Springer Series on Polymer and Composite Materials

Mariam Al-Ali AlMa'adeed
Igor Krupa *Editors*

Polyolefin Compounds and Materials

Fundamentals and Industrial Applications

Springer

Springer Series on Polymer and Composite Materials

Series editor

Susheel Kalia, Dehradun, India

More information about this series at http://www.springer.com/series/13173

Mariam Al-Ali AlMa'adeed · Igor Krupa
Editors

Polyolefin Compounds and Materials

Fundamentals and Industrial Applications

Springer

Editors
Mariam Al-Ali AlMa'adeed
Center for Advanced Materials
Qatar University
Doha
Qatar

Igor Krupa
Center of Advanced Materials
Qatar University
Doha
Qatar

ISSN 2364-1878 ISSN 2364-1886 (electronic)
Springer Series on Polymer and Composite Materials
ISBN 978-3-319-25980-2 ISBN 978-3-319-25982-6 (eBook)
DOI 10.1007/978-3-319-25982-6

Library of Congress Control Number: 2015954597

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media
(www.springer.com)

Contents

Chapter 1
Introduction

Mariam Al-Ali AlMa'adeed and Igor Krupa

1.1 What Are Polyolefins?

Polyolefins are the group of thermoplastic polymers formed by the polymerization of olefins such as propylene, ethylene, isoprenes, and butenes which are commonly obtained from natural carbon sources such as crude oil and gas. Polyolefins contain only carbon and hydrogen atoms attached together with or without side branches.

The production of polyolefins started in the research laboratories. Polyethylene was the first produced polyolefin in 1933 in the research laboratories of Imperial Chemical Company by E.W. Fawcett and R.O. Gibson, from pure ethylene by high pressure and temperature, polyethylene pellets are shown in Fig. 1.1. The production of PE is expected to reach 100 million of metric tons in 2018, and the investment of the production can reach \$1 bn for new plants.

Polyolefins are widely used in different applications since 1950 after the development of Ziegler–Natta catalysts which make it easier to produce them with low cost and high quantities and better molar mass control.

This book follows the "lifetime" of polyolefin compounds and materials: from their historical and economical input, synthesis and processing, over applications, to recycling and oxo-degradation.

M. Al-Ali AlMa'adeed (✉) · I. Krupa
Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar
e-mail: m.alali@qu.edu.qa

M. Al-Ali AlMa'adeed
Materials Science and Technology Program, Qatar University, 2713 Doha, Qatar

I. Krupa
QAPCO Professor Chair, Doha, Qatar

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_1

Fig. 1.1 Polyethylene pellets

1.2 General Information

Properties of polyolefins primarily depend on the type of monomers and route of polymerization, resulting in various molar mass and degree of crystallinity. They can be simply modified by introducing various functional groups or mixed with other polymers and fillers to get tailored properties for required applications.

Generally, polyolefins have good chemical stability and they are insoluble in water, in polar solvents as well as in unipolar organic solvents below 60 °C. They have high electrical resistivity and a high dielectric strength.

Both neat polyolefins and their blends and composites are commonly processed by blow molding, injection molding, extrusion, compression molding, rotational molding, and thermoforming. The final materials can be produced as bulk materials, fibers, and thin films.

1.3 Importance of Research in the Production and Modifications of Polyolefins

This book entitled "Fundamentals and Industrial Applications of Polyolefins" emphasizes the important relation between academia and industry for the production and improvement of the polyolefins in different applications that can help the society. Academic research all over the world developed the polyolefin industry for different uses. The knowledge and innovation provided by scientists can be translated by the industry into polyolefin products.. Industry used these ideas for financial development and marketing of real high-quality products that benefit the society. New questions and requirements are usually returned to the academia and

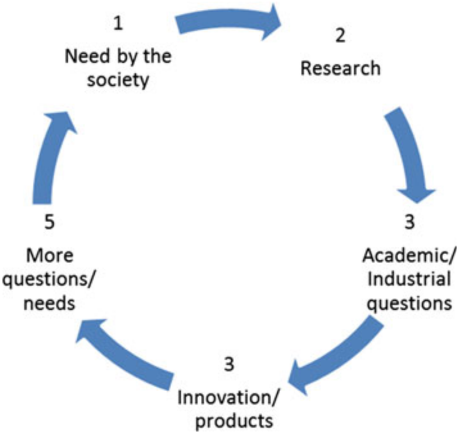


Fig. 1.2 The development of new material is a collaborative work between researches in academia and industry

different research sectors by the industry to improve the applications and have new benefits. Figure 1.2 shows the cycle of production and improvement of polyolefins by the scientists, society, and industry.

Fundamental research creates important knowledge that the industry need for new applications and for any further needs arise by the community.Open-ended exploratory research is the first step that can lead to the social and economic benefits. The time line for the production of a new polyolefin material is shown in Fig. 1.3, which starts from (i) research, (ii) new polyolefin material or polyolefin composite, (iii) production, (iv) high production, (v) mature production, and (vi) cost reduction.

Polyolefin can be considered as an interdisciplinary material that needs the collaboration from different disciplines such as chemistry, physics, computer science, and engineering. The integration of different fields leads to new advanced technology and economic competitiveness to modify polyolefins for different applications. Polyolefins are replacing many other materials in diverse uses, and the scientists are trying to find new production, processing, and applications for the polyolefins with more friendly environment routs through new polymerization processes, modified catalysts and improved additives to have a wider application of these materials.

This interaction between the academia and industry can lead to new developments in polyolefin technology and economic progress. *This book is written by academicians and industrial specialists who are experts in polyolefins and can contribute positively to the progress of the society, and this book can help the students, academics, and industrial sectors by introducing basics, applications, and uses of polyolefins.*

The book starts with the historical and economic impact of polyolefins, and examples are given from around the world. The fundamental aspects in polymerization and processing are described after that.

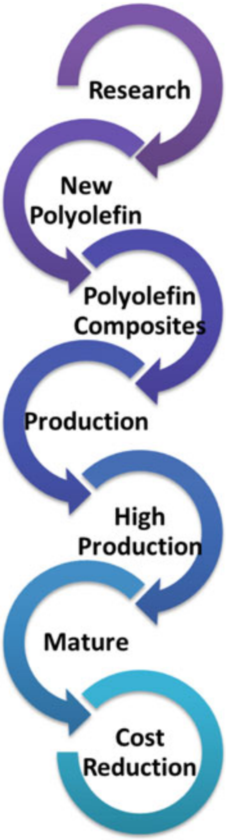


Fig. 1.3 Time line for the production, high production, and cost reduction of polyolefins

Basic and advanced knowledge in polyolefin blends and composites is explained before applications in different sectors are discussed.

New products from polyolefin were developed as explained in this book through the following areas:

- Packaging and food industry;
- Polyolefin adhesion modifications;
- Polyolefin in textiles and nonwoven industry;
- Biomedical applications of polyolefins;
- Polyolefins in automotive industry;
- Polyolefins from thermal and oxidative degradation to ignition and burning.

At the end of this book, we discuss two major important possibilities to protect the environment through recycling and oxo-degradable, which are explained according to the present status and future perspectives.

1.4 Why Polyolefins?

Production of PP and PE reached 177.5 million tons in 2015, indicating the high need in the market for different applications and the continuous economic development. This is due to the low cost and good mechanical and physical properties that can be tailored for various applications highlighted in this chapter.

Polyolefin industry contributed to economics of many countries, and one such example is Qatar which currently has the second GPD per capita due to the industrialized products from oil and gas. The industrial plants added to Qatar's development and attracted high-quality experts from around the world.

1.5 Polyolefin Blends and Composites

Polyolefins can be used in various applications, but blending polyolefins can introduce new materials with better properties for advanced applications such as in

- Medical field when blending UHMWPE with LMWPE for implants.
- Recycling by blending the waste to retain good mechanical and thermal properties.
- Blending is a common way to introduce low gas permeability for food packaging.
- Phase-change materials (PCM) can be used by blending the polyolefin matrix with a paraffin. The immiscible compatible blend can store energy through melting of paraffin, whereas polyolefin, particularly polyethylene, maintains the shape and compact solid form for different applications such as thermal comfort in buildings or food packaging.
- Partly degradable material can be achieved when blending the polyolefin with a degradable polymer such as PLA or starch; this can reduce the current polymer waste problem in the world.

Film wrapping, automobile parts, medical tubes, and coating for cable systems can be achieved by blends of two polymers such as PE and EVA which can be used in agriculture as the mix of the both polymers introduces new combined properties.

Similar applications can be achieved by blending the polyolefin with the rubber to be used in cables, wires, footwear, and automotive industry.

Future applications of blending include blending the polyolefin with other polymers such as polyaniline (PANI) to reduce oxidation in food packaging due to the fact that PANI has free radical scavenging properties.

Challenges in this application come through the immiscibility of the blends which can reduce mechanical properties. When subjected to stress, these blends fail at the interface of the immiscible components. An improvement of mutual compatibility can be insured by the addition of new additives, by reactive blending, or by adding another polymer.

Reduction in the properties can be seen when blending the polyolefin with a biodegradable component such as PLA, and this can be reduced by the addition of compatibilizers.

New opportunities of blending polyolefin can be seen in thermotropic liquid crystalline polymer (LCP) multicomponent, automobile fuel tanks, polymer solar cells, chemical sensors, polymer membrane, and foams.

Addition of micro- or nanofillers or additives to the polyolefins can improve their properties for different modern applications such as in the automotive, furniture, medical, packaging, electrical, transportation, construction, textile, and agriculture industries. These industries have been increasing over the last few decades. Additives can include different shapes such as flakes, fibers, and particulate types. It can be of natural or synthetic nature. The additives can improve the performance of the new composites or nanocomposites of the polyolefins.

For polyolefin composites, challenges include many variables such as aspect ratio of the fillers, orientation, and the interface. Controlling these properties of the additives can be an easy way to control and tailor the needed properties.

1.6 Packaging and Food Industry

The use of polyolefin materials in food packaging is very important as they have good mechanical strength to withstand the consumer handling and good thermal stability for thermal processing methods. Improving the surface properties of the polyolefins is attracting much attention as there is a need to improve wettability, adhesion to food surfaces or other materials, dye uptake, printability, antimicrobial and barrier characteristics, and glazing resistance. Surface functionalization can be arranged by different methods to improve these properties (Fig. 1.4).

Using polyolefins in food packaging has many challenges to improve the surface properties of materials maintaining their excellent bulk properties. Improvement in oxygen scavenging systems needs to be improved also to reduce the oxidation of the food and the presence of aerobic bacteria and mold growth.

1.7 Adhesion

Surface modifications of polyolefins are very important for many industrial applications such as adhesion to (1) another polymer, (2) composite, and (3) metal bonding.

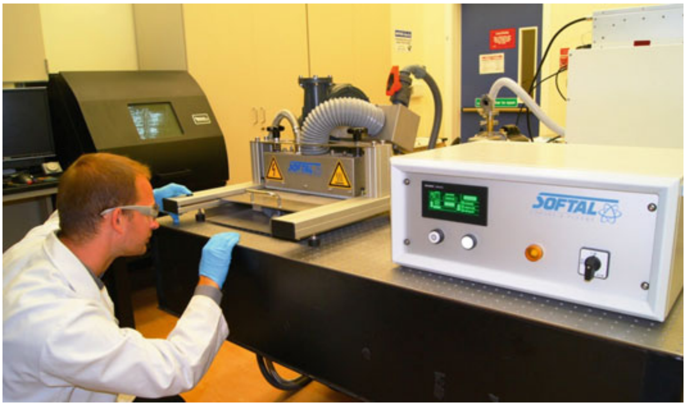


Fig. 1.4 Plasma treatment to improve the surface morphology of polyolefins

Adhesion can be modified by chemical or physical methods to increase the surface free energy. The following procedures can be used for modifying the surface: chemical treatment, ultraviolet treatment, flame treatment, and plasma treatment.

This is done by modifying the first few atomic layers in the surface of the material. The results of the surface treatment are: (1) cleaning, (2) ablation, (3) cross-linking, and (4) surface modification.

Polyolefins have in general low surface energy and poor adhesion. One of the main challenges in polyolefin adhesion modification is the functionalization process, and flexible polar groups can be added and lead to high-value applications such as fuel cells, membranes, and batteries. Other common applications include automobile painting and building industry (e.g., roofing membranes). Improving antiadhesion properties has other applications especially in the biomedical field such as in the blood-contacting equipment.

1.8 Polyolefins in Textiles and Nonwovens

Polyolefin textile fibers are usually produced through the melt spinning process with good mechanical properties and chemical and abrasion resistance. One of the main drawbacks in this industry is the fact that they are difficult to dye unless additives are used. One of the major applications of PP is the use in carpet which replaced natural fibers. Other applications include bags, sportswear, and knitwear.

Nonwovens are fabrics that are made from the fibers or webs that are made from the fibers. They are not knitted or woven. Fibers can be entangled by chemical, thermal, or mechanical methods. Current applications of nonwovens include geomembranes, filtration membranes, wipes, diapers, and medical fabrics. Advantages of this application include possible recycling, easy to clean, and wide applications.

1.9 Biomedical Applications

There are opportunities for polyolefins in biomedical applications as many types are nontoxic, non-thermogenic, non-inflammatory, non-carcinogenic, and non-immunogenic. Polyolefins are used in many applications such as artificial skin, orthopedic implants, heart valves, and disposal items used in medical applications such as syringes.

The challenge for biomedical applications of polyolefin is the need to investigate their interaction with the living tissue and their stability as medical devices. Their physical and mechanical properties can be improved by some additives or new processing techniques.

Leaching from polyolefin materials that are used to store buffer and media solutions needs to be analyzed to investigate and identify leachables to ensure the safety of the medically applied polyolefins.

1.10 Automotive Industry

Polyolefins are used in automotive industry due to their low cost, good weather resistance, and excellent properties. They can be used in many parts to reduce the vehicle weight, save fuel, increase comfort, and reduce CO_2 emission. Polyethylene (UHMWPE or HDPE), for example, is used to absorb vibration and noise and for impact protection. Polypropylene is one of the lightest polyolefins, and with a proper design, an improvement in the passenger safety can be achieved. Polypropylene can also be used in bumper systems to absorb the kinetic energy.

New trend is the use of polyolefin nanocomposites for the automotive industry in different parts such as in coatings, tires, electric and electronic equipment, breaking systems, frames, body parts, and bumper systems.

Challenges include the usual nanocomposite problems such as the adhesion of the cellulose additives to the polyolefin matrix and fiber/matrix interface optimization.

1.11 Stabilizing Polyolefin and Protection Against Ignitability

Understanding the life trajectory of the polyolefin is important to increase the lifetime of the industrial application. Protection against degradation can be achieved by adding stabilizing additives to scavenge the free radicals or hydroperoxides from the polyolefin. Two different types of antioxidants (or more than two) can be used as antioxidants. UV stabilizers can be used to eliminate the free radicals, and these include light filters, light absorbers, and quenchers.

Protection against ignitability can be increased by different techniques such as inorganic additives (magnesium hydroxide and magnesium oxide). Reducing smoke is also an important requirement for the modern society which can be achieved by different types of additives.

One major challenge is to improve flame-retardant additives added to the polyolefins which can scavenge the reactive atoms and convert them to less reactive species. This system can reduce catastrophic fires.

1.12 Recycling and Oxo-Biodegradation

Figure 1.5 shows the life cycle of polyolefins. Recycling can be more environment-friendly compared to landfilling and incineration. Recycling is highly needed to reduce emissions contributing to air, water pollution, fuel, and raw materials. The attitude of the industry is in general supportive to recycling. Recycled polyolefins can be used in non-load-bearing parts. Legal regulations and economic considerations should be arranged to encourage the recycling process of the polyolefins.

Another discussed topic in this book is the oxo-degradation which is encouraged by adding additives (metal salts) to the polyolefin material. These additives speed up the fragmentation when the material is exposed to air (oxygen). Oxo-degradation can happen after that, which is a very important step for short-service-life supplies in the market. This technique is highly needed in the modern society to reduce the negative impact of the waste on the environment.

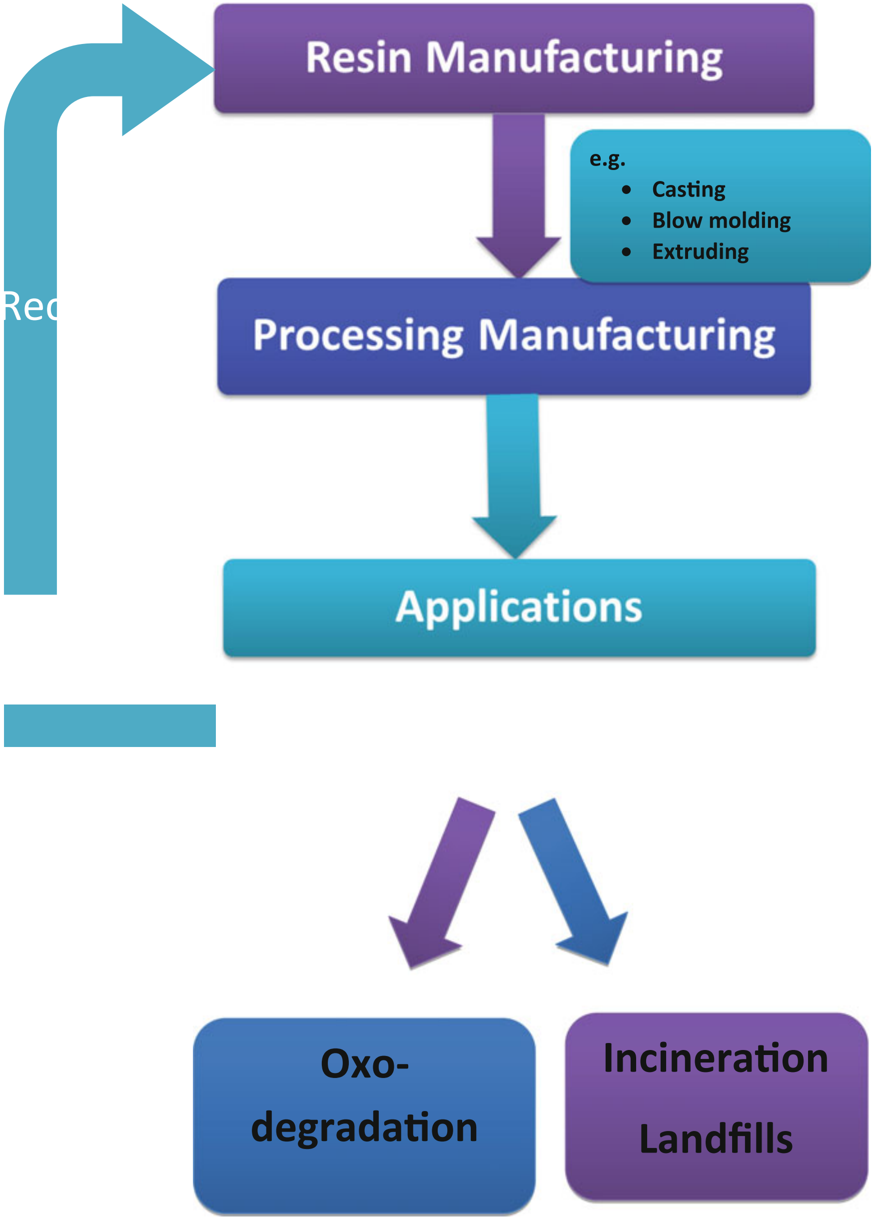


Fig. 1.5 Examples of life cycle of polyolefins

1.13 Conclusion

Polyolefins are highly applicable in the society and have a huge market share among polymeric materials. Research and innovative techniques are needed to improve these materials for different applications that can support the society and have a sustainable effect on the environment. This book discusses historical, economical, and different techniques in preparing the polyolefins with examples of current and future industrial applications. Other needs of flame retardants, recycling, and oxo-degradation are also discussed.

Chapter 2
Polyolefins—The History and Economic Impact

Trevor J. Hutley and Mabrouk Ouederni

2.1 Introduction

2.1.1 Definition

Olefins (from the French oléfiant, "oil-forming"),[1] or alkenes, are hydrocarbon molecules with at least one double carbon–carbon bond. Alpha (α-)olefins are alkenes with a double bond at the first (alpha-) carbon. Polyolefins are polymer molecules, made using either free-radical or ionic initiators or inorganic (metal oxide) or organo-metallic catalysts, to open the reactive double-bonds in these olefins, in an addition (chain-growth) polymerization reaction. These polymerisation processes produce essentially linear high molecular weight thermoplastic polymers, which are now the main topic of this chapter.

These polyolefin polymers, since their commercialization around 80 years ago, are now (2013) the major fraction (62 %) of the plastic materials which have transformed modern life [1]. In 1960, they comprised only 20 % of global polymer demand, but already by 1995, this had reached 60 % [2].

The original version of this chapter was revised: The erratum to this chapter is available at DOI 10.1007/978-3-319-25982-6_15

---

[1] Because olefins combine readily with halogens to form oily liquids

---

T.J. Hutley (✉)
Business Development Consultant, Pan Gulf Holding, Al Khobar 31952,
Kingdom of Saudi Arabia
e-mail: TrevorHutley@consultant.com

M. Ouederni
Head of Research and Development, QAPCO, Doha, Qatar
e-mail: MOuederni@qapco.com.qa

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_2

No other major material has appeared on the scene and achieved such a dominant and ubiquitous place in such a short time. As new materials, polyolefins have introduced new possibilities and benefits at attractive price points. Their annual growth rate remains exponential.

Polyolefins are used in every sector of life and are processed by every significant polymer processing technology. Whereas they are commonly perceived as commodity polymers, and their vast production and consumption volumes are testimony to this, polyolefins can also be speciality and outstanding niche materials, with unique properties and features.

2.1.2 Scope

In this chapter, we seek to demonstrate the broad and enormous economic and commercial impact of these polyolefins, by considering a number of dimensions that contribute to economic impact.

The commercial and economic impact of polyolefins is inextricably linked with the discovery, recognition, or development of properties and performance that creates value. Thus, we integrate the technical application and market development of polyolefins in our discussion.

We start with a historical perspective on how the industry evolved from the early discoveries in research laboratories in Germany and England to become a global industry of almost 170 million tons and value around $200 billion, in just over 80 years.

2.2 Polyolefins: The History and Economic Impact

2.2.1 Polyolefin Elastomer

Strictly speaking, the first high molecular weight polyolefin to be commercialized was a homopolymer of isobutylene. This polyisobutylene (PIB) was first developed by IG Farben [*Interessen-Gemeinschaft* ***Farben****industrie AG*] in 1931 using a boron trifluoride catalyst at low temperatures. We could note that the monomer, isobutylene, was discovered by Michael Faraday just over 100 years before, in 1825. PIB of medium and high molecular weight is sold under the trade name Oppanol B, a core business for BASF to this day. BASF acquired the competing Vistanex PIB business of ExxonMobil in 2003. BASF have 4 plants that make PIB, including the 18,000 ton plant at Ludwigshafen. Polyisobutylene has a low T_g (−73 °C) and does not crystallize. PIB homopolymers of high molecular weight (100,000–400,000 or more) are therefore polyolefin elastomers, not (thermo)plastics, and so fall outside of our scope. They are tough extensible rubber-like materials over a wide temperature range, with a characteristically low density of polyolefins 0.913–0.920, low permeability, and excellent electrical properties.

Polyisobutylene is used as the base of chewing gum, in adhesives, sealants, roofing, coatings, protection for optical fibre bundles, and electrical cable sheathing. In 2017, the overall polyisobutylene production is anticipated to reach 1.2 million tonnes [3].

Lower molecular weight polyisobutylene is sold by BASF as Glissopal®, as an important intermediate for the manufacture of additives for fuels and lubricants, made in plants in Antwerp and Ludwigshafen of capacities 100,000 and 40,000 tons per annum (tpa), respectively.

Polyisobutylene was later developed into butyl rubber [IIR] in 1937, by researchers William J. Sparks and Robert M. Thomas, at Standard Oil (later, ExxonMobil) by copolymerizing about 2 % of isoprene into polyisobutylene, to provide the unsaturation for vulcanization (cross-linking with sulphur). This butyl rubber was commercialized in 1943, and in 2016, the global capacity for IIR is expected to be 1.6 million tons, with 6 players. ExxonMobil has a 40 % market share. Since butyl rubber has outstanding permeability, tire inner tubes were the first major use of butyl rubber, and this continues to be a significant market today.

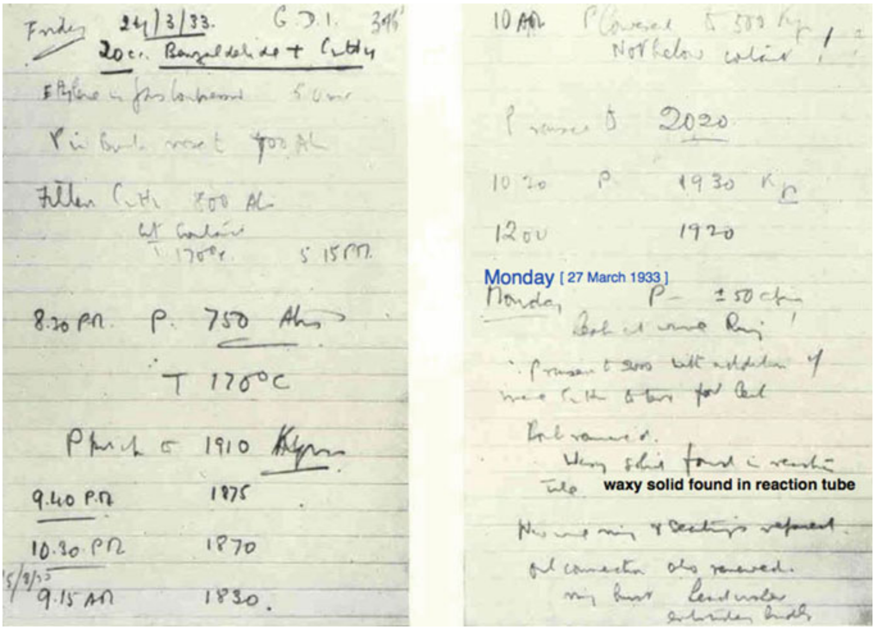
This important segment (PIB, and its derivative IIR) has clear economic impact through its unique and diverse applications and performance. Together, they total around 2.8 million tons per annum, generating a revenue of around $4bn. This segment was included here, so as to provide the full picture on the development of polyolefins, but is not a part of the commonly recognized polyolefin industry that we now turn to.

2.2.2 Polyethylene (PE)

Our story really begins with polyethylene. The first record of this word appears in the work of the French chemist Pierre Eugène Marcellin Berthelot, who reported in 1869 on his studies of ethylene exposed to boiling alkali, in which he described the olefin fraction boiling at 280–300 °C as "polyethylene" [4]. *These may have been ethylene polymers, or perhaps oligomers, but they were not solids!*

More than 60 years later, we see the first preparation of polyethylene by Prof. Marvel, a discovery that languished, and then 3 years later, the serendipitous discovery of (solid) thermoplastic polyethylene in 1933, in the research laboratories of ICI, and its commercial production by 1938.

In 1930, Professor Carl Shipp "Speed" Marvel, just starting as a technical consultant with DuPont, had assigned a graduate student [5], to prepare alkylated arsenic compounds, from tetra-ethyl-arsenium bromide and butyl lithium. One experiment involved passing ethylene gas through a solution of n-butyl lithium in a mineral oil at elevated temperature. The white powder that resulted was the first solid linear polyethylene in excellent yield by direct addition polymerization with an organo-metallic catalyst under very mild conditions. It is supposed that DuPont was both preoccupied with a number of commercially interesting polymers (including nylon, neoprene, acrylics) and that the commercial possibilities of a linear polyethylene were not seen [6, 7].



Friday 24/3/33

8.20 PM P. 750

T 170°C

1910

9.40 PM 1875

10.30 PM 1870

9.15 AM 1830

10 AM

2020

10.20 P 1930

1200 1920

Monday [27 March 1933]

waxy solid found in reaction tube

Fig. 2.1 Original laboratory notebook observation recorded by Reginald Oswald Gibson at ICI laboratories describing the waxy solid (PE) found in the reactor tube [8]

It all started with a chance observation on 27 March 1933, by Eric William Fawcett and Reginald Oswald Gibson of ICI Research in Winnington, Cheshire, England, who were investigating the effects of very high pressures—above 1000 atmospheres—on chemical reactions [8]. They had started an experiment on Friday 24 March, to react ethylene and benzaldehyde (one of 50 reactions suggested by Sir Robert Robinson, consultant to ICI, Nobel Prize in Chemistry 1947) at 170 °C and a pressure of 1900 atmospheres. On Monday 27 March, 1933, the reactor "bomb" was dismantled and Fawcett observed that the tip of the steel U-tube was coated with a waxy material. Gibson recorded in his rough notebook: "*Waxy solid found in reaction tube*" (Fig. 2.1).

Fawcett collected 0.4 g of this wax, had it analysed, and an empirical formula of CH_2 was found, with a molecular weight of at least 3700. He internally reported this (7 April 1933) as "probably polymerized ethylene". From this 0.4 gram isolated by Gibson and Fawcett in 1933, polyethylene has grown in 80 years into a global industry producing over 80 million tons per year, the largest volume thermoplastic in the world (2013 figures). This is the remarkable growth story that we proceed to outline.

It is now thought that the ethylene that Fawcett and Gibson used may have contained enough oxygen to initiate the free radical polymerization of the ethylene under this pressure [9]. This (what was originally called high-pressure PE, and what we now call low density) polyethylene was and is made by a free radical high-pressure polymerization. When "improved facilities" were available in the ICI research laboratories, this experiment, with ethylene alone, was repeated, on 20 December 1935. This time, 8.5 g of solid was prepared.

We should not forget that this discovery of polyethylene was at a time when polymer science was at the very beginning. On 26–28 September 1935, the Faraday Society held the first major conference on polymer science in the UK in Cambridge; Fawcett attended [8]. Hermann Staudinger (1953 Nobel Laureate in Chemistry) presented a paper on the first day in which he described ethylene as a stable compound which polymerizes with difficulty, giving only low molecular weight mixtures of hydrocarbons. In the discussion on Staudinger's paper, Herman Mark, the chairman of the conference, himself invoked some theoretical arguments to explain why ethylene does not polymerize. Then, Fawcett got up and told the Conference that he had actually made a solid polymer of ethylene, with a molecular weight of about 4000, by heating ethylene to 170 °C at about 2000 bar. This disclosure "elicited no reaction from the people present, the cream of England and world polymer scientists", and Staudinger, even when prompted by the chairman, declined to comment. Fawcett was apparently dismissed from ICI for this disclosure [6]. We know that in 1938, Fawcett joined BP Research.

One year after Fawcett's unauthorized statement, the ICI "process for polymerizing ethylene to (technically useful) solid polymers" was formally disclosed in British Patent 471590 (applied 4 February 1936, allowed 6 Sept. 1937) and the related US Patent 2153553 (Polymerization of olefins, Publication date 11 April, 1939 Priority date 4 Feb, 1936 Fawcett Eric William, Gibson Reginald Oswald, Perrin Michael Willcox, ICI Limited).

In November 1937, ICI started up a 9 litre reaction vessel that could produce about 10 tons per annum [tpa] of polyethylene. Continuous operation was not achieved until the first ton of polyethylene was made on 22 December 1938. We might say that the polyolefin industry had begun!

A 100-tpa polyethylene plant was started up in Wallerscote in September 1939, and the second 100-tpa plant was completed in May 1940.

These investments and significant advances in equipment design and reliability were made in parallel with the development of applications for this new material.

In 1936, (later, Sir) Michael Perrin wrote "It is felt that, of a large number of possible uses, attention should first be concentrated on those connected with the electrical industry, where the outstanding insulating properties of Alketh combined with its flexibility in the form of tape and films, and its chemical inertness, would appear to be most promising".[2]

Indeed, the first suggested use for polyethylene came from B.J. Habgood, who had joined ICI from the cable industry: the combination of electrical properties (high dielectric strength, low loss factor, and moisture resistance) and mechanical properties made it suitable as an insulator for trans-Atlantic coaxial telephone cable. The demand at that time was estimated at 2000 tons per annum. It eventually replaced the natural thermoplastic polymer gutta percha (trans-1,4-polyisoprene)

---

[2] In May 1942 ICI introduced the trademark Alkathene to replace Alketh.

which had been used in cable insulation since 1843, when it was first used to insulate the telegraph lines along the Great Western Railroad.

The submarine trans-Atlantic telegraph cables of 1857, 1858, and 1865 were insulated with gutta percha, which was the prime material for submarine cable insulation for over 80 years, until it was replaced by the new polyethylene. One of the key drivers of the growth of the polymer industry—“material substitution”—had been initiated.

The PE produced at this time by high pressure had a density of 910–920 kg/m^3 and became known as “low-density” polyethylene, once polyethylenes of greater linearity (less branching, so the chains are more easily packed together, giving high (er) density) were developed.

The submarine telephone cable application was the justification for the commercial PE plant, but in fact—with the outbreak of World War 2 in 1939—almost all of the 4000 tons of PE produced between 1939 and 1945 was used to insulate high-frequency radar cables. Commercial distribution of PE in the UK was suspended, secrecy was imposed, whilst PE was used to produce insulation for the coaxial cables of radar sets. Airborne radar, possible because of the compact cables available now with PE insulation, proved to be a critical advantage in the Battle of Britain and the Battle of the Atlantic, helping British supply ships to avoid German submarines. German Admiral Karl Dönitz told Adolf Hitler in May 1943: “What is now decisive is that enemy aircraft have been equipped with a new location apparatus … which enables them to detect submarines and to attack them unexpectedly in low cloud, bad visibility or at night” [10].

Once warfare had ceased in Europe (May 1945) and in Asia (August 1945), the military demand for PE reduced, and the search for modified products and alternative applications started. Another of the key drivers of the growth of the polymer industry—“product and application development”—had been initiated.

Calendered PE sheet (Crinothene) was used for lampshades. Winothene was a low molecular weight PE made for wax applications. Halothene was a chlorinated PE. None of these proved a growth driver for the PE business. However, a major application for PE was found once ICI Plastics started its first 122 cm (48″) film extruder. Today, extruded film (blown film, cast film, extrusion coating) is the major process/application across the main types of PE.

2.2.2.1 “Exceptional Invention”

In October 1929, DuPont signed a “patents and process agreement” with ICI “to exchange scientific and technical information on a routine basis”, which was effective until 1948, when the US Department of Justice brought antitrust pressures to bear, and it was cancelled (it was due to expire in 1949 anyway) [11].

DuPont claimed neoprene (1930) and nylon (1934) as “exceptional inventions” and so—within the understanding but not the actual contractual terms of the agreement—did not make early disclosure of these to ICI. Polyethylene was disclosed by ICI to DuPont in September 1933, but later, in 1939, ICI notified DuPont that polyethylene was an "exceptional invention", so was—likewise—outside of the scope of their agreement.

DuPont started their investigations of high-pressure polymerization in 1936 and by 1940 had developed an improved process for making PE. A 50-ton pilot plant was completed in December 1942, and a 500-ton plant was started up in March 1943 [11].

DuPont had been granted rights to grant non-exclusive sub-licences of the ICI Patents. Union Carbide approached DuPont in October 1942 for a sub-licence, whilst simultaneously contracting to supply the Navy with PE, building a 500-ton PE plant, and then improving the process and product. By the end of the war, Union Carbide had increased their capacity to six times that of DuPont, who were now making 750 tons per annum. Applications were found in extruded film, coated paper, wire and cable insulation, bottles, and pipes.

2.2.2.2 Linear Polyethylene

DuPont had discovered (patent application 739,264, filed 3 April 1947) that a more linear free radical PE—with a density of 0.955—could be made using a specific free radical initiator such as AZDN (azo-di-iso butyronitrile), under very extreme pressure conditions (their patent indicates 5000–20,000 atmospheres). They were unable to convince the patent examiners that this linear polyethylene was a patentable invention. Only after the discoveries from 1951 (publication of the various low-pressure HDPE process patents, outlined below) did this patent USP 2816883 publish. DuPont never pursued this linear polyethylene, because the extreme pressures "greatly exceeded the limits of commercial feasibility" [11].

2.3 Inorganic and Organo-Metallic Catalysts

The next major step, almost two decades after the discovery by ICI of their high-pressure free radical polymerization of ethylene, was the discovery, from 1951, of (metal oxide and organo-metallic) catalysts that produced essentially linear high molecular weight polyethylene (and other polyolefins) under much lower pressures. These catalyst discoveries occurred almost simultaneously and independently in several laboratories in the USA and Europe [12].

We briefly review these discoveries, chronologically, and see how they led to several industrial processes that were the foundation of the significant growth of the polyethylene industry since the 1950s. We then see how this technology was rapidly extended to create the polypropylene industry. The growth of the polyolefin industry in these last 60 years is the story primarily—in terms of volume and impact—of the growth of polyethylene and polypropylene.

Although from our perspective, more than 60 years later, we see polyethylene and polypropylene as quite different polymers and industries, and the commercial value of each of these polyolefin polymers is appreciated, yet from the 1950s perspective of the "new" metal oxide and organo-metallic catalyst syntheses, they were just outcomes of α-olefin polymerization. That is why the early days of polyethylene and polypropylene and these metal oxide and organo-metallic catalysts are such entwined and convoluted histories.

2.3.1 DuPont "on the Brink of a Tremendously Interesting Field of Polymer Chemistry"

Although from the patent/legal perspective, DuPont is not at the beginning of the chronology, it is described first, because the much earlier work of Prof. Marvel in 1930 might be seen as the starting point of organo-metallic catalyst synthesis of solid polymers and because the work from 1954 at DuPont was specifically derived from an earlier (1943) antecedent at BASF.

In 1954, the exploratory research section of DuPont, a group of about 10 men headed by Dr. Frank Gresham, began to investigate polymers that were of higher modulus than (low-density) polyethylene. To decrease the chain flexibility, they sought to incorporate norbornene as a "bulky" comonomer into the polyethylene chain. One chemist in the group, Nicholas G. Merckling, was assigned to find a suitable polymerization catalyst for this. Merckling found, in his literature review, that Max Fischer of BASF had been issued with a (1953) patent based on his 1943 (during WWII) improvement of a titanium and aluminium chloride catalyst for polymerizing ethylene to low molecular weight liquids. When Merckling pursued this and succeeded in making a higher modulus polyethylene using these catalysts, it was quickly recognized that he had made linear polyethylene by a relatively low-pressure process and that with this new catalyst (Gresham wrote to his boss) "we are on the brink of a tremendously interesting field of polymer chemistry". On 16 August 1954, Merckling filed a patent for the reduced (divalent) titanium catalyst and a process for polymerizing ethylene from 1 – 100 bar.[3] In one example (X), they disclosed a polyethylene of density 0.98, and in another (XIX), a molecular weight too high for the melt flow index to be measured.

2.3.2 Standard Oil of Indiana (later, Amoco)

Alex Zletz of Standard Oil of Indiana (later, Amoco) was actually the first to disclose (patent filed 28 April 1951) the use of a transition metal catalyst for the production of highly linear (what came to be called high density) polyethylene HDPE, using a molybdenum oxide catalyst supported on alumina.[4] The polymer density was 0.96. The purpose and process of their invention is very clearly stated in this patent:

---

[3] Source: US Patent 3541074.

[4] Source: US Patent 2692257.

> …to provide a relatively low temperature, low-pressure process for the conversion of ethylene-containing gases to high molecular weight resinous or plastic materials.Briefly, the inventive process comprises the conversion of ethylene principally to high molecular weight normally solid polymers by contact with an alkali metal and one or more of the oxides of chromium, molybdenum, tungsten, or uranium, extended upon a support [13].

The management was unsure of the importance of this product, and commercialization was slow. The first plant using this technology went on stream in 1961, in Japan. Three plants were eventually built between 1961 and 1971, but the process had poor economics and was soon "dead". Ironically, the first technology to market, which normally has an advantage, had little economic impact and has no place in the polyethylene technology of today.

2.3.3 Phillips Petroleum Company

On 5 June 1951, Phillips Petroleum Company (now Phillips 66, which owns 50 % of Chevron Phillips Chemical) researchers Hogan and Banks were attempting to convert propylene into gasoline (petrol), when they discovered crystalline polypropylene.

This discovery led to the development of a new catalytic process based on chromium oxide, for making both polypropylene and high-density polyethylene (HDPE) in January 1953.[5] This "Phillips (chromium) catalyst" gave a highly linear, very crystalline polymer, of density 0.963, with resultant improved mechanical properties, at low pressure. Phillips invested $50 million in developing this new technology and introduced their Marlex® HDPE in 1956. At the outset, there was only one grade available—with a melt index below 1 (a high molecular weight grade). This did not match with the already diverse market needs, so inventory began to build. It is said that Marlex® was probably "saved" by the Wham-O Company, who in 1958 made their new "craze" product, the HulaHoop, from Marlex® polyethylene tubing—lots of it: over 100 million hoops were made within 2 years. The completely unanticipated demand for Marlex gave Phillips the time necessary to resolve initial production problems and position itself as a prime source of plastic resins. This tremendous contribution by the two Phillips Petroleum scientists was commemorated by the US Postal Service (USPS) in an official stamp that features their photos (Fig. 2.2).

These Phillips discoveries were commercialized rapidly and remain a major process today, in more advanced forms: the Phillips supported chromium catalyst is used to produce some 40–50 % of the world's HDPE. The first plants were brought on stream in 1955 and 1956. However, Phillips management concluded that no one manufacturer could develop the full market potential of the Phillips HDPE and therefore decided to license the process. By 1956, nine companies in seven countries had become licensees.

---

[5] Source: US Patent 2825721.

Fig. 2.2 US postal service stamp commemorating Phillips Petroleum Scientists Robert Banks and Paul Hogan

2.3.4 Prof. Karl Ziegler

"The Ziegler catalyst was… an unprecedented break-through in … polymer synthesis" [6].

In February 1943, Prof. Dr. Karl Ziegler was invited to be the director of the Kaiser-Wilhelm-Institut für Kohlenforschung (renamed in 1949 the *Max-Planck-Institut für Kohlen-forschung*) in Mülheim an der Ruhr and appointed on 16 April 1943.

There, continuing with organo-metallic chemistry, Karl Ziegler and Hans-Georg Gellert found that triethyl aluminium could react with ethylene by stepwise insertion—what was called the "Aufbau" (building up) reaction—to produce ethylene oligomers and low molecular weight waxes or polymers (up to 100 ethylene insertions).[6]

In early 1953, in the hands of the graduate student Erhard Holzkamp, this established Aufbau reaction unexpectedly took a different course. Instead of oligomers, he obtained a quantitative yield of 1-butene, in addition to unchanged triethylaluminium! It was eventually found that this was due to minute traces of colloidal nickel in the reaction vessel, remaining from previous hydrogenation studies. This finding was later called the "Nickel-Effect". Prof. Ziegler then instigated a systematic investigation of the effect of other transition metal compounds on the Aufbau Reaction [14]. A new graduate student, Heinz Breil, was given the task of carrying out this systematic search.

On 26 October 1953, Breil carried out the reaction which was to revolutionize polymer chemistry: he treated ethylene with triethylaluminium in the presence of zirconium (acetylacetonate). The reaction was carried out under the standard conditions used for the Aufbau Reaction (100 °C, 100 bar) but took a completely different course—a white mass of polyethylene was formed. On 17 November 1953, only three weeks after Heinz Breil's original experiment, Karl Ziegler submitted a 2-claim 4-page patent (for intellectual property, Ziegler characteristically wrote and defended and negotiated himself) to the German Patent Office, claiming a

---

[6] Source: US Patent 2699457.

method to prepare high molecular weight polyethylene with an organo-metallic catalyst consisting of a trialkyl aluminium species and a transition metal compound.[7]

Karl Ziegler aggressively licensed his invention. In 1954, these agreements earned Karl Ziegler and the Max-Planck Institute for Coal Research a total of almost 9 million Deutsche Marks (compared to the Institute's then annual budget of 1.2 m Deutsche Marks), or $4.5 m at 1954 exchange rates (4.2DEM/$). The Max-Planck Institute for coal research in Mülheim was sustained for more than 40 years [15] on the proceeds of the exploitation of its patent rights dating back to 1953/1954.

However, the licence from Ziegler provided only access to catalyst knowledge, and each licensee had to develop a process. This was in stark contrast to Phillips Petroleum, who provided catalysts and process knowledge as part of their licensing strategy.

The first full-scale low-pressure HDPE plant was erected by Farbwerke Hoechst AG in Germany in late 1955. Plastic Technology reported, in September 1955, that this Hostalen® resin, with a density of 0.94 g/cc, was the talk of the Hanover Industrial Fair in Germany, where it was shown for the first time in applications such as film, pipe, tubing, and moulded household articles. This first Ziegler plant was brought on stream by Hoechst in late 1956 and the second one in 1957 in the USA, by Hercules.

By 1960, US production of HDPE via the Phillips process had reached over 91,000 tons annually, whilst 32,000 tons came from the Ziegler process.

The combination of transition metal halides and aluminium alkyls has remained at the heart of the Ziegler catalyst, and is today the world's most widely employed technology for polyolefin production [16].

2.3.5 Hercules Powder Company

Edwin J. Vandenberg describes, as a participant, his own early work in polyethylene synthesis at Hercules, noting retrospectively that his ferrous complex with cumene hydroperoxide in t-butyl alcohol produced what was "obviously the linear high-density polyethylene" that "has become a very important, large volume commercial product" [17]. But his molecular weights were too low for him to recognize the value of this linear polyethylene, and in any event, his process was too poor (low conversion and yield) to be useful. Of course, later, Hercules went on to become the first US company to make polypropylene and became in the 1980s the world's largest producer of PP.

From this brief survey of contemporaneous discoveries on polyolefin polymerization, it is evident that catalysis became a dominant technology factor to consider

---

[7] Source: German Patent 973626 K. Ziegler.

within 20 years of the discovery of high-pressure (low-density) polyethylene. These various catalysts enabled linear polyethylene of higher density and higher crystallinity and improved mechanical properties to be manufactured, without the extremes of pressure and temperature that LDPE required. These catalysts were moved quickly from the laboratory to industrial plants. We surveyed the catalyst discoveries, with patent applications submitted from April 1951 to November 1953. By early 1956, eight companies had announced the capacity of 172,000 tons to manufacture linear PE. Phillips started in late 1956, most by mid-1958. DuPont delayed manufacturing linear PE until 1960, when it captured a 10 % market share.

2.4 New Entrants

Aggressive investment in production capacity, ahead of demand growth, naturally depressed market prices, as each new entrant sought to gain or maintain market share. These new entrants included companies—such as Phillips Petroleum—moving downstream into the chemical space (as Aramco is now doing, 60 years later) or those from other sectors moving into chemicals for strategic reasons. W.R. Grace was a shipping company, used to lower margins, who found the diversification into the relatively dynamic chemical industry provided attractive returns, even in this competitive situation. In fact, the PE from W.R. Grace (“Grex”) was the original material that was used in the HulaHoop craze, before demand outstripped the Grex capacity, and Marlex became the major supplier of the PE tubing.

The creation of the HDPE industry, with so many players, such investment in capacity ahead of demand growth, and the resultant intense competition, meant that by 1970, linear polyethylene was a DuPont venture that was still $20 million in the red [10]—a considerable economic impact.

2.5 LLDPE

In January 1957, DuPont filed for a patent, based on the finding that the incorporation of higher α-olefins in PE[8] improved the product, but for DuPont, it appears that this ethylene copolymer was not really a very attractive venture compared to their other, high-margin proprietary products, like nylon. Although Du Pont of Canada introduced such a process in 1960, worldwide the products remained a small volume specialty until 1978, when Union Carbide announced their Unipol process, and actually coined the name “linear low-density polyethylene” (LLDPE). As we see later, since 1980, LLDPE has continued to increase its importance in the

---

[8] Source: US Patent 4076698

evolution of the portfolio of polyethylene products, likely to approach 1/3 of the total PE market by the end of this decade.

2.6 Progress in Catalyst Chemistries

The chromium (Phillips) and titanium (Ziegler) catalysts have remained the primary industrial catalysts for HDPE and were dominant for three decades, until the discovery in 1979 by Walter Kaminsky of methylaluminoxane (MAO) as an activator for metallocene catalysts, as this compound was far more capable of ionizing the transition metal compound. These new activated metallocenes (e.g. zirconocene)—alternatively described as single-site catalysts—were now suitable for polyolefin polymerization, up to 100 times more active than Ziegler catalysts, and the monomer insertion time (30 μs) was as fast as enzymatic processes. Kaminsky found that the homogeneous (soluble) nature of these metallocene-based catalyst systems made them "dramatically different from Ziegler–Natta catalysts". Because his catalysts led to lower polydispersities, more uniform incorporation of comonomers, giving different properties and manufacturing processes, he described them as "a revolution in the polymer industry". Metallocene catalysts have particularly found application in LLDPE, but "the resulting improvements in—clarity, strength, and lower hexane extractables—usually come at a higher price, so market penetration has not been as great as was originally predicted" [18]. Latest estimates are that perhaps 10 % of LLDPE is made using metallocene catalysts [19].

The sheer size and value of the polyethylene industry ensure that there is continued research, progress, and development in catalysis, for their potential commercial impact. Although this whole subject is not within the scope of this chapter, we mention a couple of aspects of the progress, which offer the potential to impact this industry. In 1995, DuPont introduced work, carried out with them at the University of North Carolina—via the largest patent application ever in the USA.[9] They disclosed what are described as "post-metallocene" catalysts. These are transition and late transition metal complexes with di-imine ligands, which form part of the DuPont "Versipol" technology. Such catalysts create highly branched to exceptionally linear ethylene homopolymers and linear alpha-olefins. Late transition metals offer not only the potential for the incorporation of polar comonomers, which until now has only been possible in LDPE reactors, but also their controlled sequence distribution, compared to the random composition of free radical LDPE copolymers. Such copolymers account for over 1 million tons per annum [20]. Versipol has so far only been cross-licensed and used commercially by DuPont Dow Elastomers (a former joint venture, now dissolved) in an EPDM plant.

---

[9] Source: US Patent Application WO 9623010.

2.7 The Progress of Polyethylene

We have seen the development of polyethylene, from low molecular weight polymers first mentioned by name in the literature in 1869, to the first reported solid polymers of linear polyethylene by Prof. Marvel in 1930; then the unintentional synthesis and chance observation of 0.4 g of solid polyethylene in March 1933 by ICI (prepared under high pressure, later described as LDPE); the onset of catalyst technology in the industry, from the simultaneous discoveries of transition metal catalysts a few decades later, that created the HDPE industry; the development of LLDPE copolymers; and the discovery in 1979 of metallocene catalysts for polyolefin polymerization – all of which are now part of the mainstream polyethylene industry. Post-metallocene catalysts offer the promise of branching without high pressure or comonomers; the potential to incorporate polar groups without high pressure, and to control this copolymer microstructure.

The three major segments of polyethylene (LDPE and its copolymers; HDPE; LLDPE) are now an industry of almost (2018E) 100 million tons with a value of $183bn [21].

At over 31 % of the global plastic market, polyethylene has indeed become “the world’s leading synthetic macromolecule” [22].

The outstanding growth of this polyethylene industry over an 80-year time frame is shown clearly in Fig. 2.3, based on all data available, from different sources.

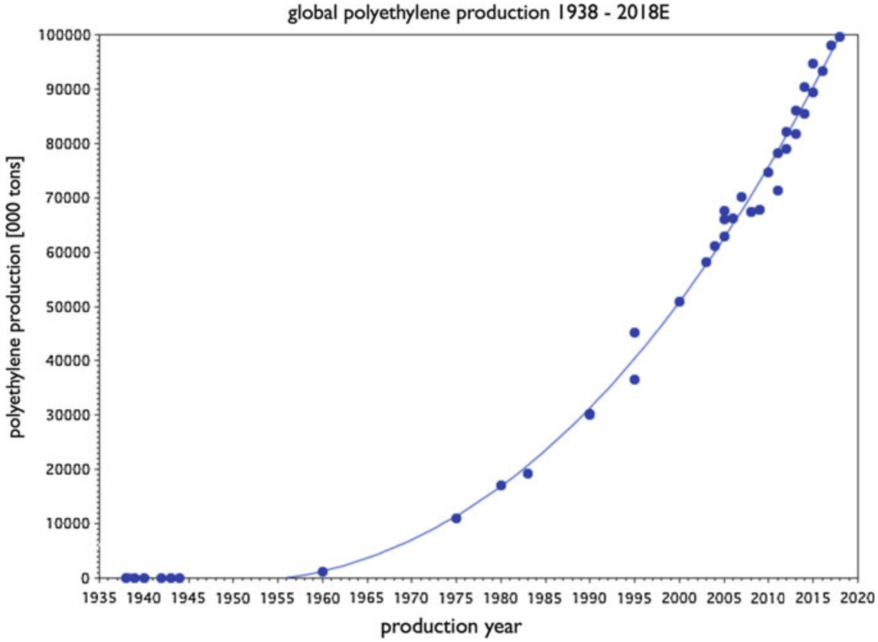
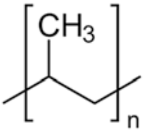


Fig. 2.3 Global polyethylene production up to 2018 (data compiled from various private and open sources)

2.8 Polypropylene (PP)

We may argue but concede that LPDE, HDPE, and LLDPE are three different kinds of polymer, albeit starting from a common monomer.



Polypropylene

This makes **polypropylene** (PP) the world's largest polymer.

Whatever our stance on this analysis, we see that polypropylene, although a comparative latecomer to the polyolefin "game", is becoming the star.

From invention in 1953 and commercialization in 1957, it has become an industry of (2018 estimate) 86 million tons (27 % of the worldwide plastic market) with a value of over $135 billion.

On the same scale as the PE growth curve just above, Fig. 2.4 shows the PP production since invention, similarly using all data available from various sources.

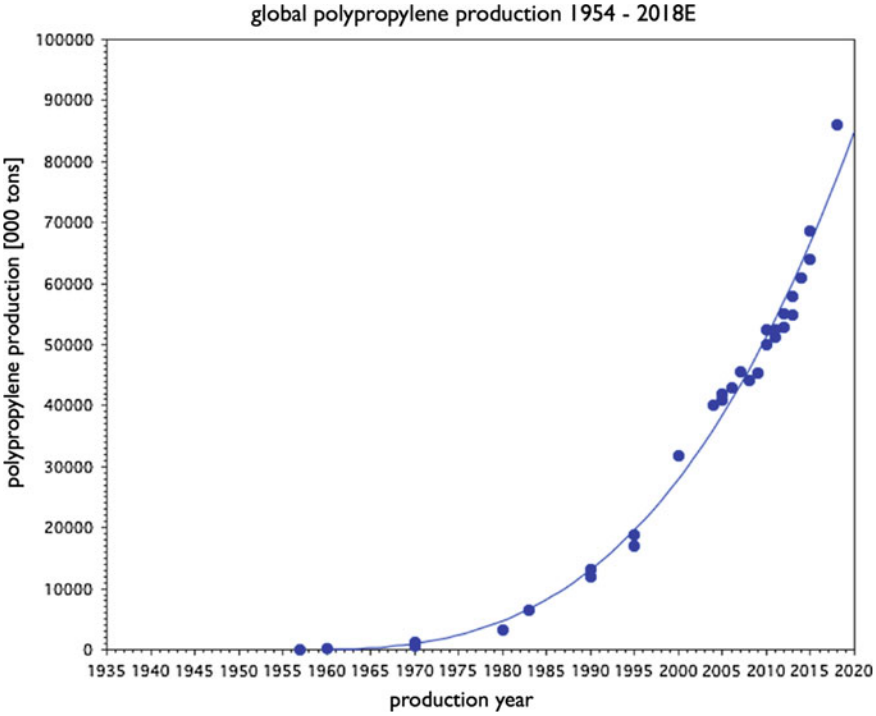


Fig. 2.4 Global polypropylene production up to 2018 (data compiled from various private and open sources)

Extrapolating, noting the faster rate of growth, we might not be surprised to find that in a decade, PP will be as big as the total PE segment.

The polypropylene story is both similar and quite different from the polyethylene story.

Let us firstly follow the strict chronology of the discoveries of crystalline polypropylene.

2.8.1 Standard Oil of Indiana

Alex Zletz noted in his laboratory journal on 18 July 1950 the suggestion that the molybdenum catalyst could be used for the polymerization of propylene. He and other colleagues carried out various experiments with propylene polymerization until July 1953, but they were not accepted as proof of priority, because later the judge ruled that “since neither the making of the product had been adequately described, nor had the product been recognized or a utility therefore been given”. The economic impact of this decision is significant and provides a salutary lesson to those designing experiments, characterizing and reporting the outcomes, and making laboratory notebook entries. The judgment is based on the US law, which provides that three criteria must be met when determining prior inventorship (priority), criteria which are also internationally respected:

(1) Production of a composition of matter satisfying the limitation of the count.
(2) Recognition of the composition of matter; and
(3) Recognition of a specific practical utility for the composition.

2.8.2 Phillips Petroleum

As we saw previously, polypropylene was first made in June 1951, unintentionally as a solid polymer, by Phillips Petroleum, who were at that time seeking to convert excess refinery gases, ethylene and propylene, to high-octane fuel. Phillips developed their chromium olefin polymerization catalyst for linear polyethylene[10], but in fact, Phillips never entered the polypropylene manufacturing business. Paul Hogan and Robert Banks recorded the invention of the process by which they produced crystalline polypropylene about an hour after their discovery. As we shall see in more detail below, their January 1953 patent application was issued[11] in March 1983 (32 years after their discovery) [11].

---

[10] Source: US Patent 2825721.

[11] Source: US Patent 4376851.

2.8.3 *Natta*

Dr. Giulio Natta was a professor at the Polytechnic Institute in Milan, who worked closely with the Montecatini Company, from where he sourced most of his research staff. In 1952, at Achema in Frankfurt, he heard Karl Ziegler lecture on the polymerization of ethylene. He immediately invited Ziegler to visit Milan, at Montecatini's expense. One outcome of this visit was an agreement for the scientific exchange of information between Ziegler and Natta, which enabled three Montecatini scientists, already assigned to Natta, to work at Ziegler's Institute. There in late 1953, they learnt about the synthesis of linear polyethylene by Ziegler, and Natta asked his research group in Milan to attempt the polymerization of propylene using "Ziegler catalysts" (so entitled by Natta). Based on experiments by Paolo Chini on 11 March 1954, Natta wrote in his own notebook "today we made polypropylene". In a subsequent visit to Ziegler (May 1954), Natta asked and persisted with the question about polymerising propylene. Ziegler said he had tried it, but "es geht nichts" (it does not work). Natta was now sure that his process was "new", and he filed Italian process and polymer patents on 8 June and 27 July 1954, respectively.

2.8.4 *Hoechst*

Hoechst was an early Ziegler licensee for linear polyethylene. Dr. Rehn, a research chemist at Hoechst, succeeded in making polypropylene using a Ziegler catalyst in March 1954. No patent was applied for, out of respect for Dr. Ziegler's research area.

2.8.5 *Ziegler*

On 27 October 1953, the day after his successful PE polymerization with zirconium, Heinz Breil also investigated propylene, but concluded "propylene cannot be converted into high molecular weight polypropylene". In June 1954, Heinz Martin used new reactors to polymerize propylene to high molecular weight in good yield and demonstrated that both pure propylene and 1-butene could be easily polymerized by the new catalysts. A sixth patent was therefore submitted 3 August 1954, extending the scope to α-olefins such as propylene and 1-butene.

2.8.6 *PCL*

Petrochemicals Ltd., in England, were Ziegler polyethylene licensees who operated a sizeable pilot plant making polyethylene. One day in 1954, just as they were ready to run the pilot plant, the ethylene line failed, and the technologist Bernard Wright decided to try propylene instead. It worked. Because of the understanding with Ziegler, that this was Dr Ziegler's research area, PCL – like Hoechst above – did not even consider patenting or publishing the result. Nor did they even inform Ziegler, who himself had just made polypropylene.

2.8.7 DuPont

Following the bold statement by Frank Gresham (mentioned previously), Stamatoff and Baxter conducted a series of experiments at DuPont, from April through August of 1954, using different catalysts for both ethylene and propylene. A large number of these experiments yielded either no polymer at all or liquid polymers (oils) only. In some cases, minute quantities of solid polymer were formed. On 21 May 1954, Baxter had converted propylene with the aid of a mixture of Grignard compounds and titanium tetrachloride, but the yield, 0.5 g of a powder, was not conclusive, even though a film was formed from this product, which was characterized as “tough and elastic”, and infrared analysis showed that it was indeed polypropylene. No evidence of crystallinity was recorded.

Later, it was a legal judgment that they “had not only failed to recognize the polypropylene product as such, but had also neglected to show any utility, as required by the rules” and that the earliest priority established by Du Pont with respect to the production of solid, crystalline polypropylene was therefore 19 August 1954. In September 1954, DuPont learned of the work of Karl Ziegler and concluded that his work was “remarkably parallel to our own”, his dates were generally earlier, and that DuPont would not dominate the Ziegler patent position. DuPont therefore paid Ziegler his customary “$50,000 to view” fee and was disappointed to find that his “process” consisted of little more than laboratory results.

2.8.8 Hercules

Hercules was one of the first Ziegler polyethylene licensees, in mid-1954. In October 1954, Edwin Vandenberg was given the assignment to do scouting work with the new Ziegler catalysts, and within a week, he had polymerized propylene with a Ziegler catalyst and had isolated an “unusual, insoluble, crystalline polymer.” As we saw previously, Hercules went on to become the world’s largest manufacturer of PP by the 1980s.

Catalyst research at Hercules led, in early 1955, to the development of improved catalysts. Vandenberg also discovered the use of hydrogen to control the molecular weight of polyolefins made with Ziegler–Natta type catalysts, which remains a principal method of molecular weight control today [23].

2.8.9 *“Interference”*

Between 1953 and 1956, five patent applications on the discovery of polypropylene had been filed at the US Patent Office (Table 2.1).

On 9 September 1958, the US Patent Office declared “interference” (a procedure carried out by US Patent law according to which the Board of Patent Appeals in the US Patent Office determines the priority of two or more inventions of identical or similar claim content with time overlap) between these five parties. Neither the parties nor the US Patent Office had considered including Karl Ziegler’s patent rights in this proceeding.

At issue was “the priority of invention of crystalline polypropylene, a plastic with considerable commercial utility and value”.

Patent Office actions and the court battle that followed lasted three decades, and produced volumes of testimony and scientific research. Indeed, the legal proceedings contained what may be the most complete scientific record of the discovery of a crystalline material. Over 1000 exhibits had been submitted and over 100 witnesses deposed in 18,000 pages of testimony by 1970. During the course of the 85-day trial conducted between 19 September 1977 and 17 May 1978, the district court received, in addition to the voluminous record compiled in the Patent Office, listed above, considerable new evidence including several thousand exhibits and the testimony of a number of experts in the area of physical and polymer chemistry.

Hercules was eliminated from the interference in 1964 by the US Patent Office because of their late discovery and patent application date. Finally (it seemed), on 29 November 1971, the board finally awarded priority of invention to the senior party, Natta et al., and US Patent No. 3,715,344 was issued to Montedison on 6 February 1973. The defeated parties then appealed the decision with a Civil Action (US District Court of the District of Delaware, Civil Action 4319). In these 1980 hearings, it was concluded that Phillips was entitled to an invention date of no later than 27 January 1953. The district court also determined that Phillips had proved that Montedison had “fraudulently withheld information from Patent Office examiners, and that this fraud was detrimental to Phillips’ case for priority of invention in the Patent Office”. However, because of the conclusion that Phillips is entitled to priority on the basis of its constructive reduction to practice, the issue of Montedison’s fraud would have no effect on Phillips’ entitlement to priority. Therefore, the court found that the crystalline polypropylene of the interference count was useful, novel, and non-obvious and therefore patentable to Phillips and

Table 2.1 PP patent filings at the US Patent Office between 1953 and 1956

Applicant	Assignee	Filing date
Natta et al.	Montedison	8 June 1954
Baxter et al.	DuPont	19 August 1954
Zletz	Standard oil	15 October 1954
Vandenberg	Hercules	7 April 1955
Hogan and banks	Philips petroleum	11 January 1956

authorized 15 March 1983 the Patent and Trademark Office to issue the patent to Phillips.[12] Phillips was able to collect $300 million in licensing revenues from polypropylene manufacturers through 1995 [24]—a considerable economic impact!

The entire story and economic impact of the ownership and licensing of polyolefin catalysts, including financial details running into millions of US dollars, have been extensively documented (297 pages) by Dr. Heinz Martin [15]. Dr. Martin mentions (p 124) that his (Max Planck) institute alone incurred expenses of more than 30 million Deutsche Marks (approximately US$ 7.5 million at the time) in the defence of its patent rights and to prosecute infringers. Even after Karl Ziegler had passed away, Dr. Martin was able to continue the patent and licensing situation in the USA, which was finally concluded after 45 years, when in 1999 a final settlement of 1.65 million US dollars was agreed with the Formosa Plastics Corp. of Texas. Among other things, they were able to compel Japanese automobile manufacturers to pay royalties for the period from 1988 to 1995, because their automobiles which were imported into the USA contained parts made of polypropylene which was produced in Japan with Ziegler catalysts!

We should perhaps note that US patent law is now internationally harmonized (since June 1995) and mandates a patent term of 20 years beginning on the date on which the application is filed, as compared to the previous "17-year term from publication, or 20 years from filing, *whichever is longer*", so such extended patent dialogues, as we have seen several examples of in this overview, with their resultant economic impact, are unlikely to be repeated.

2.9 Other Polyolefins

We have seen the development of the polyethylene industry in 80 years from 1 ton (1938) to 99.6 m tons (2018E). We saw how the original 1938 commercial polyethylene, low-density polyethylene LDPE, was complemented by the more linear, more crystalline HDPE which was discovered two decades later and then further enhanced by the reintroduction of controlled branching, through copolymerization with up to C_8 alpha-olefins, to produce still an essentially linear polymer but with short-chain branching (from the comonomer inclusion) that gave a lower density polymer, LLDPE. We will see later that this LLDPE is continuing to take share even as the total PE volume increases, approaching 1/3 of the total market of polymers made from ethylene. In parallel, we saw the development of the polypropylene sector, dominated by the Ziegler–Natta catalysis, which remains on a fast growth curve and is on track to approach the polyethylene volume within a decade.

In volume, PE and PP dominate in terms of economic impact. But they are not the entire story. We look briefly at the other polyolefins, highlighting the aspects of

---

[12] Phillips finally wins its patent—Chemical Week 23 March 1983.

their development that have special industrial application and economic or commercial impact.

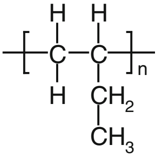
2.9.1 UHMWPE

Ultra-high molecular weight polyethylene is a linear polyethylene manufactured using a Ziegler–Natta catalyst, but with a molecular weight 10–100 times higher than conventional low-pressure polyethylene. These are very large molecules indeed: molecular weights up to 6,000,000 g/mol, a degree of polymerization of over 200,000, which means a polyethylene molecule with more than 400,000 carbon atoms in the main chain.

UHMWPE was first prepared by Karl Ziegler and commercialized as early as 1955 by Ruhrchemie AG.[13]

UHMWPE has a unique combination of properties, particularly chemical resistance, lubricity, unmatched toughness, and outstanding abrasion resistance. On account of the significant polymer entanglement due to the high molecular weight, it is not conventionally melt processible and is often fabricated by sintering (high temperature and pressure). Many industrial applications exploit the abrasion resistance of UHMWPE. A significant application, since the 1960s, when developed by Prof. (later Sir) John Charnley, has been the use of UHMWPE in hip replacements, on account of its bioinertness and outstanding abrasion resistance. This has changed the quality of life for thousands.

2.9.2 Polybutene-1



$$\left[-\mathrm{CH_2}-\mathrm{CH}(\mathrm{CH_2CH_3})- \right]_n$$

Polybutene-1, PB-1, or polybut-1-ene is another stereospecific (isotactic) polyolefin polymer, discovered by Prof. Giulio Natta in 1954. It is a linear high molecular weight crystalline thermoplastic polymer, with low density (0.91). The ethyl side groups create entanglement, which provides for the very good creep resistance of this polymer, which also has an abrasion resistance comparable to UHMWPE, and an excellent resistance to chemicals and environmental stress-cracking.

---

[13] Source: US Patent 3254070.

Polybutene was available as Vestolen BT since 1964 from Chemische Werke Hüls, who started the first industrial production in 1964 with a capacity of 3000 tpa. In 1973, Hüls withdrew Vestolen BT from the market after some manufacturing issues in their polymerization plant. Independently, Mobil Oil in the US developed their own PB-1 process technology and built a small industrial plant in Taft, Lousiana, in 1968. In the early 1970's, the plant was taken over and operated by Witco Chemical Corporation.

At the end of 1977, Shell acquired the PB-1 business from Witco, including the Taft plant. Shell then started a major investment programme to improve the product quality and to increase the production capacity to about 27,000 tpa. This Taft plant was closed in 2002, after 30 years of PB-1 production. A small Mitsui production capacity also existed in Japan. In 2004, a 45,000-tonne plant—the largest in the world—was opened by Basell in Moerdijk, the Netherlands, for less than $100 million, on the 50th anniversary of PB-1. This plant was debottlenecked in 2008 to reach a nameplate of 67,000 tpa. LyondellBasell Industries are now the primary supplier of PB-1 worldwide, claiming an 80 % market share, with Mitsui holding the balance.

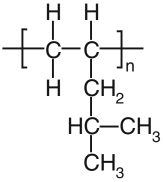
Polybutene-1 is a polyolefin with rather specialty/niche applications. A few examples are pipes for domestic and commercial hot and cold water plumbing and heating systems. Blended with PE, it forms a two-phase structure which is the basis of seal peel technology (easy-opening flexible packaging). Hot water tanks are manufactured by blow-moulding PB1.

In comparison with PE and PP, we can describe PB-1 as "a relatively unexplored polyolefin".

It remains relatively in low volume, in the scale of polyolefins that we have primarily focused on, but provides unique properties and performance, and so continues with double-digit growth.

Piping is an application example in this polyolefin industry of how legal liability has had enormous economic impact. Polybutene-1 was introduced to the European market in the 1960s, has a successful long-term record of service in pressurized hot and cold water systems, and so is widely recognized by manufacturers and installers of piping systems in Europe and Asia as the material of choice for these systems. It remains a growth area for PB1. However, polybutene piping *systems* were the subject of a large and lengthy class action legal case in the USA in the 1990s, which was actually related to the pipe connections and fittings made in acetal resin. The Polybutene Piping Systems Association (PBPSA) is focussed only on this application of PB1 and provides further detail on their Website www.pbpsa.com, where it is explained clearly that "in view of the outcome of the previous US litigation process", PB1 is not promoted (by PBPSA members) for this application in North America (in spite of historically proven intrinsic suitability).

2.9.3 TPX®



TPX® is the trade name for the polyolefin poly 4-methyl pent-1-ene.

It was originally manufactured by ICI. In 1975, Mitsui took over the entire business from ICI and the technology from BP to make the monomer. It is made solely by Mitsui today. In November 2003, Mitsui increased the annual production capacity of TPX® at Iwakuni-Ohtake Works from 68,000 tons to 75,000 tons.

A polymer of 4-methyl pent-1-ene was recorded from the earliest days (1953), as an example of the use of a transition metal catalyst to polymerize olefins.[14]

We should note that 4-methyl pent-1-ene is used as a comonomer in some grades of LLDPE.

TPX has a number of unique properties and features, but it has remained a specialty engineering polymer. It has the lowest density of any plastic material 0.835 g/cm^3. Although crystalline, it is totally transparent due to the amorphous and crystalline phases having the same density. It has very low surface energy and outstanding optical and acoustic properties. A current growth area is in films. Mitsui has a separate tradename Opulent™ for films of poly 4-methyl pent-1-ene.

2.9.4 PolyDCPD

Cyclopentadiene is a major component of the C5 stream of naphtha cracking. Because it is so reactive, it exists at ambient temperature as the stable dimer, dicyclopentadiene.

This dimer is the basis of two groups of polyolefin polymers.

The first group consists of amorphous thermoplastic engineering polymers.

These are cyclic olefin polymers (COP) or cyclic olefin copolymers (COC) with ethylene. They were commercialized, for example, as Zeonex (in 1991) and Zeonar (by Zeon), as Topas (Polyplastics), Apel (Mitsui), and Arton (JSR). Topas was originally part of Ticona, before it was sold to Daicel in 2005. A Topas plant with a capacity of 30,000 tpa started up in Oberhausen, Germany, in September 2000. Until that time, world capacity from 4 pilot-scale plants was around 10,000 tpa.

---

[14] Source: US Patent 4376851 Hogan.

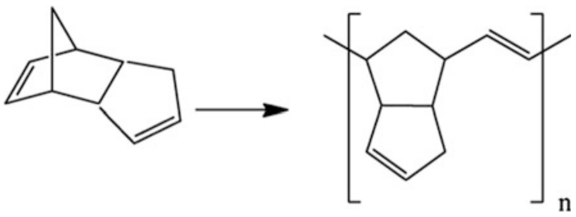


Fig. 2.5 Polymerization of DCPD into pDCPD

These cyclic olefin polymers are high-temperature (T_g up to 180 °C) polymers with good chemical resistance, outstanding optical properties, and low moisture absorption.

The early promise for COC was as a lower cost alternative to polycarbonate in optical discs, but commercialization was slow and that market has now all but disappeared.

A second group of polyolefins is made from dicyclopentadiene monomer directly, but they are thermoset polymers, processed using resin transfer moulding RTM or reaction injection moulding RIM, potentially and typically into large components in transportation (car body parts), or energy (wind turbine blades). These polyDCPD polymers are made using ring-opening metathesis polymerization (ROMP) using a Grubbs' catalyst. The process of making pDCPD is also said to be more environmentally friendly, and involving less steps, than that of making the traditional thermoset epoxy resin. Strictly speaking, they are outside the scope of this chapter, but remain a polyolefin with potential (Fig. 2.5).

2.10 The Development of the Polyolefin Industry

The economic impact of polyolefins can also be assessed by the development of the polyolefin industry—this industry is an aggregate of the companies that pioneered these materials, and the corporations that they became, or merged with. Many of the pioneering companies' names no longer exist, although new players claim their inheritance.

We have seen, as we have reviewed the development of polyethylene and polypropylene, that the commercialization, development, and manufacture of these and related polymers have involved a variety of industrial enterprises. These have been classically chemical companies (such as ICI, BASF, DuPont) diversifying into polymers; petrochemical companies moving downstream (Phillips, Standard Oil, Aramco); and other companies seeking radical diversification (W.R. Grace being an example of this, now boldly moving into polyolefin catalysts with their recent acquisition of the Unipol™ PP catalyst technology from Dow).

Over 80 years, we have seen significant activities in terms of mergers and acquisitions (M&A), asset swap, new entrants, industry consolidation, geographical diversification, the search for lower cost bases, or low-cost or available feedstock. Other drivers have been the globalization of trade and business, the opportunity to participate in emerging and fast-growing markets, as well as the globalization of industries that are primary consumers of plastics, such as the automotive (car) industry and first tier FMCG companies such as P&G and Unilever. We see examples of the drive for product diversification and portfolio extension, often followed by a focus on core business and divestment of products that are no longer part of the perceived core business strategy.

Within the scope of this chapter, it is only possible to give some selective examples of this extensive global industrial development, not to provide an exhaustive treatment, description, and analysis.

Below, we give some descriptive examples of the development of the polyolefin industry from the perspective of individual companies, some of whom have remained in polymers but have largely exited their early polyolefin activities (such as DuPont), no longer even participate in the industry of which they were an early member (such as Hoechst AG or Monsanto, which went on to become a life science or agricultural company, respectively) or were a founding member, but no longer even exist (ICI being a prime example).

Anyone entering the polyolefin industry today, and seeing the major players of today, would be unaware of the trauma and change that this industry has seen, particularly in the last 30 years.

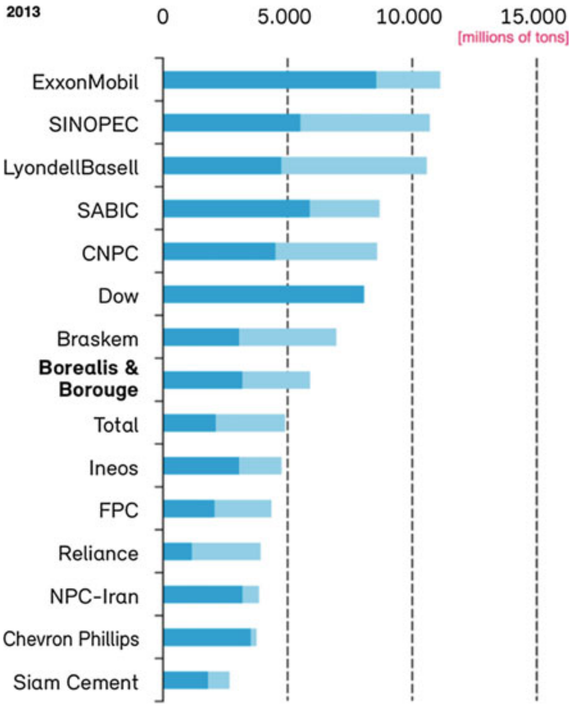
One way to describe the polyolefin industry today is to look at the main polyolefin producers. The (2013) Fig. 2.6 shows the top 15 polyolefin producers in the world.

By "recognizable name", only two of the early players in the polyolefin industry are listed: ExxonMobil—formerly Exxon, previously Esso, previously Standard Oil (S.O.)—at the head of the list; and Chevron Phillips, which was formed 1 July 2000 by merging the chemical operations of Phillips Petroleum Company and Chevron Corporation. Dow Chemical purchased Union Carbide Corporation for $9.3bn in 2001 and through that acquisition can claim to have been an early participant in this polyolefin industry (recalling that Union Carbide was rapidly developing ICI low-density polyethylene plants during WWII under sub-licence from DuPont).

LyondellBasell, the third largest polyolefin company in the world, has accumulated a rich heritage from the polyolefin industry through a complex history, and moreover, its formation from Basell and Lyondell in 2007 is one of the industrial deals that has made considerable economic impact. We briefly trace the Lyondell and Basell streams from the earliest days and then look at the trauma of formation, bankruptcy, and emergence as a major high-performing polyolefin producer. Figure 2.7 attempts to capture the history and ancestry and mergers related to LyondellBasell in one image.

We can start one thread in 1955, when the Texas Butadiene and Chemical Corporation bought the Lyondell Country Club in Channelview, Texas, and built a plant on that site. Sinclair Petrochemicals then purchased the Channelview site in 1962. Atlantic Refining Company and Richfield Oil Corporation formed Atlantic Richfield (ARCO) in 1966, which merged in 1969 with Sinclair, so the Channelview

Fig. 2.6 Top 15 polyolefin producers in the world



plant then became a part of ARCO Chemical Company [25]. In 1985, Atlantic Richfield Company (ARCO) separated its olefins operations from ARCO Chemical Company, forming a new subsidiary, finally renamed Lyondell Petrochemical Company, 50 % of which was sold to the public in a $1.4 billion IPO in 1989 [26].

The next year, 1990, Lyondell purchased, from the Rexene Products Company, the low-density polyethylene and polypropylene plants built in Bayport, Texas, by El Paso Products Company in the 1970s. In 1995, the Alathon® HDPE business was acquired from Occidental Chemical Corporation for $356 million. In 1997, Lyondell combined its petrochemical and polymer businesses with those of Millennium Chemicals (which itself had recently been formed from the Quantum Chemical Company, which had been the largest producer of polyethylene in the USA) to form Equistar Chemicals as a joint venture. Occidental Chemical's petrochemical business became the third part of Equistar in 1998.

As a result of the merger, Equistar controlled $7 billion in assets with *pro forma* sales in 1997 of $6 billion. It was now North America's largest olefins producer and the second largest in the world. Lyondell acquired ARCO Chemical in 1998 for $5.6 billion, and the company changed its name to Lyondell Chemical Company. Lyondell bought the Occidental Stake in Equistar in a $400 m stock deal in 2002, and in 2004, Lyondell acquired Millennium, thus gaining 100 % ownership of Equistar.

Three tributaries flow into the Basell stream. We should perhaps start with Montecatini, to whom Natta assigned his PP patents, Montecatini merged with

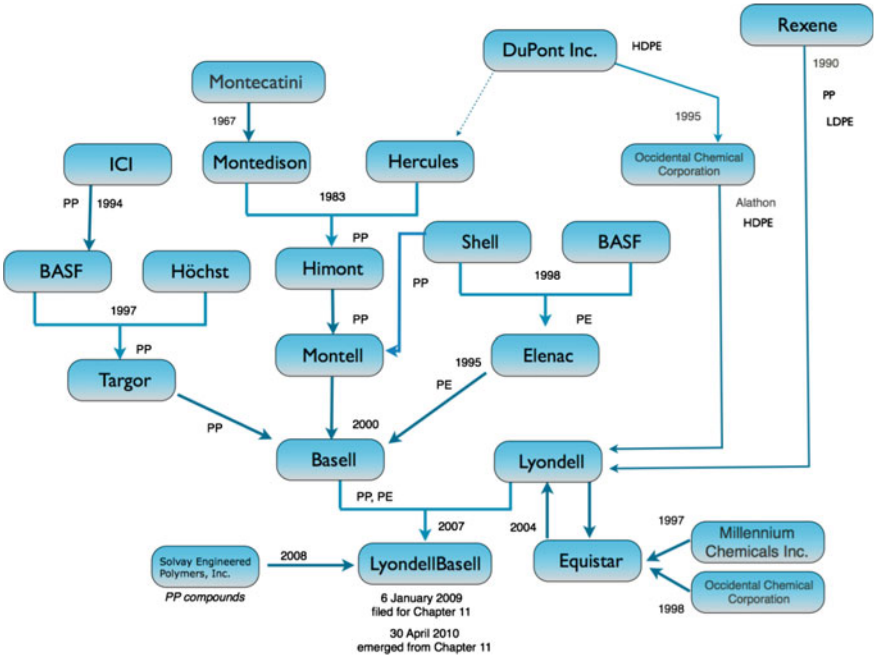


Fig. 2.7 The historical development of LyondellBasell

Edison and became Montedison in 1967. Hercules Powder Company merged their PP interests with Montedison in 1983, to form Himont, which later merged with the PP interests of Shell in 1995 to form Montell.

The second tributary is the PP thread from the early days of polypropylene at BASF, and the 1994 acquisition by BASF of the 300,000-ton PP business from ICI (who had already exited PE in 1982, when it swapped its PE business for the PVC business of BP), which acquisition doubled the size of the BASF PP business to 600,000 t. BASF merged their PP business with that of Hoechst in a venture called Targor, in 1997.

A third tributary is the polyethylene business Elenac, formed in 1998 by the merger of the polyethylene interests of BASF and Shell.

These three—Montell, Targor, and Elenac—came together as the Dutch-based company Basell in 2000. Basell was then the world's largest polypropylene maker, with 7.8 million tons of annual capacity, and the largest polyethylene producer in Europe. Basell was also a world leader in polypropylene licensing; 40 % of installed capacity worldwide used Basell technologies, such as Spheripol.

Basell lost money in two of its first three years of operation, but in 2004, generated profits of about $175 million on sales of $8.2 billion.

In late 2005, Access Industries, a privately held industrial group founded and led by Ukrainian-born, Harvard-educated financier Len Blavatnik, purchased Basell in a $5.4 billion 80 % leveraged buyout, putting down $1.1 billion in the deal. This was the largest leveraged buyout that the chemical industry had seen. Over the two years from acquisition until December 2007, $463 million of cash was withdrawn from Basell in the form of dividends and management fees.

In 2006, Basell was the world's largest producer of polypropylene and of polyethylene, and a global leader in the development and licensing of polypropylene and polyethylene processes, and catalysts.

The next stage is what has become known as "The Lyondell Play". In July 2007, Blavatnik proposed to acquire Lyondell at $48 per share, a 45 % premium on the share price on 16 July 2007. Including the $12.2 billion to purchase these shares, a total funding of $21bn was required. Pursuant to the merger agreement, on 20 December 2007, LyondellBasell Industries (LBI), the third largest chemical company in the world, were formed by this merger of Basell and Lyondell.

In 2008, the revenue of LBI was $50.710bn with an EBITDA of $3.398bn.

It was the merger timing that was unfortunate—LBI had an enormous debt ($23.6bn), at a time when the Lehman Brothers collapse in September 2008 was precipitating a global financial crisis. Because some of the debt was asset-backed, eroding inventory values resulted in a severely diminished borrowing base and triggered LBI's obligation to repay the lenders. Lack of liquidity meant that repayments were increasingly difficult, and LyondellBasell filed for Chap. 11 bankruptcy protection on 6 January 2009.

Chapter 11 enabled a "fresh start" for LBI on many fronts, and LBI was able to exit from Chap. 11 on 30 April 2010 with a "favourable capital structure".

LBI was also well placed to benefit from the emergence of low-cost shale gas (ethane) at that time, to feed the six crackers it had in the USA. They were converted for minimal capital investment, to be able to run 90 % of the time on ethane.

Quickly recognizing and taking advantage of this new feedstock opportunity significantly improved margins and profitability, such that other investors are challenging companies like Dow, asking why they are not performing as well as LBI.

LyondellBasell was listed on the New York Stock Exchange starting 14 October 2010, opening around $27. In September 2014, a peak of $115.40 was achieved.

Figure 2.7 shows the polyolefin thread of the historical development of LyondellBasell.

2.10.1 *The Development of the Polyolefin Industry in the Gulf Cooperation Council (GCC)*

We have looked in some detail at how the polyolefin industry has developed from those who originated it. We now turn to the GCC region, which has developed a polyolefin industry from nothing in the last 20 or 30 years. There is a major polyolefin industry in Saudi Arabia, but within the constraints of this chapter, we have selected two examples, and for each, we illustrate the progress and status through a chart similar to the one we prepared for LyondellBasell Industries. The first is Qatar, the first GCC country to have a polyolefin industry. The second is the

UAE, where the sovereign wealth fund has acted strategically and boldly, and has created a polyolefin group with global and regional impact.

2.10.2 Qatar

The State of Qatar was the first GCC state to have a polyolefin industry. The first production of polyolefin in the GCC was an LDPE plant inaugurated by QAPCO in 1981. In Fig. 2.8, we attempt to show in one image the historical development and ownership of this polyethylene industry. The strong French partnership is evident. The outcome, after 35 years, is the emergence of a major plant for each major kind of polyethylene.

2.10.3 The United Arab Emirates (UAE)

The International Petroleum Investment Company (IPIC) is the long-term strategic investment arm of the government of Abu Dhabi, established by the visionary Sheikh Zayed 30 years ago. In the last 20 years, IPIC has purchased, developed,

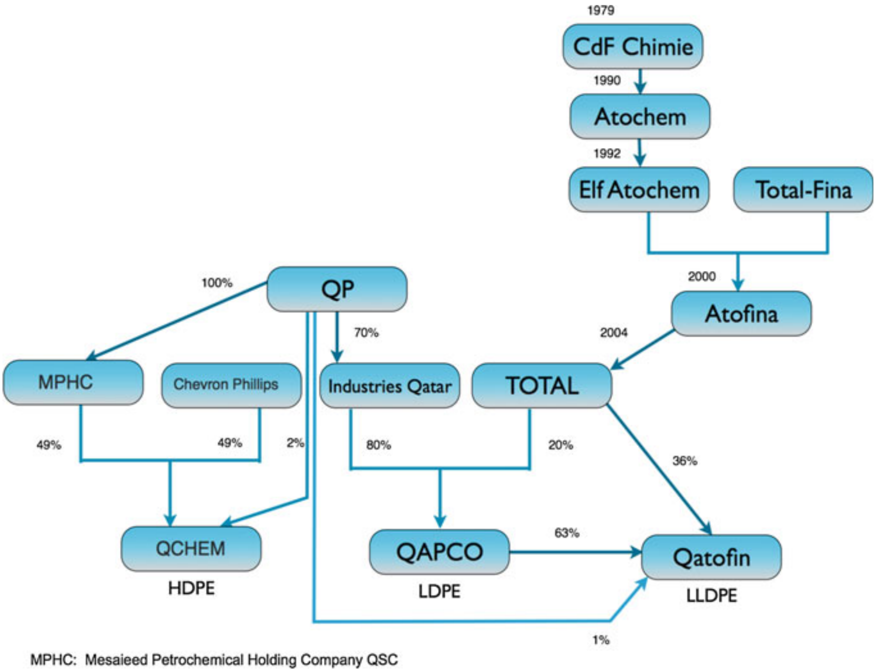


Fig. 2.8 Development of the polyolefin industry in the State of Qatar

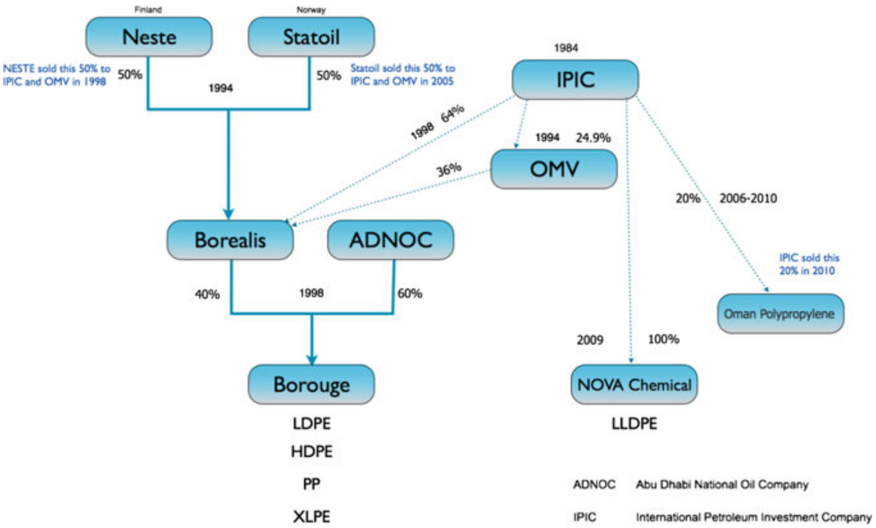


Fig. 2.9 Development of the polyolefin industry in the UAE

and nurtured a portfolio of companies in the polyolefin industry. Today, the IPC portfolio consists of Nova Chemicals, Borealis, and Borouge. Little effort seems to have been made in the 5 years since acquiring Nova to integrate it within the Borealis/Borouge sphere, or develop any synergy between these three companies (Fig. 2.9).

2.11 Industrial Economic Impact

We have seen how the economic impact of polyolefins can be assessed by the development of the polyolefin industry, in terms of company development and merger and acquisition activity. Numerous M&A transactions have cumulatively resulted—from the time perspective of decades—a radical transformation and reshaping of the industry.

One characteristic of the polyolefin industry is that it is capital-intensive. This is a dimension of economic impact—the amount of money to be invested to create this industry. Unlike the downstream polymer processing and converting industry (where the classical start-up might be imagined as one small moulding machine in a garage), even the smallest polyolefin manufacturing process (the Hüls PB-1 plant at start-up was just 3000 tons per annum) involves capital investment in the order of millions of dollars.

World-scale plants today for PE and PP are very much bigger than when the industry started, of course, by more than three orders of magnitude. Recall that the earliest ICI LDPE plants were 100 tons per annum! The first 1957 polypropylene plant was 6000 tons per annum. By 1965, typical new polyolefin plant capacities were 10,000 tons per annum; in the early 1970s, around 25,000 tons per annum, and by 1985, we were at 80,000 tons. By 1990, 100,000 tons per annum was the norm, increasing to 300,000 tons by 2000. The newest plants being built now are more than 450,000 and up to 750,000 tons per annum.

Despite these changes in production capacity, the *basic* process for making polyolefins has really changed little since 1960 [27]. What has happened is that the cost per unit of output has been reduced through the massive increase in the scale of the plant. In addition, improvements in process, process control and automation, process equipment, and catalyst technology have all contributed to lower polymer conversion cost, and improved and more consistent product quality.

In spite of significant capital investment (we now need to think in the investment range of $500–1000 million per world-scale state-of-the-art plant), these highly automated plants provide only minimal employment opportunities. They offer interesting, challenging, demanding, and well-paid positions, but relatively few of them, and only for appropriately qualified and experienced professionals. The polymers, if converted locally, provide many further opportunities for employment, so that the plant and its downstream value chains make a significant contribution to the local economy, whether through local consumption or for export.

How many of these polyolefin production plants have been installed since the beginning of this industry? One way to develop the answer to this question, which we do not pursue in depth here, is to follow the technology licensors. For example, we know that ICI were active in licensing LDPE and that by 1977, they had 23 licensees, and a total installed capacity of 812,000 tons. However, their founding technology was based on the stirred tank reactor (autoclave), and this could not be scaled up in the same way that tubular reactors, developed by others, could. By 1980, ICI had lost the "first producer advantage", had not led the way in technology development, and in 1982, exited the PE business.

It is estimated (GEM-CHEM) that there are 170 polypropylene sites and 376 polyethylene plants, worldwide. We have seen above that the additional polyolefins (polybutene-1, TPX, pDCPD) are made in only a handful of plants around the world, so it is likely that there are over 500 plant sites around the world producing polyolefins.

2.12 Globalization, Feedstocks, and Feedstock Availability

The synthetic polymer industry started in 1910 when the thermoset moulding resin Bakelite® was commercialized and has become a global industry in the intervening 100+ years. The synthetic thermoplastic polymer industry started in Europe and developed in Europe and the Americas and Japan. Then, there was a shift of production and consumption to Asia-Pacific, particularly China, and a shift in production to the Middle East, in the last 30 years. The polyolefin industry has perhaps even led this shift. Five of the major polyolefin producers (in the list of the top 15, we saw previously) are from Asia-Pacific, and three of them are based in the Middle East. That is a radical reshaping of the industry. This globalization is an irreversible process.

The shift to Asia is now supported by local regional demand, not just driven by the availability and low cost of labour, so we do not expect to see anything but an increasing demand from this region, as the per capita income increases, the middle class develops, and consumer expectations increase in these populous nations. China became the world's largest market for polymers as far back as 2002 and as of 2013 has a share of 30 %, compared with just 6 % back in 1983. The rest of Asia-Pacific accounts for another 15 %.

However, the shift of production to the Middle East was driven almost entirely by the availability of abundant and low-cost feedstock and investment capital, supplemented to a small extent by low-cost energy, but not by regional demand. The Middle East industries are still primarily export driven. Now that hydrocarbon feedstocks are less available in the Middle East, the capital will in future seek out alternative feedstocks based on cost and availability.

We see two feedstock factors already at play. First, we saw how the availability of low-cost ethane (shale gas) dramatically improved the economic performance of LBI after emerging from Chap. 11. We did not so far discuss Ineos, but they were, at a similar time, also heading for financial difficulties, after their $9bn acquisition of Innovene, which immediately resulted in a downgrading of their credit rating because of the leverage. Shale gas was also their saviour. It is clear that the availability and low cost (not as low cost as the Middle East, but 1/3 or 1/4 of what it was in North America not so long ago) of feedstock are drawing investment and have led to some moth-balled crackers being returned to operation. That story has only just begun and may soon build a momentum and investment direction for the next decade.

The second feedstock factor is the use of coal in China. The quantity is vast and the cost is low, both of these positive factors being offset by logistics (it is stranded coal) and concern about the quality of both the feedstock and the impact of the low quality on the environment. Oil has been the feedstock of choice for most of the world since WWII or earlier, except for a few countries, notably South Africa where political factors forced the development of an entire chemical industry based on coal. It has been remarkable to see the development of a chemical industry in China based on coal in perhaps just 10 or 15 years. "Coal to olefins" (CTO) is a reality there. Synthesis gas is produced from coal and then used to make methanol, which is then converted to olefins (ethylene or propylene). Coal to olefins is happening fast in China, it is happening widely (over three dozen projects are described), and it is likely to be as significant or more significant than the North American shale gas phenomenon.

Both of these trends— shale gas and coal to olefins—will likely be impacted by the recent (2014) drop in oil price from over $100/barrel, down to (almost) $45/barrel. Such very low oil prices make shale oil, shale gas, and deep sea drilling less attractive or even uneconomic.

Other feedstocks are there. Some polyethylene is made now in Brazil from ethylene made from ethanol from sugar cane. That is marketed and touted as though it is a revolutionary step forward. In fact, it is just returning to the roots, but perhaps that is unknown to many. The very first polyethylene made at ICI in 1933 was made from ethylene that was made by dehydrating ethanol produced by the fermentation of molasses. The tar sands continue to be an alternative hydrocarbon source, even if it is not daily in the headlines. Almost no one is looking at the 20 gigatons of methane hydrate in the oceans or tundra.

Although it is said (for example in Saudi Arabia) that there is no natural gas available anymore, that is, at best, an inaccuracy. The fact is about 3/4 of the natural gas available in Saudi Arabia is burnt in power stations, rather than turned into valuable petrochemical feedstocks and specialty materials. The industry needs the critical feedstock for growth, and if the feedstock is not available in adequate quantities, investors will take that industry to an available feedstock source.

2.13 The Future of the Polyolefin Industry

From the materials point of view, we have clearly seen that both the total polyethylene and the polypropylene industries are still on an ascending curve, far away it seems from a plateau in terms of growth. This is clear from production forecast data in Figs. 2.2 and 2.3 discussed earlier in this chapter.

Indeed, it seems that PP, even as the latecomer, may be developing more rapidly, and we suggested that in perhaps another decade, we might see both industries of a similar size.

By then, we will have a polyolefin industry of over 200 million tons and a value above $250 billion.

The profile of the polyethylene industry itself is likely to change, in line with trends that are well developed. LLDPE continues to take share, whilst LDPE still

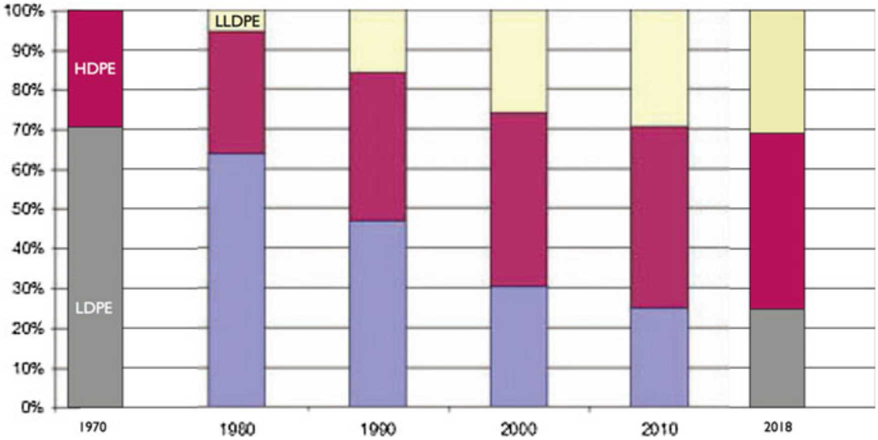


Fig. 2.10 Evolution of the polyethylene industry by PE type up to 2018

continues to grow absolutely albeit slowly from a large base. The evolution of the polyethylene industry from 1970 with an estimate forward to 2018 is shown in Fig. 2.10.

We expect that by the end of this decade, LLDPE may comprise fully 1/3 of the PE industry.

2.14 Concluding Remarks

We have considered the historical development of polyolefin polymers, looking in some detail at those who were at the forefront of this industry—some by purpose and intent, quite a number by serendipity and chance. We have explored some examples of how companies and countries have developed their polyolefin position and heritage.

We noted that the polyolefin industry developed at the same time and in parallel with the scientific recognition of polymers as giant molecules. We identified early on what have become important drivers to this day for the growth of the polymer and polyolefin industry—such themes as materials substitution; such activities as product and application development, achieved through understanding customer needs as well as the properties, processing and economics of the polymers.

We touched on various aspects of intellectual property such as patents and licensing, and how they determined the development and more importantly ownership of the new technologies.

Globalization and changes in geographical and regional importance were identified. Feedstocks—changes in the variety, the availability, and the economics—were found to be remain a fundamental driver for the polyolefin industry, and we noted that we are at several critical junctures on this topic, as we write.

The polyolefin industry is capital-intensive, for building plants, developing and upgrading them, and for investment in research, technology, and innovation for a competitive future. This industry itself provides promising and challenging careers and employment opportunities, and the associated downstream value chain—polymer conversion and processing—provides additional and more numerous employment opportunities.

Polyolefins have had a great economic and global impact as was demonstrated in this chapter. They continue on a strong growth curve, and we expect that they will have even a greater impact in the future. We concur with this statement:

> Polyolefins are indispensable in our daily lives (Borealis 2014)

We trust that you have seen and observed that polyolefin polymers are indeed now ubiquitous and indispensable in every aspect of our lives, and we hope that you have enjoyed this unique and unusual journey with us, as we have illustrated the development and economic impact of this vast polyolefin industry from its inception about 80 years ago, as much as we have been enriched as we have developed it for you.

List of Patents Referenced in the Chapter

US Patent 2816883
Product and process of polymerizing ethylene
Arthur W. Larcher and Donald C. Pease
E. I. du Pont de Nemours & Co., Inc.
Filed 2 August 1951, Published 17 December 1957
Continuation-in-part of application 739,264, filed 3 April 1947

US Patent 2153553
Polymerization of olefins
Eric William Fawcett, Reginald Oswald Gibson, Michael Willcox Perrin
ICI Limited
Priority date 4 February 1936, Published 11 April 1939

US Patent 4076698
for what we now call LLDPE
Arthur William Anderson, Gelu Stoeff Stamatoff
DuPont
Filed 4 January 1957, Published 28 February 1978
Continuation-in-part of application 568,707, filed 1 March 1956

US Patent 3012023
Production of Oleﬂn Polymers
John Macmillan Bruce, Nicholas George Merckling, William Lawrence Truett, Arthur William Anderson
E. I. du Pont de Nemours and Company
Filed 25 January 1955, Published 5 December 1961

US Patent 3541074
Olefin polymerization catalysts comprising divalent titanium and process for polymerization of ethylene therewith
Arthur William Anderson, John Macmillan Bruce Jr, Nicholas George Merckling, William Lawrence Truett
I. du Pont de Nemours and Company
Filed 16 August 1954, Published 17 November 1970

US Patent 2692257
Ethylene polymerization with conditioned alumina-molybdena catalysts
Alex Zletz
Standard Oil Company of Indiana
Filed 28 April 1951, Published 19 October 1954

Max Fischer, German Patent 874,215, Published 20 April 1953

US Patent 2699457
Polymerization of ethylene
Karl Ziegler, Hans-Georg Gellert
Filing date 19 June 1951, Publication date 11 January 1955

German Patent 973626
Verfahren zur Herstellung von hochmolekularen Polyäthylenen
Process for Preparing High-Molecular Polyethylenes
Karl Ziegler, Heinz Breil, Erhard Holzkamp, Heinz Martin
Filed 18 November 1953, Published 14 April 1960

US Patent 2825721
Polymers and production thereof
John Paul Hogan, Robert L. Banks
Phillips Petroleum Company
Continuation-in-part of application Serial No. 333,576, filed 27 January 1953
Publication date 4 March 1958

US Patent Application WO 9623010
The following US patents are all divisionals of that initial broad US filing.
As a result of the procedures to handle divisional cases in the US Patent Office, they all contain the same examples though the claims (which are of interest to the community of those who patent) will be different.
With some indication of the claims, the divisionals are as follows:

(a) Arthur, S. D.; Bennett, A. M. A.; Brookhart, M. S.; Coughlin, E. B.; Feldman, J.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A. U.S. Patent 5866663, Feb 2, 1999 to DuPont (Polymerizations).
(b) Brookhart, M. S.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A.; McCord, E. F.; McLain, S. J.; Tempel, D. J. U.S. Patent 5880241, May 3, 1999 to DuPont (Polymer compositions).
(c) Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; Wang, L.; Yang, Z.-Y., U.S. Patent 5880323, March 9, 1999 to DuPont (R-Olefins).
(d) Arthur, S. D.; Bennett, A. M. A.; Brookhart, M. S.; Coughlin, E. B.; Feldman, J.; Ittel, S. D.; Johnson, L. K.; Killian, C. M.; Kreutzer, K. A.; Parthasarathy, A.; Tempel, D. J. U.S. Patent 5886224, March 23, 1999 to DuPont (Ligand compositions).
(e) Arthur, S. D.; Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; McCord, E. F.; McLain, S. J. U.S. Patent 5891963, April 6, 1999 to DuPont (Copolymers)

US Patent 4376851
High density, heat resistance polypropylene
John P. Hogan, Robert L. Banks
Phillips Petroleum Company
Continuation-in-part of applications Serial No. 333,576, filed 27 January 1953
Publication date 15 March 1983

US 4342854
Solid polymers of 4-methyl-1-pentene
John P. Hogan, Robert L. Banks
Phillips Petroleum Company
Continuation-in-part of applications Serial No. 333,576, filed 27 January 1953

Publication date 3 August 1982

US Patent 3112300
Isotactic polypropylene
Natta Giulio, Pino Piero, Mazzanti Giorgio
Montecatini-Societa Generale per lIndustria Mineraria e Chimica
Priority date 8 June 1954 *on the basis of an Italian application filed on that date*
Published 26 November 1963

US Patent 3112301
Prevailingly Isotactic polypropylene
Natta Giulio, Pino Piero, Mazzanti Giorgio
Montecatini-Societa Generale per lIndustria Mineraria e Chimica
Filed 8 June 1954 *on the basis of an Italian application filed on that date*
Published 26 November 1963

US Patent 3113115
Polymerization catalyst
Ziegler Karl, Breil Heinz, Martin Heinz, Holzkamp Erhard
Priority date 19 January 1954
Published 3 December 1963

US Patent 3715344
Regular linear head-to-tail polymerizates of certain unsaturated hydrocarbons and filaments comprising said polymerizates
G Mazzanti, G Natta, P Pino
Priority date 8 June 1954
Published 6 February 1973

US Patent 2691647
Conversion of ethylene and/or propylene to solid polymers in the presence of group 6a metal oxides and alkali metals
Field Edmund, Feller Morris
Standard Oil of Indiana
Priority date 6 December 1952
Published 12 October 1954

References

1. Polyolefins Report. IHS Chemicals (2014)
2. P. Galli, J.C. Haylock, E. Albizzati, A. Denicola, High performance polyolefins: polymers engineered to meet needs of the 21st century. Macromol. Symp. **98**(1), 1309–1332 (1995)
3. Polyisobutylene: 2014 World Market Outlook and Forecast up to 2018, Research & Markets. January, 2014
4. H. Morawetz, *Polymers the Origins and Growth of a Science*. Wiley-Interscience (1985) pp. 20–132-3, ISBN 0-471-89638-1

5. M.E.P Friedrich, C.S. Marvel, J. Am. Chem. Soc. **52**, 376 (1930)
6. R.B. Seymour and T.C. Cheng, *History of Polyolefins The World's Most Widely Used Polymers*. (D Reidel Publishing Company, Dordrecht NL, 1986) ISBN-13: 978-94-010-8916-6, doi: 10.1007/978-94-009-5472-4
7. F.M. McMillan, *The Chain Straighteners, Fruitful Innovation: The Discovery of Linear and Stereo-Regular Synthetic Polymers*. (Macmillan Press, London, 1979), ISBN 0-333-25929-7
8. L. Trossarelli, V. Brunella, *Polyethylene: discovery and growth, UHMWPE Meeting* (University of Torino, Italy, 2003)
9. C. Flavell-While, Plastic Fantastic. www.tcetoday.com Nov 2011, pp. 49–50
10. M. Lauzon, PE: the resin that helped win World War II. Plastics News **19**(23), p27 (2007)
11. D.A. Hounshell, J. Smith, *Science and Corporate Strategy*: *Du Pont R&D*, *1902–1980*. (Cambridge University Press, Cambridge, 2006)
12. S. Ali, Polyolefin catalyst market overview. Catal. Rev. **27**(4), 91–6 (2014) ISSN 0898-3089
13. A. Clark, Olefin polymerization on supported chromium oxide catalysts. Catal. Rev. Sci. Eng. **3**, 145–173 (1970) doi:10.1080/01614947008076858
14. M.W. Haenel, *Historical Landmarks of Chemistry: Karl Ziegler* (Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, 2008)
15. H. Martin, *Polymers, Patents, Profits: A Classic Case Study for Patent Infighting*. (Wiley-VCH Verlag GmbH & Co. KGaA, 2007), ISBN: 9783527318094, doi: 10.1002/9783527610402
16. M. Gahleitner, W. Neissl, C. PAULIK, *Two Centuries of Polyolefins*. (Kunststoffe international, 2010), pp. 8–11
17. E. Vandenberg, *History of Polyolefins Chapter 5*. (D Reidel Publishing Company, Dordrecht NL, 1986), ISBN-13: 978-94-010-8916-6
18. W. Kaminsky, *The Discovery of Metallocene Catalysts and Their Present State of the Art, Institute for Technical and Macromolecular Chemistry*. (University of Hamburg, May 2004), doi:10.1002/pola.20292
19. A. Shamiri, M.H. Chakrabarti, S. Jahan, M.A. Hussain, W. Kaminsky, P. Aravind, W. Yehye, The influence of ziegler-natta and metallocene catalysts on polyolefin structure. Prop. Process. Ability Mater. **7**, 5069–5108 (2014). doi:10.3390/ma7075069
20. G.M. Benedikt, B.L. Goodall, *Metallocene Catalyzed Polymers: Materials, Processing and Markets*. (Cambridge University Press, Cambridge, 2008), ISBN 0080950426
21. World Polyethylene, *Demand and Sales Forecast, Market Share Market Sixe, Market Leaders* (The Freedonia Group, Report, 2014)
22. J.C. Sworen, *Modeling Linear Low Density Polyethylene: Copolymers Containing Precise Structures*, PhDDissertation, University of Florida (2004)
23. J. Karger-Kocsis, *Polypropylene: Structure, blends and Composites,* vol 1, 2, 3. (Springer Science & Business Media, 1995)
24. C.W. Adams, Allocating Patent Rights Between Earlier and Later Inventions. St. Louis U.L. J. **54**, 47–55 (2010)
25. H. Sailors, J.P. Hogan, History of polyolefins. J Macromol Sci Part A Chem **15**(7), 1377–1402 (1981). doi:10.1080/00222338108056789
26. C. Freeman, L. Soete, *The Economics of Industrial Innovation, 3rd Edition*. Routledge, Polyethylene §5.7 pp. 123–124 (1997), ISBN-10: 1855670704
27. J. Soarez, T. McKenna, *Polymer Reaction Engineering*. *"Polyolefin Reactors and Processes*". (Wiley, Hoboken, 2012) doi:10.1002/9783527646944.ch4

Chapter 3
Olefin Polymerization

Hani D. Tabba, Yousef M. Hijji and Adnan S. Abu-Surrah

3.1 Introduction

Polyolefins are among the top 10 products in chemical industry. The annual production of polyethylene (PE) and polypropylene (PP) occupies 50 % of plastic production worldwide and will be 60 % upon including polystyrene. The annual production of PE and PP is estimated to exceed 130 million tons as they are the most widely used polymers in the world. They are commonly produced using Ziegler- and chromium-based catalysts. The continued increase in global production and consumption (about 7 % annual increase) of polymeric and petrochemical materials in the last two decades has resulted in widespread academic and industrial research activities, particularly in the field of polyolefins [1, 2]. During the last few decades, development of knowledge in olefinic polymers passed through several distinct periods. This chapter will be concerned with the comprehension of the developing chemistry of olefin polymerization in some details.

3.2 Principles of Polymerization

The basic implication for occurrence of polymerization is to have a monomer capable of linking by chemical reaction. Keeping this concept into account, many polymers comprising various properties have been prepared. Addition polymerization processes can take place through more than one type of mechanism based on the initiator. In the addition polymerization, the produced polymers have identical empirical formula to that of the monomers from which they are formed.

H.D. Tabba (✉) · Y.M. Hijji · A.S. Abu-Surrah
Department of Chemistry and Earth Sciences, Qatar University, Doha, Qatar
e-mail: tabbah@qu.edu.qa

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_3

The more commonly used descriptive name "chain-growth polymerization" is given to these addition polymerization synthetic methods.

In this polymerization, chain will grow after an initiating step. As a result, a macromolecule with a reactive end-group that can be an anion, radical, or cation is formed. In the sections below, the detailed mechanism for each type of polymerization will be discussed.

3.2.1 Free Radical Mechanism

A free radical is a short-lived intermediate. It is a species possessing an unpaired electron due to deficiency of one electron and usually results from homolytic cleavage of a covalent bond or addition of radical to a multiple bond. A typical carbon radical is sp^2 hybridized with the unpaired electron in the perpendicular unhybridized p-orbital.

Radical polymerization is the most widely practiced method at the present and in the old times [3]. It is commonly adopted in polymerization of olefins because C=C bond is most susceptible to be attacked by a radical during polymerization. This would result in a new radical active center (then the process will go on and on), as demonstrated in Scheme 3.1.

With every addition of radical to an olefinic monomer, the radical active center is transferred to a newly formed chain end [3, 4].

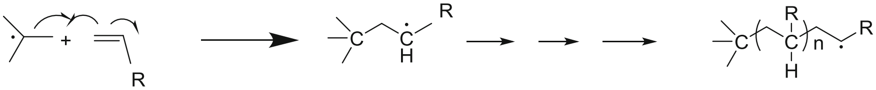
As of 1990, this conventional free radical polymerization is developed to the newer reversible deactivation radical polymerization. More details of each will be discussed here.

3.2.1.1 Mechanism of Conventional Free Radical Polymerization

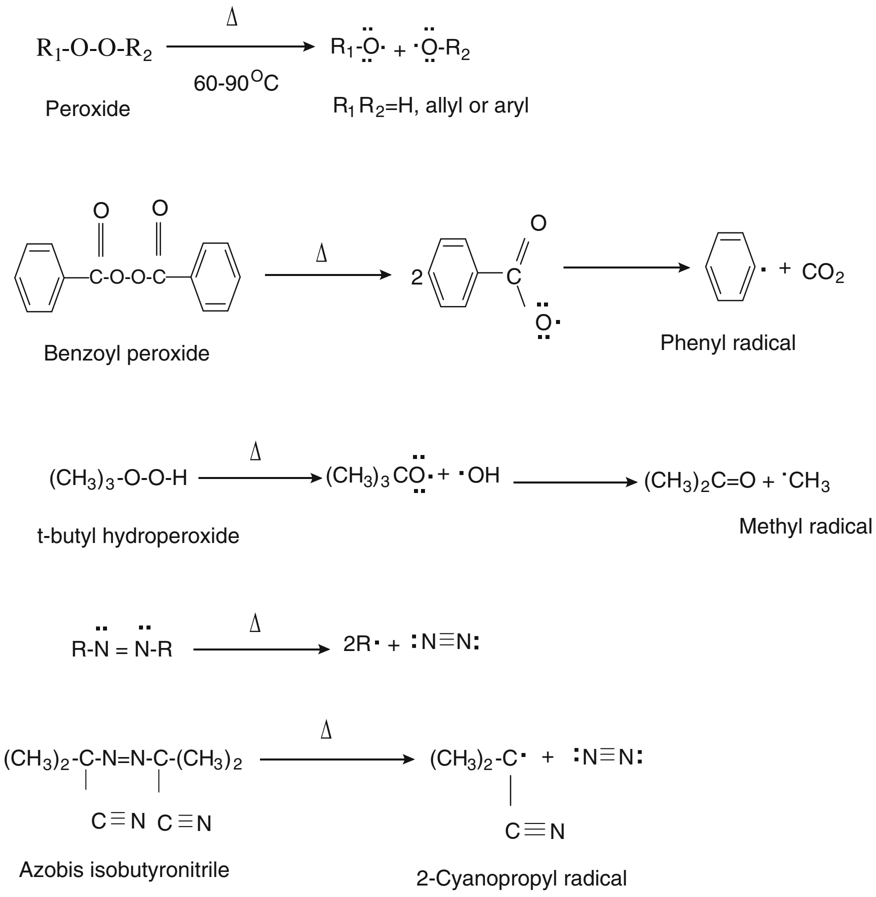
This method is divided into three distinct steps, namely initiation, propagation, and termination [5].

(A) **Initiation**

It mainly comprises the formation/creation of the free radical active center by the addition of radical initiator to the monomer molecule. The following list of reactions shows the formation method of most commonly used radical initiators.



Scheme 3.1 Free radical polymerization propagation step

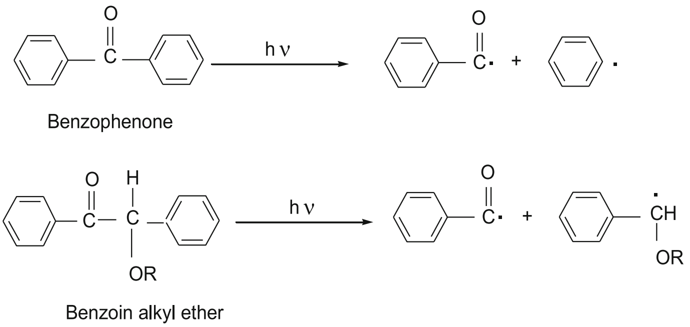


Scheme 3.2 Free radical initiators through thermal homolytic cleavage

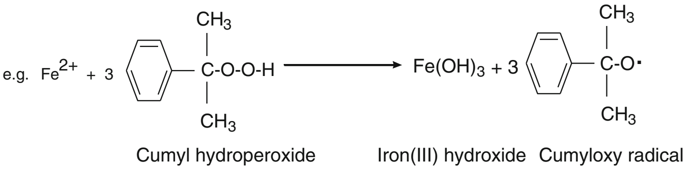
(i) **Homolysis (thermal homolytic cleavage)**
This process takes place under the influence of heat (thermolysis) or ultraviolet radiation (photolysis). The most common examples are shown in Scheme 3.2.

(ii) **Photolysis (photochemical initiators)**
Homolytic bond cleavage could be brought about through ultraviolet radiation rather than heating, and examples are shown in Scheme 3.3.

(iii) **Redox reactions (single-electron transfer)**
This process is usually adopted when heating or photolysis is not appropriate. Free radical is produced through a redox reaction including an electron transfer process (see Scheme 3.4).
Redox reactions are also observed when (Fe^{2+} or Co^{2+}) is added to peroxides or hydroperoxides.

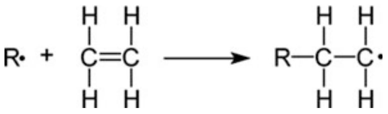


Scheme 3.3 Radical initiators produced through photolysis



Scheme 3.4 Radical initiators through single-electron transfer

The generated radical initiator now attacks the olefinic monomer so that it adds to the least hindered carbon and produces the more stable radical. Steric and mesomeric (electronic) effects contribute to location of radical addition as demonstrated in the following diagram:



$$R\cdot + H_2C{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2\cdot$$

(B) **Propagation**

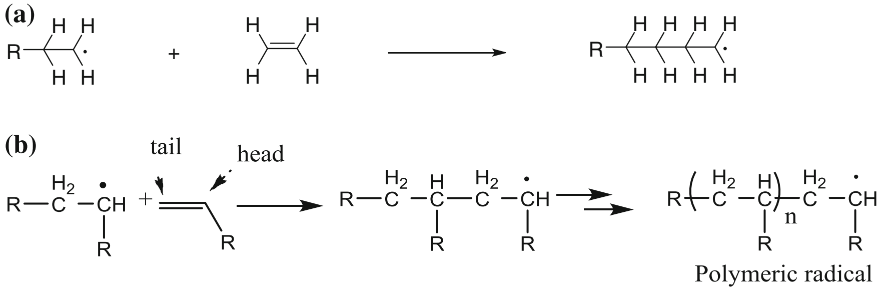
This step involves a fast sequence of monomer additions leading to molecular growth and eventually to polymer. Several thousands of monomers can be added in few seconds to ethylene (a) or higher alkenes (b) as shown in Scheme 3.5.

(C) **Termination**

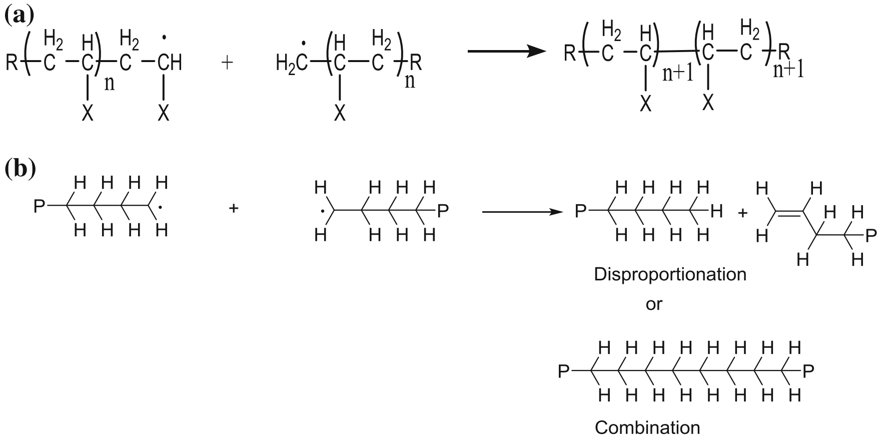
Termination process can take place via either (a) coupling of two macroradicals or (b) disproportionation reaction, thus destroying the active center. Coupling of two growing chains would lead to a single linear polymer chain both with initiator fragment and with the other chain end, as shown in Scheme 3.6.

Chain termination can also occur through chain transfer mechanisms by which the radical electron is transferred to other chain or molecule in the reaction medium.

Detailed strategies for performing industrial free radical polymerization are beyond the scope of this chapter.



Scheme 3.5 **a** Propagation of addition reaction of olefin and **b** propagation of higher olefins (R=alkyl group) head to tail addition

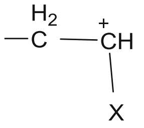


Scheme 3.6 Chain termination reactions

3.2.2 *Ionic Polymerization*

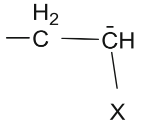
In this type, olefinic polymerization proceeds via ionic active center. Ionic active center could be cationic or anionic depending on the stabilization affected by substituent. Stabilization can take place by inductive and/or mesomeric effects.

Cationic active center will be stabilized by electron-donating substituents that delocalize positive charge, while anionic active center is favored with electron-withdrawing or electronegative substituents which delocalize negative charge as shown in the following (a) carbocationic and (b) carbanionic structures:



X = e⁻ donating

carbocation



X = e⁻ withdrawing

carbanion

Both cationic and anionic polymerization can be utilized when substituent on active center is capable of delocalizing both positive and negative charges (e.g., styrene and 1, 3-butadiene). The counterion in ionic polymerization has a significant effect on the stereochemistry of the resulting polymer.

Termination step of ionic polymerization takes place through a different path from that of radical polymerization. The following discussion will shed some light on ionic polymerization.

3.2.3 Cationic Polymerization Mechanism [6, 7]

(A) **Chain initiation**

The cationic active center will be the product of adding an electrophile to the alkylated olefin (e.g., adding H^+ from sulfuric or perchloric acid) as initiator. More commonly used initiators are Lewis acids such as $AlCl_3$, BF_3, or $SnCl_4$ which are used with water or alkyl halide.

$$H_2O + BF_3 \longrightarrow H^+(BF_3.OH)^-$$

$$R\text{-}X + AlX_3 \longrightarrow R^+AlX_4^-$$

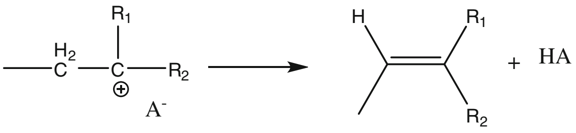
(B) **Chain propagation:**

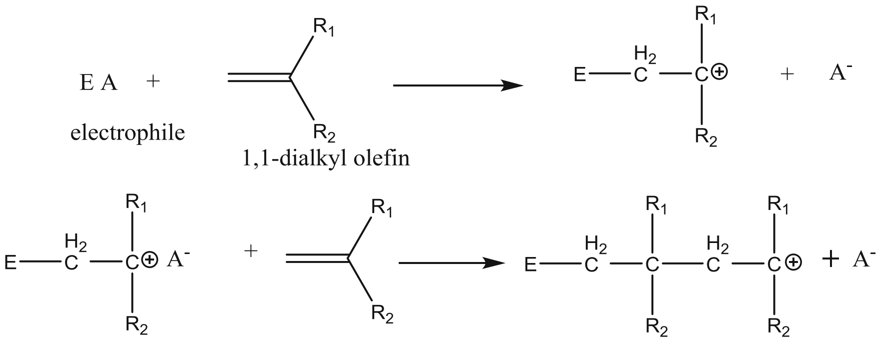
An attack on the olefinic monomer by the electrophile (H^+ or R^+) will generate the cationic active center (carbocation). The addition of the electrophile is oriented toward production of the more stable carbocation (Markovnikov orientation) as given in Scheme 3.7.

(C) **Chain termination step:**

Chain reaction termination could be accomplished by two plausible mechanisms, namely

(a) removal of vicinal hydrogen to give terminal C=C bond at the end of the polymer

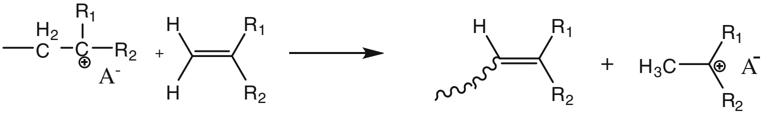




$A^- = (BF_3OH)^-$ or AlX_4^-

Scheme 3.7 Chain propagation step in cationic polymerization

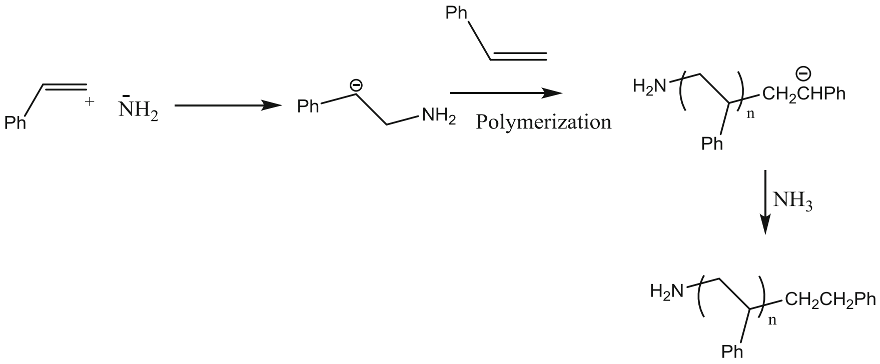
(b) chain transfer of vicinal (H^+) to a molecule of the monomer which results in the formation of monomer carbocation according to the following equation:



3.2.4 *Anionic Polymerization*

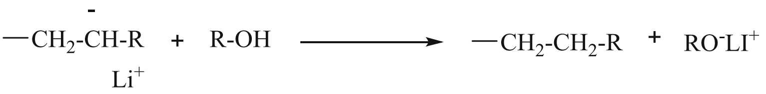
Bases were used as polymerization catalyst since early days of polymerization studies, but showed limited usefulness due to the encountered low extent of polymerization. Reaction conditions are adjusted to enhance living anionic polymerization as applied to styrene in liquid ammonia through initiation by $K^+NH_2^-$. Addition of the K^+ NH_2^- to olefinic part of the monomer generates the intermediate carbanion which propagates until termination is attained by abstraction of proton by the anion from the ammonia. If this type of termination occurred fast, then a limited polymerization process would be attained as shown in Scheme 3.8.

In the absence of ammonia, the carbanionic polymer would stay alive and will grow again if more monomer is added. Butyl lithium was also used as initiator for anionic polymerization by adding the Bu^- to the vinylic group of styrene (using THF as solvent would coordinate with Li^+ ion).



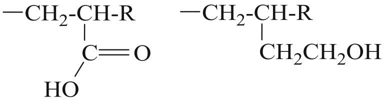
Scheme 3.8 Anionic polymerization mechanism

In the termination step, the living carbanionic polymer can be deactivated by proton abstraction from protic solvent, by which process the end of the polymer is saturated.



$$-CH_2\text{-}\overset{-}{CH}\text{-}R \quad + \quad R\text{-}OH \longrightarrow -CH_2\text{-}CH_2\text{-}R \quad + \quad RO^-LI^+$$
$$\qquad Li^+$$

Another way to deactivate carbanion is by reaction of the carbanion with carbon dioxide and dilute acid to give carboxylic terminal group or by reaction with alkene oxide (epoxide) to give a terminal alcohol.



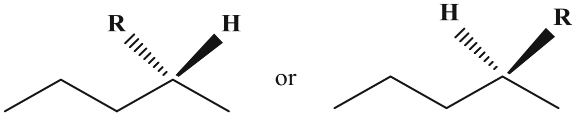
$$\begin{array}{l} -CH_2\text{-}CH\text{-}R \\ \qquad\quad | \\ \qquad\quad C{=}O \\ \qquad\ / \\ \quad HO \end{array} \qquad \begin{array}{l} -CH_2\text{-}CH\text{-}R \\ \qquad\quad | \\ \qquad\quad CH_2CH_2OH \end{array}$$

3.3 Stereochemical Implications and Tacticity

Polymerization of olefins results in the variation of geometrical and configurational arrangements (named tacticity) [8]. Having control of these arrangements is an issue of particular importance because tacticity affects the physical properties of the polymer.

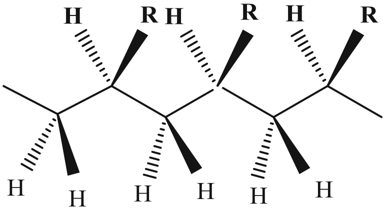
Atactic polymers are generally amorphous, soft, and flexible. Isotactic and syndiotactic polymers on the other hand are more crystalline (less flexible).

When the monomer comprises an olefinic carbon attached to two different groups (R and H), a chiral carbon will result upon polymerization. The groups R and H in the polymer can have either one of the two arrangements.

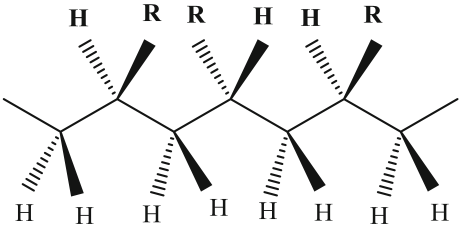


Upon polymerization, the resulting type of isomeric form (of the repeating monomer) will be important and might lead to any of the three modes of tacticity, namely

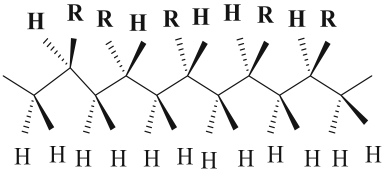
1. **Isotactic:** In this mode, all repeated units show same configuration.



2. **Syndiotactic:** Configuration of repeated units alternates between unit and the next in a synchronized manner.



3. **Atactic:** In this mode, configuration of repeated units is placed randomly (irregularly) in an unpredictable manner.



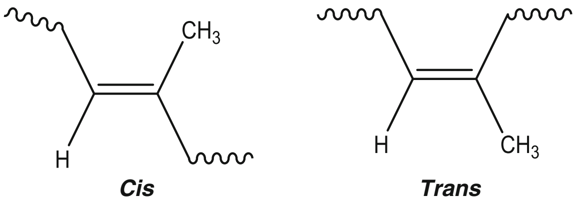
In commercial application of polymers, isotactic is the most desired mode due to its crystalline nature and good mechanical properties (e.g., propylene). The atactic analogue with its irregular structure is found as amorphous material, waxlike (not very useful mechanical properties).

When the counterion is strongly coordinating with the active center of polymer's terminal unit and the incoming monomer, isotactic polymer will be more favored. This task is hard to achieve when nonpolar monomers are incorporated. Polarity is attained when cationic or anionic polymerization mechanism is adopted. It is also useful to employ nonpolar solvent at low-temperature conditions. Polar solvents would disrupt coordination and consequently lose stereochemical control leading to syndiotactic or atactic polymer.

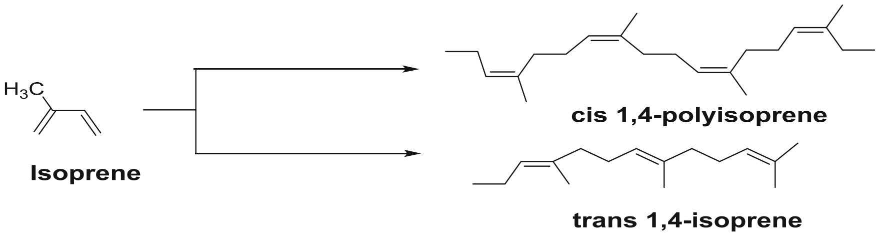
3.4 Stereo Chemistry of Conjugate Diene Polymerization

Conjugated dienes upon polymerization would result in either *cis* or *trans* isomeric polymer. One of the most important examples of this class is isoprene. Example of these isomeric polymers is shown in Scheme 3.9.

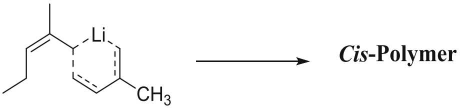
Natural polymerization of isoprene (natural rubber) produces the less symmetrical *cis* isomer as can be seen in the up- and down-orientation of the methyl group. This will result in the amorphous natural rubber. The synthetic more symmetrical *trans* isomer is a crystalline hard and rigid solid and will be obtained upon polymerization at low temperature. This transoid geometry is more stable than the cisoid due to the existence of the methyl group which facilitates the addition upon *trans* orientation.



Anionic isoprene polymerization using nonpolar solvent and Li^+ counterion leads to predomination of the *cis* polymer. This is due to the formation of the coordinated intermediate shown below:



Scheme 3.9 *Cis* and *Trans* isomeric polymers of isoprene



Coordination effect on stereochemistry of polymers inspired scientists to look for various catalysts that would result in a selected type of polymer. In the following section, the application of transition metal-based catalysts in polymerization of olefins will be demonstrated.

3.5 Coordination Polymerization

Coordination polymerization of olefins was first proposed in 1956 for the unusual, at that time, low-pressure polymerization of ethylene and polymerization of propylene with the transition metal catalysts discovered by Ziegler in 1953, and for the ferric chloride catalyzed ring-opening polymerization of propylene oxide to crystalline polymer reported by Pruitt et al. in a Dow patent. Polymerization carried out in the presence of a coordination catalyst is referred to as “coordination polymerization”. This term is used when each polymerization step involves the complexation of the monomer before its enchainment at the active site of the catalyst [9].

The majority of polyolefins is produced with titanium (Zeigler catalysts) and zirconium (metallocene catalysts) or by a free radical process (low-density polyethylene (LDPE)). Recently, late transition metals (LTMs), in particular nickel and palladium [10, 11], and iron and cobalt, are seeing a renewed interest as olefin polymerization catalysts [12, 13].

Interestingly, the discovery of methylaluminoxane (MAO) in 1980 played a crucial role in determining the course of action in polymer science [14]. This co-catalyst replaced the alkyl aluminum compounds because it acts not only as alkylating agent, but also as scavenging agent that led to a remarkable increase in the activity of the catalysts.

Unbridged metallocenes, in which the backbone of the catalyst is loosely bound, were the driving force for the development of the next generation of polymerization catalysts because of different microstructures produced due to the change in the symmetry of the active site of the metal center involved. Thus, a new horizon was born toward the synthesis of controlled microstructures.

In 1984, Ewen first reported the use of metallocene-based catalysts for the isospecific polymerization of propylene [15] and the polymerization of propylene at −45 °C using a Cp_2TiPh_2 (Fig. 3.1) and MAO. The catalyst system produced a partially isotactic polymer with a pentad content (mmmmm) of about 52 %, and a probability of finding meso dyads is $P_m = 0.85$.

Kaminsky et al. [16] reported the production of highly isotactic PP from the activated zirconium-based metallocene [ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium(IV) dichloride]; [(*ether*)$ZrCl_2$], (Fig. 3.2) MAO serves as a co-catalyst.

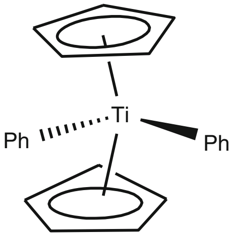
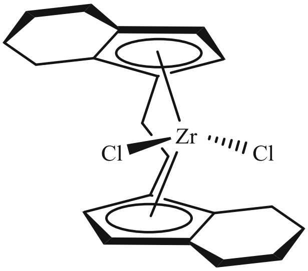


Fig. 3.1 C_{2v}-Ewen's precursor for the synthesis of partially isotactic polypropylene

Fig. 3.2 Structure of a bridged C_2-(*ebthi*) $ZrCl_2$) precatalyst



Their publication in *Angewandte chemie* can be considered as the starting point for a worldwide competition in the search for molecularly defined polymerization catalysts and for new materials [16].

MAO can form a complex with the metallocene even at −60 °C as proved by IR measurement, followed by a rapid alkylation of the transition metal center and dissociation of the complex into an ion pair (equations below). This pathway is considered as the initiation step in α-olefin polymerization with the aid of MAO [17].

$$L_2ZrCl_2 + 2MAO \rightarrow L_2Zr(CH_3)_2 + 2MAO{-}Cl$$
$$L_2Zr(CH_3)_2 + MAO \rightarrow L_2Zr(CH_3)^+ + MAO{-}CH_{3^-}$$

According to this pathway, the Cl^- or CH_3^- can be abstracted by the bulky co-catalyst MAO (Me_2AlO-$(MeAlO)_x$-$OAlMe_2$ with high molecular weight and $5 < x < 20$) or borate under the formation of the bulky co-catalyst anion and a metallocene cation with a weak back-donation. The polymerization then happens by the coordination and subsequent insertion of the olefin into the metal–carbon bond of the catalytic active species, L_2Zr-$CH2R^+$. Most conventional MAO-activated metallocenes require a large excess of MAO with [Al]/[M] molar ratios >100 in order to shift the equilibrium toward the formation of active cationic metallocenes at the expense of inactive neutral complexes.

Many new developments on the so-called constrained geometry catalyst (CGC) (Fig. 3.3) system have been reported in the patent literature and were reviewed [18].

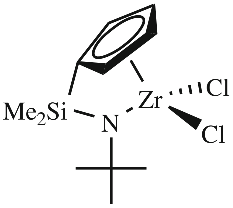


Fig. 3.3 Structure of the constrained geometry catalyst: [{(*tert*-butylamido-*N*-dimethylsilyl}-(η^5-cyclopentadienyl) zirconium (IV) dichloride]

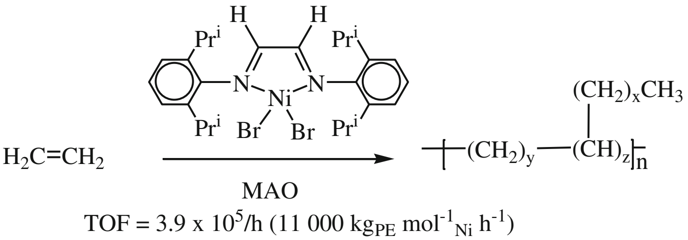
Worldwide research accomplishments on single-site metallocene-based catalysts have led to convincing improvements of poly(α-olefin) materials as well as to understanding of basic reaction mechanisms responsible for the growth of a stereoregular polymer chain at a metal center [10, 11, 16]. However, this catalyst generation allows only the use of a limited number of polar monomers bearing sterically hindered functionalities due to the sensitivity of early transition metal complexes to electron-donating functional groups [19]. Thus, copolymers of technically important polar monomers with ethylene are produced exclusively by radical polymerization routes in high-pressure processes. Therefore, there is still an unlimited interest to discover and develop new families of polymerization catalysts that can allow more control on the polymer material properties. Subsections below represent some of the most successfully applied transition metal-based polymerization catalysts.

3.6 Development of Polymerization Catalysts

3.6.1 α-Diimine-Based Catalysts

LTM-based catalysts are not as sensitive as Ziegler–Natta and metallocene catalysts to functional groups. Therefore, and because of the weak oxophilicity character, late transition metal complexes are the most attractive candidates because of their tolerance toward polar functionalities. However, until mid-1990s, only few reports were introduced utilizing these compounds as catalysts for the polymerization of α-olefins and ethylene [10, 11]. This could be due to the fact that these catalysts generally exhibit reduced activities for olefin insertion and *β*-hydride elimination, which steadily competes with chain growth resulting in the formation of oligomers.

In 1995, the quantum leap happened in the utilization of LTMs in the polymerization of ethylene, after the discovery of the α-diimines-based palladium(II) and nickel(II) catalysts (Scheme 3.10) which became the first polymerization catalysts to give high molar mass PE. This was attained by the application of sterically *o*-protected auxiliary ligands of the imino moiety, in such a way that the bulky



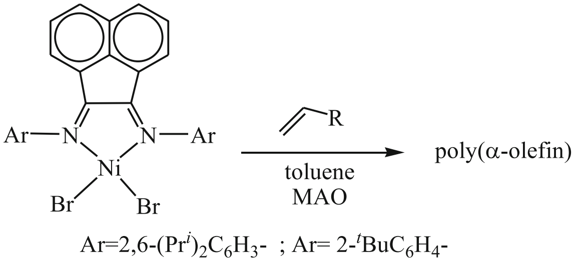
Scheme 3.10 The highly active nickel (II) α-diimine-based catalysts reported by Johnson et al. for the polymerization of ethylene

substituents on the aryl groups of the ligands block an associative olefin exchange, thus effectively retarding chain transfer processes [20].

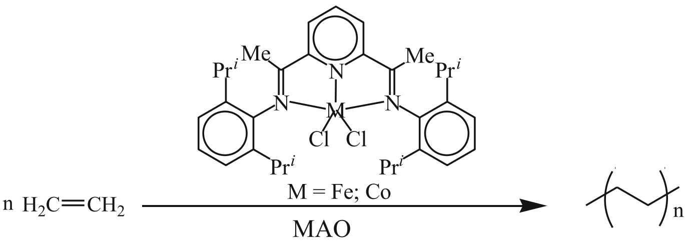
Killian et al. [21] described the well-performing α-diimine-based catalysts after the development of a procedure for the living polymerization of α-olefins based on Ni α-diimine catalysts and application of this procedure to the synthesis of diblock and triblock poly(α-olefins) (Scheme 3.11). Moreover, they found that the ratio of 1,2—versus 2,1-insertion is sensitive to the nature of the α-diimine ligand [21].

3.6.2 2,6-Bis(Imino)Pyridine-Based Catalysts

LTM complexes have attracted increasing attention [22, 23], especially after the reports of Brookhart and Gibson about new Fe (II)-based complexes containing 2,6-bis(imino) pyridyl ligands as efficient catalyst precursors for ethylene polymerization (Scheme 3.12). After MAO activation, the complexes show high activity and produce strictly linear PE [24]. The parent catalysts that were based on iron(II)- and cobalt(II)-based precursors showed that there is a clear relationship between the molar mass of the polymer produced and the bulky groups on the *ortho* position of the aromatic auxiliary ligands.



Scheme 3.11 Polymerization of α-olefins by α-diimine Ni^{II}-based catalyst



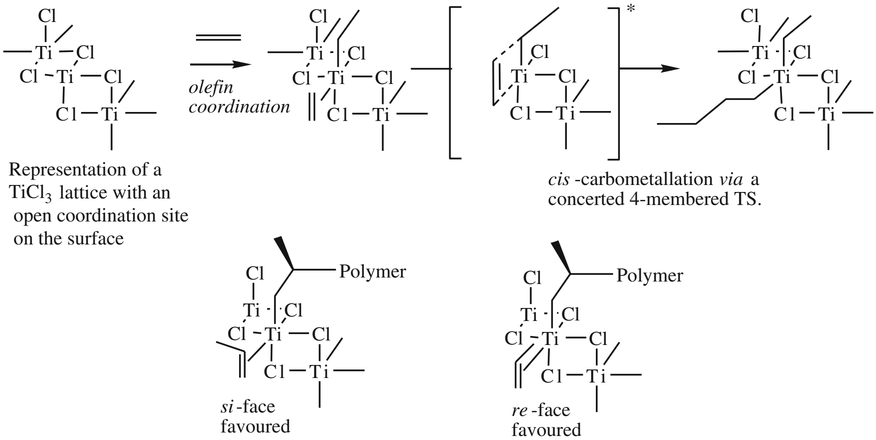
Scheme 3.12 Brookhart/Gibson-type BIP polymerization catalyst

The presence of the two di-*iso*-propyl groups on the *ortho* position of the imino moiety produces strictly linear PE, thus blocking the chance of the *β*-hydride elimination step.

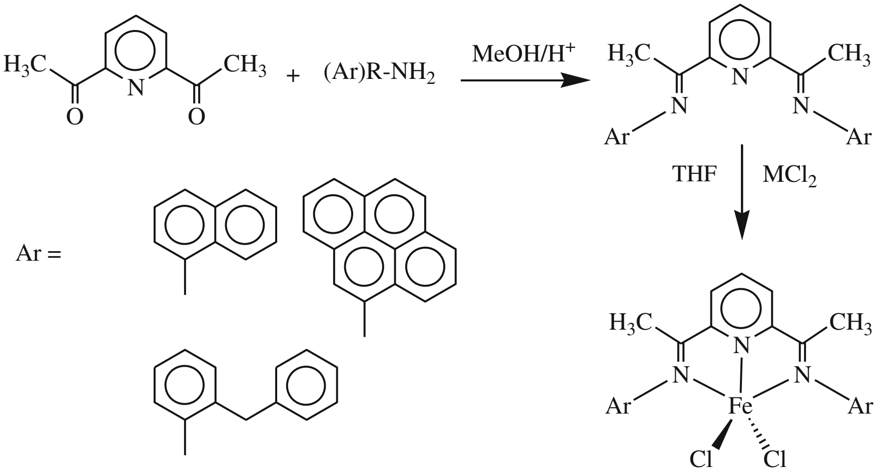
Following that year, many work groups studied the theoretical concepts concerning this type of catalytic system. Griffiths et al. [27] presented the first theoretical studies on this catalyst system, having assumed the generally accepted Cossee–Arlman polymerization mechanism [25–27] (Scheme 3.13).

Abu-Surrah et al. [29] also reported on highly active 2,6-bis(arylimino) pyridine iron(II)- and cobalt(II)-based ethylene polymerization catalysts which lack the *ortho* alkyl substituents on the aryl groups. Modifications of the steric bulkiness of the aromatic groups in the tridentate ligands influenced not only the catalytic activity, but also the molecular weight, and for the first time the microstructure of the resulted material (Scheme 3.14) [28].

McTavish et al. [30] reported another form of catalysts containing BIP-based ligands. The resultant iron dichloride complexes were highly active ethylene polymerization catalysts after the activation with methylaluminoxane (MAO).



Scheme 3.13 Cossee–Arlman mechanism (Ziegler–Natta Ti-based catalyst), *asterisk* The other Ti atom was omitted for clarity



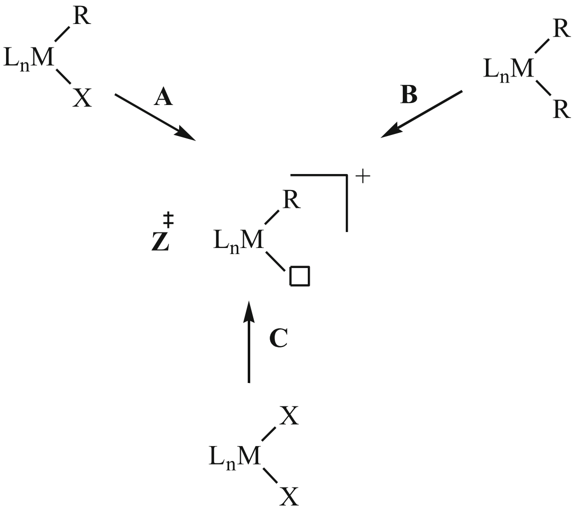
Scheme 3.14 2,6-bis(arylimino)pyridineiron(II)- and cobalt(II)-based ethylene polymerization catalysts which lack the *ortho* alkyl substituents

Activities in the range of 3000–18,000 g/mmol bar h were reached. The molecular weights (M_n) of the resultant PEs lie in the range of 6500–24,000 with broad molecular weight distributions (16.5–38.0). The nature of the imine carbon substituent has a marked effect on the polymer molecular weight, whereas the catalyst activity is largely unaffected by changes to this substituent [29].

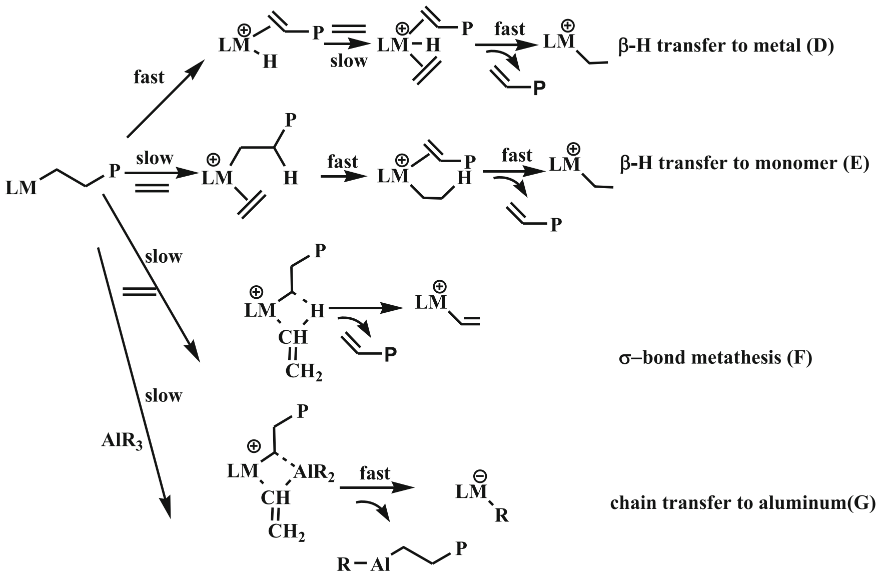
The catalytically active species formed by the treatment of 2,6-bis(imino) pyridine iron(II) chloride complexes with MAO is generally proposed to be a highly reactive monomethylated iron(II) cation $[LFe\text{-}Me]^+$ (L = 2,6-bis(imino)pyridine ligand) bearing a weakly coordinating counteranion $[Me\text{-}MAO]^-$. Both monochloride and monoalkyl cationic species are expected to be present in the solution, their relative concentration depending on the MAO/Fe ratio [24].

At high loadings, the active species will be the dimethylated product, which does not polymerize ethylene alone, followed by reductive elimination (path **B**) with aluminum metal center to give the active species (**Z**; Scheme 3.15), which is presumably the same for metallocene-mediated MAO polymerization [23].

Scheme 3.16 represents different chain termination pathways, in which path (**D**) represents a propagation mechanism following a Cossee–Arlman mechanism involving migratory insertion of ethylene into a metal alkyl bond. The latter pathways are chain transfer pathways: β-H transfer reactions to the metal (two types of path **E**) or the monomer (path **F**) give one double bond per polymer chain (vinyl end groups), whereas chain transfer to aluminum (path **G**) gives saturated polymer chains. NMR and computational studies of cobalt complexes by Gibson and co-workers [30] have shown that β-H chain transfer proceeds via a stepped mechanism involving a cobalt hydride species (path **E**).



Scheme 3.15 General mechanism for the activation processes, where *open square* represents the vacant coordination site



Scheme 3.16 Different chain termination pathways

3.6.3 Salicyldimine-Based Complexes

Salen-type complexes are a fundamental class of compounds in coordination chemistry, known since 1933. They have been extensively studied, and more than 2500 have been synthesized. Interest in salen-type complexes intensified in 1990 when the groups of Jacobsen and Katsuki discovered the enantioselective epoxidation of unfunctionalized alkenes using chiral Mn(*salen*) complexes as catalysts. Since that time, an extremely wide variety of reactions catalyzed by salen complexes have been investigated.

3.6.4 Early Transition Metal-Based Phenoxy-Imines

In 1998, ligand-oriented design led to the discovery of phenoxy-imines that were utilized using group 4 metals initiated by Mitsui Chemicals led by T. Fujita and co-workers under the name "***FI*** catalysts" which stands for the Japanese pronunciation of the ligand "Fenokishi-Imin Haiishi" and, at the same time, for "Fujita group Invented catalysts" [31, 32].

Phenoxy-imine ligands have the advantageous properties of diversity and tunability. Within the framework, there are three readily changeable substituents, which will sterically and electronically affect polymerization reactions (R_1–R_3, Fig. 3.4).

Those types of catalysts were based on continuous *trial and error*, and they found that group 4 transition metal complexes having phenoxy-imine ligands displayed very high activity for ethylene polymerization at 25 °C under atmospheric ethylene pressure. e.g. (**complex 1**, Fig. 3.5) bis[N-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride, exhibited 519 $\mathrm{kg_{PE}/mmol_{Zr}} \times \mathrm{h}$ of activity, which is almost 20 times higher than the activities observed with Cp_2ZrCl_2/MAO (27 $\mathrm{kg_{PE}/mmol_{Zr}\ h}$) under the same polymerization conditions [33].

Fujita and co-workers reported on the catalytic behavior of fluorinated bis (phenoxy-imine) titanium complexes bearing a series of substituents *ortho* to the phenoxy oxygen for ethylene/higher α-olefin (i.e., 1-hexene, 1-octene, and 1-decene) (co)polymerization (Fig. 3.6) [27].

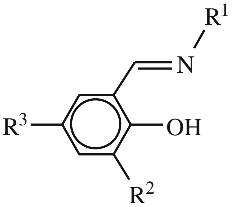


Fig. 3.4 General structure of the *FI*-salicyldimine-based ligand

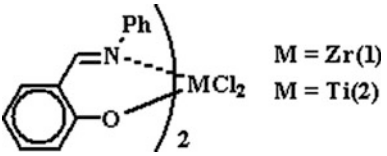
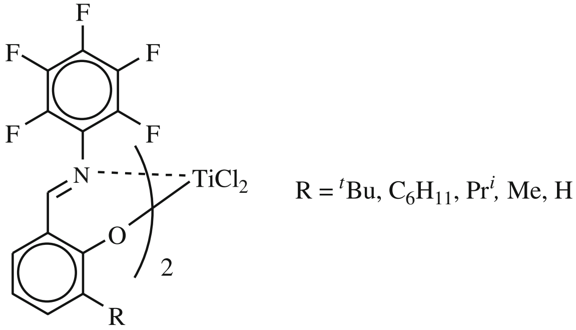


Fig. 3.5 Structure of *FI*-zirconium (IV) and its Ti(IV)-phenoxy-imine correspondent

Fig. 3.6 General formula of the fluorinated *FI*-Ti(IV)-based catalysts



Independent of the magnitude of steric bulk of the *ortho* substituent, also, all complexes that were investigated produced PEs and ethylene/higher α-olefin copolymers with very narrow molecular weight distributions [e.g., PEs, M_w/M_n = 1.05–1.16, M. 44,000–412,000; ethylene and 1-hexene copolymers, M_w/M_n = 1.07–1.19, M_n 49,000–102,000, 1-hexene content 3.2–22.6 mol%], indicative of living polymerization. The incorporation ability for higher α-olefins is highly dependent on the nature of the *ortho* substituent, and Ti complexes with a sterically less encumbered *ortho* substituent incorporated a higher amount of higher α-olefins. A number of unique block copolymers consisting of linear PE and ethylene/1-hexene copolymer segments were prepared using one of the living catalysts with enhanced incorporating capability for higher α-olefins. These block copolymers exhibited lower peak melting temperatures (T_m) relative to the corresponding homo-PE.

3.6.4.1 Late Transition Metal Salicyldimine Complexes

Complexes containing ligands of N,O-chelate are particularly interesting and challenging for catalysis by mixed-donor ligand complexes, such as the Ni-based systems were shown to be effective in ethylene polymerization, because of their ease of preparation and simple modification of both steric and electronic effects.

Several nickel(II) salicylaldiminato systems have been developed which are highly active for the polymerization of ethylene (Fig. 3.7). Furthermore, bulky substituents in the 3-position of the salicylaldiminate ring were found to enhance

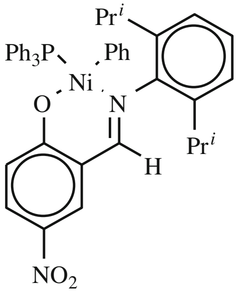


Fig. 3.7 Structural representation of the most productive catalyst reported in the study, using (Ni (COD)$_2$ as a co-catalyst)

the activity of the catalyst and lower the number of branches in the resulting PE. An electron-withdrawing group in the 5-position of the salicylaldiminate ring also increases catalyst activity. With these systems, moderately high molecular weight polymer with about 10–50 branches per 1000 carbons can be obtained. As observed in other late metal systems, branching can be controlled by the variation of both temperature and pressure [34].

Zhang et al. [36] reported that a series of neutral Ni (II) complexes derived from anilino-substituted enone ligands bearing electron-withdrawing trifluoromethyl and trifluoroacetyl groups have been synthesized (Fig. 3.8). When activated with either Ni (COD)$_2$ or B(C$_6$F$_5$), these complexes were active for the polymerization of ethylene to branched PEs. Complex is especially active and long-lived, with a turnover frequency (TOF) of 5 × 10^5 at 60 °C and 200 psig of ethylene, a half-life exceeding 15 h at 35 °C, and a total turnover number exceeding 10^6 at 35 °C and 200 psig [35].

3.6.5 *Quinaldimine-Based Complexes*

Quinaldimines are attractive special type of aldimine family that are used as backbone for the preparation of catalytically active material for the polymerization of ethylene or those containing polar functionalities especially (meth) acrylates.

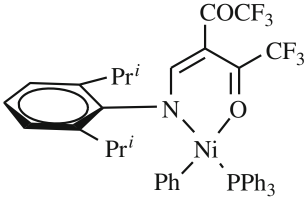
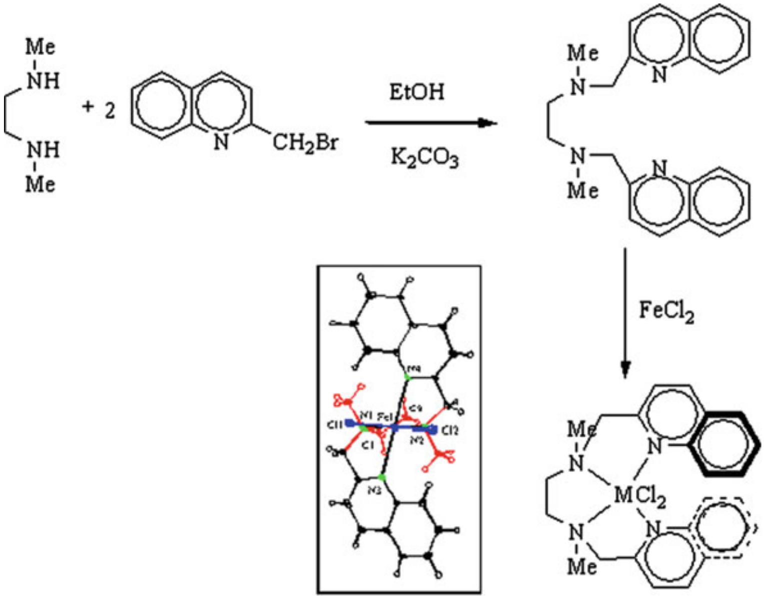


Fig. 3.8 Synthesis of substituted enone SD-Ni^{II}-based complex

Abu-Surrah et al. [37] reported the synthesis of C_2-symmetric iron (II) and cobalt (II) complexes bearing new tetradentate ligands based on 2-bromomethylquinoline. The isolated complexes were the first C_2-symmetric octahedral complexes that resemble the structure of the tetrahedral, C_2-symmetric metallocene-based catalysts (Scheme 3.17) [36].

Britovsek et al. [38] reported a bidentate imino quinolinyl nickel dibromide complex (Fig. 3.9) for the polymerization of ethylene, but it showed moderate activity toward the formation of oligomers rather than polymers [37].

Yliheikkila et al. [39] reported a series of manganese (II) dichloro complexes for ethylene polymerization using MAO as a co-catalyst (Fig. 3.10) [38]. From the series are two of the most active octahedral manganese (II) complexes and those bearing tetradentate nitrogen ligands with chiral backbone [39], (Abu-Surrah et al. [40]). The highest activity in ethylene polymerization $\left(67.0\,\mathrm{kg_{PE}}\,\mathrm{mol_{Mn}^{-1}}\,\mathrm{h}^{-1}\right)$ was obtained with $\mathbf{A}^{\mathbf{1}}$/MAO at 80 °C under 5 bars of ethylene pressure.



Scheme 3.17 Fe(II)-quinaldimine-based complex

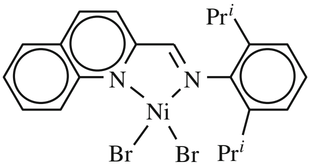


Fig. 3.9 Structural representation of the bidentate Ni(II)-based complex

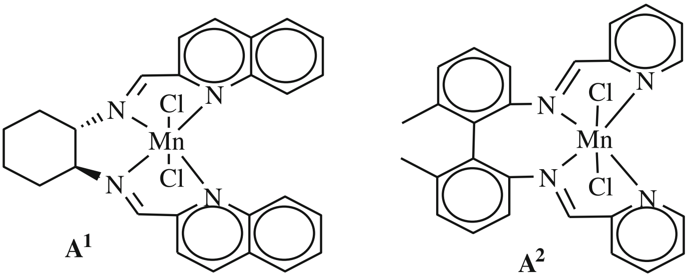
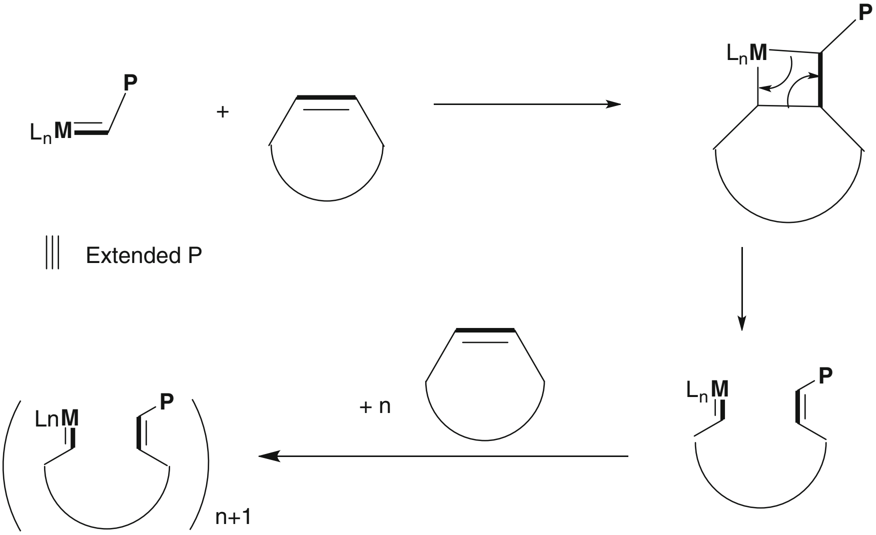


Fig. 3.10 Quadridentate octahedral Mn(II)-based complexes

3.6.6 Ruthenium-Based Polymerization Catalysts

Olefin metathesis (carbene) polymerization is also known as ring closure metathesis. It was introduced by Grubbs and his co-workers in the 1970s and became an important organic synthesis tool. It included the stable ruthenium-based catalyst [40]. Later, it was subjected to much advancement and became more versatile tool to make new polymers versatile [41].

In metathesis polymerization, the catalytically active species is a stable metal–carbene bond that is formed between the metal and the alkene. Upon reaction with cycloalkane, a living moiety capable of chain growth is formed. The olefin metathesis reaction mechanism is shown in Scheme 3.18.



Scheme 3.18 Ring opening metathesis polymerization mechanism

Applications of Grubbs catalyst in ring closure metathesis and its second-generation catalyst for phase-transfer ring closure metathesis were the subject of more recent reports [42, 43].

3.7 Remarks and Outlook

Over the last 60 years, only few discoveries have had such a visible impact on the development of our modern society than Ziegler–Natta olefin polymerization catalysts. They have facilitated large-scale production of synthetic polyolefins and rubbers and subsequently the introduction of cheap commodity materials in our everyday life.

The discovery of a highly active family of catalysts based on iron, a metal that had no previous track record in this field, has highlighted the possibilities of further new catalyst discoveries. The search for new catalysts be restricted to metals that have a history of giving polymerization-active centers was no longer needed. The LTMs especially are likely to provide fertile ground for future development, and the greater functional group tolerance of the LTMs also offers the attractive prospect of polar co-monomer incorporation. A relatively small amount of functionality can dramatically transform the adhesion and wettability properties of polyolefins; more heavily functionalized products offer the prospect of materials with totally new properties and performance parameters. It is clear that, for olefin polymerization catalysis, the process of catalyst discovery and development is far from over.

Still, pollution caused by these nondegradable common plastics, oil stock declining, and concerns about greenhouse effect have directed research efforts toward sustainable alternatives to polyolefins and other fossil feedstock-derived polymers [44].

Ideally, sustainable materials should match or exceed the physical and mechanical properties of the replaced polymer, be available at a competitive price, be issued from renewable resources, and be environmentally friendly, i.e., entirely recyclable without the release of hazardous and persistent substances [45, 46].

The contemporary advancements in “olefin polymerization” impose several challenges to be faced by polymer industries.

The following is the list of the most urgent tasks:

1. Reduce process variability (while retaining cost-effectiveness).
2. Inefficiency and improvement of product.
3. Produce prime product, while keeping up with customer demand.
4. Polymer recycling and sustainability of material feedstock.
5. Manufacturers are skeptical about using the latest technology.
6. Gearing toward reducing pollution caused by industry and to produce less wastage.

7. High demand for new and advanced material with the need to find solutions to growing market and upscaling production.
8. Quality of material on demand; high-weight material with controllable properties through structural and functional capability.

3.8 Conclusion

Olefin polymerization is becoming one of the most significant concerns in research and development of chemical industries.

The history and early developments in the pioneering work of polymers up to the most recent advancements are covered. Olefin polymerization started about 100 years back without involvement of metals, following anionic or radical pathways. The contemporary olefin polymerization industry depends mainly on the use of metal complexes as catalysts. At the present time, metal-catalyzed polymerization represents the most successful, conceivable, and sustainable procedure toward the synthesis of polyolefins. Nowadays, the list of metals includes several transition metals in the generation of catalysts. In doing their catalytic role, they follow various mechanisms that lead to a wide range of polymeric products.

The 1950s witnessed the introduction of heterogeneous metal catalysts, leading to a broad range of applications. Two decades later, metallocene led to active homogeneous catalysts which allowed the rational of specific polymer structures.

The better understanding and evolution in the 1990s led to new industrial implementations of the new post or nonmetallocenes, which is the outcome of the recent advancements. They are easier to assemble and produce higher control and activity over the desired polymer structures. This would also be reflected in endless applications of these polymers in many aspects of our life.

In conclusion, it must be emphasized that coordination polymerization of olefins is now considered among the most important areas in polymer research. This area occupies the most prominent place in polymer science and technology that chemical industries intend to cope with.

References

1. G. Odian (ed.), *Principles of Polymerization*, 4th edn. (Wiley, Hoboken, 2004) 832 p, ISBN 978-0-471-27400-1
2. R.J. Young, P.A. Lovelle, *Introduction to Polymers*, 3rd edn. (CRC press, Boca Raton, 2011), ISBN 978-0-8493-3929-5
3. K. Matyjaszewski, T.P. Davis (eds.), *Handbook of Radical Polymerization* (Wiley, Hobken, 2002)

4. G. Moad, D.H. Soloman, *The Chemistry of Radical Polymerization*, 2nd edn. (Elsevier, Oxford, 2006)
5. A.A. Gridnev, S.D. Ittel, Catalytic chain transfer in free radical polymerization. Chem. Rev. **101**, 3611 (2001)
6. K. Matyjaszewski, P. Sigwalt, Unified approach to living and non-living cationic polymerization of alkenes. Polym. Int. **35**, 1 (1994)
7. M. Sawamoto, Modern cationic vinyl polymerization. Prog. Polym. Sci. **16**, 111 (1991)
8. L.S. Baugh, J.M.M. Canich (eds.), *Stereoselective Polymerization with Single Site Catalyst* (CRC Press, Boca Raton, 2008)
9. W. Kuran, *Principles of Coordination Polymerization* (Wiley, Hoboken, 2001) ISBN 0-479-84141-9
10. A. Abu-Surrah, B. Rieger, Late transition metal complexes: catalysts for a new generation of polymers. Angew. Chem. Int. Ed. Engl. **35**, 2475–2477 (1996)
11. L. Johnson, C. Killian, M. Brookhart, New Pd (I1)- and Ni(I1)-based catalysts for polymerization of ethylene and α-olefins. J. Am. Chem. Soc. **117**(23), 6414–6415 (1995)
12. B. Small, M. Brookhart, A. Bennett, Highly active iron and cobalt catalysts for the polymerization of ethylene. J. Am. Chem. Soc. **120**, 4049–4050 (1998)
13. G. Britovsek, V. Gibson, B. Kimberley, P. Maddox, S. McTavish, G. Solan, A. White, D. Williams, Novel olefin polymerization catalysts based on iron and cobalt. Chem. Commun. **7**, 849–850 (1998)
14. W. Kaminsky, The discovery of metallocene catalysts and their present state of the art. J. Polym. Sci. A: Polym. Chem. **42**, 3911–3921 (2004)
15. J. Ewen, Mechanisms of stereochemical control in propylene polymerizations with soluble group 4B metallocene/methylalumoxane catalysts. J. Am. Chem. Soc. **106**(21), 6355–6364 (1984)
16. W. Kaminsky, K. Külper, H.H. Brintzinger, F. Wild, Polymerization of propene and butene with a chiral zirconocene and methylalumoxane co-catalyst. Angew. Chem. Int. Ed. Engl. **24** (6), 507–508 (1985)
17. W. Kaminsky, A. Funk, H. Haehnsen, New application for metallocene catalysts in olefin polymerization. Dalton Trans. **41**, 8803–8810 (2009)
18. A. McKnight, R. Waymouth, Group 4 *ansa*-cyclopentadienyl-amido catalysts for olefin polymerization. Chem. Rev. **98**, 2587–2598 (1998)
19. M. Kesti, G. Coates, R. Waymouth, Homogeneous Ziegler-Natta polymerization of functionalized monomers catalyzed by cationic Group IV metallocenes. J. Am. Chem. Soc. **114**, 9679–9680 (1992)
20. L. Johnson, C. Killian, M. Brookhart, New Pd(I1)- and Ni(I1)-based catalysts for polymerization of ethylene and α-olefins. J. Am. Chem. Soc. **117**(23), 6414–6415 (1995)
21. C. Killian, D. Tempel, L. Johnson, M. Brookhart, Living polymerization of α-olefins using NıII α-diimine catalysts. Synthesis of new block polymers based on α-olefins, J. Am. Chem. Soc. **118**(46), 11664–11665 (1996)
22. C. Pellecchia, M. Mazzeo, D. Pappalardo, Isotactic-specific polymerization of propene with an iron-based catalyst: polymer end groups and regiochemistry of propagation Macromol. Rapid Commun. **19**(12), 651–655 (1998)
23. V. Gibson, C. Redshaw, A. White, D. Williams, Novel aluminum containing ring systems: an octanuclear structural analogue of calix [4]pyrrole. Angew. Chem. Int. Ed. Engl. **38**(7), 961–964 (1999)
24. V. Gibson, S. Spitzmesser, Advances in non-metallocene olefin polymerization catalysis. Chem. Rev. **103**(1), 283–315 (2003)
25. B. Small, M. Brookhart, A. Bennett, Highly active iron and cobalt catalysts for the polymerization of ethylene. J. Am. Chem. Soc. **120**, 4049–4050 (1998)

26. G. Britovsek, V. Gibson, B. Kimberley, P. Maddox, S. McTavish, G. Solan, A. White, D. Williams, Novel olefin polymerization catalysts based on iron and cobalt. Chem. Commun. **7**, 849–850 (1998)
27. E. Griffiths, G. Britovsek, V. Gibson, I. Gould, Highly active ethylene polymerization catalysts based on iron: an *ab-initio* study. Chem. Commun. **14**, 1333–1334 (1999)
28. P. Cossee, Ziegler-Natta catalysis I. Mechanism of polymerization of ☐-olefins with Ziegler-Natta catalysts. J. Catal. **3**, 80–88 (1964)
29. A. Abu-Surrah, K. Lappalainen, U. Piironen, P. Lehmus, T. Repo, M. Leskela, New bis (imino)pyridine Iron(II) and Cobalt(II)-based catalysts: synthesis, characterization and activity towards polymerization of ethylene. J. Organomet. Chem. **648**, 55–61 (2002)
30. S. McTavish, G. Britovsek, T. Smit, V. Gibson, A. White, D. Williams, Iron-based ethylene polymerization catalysts supported by Bis(imino)pyridine ligands: derivatization *via* deprotonation/alkylation at the ketimine methyl position. J. Mol. Cat. A: Chem. **261**, 293–300 (2007)
31. K. Tellmann, M. Humphries, H. Rzepa, V. Gibson, Experimental and computational study of β-H transfer between cobalt (I) and alkenes. Organometallics **23**(23), 5503–5513 (2004)
32. V. Gibson, K. Tellmann, M. Humphries, D. Gould, Bis(imino)pyridine cobalt alkyl complexes and their reactivity towards ethylene: a model system for β-hydrogen chain transfer. Chem. Commun. **20**, 2316-2317 (2002)
33. R. Furuyama, M. Mitani, J.-I. Mobri, R. Mori, H. Tanaka, T. Fujita, Ethylene/higher α olefin copolymerization behavior of fluorinated bis(phenoxy- imine) titanium complexes with methylalumoxane: synthesis of new polyethylene-based block copolymers. Macromolecules **38**(5), 1546–1552 (2005)
34. H. Makio, N. Kashiwa, T. Fujita, FI catalysts: a new family of high performance catalysts for olefin polymerization. Adv. Synth. Catal. **344**(5): 477–493 (2002)
35. C. Wang, S. Friedrich, T. Younkin, R. Li, R. Grubbs, D. Banseleben, M. Day, Neutral nickel (II)-based catalysts for ethylene polymerization. Organometallics **17**(15), 3149–3151 (1998)
36. L. Zhang, M. Brookhart, P. White, Synthesis, characterization, and ethylene polymerization activities of neutral nickel(II) complexes derived from anilino-substituted enone ligands bearing trifluoromethyl and trifluoroacetyl substituents. Organometallics **25**(8), 1868–1974 (2006)
37. A.S. Abu-Surrah, B. Rieger, R. Fawzi, M. Steiman, Synthesis of chiral and *C2*-symmetric iron (II) and cobalt(II) complexes bearing a new tetradentate amine ligand system. J. Organomet. Chem. **497**, 73–79 (1995)
38. G. Britovsek, S. Baugh, O. Hoarau, V. Gibson, D. Wass, A. White, D. Williams, The role of bulky substituents in the polymerization of ethylene using late transition metal catalysts: a comparative study of nickel and iron catalyst systems. Inorg. Chimica Acta **345**, 279–291 (2003)
39. K. Yliheikkila, K. Axenov, M. Raisanen, M. Klinga, M. Lankinen, M. Kettunen, M. Leskela, T. Repo, Manganese(II) complexes in ethene polymerization. Organometallics **26**, 980–987 (2007)
40. A. Abu-Surrah, T. Laine, R. Fawzi, M. Steiman, B. Rieger, An enantiomerically pure Schiff base ligand. Acta Cryst. **C53**, 1458–1459 (1997)
41. R.H. Grubbs, Olefin Metathesis catalyst for the preparation of Molecules and Materials. Angew. Chem. Int. Ed. **45**, 3760–3765 (2006)
42. G.C. Vougioukalakis, R.H. Grubbs, Ruthenium-based heterocyclic carbene- coordinated olefin metathesis catalysts. Chem. Rev. **110**, 1746–1787 (2010)
43. E. de Brito Sa', J.M.E. de Matos, Ring closing metathesis by Hoveyda-Grubbs catalysts: a theoretical approach of some aspects of the initiation mechanism and the influence of solvent. Inorg. Chim. Acta **426**, 20–28 (2015)
44. Y. Kobayoshi, S. Inukai, T. Watanabe, Y. Sogiyama, H. Hamamoto, T. Shioiri, M. Matsugi, A medium fluorous Grubbs-Hoveyda 2nd generation catalyst for phase transfer catalysis of ring closing metathesis reactions. Tet. Lett. **56**(11), 1363–1366 (2015)

45. S. Mecking, Nature or petrochemistry?-biologically degradable materials. Angew. Chem. Int. Ed. **43**(9), 1078 (2004)
46. A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W. J. Frederick Jr, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, The path forward for biofuels and biomaterials. Science **311**, 484 (2006)
47. A.K. Mohanty, M. Misra, L.T. Drzal, Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J. Polym. Environ. **10**(1–2), 19–26 (2002)

Chapter 4
Processing Techniques for Polyolefins

Tomáš Sedláček

4.1 Introduction

In 1975, a study conducted by the plastic industry predicted that the future of plastic industry was hidden in special types of high-performance plastic materials with enhanced properties (such materials should occupy about 50 % of market share of polymer industry). The continuous development in polyolefins science revealed that time unimaginable secrets and potential for polyolefins to meet the high-performance needs expected from technical and speciality plastics. Thus, the latest trend in plastic goods processing is pronouncedly controlled by polyolefin producers (while high-performance plastics accounted in 1997 was about 0.25 % of polymer market) [1].

Easiness of polyolefin processing connected with relatively high melt stability and low processing temperature, possibility to modify properties of final products via molecular tailoring, copolymerization, alloying, grafting, cross-linking and high recycling potential guarantee further successful future for polyolefins—high-density polyethylene (HDPE); low-density polyethylene (LDPE); linear low-density polyethylene (LLDPE); medium-density polyethylene (MDPE); ultra-high molecular weight polyethylene (UHMWPE); metallocene polyethylene (mPE); cross-linked polyethylenes (xPE); cyclic polyolefins (COC); syndiotactic, isotactic and atactic polypropylene (sPP, iPP, aPP); random and homopolypropylene (rPP, hPP); thermo-elastic polyolefins (TPO), as well as other special type of polyolefins as for example poly-1-butene (PB), in addition, the number of potential polyolefin blends as well as masterbatches based on them—for a wide range of applications.

T. Sedláček (✉)
Centre of Polymer Systems, Tomas Bata University in Zlin, Trida T. Bati 5678,
760 01 Zlín, Czech Republic
e-mail: sedlacek@cps.utb.cz

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_4

Without any doubts, it could be stated that there is no other type of polymeric materials traded all around the world and processed into such amount of products:

- blown packaging and agriculture films;
- extruded into hygienic foils, building and automotive industry sheets and foams, or pressure pipes;
- blow moulded into containers, tanks, detergent bottles or car's defrost air systems;
- spread onto wires and cables as insulation;
- injection moulded into countless consumer (end-use) products;
- melt-blown into non-woven fabrics; and
- used for paper coating, laminations, gluing or its substitution.

Examples of utilization include automobile headlights; taillights; disc brake pads and bumpers; carpets; CDs and optical discs; clear film food wrap; eyeglasses; flexible foams used in bedding and furniture; rigid foam insulation; impact-resistant and bulletproof windows; moulded plastic goods such as buckets, food containers, kitchen utensils and wastebaskets; elastic hoses; seals and gasket; protective coatings; grocery bags; synthetic fibres for blankets; sweaters, socks and fleeces; water cooler bottles; and wood products such as plywood, oriented strand board and laminates.

4.2 Principle of Processing

While manufactured polyolefins are processed by their producers, with no or only basic amount of additives (lubricants, stabilizers, antistatic agents and slip/antiblock agents), into the form of granules using powerful extruders equipped usually with giant melt pelletizing heads [2, 3], polyolefins in the form of powder [4], could be produced utilizing mechanical grinding of granules [5] or extraordinary without necessity of the mentioned thermoplastic process directly during polymerization [6]. Larger amount of stabilizers, organic or inorganic fillers, pigments, flame retardants, or other additives, which could be desirably added into the prepared polymeric systems—masterbatches, compounds or alloys, are mixed with the pure polyolefins by compounders utilizing a variety of processing technologies [7]—mixers, single- or twin-screw extruder (parallel co-, counter-rotating [8] or conical [9, 10]), planetary system extruders [11, 12], and kneader extruders (e.g. single-screw co-kneader [13–15]) equipped with melt or strand pelletizing head [16]—regarding required size of desired batch, temperature sensitivity of processed components, sensitivity to shear deformation, etc. Such polymeric materials are further processed into the form of final products by small local to huge international plastic convertors employing various thermoplastic forming technologies. For various processing technologies as well as countless numbers of production aspects, the knowledge of processed material flow behaviour is important and crucial. Connection of rheology of polymer melts with set-up and optimization of processing conditions as well as with final products' properties nevertheless requires not only the comprehension of polymer melt flow complexion during manufacturing process but also the understanding of processed polymer molecular structure/composition and its role in physical and mechanical properties of the prepared resolidified unorganized/organized material structure.

Solid polyolefin (plastics in general) pellets/powder obtained during polymerization step at the start of converting phase is fed into the processing device (extruders, injection moulding machines, presses, etc.). Usually, air-driven pneumatic filling systems, equipped with gravimetric or volumetric dosing technology (see, e.g. [17]), are utilized for fabricated materials supply from bags, big-bags or storage bins into the still or vibrated hoppers. Contrary to polar plastics, the unexceptionable advantage of polyolefins, namely for centrally supply production where tube distribution to various processing machines is provided from central—even outside—material sources, consists in their low wettability, thus possibility to convert them usually without necessity of dryers' or dehumidifiers' utilization. The exception occurs in the case of polyolefins filled with high amount of hydroscopic additives or ions, polyolefin-based blends containing hydrophilic component, or applications where optical appearance of products with huge surface dimensions is critical.

The processing devices at the first step are used for heat transfer—achieved via heat conduction from tempered parts of employed technologies and dissipation from processed material friction movement—of solid-state particles into polymer melt. Since it is essential to efficiently convert all materials processed in the device to polymer melt, the correct and optimized geometry of manufacturing device set-up is advisable to be utilized in order to achieve trouble-free production. In addition, to achieve maximum performance of the process, the plastic materials should be converted into the melt at appropriate time (screw position) [18, 19], and its temperature to be homogenized as much as possible in order to minimize troubles in further polymer formation steps, especially in the temperature-sensitive processes, as for example foam extrusion [20], film blown extrusion [21, 22], or in the cases that highly affected by heat friction or viscosity increase as for example during mixing of highly filled compounds [23, 24].

4.3 Employment and Role of Polymer Melt Rheology

Rheology is utilized as a fundamental instrument for conversion technology design optimization according to materials or technology process type used. Moreover, rheology point of view in polymeric solid-state conversion could be used not only for correct proposition of processing equipment design, but also for suitable proposal of manufacturing conditions, such as temperature process window definition, material flow rate maximization [25]. Here, the software process simulations, represented, for example, by Virtual Extrusion Laboratory from COMPUPLAST INTERNATIONAL a. s. [26], POLYFLOW from ANSYS, Inc.

[27], Moldflow from Autodesk, Inc. [28], or Ludovic from Sciences Computers Consultants [29], play unsubstitutable and important role. Nevertheless, it should be kept in mind that even the task to quantify the flow and heat transfer during the manufacturing steps is perceived as complex enough, the fact that material properties could differ for a particular resin from batch to batch for various moisture content could complicate it even much more. In this respect, standard laboratory rheological properties characterization, carried out using laboratory offline rheometers (single-screw extruders, high-pressure capillary (circular or slit die) viscometers and/or rotational rheometry apparatuses—depending on real processing conditions), could be apprehended as not enough flexible tool for manufacturing control, and the utilization of online or in-line rheometers applied directly into the processing lines could be required [30]. Commercially attainable in industry that could be included ViscoSensor by Dynisco (return-stream capillary instrument [31]), Online viscometers by Gneuss (bypass slit capillary device [32]), or viscometers by Hydramotion (in-process viscometer operating on principles of rotation [33]).

4.3.1 Viscoelasticity

For simulation purposes and process control, the material behaviour is usually described by the help of complex physical viscoelastic models [34], where the influence of processing conditions (e.g. temperature, pressure, material output) as well as material properties (elasticity, strength, etc.) affected by molecular structure play crucial role.

Before rheology could be successfully employed for processing optimization, one should be familiarized with the aspects of viscoelastic behaviour of polymer (polyolefins) melts in connection with implication of processing characteristics. Polymer melts are viscoelastic fluids behaving viscous or elastic in response to how fast they flow through processing device or are deformed during the process. The silicone putty test could be presented as a good demonstration of this phenomenon. If a silicone ball is rapidly deformed, for example via bouncing, it behaves like an elastic body. Stored energy caused the recoverable elastic deformation and makes the ball bounce. If the silicone ball is left at rest for a longer period of time, viscous behaviour, connected with gravity, causes its flow like a fluid. Whether a material behaves more elastic or viscous which depend on the timescale of the deformation and on the ratio of process time and material time, referred to as Deborah or Weissenberg number. If the material time is short in relation to the process time, the material shows predominantly viscous behaviour. If the Deborah number equals unity or larger, the elastic behaviour of the fluid increases and becomes dominant.

4.3.2 Shear Viscosity

In general, the flow behaviour, expressed via viscosity—resistance to flow, of low monodisperse molecular weight fluid is independent of the shear rate. Here, only one unique value is necessary to be determined in order to describe and predict flowability of these Newtonian fluids. On the other hand, polymer melts as polydisperse molecular weight fluids are typical for shear rate–dependent flow behaviour. This phenomenon could be manifested via help of entanglement of macromolecules. Rate of entanglements/disentanglements of polymer chains with one another, described via relaxation time, is proportional to viscosity change. While polymer melt viscosity stays Newtonian in the region of low shear rates, also known as the zero-shear viscosity, where disentanglement is fully balanced with formation of chain entanglements, with increasing shear rate entanglement formation velocity does not achieve the rate of their extinguishment causing thus polymer melt viscosity decrease. Viscosity declines with increased deformation rate, a phenomenon called shear thinning (the most important non-Newtonian property in polymer processing because it speeds up material flow together with reduction in heat generation and energy consumption during processing), up to a point where all entanglements are lapsed and viscosity becomes shear rate independent again, region known as second Newtonian plateau. However, in this region viscosity behaviour, due to too high shear rates, is usually complicated with flow instability origination.

It should be stressed here that complex flow behaviour strongly depends on polymer chain structure and as such, all aspects as for example chemical nature, average molecular weight, molecular weight distribution and additives or filler presence, need to be taken into account for further utilization of viscosity variation role in plastics converting and processing demands purposes [35]. For example:

- broadening of a polymer's molecular weight distribution to ensure improvement of moulding and extrusion process as well as to modify surface smoothness of extruded and moulded goods or optical properties as sag and haze of blown films,
- even the small variation in polymer chain structure could cause change in specific flow region, including, but not limited to the case when small difference in long-chain branching or a small amount of high molecular weight component stand for variation in product weight of blown product although no visible change could be found in shear viscosity behaviour.

Considering mentioned findings, it is clear that not only melt flow index, defined as one point on the curve describing shear rate–dependent viscosity, is definitely insufficient tool for determination of specific processing problems sources, but even standard viscosity measurements carried out with the help of capillary viscometer could not be enough and appropriate approach required to be chosen according to correspondent processing deformation behaviour defying material response.

Beside deformation characteristics, further manufacturing specifications influencing viscosity dependences, such as temperature and pressure profiles, which should be known, described and evaluated for each processed materials besides shear rate variation (controlled by demanded material processing flow rate). In general and for simplification of viscosity behaviour comprehension, it could be presumed that while temperature increases decline in viscosity, pressure arises which causes viscosity to increase. These variations could be connected with amount of free space contained in flowing material. Since higher amount of free space evokes easier flowability due to extended possibility, energetically promoted by temperature arise or pressure drop, for chain segments to occupy positions in flow direction, one could expect proportional behaviour also for viscosity dependency. Exceptions are caused by chemical reactions when polymer cross-linking or other restriction of free movement occurs. While temperature and shear rate dependencies are ordinarily determined by the help of commercially accessible rheological analysers, pressure effects could be characterized with several limitations [36].

4.3.3 Extensional Viscosity

Even majority of the rheological characterizations is carried out in shear mode using rotational or capillary rheometers, flows of processed materials are usually complicated by extensional deformations important especially in processes like film blowing, fibre spinning, foam manufacturing or blow moulding. Since elongational viscosity behaviour has its own specification, it could vary significantly from shear flow dependencies concerning in particular the case of branched polymer macromolecules. The suitable available rheometers evaluate elongational viscosity from uni-axial stretching of filament or strip in air or liquid environment. For this type of measurement, homemade or commercial single-purpose devices designed based on Munstedt [37] or Meissner and Hostettler [38] ideas, known as MTR and RME instruments, respectively, could be employed. Another possibility is to use Sentmanat test fixture (SER), based on fibre windup technique first described by Macosko and Lorntson [39], mounted on the transducer of a conventional torsional rheometer. Finally, as further option available for determination of extensional flow behaviour also Rheotens and haul-off testing accessories of capillary rheometers could be used. Benefits as well as disadvantages of each mentioned devices (extensional rate limitation, temperature uniformity attainability, gravity impact and many others) should be carefully taken into account according to process which should be simulated or optimized.

4.4 Polyolefin Processing Technologies

As it was already mentioned, raw polyolefin-based materials in the form of granules obtained consequently to polymerization process or custom blends and/or compounds, prepared with the addition of various polymers and/or additives including, for example processing aids, heat and UV stabilizers, are advantageously converted into the form of semi-products or final fabrics employing commercially accessible to technologies and production lines. In general, polyolefin conversion is achieved by the help of all the standard thermoplastic technologies (e.g. extrusion process, injection moulding, extrusion blowing or rotation moulding) without necessity of any special technical requirements.

In the case of periodic processes (e.g. injection, blow, and rotational moulding), polyolefin melt closed in the mould is solidified exactly in the final product shape given by the mould design. The injection moulding process is one of the most cost-effective processes to produce plastic articles, and thus, it is used to make parts for practically every major industry existing today. Obtained products such as containers; food and chemical packaging; toys; crates; capes; closures; and various parts for automotive such as bumpers, sun shields and dashboards, achieve their final properties in short timescale. The polymer melt viscosity thus became significantly affected by time dependency, in accordance with the set processing parameters (injection rate and pressure, holding pressure, mould temperature, etc.). While filling stage of process could be regarded and simplified via the melt flow through closed channels which is determined by high shear rate–viscosity behaviour, because usually shear rates in order of thousands of reciprocal seconds are considered, the solidifying process is rather affected by melt visco-elasticity and crystallization kinetics. Settling and suitable combination of injection moulding process conditions are thus crucial for polyolefin products manufacturing. Polyolefins with higher melt flow index, such as the trivial value characterizing flowability of polymer melt, are usually chosen as suitable candidates for injection moulding of thinner and more spacious products. However, since the melt solidifying is primarily determined by the thermal properties of employed materials together with the mould temperature rather than polymer melt flow behaviour itself, preferable and frequently used method for characterization of processed materials is the spiral flow test enabling evaluation of the melt flowability together with its solidification kinetics under desire processing conditions [40]. Even the polyolefin product manufacturing qualities, such as mechanical, optical, barrier, thermal and other pursued properties given by employed material properties could be partially modified by the thermal condition (mould temperature) setting, most of the modifications are attained via material changes utilizing fillers (inorganic particles, glass fibres and beads, metal powder), additives (nucleation and blowing agents, pigments) and/or other components.

On the other hand, during continuous processes (e.g. profiles, pipes, sheets, films and foams extrusion) the solidification occurs in gradual procedure enabling not only forming of final shape in longer timescale usually by the help of additional accessories (cooling rolls and calibres, internal positive pressure), but also affecting final properties of films, foils, sheets and other extrudates (impact and tear resistance, toughness, optical clarity, sealability); this is determined via both molecular architecture (molecular weight distribution and its modality, length of branches, branching level, etc.) and reached supramolecular structure (e.g. oriented fibrils created in fibres or stretched ribbons, achieved crystallinity/amorphousness rate). Deeper discussion of selected individual continuous processes concerning selected polyolefin product manufacturing is presented further in the text.

4.5 Blown Film

Since the packaging is the world's most widespread polymer application, with the Europe plastic total demand of almost 40 % [41], the blown film process, sketched in Fig. 4.1, is the most diverse conversion procedure where polyolefins, namely polyethylenes, play the major role.

Via the highly efficient and economical tubular blown film process (according to ASTM terminology [42], films are defined as sheeting having a nominal thickness no greater than 0.254 mm), polyolefins can be produced into the light films of thickness of microns or into the heavy construction films with thickness of hundreds of microns, all with width exceeding 12 m.

In general, there are different requirements demanded from blown films. Food and retail packaging applications need higher clarity, while industrial packaging applications do not. Some food packaging needs strength, others need tearability,

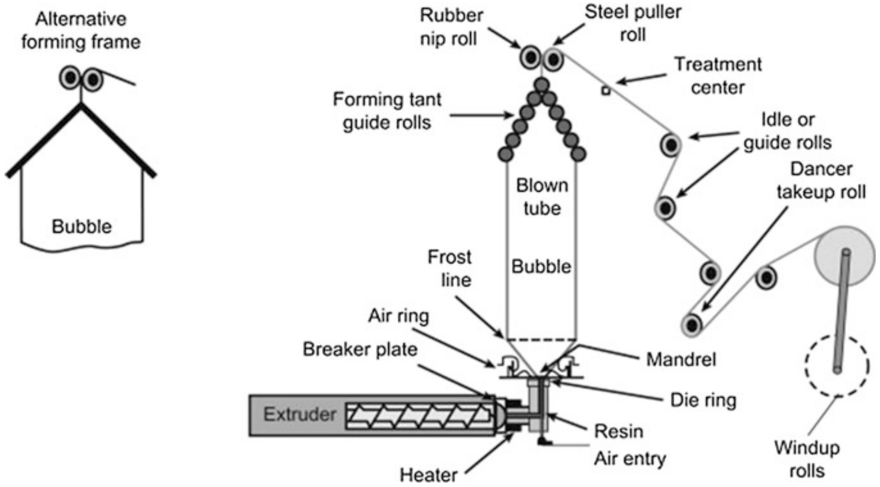


Fig. 4.1 Scheme of blowing line [43]

oxygen barrier or breathability to specific gas or aroma. Non-packaging applications range from agricultural to hygiene films, both with very different optical, barrier and mechanical respond requirements. Such diversity in property demands could not be ensured only through the thickness variations of polyolefin films, but rather via the utilized macromolecule chain structure, polymer molecular weight distribution and/or film construction.

In terminology connected with blown film process, graphically introduced in Fig. 4.2, several terms are utilized and one should be familiar with them; (1) the blow-up ratio (BUR) which is given by ratio of bubble and die diameters or ratio of 0.637 times the lay-flat width (width of the collapsed film) and the die diameter; (2) the drawdown ratio (DDR) given by the gage reduction of the extruded tube into the final thickness of blown film (ratio of width of die gap and finished film thickness connected with the thickness reduction of the melt during blowing process) divided by BUR; and (3) the orientation of the film, which could be distinguished in the direction of drawing (machine direction, MD) or blowing (transverse direction, TD).

During blown film extrusion, polymer granules are melted and transported by the help of one (monolayer film) or several extruders (multilayer film) through an annular or ring-shaped die. While the blowing is usually carried out vertically upwards, also downward extrusion processes are becoming common lately [45]. Monolayer films have limited applications due to limited possible combined properties. Multilayer co-extrusion technologies, on the other hand, lay the groundwork for the many possibilities to approach various applications demands, but their processing is usually sophisticated and requires purpose-made line.

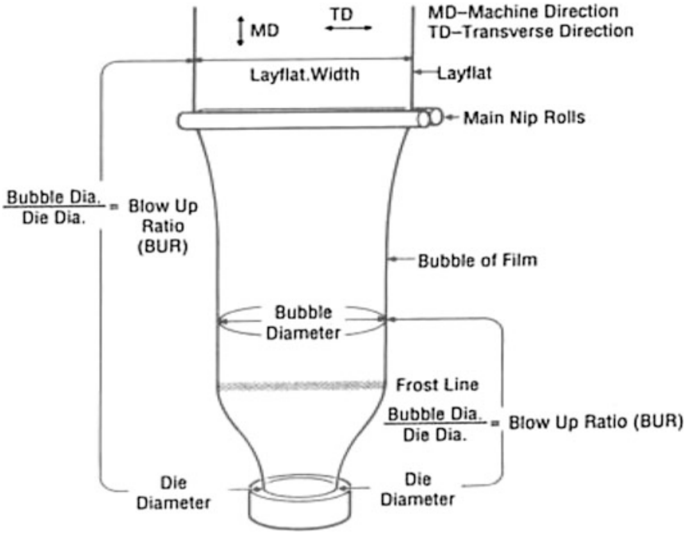


Fig. 4.2 Selected terminology from blown film production [44]

Even utilized extruders have usually smooth bore, grooved feed one, guaranteeing increase friction between the polymer and the barrel surface, can be also used for the process optimization with increased production rates where reduced temperature positively increases stability of process, specially of polyolefins with high viscosity such as high molecular weight polymers [22]. In order to increase melt quality or stability of generated material flows, the gear pumps, also called melt pumps, could be inserted between the end of the extruder and the die head. The pumps then deliver a stable, surge-free melt output, thus guaranteeing excellent layer uniformity, which is the vital fact especially for continuous multilayer extrusion processes. The benefits are particularly important for the extrusion of the very thin layers, as for example in the case of barrier or adhesive tie—layer preparation.

Thin film is inflated from extruded tube consequently to the die exit. The blown film dies could be in general divided to spider and spiral types, as presented in Fig. 4.3. Since spiral dies provide more uniform melt distribution and eliminate weld or knit lines caused by the spider holding the mandrel, they almost replaced the former ones [43, 46].

While diameter of extruded tube increases due to blowing via inner air (for higher product efficiency its temperature could be controlled), it is in meantime withdrawn away from the die and cooled from outside. The finished film is thus formed between the die and frost line, defined as point where film is changed from the melt to the solid state, by the simultaneous blowing and drawing of the tube of hot melt extruded from the die.

Product efficiency is determined by the cooling of the bubble. In other words, the higher production speed is demanded and the more intensive cooling is required. While the most of polyethylene films are cooled down by air, polypropylene blown films are commonly cooled via tubular water quenching. Air cooling efficiency is usually intensified employing double air ring or internal cooling supplemented with exchanging of the air inside the bubble while maintaining the internal pressure. It should be noted that attempts to increase the cooling rate via cooling ring air flow increase usually evoke bubble vibration and instability deforming the "bubble" and causing its defects, similarly to any other even small outside forces (light air currents, heat, stretching). Other factors besides bubble stability affecting

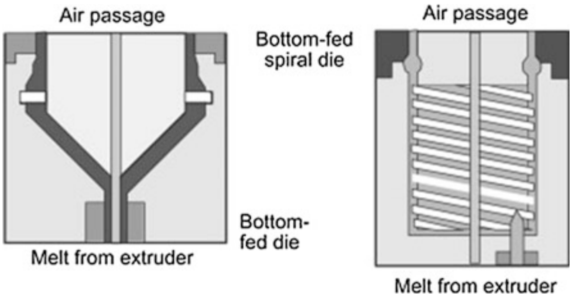


Fig. 4.3 Schematic of spider and spiral blown film dies [43]

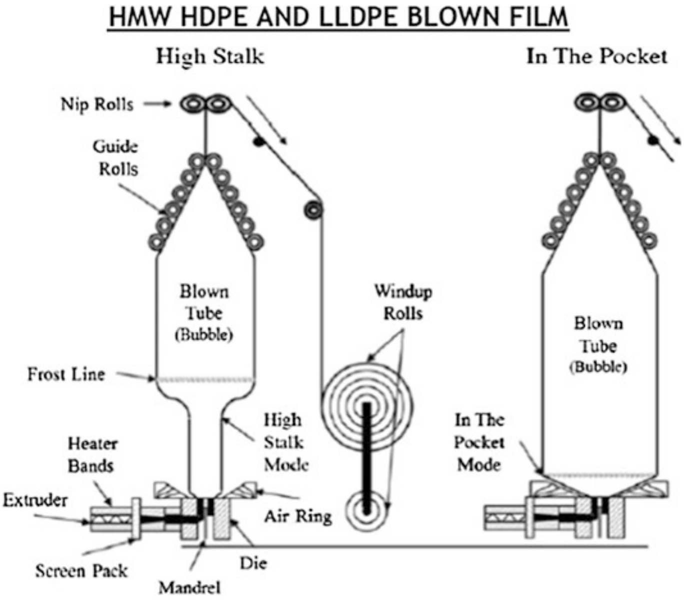


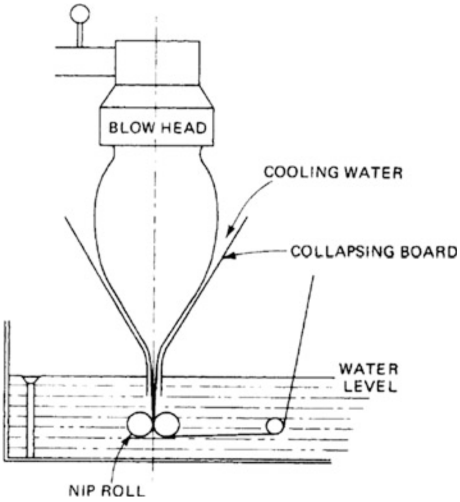
Fig. 4.4 Typical shape of HDPE and LDPE blown tube [47]

processability as well as film properties are frost-line height, bubble air temperature and bubble sizing cage [22].

As it is shown in Fig. 4.4, blowing of linear macromolecules, such as HDPE, causes film lines to have a typical "high-stalk" bubble shape, while on the other hand, branched polymers tend to be blown into the form of the "pocket" shape. The stalk height recommended for HDPE blown film lines is 7 times to 9 times the die diameter [47]. Moreover, the HDPE blown film lines typically have small diameter dies to achieve the relatively high BUR ratios required to obtain optimum film properties, contrary to LDPE and LLDPE lines, normally operating at much lower BURs of 2–3. Analogously, the typical die gaps for HDPE blown film lines are in the region of 1.0–1.5 mm, which is narrower than die gaps used for conventional blown film lines converting LDPE and LLDPE (1.5–3 mm).

When the bubble is cooled enough, it is flattened by collapsing frames drawn through nip and idler rolls to a winder, thus introducing further process stability factors such as type of collapsing frame, parameters of winder and tension control of final film. For example, in the case of PP when the blowing process is carried out downwards, as it is shown in Fig. 4.5, nip rolls are situated under level of cooling water. Since it is virtually impossible to fabricate blown film with a constant thickness, it is important, particularly in industrial practice, to eliminate accumulation of gauge variation on one place as they continuously overlap, resulting in unacceptable geometry of final roll. Utilizing different ways to randomize

Fig. 4.5 Technological settlement for water-quenched PP film blowing [48]



irregularities, localization can be ensured via several basic ways with higher or lesser efficiency as for example oscillation of extruder, rotating or oscillating die or nip system, rotating tower with winder. Consequently, based on further application of the produced film, it is finally either spooled as a flattened tube (for products such as seamless bags), slit to form one flat film or split into two separate layers during final roll winding. However, formerly winding film up to the roll for further utilization and distribution, non-polar surface of polyolefins is usually modified by the help of corona, plasma or other surface treatment which is crucial, namely prior further operations as printing, lamination, coating or other finishing operation [22].

It should be kept in the mind that appropriate balance of the blown film's physical properties is achieved in case of bi-axial orientation of macromolecules connected with high BUR ratios applied during processing. High orientation level of macromolecules in solid state is also guaranteed by low temperature of the processed melt on account of longer relaxation time. Due to differences in the polymer structures (lack of long side chains), it is much more difficult to reach balanced bi-axial orientation of HDPE films with comparison to LDPE or LLDPE films. While HDPE blown film is oriented in the machine direction after die exit forming long stalk, relaxation of macromolecules orientation in still enough heat melt occurs. On the other hand, orientation of stretched macromolecules in transverse direction is because of significant cooling of the HDPE film preceding blowing into the final bubble diameter preserved. The cooler the polymer melt reaching the top of the stalk, the higher amount of TD orientation is generated in the finished blown film. On the other hand, if the film is processed at higher temperature (relaxation time of macromolecules is shorter), TD orientation of the final product is significantly reduced [43].

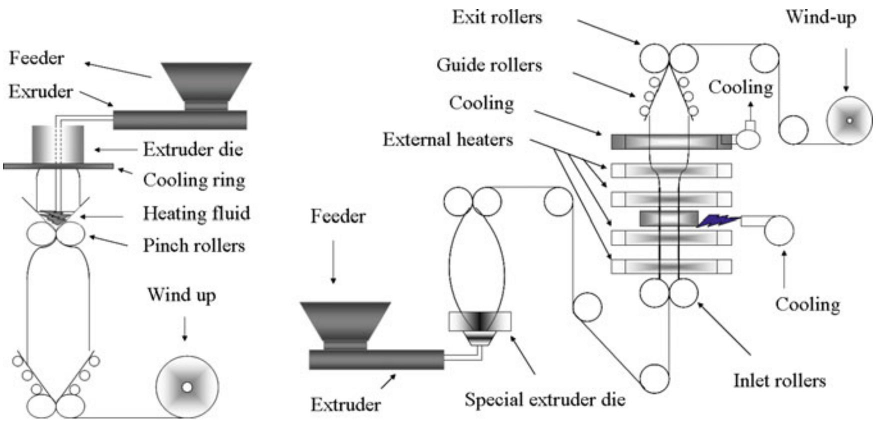


Fig. 4.6 Scheme of double-bubble blown film process [50, 51]

Since above the frost line the processed blown film is already solidified and it is stretched only in the MD direction, the orientation in this direction could be stressed significantly by this fact even in the case of low strain of the bubble. This type of orientation is deliberately induced online during blowing process or offline in consequent technology step utilizing additional drawing equipment (usually pre-heated rollers, where stretching of the film in the gap between a fast-draw roller and a slow-draw roller is determined by their turning speed ratio) in order to achieve meaningful increase of barrier properties, flatness, stiffness, elongational strength and other film features. However, to secure orientation and to preserve enhanced properties, careful control of temperature conditions together with suitable material selection, are important critical parameters [49].

Other level of orientation (MD as well as TD) could be achieved by the help of the double-bubble process. Thin, tough and elastic polymer films with attainable shrinkage ability, exploited during film applications via its heating above the orientation temperature, are obtained by this process. In this case consequently to blown film process described above, the film is re-heated above its orientation temperature. The heating can be accomplished by the use of heated air, liquid reservoir or sock disposed at the lower end of the primary bubble, inside the bubble (see Fig. 4.6). The hot blown heated film is then passed through a first set of pinch rolls, re-inflated into a blown bubble, and collapsed at a second set of pinch rolls. It should be noted that when the heated hot blown film is expanded into secondary bubble, the film can be either monoaxially or bi-axially stretched, depending on chosen combination of stretching ratios, usually set up in the range of 1:1–9:1 for the MD and 1:1–5:1 for TD. Additionally, the degree of TD or MD stretching in secondary bubble is substantially independent from the blow ratio in primary bubble, so that many combinations of blow-up ratios in the primary and secondary bubble are achievable [49–51].

4.6 Cast Film Extrusion, Extrusion Coating and Lamination

The other way to produce polyolefin films is to cast them using chill rolls. In this manufacturing process, the fabricated film could be extruded into the form of separated film (monolayer or multilayer) or connected during extrusion coating or lamination process to some substrate as a cover or binding layer, as it is presented in Fig. 4.7. The initial procedure of the cast film process, extrusion coating and lamination runs under the same routine as the film blowing. In the first step, the employed plastic materials are transferred to the polymer melt and conveyed towards the shape forming die by the help of the employed extruders eventually the melt pumps, as it was described in the previous chapter.

Nevertheless, in the consequent step the stream of polymer melt is using flat wide die with narrow opening design to provide smooth melt flow with constant cross-sectional profile, constant pressure profile, minimal chance to overheat the processed material and maximal temperature homogeneity—formed into the final form, the thin hot film. The utilized flat die usually consists of die body, heaters, feed block, mandrel, die lips or jaws for adjusting the die opening, thus controlling film thickness uniformity profile and generating optimal resistance to the flow. Since the modern feed-block technology allows the flow from one extruder split into two or more layers in the final co-extrudate, the number of employed extruders is governed by the number of different materials being extruded rather than required number of layers. For example, in order to achieve a high oxygen barrier it is necessary for polyolefin film structure to incorporate co-extruded layer of polymer like EVOH. Even the co-extruded films typically contain up to seven layers, the structure of more layers is becoming common lately [53].

Extruded film, known as a web, is noticed immediately after die exit quenched, as it is pressed usually by the help of air knife to tempered chill roll (eventually multiple chill rolls) potentially to chill roll partially submerged in a water bath, or just water bathed as schematically depicted in Fig. 4.8, allowing (compare to blown film, in general) higher film manufacturing production rates. Due to higher amorphous level that can provide heat seal film with excellent puncture resistance and amazing optical properties as important advantage aspects, for example, in food and retail packaging applications, the quality of the fabricated film is directly connected to the melt thickness uniformity, melt velocity profile at the die exit as well as the

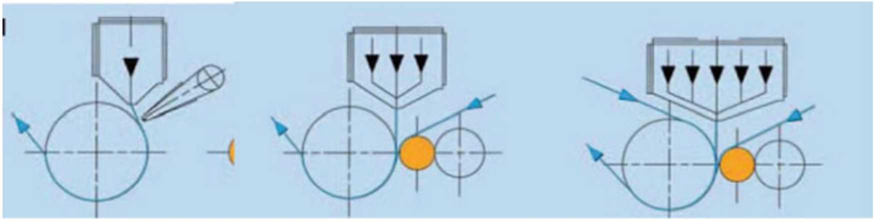


Fig. 4.7 Scheme of casting, coating and laminating manufacturing process [52]

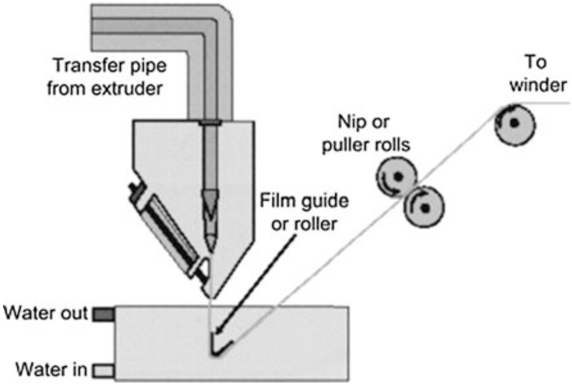


Fig. 4.8 Schematic of water bath cooling of casted film [43]

quality of chill roll which must be very smooth without any pitting or irregularities on its surface. Due to the contact of the film with chill roll on one side, different surface properties could be expected on each side of manufactured film. If a water bath is used instead of a chill roll, as it is depicted in Fig. 4.9, the quenching of the melt on both sides at the same time ensures processing of the film with the very similar surface properties on each side.

Since the temperature set for these technologies, contrary to film blowing, could be quite high (up to 300 °C specially during extrusion coating and lamination), it is necessary to ensure maximal temperature control and uniformity (usually one heat zone at least each 20 cm). Specially for the manufacturing of thin film under high processing speed, for example in the case when polypropylene is processed for food or other applications with adequate optical properties requirements, efficient homogenization of the polymer melt is crucial. In order to increase temperature homogeneity of polymer melt coming out of extruder or extruders into flat die, various types of mixing elements could be employed and some examples are presented in Fig. 4.9. In general, there are two basic types of mixing sections, one with dispersive mixing (e.g. Maddock mixer) usually causing beside high-pressure variations similarly to barrier screws significant reduction in molecular weight during extrusion process due to the high shear stresses as melted materials flow

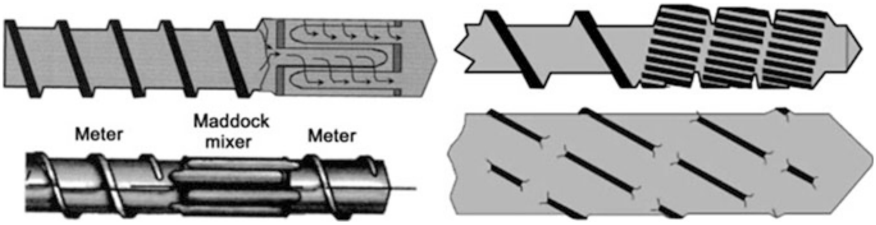


Fig. 4.9 Extrusion screw mixing elements. Maddock mixer [55]. Saxton mixers [56]

through narrow gaps, and the other one—distributive mixing sections—based on elongational mixing elements required for flow splitting and reorientation as generally more processed material considering choice. Deeper overview of available mixing possibilities together with comparison of pros and cons could be found in [54]. Another critical aspect covers ensuring constant flow of melt in the extruder, since even a small variations (as low as 1 %) in the volume flow typically result in unstable pulsating flow. Flow stability is directly driven by extruders' geometry and settlement of processing conditions.

Beside extruders design, appropriate web thickness uniformity and velocity profile are driven by the utilized concept of the die, which is another crucial factor guaranteeing trouble-free and effective production. First, the filtration system is used to prevent downstream passage of melt impurities, for example due to insufficient fillers mixing, and/or gels formation during the extrusion process. Proper control at this stage is imperative to prevent melt contamination. The most common filters are those containing metallic meshes. The case hosting the filter body has capacity of bearing the forces exerted by the polymer flow under the condition of the maximum pressure arisen by the extrusion process. The continuously regenerated screen changers minimizing the replacement time of the screen pack could be incorporated with advantage [53].

If the feed-block system is used, it is usually supplied from connected extruders by the means of melt transfer adapters. These heated and usually insulated connections should be proposed with respect to the amount of material transferred regarding not only optimal size of heating elements, but also diameter and length of pipes. Here, it should be kept in mind that even increased diameter could positively affect pressure consumption, prolonged residual time could increase tendency to degradation. Concerning feed-block proposal, it should be highlighted that while the variable feed blocks equipped with selector plug or spool could bring increased production efficiency, namely in the case when broader material portfolio is processed using the die or in the case when various additives modifying final properties of prepared film are added, the fixed feed-block geometry is more reliable and stable from process point of view, even they need to be mechanically modified when extruded profile parameters are changed. Nevertheless, it should be kept in mind that the optimal co-extruded film production is bonded to conjunction of the feed block with the rest of a properly designed die. A suitably designed flat die having the coat hanger, fishtail or T (typically utilized for coating and lamination) shape manifold (see Fig. 4.10) must ensure laminar spreading of the co-extruded material layers from the feed-block proportion, keeping the flatness of each individual layer maintained without onset of the melt flow instabilities, into the extension govern by die lips width or additionally restrict via a deckling system. Furthermore, the melt residence time should not be idly prolonged, thus preventing degradation problems or in some cases undesired heat transfer between layers. And finally, another pursued aspect is keeping a pressure drop stabilized and under an extrusion standard level, since not only any variation in melt temperature, but also pressure instability is passed through the die with little to no damping and causing

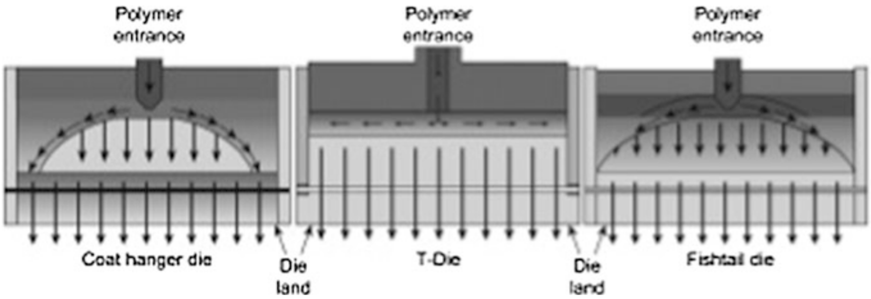
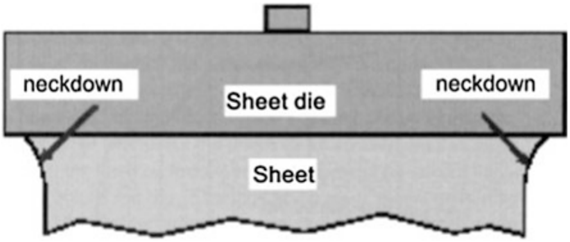


Fig. 4.10 Coat hanger, T and fishtail shape extrusion die geometry [43]

potential web processing troubles. Several adjustments could be utilized in order to overcome inevitable variations in flow and limitations of dies machining to increase the quality of the produced films. Thus, the dies are commonly equipped with adjustable choke or restriction bars for melt flow correlation (pressure drop and shear rate) in the manifold section and adjustable lips in the terminal section. There are various types of bolts available for adjusting control. They could be set manually by the help of push only/push–pull bolts, or automatically adjusting systems utilize heated/cooled bolts (push only/push–pull) [43].

When web comes out of die gap, it is stretched in the air gap due to velocity ratio of chill roll take-up and extrudate at die lips (defining drawdown ratio) determine not only thickness of the film on the chill roll (equal to die gap thickness and drawdown ratio proportion), but also narrowing of the molten web due to "necks-in" and implicating moderate anisotropy-level film properties (Fig. 4.11). Because edging profile inhomogeneity exists, usually the thickening of edges compared to the centre is due to mentioned necks-in and/or in the case of co-extrusion non-uniformity of layers occurrence is connected with encapsulation phenomenon caused by variety in viscosity of processed materials [57], it is important to detach them from the rest of the film. Though the modern flat dies technology minimized problem with the film edges trimming, still there exists disadvantage, particularly in multilayer film manufacturing using co-extrusion process, linked to the wasting of trimmed material which cannot be recycled and reused in the same film production.

Fig. 4.11 Web neck-in [43]



Casted polyolefin films are commonly characteristic by high-gloss, brilliant optics, excellent heat sealing performance, and good dimensional stability. Nevertheless, as it was already mentioned, the process significantly differs from the film blowing due to the achieved orientation of manufactured film which is ordinarily conducted with unoriented or slightly unidirectional orientated structure. While casting process guarantees the much more convenient uniform film thickness distribution, compared to blowing process, due to the reduced level of orientation, the achieved mechanical properties are lower. Thus, films with higher tensile strength and stiffness, better optical and barrier properties are demanded, as for example cellophane substitution, production of uni-axially and bi-axially oriented films is possible using modified process and customized manufacturing line composed of tenter-frame oven. In the tenter-frame process, an extruded quenched extrudate is stretched after reheating in the MD (usual stretch ratio is kept between 4:1 and 6:1) using either a series of tempered orienting rolls with consequent stretching in the TD (with ratio of 8:1–10:1) or one-step bi-axial stretching in the air-heated tenter-frame unit by the help of a rail-guided chain with clips [58]. Even the bi-axially oriented film lines based on the tenter-frame process tend to be very large and complex, for PP film manufacturing they are used predominately to double-bubble process-type lines.

One of typical applications of polyolefin films is to consequently use them in the form of tapes which are prepared after melt quenching by film slitting with a row of equally spaced blades. Tapes are often after their preparation abraded for gloss loosing via their passing through a set of rolls with fine grit sandpaper with surface speed higher than the speed of the tapes. The resulting abrasion both reduces the gloss (undesirably, e.g. for products such as primary carpet backing) and increases yarn-to-yarn friction coefficients. The tapes are then heated and drawn out at ratios of 5:1 (yarns for carpet backing) up to 18:1 (cordage), depending upon the tensile properties required for the final product and usually fibrillated via multiple short cuts or splits parallel to the yarn axis, which is accomplished by passing the drawn tape over a roller with rows of sharpened pins, which after the tape penetration slice it for a length given by the speed ratio of fibrillator roll and movement of the yarn and resulting in a “fishnet” pattern. After drawing (or fibrillation), the tapes are finally reheated in order to relax the drawing stresses according to demanded properties of the final product [59].

Another utilization of casted films is to use them for consequent lamination purposes. Contrary to extrusion coating process, where thin layer of extruded polymer melt is coated onto a substrate (usually paper, aluminium foil or plastic film), in the lamination process, molten extruded polymer layer is used for adhering of the substrate with the preheated previously prepared covering casted film. Processing conditions of extrusion lamination and coating are very similar, and compared to cast film extrusion, several differences could be identified. The lamination/process is generally run under higher production speed (up to 900 m. min^{-1}) with the longer distance between the flat die and chill roll (usually 120–300 mm instead of standard casting gap of 25-65 mm). As it was already mentioned, the temperature of polymer melt is rather higher (around 300 °C). Even the maintenance of polymer stability is important from the processing point of view, and the possible moderate material oxidation positively promotes its adhesion to substrate [60]. Nevertheless, also the viscosity of polymer melt reduction with more intensive stretching (neck-in behaviour) due to bigger air gap is connected with enhanced requirement on polymer melt strength. Increase of melt strength, generally denoted as pronounced strain-hardening behaviour, which is desirable much like in blown film process, could be achieved by addition of materials with higher long-chain branching level, as for example in case of autoclave LDPE, by polymer treatment using high energy radiation (usually electron beam) or by utilization of processing cross-linking agent, as for example small amount of peroxide.

4.7 Sheets, Pipes, and Other Profile Extrusion

Preparation of flat plastic sheets, insulation films, tubes, cardboards, frames, and many other profile shapes from a variety of polyolefin-based materials (polymeric in common) is in general referred further in this chapter. By using the same principles of the initial steps, polymer particles transferred into the melt and then transported forward to die exit; already discussed in more detail within the description of processes for films production, thin coating and lamination layers preparation are valid also for the extrusion of sheets, pipes or other profiles. The main difference is in the thickness of manufactured extrudates and speed of the extrusion lines directly determined by their total production potential with limitation given by extruder geometry, cooling capacity, etc. Moreover, contrary to the production of thin films where addition of high volume of fillers is definitely not usual, as exception could be, however, introduced breathable hygienic (water vapour permeable) films extrusion from LDPE and calcium carbonate powder compounds, fabrication of filled polyolefins is often employed for the profile production, particularly in order to increase modulus, impact resistance and strength of final products, or merely to safe polymer matrix expenses.

Behind the lip of die exit, the processed material is cooled down to a temperature that guarantees the desired shape using chill rolls, cooling baths, spray cooling tanks or air racks regarding required rate and amount of energy removal from manufactured polymer melt [61]. The polymer melts because of internal relaxation processes governed by the polymer structure and die design undergoes die swell (expansion) before its cooling as the pressure is released. Nevertheless, it is also reduced mainly according to velocity difference of extruded web and draw-off mechanism. In order to ensure demanded size of final products, the shape of extruded profile is typically controlled using the dry, wet or combined calibration tool which can be on top designed with independent water temperature control [62], eventually in the case of elastomeric materials, profiles could be free sized with no or few constrains [63, 64]. While avoidance of permanent deformation of the final products is pursued, the draw-off profile is cooled to a temperature necessary for the achievement of mechanical properties required for post-processing operations as cutting into transportable lengths, drowning onto a take-up roller, and/or packaging [65].

For sheets, thick films, and other flat profile fabrication, the similar flat dies together with cooling rolls are utilized as in the case of thin film manufacturing. While the thinner gauge sheets are often applied for further thermoforming process important for packaging applications such as drink cups, deli containers, produce trays, baby wipe containers or margarine tubs, thick sheets are usually applied for industrial and recreational applications such as truck bed liners, pallets, automotive dunnage, playground equipment and boats. The further important utilization of extruded polyolefins sheets is their application in building (road, tunnels and dam constructions), mining industry and for municipal waste disposal in the form of insulation films or geomembranes welded into large containment systems.

Concerning tube and pipe extrusion, polyolefin mono- or multilayer pipes of small diameter in units of millimetre up to diameter more than 2 metres are produced mainly due to their chemical resistance properties, easiness of installation, durability and cost saving comparing to metal or ceramic ones. HDPE as tough, abrasion-resistant and enough flexible choice, even at subfreezing temperatures, represents in this sector the most employed polyolefin type. Important applications cover water mains, gas distribution, storm and sanitary sewers, interior plumbing, electrical conduits, power and communications ducts, chilled water piping and well casing [66]. Since the combined impact of internal pressure excessively supplemented with chemical aggressive medium could occur in the case of pipes application in chemical industry, environmental stress cracking resistance could be one of the pursued critical parameter. Similarly, the supply with hot water could induce increased demands on the mechanical long-term stability. Satisfying level of resistance to mechanical and environmental stress is achieved by utilization of polymeric materials with enough extensive volume of high molecular weight portion or in order to ensure appreciable process readiness, materials with bimodal distribution could be advised with advantage [67]. Further possibility is an addition of poly(1-butene), guaranteeing increase of mechanical stiffness as supplementation effect attending its spontaneous polymorphic transformation, into the processed material or utilization of cross-linked polyethylene (PEX) with built-up macromolecules network as a result of additional treatment via either radiation or introduction of processing (peroxides) or post-processing (silane-based materials) cross-linking additives [67–70].

Usually, standard extrusion line employed for wood–plastic composite (WPC) profile fabrication (including decking, windows and doorframes, fencing, and sheets for thermoforming of, for example, automotive components) is the integral part of the WPC compounders manufacture side, historically more extended in North America but recently swiftly wide-spreading all over the world [71]. Just well-known WPC preparation employing some of the available compounding technologies and its manufacturing is another important application of polyolefins, since general plastic utilization is divided approximately by 70, 13 and 17 %, between PE, PP and PVC resins, respectively [72]. Building and structural WPC end product properties are tailored via compounding of polyolefins with wood flour, sawdust, or rice hulls together with additives such as colorants, coupling agents, thermal and UV stabilizers, lubricants, and sometimes also blowing agents or reinforcing agents, as well as mineral fillers [73, 74].

4.8 Foam Extrusion

One of the most recently developing polymer manufacturing industrial process is foam extrusion. Driving forces for innovation tendencies in this sector could be attributed not only to increasing demands on sound, mechanical and thermal insulation properties of extruded polyolefins foams, but also to material weight reduction efforts in relation to a hunting for possible economically based cost savings. Foam extrusion varies significantly from the previously described processes. The main differences are caused by necessity to (a) incorporate gas phase into the processed polymeric materials, (b) ensure demanded size and shape of prepared extruded profile complicated by the extrudate growth on the exit from the die in connection with the foaming process and (c) provide enough time to solidify shape and size stabilized foamed profile before its collapse.

From processing point of view, there exist two basic ways for the foaming production: firstly, utilization of chemical blowing agents (CBA), producing gas as a product of their thermal decomposing; and the second method is the dissolution of physical foaming agents (PFA or PBA) in the polymer melt [75]. In more details, the utilization of CBA is limited to several chemical substances that produce sufficient amount of gas phase after thermal decomposition. For a long time, azodicarbonamide is widely employed all around the world since it offers beside suitable decomposition temperature the extensive amount of decomposed gas phase consisting of nitrogen and carbon monoxide. Moreover, decomposition temperature could be modified regarding to processed materials through the incorporation of various additives (e.g. zinc oxide or zinc stearate) in the region from 130 up to 210 °C [76]. Employment of CBAs requires prior to own cell creation process during polymer melt forming into the final product shape, their thorough and homogenous incorporation into the polymer matrix as well as melt strength increase via generation of a specific cross-linking level either by peroxide addition or by high energy radiation. Necessity to increase stability of polymer melt via cross-linking is connected to the fact that CBA decomposition is often exothermic chemical reaction causing viscosity decline; moreover, melt viscosity drops as gas phase is dissolved within the polymer, but also due to lowered heat conduction ability of foam, thus prolonging cooling time for its stabilization and solidification [77].

In general, using both blowing agents (1) either high-density, usually closed cell structure, foams insuring only moderate reduction of mechanical properties with relevant polymer weight saving or (2) low-density foams that provide significant mechanical properties modification (closed, opened or closed/opened cell structure) and acoustical absorption and/or thermal insulation (open cell structure) could be

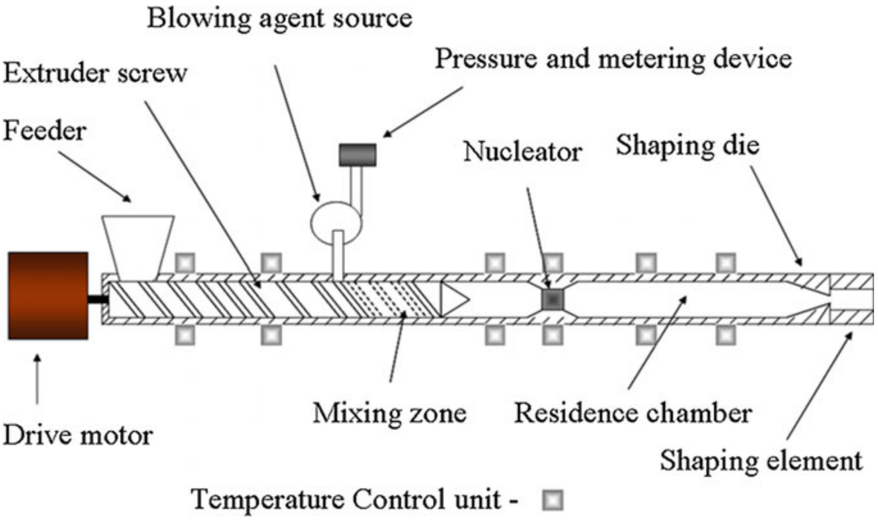


Fig. 4.12 Schematic of extrusion system with multihole nucleator, residence chamber [79]

produced. However, employment of PBA seems to offer several advantages over CBA particularly due to the possibility to employ commercially accessible devices (schematically shown in Fig. 4.12), as for example supplies Promix Solutions AG [78] or Trexel Inc. [79] together with inexpensive CO_2 or other gas dosing (e.g. low molecular weight hydrocarbons as propane, butane or pentane) instead of utilization of chemical substances [80] which use could be potentially legislatively restricted as it is actually relevant within EU for azodicarbonamide. While in the foam extrusion process, firstly the solid polymer granules are melted in the same way as it is common in other extrusion process, dissolution of the PBA, injected under the pressure into the polymer melt, is necessary. Satisfying level of melt/gas solution homogenization is highly desirable, since concentration of PBA significantly effects drop of melt viscosity, thus minimizing local viscosity variations. Appropriate gas solution, directly driven by its solubility [81], is achieved either via employment of twin-screw extruders, long-screw geometries, static mixers or residence chamber. Since this gas incorporation and dissolution into the polymer melt causes its plasticization connected with the significant viscosity to decrease (30–70 % compared to the same melt without blowing agents [82]), melt temperature prior to its foaming, after satisfactory gas distribution and thorough homogenization, decreased in order to increase the foamed structure stability. Therefore, the utilization of tandem arrangement of extruders or extruder in combination with static mixer is convenient in order to reach the lowest permissible temperature decline providing maximal increase of melt stability for the final processing stage when foaming structure is formed.

When the pressure falls as the melt reaches the die exit, gas starts to diffuse out of the melt and bubbles are nucleated and formed. Cells grow rapidly and consequent retention of the foamed structure is from the stability point of view, due to bi-axial extension of the bubble wall, dependent mainly on the melt strength [83]. Employment of branched polymers as LDPE, metallocene PE or high-melt-strength PP, typical for their strain-hardening behaviour, is thus the right choice for the successful foam extrusion process. In this respect, also blending of processed polymers with branched ones or introducing cross-linking bonds via in-line branching reactions could be the proper instrument positively effecting extrusion process. During bubble nucleation, which could be positively influenced by the utilization of nucleation additives, further stabilization of the foaming process is achieved due to the gas exclusion into the cells causing melt viscosity and strength increase. Maintenance of the cell structure to resist rupture before polymer crystallization during the cooling phase is another critical aspect restraining foamed profile collapse because of the cell coalescence [84]. Finally, since the permeation of hydrocarbons PBA through polyolefins is faster compared to air, the ageing of polyolefin foam needs to be considered to avoid post-processing shrinkage. As it was described by Cronin [85] and Park [86] utilization of fatty acid esters, fatty acid amides and fatty acid derivatives stabilizes the foams by modifying the permeability of polymer, ideally causing matching of permeability of foaming gas and air. Here, also blending of polyolefins with other polymers as for example acrylic resins or ionomers could be helpful in foam manufacturing processes [87].

4.9 Fibre Production

Fibre manufacturing is another intensively evolving polymer processing area. The advantage of polyolefin fibres is not only their durability, chemical resistance, and lightweight but particularly a positive production economic aspect. Their manufacturing is possible via all the typical fibres and filaments production technologies utilized for synthetic polymeric materials, beside polyolefins, mainly polyesters, polyamides, or polyacrylics could be mentioned. While melt spinning, as for example non-woven technologies as melt-blowing and spunbond, is used dominantly, dry and wet spinning technologies are employed for only a limited amount of applications. For example, the low entangled polymer gel-spun UHMWPE filaments are crystalized (after their coagulation in one- or multiple-step drawing process at an appropriate temperature) in the form of highly oriented high-performance fibres during the wet spinning process known as solution-gel spinning technology [88].

Contrary to the tape fibrillation process described previously in the chapter for cast film process, in the melt spinning manufacturing, the polyolefin matrix after its melting is extruded at very high speed through a spinneret (multiple hole extrusion die having thousands of tiny openings per spinning position guaranteeing production of thin fibres structure) in the form of very fine one or bicomponent

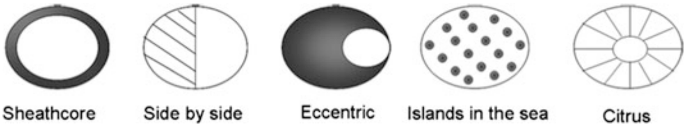


Fig. 4.13 Cross section of bicomponent fibres [90]

filaments with several possible cross-sectional shapes (e.g. circular, triangles, hollow, C or Y) and structures (sheath-core, side-by-side, excentric, islands-in-the-sea, citrus, etc. as depicted in Fig. 4.13), which are further reinforced via drawing process [89].

After their drawing via air jet, prepared fibres are collected in the form of continuous fibres randomly arranged and bonded together through self-binding, heat sealing with binder fibres or externally bonded using vinyl or acrylic compounds into a continuous sheet using calenders, ultrasonic techniques, short ovens and suction drum units in the spunbond process creating spunlaid fabrics. On the other hand in the melt-blown process, ultra-fine choppy microfibers of diameters in the range of 2–4 µm, generally made of polypropylene with high melt flow index, collected in a self-bonding web via a conveyor or take-up screen are formed by the help of spinneret or spray gun using high-velocity hot air jet. Since big efforts have been devoted recently to the melt-blown fibres processing development, production of microfibers as small as 0.1 µm and as large as 10–15 µm is also possible. Due to the lower strength compared with spunbond, combination of various non-woven fabric structures is often utilized, as for example spunbond/melt-blown/spunbond (SMS), where spunbond layers are applied for mechanical strength ensuring and centre melt-blown layer for increasing barrier properties, which affects filtration characteristics and resistance to penetration by aqueous liquids [91]. Since polyolefin fibres extruded via melt spinning process through the spinneret are neither oriented nor drawn, several consequent steps are usually required before the finished fibre is ready for conversion in the textile industry. This is done via the conventional two-stage process, when final drawing of fibres are carried out using the addition fibre line, or via the single-stage compact process, when spun material is directly further processed as for example stretched, winded and/or crimped [92].

Prepared filaments and fibres are applied not only in the floor coverings as the most important utilization for PP, but also medical, hygienic, apparel, automotive and/or agricultural sectors became crucial, for applications such as disposable diapers, sports underwear and equipment, artificial grass, geo textiles, ropes, car seats, oil wipes, wet and dry filters or membranes. Physical and chemical properties of polyolefins fibres are developed for many applications, in order to increase comfort characteristics, tensile strength, and/or other utility properties they are often blended, co-processed or combined with other materials such as polar acrylics, wool, bonding agents, hydrophilic fillers, or stabilizers.

References

1. G.W. Ehrenstein, *Polymeric Materials: Structure-Properties-Applications* (Carl Hanser Verlag, Munich, 2001)
2. http://www.psgdover.com/en/maag/automatik-pelletizing-systems/sphero-underwater-pelletizing-system/sphero-220350560
3. http://www.coperion.com/en/compounding-extrusion/machines-systems/pelletizers/ug-underwater-pelletizer
4. http://www.lyondellbasell.com/Products/ByCategory/polymers/type/Polyethylene/Polyolefin-Powders
5. US 20120172534 A1, Powdered thermoplastic polyolefin elastomer composition for slush molding processes
6. WO 2005123822 A1, Process for the production of stabilised filled polyolefins
7. T.A. Osswald, G. Menges, *Materials Science of Polymers for Engineers* (Carl Hanser Verlag, Munich, 2003)
8. http://www.ptonline.com/articles/no-5—twin-screw-extrusion
9. http://www.kraussmaffeiberstorff.com/media/files/kmdownloadlocal/en/EXT_BR_Conical_Profile_en.pdf
10. http://www.milacron.com/plastics/sites/default/files/product-files/Extrusion Brochure_FINAL.pdf
11. http://entex.de/fileadmin/user_upload/pwe._engl..pdf
12. http://www.takimsan.com/en/planetary-extruder.html
13. http://www.busscorp.com/en/quantec2.htm
14. US 3749375 A, Process for mixing, kneading and granulating thermosetting plastic material in continuous operation
15. WO 2012113086 A1,Mixing and kneading machine for continuous conditioning processes and method for conditioning metals
16. http://www.coperion.com/en/compounding-extrusion/machines-systems/pelletizers/strand-pelletizer
17. http://www.imeco.org/industry-solutions/chemicals/plastic-granules
18. R.F. Dray, How to compare barrier screws. Plast. Technol. (2002)
19. J. A. Colbert, *Scale up of Extruders, Practicalities and Pitfalls*. Screws For Polymer Processing II, A One-Day Seminar (Rapra Technology Limited, Shawbury, 1998)
20. S.T. Lee, C.B. Park, *Foam Extrusion: Principles and Practise*, 2nd edn. (CRC Press, Taylor and Francis Group, 2014)
21. R. Knittel, Get rid of wrinkles in blown film. Plast. Technol. (2007)
22. P. Waller, *A Practical guide to Blown Film Troubleshooting* (Plastics Touchpoint Group Inc., Ontario, 2012)
23. M.K. Atesmen, Everyday heat transfer problems: sensitivities to governing variables (2009)
24. J. Frankland, How fillers impact extrusion processing. Plast. Technol. (2011)
25. J. Aho, Rheological characterization of polymer melts in shear and extension: measurement reliability and data for practical processing. Ph.D. thesis, Tampere University of Technology, Finland, 2011
26. http://www.compuplast.com/
27. http://www.ansys.com/Products/Simulation+Technology/Fluid+Dynamics/Specialized+Products/ANSYS+Polyflow
28. http://www.autodesk.com/products/simulation-moldflow/overview
29. http://www.scconsultants.com/en/ludovic-twin-screw-simulation-software.html
30. R. Gendron, L.L. Daigneault, M. Dumoulin, J. Dufour, On-line rheology control for the peroxide degradation of polypropylene. Int. Plast. Eng. Technol. **2**, 55–75 (1996)
31. http://www.dynisco.com/online-rheometer-viscosensor
32. http://www.gneuss.de/index.php?lang=en&m=2&processing=online-viskosimeter
33. http://www.hydramotion.com

34. E. Riande, R. Diaz-Calleja, M.G. Prolongo, R.M. Masegosa, C. Salom, *Polymer Viscoelasticity: Stress and Strain in Practise* (Marcel Dekker, Basel, 2000)
35. J.M. Dealy, R.G. Larson, *Structure and Rheology of Molten Polymers: From Structure to Flow Behavior and Back Again* (Carl Hanser Verlag, Munich, 2006)
36. T. Sedlacek, T.M. Zatloukal, M.P. Filip, P.A. Boldizar, P. Saha, On the effect of pressure on the shear and elongational viscosities of polymer melts. Polym. Eng. Sci. **44**, 1328–1337 (2004)
37. H. Munstedt, New universal extensional rheometer for polymer melts. Measurements on a polystyrene sample. J. Rheol. **23**, 421–436 (1979)
38. J. Meissner, J. Hostettler, A new elongational rheometer for polymer melts and other highly viscoelastic liquids. Rheol. Acta **33**, 1–21 (1994)
39. C.W. Macosko, J.M. Lorntson, The rheology of two blow molding polyethylenes. SPE Tech. Pap. **19**(197), 461–467
40. S.Z. Gebrehiwot, Manufacturing and rheological analysis of spiral flow test piece. Degree Thesis, ARCADA, 2014
41. Plastics—the Facts 2013, An analysis of european plastics production, demand and waste data for 2012, Plastics Europe—Association of Plastics Manufactures (2013)
42. ASTM D883-12, Standard terminology relating to plastics
43. J.R. Wagner, E.M. Mount III, H.F. Giles Jr., *Extrusion (Second Edition): The Definitive Processing Guide and Handbook* (Plastics Design Library, William Andrew, Elsevier, 2014)
44. How to Solve Blown Film Problems, (Lyondell Chemical Company, Cincinnati Technology Center, Cincinnati, OH, USA, 2013)
45. M. Chanda, S.K. Roy., *Plastics Technology Handbook*, 4th edn. (CRC Press, Taylor and Francis Group, Florida, 2007)
46. US4201532 A, Extrusion dies of spiral mandrel type
47. Polyethylene Film Processing Guide: Quality, Value and Performance, (Formosa Plastics Corporation, Livingston, NJ, USA, 2014)
48. J.A. Brydson, *Plastics Materials* (Elsevier, 2013)
49. J.H. Schut, MDO Films: lots of promise, big challenges. Plast. Technol. (2005)
50. US 5674607 A, Double bubble process for making strong, thin films
51. EP 1476294 B1, Polypropylene biaxially oriented film
52. A. Christie, *Flat Die Extrusion Cast Film* (Coating & Laminating, Tappi, 2009)
53. Fundamentals of cast film extrusion technology. Macro White Papers, http://www.macroeng.com/fundamentals-of-cast-film-extrusion-technology.php
54. Ch. Rauwendaal, *Polymer Mixing: A Self-Study Guide* (Hanser Publishers, Munich, 1998)
55. Feedscrews, Davis-Standard Corporation. Pawcatuck, CT, 1997
56. Plasticating Components Technology. Spirex Corporation, Youngstown, OH, 1977
57. J.R. Wagner, Jr., *Multilayer Flexible Packaging: Technology and Applications for the Food, Personal Care, and Over-the-Counter Pharmaceutical Industries* (William Andrew, 2009)
58. C. Maier, T. Calafut, *Polypropylene: The Definitive User's Guide and Databook* (Taylor & Francis, 2008)
59. Polypropylene Processing Guide, (INEOS Olefins & Polymers USA, Technical Center, LaPorte, TX, USA, 2007)
60. I.M. Ward, *Structure and Properties of Oriented Polymers* (Springer Science & Business Media, 2012)
61. W.J. Sipe, Polymer extrusion cooling for the 21st century. Novatec White Paper (2002)
62. A.N. Wilkinson, A.J. Ryan, *Polymer Processing and Structure Development* (Springer Science & Business Media, 1998)
63. US 6485282 B2, Device for the extrusion of plastic profiles
64. D. Cykana, How to size & calibrate profile parts. Plast. Technol. (2011)
65. Z. Tadmor, C.G. Gogos, *Principles of Polymer Processing* (Wiley, 2013)
66. High-density polyethylene pipe systems: meeting the challenges of the 21th century. Plastics Pipe Institutes, www.plasticpipe.org

67. S. Joseph, *How Do Bimodal Polyethylene Resins Provide Improved Pipe Properties* (Lyondell, 2005)
68. L. Hojer, N. Jansen, J. Oderkerk, T. Venator, *Copolymerized silane PEX technology a new innovation for production PEX pipes* (Borealis0
69. www.pexinfo.com
70. Organic Peroxides for PEX—A Pipe and Tubes, AkzoNobel
71. P. Mapleston, It's one hot market for profile extruders. Modern Plastics **78**, 49–52 (2001)
72. J. Patterson, New opportunities with wood-flour-foamed PVC. J. Vinyl Add. Tech. **7**, 138–141 (2001)
73. A.A. Klyosov, *Wood-Plastic Composite* (Wiley-Interscience, 2007)
74. M.W. Chastagner, Slit die rheology of HDPE and ABS based wood plastic composites. M.Sc. thesis, Washington State University, 2005
75. D. Eaves, *Handbook of Polymer Foams* (iSmithers Rapra Publishing, 2004)
76. US 3321413 A, Activated azodicarbonamide blowing agent compositions
77. N.M. Mills, *Polyolefin Foams*, vol. 14 (Smithers Rapra Publishing, 2003)
78. http://www.promix-solutions.ch/
79. US 6284810 B1, Method and apparatus for microcellular polymer extrusion
80. US 7045556 B2, Polyolefin foams made with isopentane-based blowing agents
81. G. Li, F. Gunkel, J. Wang, C. B. Park, V. Altstädt, Solubility measurements of N_2 and CO_2 in polypropylene and ethene/octene copolymer. J. Appl. Polym. Sci. **103**, 5–13 (2007)
82. S.T. Lee, N.S. Ramesh, *Polymeric Foams, Mechanism and Materials* (CRC Press, Taylor and Francis Group, 2004)
83. J.M. Dealy, J. Wang, *Melt Rheology and its Applications in the Plastics Industry*, 2nd edn. (Springer Science+Business Media, Dordrecht, 2013)
84. W. Michaeli, *Extrusion Dies for Plastics and Rubber*, vol. 52 (Hanser, 2003)
85. US 3644230 A, Extrusion process for polyolefin foam
86. US 4640933 A, Expandable polyolefin compositions and preparation process utilizing isobutane blowing agent
87. WO 2000027905 A2, Polyolefin/ionomer extruded foam blend
88. J. Furukawa, *Physical Chemistry of Polymer Rheology* (Springer, Heidelberg, 2003)
89. I.M. Hutten, *Handbook of Nonwoven Filter Media* (Elsevier, 2007)
90. M. Lewin, J. Preston, *Handbook of Fiber Science and Technology: High Technology Fibers*, vol. 3 (CRC Press, Taylor and Francis Group, 1996)
91. C. Vasile, *Handbook of Polyolefins*, 2nd edn., Revised and Expanded (CRC Press, Taylor and Francis Group, 2000)
92. M. Lewin, *Handbook of Fiber Chemistry*, 3rd edn. (CRC Press, Taylor and Francis Group, 2006)

Chapter 5
Polyolefin Blends

Adriaan S. Luyt

5.1 Introduction

Polymer blend is a very important application in the field of materials, and this has been widely investigated. The preparation of polymer blends gives the opportunity for preparing new materials with a good mix of the best properties of the component polymers in the blends. The extent to which the properties of the material are improved depends mainly on the morphology of the blend and the interaction between the different components in the blend. The best mix of properties is obtained when the polymers in the blend are completely miscible, but there are only very few polymer pairs that form completely miscible blends.

Immiscible polymer blends normally have a sea-island structure, where one polymer is dispersed as (normally spherical) ‘particles’ in the other polymer, which forms the matrix, or a co-continuous structure, where both polymers are equally distributed in the blend without one polymer forming a continuous phase. For the blends to have good mechanical properties, it is also important that there is good interaction between the different components in the blend. To ensure this, researchers have tried a variety of methods to compatibilize the polymers in blends. The most used method is to add a third polymer, which interacts well with the other two polymers, into the blend. Reactive blending is another well-used method, and recently, a lot of investigation went into the use of (especially clay) nanoparticles to improve the interaction between the polymer components by locating themselves on the interfaces between the polymers.

This chapter describes the recent research on the morphologies, properties and morphology–property relationships of a variety of blends having at least one

---

A.S. Luyt (✉)
Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar
e-mail: aluyt@qu.edu.qa

M. Al-Ali AlMa’adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_5

polyolefin (polypropylene or one of the polyethylenes) as a blend component. It also highlights the possible applications of polyolefin/polyolefin blends and polyolefins blended with a number of other commercial polymers.

5.2 Polyolefin/Polyolefin Blends

5.2.1 *Blends with Ultra-High Molecular Weight Polyethylene (UHMWPE)*

UHMWPE has excellent friction and wear characteristics, as well as good notched impact strength, energy absorption capacity at high loading rates, and very low embrittlement temperatures [1]. It is used in ballistics composite materials, bearing components, and medical materials in total joint replacement. It has a very high melt viscosity (108 Pa s), and it hardly flows above its melting point because of its high molecular weight. UHMWPE powders suspended in liquid LDPE or LLDPE, and their blends, show two-phase morphologies on the mesoscale. The mixture is therefore processable by conventional injection moulding machines and screw extruders. Due to the thick interfaces of UHMWPE/normal molecular weight polyethylene (NMWP) blends, there is no significant reduction in their excellent mechanical properties such as tensile and impact strength.

There is also interest in the development of different crystal structures in these systems. Such investigations are especially important to understand the morphology development during injection moulding. Both shish-kebabs and β-cylindrites are flow-induced crystals and are formed from stretched chains [2, 3]. A good understanding of the factors that influence the final morphologies that grow from the stretched chains provides more insights into the mechanism of flow-induced crystallization as well as valuable guidance in controlling the final morphology of products in industrial production.

Isotactic polypropylene (iPP) is among the most used polymers because of its high stiffness, excellent water and chemical resistance, low density, ease of processability, and superior performance-to-cost ratio. However, low heat distortion resistance and poor impact behaviour limit its applications. Injection-moulded samples of iPP/UHMWPE blends were prepared by a mini-injection moulding machine, which can provide high mechanical stresses to induce the formation of stretched chains, in order to investigate the coexistence of the shish-kebab and β-cylindrite structures [2, 3]. UHMWPE was added into an iPP matrix in order to enhance the flow-induced crystallization of iPP. The density of row nuclei was found to be critical for the formation of shish-kebab-like structures, β-cylindrites, and β-spherulites in mini-injection-moulded iPP/UHMWPE samples. When the row nuclei was dense enough, shish-kebab-like structures formed. As the density decreased, β-cylindrites and β-spherulites appeared. At low densities, or when no row nuclei existed, β-crystals disappeared and α-spherulites dominated. It was also found that during isothermal and non-isothermal crystallization processes, the overall crystallization rates of iPP increased with the addition of UHMWPE. Different nucleation mechanisms were observed for isothermal and non-isothermal crystallization. In non-isothermal crystallization, the primarily formed UHMWPE crystals acted as nucleating agents, largely increasing the number of heterogeneous nuclei for iPP crystallization, while during isothermal crystallization the UHMWPE in the blends was in an amorphous molten state. It was proposed that the interfaces between the iPP and the UHMWPE phase domains preferentially induced iPP crystal nuclei, which effectively enhanced the isothermal crystallization rate [4].

As already mentioned, the special composite microstructure of UHMWPE, where long, regular, and non-polar chains always connect different lamellae through the amorphous phase, gives it outstanding mechanical properties, very low friction and wear rate, excellent fatigue resistance, and recognized biocompatibility [5, 6]. UHMWPE is therefore used for load-bearing, articulating surfaces for the metal/articular pair in total joint arthroplasty. However, the use of UHMWPE implants in the case of high-stress applications such as total knee implants, especially in younger and more physically active patients, is limited. The damage to UHMWPE in vivo caused by wear debris, oxidation, or mechanical performance degradation adversely affects the long-term performance of the reconstructed joint. It is therefore important to enhance the mechanical properties of the UHMWPE implants without sacrificing the wear resistance and oxidation stability. Xu et al. [5, 6] successfully improved a number of properties of UHMWPE/low-molecular-weight polyethylene (LMWPE) blends through the formation of an interlocking shish-kebab self-reinforced superstructure by applying shear flow during the injection process. This superstructure made the PE blend samples very strong, and its rigidity improved the wear resistance along the direction of shear flow. When low-molecular-weight, low-density polyethylene (LMWPE) was solution-blended with UHMWPE and the film studied under a controlled temperature-gradient field, it was found that no clear lamellae were formed in the β-LMWPE-rich phase due to complex interactions such as solvent evaporation, crystallization, and phase separation [7]. However, the lamellae in the UHMWPE-rich phase became more disordered as the temperature was increased. The preferred orientation of the lamellae also strongly depended on the annealing temperature, and they stacked regularly and oriented parallel to the film surface at lower temperatures. However, the lamellae preferably oriented along the normal to the film surface, with a random distribution around that direction at higher temperatures. The film drawability was also influenced by this arrangement, as shown in Fig. 5.1.

When studying UHMWPE blended with low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), it was found, using analysis of the log–additive rule, Cole–Cole plots, Han curves, and Van Gurp's plot, that the LDPE/UHMWPE blends were miscible in the melt [8]. However, the thermal properties and morphology of the blends were not consistent with the rheological properties. The latter showed liquid–solid phase separation as a result of the different rates of crystallization of LDPE and UHMWPE. However, the rheological properties and electron microscopy images of LLDPE/UHMWPE blends showed

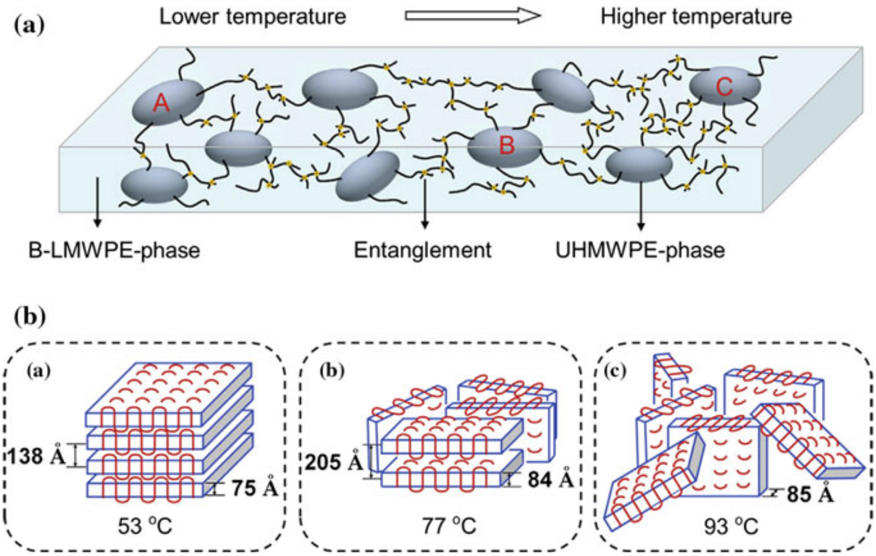


Fig. 5.1 Schematic of **a** the entanglements between UHMWPE-rich phases, where the ellipsoid represents the UHMWPE-rich phase and the nets between the ellipsoids are the entangled chains of UHMWPE, and **b** lamellae development in UHMWPE-rich phase under a T-gradient field, where *A*, *B,* and *C* correspond to the annealing temperatures 53, 77, and 93 °C, respectively [7]

partial microphase separation, with the extent of phase separation depending on the LLDPE content.

UHMWPE can also be blended with random ethylene co-polymers, but it is difficult because of a sudden decrease in the crystallinity with an increase in the incorporated monomer content [9]. This leads to a significant change in the co-polymer mechanical properties and deformation. A metallocene/methylaluminoxane (MAO) catalyst normally provides high-yield synthesis of polyolefins and olefin co-polymers, with a high incorporated α-olefin content. These catalytic systems allow one to control the structure and properties of the blend components and, therefore, to control the crystallization processes, morphology, and overall properties of the reactor blends. The precatalyst nature determines the molecular weight of the product. Ushakova et al. [10] found that the introduction of random ethylene/1-hexene co-polymers (CEHs) led to the modification of nascent reactor-blended crystalline and amorphous phases. The possibility to widely vary the composition and morphology of the co-polymer fraction from semicrystalline to completely amorphous in the polymerization with a zirconocene catalyst allowed them to change the material crystallinity and density. The tensile properties and melting indices of these blends depended on the properties of the UHMWPE fraction and the content of the CEH fraction, and on the co-polymer composition. These blends showed a high enough strength because of the presence of many interlamellar tie-molecules in the UHMWPE fraction.

5.2.2 Shape Memory Applications

Shape memory (SM) functionality is the ability of a material to fix one or more 'temporary' shapes after a quasi-elastic deformation and to recover its original ('permanent') shape through stored elastic and viscoelastic stresses that drive SM recovery after the application of an external thermal stimulus. This is normally linked to a thermal transformation like melting/crystallization or glass transition in the polymer that has a covalent or physical network. Radusch et al. [11] created SM polymers through covalently crosslinked polyolefin blends. Distinct multiple SM behaviour with high performance was obtained by blending polycyclooctene (PCO), which is thermodynamically incompatible with polyethylenes and has a low viscosity in the melt, with the polyethylenes. All the investigated materials were either quenched or slowly cooled from the melt before crosslinking. The subsequent crosslinking was performed by electron beam radiation at room temperature to fix the phase morphology, which was generated during mixing and thermal treatment. They found multiple SM behaviour only through the blending of thermodynamically incompatible materials. They also found that thermal history alone was not sufficient to improve the phase separation in thermodynamically compatible blends, which is a requirement for pronounced multiple SM behaviour. Their blends seem to have good potential for applications requiring multiple shape changes between 60 and 135 °C.

SM effects can also be induced by mixing two polymers with widely different melting points, such as LLDPE (122 °C) and PP (165 °C). A new shape memory mechanism for an LLDPE/PP/LLDPE-PP ternary SM blend was proposed [12], in which the two components that had quite different melting points both contributed to the SM performance. The PP acted as a fixed phase, the LLDPE was the reversible or switch phase, and the LLDPE-PP acted as compatibilizer to improve the compatibility of the blends. The strong interaction between the fixed and reversible phases, and appropriate blend ratios was important for the good shape memory effect of the blends. It was found that during the deformation process, the droplets of the fixed phase were unchanged, while molecular orientation occurred in the reversible phase (Fig. 5.2). Consequently, heating the material and releasing the stress reversed the shape back to the original.

Triple SMPs have one permanent shape and two temporary shapes, compared to the traditional double shape memory polymers (SMPs) that have only one permanent and one temporary shape. Triple SMPs can therefore provide more complex actuation than double SMPs. While double SMPs only need one reversible phase, triple SMPs generally need two reversible phases. Zhao et al. [13] first built a co-continuous architecture in immiscible polyethylene (PE)/polypropylene (PP) blends, and then prepared triple SMPs through chemical crosslinking of the blends. The co-continuous window of typical immiscible PE/PP blends is a volume fraction of PE of approximately 30–70 vol.%. This architecture can be stabilized by chemical crosslinking. Different initiators, 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane (DHBP), dicumylperoxide (DCP) coupled with divinylbenzene (DVB) (DCP-DVB), and their

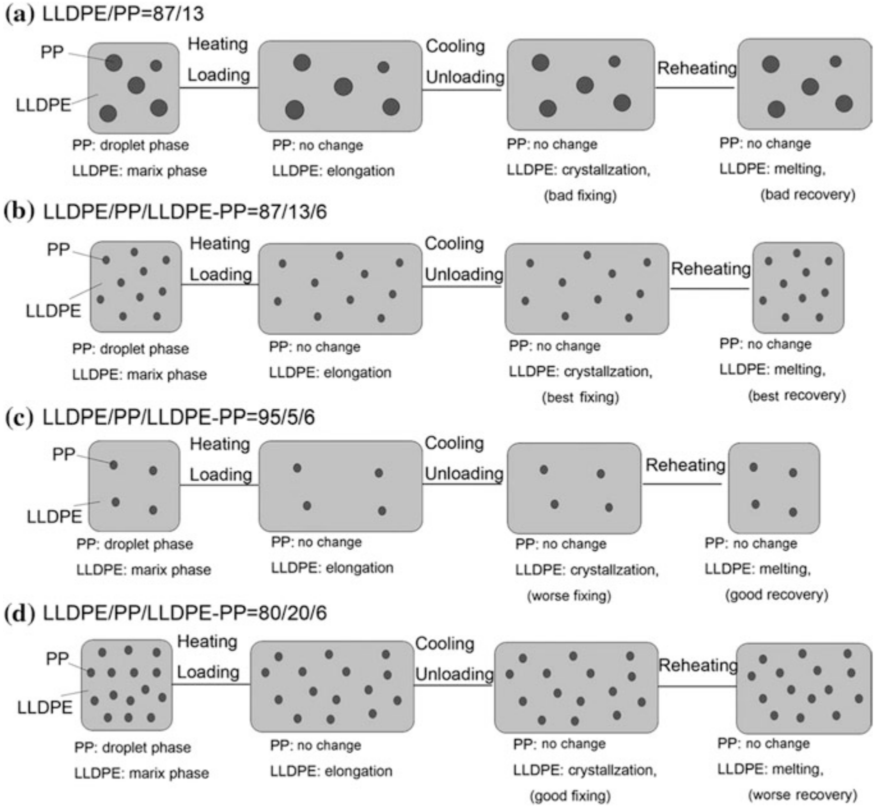


Fig. 5.2 Schematic figures of the shape memory mechanism of LLDPE/PP/LLDPE-PP blends [12]

mixture (DHBP/DCP-DVB) were used for the crosslinking. They found that DHBP produced the best crosslinking, and DCP-DVB the worst. The chemical crosslinking caused lower melting temperatures (T_m) and smaller melting enthalpies (ΔH_m). A similar investigation [14] looked at the multiple-shape memory capability of polyethylene blends that were crosslinked at the interface between a thermoplastic and an elastomer. An optimized composition containing 80 wt% ethylene octene co-polymer (EOC), 15 wt% LDPE, and 5 wt% HDPE was lightly crosslinked using DCP. The blend was found to contain finely dispersed crystalline phases, which selectively melted at distinct temperatures. The crosslinked blend was successfully programmed to a dual-, triple-, and quadruple-shape memory effect. The triple- and quadruple-shape memory showed well-defined intermediate temporary shapes (retraction $< 0.5\ \%\ K^{-1}$) over a significantly broad temperature range (up to 30 K), large storable strains (up to 1700 %), and nearly full recovery of all the shapes (>98.9 %).

HDPE, poly(ε-caprolactone) (PCL) (which is not a polyolefin, but is included here because of its shape memory behaviour) and binary HDPE/PCL blends containing the crosslinking agent dehydrobenzperidol peroxide (DHBP), with different mass ratios of the components, were investigated for their two-way shape memory behaviour [15]. Two-way SMEs show, on the one hand, anomalous elongation of a sample initiated by non-isothermal crystallization during cooling under load (at a constant force) and, on the other hand, the expected contraction of a sample during heating under the same load triggered by melting of the oriented crystalline phase. In contrast to irreversible one-way SMEs, invertible two-way SMEs can be reproduced repeatedly as long as the sample is loaded and the temperature change is enough to cause consecutive crystallization and melting of the sample. The SME performance of crosslinked semi-crystalline polymers therefore strongly depends on the properties of the crystalline structure and of the covalent polymer network generated in the material.

5.2.3 Compatibilization

Compatibilization of polymer blends is not a new concept, but some recent studies proposed innovative ways of compatibilizing polyolefin–polyolefin blends. Recently, the Dow Chemical Company developed a chain-shuttling catalyst technology to synthesize novel olefin block co-polymers (OBC) in a continuous process [16]. The OBC contains crystallizable ethylene/octene blocks with a very low octene content and a high melting temperature, alternating with amorphous ethylene/octene blocks with a high octene content and a low glass-transition temperature. Compared to statistically random ethylene/octene co-polymers, the OBC was much more effective in compatibilizing PP and high-density polyethylene (HDPE) blends. The adhesion of four OBCs to PP and HDPE was studied using microlayered PP/OBC/HDPE tapes [16]. Adhesive delamination occurred at the PP/OBC interface for all these OBCs. Two regimes were defined based on the tie-layer thickness. The delamination toughness increased linearly with increasing tie-layer thickness for all the OBCs in the thick tie-layer regime, which indicated that the energy was dissipated by deformation of the entire tie-layer, while the delamination toughness decreased more rapidly with decreasing tie-layer thickness in the thin tie-layer regime due to a highly fibrillated damage zone morphology.

5.2.4 Epitaxial Crystallization

Heterogeneous epitaxy is a specific interfacial crystallization between different polymer pairs due to lattice matching. Heterogeneous epitaxy at interfaces may be an active way to improve the mechanical properties of polymer blends, especially for incompatible systems. The epitaxial growth of HDPE and LLDPE on the oriented iPP lamellae, to obtain epitaxy during industrial processing and to obtain super polyolefin blends, has been clearly demonstrated, and it was shown that chain orientation induced by shearing facilitates epitaxy [17]. The crystallization of propylene-ethylene random co-polymer (PPR) is significantly promoted by flow and occurs before that of HDPE in their blends, and this sequence determines the epitaxial growth of HDPE on the PPR crystals. In a blend with HDPE as matrix, however, the epitaxial growth of HDPE under flow competes with the shear-induced formation of shish-kebabs. If shear-induced crystallization is activated, the epitaxial growth of HDPE will be suppressed and the crystallization sequence will have little effect.

Heteroepitaxy of polymers is a method to improve the mechanical properties of polymer blends, especially for incompatible systems. The epitaxy mechanism of iPP/HDPE was found to be clear [18, 19]. The epitaxially grown HDPE chains interact with rows of methyl groups that populate the iPP (010) alpha plane, since the PE chains exactly fit into the valleys formed by the methyl groups. However, well-defined epitaxial growth can only be obtained by either (a) vacuum deposition/casting film crystallization of iPP (or HDPE) onto single crystals or oriented films of HDPE (or iPP), or (b) annealing of drawn blends of iPP/HDPE and sandwiched films of iPP/HDPE. No well-defined heteroepitaxy has been achieved in polymer blends produced by traditional processing methods (such as injection moulding and extrusion). Deng et al. [18, 19] performed experiments to investigate the possible epitaxial growth between iPP and HDPE by using micro-injection moulding, which can prepare highly oriented samples, and they managed to achieve epitaxial growth at high shear and suitable temperatures. Another group [20], in a similar study, illustrated successful control of the blend superstructure via dynamic packing injection moulding. The crystalline and oriented structure in moulded bars of LLDPE/iPP blends was identified with the aid of two-dimensional wide-angle X-ray diffractometry. The iPP, which was the dominant phase, was highly oriented in the blends. The LLDPE was epitaxially crystallized on the oriented iPP and the contact planes were $(100)_{\mathrm{LLDPE}}$ and $(010)_{\mathrm{iPP}}$, resulting in an inclination of the LLDPE chains, about 50° to the iPP chain axis. Since iPP was the minor phase, it had a low level of orientation and there was no epitaxial growth between iPP and LLDPE, and the LLDPE remained oriented. The observed epitaxial growth of LLDPE on the oriented iPP was due to (1) the effect of the crystallization sequence, (2) the composition dependence of the oriented iPP structure, and (3) a ‘mutual nucleation’ phenomenon, where the two components acted as nucleating agents for each other.

The epitaxial growth and the formation of a shish-kebab structure were also investigated in high molecular weight iPP (HMW-iPP)/low-molecular-weight LLDPE (LMW-LLDPE) blends [21]. The formation of the initial crystallization precursor structure was investigated by using synchrotron WAXS/SAXS techniques at 130 and 140 °C. Shear was applied at temperatures above the cloud points of these blends, and therefore, the HMW-iPP chains could form a flow-induced crystalline structure in the blends only at 6 and 9 wt% of HMW-iPP; LMW-LLDPE merely served as the amorphous matrix (Fig. 5.3). When the HMW-iPP

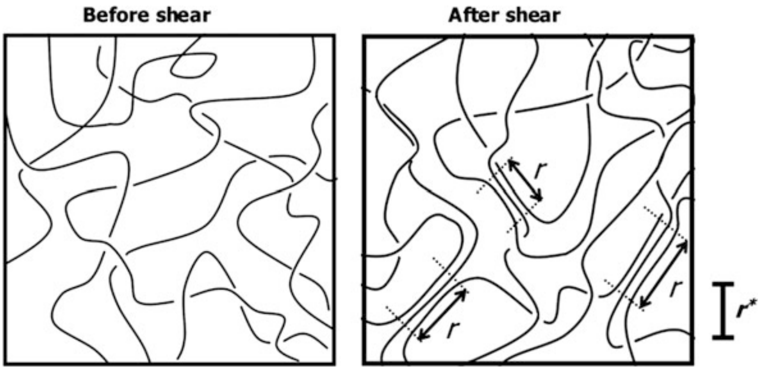


Fig. 5.3 Schematic illustration of initial crystallization precursor structure (stable critical nucleus) formation in HMW-iPP/LMW-LLDPE blends after cessation of flow. Before flow, HMW-iPP chains (*solid lines*) form a network with a given entanglement density in the LMW-LLDPE matrix (*blank area*). During shear, stretched chain segments begin to form initial crystallization precursor structure via local parallel packing. r and r^* represent the sizes of initial precursor and critical nucleus for crystallization, respectively. When $r \geq r^*$, the precursors can further develop into crystals [21]

concentration was low, no flow-induced crystallization was observed at both temperatures. When the concentration of HMW-iPP increased above 3 wt%, the flow-induced nucleation, crystallization kinetics, crystallinity, and lamellar orientation were all significantly improved.

During the extrusion of linear polyethylene (LPE) and iPP blends, the epitaxial crystallization of these blends yielded two types of epitaxial structures: (1) homoepitaxy of both components where the branches, shorter in iPP and longer in LPE, were initially oriented perpendicular to the extrusion direction, and (2) heteroepitaxy of LPE on initially crystallized iPP fibrils [22]. The positive mutual interaction of iPP and LPE was the result of the solid iPP representing a heterogeneous nucleation surface for LPE crystallization such that its lamellae were inclined ±50° to the extension direction. The limited mutual solubility of the two blend components influenced the crystallization and melting behaviour of the blend. The blend extrusion led to the iPP phase being slightly oriented towards the extrusion direction. The relatively short crystallization time resulted in a higher amorphous content and lower crystallinity, crystal size, and melting temperatures than in other highly oriented or annealed samples of iPP or LPE.

5.2.5 Other Crystallization Phenomena

As already described in the previous section, crystallization of the different components in a blend is a very important factor in determining the interaction between the different components and the blend properties. Generally, higher molecular weight will give rise to better final mechanical properties, but it also results in high melt viscosity and poor processability, which limits the application of PE [23]. Polyethylene with bimodal molecular weight distribution (defined as bimodal PE) can address this conflict between mechanical properties and processability. In bimodal PE, the low-molecular-weight fraction contributes to the stiffness and creep resistance in the crystalline state, and reduces the melt viscosity during processing. The high molecular weight fraction forms the tie-molecules that connect the crystal lamella mainly formed by the low-molecular-weight fraction, enhancing the impact strength and stress cracking resistance. Bimodal PE is produced through two methods in industry: the reactor in series configuration and the single reactor with dual site catalysts.

There was a fair amount of research into the crystallization behaviour of the low and high molecular weight components in bimodal polyolefin blends. In one such an investigation [24], differential scanning calorimetry was used to investigate the non-isothermal crystallization behaviour of blends containing low-molecular-weight polyethylene (LMWPE) and high molecular weight polyethylene (HMWPE). When LMWPE was added, the molecular weight (MW) of the blends decreased and the molecular weight distribution (MWD) broadened. Meanwhile, the low-molecular-weight fractions also increased, and the blends gradually showed obvious bimodal MWD (Fig. 5.4). The Avrami analysis modified by the Jeziorny theory and Mo's method successfully described the non-isothermal crystallization process of these bimodal PE blends, although some complicated relationships between the MW and the different analysis parameters were obtained.

In bimodal polyethylene (BPE) blends, the high molecular weight fraction with a higher degree of branching gives BPE better toughness and environmental stress crack resistance, while the low-molecular-weight fraction with a more linear chain structure ensures good processability of the material [25]. When blending an HDPE sample and an LLDPE sample with almost the same molecular weight distribution, but with a considerable difference in the short-chain-branching (SCB) content,

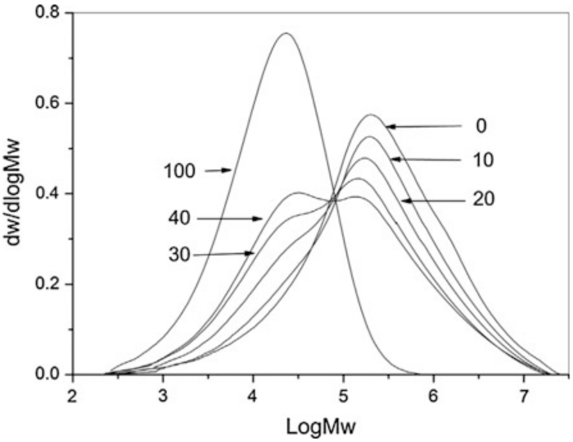


Fig. 5.4 MWD curves of HMWPE/LMWPE blends and their components (weight fraction of LMWPE indicated) [24]

blends with a bimodal chain branch distribution and a normal unimodal molecular weight distribution were obtained. A certain degree of co-crystallization was observed for all the blends, even after thermal fractionation, and crystal perfection was improved by the co-crystallization because the crystallizable fragments formed more prefect lamellae in the blends. The co-crystallization behaviour of this blend system effectively promotes fracture toughness, because the work of fracture (w_e) of the different blends was much higher than those of pure LLDPE and pure HDPE.

It is known that increasing MW brings good stress crack resistance and toughness to PE, but results in difficulty in processing. On the other hand, lower MW, which normally improves stiffness and ease of processing, reduces the toughness. In order to balance the relationship between processing and mechanical performance, one should simultaneously consider the MW and chain-branching parameters. With this in mind, the melt-blending of different PEs has been successfully applied in industry. However, since the crystalline phase accommodates only linear chain segments, a slight variation in the chemical structure of the PE segments that participate in the crystallization may cause these segments to be rejected by the crystalline phase, resulting in individual crystalline phases and/or segregation. In the absence of any force between the chain segments, the compatibility of different PEs depends on the accommodation of different chain segments in the crystalline phase. Analysis of the melting curves of HDPE/LLDPE blends after successive self-nucleation and annealing (SSA) treatment showed co-crystallization through a variation in the relative amount of each melting fraction [26]. When enough HDPE was added into the blends to make the number of melting peaks increase, co-crystallization occurred because the interaction between the HDPE and LLDPE molecules resulted in a new fraction forming with intermediate lamellar thickness. Once a new thermal fraction with much thicker lamella appeared through variation of the blend composition, the thickness of the original fraction slightly decreased, indicating that some long linear methylene segments were affected by the presence of HDPE and transferred from the original fraction to the newly formed fraction.

Liquid–liquid phase separation and crystallization are basic phase transitions in polymer blends. The interplay of these two processes to a large extent controls polymer morphologies. During isothermal crystallization, with the exception of very low-molecular-weight materials, co-crystallization also occurs between different materials. A study of the crystallization and melting behaviour of linear and branched polyethylenes, and their blends, using DSC and synchrotron SAXS techniques showed that co-crystallization occurred in a blend of linear polyethylene and branched polyethylene of 4.8 % hexene, whereas a blend of linear polyethylene and branched polyethylene of 15.4 % hexene showed macroscopic liquid–liquid phase separation [27]. SAXS results indicated that a large decrease in the long period in the initial stage of crystallization occurred during cooling, which gradually levelled off in the final stage. This has been explained by the lamellar insertion model, where additional thin lamellae are inserted into the thicker primary stack yielding a significant decrease in the long spacing (d_{ac}) of average lamellar stacks, and the average lamellar thickness (d_c).

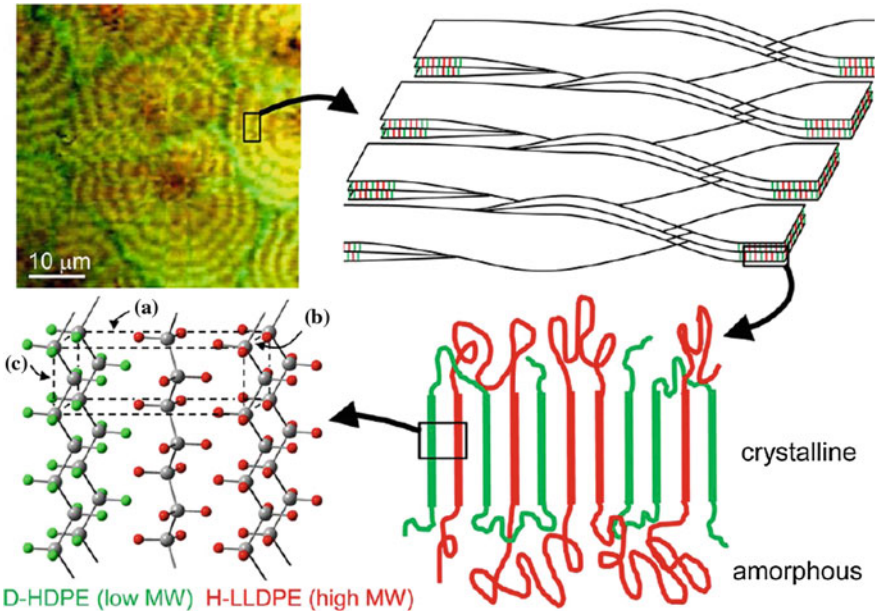


Fig. 5.5 Schematic hierarchy of microscopic structure of PE blend spherulites consisting of semicrystalline lamellar ribbons. *Green* in the composite image indicates D-HDPE, and *red* indicates H-LLDPE. The *dotted rectangular box* in the molecular structure indicates the unit cell of crystalline PE, with the unit cell parameters (*a*, *b*, *c*) as indicated [28]

The actual crystalline structure of polyolefin blends can be investigated through broadband coherent Raman (CARS) microscopy, which is a 3-D chemical imaging technique with high efficiency, developed to acquire simultaneous compositional and orientational images of multicomponent biological and materials systems [28]. CARS microscopy can simultaneously be an image of chemical composition and molecular orientation of the high and medium MW chains in a polyethylene semicrystalline blend. It was found that there was a gradual exclusion of the medium MW chains from the spherulite centre and its amorphous characteristics, a higher degree of crystallinity of the medium MW chains in the ring banding, and a filling of the interstack amorphous regions by medium MW chains (Fig. 5.5).

5.2.6 Waste and Recycling

Blending of polyolefins is increasingly used to produce usable materials from polymer waste, to improve the processing and to retain the good thermal and mechanical properties. Blend prepared from virgin and/or recycled components is a well-established strategy to handle post-consumer and post-industrial polymeric wastes. HDPE and PP constitute a significant portion of post-consumer waste [29].

PP is widely used for carpeting, packaging, and other applications, while HDPE is mostly used in the packaging of consumer and industrial products. Their occurrence in mixed scraps is likely to occur, and a complete separation of these two polyolefins is costly and almost impossible because of their close densities and similarity of other physical properties. PP shows a relatively low modulus, yield strength, and resistance to creep that limits its applications, but these properties can be improved by mechanical blending with PE.

Fang et al. [30] blended waste PP and investigated the mechanical and thermal properties of this binary blend. They wanted to improve the compatibilization of the binary blend through adding different compatibilizers (EPDM and PE-g-MAH) and a montmorillonite nanofiller, and comparing the different compatibilization effects. They blended the waste PP and PE with the different compatibilizers in a twin-screw extruder. The tensile and impact strength of the uncompatibilized blends showed a slight improvement, but the compatibilizer improved only the impact strength. The waste PP reduced the thermal stability of the blends. When the amount of waste PP was 60 wt%, the thermal stability almost reached the level of pure waste PE, but the presence of the O-MMT improved the thermal stability. EPDM had a better compatibilization effect than PE-g-MAH, but the PE-g-MAH more significantly improved the mechanical properties. Crosslinking through electron beam irradiation was also used to compatibilize waste polymers in a blend [31]. It was found that blending of waste PE with virgin HDPE and LDPE, and irradiated with an electron beam, increased the crystallinity and induced crosslinking in the blends.

5.2.7 Rheological Properties

LDPE, produced by radical polymerization at a high temperature and pressure, having a broad molecular weight distribution and long-chain branches, shows good foaming, blow-moulding, film-blowing, and extrusion coating processability. The melt elasticity of LDPE is normally enhanced by blending with LLDPE or HDPE, although both LLDPE and HDPE normally have a narrow molecular weight distribution and no long-chain branches. Mieda et al. [32] investigated the flow instability at capillary extrusion of blends composed of LDPE, as a long-chain-branched polyethylene, and three types of linear polyethylenes having different molecular weights. The effect of shear viscosity of the linear polyethylenes, which plays an important role in anomalous behaviour, on the flow instability at capillary extrusion was studied in detail. The blends containing linear PE with a high shear viscosity showed a synergetic effect, i.e. an enhanced zero-shear viscosity and marked strain-hardening. The blends showing an anomalous rheological response exhibited shark-skin failure at low shear stress, which was explained by the high Deborah number for the blends. The blends showed severe melt fracture compared to branched PE. Increased strain-hardening in elongational viscosity and a large entrance angle at the die entry were found to be responsible for this observation.

Rheological measurements were also used to detect subtle viscoelastic changes in two metallocene polyolefin co-polymers, poly(ethylene-co-hexene) (PEH), poly (ethylene-co-butene) (PEB) and their 50/50 w/w blend, by changing the moulding conditions [33]. A low level of long-chain branching (LCB) was detected in the PEB component (with higher short-chain branching (SCB) level), because of the active tertiary carbon atoms on its backbone. Since the relaxation and diffusion of polymer chains can be significantly retarded by LCB, this structure is expected to further affect the phase separation kinetics of these blends. Since PEB is less stable than PEH for moulding at temperatures above 100 °C, thermal oxidation-induced LCB was detected on PEB and the blend by rheological measurements that were more sensitive to detect the low level of LCB than other methods such as FTIR, gel extraction, and GPC. Gel extraction and GPC results indicated that there was no crosslinking for all the PEB and blend samples, which indicated that the slight LCB retarded the development of phase separation. Once LCB was beyond a certain level, the readily formed LCB entanglements prevented chain diffusion of PEB, and then phase separation could hardly occur.

Another investigation looked at the influence of different LDPE dispersed phases on the linear viscoelastic behaviour and elongation in the melt of LLDPE/LDPE blends [34]. In the case of blends of Ziegler–Natta LLDPE with LDPE, the linear viscoelastic spectrum showed an additional contribution, which could not be explained by the assumption of a simple dispersion of LDPE droplets in the LLDPE matrix. This contribution was not present when the matrix was a homogeneous LLDPE obtained by means of a single-site catalyst. It was therefore probably due to the existence of a thick interphase formed by a fraction of the longest linear molecules of the LLDPE matrix and the shortest, less branched molecules (rich ethylene sequences) of the LDPE minor phase. This interphase then gave rise to a long relaxation time tail, which could be explained by a viscoelastic model that includes the effect of non-isotropic interfacial effects with a significant elastic character.

5.2.8 Barrier Properties

Common routes to reduce gas permeability consist of combining materials, capable of giving higher barrier than the individual components, through lamination, coating, or co-extrusion. However, total barrier is no longer the main goal of food packaging, but rather the saving of freshness. This is the case, for example, with cheese and meat that must be consumed within a limited number of days, in contrast to the bakery products that are supposed to last several months. It is therefore important to investigate the modulation of the film permeability to meet specific requirements for different foods. Taglialatela Scafati et al. [35] attained the modulation of permeability by melt-blending a commercial polymer for packaging with a high-barrier material. Melt-blending is less complicated and less costly than lamination or coating, and monolayer films based on blends are attractive alternatives to multilayer co-extruded films. An LDPE/LLDPE blend was melt-blended with an ethylene/norbornene co-polymer (COC). COCs are characterized by excellent transparency, high rigidity, good thermal stability, and resistance to acids and bases. A significant decrease in O_2 and CO_2 permeability was observed with COC content ranging from 5 to 20 wt%, and the desired value of diffusional properties was obtained by adding a proper amount of COC.

5.2.9 Polyolefin Blends as Models for High-Impact Polypropylene Co-polymers (HIPCs)

HIPCs are PE-grafted PP co-polymers made through a dual-reactor process. In this way, the toughness of the material can be improved while retaining reasonable stiffness and expanding the application temperature range. A lot of research these days is aimed at unravelling the morphology and structure of these co-polymers. In some of the research, PP/PE blends are investigated as model systems for HIPCs. One investigation of such blends concentrated on the relation between the composition and mechanical performance of a series of binary polyolefin blends [36, 37]. These model compounds were fractionated with temperature rising elution fractionation (TREF) to study the possibility of fractionating industrially relevant heterophasic polyolefin systems. The separation quality, based on molecular structures or chemical composition, was found to be good for most of the systems. However, the separation of an ethylene-propylene random co-polymer and a high-density polyethylene was difficult if not impossible. Mechanical characterization, including the determination of brittle-to-ductile transition curves, showed significant effects of modifier type and amount. Toughness effects were primarily related to the modulus differences between the modifier and matrix. Compatibility and particle size were found to have a secondary influence, but were considered for a detailed interpretation of the mechanics of the investigated systems.

5.3 Polyolefin/Ethylene Vinyl Acetate (EVA) Blends

HDPE is a thermoplastic material with unique properties, such as excellent mechanical properties, ozone resistance, good electrical properties, and chemical resistance. EVA shows high impact strength, stress crack resistance, good ageing resistance, low-temperature flexibility, improved clarity, permeability to oxygen and vapours, high moisture absorption, and good electrical resistance [38–40]. Blending these two polymers should give rise to a product with a good property mix, but which should undergo much faster degradation when being disposed of.

These blends are widely used in shrinkable films, multilayer packing, and wire and cable coating. Although PE and EVA are immiscible, the vinyl consequence in EVA gives the same crystal structure as PE and partial miscibility at the interface of PE/EVA blends. Addition of EVA to HDPE could improve transparency, environmental stress cracking resistance, capacity of filler carrying, and impact properties, but usually reduces the tensile strength.

Although PE crystallinity could reach 65 %, EVA with about 50 wt% VA is completely amorphous [38]. The polarity of EVA increases as the VA content increases because of the polar nature of the acetoxy side chain. This allows manipulation of important properties such as flexible shrink wrap, agricultural films, coatings, paints, footwear soles, hot melt and heat seal adhesives, semipermeable films, flexible toys and tubing, and crosslinked foamed tyres. The addition of EVA to PE can improve its transparency, flexibility, thermal resistivity, environmental stress cracking resistance, and loading capacity of fillers. These blends possess good thermo-shrinkage and stability when subjected to ageing, weathering, and aggressive media, and are therefore used in many applications such as high-voltage cable systems, multilayer packaging films and sheets, car parts, agricultural films, and medical tubes.

The addition of PE provides a higher rigidity to the products and at the same time improves the flowability of the melt during processing. Since EVA is more expensive than PE, blending can be an effective way for cost saving [39]. Most polymer blends have some degree of immiscibility, giving rise to a multiphase morphology, and this strongly affects the rheological behaviour and mechanical properties that depend on the type of morphology and on the interfacial interaction between the phases. On increasing the EVA content, the morphology of these blends changes from a two-phase structure, if EVA is dispersed, to a co-continuous morphology and, at large EVA content, a two-phase morphology again with LDPE dispersed as domains in the EVA. This influences the rheology of the melt and the mechanical properties of the solid state. The crystallization behaviour of these blends is also influenced by the morphology, with the crystallization behaviour depending on the composition.

DSC results showed a melting temperature depression of HDPE caused by the dilution effect of the non-crystalline EVA and the probable co-crystallization of some EVA chains with HDPE chains [38, 40]. Changes in the crystallization and melting temperatures of EVA were determined mainly by the nucleation effect of HDPE crystals and the effect of partial miscibility between these polymers. Crystallization kinetics results showed that the addition of more HDPE into an EVA matrix caused more heterogeneous nucleation, while the addition of EVA would delay the nucleation of HDPE at the beginning of the cooling process. Intermolecular interaction in the melt facilitated the crystallization of both EVA and HDPE.

SEM images of HDPE/EVA blends showed that these samples have two distinctive crack propagation zones: slow and fast [38]. The lengths of these zones were affected by the EVA content. The slow crack propagation zone length increased with increasing the EVA content, and matrix fibrillation was thick and short for blends containing a smaller amount of EVA. Increasing EVA content gave rise to thinner and longer fibrils.

A rheological study showed that PE was significantly less viscous than EVA at all the shear rates, justifying blending for reducing the viscosity [39]. The viscosity of the blends can be described by a logarithmic mixing rule $\log (\eta_{\mathrm{blend}}) = \sum w_i \log \eta_I$, where w_i is the mass fraction and η_I is the viscosity of the pure component. At EVA contents lower than 75 %, the blends presented a negative deviation from the mixing rule. The stress–strain curves gradually passed from a plot representative of pure PE to that representative of pure EVA. On increasing the EVA fraction, the modulus data followed the behaviour of a system in series and, at EVA fractions higher than 75 %, the system was well described by the parallel model. The positive and negative deviations from the mixing rules could not be ascribed to crystallinity, because the crystalline content linearly depends on the EVA fraction. At small EVA fractions, PE-rich phases form and induce blend properties closer to those of PE. The increase in elastic modulus of the solid blends is probably due to strong interfacial interactions with the other phase, and these interactions are probably the result of co-crystallization.

It was further shown that the complex viscosity of the blends increased with increasing EVA content [38]. All the blends behaved as shear thinning materials and could be divided into two regions: (i) high shear thinning at lower frequencies and (ii) low shear thinning at higher frequencies. The viscosities of the EVA rich blends were higher than those of the neat polymers, which was due to a restriction of the molecular mobility and a reduction of the free volume induced by the addition of EVA. As the amount of EVA increased, the storage modulus, Young's modulus, and hardness decreased—all these properties are related to the crystallinity of the material which decreased with increasing EVA content.

LDPE and EVA are used in the manufacture of polymeric foams; an LDPE/EVA foam possesses higher flexibility and impact resistance [41]. Crosslinked polyethylene foams have better heat resistance than the uncrosslinked ones. Crosslinked EVA usually shows better nucleation control and the formation of cells with uniform size in the foaming of EVA. Scission and crosslinking of polyethylene molecular chains can occur simultaneously when it is subjected to irradiation by γ-rays. Chain scission occurs mainly at a low dose, and chain crosslinking at a higher dose. Crosslinking results in the formation of a three-dimensional network in the LDPE/EVA blends, leading to an increase in the melt viscosity and strength of the blend. It was found that LDPE/EVA foams irradiated to 50 kGy had the most uniform cell morphology, giving the best cell size uniformity (Fig. 5.6). The crosslinking improved the melt viscosity and strength, leading to a higher resistance to bubble expansion and an obstacle to coalescence of neighbouring cells, giving rise to smaller cell sizes and a higher cell densities in the foams. An increase in EVA content resulted in a decrease in the melt viscoelasticity of the blend. The cell expansion in the foams therefore becomes easier due to lower resistance to cell expansion. Cells can also fuse and break due to poor melt strength. After irradiation

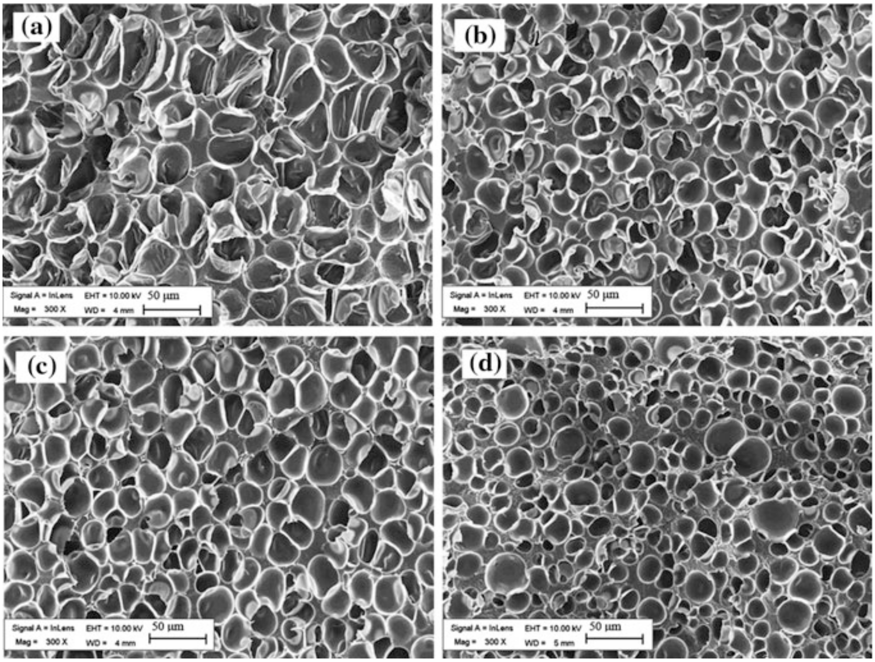


Fig. 5.6 SEM micrographs for the LDPE/EVA blend (70/30) foams produced at 105 °C and 23 MPa: **a** 25 kGy, **b** 50 kGy, **c** 75 kGy, **d** 100 kGy [41]

of the blends, the melt viscosity and strength of the blends were improved through a crosslinked network. Crosslinking gave rise to a remarkable improvement in the cell structure of the foams with higher EVA contents.

Crosslinking can improve the interfacial adhesion between two phases, giving rise to improved tensile strength but reduced elongation at break due to a decrease in molecular mobility [42]. Crosslinked polymers also have better heat resistance and mechanical properties, but poor reprocessability. The mechanical properties of crosslinked polymers are determined by their crystal structure and crosslinking degree. Properties dominated by crystallinity, such as tensile modulus and yield stress, normally decrease. It was found that for uncrosslinked HDPE/EVA blends, the tensile modulus, stress at yield, and stress at break decreased markedly, while the elongation at break only slightly decreased with increasing w_{EVA} due to the presence of the soft EVA phase [42]. The tensile modulus and yield stress did not change markedly, because the crystallinity of HDPE was little influenced by crosslinking. The impact strength is increased with increasing w_{EVA} and DCP contents. The presence of crosslinked EVA gel not only improved the toughness, but also enhanced the interfacial strength due to co-crosslinking.

5.4 Polyolefin/Paraffin Blends

Polyolefin/paraffin blends are mostly used as phase-change materials (PCM) for thermal energy storage. They are a good combination because of the paraffinic nature of their respective chains, and therefore, they are compatible but not miscible, which is a requirement to ensure stable blends with separately crystallized paraffin. Energy is stored and released through the melting and recrystallization of the paraffin, while the polyolefin matrix contains the paraffin so that it does not leak during the melting process. During the last two decades, these systems have been extensively investigated, with recent studies concentrating on the influence of thermally conductive fillers on the properties and behaviour of these blends.

Chen and Wolcott [43] investigated blends of a low molar mass paraffin with HDPE, LDPE, and LLDPE to be used in energy conservation in buildings. When the building's interior temperature approaches the melt temperature of the PCM, the PCM changes from solid to liquid and, in doing so, absorbs energy. Later, when the ambient temperature drops, the PCM begins to crystallize, releasing stored thermal energy to the building and stabilizing the interior temperature. The PCM temperature will be maintained closer to the desired temperature during each phase transition period until the phase change is complete. In this manner, the PCM decreases interior temperature fluctuations, maintaining human comfort while conserving energy through the reversible phase change. HDPE, LDPE, and LLDPE were all found to be partially miscible with the paraffin. The HDPE/paraffin blend had the lowest miscibility of the three systems. Because of the influence of miscibility on the thermal behaviour of the paraffin, it was suggested to use HDPE in PE/paraffin-form-stable PCMs to maintain the energy-saving behaviour of the paraffin in building applications for reducing interior temperature fluctuations.

In another recent investigation [44], injection moulding was proposed as a profitable method to process phase-change materials, because of the ease of processing and good properties of the final parts. Blends containing 5 to 50 vol.% of wax were extruded, and in spite of the different melting temperatures of the two components, no wax loss was detected after processing. All the prepared blends were pseudoplastic, and therefore, all of them were suitable to be injection moulded. The glass-transition temperatures of the two components in the blend were detected by dynamic mechanical analysis, confirming their immiscibility.

Ternary blends containing polyethylene and a paraffin were also investigated [45]. As a third component, dibenzylidene sorbitol (DBS) was used, which is an amphiphilic molecule derived from the sugar alcohol D-glucitol. Due to the butterfly shape and propensity to undergo intermolecular hydrogen bonding between the terminal hydroxyl group and the acetal oxygens, DBS molecules can strongly interact in the presence of an organic solvent to form a physical gel through self-assembling into a fibrillar network, with the fibrillar diameter in the nanoscale. UHMWPE and liquid paraffin (LP) have excellent affinity due to their similar chemical structures and solubility parameters. The multiple phase transitions, i.e. self-assembly of DBS, liquid–liquid phase separation between UHMWPE and LP

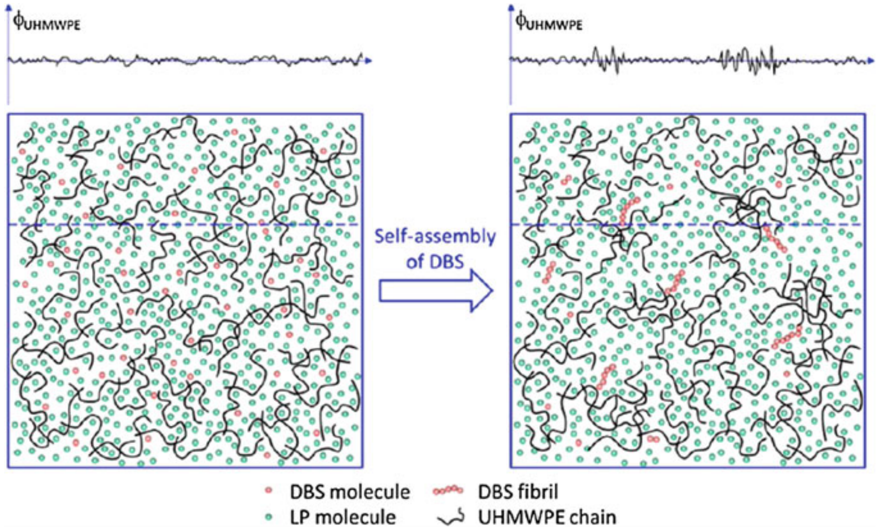


Fig. 5.7 Scheme of liquid–liquid phase separation assisted by self-assembly of DBS in the early stage [45]

assisted by the self-assembly of DBS (Fig. 5.7), and the crystallization of UHMWPE were studied. A complex relationship was found between the multiple phase transitions.

5.5 Polyolefin/Polyamide Blends

Polyolefin/polyamide blends can be used for a variety of applications where one polymer will enhance the properties of the other polymer. Research on these blends has so far been very fundamental, exploring different possibilities to compatibilize and improve the properties of otherwise very incompatible polymers.

Polyamide 6 (PA6) has good mechanical and thermal properties while LLDPE has good low-temperature flexibility and good resistance to moisture permeation. One study focused on compatibilizing an immiscible PA6/LLDPE blend through electron beam irradiation with glycidyl methacrylate (GMA) for cross-copolymerization [46]. The GMA has two reactive sites, which are an epoxy functional group and a double bond. The epoxy group can react with other functional groups in polymers during melt mixing and the double bond can be easily opened by a radical and then cross-copolymerization takes place at the interface (Fig. 5.8). GMA is also a low-molecular-weight material, which can easily diffuse to the interface during melt mixing. Another investigation on PA6/LLDPE blends looked at the use of these blends as shape memory polymers [47]. Shape memory transition temperatures were in the range of 120–130 °C, and a shape memory

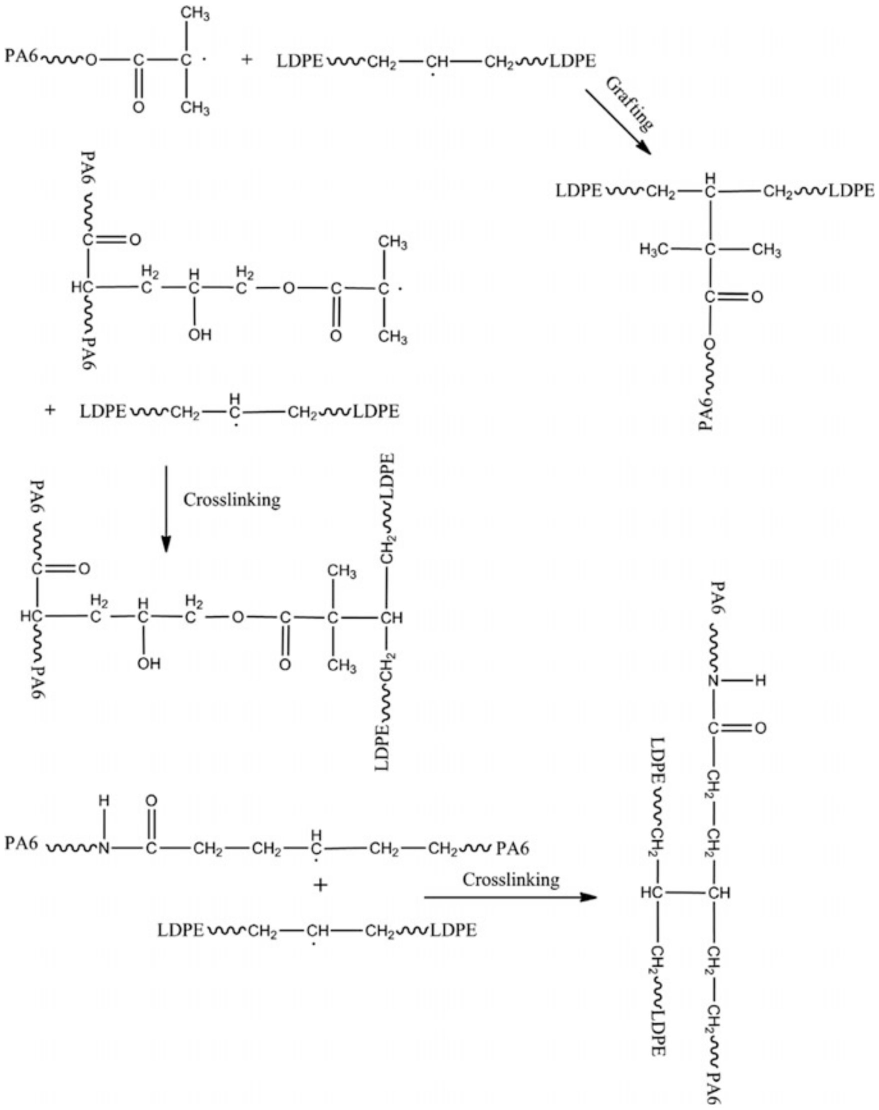


Fig. 5.8 Expected mechanisms of cross-co-polymerization at the interface between LLDPE and PA6 [46]

mechanism for this type of polymer blend SMP proposed that the LLDPE in the blend contributes to the shape memory fixing and that the PA6 in the blend with the help of PE-g-MA contributes to the shape memory recovery. The PA6 provided the stretching and recovery effects, while the LLDPE provided the fixing and unfixing effects.

PA6/HDPE blends have been widely investigated. PA6 shows good tensile strength and barrier properties, while HDPE shows good impact resistance and low-temperature flexibility. PA6/HDPE blends are thermodynamically immiscible and generally have poor ultimate mechanical properties. When these immiscible blends are subjected to stress, the stress concentrates at the interface of the immiscible blends and serves as failure initiation points. An investigation on twin-screw extruded 50/50 w/w PA6/HDPE blends containing different amounts of functionalized multiwalled carbon nanotubes (FMWCNTs) showed that, at relatively low FMWCNT contents (0.5 and 1.0 wt%), the addition of FMWCNTs had no influence on the phase morphology of the blend [48]. The PA6 still formed the continuous phase while the HDPE formed the dispersed phase. At moderate FMWCNT contents (2.0 and 5.0 wt%), the nanocomposites showed typical co-continuous morphology, and at high FMWCNT contents (10 wt%), the PA6 formed the dispersed phase and HDPE formed the continuous phase, indicating the occurrence of phase inversion. Further results showed that the FMWCNTs selectively distributed in the PA6 phase due to the lower interfacial tension between the PA6 and the FMWCNTs. As a consequence, the crystallization behaviour of the PA6 component changed. Rheological measurements showed the formation of an FMWCNT network structure, which was the main reason for the formation of the co-continuous morphology. It was also found that the incorporation of FMWCNTs significantly improved the ductility of the immiscible blend. The FMWCNTs induced a change in the crystallization behaviour of the PA6 component and a two-step crystallization process occurred, while the crystalline structures of both the HDPE matrix and the PA6 dispersed particles were varied insignificantly. The much improved interfacial adhesion was ascribed to a nanobridge effect of the FMWCNTs on the interfaces, which prevented crack initiation and propagation along the interfaces under stress.

Argoud et al. [49] investigated the morphologies of these blends, but they used MA-g-HDPE as reactive compatibilizer. They observed two characteristic sizes. At the larger scale, the characteristic domain sizes varied from 10 μm down to ~ 1 μm, specifically in case of co-continuous morphologies, depending on the compatibilizer/HDPE ratio. The composition (the PE/PA6 volume ratio) was the predominant system parameter which determined the type of morphology, and the morphology depended very little on the amount of compatibilizer (for a compatibilizer structure which does not induce a strong curvature at the interface). As expected, by increasing the compatibilizer amount, the characteristic size became smaller. The compatibilizer also suppressed coalescence and stabilized the micrometer scale morphologies. Under load, a crack usually initiates and propagates along the interface, leading to failure of the materials [50]. The minor phase of the blend forms dispersed particles with large diameters. This is unfavourable for the improvement of the mechanical properties of the blend. Improvement of the interfacial strength and decreasing the diameter of the dispersed particles are the key issues to obtain materials with excellent mechanical properties. The presence of clay did not seem to improve the interfacial adhesion, and the main reason for the improvement in mechanical properties was the change in the morphology. For an immiscible HDPE/PA6 blend containing both clay and HDPE-g-MA compatibilizer, the blend morphology was determined by a competition between and/or synergistic effects of the clay and the compatibilizer. The most acceptable model is that the clay functions first, decreasing the average diameters of the dispersed particles and stabilizing the morphologies of the blends. The compatibilizer effect then follows, strengthening the interfacial adhesion between the dispersed particles and the matrix.

Instead of using a reactive compatibilizer, silane grafting can also be used with nanoclay to improve the morphology of HDPE/PA6 blends [51]. Both these modifications play a significant role in the morphology of the HDPE/PA6 blends, where nanoclay acts as a nucleating agent and/or barrier to coalescence of PA6 droplets, and silane grafting along with the location of the clay at the interface mediates the polarity between the two phases and causes improved interfacial adhesion. The presence of organoclay and/or PA6 reduced the gas permeability of the samples. Silane grafting of the HDPE enhanced the barrier properties of the blends because of its compatibilizing effect, which caused a finer blend morphology or more delaminated clay in the nanocomposites. These blends exhibited excellent permeation resistance to both cyclohexane and oxygen.

Neutralization of acrylic acid, methacrylic acid, and/or maleic anhydride (MAH) functional groups with a metal salt or alkaline bases forms ionomers from polyethylene. Ionomers are an attractive way of compatibilizing PA6 and PE, because the amide functional groups in PA6 can interact with the ionomer via hydrogen bonding, ion–dipole interaction, and/or metal ion coordination during melt-blending. Charoenpongpool et al. [52] studied the effect of zinc neutralization of hydrolysed anhydride acid groups in MAH-grafted HDPE (MAH-g-HDPE) on the efficiency of compatibilization. When using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as the neutralizing agent, they found that the dispersed phase sizes decreased with added compatibilizer and with increasing compatibilizer content. Compatibilization improved the mechanical properties, and significantly improved the melt viscosity of the high PA6 content blend.

An in-depth study [53] focused on the compatibilization mechanism of clay particles on the PE/PA interface. The clay-filled PE/PA blends exhibited an interphase composed of clay particles intercalated by PA chains. No emulsifying effect was obtained if the degree of exfoliation of the clay particles was too high, which was shown to happen (i) when a high viscosity polyamide was used, favouring the presence of the clay particles in the PA nodules and (ii) when a low-viscosity polyethylene was used, making deformation and break-up of the PA nodules more difficult. These results highlighted the role played by the molecular characteristics of both polyamide and polyethylene chains in the structure and properties of the intercalated PA/clay interphase. The viscoelastic properties of the PE/PA blends were significantly influenced by clay addition and content, through various mechanisms that involve changes in (i) dispersed phase interfacial area, (ii) blend morphology, (iii) clay localization, and (iv) interphase structure.

It was also found that orientation during film blowing can significantly change the ductility of the PE/PA6 blends [54]. The elongation at break in the machine direction significantly increased compared to the anisotropic value, but it tended to decrease with increased degrees of orientation. The sample, however, remained brittle in the transverse direction. The ductility was interpreted in terms of the orientation of the matrix macromolecules and the dispersed phase particles, which gave a morphology with reduced defects in the orientation direction. In an investigation of the morphologies of injection-moulded PE/PA6 blends [55], it was found that the physical properties of a water-assisted injection-moulded part can be strongly influenced by its microstructure such as molecular orientation and morphology. The microstructure is formed by a complex thermal and deformation history that a polymer has undergone during the moulding process, and it varies depending on the location in a moulded part and on the moulding conditions. Distinct skin layers, core regions, and channel layers were observed across the thickness in both gas- and water-assisted injection-moulded tubes. The shape and size of the dispersed phase depended on the position across the part thickness and along the flow direction. Small and large particles coexisted in the skin and channel layers, indicating that both coalescence and disintegration of the dispersed phase occurred in these layers. Water-moulded parts exhibited a smaller polyamide particle distribution than gas-moulded parts, and high water pressures were found to mould parts with smaller polyamide phase domains.

Grafting and crystallization effects play a very important role in the compatibility of PE and PA and the resultant mechanical properties. By an appropriate choice of the molecular parameters of the two functionalized polymers, it is possible to control the grafting reaction at the interface and thus the amount of graft co-polymer [56]. Various morphologies can be obtained, from sub-micrometer dispersion for a low graft co-polymer content to a co-continuous nanostructured morphology for a high graft co-polymer content. A co-continuous blend constituted of functionalized PE (the majority component) and PA (the minority component) showed outstanding mechanical properties at low and high temperatures. It is possible, through morphology control provided by reactive blending, to produce stable co-continuous morphologies and also sub-micrometer droplet dispersions in PE/PA blends (Fig. 5.9). Since both blend components can crystallize, there should be an influence on the nucleation and overall crystallization kinetics of the blend, depending on which component crystallizes first. The nucleation and crystallization of PA chains strongly depend on the surrounding environment. When they are in the bulk state, they nucleate heterogeneously and crystallize at low supercoolings. When they are confined with functionalized PE in a sub-micrometer co-continuous morphology (and compatibilized by a graft co-polymer between the phases), their crystallization rate is depressed and larger supercoolings are needed for their crystallization. There was a correlation between the Avrami index and the confinement of the PA chains. As the confinement increased (on going from the bulk state to a co-continuous phase to dispersed sub-micrometer particles), the Avrami index decreased.

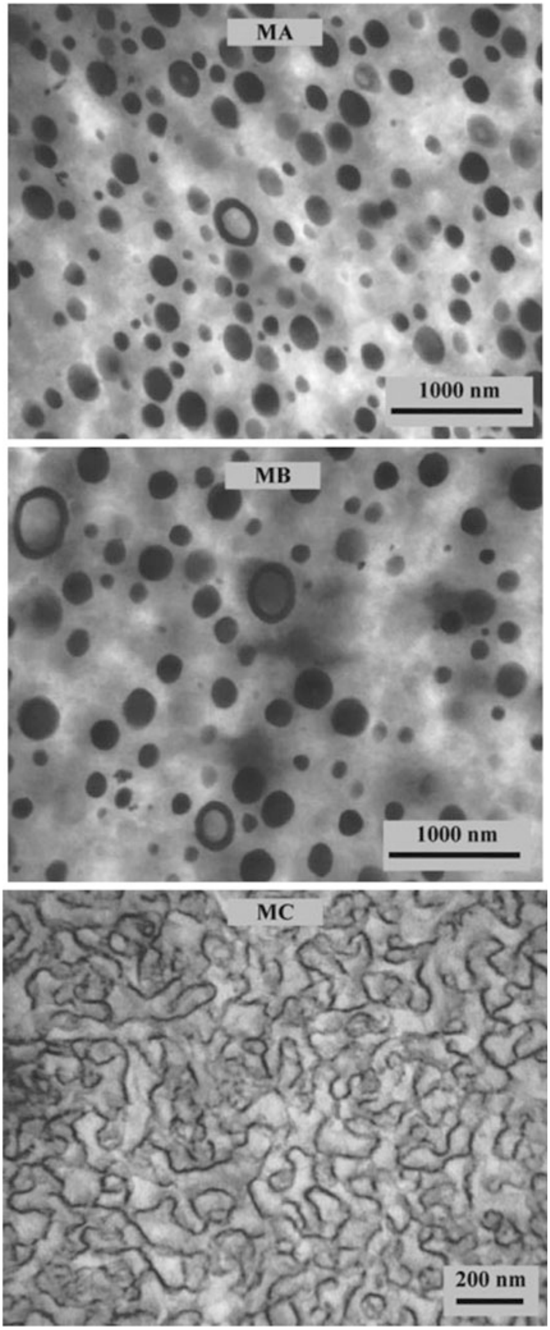


Fig. 5.9 TEM micrographs for the three PE/PA blends prepared by reactive extrusion [56]

5.6 Polyolefin/Rubber Blends

Thermoplastic elastomeric materials based on blends of ethylene propylene diene terpolymer (EPDM) and polyolefins combine the processing advantages of thermoplastics with the excellent physical properties of elastomers, giving rise to materials with excellent properties for use in the automotive industry, extruded profiles for windows, electrical cables and wires, packing materials, and footwear [57–60]. Car parts remain the largest market for thermoplastic elastomer compositions. EPDM exhibits excellent resistance to weather, ozone, acids, and alkalis while accommodating high volume fractions of filler and liquid plasticizers and retaining desirable physical and mechanical properties. The blending of EPDM with HDPE was found to improve the physical and mechanical properties of EPDM.

Stelescu et al. [57] found an increase in elongation at break and tear strength values of EPDM/HDPE blends, compared to the uncompatibilized sample. Incorporation of PE-g-MA or dynamic vulcanization led to an increase in contact angle, indicating an increase in the hydrophobicity of the composite surface. Addition of PE-g-MA or an increase in PE content determined the increase in the percentage crystallization in EPDM/HDPE blends. Solvent vapour permeation is an energy-saving process to remove volatile organic components (VOC) from contaminated air streams, and it is much more effective than classical VOC control processes such as incineration, oxidation, and active carbon absorption. Analysis of the equilibrium sorption of a vapour by an HDPE/EPDM blend can provide information regarding polymer–polymer interactions [58–60]. The amount of sorbed vapour is related to its interactions with the blend. It was found that the permeability and sorption coefficients increased with an increase in the EPDM concentration, and the permeation rate decreased with an increase in the molar mass of the penetrants, and as the degree of crosslinking increased, the permeability decreased (Fig. 5.10).

Thermoplastic elastomers have a large number of applications due to their unique combination of mechanical properties and processability [61]. The modulus values, from low temperatures near the glass transition of the rubber to higher temperatures around the softening point of the plastic, are comparable with those of reinforced-vulcanized rubbers. During processing, thermoplastic elastomers are in the molten state and they can be processed with plastic processing equipment. Non-irradiated LDPE blends in different compositions with SEBS and SEBS-g-MA block co-polymers showed better mechanical, thermal, and volume resistivity properties than pure LDPE. The improvement in the properties of the non-irradiated blends by using SEBS-g-MA was more significant than when using SEBS. The mechanical, thermal, and electrical properties were further improved after electron beam irradiation.

Polyethylene can also be blended with a number of other rubbers. When ozonolysed natural rubber is blended with polyethylene and cured, it was found that sulphur dynamic vulcanization was better than peroxide curing, with a higher crosslink density resulting in a change in the LDPE crystallization behaviour [62].

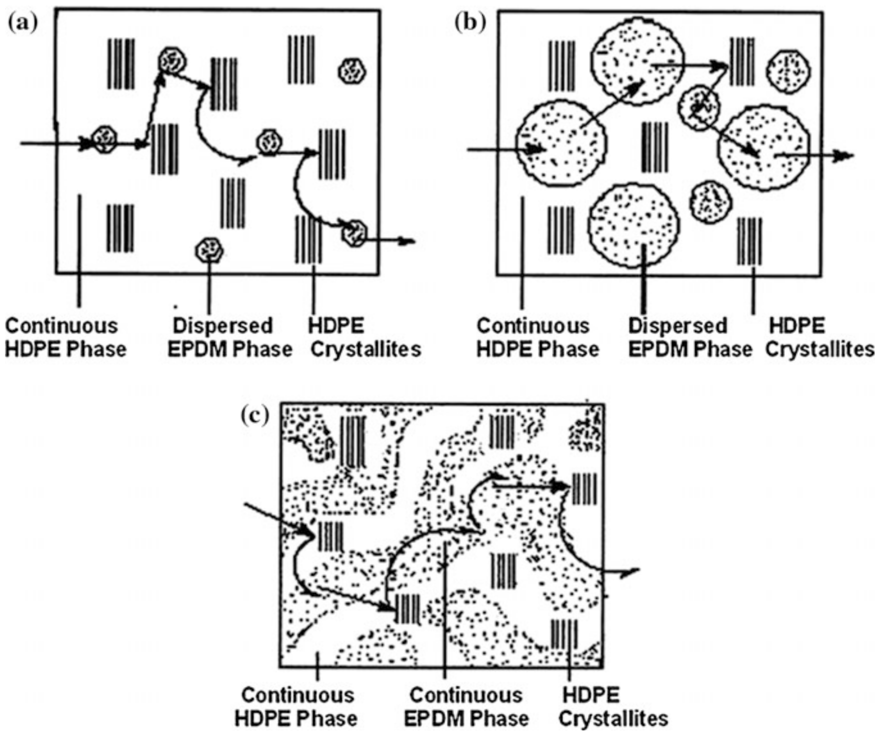


Fig. 5.10 Schematic representation of the tortuous path exhibited by the crystalline HDPE phase to the transport of solvent [60]

The α-temperature of LDPE shifted when the ozonolysed NR loading reached 50 % w/w for peroxide curing and 40 % w/w for sulphur vulcanization. The tensile strength and elongation at break of the peroxide-cured blends were much better than those after sulphur curing. The tensile strength and elongation at break of the peroxide-cured blends significantly increased with the ozonolysed NR content in the blends.

When a radiation-crosslinked semicrystalline polymer is stretched, the molecules are oriented in the stretching direction gets frozen in its extended form. If the stretched sample is heated (without any mechanical force), the material shrinks. Such heat-shrinkable polymers find applications in the packaging and cable industries and in heat-shrinkable tube production. When nitrile butadiene rubber (NBR) was mixed with HDPE, the tensile modulus increased with increasing HDPE content and increasing radiation dose [63]. Radiation dose had little effect on the elongation at break at high HDPE contents, but this property decreased with increasing radiation dose up to 150 kGy at high NBR contents. The hardness increased significantly with HDPE content, but only slightly with increasing radiation dose. Permanent set decreased with increasing HDPE content and radiation dose.

It was also found that the addition of up to ~30 wt% SBR delayed nucleation, but accelerated the rate of crystallization of HDPE [64]. An SBR amounts >30 wt% in the blends delayed the crystallization of the matrix polymer. The presence of small rubber particles, dynamically crosslinked, accelerated the crystallization of the matrix, and this was attributed to the formation of more nuclei. The nucleation effect caused an increase in the overall crystallization rate. However, due to the increased rigidity of the crosslinked amorphous component, it was unable to diffuse into the spherulitic growth sites, thereby obstructing spherulitic growth. Another rubber used for heat-shrinkable materials is bromobutyl rubber (BIIR). An investigation into LDPE/BIIR blends cured through γ-irradiation showed that (i) crosslinking was induced in all the samples by the irradiation, and the extent of crosslinking increased with increasing irradiation dose and LDPE content in the blend, (ii) blending of LDPE with small amounts of BIIR gave better mechanical properties than BIIR alone, but the improvement in properties depended on the irradiation dose, (iii) the heat shrinkability increased significantly when the blend was crosslinked by gamma irradiation, and (iv) an increase in the elastomer content in the blend improved the heat-shrinkable properties [65].

5.7 Polyolefin/Natural Polymer Blends

The degradation of polyolefins involves two stages: oxidative degradation (oxo-degradation) and biodegradation [66]. Oxo-degradation incorporates oxygen into the carbon chain, which results in the formation of oxygen containing functional groups. This process can be accelerated by ultraviolet (UV) light or heating. When the molar mass of a polymer is reduced to a certain level through oxo-degradation, the oxidation products can be biodegraded by microorganisms that consume the oxidized carbon backbone fragments to form CO_2, H_2O, and biomass. This is one of the main reasons for investigating blends of polyolefins with natural polymers.

5.7.1 Starch

Starch is a natural carbohydrate storage material accumulated by green plants in granular form and is composed of amylose (linear molecules) and amylopectin (branched molecules). It is a renewable, inexpensive natural polymer that can be blended with synthetic polymers to decrease their relative amount and to lower the cost of the final product [67]. It is possible to improve their compatibility through the addition of a suitable interfacial modifier. It has been considered as a partial substituent for synthetic polymers in packaging, agricultural mulch, and other low-cost applications. The crystalline structure of starch can be disrupted through gelatinization, during which the starch is first mixed with water and subsequently stirred and heated, resulting in the formation of hydrogen bonds between the water molecules and the free hydroxyl groups of starch. Gelatinized starch, which can flow, can then be plasticized by the addition of a suitable plasticizer such as glycerol. Thermoplastic starch (TPS) can flow at high temperatures and shows good ductility, making it suitable for melt-processing. Blends of TPS and polyolefins have relatively high interfacial tensions because of the high incompatibility between the non-polar polyolefin and the highly polar TPS.

LDPE–starch blends are biodegradable because the starch moiety is a carbon source that is consumable by microorganisms [68, 69], and it is considered a feeding stimulant for insects possessing specific amylase digestive enzymes. Subsequently, the remaining synthetic polymer matrix is more easily attacked by natural elements such as thermal oxidation and ultraviolet photodegradation. PE–starch materials are suitable for the manufacturing of any kind of home and light industrial plastic containers, bottles, dishes, glasses, and cups through injection moulding. There should, however, be a specific starch concentration for each application because there are specific needs in terms of the mechanical, thermal, and water resistance properties. Weight loss during exposure normally increases with starch content and time. It is expected that about 12 years are required for the complete degradation of a sample containing 40 % starch. Even though this is a long time for biodegradable materials, it is realistic for end products with possible applications that need a longer lifetime.

Various pro-degradants have been developed to accelerate the oxidation of polyolefin under UV light [66]. A pro-degradant can be divided into two groups: (1) transition metal systems such as transition metal salts, ferrocene, and metal oxides; (2) metal-free systems such as ketone co-polymers, chemicals containing oxo-hydroxy groups, peroxides, and unsaturated alcohols or esters. Yu et al. [66] investigated the influence of the distribution of Fe- and Co-based pro-degradants in the different phases of PE/starch blends on the ultraviolet (UV) photo-oxidative degradation. The distribution in the different phases was varied by a dual step process using a side-feed on a reactive extruder. They found that the mechanical properties varied more when the pro-degradants were distributed in the PE phase, the concentration of the carbonyl groups increased as a function of UV exposure, and the concentration of carbonyl groups was higher when the pro-degradants were distributed in the PE phase.

Another investigated blend system is TPS/HDPE/NR compatibilized with PE-g-MA [70–76]. A blend of thermoplastic natural rubber (TPNR) and HDPE gives rise to a new material that exhibits good tensile properties and improved impact resistance. Incorporation of starch into TPNR should also enhance the biodegradability of the blend. Kahar et al. [70, 71] observed the occurrence of covalent bonding between the functional groups of PE-g-MA and the hydroxyl groups of starch, which confirmed reactions between these two polymers. The compatibilized blends showed better tensile properties and improved surface morphology, while the compatibilized blends with 5 and 10 % TPS showed significant improvements in tensile strength. This was attributed to better interaction at the interphase between TPS and HDPE/NR, allowing stress transfer between the phases. Another compatibilization method used for this system is dynamic sulphur vulcanization [72, 73]. Morphology studies showed that the TPS particles were homogeneously dispersed and well-embedded in the vulcanized HDPE/NR matrix, and that the tensile strength improved significantly, which was attributed to the crosslinking reactions in the NR phase. Compatibilization in these systems was also achieved through citric acid modification of starch (TPSCA) [74]. Starch hydrolysis and acetylation between the starch and citric acid were observed. The modified TPS blends showed better tensile properties and surface morphology than HDPE/NR/TPS, and the blends with 5 and 10 % TPSCA loading showed tensile strength almost the same as that of the HDPE/NR blend. This was attributed to the low viscosity of TPS, which allowed it to easily disperse when blended with the HDPE/NR matrix. The blends with TPSCA showed better dispersion of the starch in the HDPE/NR matrix.

Starch can also be propylated and blended with polyolefins. Propylated starch–LDPE blend films were prepared and the effect of the degree of substitution (DS) and starch concentration on the mechanical properties, morphology, water absorption capacity, and biodegradability of the blend films was investigated [75]. The tensile strength, elongation, and melt flow index of the propylated starch blend films were higher than those of the corresponding native starch blend film, and these properties improved with an increase in DS from 1.56 to 2.51. The propylated starch blend films were thermally more stable than the native starch blend films, and the water absorption capacity decreased for the films containing propylated starch at high DS. The biodegradability of the films increased with an increase in the starch concentration, but decreased with an increase in the DS (Fig. 5.11). LDPE-g-MA was also used as compatibilizer in corn starch (TPCS)–LDPE blends [76]. The tensile properties and impact strength of the samples decreased with increasing the TPCS concentration, but addition of up to 25 wt% TPSC gave rise to similar mechanical properties than those of pure LDPE. A linear relation was found between the reduction in melt flow index and the starch content in the blends. The

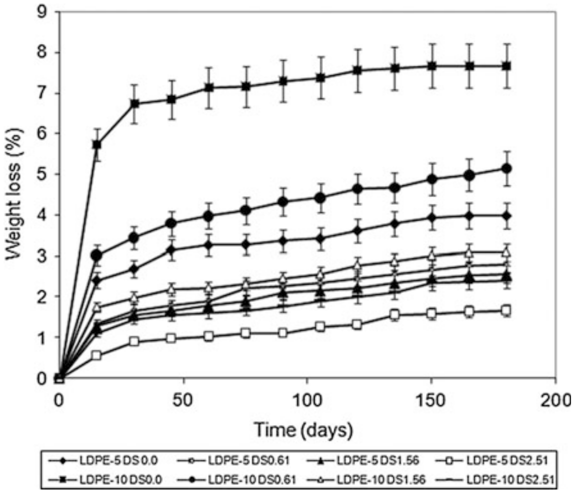


Fig. 5.11 Weight loss of starch–LDPE films during soil burial test [75]

apparent viscosity of the blends increased by increasing the starch concentration and by decreasing the shear rate.

As was the case of some previously described blends, nanofiller was included into PE–starch blends to improve the compatibility of the different components in the blends and the mechanical properties of the blends. Recently, Zeolite 5A [77] and sepiolite [78] were used for this purpose, and improved properties were generally observed.

Glycerol has mainly been used as plasticizer in TPS, but glycerol is very hydrophilic, has a low thermal stability, and it migrates to the surface with time, especially in thin films. TPS formulations, with diglycerol and polyglycerol plasticizers, were blended with HDPE at a concentration of 20/80 w/w TPS/HDPE and a range of interfacial modifier contents via a one-step extrusion process [79]. The emulsification curves of the blends that track the volume and number average diameter of the dispersed TPS as a function of per cent interfacial modifier showed significantly different profiles. The addition of small amounts of interfacial modifier to the blends gave rise to TPS droplets in the order of 200–300 nm coexisting with droplets of 5–7 μm. This wide polydispersity is indicative of an erosion-type droplet formation mechanism, where small parts of the TPS droplet break off the surface of the droplet. Blends prepared with glycerol-TPS and sorbitol-TPS did not show this behaviour. Dynamic mechanical analysis showed miscible behaviour for diglycerol-TPS and polyglycerol-TPS, and partially miscible behaviour for glycerol-TPS. This was attributed to the presence of ether bonds in the chemical structure of diglycerol and polyglycerol. The increased chain flexibility and lower cohesive energy forces of diglycerol and polyglycerol led to a more homogeneous TPS phase and to the erosion-type compatibilization at the interface. The mechanical properties of the blends prepared with polyglycerol and diglycerol showed a similar overall behaviour to that of glycerol.

5.7.2 Chitosan

Polyolefin/chitosan blends have not been investigated as extensively as polyolefin/starch blends. Chitosan is a polysaccharide more commonly found in nature, and its films can be used as packaging material because of their antimicrobial activity, non-toxicity, and biodegradability [80, 81]. The mixing of chitosan, a biodegradable polysaccharide, with LDPE decreases the fluidity of the molten polymer [80]. Mixing of PE-g-MA into this blend allows easy processing of the polyethylene/chitosan mixtures into films in standard extrusion equipment. It is therefore possible to obtain films with a maximum content of 20 wt% chitosan. The use of an anhydride-based coupling agent, extensively used to compatibilize polymer blends, was effective in improving the mechanical properties of the chitosan composites, especially the deformation at break, which makes these compositions suitable for the preparation of biodegradable films and other biodegradable items intended for short-term applications. PE films containing

15 wt% of chitosan were severely degraded in less than 6 months of exposure to natural weathering [81]. The oxidative degradation produced a significant increase in the content of carbonyl groups, and the exposure also led to the formation of microfractures and polymer embrittlement with the concomitant variation in mechanical properties. The extremely high temperatures and radiance recorded in the weathering location during the test period, and the use of PE-g-MA as a compatibilizer, accelerated the degradation rate of the films.

5.7.3 Poly(Lactic Acid) (PLA)

Although not strictly a natural polymer, PLA is a biodegradable polymer derived from natural resources. PLA is a linear aliphatic polyester derived from the fermentation of plant starches and can be bio-degraded into environmentally manageable compounds [82–84]. It has some unique properties such as good strength and stiffness, and resistance to fats and oil. Applications of PLA are limited in the commodity industries due to its brittleness, poor thermal resistance, low viscosity, high moisture sensitivity, medium gas barrier properties, high cost, and low solvent resistance compared to those of non-biodegradable polymers such as polyolefins, polyethylene terephthalate, polycarbonate, and nylon. So far PLA, because of its non-toxicity, biodegradability, and biocompatibility, has been used in biomedical and pharmaceutical applications such as implants, drug delivery carriers, and scaffolds for tissue engineering. Polyolefin/PLA blends have mainly been investigated with the aim of producing materials that have acceptable properties, but that have at least one biodegradable component. This has become necessary because of the huge plastics waste problem the world currently facing.

In an investigation of single-screw-extruded LDPE/PLA blends, it was found that the stress at break and Young's modulus values were below the mixing rule line, which is typical for incompatible polymer blends [82]. Rheological results showed that these blends were pseudoplastic in nature; their viscosity decreased with increasing shear rate similar to most polymer melts. The true viscosity of PLA decreased sharply with increasing temperature, whereas the true viscosity of LDPE varied only slightly with temperature. The true viscosity of the blends decreased with increasing PLA content, and this was attributed to the low viscosity of PLA. Adding acrylonitrile–butadiene–styrene as compatibilizers in these blends gave rise to similar observations [83]. Jiang et al. [84] did a similar investigation by using a single-screw extruder with different screw elements. They found that the different screw configurations gave rise to different morphologies, different rheological properties, and different crystallinities.

It was proposed [85] that PLA could improve the properties of PP/HDPE/EVA blends. The mechanical properties showed that the polymer blend had optimum tensile and burst strengths at 4 wt% PLA incorporated into the PP/HDPE/EVA blend. The tear strength decreased with increasing PLA content in both the machine and the transverse directions. The friction coefficient was found to be the lowest at 4 wt% PLA loading in the blend, probably because of better PLA dispersion at this loading. The modification of PP/HDPE/EVA blends with PLA caused a gradual increase in haze.

When adding an ethylene–glycidyl methacrylate–vinyl acetate co-polymer as compatibilizer into a metallocene polyethylene elastomer co-polymer (mPE)/PLA blend, the results from SEM, FTIR, and rheological studies revealed that the interaction between the mPE matrix and the dispersed PLA was enhanced with the addition of the compatibilizer [86]. The addition of the compatibilizer completely hindered the cold crystallization and rearrangement crystallization of PLA, even though the additional annealing effect of mPE/PLA blends in the injection moulder tended to increase the crystallization of PLA. The synergistic effect of compatibilization and annealing treatment significantly improved the tensile strength and Young's modulus of the blends.

In a study of ternary LDPE/PLA/poly(ethylene-co-glycidyl methacrylate) (EGMA) blends [87], it was found that there was a reaction between the epoxy groups of GMA and the functional groups (hydroxyl and carbonyl) of the PLA, which led to a good compatibilization of the blend. The SEM results supported the FTIR results and showed that the incorporation of EGMA in a 60/40 w/w LDPE/PLA blend, at a level higher than 7 phr, led to further connections between the blend phases giving rise to almost indistinguishable component domains. The uncompatibilized blends showed the typical behaviour of immiscible blends with a sharp drop in the tensile and impact properties. However, the 60/40 w/w LDPE/PLA blend containing 15 phr of EGMA showed very good mechanical strengths (Fig. 5.12). The micro-hardness characteristics of the different blends were in good agreement with the macroscopic mechanical properties such as yield stress, Young's modulus, and impact strength. Similar observations were made in the case of HDPE/PLA blends compatibilized with maleic anhydride-grafted PE [88].

The mechanical and physical properties of PLA are severely degraded when subjected to electron beam irradiation [89], because the dissipated energy from the irradiation easily causes chain scission of the backbone chain of PLA and forms free radicals. Additional additives, such as a crosslinking agent, are therefore

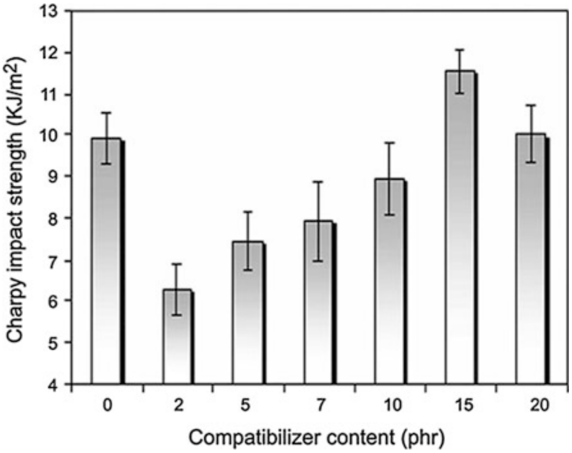


Fig. 5.12 Effect of the compatibilizer content on Charpy impact strength of 60/40 (LDPE/PLA) blend [87]

necessary to promote irradiation-induced crosslinking in PLA. LDPE is widely used in various applications due to its excellent electrical insulation, good mechanical properties and processability, and resistance to chemicals and irradiation. It tends to crosslink when exposed to high-energy electron beam irradiation and is able to withstand the application of an electron beam radiation dosage of up to 300 kGy without undergoing degradation. When the percentage of LDPE added to PLA was gradually increased, the gel content of the irradiated PLA/LDPE blends significantly increased compared to that of pristine PLA. Increasing amounts of LDPE marginally increased the crystallinity of the PLA/LDPE blend by introducing new crystalline structures to PLA. The application of irradiation significantly increased the crystallinity of these blends because of the formation of crosslinked networks that acted to converge the random structures into a highly ordered arrangement.

Poly(L-lactic acid) (PLLA) is environmentally biodegradable through a two-step process that begins with the high molecular weight polyester chains hydrolysing to lower molecular weight oligomers in an appropriate temperature and moisture environment. Microorganisms then convert these lower molecular weight components to carbon dioxide, water, and humus. LLDPE and PLLA were melt-blended in an extrusion mixer with a post-extrusion blown film attachment, with and without LDPE-g-MA [90]. Varying degrees of property modifications were achieved by blending these polymers. The most important observation was a significant increase in biodegradability of these blends, especially at higher pH values. Singh et al. [91] reported similar observations.

5.7.4 Other Biodegradable Polymers

Poly(vinyl alcohol) PVA and poly(hydroxyl butyrate-co-valerate) (PHBV) are also not natural polymers, but they are biodegradable and useful for various applications in packaging such as for foods, pharmaceuticals, chemicals, detergents, cosmetics, compost bags, grocery bags, shipping bags, cutlery, plates, and toys [92, 93]. Polymers such as polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl alcohol (PVA) are most frequently used for packaging because of their excellent thermal and mechanical properties, but they persist in the environment even after many years of disposal, contributing to the waste disposal management problem. Within the PE family, LLDPE is widely utilized in packaging applications, but its resistance to biodegradation causes serious problems. Poly(vinyl alcohol) (PVA) is a water soluble polymer which is also widely used in packaging applications because of its strength and biodegradability. The packaging applications of PVA are potentially limited because of its low resistance to humidity and its poor processability [92]. These problems can be solved by blending these two polymers with in situ silane crosslinking. Biodegradable plastics like poly(hydroxybutyrate-co-valerate) (PHBV) can be used to improve the gas barrier properties of PE without sacrificing the other properties (Fig. 5.13) [93].

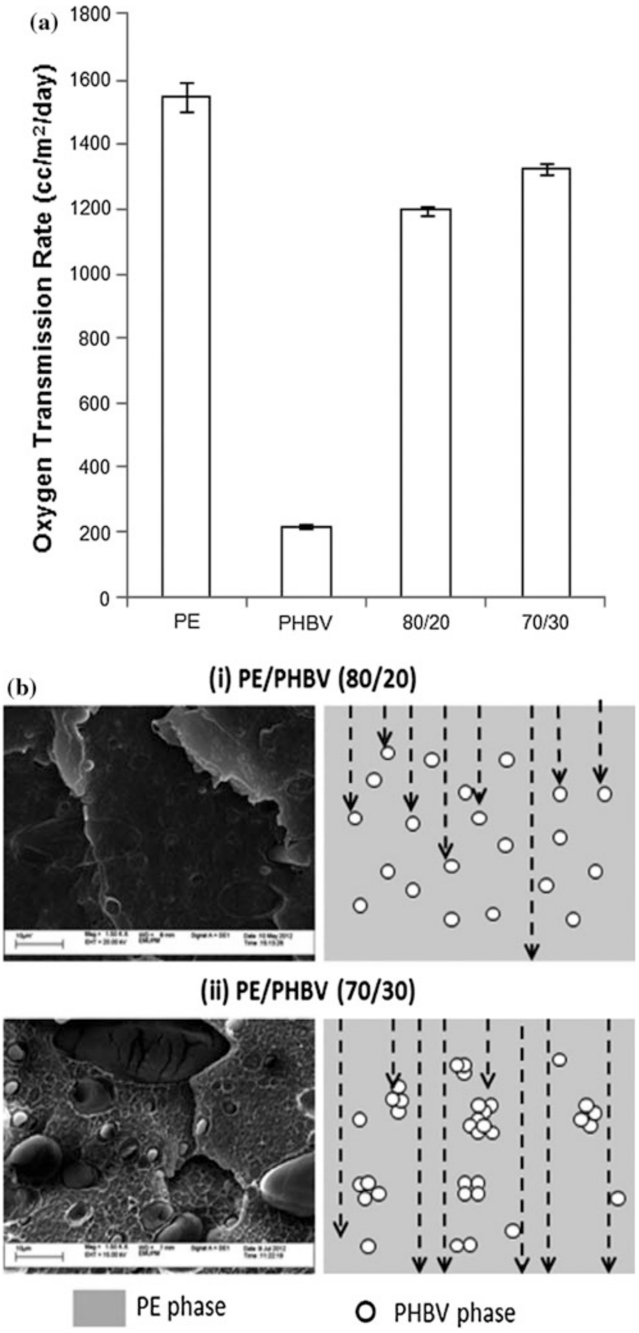


Fig. 5.13 **a** Oxygen transmission rate (cm^3 per m^2 per day) of PE, PHBV, and PE/PHBV blends (20 and 30 wt% PHBV). **b** PHBV distribution within the polymer matrix at different PHBV compositions and its effect on oxygen transmission rate [93]

Poly(butylene succinate) (PBS) is another biodegradable polymer which is not commonly blended with polyolefins. However, Yang et al. [94] investigated the effect of PBS content, extrusion rate, and extensional strain rate on the melt strength and extensional viscosity of LDPE/PBS blends using a melt-spinning technique, and developed extensional master curves. Based on both the extensional master curve and a neural network method, they compared the predicted extensional viscosities with the experimental data of the LDPE/PBS blends.

5.8 Polyolefins Blended with Other Polymers

A number of other polymers have been blended with polyolefins for a number of applications. Space does not allow one to give too many details about work done on these systems. This section will therefore summarize the proposed applications for these systems, and some very interesting observations will be included.

5.8.1 Polyaniline (PANI)

Active food-packaging systems contain agents such as antioxidants or antimicrobials, either in sachets, functionalized on the surface or incorporated directly in the packaging matrices [95, 96]. These systems do not simply provide an inert barrier to external elements, but can interact dynamically with the products or their immediate environment to enhance product shelf life. PANI, an intrinsically conducting polymer, also has antimicrobial and free radical scavenging properties. It is also relatively cheap and easy to prepare [97]. It can exist in a continuum of oxidation states and can be easily switched between the reduced and the oxidized states. It has good chemical, electrical, and optical properties that are associated with its insulating and conducting forms. The oxidation of food stuff is induced by oxygen-containing radicals, and therefore, radicals scavenging can be an effective strategy to inhibit the oxidation of food stuff, because the propagation of the oxidation reaction is prevented. Incorporating PANI in polymers such as LDPE, one of the most widely used packaging materials in the food sector, can yield antioxidant and antimicrobial active packaging systems. However, PANI's insolubility in common solvents and its poor mechanical properties make its processing very difficult. Several conventional thermoplastics, such as PE, PP, nylon 12, and polystyrene, have been combined with PANI to obtain materials with a proper balance between electrical and mechanical properties. Blends of LDPE and PANI showed particularly attractive properties as antistatic materials, for gas-separation and ion-exchange membranes, as transducers in sensor devices, and for flexible electrochemical systems.

5.8.2 Thermoplastic Polyurethane (TPU)

Some of the applications, like automotive and consumer goods, where polyolefins are used, demand that the part is painted. The non-polar surfaces of polyolefins, however, lead to poor paint adhesion. In order to enhance the adhesion between a polyurethane paint and an olefin block co-polymer (OBC), TPU can be blended into OBC [98]. TPUs are an important class of materials with desirable properties such as high strength, good abrasion, tear, oil and solvent resistance, and low-temperature flexibility. The advantage of TPU over conventional PU is that it can be melt-processed in conventional melt-processing equipment such as extruders and mixers. It has already been used extensively in cars, electronics, medicine, glazing, textiles, footwear, cable sheathing, and tubing. However, extruded TPUs do not have the desired properties for applications such as transmission or hoisting belts. UHMWPE is a material with good strength, low creep, low friction coefficient, low abrasion, and reduced wear, and the incorporation of UHMWPE into TPU can improve the tribological properties, while retaining most of the mechanical properties of the matrix [99].

5.8.3 Poly(Ethylene Terephthalate) (PET)

One of the recent applications in which recycled plastics were utilized is the production of plastic lumbers that can be used in applications where treated wood was previously used [100]. Railroad cross-ties are one of these applications. The patents on this subject claim that the appropriate material for this application is a proper combination of different disposed polymers such as ‘waste polyolefins’, mainly HDPE, as well as polystyrene (PS) and thermoplastic polyesters (PET or PBT). Since HDPE is the main source of plastic waste and has suitable mechanical properties at a reasonable price, it is a good candidate for plastic recycling on a large scale. However, the production of PET rapidly increased with the expansion of the packaging industry [101]. The short life cycle of beverage bottles also leads to the accumulation of post-consumed PET bottles, which inevitably creates serious environmental problems. The recycling of waste PET therefore also became important, and blending of recycled PET with PE is very attractive because of their relatively low cost and excellent properties [102]. The amount of waste from post-consumer PET and PP, especially in the beverage and packaging industry, stimulated an in-depth investigation into the production of innovative new products from recycled PET and recycled PP.

The thermal degradation stability and moisture absorption characteristics of thermoplastics are not only related to their chemical composition, but also to the effect of the dispersed phase size in polymer blends. The various forms and sizes of thermoplastic raw materials, e.g. pellets, flakes, or powder, can also have an effect on their thermal degradation stability. Smaller pellets can easily absorb moisture due to their large surface area and their surface roughness. They are therefore more susceptible to hydrolysis when exposed to high temperatures, especially in the presence of O_2. However, these small pellets can dry more quickly and thoroughly than larger pellets under similar drying conditions. These considerations led to an investigation into the thermal degradation stability and moisture absorption characteristics of PET/PP blends [103]. PP/PET blends were also investigated as shape memory polymers, which were already discussed earlier in this chapter. The shape-recovery value of the PP/PET blends increased rapidly up to 98.5 % with increasing POE-g-MAH content. The recovery rate increased with increasing recovery temperature [104].

5.8.4 Polyethylene Acrylic Acid (PEA)

PEA is well known for its use in conventional extrusion coating, co-extrusion coating, and extrusion lamination [105]. The beneficial properties of PEA, such as excellent adhesion to various substrates such as foils, paper, and films, can add value to other polymers that require these properties for specific applications. PEA/LDPE blends have many industrial uses because of their good mechanical strength, processability, and impact strength.

5.8.5 Liquid-Crystalline Polymers (LCP)

There are several reasons for the development of thermotropic LCP-modified thermoplastics [106]. LCP multicomponent mixtures with polymers such as PE, PP, PS, polycarbonate (PC), PET, poly(butylene terephthalate) (PBT), PA, poly(ether imide) (PEI), poly(ether ether ketone) (PEEK), and elastomers showed improvements in the rheological, mechanical, and barrier properties, and in the dimensional and thermal stabilities of the polymers. To effectively reduce the viscosity and hence facilitate processing, the LCP inclusions should be in the nematic state with a critical concentration oriented in the flow direction. Enhanced barrier properties are the result of the dense packing of the rigid LCP chains and the continuity and lamellar shape of the LCP phase, while the improved mechanical properties are the result of the formation of extended LCP fibrils in the matrix polymer. A self-reinforcing effect was obvious during extrusion and subsequent drawing of the compositions containing considerable amounts of LCPs.

5.8.6 *Fluorothermoplastics*

Blend properties are normally controlled by the morphology and phase sizes developed during the blending of two or more polymers. The polymer blend processing parameters can be controlled to a large extent by understanding the rheology of the blend. Fluorothermoplastic (THV) blends are considered a cost-effective replacement of engineering materials, especially in the fabrication of vehicle fuel tanks [107]. THV in a PE matrix has very good barrier properties that will enhance the permeability resistance of PE containers. The mechanical properties of these blends depend on the type of THV used, which determines the size and dispersion of the THV spheres in the PE matrix (Fig. 5.14).

5.8.7 *Poly(3-Alkylthiophenes) (P3ATs)*

Conjugated polymers and, especially, regioregular P3ATs demonstrated intriguing electrical and optical properties that led to a number of potential applications in high-performance organic thin film transistors, polymer solar cells, and chemical sensors [108]. Both the electrical and the optoelectrical properties of the P3AT-containing blends are significantly influenced by their morphology and phase behaviour. If the miscibility between P3AT and a non-conducting polymer becomes very poor, the conductivity of the blend is low. Since perfect mixing on a molecular level is not possible, a conductive network of P3AT cannot be easily formed. Poly(3-butylthiophene) (P3BT) has a limited miscibility with polyethylene, and the very small spherulites of the pure PE were changed into large, ring-banded 2D-spherulites in the thin films by blending with P3BT (Fig. 5.15). The limited miscibility created the necessary conditions for improving the growth of PE-ringed spherulites and resulted in PE lamellar twisting during crystallization with the period decreasing with increasing P3BT content.

5.8.8 *Speciality Blends for Membranes and Foams*

Block polymers containing an etchable block have been used as precursors for nanoporous polymers [109]. Because nanoporous polymers have large internal surface areas, large pore volumes, and uniform pore dimensions, these materials were studied as separation/purification media, battery separators, templates for nanostructured materials, low dielectric materials, and low refractive index materials. Both pore wall functionality and robustness of the matrix are important for the practical use of nanoporous polymers. As shown in Fig. 5.16, PLA was selectively etched from a blend with reactive block co-polymers to form a nanoporous material,

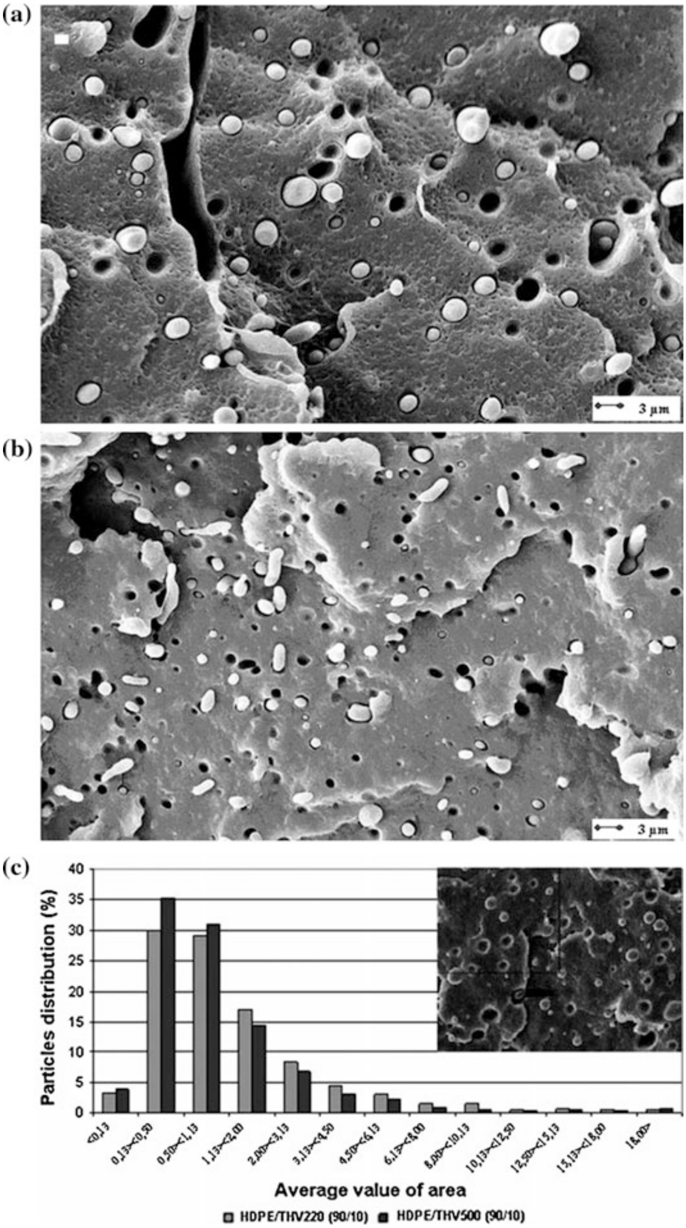


Fig. 5.14 SEM pictures of a HDPE/THV500 (90/10) blend (**a**), HDPE/THV220 (90/10) blend (**b**) and particle distribution of blends (**c**) [107]

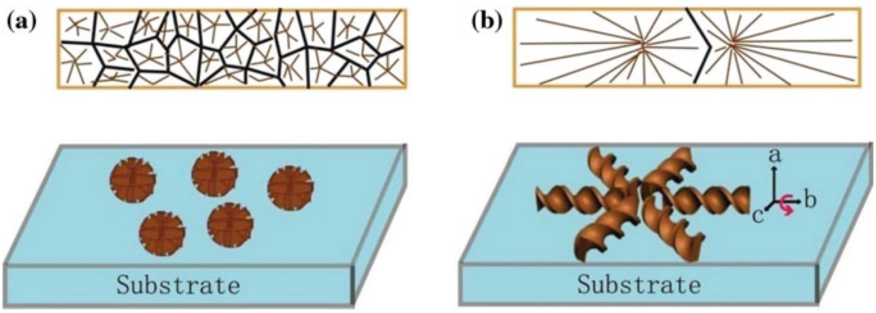


Fig. 5.15 Schematic illustration of structures of small (**a**) and large (**b**) PE spherulites in PE/P3BT blend films with 4 μm of thickness. *Top panel* cross section of surface; *bottom panel* overall view [108]

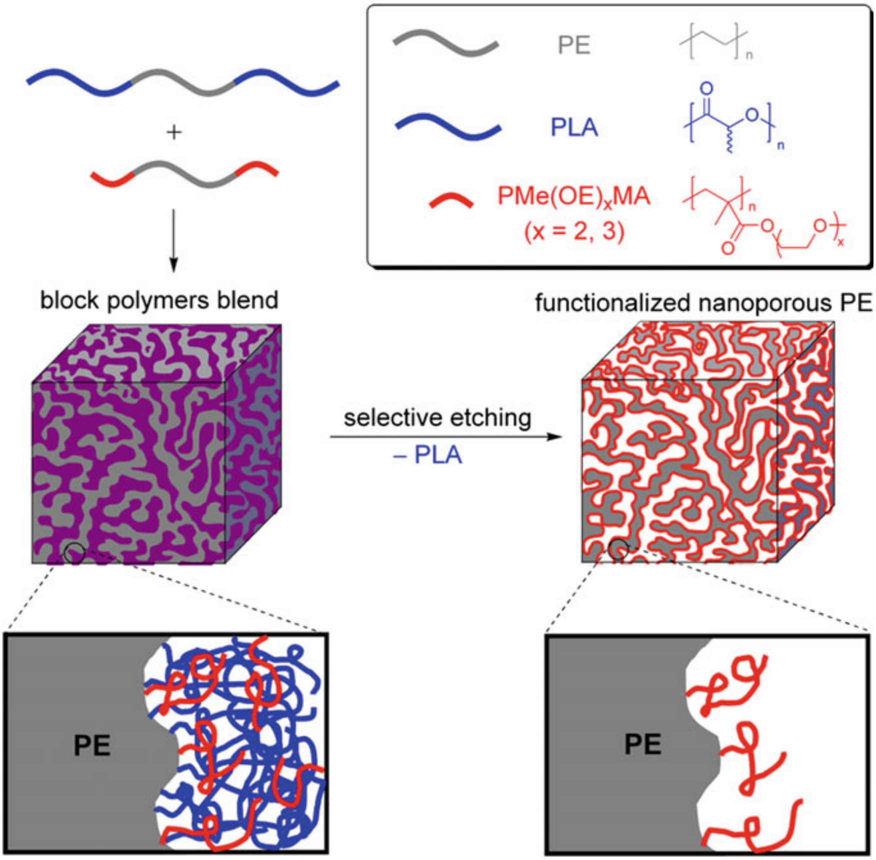


Fig. 5.16 Preparation strategy of the nanoporous polyethylene whose pore wall is lined with poly [2-(2-methoxyethoxy)ethyl methacrylate] and poly{2-[2-(2-methoxyethoxy)ethoxy]-ethyl methacrylate} PMe(OE)$_x$MA (x = 2, 3) by the PLA selective etching from the reactive block polymer blends [109]

which showed improved water uptake because of the hydrophilic PMe(OE)xMA on the pore walls.

The hydrophobic properties of polyethylene (PE) are considered to be the key factor limiting the application of PE membranes, especially for water treatment [110]. The hydrophobicity of the membrane causes (i) high energy consumption during its use, because a higher pressure is required for water to penetrate the membrane and (ii) membrane fouling which leads to a rapid decay of the flux. Hydrophilic modification is therefore an important direction for research into high-performance PE membranes. Extensive studies focused on amphiphilic co-polymers (e.g. PE-b-PEG), because the hydrophobic segments usually have good compatibility with the matrix and can act as anchors in the membrane matrix to prevent the loss of the co-polymer during the membrane preparation and operation processes. Meanwhile, the hydrophilic moiety always enriches the surface of the membrane, giving the membrane improved hydrophilicity.

A foamed plastic is called an open-cellular foam when its pores are interconnected with one another; otherwise, this plastic is called a closed-cellular foam [111]. Open-cellular plastic foams are applied in the field of acoustic insulation. Two different mechanisms of bubble nucleation exist: homogeneous and heterogeneous nucleation. Several nucleating agents have been used to enhance heterogeneous bubble nucleation. PS/PE blends with dispersed PE domains were studied to observe the effects of a dispersed domain polymer on heterogeneous bubble nucleation, as well as on cell wall opening. PS and PE are immiscible, and the interfacial tension between these polymers is higher compared to blends such as PMMA/PS or PP/PE. The viscosity difference between the dispersed domain and the matrix could be altered by changing the processing temperature and the PE grade.

5.8.9 Chlorinated Polyethylene (CPE)

CPE is a special class of elastomer prepared from polyethylene by random chlorination in an aqueous medium, and it is always available in a powder form [112]. It possesses a number of advantageous properties over other unsaturated and saturated elastomers. The saturated backbone of CPE imparts excellent weather, ozone, oxidation, chemical, and hydrocarbon oil resistance, as well as very good compression set, low-temperature flexibility, heat-ageing resistance, and very good processability. The presence of chlorine atoms in the backbone of CPE gives inherent flame retardancy. Ethylene methacrylate co-polymer (EMA) also has a saturated backbone, and therefore, it has very good age, oil, and thermal degradation resistance. It further has excellent low-temperature flexibility which is much better than that of CPE, even without any plasticizer. All halogen-containing polymers produce toxic and corrosive gases once it burns, and therefore, CPE is not always a good choice in a number of applications. Blending of EMA with CPE should reduce the adverse effect of halogen in a polymer used for wire and cable covers and jacketing, while combining the beneficial properties of the two polymers.

PVC is a widely used commodity polymer because of its excellent properties such as high stiffness, good transparency, low flammability, and favourable price [113]. PVC is recyclable, but incompatible contaminations reduce its mechanical properties. Polyethylenes, with their low glass-transition temperatures, should be good impact modifiers of PVC, but the incompatibility of these two polymers makes the preparation and application of such a blend almost impossible. The thermal stability of PVC is limited, and it requires special care during processing to prevent thermal degradation by dehydrochlorination. CPE was found to be a very good compatibilizer in PVC/polyethylene blends because it contains a broad range of different structural units on the same molecule.

5.9 Conclusions

This chapter described recent research on polyolefins blended with other polyolefins and with a variety of other polymers, including natural and biodegradable polymers. Most of the research concentrated on morphology–property relationships and on understanding the different morphologies and their influence on obtaining the required properties for specific applications. From this chapter, it is clear that polyolefin blend research during the first decade of the twenty-first century was concerned with (i) improving the usability of known polyolefin blends for certain applications, (ii) obtaining a better understanding of blending technology for recycling of polyolefins, and (iii) increasing the biodegradability of polyolefins through blending with natural or biodegradable polymers, without sacrificing the excellent properties of the polyolefins.

References

1. J.-G. Gai, Y. Zuo, Metastable region of phase diagram: optimum parameter range for processing ultrahigh molecular weight polyethylene blends. J. Mol. Model. **18**, 2501–2512 (2012)
2. Y. An, R.-Y. Bao, Z.-Y. Liu, X.-J. Wu, W. Yang, B.-H. Xie, M.-B. Yang, Unusual hierarchical structures of mini-injection molded isotactic polypropylene/ultrahigh molecular weight polyethylene blends. Eur. Polym. J. **49**, 538–548 (2013)
3. Y. An, L. Gu, Y. Wang, Y.-M. Li, W. Yang, B.-H. Xie, M.-B. Yang, Morphologies of injection molded isotactic polypropylene/ultra high molecular weight polyethylene blends. Mater. Des. **35**, 633–639 (2012)
4. W. Shao, Y. Zhang, Z. Wang, Y. Niu, R. Yue, W. Hu, Critical content of ultrahigh-molecular-weight polyethylene to induce the highest nucleation rate for isotactic polypropylene in blends. Ind. Eng. Chem. Res. **51**, 15953–15961 (2012)
5. Y.-F. Huang, J.-Z. Xu, J.-Y. Xu, Z.-C. Zhang, B.S. Hsiao, L. Xu, Z.-M. Li, Self-reinforced polyethylene blend for artificial joint application. J. Mater. Chem. B **2**, 971–980 (2014)

6. D. Xu, Y. Song, X. Shi, P. Tang, M. Matsuo, Y. Bin, Temperature dependence of lamellae orientation of a branched low molecular weight polyethylene/ultrahigh molecular weight polyethylene blend film under a controlled temperature gradient. Polymer **54**, 4037–4044 (2013)
7. D. Xu, Y. Song, X. Shi, P. Tang, M. Matsuo, Y. Bin, Temperature dependence of lamellae orientation of a branched low molecular weight polyethylene/ultrahigh molecular weight polyethylene blend film under a controlled temperature gradient. Polymer **54**, 4037–4044 (2013)
8. Y. Chen, H. Zou, M. Liang, P. Liu, Rheological, thermal, and morphological properties of low-density polyethylene/ultra-high-molecular-weight polyethylene and linear low-density polyethylene/ultra-high-molecular-weight polyethylene blends. J. Appl. Polym. Sci. **129**, 945–953 (2013)
9. Yu.V. Zavgorodnev, K.A. Prokhorov, G.Yu. Nikolaeva, E.A. Sagitova, P.P. Pashinin, T.M. Ushakova, L.A. Novokshonova, E.E. Starchak, V.G. Krasheninnikov. Raman structural study of reactor blends of ultrahigh molecular weight polyethylene and random ethylene/1-hexene copolymers. Laser Phys. **23**, 025701 (8 pp) (2013)
10. T.M. Ushakova, E.E. Starchak, V.G. Krasheninnikov, V.G. Grinev, T.A. Ladygina, L.A. Novokshonova, Influence of copolymer fraction composition in ultrahigh molecular weight polyethylene blends with ethylene/1-hexene copolymers on material physical and tensile properties. J. Appl. Polym. Sci. **131**, 40151 (2014)
11. H.-J. Radusch, I. Kolesov, U. Gohs, G. Heinrich, Multiple shape-Memory behavior of polyethylene/polycyclooctene blends cross-linked by electron irradiation. Macromol. Mater. Eng. **297**, 1225–1234 (2012)
12. H. Liu, S.-C. Li, Y. Liu, M. Iqbal, Thermostimulative shape memory effect of linear low-density polyethylene/polypropylene (LLDPE/PP) blends compatibilized by crosslinked LLDPE/PP Blend (LLDPE–PP). J. Appl. Polym. Sci. **122**, 2512–2519 (2011)
13. J. Zhao, M. Chen, X. Wang, X. Zhao, Z. Wang, Z.-M. Dang, L. Ma, G.-H. Hu, F. Chen, Triple shape memory effects of cross-linked polyethylene/polypropylene blends with cocontinuous architecture. ACS Appl. Mater. Interfaces **5**, 5550–5556 (2013)
14. R. Hoeher, T. Raidt, C. Krumm, M. Meuris, F. Katzenberg, J.C. Tiller, Tunable multiple-shape memory polyethylene blends. Macromol. Chem. Phys. **214**, 2725–2732 (2013)
15. I. Kolesov, O. Dolynchuk, S. Borreck, H.-J. Radusch, Morphology-controlled multiple one- and two-way shape-memory behavior of cross-linked polyethylene/poly(ε-caprolactone) blends. Polym. Adv. Technol. doi:10.1002/pat.3338
16. Y. Lin, G.R. Marchand, A. Hiltner, E. Baer, Adhesion of olefin block copolymers to polypropylene and high density polyethylene and their effectiveness as compatibilizers in blends. Polymer **52**, 1635–1644 (2011)
17. R. Su, Z. Li, H. Bai, K. Wang, Q. Zhang, Q. Fu, Z. Zhang, Y. Men, Flow-induced epitaxial growth of high density polyethylene in its blends with low crystallizable polypropylene copolymer. Polymer **52**, 3655–3660 (2011)
18. P. Deng, B. Whiteside, F. Wang, K. Norris, J. Zhang, Epitaxial growth and morphological characteristics of isotactic polypropylene/polyethylene blends: Scale effect and mold temperature. Polym. Testing **34**, 192–201 (2014)
19. P. Deng, K. Liu, L. Zhang, H. Liu, T. Wang, J. Zhang, Micro and macro injection molded parts of isotactic polypropylene/polyethylene blends: Shear-induced crystallization behaviors and morphological characteristics. J. Macromol. Sci. Part B Phys. **53**, 24–39 (2014)
20. R. Su, K. Wang, Q. Zhang, F. Chen, Q. Fu, N. Hu, E. Chen, Epitaxial crystallization and oriented structure of linear low-density polyethylene/isotactic polypropylene blends obtained via dynamic packing injection molding. Polym. Adv. Technol. **22**, 225–231 (2011)
21. J.K. Keum, Y. Mao, F. Zuo, B.S. Hsiao, Flow-induced crystallization precursor structure in high molecular weight isotactic polypropylene (HMW-iPP)/low molecular weight linear low density polyethylene (LMW-LLDPE) binary blends. Polymer **54**, 1425–1431 (2013)

22. F. Rybnikar, M. Kaszonyiova, Epitaxial crystallization of linear polyethylene in blends with Isotactic polypropylene. J. Macromol. Sci. Part B Phys. **53**, 217–232 (2014)
23. H.-W. Shen, B.-H. Xie, W. Yang, M.-B. Yang, Thermal and rheological properties of polyethylene blends with bimodal molecular weight distribution. J. Appl. Polym. Sci. **129**, 2145–2151 (2013)
24. H. Shen, B. Xie, W. Yang, M. Yang, Non-isothermal crystallization of polyethylene blends with bimodal molecular weight distribution. Polym. Testing **32**, 1385–1391 (2013)
25. G. Shen, H. Shen, B. Xie, W. Yang, M. Yang, Crystallization and fracture behaviors of high-density polyethylene/linear low-density polyethylene blends: The influence of short-chain branching. J. Appl. Polym. Sci. **129**, 2103–2111 (2013)
26. X. Sun, G. Shen, H. Shen, B. Xie, W. Yang, M. Yang, Co-crystallization of blends of high-density polyethylene with linear low-density polyethylene: An investigation with successive self-nucleation and annealing (SSA) technique. J. Macromol. Sci. Part B Phys. **52**, 1372–1387 (2013)
27. Y. Sun, S. Fischer, Z. Jiang, T. Tang, S.S. Funari, R. Gehrke, Y. Men, Morphological changes of linear, branched polyethylenes and their blends during crystallization and subsequent melting by synchrotron SAXS and DSC. Macromol. Symp. **312**, 51–62 (2012)
28. Y.J. Lee, C.R. Snyder, A.M. Forster, M.T. Cicerone, W.-L. Wu, Imaging the molecular structure of polyethylene blends with broadband coherent Raman microscopy. ACS Macro Lett. **1**, 1347–1351 (2012)
29. N.K. Madi, Thermal and mechanical properties of injection molded recycled high density polyethylene blends with virgin isotactic polypropylene. Mater. Des. **46**, 435–441 (2013)
30. C. Fang, L. Nie, S. Liu, R. Yu, N. An, S. Li, Characterization of polypropylene–polyethylene blends made of waste materials with compatibilizer and nano-filler. Compos. B **55**, 498–505 (2013)
31. S. Satapathy, G.B. Nando, A. Nag, Dynamic mechanical analysis of electron beam irradiated waste polyethylene and its blends with virgin high density and low density polyethylene. J. Elastomers Plast. **43**, 33–48 (2011)
32. N. Mieda, M. Yamaguchi, Flow instability for binary blends of linear polyethylene and long-chain branched polyethylene. J. Nonnewton. Fluid Mech. **166**, 231–240 (2011)
33. Y.-H. Niu, Z.-G. Wang, X.-L. Duan, W. Shao, D.-J. Wang, J. Qiu, Thermal oxidation-induced long chain branching and its effect on phase separation kinetics of a polyethylene blend. J. Appl. Polym. Sci. **119**, 530–538 (2011)
34. N. Robledo, J.F. Vega, J. Nieto, J. Martínez-Salazar, Role of the interface in the melt-rheology properties of linear low-density polyethylene/low-density polyethylene blends: Effect of the molecular architecture of the dispersed phase. J. Appl. Polym. Sci. **119**, 3217–3226 (2011)
35. S. Taglialatela Scafati, L. Boragno, S. Losio, S. Limbo, M. Castellano, M.C. Sacchi, P. Stagnaro. Modulation of barrier properties of monolayer films from blends of polyethylene with ethylene-co-norbornene. J. Appl. Polym. Sci. **121**, 3020–3027 (2011)
36. C. Kock, N. Aust, C. Grein, M. Gahleitner, Polypropylene/polyethylene blends as models for high-impact propylene-ethylene copolymers, Part 2: Relation between composition and mechanical performance. J. Appl. Polym. Sci. **130**, 287–296 (2013)
37. C. Kock, M. Gahleitner, A. Schausberger, E. Ingolic, Polypropylene/polyethylene blends as models for high-impact propylene-ethylene copolymers, Part 1: Interaction between rheology and morphology. J. Appl. Polym. Sci. **128**, 1484–1496 (2013)
38. O.Y. Alothman, Processing and characterization of high density polyethylene/ethylene vinyl acetate blends with different VA contents. Adv. Mater. Sci. Eng., 635693, 10 pp (2012)
39. A. Iannaccone, S. Amitrano, R. Pantani, Rheological and mechanical behavior of ethyl vinyl acetate/low density polyethylene blends for injection molding. J. Appl. Polym. Sci. **127**, 1157–1163 (2013)

40. Y. Chen, H. Zou, M. Liang, Y. Cao, Melting and crystallization behaviour of partially miscible high density polyethylene/ethylene vinyl acetate copolymer (HDPE/EVA) blends. Thermochim. Acta **586**, 1–8 (2014)
41. B. Wang, M. Wang, Z. Xing, H. Zeng, G. Wu, Preparation of radiation crosslinked foams from low-density polyethylene/ethylene vinyl acetate (LDPE/EVA) copolymer blend with a supercritical carbon dioxide approach. J. Appl. Polym. Sci. **127**, 912–918 (2013)
42. X. Zhang, H. Yang, Y. Song, Q. Zheng, Influence of crosslinking on crystallization, rheological and mechanical behaviours of high density polyethylene/ethylene-vinyl acetate copolymer blends. Polym. Eng. Sci. (2014). doi:10.1002/pen.23843
43. F. Chen, M.P. Wolcott, Miscibility studies of paraffin/polyethylene blends as form-stable phase change materials. Eur. Polym. J. **52**, 44–52 (2014)
44. M.E. Sotomayor, I. Krupa, A. Várez, B. Levenfeld, Thermal and mechanical characterization of injection moulded high density polyethylene/paraffin wax blends as phase change materials. Renewable Energy **68**, 140–145 (2014)
45. S. Liu, W. Yu, C. Zhou, Molecular self-assembly assisted liquid–liquid phase separation in ultrahigh molecular weight polyethylene/liquid paraffin/dibenzylidene sorbitol ternary blends. Macromolecules **46**, 6309–6318 (2013)
46. B.Y. Shin, D.H. Han, Morphological and mechanical properties of polyamide 6/linear low density polyethylene blend compatibilized by electron-beam initiated mediation process. Radiat. Phys. Chem. **97**, 198–207 (2014)
47. G.-M. Lin, G.-X. Sui, R. Yang, Mechanical and shape-memory properties of polyamide/maleated polyethylene/linear low-density polyethylene blend. J. Appl. Polym. Sci. **126**, 350–357 (2012)
48. F. Xiang, Y. Shi, X. Li, T. Huang, C. Chen, Y. Peng, Y. Wang, Cocontinuous morphology of immiscible high density polyethylene/polyamide 6 blend induced by multiwalled carbon nanotubes network. Eur. Polymer J. **48**, 350–361 (2012)
49. A. Argoud, L. Trouillet-Fonti, S. Ceccia, P. Sotta, Morphologies in polyamide 6/high density polyethylene blends with high amounts of reactive compatibilizer. Eur. Polymer J. **50**, 177–189 (2014)
50. S. Mallick, B.B. Khatua, Morphology and properties of nylon6 and high density polyethylene blends in absence and presence of nanoclay. J. Appl. Polym. Sci. **121**, 359–368 (2011)
51. A. Sharif-Pakdaman, J. Morshedian, Y. Jahani, Effect of organoclay and silane grafting of polyethylene on morphology, barrierity, and rheological properties of HDPE/PA6 blends. J. Appl. Polym. Sci. **127**, 1211–1220 (2013)
52. S. Charoenpongpool, M. Nithitanakul, B.P. Grady, Melt-neutralization of maleic anhydride grafted on high-density polyethylene compatibilizer for polyamide-6/high-density polyethylene blend: effect of neutralization level on compatibility of the blend. Polym. Bull. **70**, 293–309 (2013)
53. I. Labaume, J. Huitric, P. Médéric, T. Aubry, Structural and rheological properties of different polyamide/polyethylene blends filled with clay nanoparticles: a comparative study. Polymer **54**, 3671–3679 (2013)
54. F.P. La Mantia, P. Fontana, M. Morreale, M.C. Mistretta, Orientation induced brittle-ductile transition in a polyethylene/polyamide 6 blend. Polym. Testing **36**, 20–23 (2014)
55. S.-J. Liu, W.-R. Lin, K.-Y. Lin, Morphological development in water assisted injection molded polyethylene/polyamide-6 blends. Polym. Adv. Technol. **22**, 2062–2068 (2011)
56. M.E. Córdova, A.T. Lorenzo, A.J. Müller,* L. Gani, S. Tencé-Girault, L. Leibler, The influence of blend morphology (co-continuous or sub-micrometer droplets dispersions) on the nucleation and crystallization kinetics of double crystalline polyethylene/polyamide blends prepared by reactive extrusion. Macromol. Chem. Phys. **212**, 1335–1350 (2011)
57. D.M. Stelescu, A. Airinei, M. Homocianu, N. Fifere, D. Timpu, M. Aflori, Structural characteristics of some high density polyethylene/EPDM blends. Polym. Testing **32**, 187–196 (2013)

58. P.V. Anil Kumar, S. Anil Kumar, K.T. Varughese, S. Thomas, Permeation of chlorinated hydrocarbon vapors through high density polyethylene/ethylene propylene diene terpolymer rubber blends. Sep. Sci. Technol. **47**, 811–818 (2012)
59. P.V. Anil Kumar, S. Anil Kumar, K.T. Varughese, S. Thomas, Transport properties of high-density polyethylene/ethylene propylene diene terpolymer blends. J. Mater. Sci. **47**, 3293–3304 (2012)
60. P.V. Anil Kumar, S. Anilkumar, K.T. Varughese, S. Thomas. Transport behavior of aromatic hydrocarbons through high density polyethylene/ ethylene propylene diene terpolymer blends. Journal of Polymer Research 2012; 19:9794
61. M.M H. Senna, Y.K. Abdel-Moneam, Y.A. Hussein, A. Alarifi. Effects of electron beam irradiation on the structure–property behavior of blends based on low density polyethylene and styrene-ethylene-butylene-styrene-block copolymers. Journal of Applied Polymer Science 2012; 125:2384–2393
62. S. Utara, P. Boochathum, Novel dynamic vulcanization of polyethylene and ozonolysed natural rubber blends: Effect of curing system and blending ratio. J. Appl. Polym. Sci. **120**, 2606–2614 (2011)
63. E. Elshereafy, M.A. Mohamed, M.M. EL-Zayat, A.A. El Miligy. Gamma radiation curing of nitrile rubber/high density polyethylene blends. J. Radioanal. Nucl. Chem. **293**, 941–947 (2012)
64. T.K. Jayasree, P. Predeep, Non-isothermal crystallization behavior of styrene butadiene rubber/high density polyethylene binary blends. J. Therm. Anal. Calorim. **108**, 1151–1160 (2012)
65. A.M. Maysa, Radiation vulcanization of thermoplastic low-density polyethylene/bromobutyl rubber blends. J. Thermoplast. Compos. Mater. **27**, 364–378 (2014)
66. L. Yu, X. Liu, E. Petinakis, S. Bateman, P. Sangwan, A. Ammala, Ka. Dean, S. Wong-Holmes, Q. Yuan, C.K. Siew, F. Samsudin, Z. Ahamid. Enhancement of pro-degradant performance in polyethylene/starch blends as a function of distribution. J. Appl. Polym. Sci. **128**, 591–596 (2013)
67. C. Cercléa, P. Sarazinb, B.D. Favis, High performance polyethylene/thermoplastic starch blends through controlled emulsification phenomena. Carbohydr. Polym. **92**, 138–148 (2013)
68. H. Vieyra, M.A. Aguilar-Méndez, E. San, Martín-Martínez. Study of biodegradation evolution during composting of polyethylene–starch blends using scanning electron microscopy. J. Appl. Polym. Sci. **127**, 845–853 (2013)
69. G. Li, P. Sarazin, W.J. Orts, S.H. Imam, B.D. Favis, Biodegradation of thermoplastic starch and its blends with poly(lactic acid) and polyethylene: Influence of morphology. Macromol. Chem. Phys. **212**, 1147–1154 (2011)
70. A.W.M. Kahar, H. Ismail, N. Othman. Effects of polyethylene-grafted maleic anhydride as a compatibilizer on the morphology and tensile properties of (thermoplastic tapioca starch)/(high-density polyethylene)/(natural rubber) blends
71. M. Kahar, A. Wahab, H. Ismail, N. Othman, Compatibilization effects of PE-g-MA on mechanical, thermal and swelling properties of high density polyethylene/natural rubber/thermoplastic tapioca starch blends. Polymer-Plastics Technology and Engineering **51**, 298–303 (2012)
72. M. Kahar A. Wahab, H. Ismail, N. Othman. Effects of dynamic vulcanization on the physical, mechanical, and morphological properties of high-density polyethylene/(natural rubber)/(thermoplastic tapioca starch) dlends. Journal of Vinyl Additive Technology 2012; 18:192–197
73. A.W.M. Kahar, H. Ismail, N. Othman, Properties of HVA-2 vulcanized high density polyethylene/natural rubber/thermoplastic tapioca starch blends. J. Appl. Polym. Sci. **128**, 2479–2488 (2013)
74. A.W.M. Kahar, H. Ismail, N. Othman, Morphology and tensile properties of high-density polyethylene/natural rubber/thermoplastic tapioca starch blends: The effect of citric acid-modified tapioca starch. J. Appl. Polym. Sci. **125**, 768–775 (2012)

75. S. Garg, A. Kumar, Jana. Effect of propylation of starch with different degrees of substitution on the properties and characteristics of starch-low density polyethylene blend films. J. Appl. Polym. Sci. **122**, 2197–2208 (2011)
76. M. Sabetzadeh, R. Bagheri, M. Masoomi, Effect of corn starch content in thermoplastic starch/low-density polyethylene blends on their mechanical and flow properties. J. Appl. Polym. Sci. **126**, E63–E69 (2012)
77. R. Thipmanee, A. Sane, Effect of zeolite 5A on compatibility and properties of linear low-density polyethylene/thermoplastic starch blend. J. Appl. Polym. Sci. **126**, E251–E258 (2012)
78. S. Mir, T. Yasin, P.J. Halley, H.M. Siddiqi, O. Ozdemir, A. Nguyen, Thermal and rheological effects of sepiolite in linear low-density polyethylene/starch blend. J. Appl. Polym. Sci. **127**, 1330–1337 (2013)
79. A. Taghizadeh, P. Sarazin, B.D. Favis, High molecular weight plasticizers in thermoplastic starch/polyethylene blends. Journal of Materials Science **48**, 1799–1811 (2013)
80. J.M. Quiroz-Castillo, D.E. Rodríguez-Félix, H. Grijalva-Monteverde, T. del Castillo-Castro, M. Plascencia-Jatomea, F. Rodríguez-Félix, P.J. Herrera-Franco, Preparation of extruded polyethylene/chitosan blends compatibilized with polyethylene-graft-maleic anhydride. Carbohydr. Polym. **101**, 1094–1100 (2014)
81. D.E. Rodríguez-Félix, J.M. Quiroz-Castillo, H. Grijalva-Monteverde, T. del Castillo-Castro, S.E. Burruel-Ibarra, F. Rodríguez-Félix, T. Madera-Santana, R.E. Cabanillas, P. J. Herrera-Franco, Degradability of extruded polyethylene/chitosan blends compatibilized with polyethylene-graft-maleic anhydride under natural weathering. J. Appl. Polym. Sci. **131**, 41045 (2014)
82. K. Hamad, M. Kaseem, F. Deri, Poly(lactic acid)/low density polyethylene polymer blends: Preparation and characterization. Asia-Pac. J. Chem. Eng. **7**, S310–S316 (2012)
83. K. Hamad, Y. Gun, Ko, M. Kaseem, F. Deri. Effect of acrylonitrile–butadiene–styrene on flow behaviour and mechanical properties of polylactic acid/low density polyethylene blend. Asia-Pac. J. Chem. Eng. **9**, 349–353 (2014)
84. G. Jiang, H.-X. Huang, Z.-K. Chen, Rheological responses and morphology of polylactide/linear low density polyethylene blends produced by different mixing type. Polym. Plast. Technol. Eng. **50**, 1035–1039 (2011)
85. Monika, P. Upadhyaya, N. Chand, Vi Kumar, Effect of poly lactic acid on morphological, mechanical, and optical properties of compatibilized polypropylene and high density polyethylene blend. Compos. Interfaces **21**, 133–141 (2014)
86. S.-M. Lai, K.-C. Hung, H.C. Kao, L.-C. Liu, X.F. Wang, Synergistic effects by compatibilization and annealing treatment of metallocene polyethylene/PLA blends. J. Appl. Polym. Sci. **130**, 2399–2409 (2013)
87. S. Djellali, N. Haddaoui, T. Sadoun, A. Bergeret, Y. Grohens, Structural, morphological and mechanical characteristics of polyethylene, poly(lactic acid) and poly(ethylene-co-glycidyl methacrylate) blends. Iran. Polym. J. **22**, 245–257 (2013)
88. G. Madhu, H. Bhunia, P.K. Bajpai, Blends of high density polyethylene and poly(L-lactic acid): mechanical and thermal properties. Polym. Eng. Sci. (2013). doi:10.1002/pen.23764
89. S.-T. Bee, C.T. Ratnam, L.T. Sin, T.-T. Tee, W.-K. Wonga, J.-X. Lee, A.R. Rahmat, Effects of electron beam irradiation on the structural properties of polylactic acid/polyethylene blends. Nucl. Instrum. Methods Phys. Res., B **334**, 18–27 (2014)
90. G. Singh, H. Bhunia, A. Rajor, V. Choudhary, Thermal properties and degradation characteristics of polylactide, linear low density polyethylene, and their blends. Polym. Bull. **66**, 939–953 (2011)
91. G. Singh, N. Kaur, H. Bhunia, P.K. Bajpai, U.K. Mandal, Degradation behaviors of linear low-density polyethylene and poly(L-lactic acid) blends. J. Appl. Polym. Sci. **124**, 1993–1998 (2012)
92. R. Nordin, H. Ismail, Z. Ahmad, A. Rashid, Performance improvement of (linear low-density polyethylene)/poly(vinyl alcohol) blends by in situ silane crosslinking. J. Vinyl Add. Tech. **18**, 120–128 (2012)

93. M.N.F. Norrrahim, H. Ariffin, M.A. Hassan, N.A. Ibrahimc, H. Nishida, Performance evaluation and chemical recyclability of a polyethylene/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blend for sustainable packaging. RSC Adv. **3**, 24378–24388 (2013)
94. J. Yang, J.-Z. Liang, F.-J. Li, Melt strength and extensional viscosity of low-density polyethylene and poly(butylene succinate) blends using a melt-spinning technique. J. Macromol. Sci. Part B Phys. **51**, 1715–1730 (2012)
95. A.V. Nand, S. Swift, B. Uy, P.A. Kilmartin, Evaluation of antioxidant and antimicrobial properties of biocompatible low density polyethylene/polyaniline blends. J. Food Eng. **116**, 422–429 (2013)
96. A.V. Nand, S. Ray, J. Travas-Sejdic, P.A. Kilmartin, Characterization of antioxidant low density polyethylene/polyaniline blends prepared via extrusion. Mater. Chem. Phys. **135**, 903–911 (2012)
97. T. Del Castillo-Castro, M.M. Castillo-Ortega, P.J. Herrera-Franco, D.E. Rodríguez-Félix, Compatibilization of polyethylene/polyaniline blends with polyethylene-graft-maleic anhydride. J. Appl. Polym. Sci. **119**, 2895–2901 (2011)
98. J. Songa, A. Batrab, J.M. Regoc, C.W. Macosko, Polyethylene/polyurethane blends for improved paint adhesion. Prog. Org. Coat. **72**, 492–497 (2011)
99. X. Wang, B. Mu, Hg Wang, Preparation and properties of thermoplastic polyurethane/ultra high molecular weight polyethylene blends. Polym. Compos. (2014). doi:10.1002/pc.23009
100. S. Razavia, A. Shojaeia, R. Bagheri, Binary and ternary blends of high-density polyethylene with poly(ethylene terephthalate) and polystyrene based on recycled materials. Polym. Adv. Technol. **22**, 690–702 (2011)
101. Y. Zhang, H. Zhang, W. Guo, C. Wu, Effects of different types of polyethylene on the morphology and properties of recycled poly(ethylene terephthalate)/polyethylene compatibilized blends. Polym. Adv. Technol. **22**, 1851–1858 (2011)
102. K.A. Tawab, S.M. Ibrahim, M.M. Magida, The effect of gamma irradiation on mechanical, and thermal properties of recycling polyethylene terephthalate and low density polyethylene (R-PET/LDPE) blend compatibilized by ethylene vinyl acetate (EVA). J. Radioanal. Nucl. Chem. **295**, 1313–1319 (2013)
103. Y. Zhang, H. Zhang, W. Guo, C. Wu, Effects of different types of polyethylene on the morphology and properties of recycled poly(ethylene terephthalate)/polyethylene compatibilized blends. Polym. Adv. Technol. **22**, 1851–1858 (2011)
104. Y.-Y. Cui, B.-J. Dong, B.-L. Li, S.-C. Li, Properties of polypropylene/poly(ethylene terephthalate) thermostimulative shape memory blends reactively compatibilized by maleic anhydride grafted polyethylene-octene elastomer. Int. J. Polym. Mater. Polym. Biomater. **62**, 671–677 (2013)
105. Siddaramaiah, M.N. Satheesh Kumar, G.B. Nando, Rheological and mechanical properties of poly(ethylene acrylic acid) and low density polyethylene blends. J. Appl. Polym. Sci. **121**, 3070–3077 (2011)
106. T. Ivanova, J. Zicans, I. Elksnite, M. Kalnins, R. Maksimov, Mechanical properties of injection-molded binary blends of polyethylene with small additions of a liquid-crystalline polymer. J. Appl. Polym. Sci. **122**, 3564–3568 (2011)
107. S. Siengchin, T.N. Abraham, Morphology and rheological properties of high density polyethylene/fluorothermoplastics blends. J. Appl. Polym. Sci. **127**, 919–925 (2013)
108. Y. Wang, Z. Chen, J. Chen, Y. Qu, X. Yang, Miscibility, crystallization, and morphology of the double-crystalline blends of insulating polyethylene and semiconducting poly (3-butylthiophene). J. Macromol. Sci. Part B Phys. **52**, 1388–1404 (2013)
109. T. Kato, M.A. Hillmyer, Functionalized nanoporous polyethylene derived from miscible block polymer blends. ACS Appl. Mater. Interfaces **5**, 291–300 (2013)
110. J.-L. Shi, L.-F. Fang, H. Zhang, Z.-Y. Liang, B.-K. Zhu, L.-P. Zhu, Effects of the extractant on the hydrophilicity and performance of high-density polyethylene/polyethylene-b-poly (ethylene glycol) blend membranes prepared via a thermally induced phase separation process. J. Appl. Polym. Sci. **130**, 3816–3824 (2013)

111. D. Kohlhoff, M. Ohshima, Influence of polyethylene disperse domain on cell morphology of polystyrene-based blend foams. J. Cell. Plast. **50**, 241–261 (2014)
112. P. Bhagabati, T.K. Chaki, Compatibility study of chlorinated polyethylene/ethylene methacrylate copolymer blends using thermal, mechanical, and chemical analysis. J. Appl. Polym. Sci. **131**, 40316 (2014)
113. M. Kollár, G. Zsoldos, Investigating poly-(vinyl-chloride)-polyethylene blends by thermal methods. J. Therm. Anal. Calorim. **107**, 645–650 (2012)

Chapter 6
Polyolefin Composites and Nanocomposites

Noora J. Al-Thani, Jolly Bhadra and Khadija M. Zadeh

6.1 Introduction

Polyolefin composites (POCs) are defined as materials that contain two or more phases (chemically and physically) and have a distinct boundary. The careful combination of different systems results in improved structure and function over the individual constituents alone. Polyolefins have a wide range of applications, are inexpensive, and possess a diverse range of features [1, 2]. One of the primary advantages of polyolefins is that they are recyclable. Their properties can also be improved through composite engineering [3]. Polyolefins may be classified into different groups of thermoplastics and elastomers depending on the type of monomer and their structure [4]. Polyethylene (containing an ethylene monomer unit) and polypropylene (containing propylene monomer units) are two widely used polyolefins with diverse applications [5].

Composites are engineered materials that contain two or more constituents with different properties that remain distinct from one another within the structure. POCs are a subset of the larger polymer composites group. The increased synthesis of POCs with different additives is necessary to satisfy the industrial demand that cannot be fulfilled by pure polymers. Additive materials can be classified as micro- and nanofillers depending on the applications of the composites. The fillers may be further subdivided as natural (plant fibers) or synthetic (glass fibers, CNT, etc.), different shapes (long or short length), flaky, fibrous, and spherical or disk-like [6]. The conventional addition of filler materials lowers the cost and improves the

---

N.J. Al-Thani · J. Bhadra (✉) · K.M. Zadeh
Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar
e-mail: jollybhadra@qu.edu.qa

N.J. Al-Thani
e-mail: n.al-thani@qu.edu.qa

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_6

mechanical, rheological, electrical, thermal, solvent resistance, and fire retardant properties compared to the pure polymer [7].

Polyolefin-based composites with natural fillers are gaining interest in a number of sectors because they are novel materials with automotive, building, textile, consumer, packaging, medical, and agricultural applications [8]. The advantages of natural fiber composite materials are their biodegradability, ecofriendly nature, renewability, reduced cost, and low density [9]. Higher content fillers can improve composite properties, but they result in composites that are more opaque and bulky. These characteristics restrict the use of these materials in food packaging. Another emerging field is polymer-layered clay nanocomposites. These materials have a number of advantages over polyolefins (inexpensive, straightforward to process and lightweight) that make them a suitable choice for both packaging and engineered applications. Current research focuses on polymer/clay nanocomposites using various polymers [10, 11]. Table 6.1 illustrates typical POCs found in the literature. These composites may involve different types of polyolefins. The selection of composites in Table 6.1 is random, without a classification system.

POCs and nanocomposite materials are useful in almost every aspect of daily life. These applications include transportation (aerospace, automotive, and marine), medical, packaging industries, construction industries (concrete, building blocks),

Table 6.1 POCs, types of fillers, and their applications

Polyolefin	Filler materials	Applications
Polyethylene	Wood fiber	Tubular concrete pole [12]
Polyethylene	Clay/cellulosic fiber	Food packaging [13]
Polyethylene	Glass fiber	Consumer [14]
Polyethylene (LDPE)	Palm fiber	Construction and consumer [15]
Polypropylene	Date palm fiber	Automotive industry [16]
Polymethylpentene	Minerals (karolin)	Microwave cooking ware [17]
Polyisobutylene	Glass fiber	Electronics industry [18]
Ethylene propylene rubber	Ferrite/carbon black	Electronics industry [19]
Polyethylene	Magnesium hydroxide	Textile industry [20]
Polyvinyl chloride	Glass fiber	Construction industry [21]
Polybutene-1	Wood flour	Construction industry [22]
Polypropylene	Wood fiber	Automotive industry [23]
Polypropylene	Paraffin wax	Construction industry (Thermal Insulation) [24]
Ethylene propylene diene monomer (M-class) rubber	Magnetite	Electronics industry [25]
Polypropylene	Kenaf fiber	Agriculture industry [26]
Polyethylene	Hydroxyapatite	Medical (bone substitution) [27]

consumer products (toys, home appliances, etc.), electronic industries, cable and wire coating, thermal and acoustic insulation, textile, and agriculture (12–27). Different processing techniques include extrusion for preparing polyolefin filaments (fibers) and casting and blowing pipes/profiles. Another advantage of polyolefins is that they can be molded into various shapes and sizes using physical and chemical foaming/blowing agents and they can be foamed and/or coated onto other materials. This chapter focuses on the preparation, processing, property characterization (mechanical, morphological, electrical, and thermal), and application of POCs and nanocomposites.

6.2 Definition and Classification

POCs are composed of two or more phases. The **matrix** is the polyolefin with a continuous phase that surrounds the other phases. The **filler** *could be a reinforcement* material for the entire composite. The properties of the polyolefin composite are dependent upon the filler type (organic or inorganic), geometry (fiber, flake, particulate, or sphere), the type of matrix, and the size of filler (micro or nano). Figure 6.1 depicts a simple schematic classification of a polyolefin composite [28].

6.2.1 Particulate Composite

The addition of rigid particles into the polyolefin matrix can result in a number of desirable effects on the composite including increased stiffness, improved flame retardancy, and enhanced electrical properties.

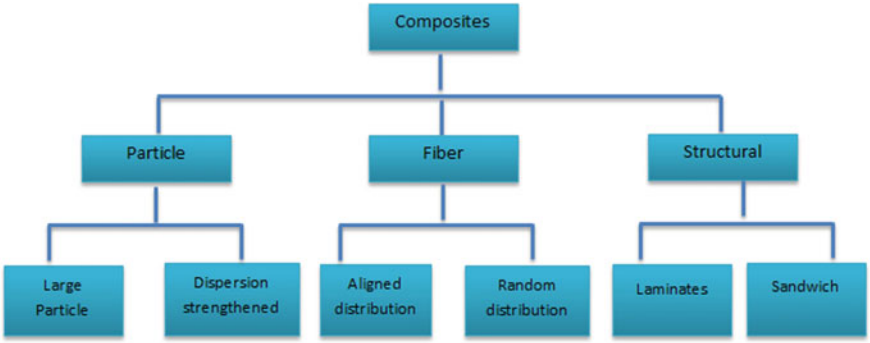


Fig. 6.1 Classification of the various composite types discussed in this chapter

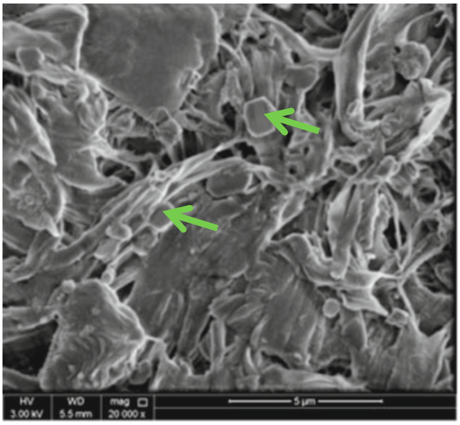


Fig. 6.2 SEM micrograph of MgOH particulate in PO matrix

Particle reinforcement in polymeric materials was first recognized for rubber compounds. This technique became possible when the relationship between structure and properties was understood for carbon black-filled natural rubber. The viscous component of the viscoelastic properties demonstrated that an enhancement in modulus was analogous to an increase in viscosity [29].

Particulate filler comes in a variety of geometries as shown in Fig. 6.2. For effective reinforcement, they should be approximately the identical dimensions in all directions. Examples of particulate filler include talc, calcium carbonate ($CaCO_3$), mica, and natural silica [30]. Their strength depends on the stress transfer between the particles and the matrix. The applied stress can be effectively transferred to the well-bonded particles from the matrix (Table 6.2).

Table 6.2 Types of fillers and their effect on PO matrix properties

Filler	Common materials	Effects on PO matrix properties
Reinforcements	Baron, carbon fiber, glass fiber, mineral fiber, Kevlar	• Increases tensile strength, flexural modulus, and heat deflection temperature (HDT)
Electrical/thermal conductive fillers	Metallic powders, carbon fiber, graphite, graphene	• Improves electrical and thermal conductivity
Flame retardants	Mineral hydroxide ex: $Mg(OH)_2$, AL_2O_3 Chlorine, bromine, phosphorous	• Reduces the occurrence and spread of combustion

6.2.2 Fiber Composite

Fibers are classified as natural or synthetic. Fibers are used as a reinforcement material to increase the mechanical properties of polymer composites [31]. Synthetic fibers have been successfully used as the reinforcing material in composites such as carbon fiber, glass fiber, and Kevlar fiber. Glass fiber is a well-known example of a reinforcement material for polyolefin matrix. Polypropylene is a composite of increasing interest in automotive and other applications [32]. Figure 6.3 illustrates a glass fiber-reinforced polypropylene matrix.

Factors affecting the properties of a fiber-reinforced thermoplastic composite

1. Fiber aspect ratio
2. Fiber distribution and fiber loading
3. Fiber interface with matrix

Fiber aspect ratio is defined as the ratio of fiber length divided by its diameter (L/D). A higher aspect ratio denotes a higher strength composite. The distribution or orientation of fiber and the loading both have significant influence on the strength of the composite. Fiber alignments include transverse, parallel, or random distributions. The following figure illustrates that the force direction and fiber arrangement are related to composite properties. The highest mechanical properties are achieved with aligned fibers, and the minimum strength occurs for fibers with a perpendicular alignment.

The interface region between fiber and polymer matrix is also an important factor affecting composite strength. For example, the use of a coupling agent or the chemical treatment of the fiber surface is essential to increase the degree of cross-linking at the interface region between a natural fiber with a polar nature and a nonpolar polyolefin matrix [34] (Fig. 6.4).

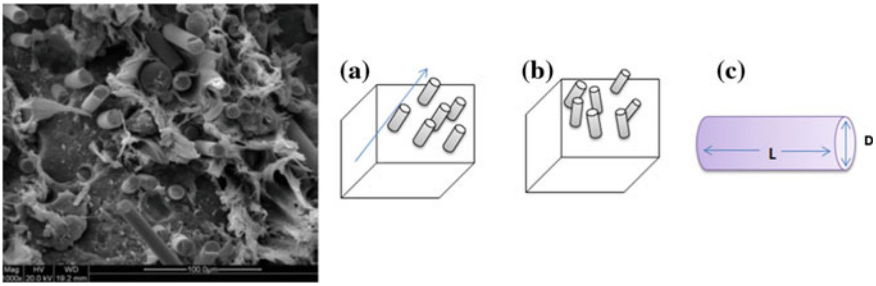


Fig. 6.3 Glass fiber-type E embedded in PP matrix as a reinforcing material [33]

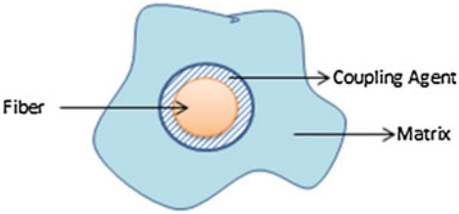


Fig. 6.4 Cross section of a natural fiber-reinforced polyolefin matrix with coupling agent

6.2.3 *Structural Composite*

A structural composite is composed of layers of homogenous or composite materials, with properties that depend on the characteristics of the composite and also the geometrical design of various structural laminar composites. Figure 6.5a shows a diagram of the layers of a sandwich composite and (b) illustrates a long fiber composite and (c) a laminar fiber composite.

Laminar composites are combinations of several layers of composite sheets that are bonded together. **Polyolefin sandwich** structures are a laminar composite. They are composed of two or more layers of polyolefin with a different material in between the layer (long fiber mat or short fiber). Sandwich panel and laminar composites are common methods for thermoset resins and thermoplastic composites. This simple method can be applied to natural fiber-reinforced thermoplastic composites using the hot press method. The addition of a reinforcement material between polyolefin layers does not require extrusion or injection molding and minimizes fiber degradation [35, 36].

6.3 Applications

Recent research in the field of polyolefins has focused on polyolefin synthesis. Polyolefins have been designed in different forms such as homopolymers, copolymers, and terpolymers. Careful control of the chain has resulted in a universal polymer. POCs, a subset of polymer composites, have evolved to meet

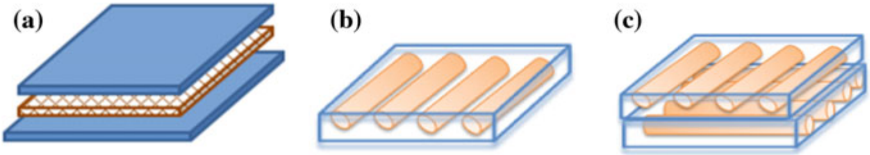


Fig. 6.5 **a** Layers of a sandwich composite. **b** Long fiber composite and **c** Laminar fiber composite

current application requirements. The advantages over other POCs include lower density, low cost, straightforward processing, and an overall suitable combination of chemical, physical, and mechanical properties. The research and application of POCs have significantly increased because of new emerging opportunities in the fields of agriculture, medicine, construction, and transportation. The following sections briefly describe the application of POCs and nanocomposites in different sectors.

6.3.1 Consumers

POCs and nanocomposites have many applications in our daily life including different consumer products such as park benches and tables, home furniture, musical instruments, playground equipment, cooking ware, bathroom materials, trash bins, landscape timbers, railroad ties, toys, and home appliances. Natural fillers such as wood POCs and synthetic fillers such as glass fiber POCs are the two most common composites of the current plastic industry [14, 15]. These polyolefin and filler composites possess many advantages such as:

- They are a convenient way to protect a wooden product or furniture used in a high-moisture environment from rot and swelling deformation.
- They are resistant to termites.
- They come in many colors including a natural wood texture.
- They are easily molded to any shape and size.
- They are environmentally friendly, pollution free, and recyclable.
- They are an effective flame retardant, fireproof, and self-quenching and produce no toxic gases.
- They possess excellent workability. They can be set, sawed, and drilled, and the surface can be painted.
- They are simple to install, and their convenient construction technology saves on installation time and cost.
- They resist cracking, swelling, and deformation and require no repair and maintenance. They are easy to clean.

Wood polyolefin composites (WPCs) are polymer mixed with wood fiber. WPCs exhibit the advantages of wood with the cost of plastic. They can be obtained by extrusion or compression molding using wood flour and polymer. The development of wood polymer composites reduces natural wood use by recycling old wood powder and plastic and protects our limited forest resources. Wood fiber and plant fiber sources are abundant, inexpensive, and lightweight, have good dimensional stability and electrical insulation, are non-toxic, can be repeatedly processed, and are biodegradable. WPC outdoor gazebos are increasingly popular because of these advantages. WPCs are prepared using a fine wood powder (such as fillers based on cellulose fiber), hardwood, softwood, plywood, peanut hulls, bamboo, rice straw, or date palm mixed with various polymers (PP, PE, PVC) [37]. The obtained mixture

Fig. 6.6 Table of wood–polyethylene composites

is extruded or injection molded into a dough-like consistency and then extruded or molded to the desired shape and size. Additional additives include colorants, coupling agents, stabilizers, blowing agents, reinforcing materials, foaming agents, and lubricants to help tailoring the polymer for a specific application. Figure 6.6 lists typical wood–polyethylene composites.

Another example of POCs includes polypropylene biofiller composite. The properties of these composites are comparable to that of mineral filled and glass fiber-reinforced PP composites. Lignocelluloses are biofibers from jute fiber, flax fiber, or sisal fiber and reinforce the polymer. POCs can be obtained using a reactive extrusion method. Activated coupling agents are used to obtain good interfacial adhesion between polymer and biofiber. Coupling agents such as MagPP can modify the PP matrix and create adhesion to the silane-modified surface of the lignocellulose component. Mechanical tests of strength and toughness resulted in increased impact and tensile strengths. These biofiber-based polymer composites have been used in a wide range of applications including furniture (chair backs or seats), luggage, and musical instruments [38] (Fig. 6.7).

Thermoforming sheets from polyolefin glass fiber (POGF)-reinforced composites are another common application of composites. There are two types of glass fibers: long glass fibers (LGFs) and short glass fibers (SGFs). LGF is ideal for the production of thermoformed parts because the shear forces in the reinforced parts are transmitted through the polymer to the reinforcing fibers. LGFs are lighter and stiffer than other formable materials. These synergetic properties of LGF/PP composites make them suitable for fan blade applications (low volume and high stiffness is required) [39, 40]. Hemp fiber, as a reinforcement filler, is used in an increasing number of polymer composites. This composite (e.g., hemp fiber with polypropylene) can be compression molded to form nonwoven (felt) mat that forms a three-dimensional part used in automotive interior substrates, furniture, door panels, window pillars, package trays, trunk liners, and other consumer products [41].

Fig. 6.7 Images of indoor furniture composed of POCs **a** office chair, **b** cupboard, and **c** office partitions

6.3.2 Medical

The use of glass and metals in medical applications both in vitro and in vivo has declined recently, whereas the use of polymers drastically increased. This phenomenon is because of the versatility of polymer properties. The potential to customize polymers according to the desired application by choosing the best filler materials has created lucrative opportunities. The growth in the polymer composite industry has been driven by the increasing use of polymers in medical devices. These polymers may be pure polyolefin (PP, PE, and PVC) and composites. The need for portable and impact-resistant devices has led an increase in the utility of polymer composite materials. Research in this field revealed that POCs have the ability to overcome all healthcare material requirements. This polymer is versatile and can be formed into foams, films, gels, and bulk materials. POCs are the most favorable material in medical applications and possess a wide range of advantages over conventional materials such as:

- POCs have enhanced chemical and impact resistance, and superior mechanical and thermal properties.
- POCs can be customized to have properties such as exceptional durability, flexibility, and strength. They can be lightweight and portable.
- POCs are resistant to hydrolysis and body fluids because they are biocompatible. They have excellent mechanical properties (high tensile strength, highly elastomeric) and a low degree of degradation.

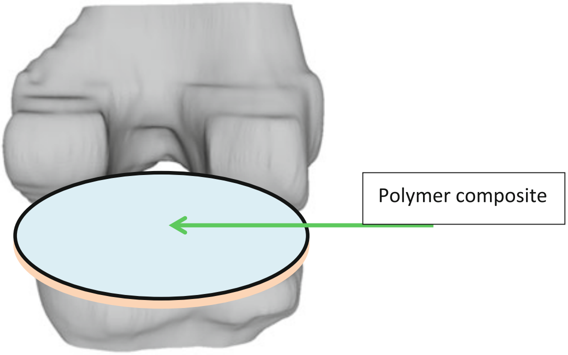


Fig. 6.8 Schematic diagram of bone orthopedic implantation

The initial increase in the research and advancement of polymer composite materials for medical applications started in the field of orthopedic implantation. Metal alloys were conventionally used in implants/prostheses such as bone fracture fixation plates, bone replacement substitute, and total hip and knee replacement (Fig. 6.8). The metal alloys used for bone plates are approximately 15 times stiffer compared to bone. This mismatch leads to stress-shielding effects because of the implanted metal alloy. Stress-shielding affects bone remodeling and healing processes and causes an increase in bone porosity [42–83]. This issue can be resolved using implant materials with a stiffness that matches the host tissue [45]. Polymer materials often exhibit low stiffness and low strength, which limits their potential use. Similarly, low fracture toughness and load strength restrict the use of ceramic materials in orthopedic applications. Because the constituent (polymer composite) exhibits low stiffness and high strength simultaneously, they are suggested for many orthopedic applications. Polymer composite materials have the additional advantage of tailoring their properties by varying the volume fraction and the arrangement of the filler materials within the polymer matrix. These modifications can match the mechanical and anatomical features of the host tissue. Adverse tissue reactions caused by metal ions ultimately loosen the implant and cause discomfort for the patient. This reaction is not observed for polymer composite materials. Metal alloys and ceramics are radio opaque and cause unwanted noises in X-ray radiography. Polymer composite materials are transparent to radio signals and can be tuned by the addition of a contrast medium to the polymer. Polymer composites are compatible with the diagnostic methods employed in orthopedic treatment such as computed tomography (CT) and magnetic resonance imaging (MRI).

Bonfield et al. [45] reported the synthesis and application of natural and synthetic hydroxyapatite powder (HA)–polyethylene composites (HA–PE) (containing a volume fraction of HA ranging from 0.10 to 0.60) by a mixing technique. The variation of Young's modulus is linearly proportional to the volume fraction. At the 0.6 volume fraction level, HA/PE has the highest Young's modulus more than that of transversely orientated bone [45, 46]. High-density polyethylene composite reinforced by bioglass (SiO_2, Na_2O, CaO, and P_2O_5) is being investigated as a new material for bonding soft tissue. This composite quickly forms a strong bond between the implant and the tissue. Composite containing 30 vol.% of bioglass shows the best level of elastic compliance, tensile strength, and fracture strain compared to soft connective tissue [47]. Polyethylene composite with apatite–wollastonite glass ceramic (AWGC) has excellent mechanical properties and high bioactivity [46] and is used as a tissue bonding material. Young's modulus and microhardness of the composite increases with increasing AWGC volume fraction while decreasing tensile strength and fracture strain. This composite system has applications in vitro [47].

Another type of POCs in medical applications is PP glass fiber (GF)-reinforced sheet. The composite's strength is a function of the adhesion of the polymer to the surface fibers through shear strength. This composite is found in safety shoe toe caps prepared by injection molding (GF/PP). Other applications of this lightweight, high volume, and stiff thermoforming composite are custom-fit orthotic supports (i.e., arch supports) and external orthopedic supports [i.e., knee braces (Fig. 6.8)] [48]. Ahmad et al. [49] researched ultrahigh molecular weight and high-density polyethylene (UHMWPE/HDPE) blends prepared using polyethylene glycol (PEG) as the processing aid and hydroxyapatite (HA) as the reinforcing filler. These composites were highly processable using a conventional melt processing method. The composite is used in orthopedics as a bearing liner because of its low friction and high wear resistance.

6.3.3 Agriculture

To meet the growing demand of food security, researchers are trying to find possible solutions. Plastic technology has applications in the agricultural field such as plastic films for greenhouses, walk-in tunnels, low tunnel covers, and mulching; nets for protection and for harvesting and post-harvesting practices, shade nets, windshield nets, crop covers, plant nets, root ball nets, harvesting nets, anti-hail nets, turf protection nets; and pipes for the transport of water [50]. Polymer chemistry in agriculture may help obtain a maximum yield from a small amount of land by reducing the water needs without hampering the environment and natural resources [6]. The advantages of using POCs in agricultural field applications are as follows:

- An increase in yield while reducing water and fertilizer needs.
- A reduce in the labor costs through simple maintenance and control.
- Less disease, resulting in a reduction in disease control and insecticide costs.
- Improved cultivation of problematic topography, problematic soil, and diverse climatic conditions.
- Reduced crop damage because of wind, hail, birds, and insects.
- Customization of the quality and quantity of light can be achieved by changing the netting densities resulting in enhanced photosynthesis.

- Increased productivity, by moderating extreme climatic conditions (temperature, sun burn, and frost damage).
- Improved stability, because these materials have ultraviolet stabilizing properties that prevent decay because of sunlight, reduce moisture absorption, ensure consistent color, and prevent curling.

Glass fiber-reinforced polymer (GRP) pipe is used for the transport of water and wastewater in pressure and non-pressure systems. This composite is composed of glass fiber and PP, PE, or PVC resins. These pipes are lightweight, corrosion resistant, and straightforward to install and have a long and effective service life and low maintenance costs. These features make GFR POCs, a strong candidate for piping applications in environments with acidic soil [51].

Textile fabric has a long history of application in agriculture. Textiles such as knits, wovens, nonwovens, extruded sheets, molded products, ropes, and belts are used for many agricultural applications. The agrotextile sector is composed of all textiles that are used in the growing, harvesting, protection, and storage of either crops or animals. Agrotextiles help to maintain sufficient soil humidity and increase the soil temperature. Polyethylene and polypropylene are types of polyolefin used in agricultural applications. Polyolefin is extensively used in agricultural applications. Jute and wool are also used because they degrade and act as a natural fertilizer. The advantages of man-made fibers over natural fibers include their favorable price/performance ratio, ease of transport and setup, space saving storage, and long service life.

The US patent discloses a partially degradable type of polyolefin composite with netting composed of metal carboxylate, an aliphatic polyhydroxy-carboxyl acid and polyethylene. This degradable extruded netting material has sufficient flexibility and withstands cold stretching when bent or folded [52]. Another type of polyolefin-based film for greenhouse applications can be prepared using two types of organo-modified clays: cloisite 15A and cloisite 20A. Filler enhances the rigidity and tear strength of the films, and the effect of harmful radiation is reduced, maintaining transparencies in the visible range. The greenhouse effect increases because of the presence of clay material, and it restricts the thermal emission from the soil to outside the greenhouse at night. The presence of clay did not affect the wettability of the soil [50].

6.3.4 Packaging

The packaging industry extensively uses both pure polyolefin and its composites. Applications include packaging, food and easy peel packaging, electronics packaging (pre-mold plastic packaging for electronic devices), shrink film, tubing, blister packs, sales packaging, transport packaging, consumer packaging, and industrial packaging. High-performing packaging materials must be rigid, retain flavor and aroma, and be heat sealable, etc. [53–60]. Polymer composite materials have several advantages over conventional packaging materials (pure polymers, glass, metals, and ceramics) including the following:

- They have high specific strength, are lightweight, resistant to water and waterborne microorganisms, and are durable.
- They are biodegradable, recyclable, and easy to dispose of.
- As a packing material, they are flexible, protecting the product inside the package.
- Polymer packaging material is easy to seal, allowing the contents to remain fresh for longer times and during transportation.
- They are compatible with food stuff and prevent dust, contaminants, and insects from getting inside the package.
- They are easily molded into different shapes and sizes. The item is therefore easy to identify from the package.
- They can be formulated in different shapes to attract the consumer.

Adding composite materials to the polymer enhances the processing, performance, and appearance and results in stronger packaging materials [53]. Films molded containers and cushioning are various forms of polymeric materials used in the packaging industry [54]. Low-cost filler materials can replace the volume of more expensive materials and reduce the cost. Filler materials used in the packaging industry include wood, silica, glass, clay, glass fiber, and natural fibers. These fillers improve processing, abrasion resistance, density control, dimensional thermal stability, and optical effects [55].

Majeed et al. [56] reviewed natural fiber-/nanoclay-reinforced polymeric materials and their application in food packaging. The biodegradable hybrid material obtained by mixing natural fibers with nanoclay particles exhibits improved barrier properties. This combination demonstrates excellent dispersion, compatibility with the matrix, and mechanical strength at low costs and is suitable for use with vapor-sensitive materials (electronic goods and pharmaceutical packaging) [56].

Calcium carbonates ($CaCO_3$), with a density of 2.7 g/cm^3, are commonly used filler materials for packing applications [57, 58]. $CaCO_3$ filler improves flex modulus, impact strength, stiffness, tear strength, gas and water barrier properties, and printability. PE/carbonates are commonly used in the food packaging industry.

6.3.5 Transportation

Polymers are common materials on land, sea, air, and space. Almost all cars, buses, light trucks, trailers, motorcycles, trains, boats, airplanes, and space shuttles contain plastics. POCs are found in the bumpers, fenders, doors, headlights, and wheel covers of automobiles, and their incorporation has reduced vehicle weight by approximately 250 pounds. The weight reduction also reduces fuel consumption and lowers the carbon dioxide (CO_2) emissions. The advantages of using POCs over conventional materials in transport industry are the following:

Table 6.3 Different car parts and POC compositions [61]

	Car parts	Composition
1	Car bumper	Talc/rubber/PP
2	Inside part—engine	Glass fiber/PP
3	Doors	Nanoclay/PP or LWGF/PP

- They are durable and resist corrosion, tough, easily colored, resilient, and lightweight.
- Their reduced weight leads to fuel savings and reduced in CO_2 emissions.
- They demonstrate design flexibility and high performance at low cost.

Several researchers seek to design materials with high performance, greater efficiency, low costs, and lower overall automotive weight, resulting in reduced fuel consumption and CO_2 emissions. Most car parts are composed of plastic composite materials. Chevrolet Impalas contain doors with thermoplastic polyolefin nanocomposite. General Motors and Basell published the application of clay/polyolefin nanocomposites as a step assistant component for GMC Safari and Chevrolet Astro vans in 2001 [61–63].

Polyolefin nanocomposites are a large, fast-growing market with many innovations in diverse applications. PP is the most common thermoplastic material used in automotive parts. By adding SGF to PP [32], the threshold of heat resistance increases to the melting point of PP. This type of PP can be used in automotive parts exposed to severe heat (engine compartment) [64].

Table 6.3 summarizes different cars parts and their POC composition. The bumper back beam is the structure that absorbs collision energy [65, 66].

Fifty percent of a Boeing 777 airplane is composed of polymer composites (mainly thermoset composites) because they must be lightweight and strong. The interior part is composed of POCs. Carbon fiber and fiber glass filler are used as a reinforcement material to increase the rigidity and impact resistance of the composite. The most common types of glass fiber used for reinforcement are E-glass and S-glass fiber. E-glass fiber has the lowest cost of all commercially available reinforcing GFs. Their affordability is the reason for their widespread use in the fiber-reinforced plastic industry. S-glass, originally developed for aircraft components and missile casings, has the highest tensile strength among all fibers in use. However, the compositional difference and higher manufacturing cost make it more expensive than E-glass [67, 68].

6.3.6 Electrical

Most of polymers are poor electrical conductors because of the absence of free electrons. Recently, polymeric composite materials have been synthesized as conductor materials by adding metallic fillers. The number of electrical and electronic industry applications of POCS is increasing. POCs are inherently insulators. The properties of the filler (type, size, shape, and orientation within a matrix such as carbon fiber, graphene, or metallic fillers) determine the conductivity of the composite. The resulting composites can have applications in metal dominated areas, such as electrode materials, electromagnetic interference (EMI) shielding, protection from static electricity, and resistors for microelectronics. The electromagnetic properties of materials are important because of their commercial, military, communication, and environmental protection applications [69–72]. The metal-based screening materials previously used in EMI shielding can be replaced by POCs.

The advantages of using these materials include the following:

- Lightweight, resistant to corrosion, and can be adapted to the needs of a specific application.
- Flexibility of the material.
- Easily molded into the desired shape and size.
- Recyclable.

Electrical and electronic appliances composed from POCs are shown in Fig. 6.9. Composite electrodes are an important application of conducting POCs. Electrode materials must be conductive, have mechanical integrity, low permeability, and electrochemical activity, and be stable in the electrolytic environment. Material selection plays an important role in the fabrication process. High-density polyethylene (HDPE)/ethylene propylene diene monomer (EPDM) with a blend ratio (70/30) filled with carbon black is the standard material [73]. This combination has a low percolation threshold and volume resistivity compared to carbon black filled HDPE and EPDM because of a double percolation effect. Carbon black was added to enhance the conductivity and mechanical properties [73]. EMI shielding is another important application. Los et al. [74] demonstrated a novel metamaterial that is composed of polyolefin (LDPE, LLDPE and PP) and micrometer and/or nanometer-size copper flakes as conducting inclusions, by using reverse pulse electrolysis methods [74]. Graphene in polyolefin matrix (normally a poor electrical conductor) for EMI shielding is another composite filler commonly used in the electronic industry. Anti-static agents can be used to attract moisture and reduce static charge. Graphene is an excellent fast conductor (compared to silicon chips) and fine-scale material that may revolutionize electronics [75, 76].

Fig. 6.9 Different types of electrical appliances

6.3.7 Construction

The building and construction industry commonly uses polyolefin microcomposite and nanocomposite as reinforcement materials to enhance the physical properties (tensile strength, modulus, and damping) of POCs. There are many current and future applications of POCs in construction including walling, roofing, outdoor furniture, and timber. These composites can be molded into sheets, frames, pellets, structural shapes, and others [77].

The following are the advantages of using POCS in the construction industry over conventional materials:

- They are durable, lightweight, corrosion resistant, strong, and require little maintenance.
- They are resistant to fire and ultraviolet (UV) rays.
- They offer moisture protection.
- They come in a variety of colors and shapes.

Natural fiber-reinforced polyolefins are commonly applied to automotive and construction applications. The most abundantly used additive is fire retardant. Flammability is an important factor that often limits the application of composites to a specified field. Magnesium hydroxide is the most common flame retardant material used in the construction industry. This filler responds well to surface modifiers and decomposes by an endothermic reaction that releases water at temperatures close to the polymer degradation temperature as show in Eq. 6.1. Rothon et al. [78] studied the effects of magnesium hydroxide on polypropylene as a flame retarder of 60 % by weight. The study found less heat emission at 100 kWm^2 after 6 min of fire exposure compared to filled PP without $Mg(OH)_2$ at 500 kWm^2.

$$Mg(OH)_2 \rightarrow MgO + H_2O \; (\sim 380\,^{\circ}C) \qquad (6.1)$$

Figure 6.10 depicts the morphology of POCs reinforced with date palm fiber (DPF) and $Mg(OH)_2$ added as flame retardant. The SEM micrograph shows the structure of (a) pure MgOH flame retardant as filler, (b) natural fiber as a reinforcement material in PO matrix, and (c) distribution of MgOH in PO matrix. Figure 6.11 shows the use of POCs with fire retardant filler.

POCs as insulation in the construction industry are described below.

Thermal insulation is used to ensure a pleasant indoor hygienic climate at low ambient temperatures. Thermal insulation is essential to protect construction elements from thermal impact and damage from moisture. Thermal insulation is necessary for energy conservation during summer. Examples include WPC with natural fiber or a phase change material (PCM), which has capability of storing and releasing large amounts of energy. PCM can be specified by the latent heat capacity. Several researchers examined paraffin wax as a PCM filler in polyolefin matrix, resulting in an excellent thermal insulation material [79–81].

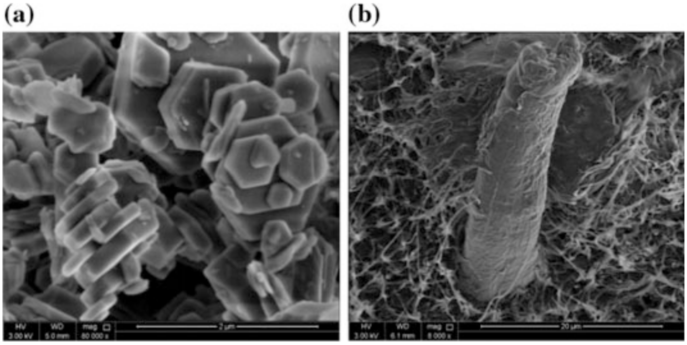


Fig. 6.10 Shows **a** microsize $Mg(OH)_2$ flakes **b** date palm fiber-reinforced PO matrix filled with $Mg(OH)_2$

Fig. 6.11 Cable from LDPE filled with $Al_2(OH)_3$

6.3.8 Textiles

The versatile nature of POCs lends itself to textile and fiber applications. The property modifications of POCs (combining the virgin polymer with the right filler material) meet end-user requirements. POC textile is used in sportswear. These flexible, high-tech fibers have a long life and are colorfast, resistant to different chemicals, inexpensive, and safe for the environment. The advantages of POCs in the textile industry are as follows:

- They are naturally hydrophobic and do not decompose in a wet environment.
- They evacuate moisture by transferring it to the outside promoting evaporation.
- Their chemical resistance makes them resistant to soiling.
- POCs are well tolerated, and from a health and safety point of view, they are harmless.

PP is the most used polymer in the polyolefin family for textile applications. Fabric and fibers composed of POCs keep carpets clean and dry. They maintain germfree environments and can soak up industrial spills. POC-based textiles and fabrics are used in flexible intermediate bulk containers (FIBCs) for transporting industrial and construction materials in bulk [82]. PP-based polyetheresteramide composites are taped into fine fabric and can be sewed into large bags. These bags are used to transport bulk materials. Sacks of PP and jute composites formed by compression molding are used for the transportation of chemicals, fertilizers, and dyestuffs [83]. Fabrics, containing PP and jute composites, are sewed into sacks. POCs are used in carpets and carpet backing. Woven or tufted multifilament yarns or spun yarns are used, or obtained from staple fibers by a needle punching technique. The heat setting technique is used to further improve its characteristics [84]. These carpets are stain resistant, resilient, inexpensive, and colored during the preparation, reducing costs and sensitive dyeing techniques. POCs used in carpet backing provide stability, comfort, and cushioning [85]. POCs can also be used in ropes, twines, and nets, composed of multifilament, monofilament, or tape forms of composite (Fig. 6.11). PP and PE are used for the above-mentioned applications because they are strong and resistant to chemicals and water. They are useful as twine for agricultural baler and fishing and packaging nets because they can float on water [85]. Artificial sport surfaces and artificial grass also use POCs [86]. Yarns composed of both PE and PP with colorant, UV-resistant, and other composite fillers (glass fiber and carbon fiber) are used to obtain multifilament or fibrillated tape. These polymer yarns are used to manufacture a playing surface that is soft and flexible [87]. POCs are used in geotextiles and agrotextile fabric. Geotextile includes textile used during construction and civil engineering projects. They are used to stabilize soil, to separate different materials layers, and to assist drainage. The demand for agrotextiles in agriculture is increasing. These materials are used in greenhouses, walk-in tunnels, low tunnel covers, mulching, nets for protection and for harvesting and post-harvesting, shade nets, windshield nets, crop covers, plant nets, root ball nets, harvesting nets, anti-hail nets, and turf protection nets [51]. PP- and PE-based composite textiles have hygiene and medical applications.

Some examples include disposable diapers and wipes and disposable garments. POCs provide resistance to unhygienic staining and can hold liquids without absorbing them. Bioactive additives such as ammonium biocide, antimicrobial N-halamine alkyl carboxylate, alkyl sulfate, alkyl sulfonate, alkyl phosphate, or alkyl phosphite can further improve hygienic properties [88, 89].

6.4 Conclusions

This book chapter evaluates the definition, classification, and scope of POCs in different applications. POCs represent one of the most widely used polymeric materials. Synergistic reactions between the polymer matrix and filler materials (particulate, fiber, and structural fillers) result in modified properties. This book chapter contributes a brief introduction followed by a definition of processing and an extensive illustration of the different applications of POCs in a variety of fields (consumer, medical, agricultural, packaging, transportation, electrical, construction, and textile). POCs with natural wood fiber are widely used in consumer applications. They result in wood-like texture and properties with the cost of plastic.

Properties such as biocompatibility, high resistance against hydrolysis and body fluids, excellent mechanical properties (high tensile strength, highly elastomeric), and a low degree of degradation make POCs ideal for the medical field. Polymer chemistry in agriculture promotes maximum yield from a small amount of land by reducing water requirements without harming the environment and natural resources. POCs are finding increasing applications in packaging, because of their high specific strength, low weight, durability, and resistant to water, dust, and waterborne microorganisms. POCs are used in various parts of automobiles such as bumpers, fenders, doors, headlights, and wheel covers. They reduce vehicle weight, fuel consumption, and carbon dioxide (CO_2) emissions. POCs are used for EMI shielding because they are light, resistant to corrosion, flexible, and recyclable. Durability, lightweight, corrosion resistance, high strength, and low maintenance are important features of POCs that make them ideal in the construction industry. POCs are naturally hydrophobic and are therefore useful in the textile industry for footwear and carpets. The type and quantity of filler can be customized for requirements such as low cost, biodegradability, rigidity, flame, and UV retardant properties, and weight. Future research will explore new applications of POCs in all aspects of human civilization.

References

1. M. Robert, R. Roy, B. Benmokrane, Environmental effects on glass fiber reinforced polypropylene thermoplastic composite laminate for structural applications. Polym. Compos. **31**, 604–611 (2010)
2. E.P. Gellert, D.M. Turley, Seawater immersion ageing of glass—fiber reinforced polymer laminates for marine applications. Compos. Part A—Appl. Sci. **30**, 1259–1265 (1999)
3. A.M. Hugo, L. Scelsi, A. Hodzic, F. Jones, R.R. Dwyer-Joyce, Development of recycled polymer composites for structural applications. Plast. Rubber Compos. **40**, 317–323 (2011)
4. J.B.P. Soares, T.F.L. McKenna, *Polyolefin Reaction Engineering*, 1st edn. (Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, 2012)
5. G. Saman, N.S. Kazemi, M. Behbood, T. Mehdi, Impact strength improvement of wood flour–recycled polypropylene composites. J. Appl. Polym. Sci. **124**, 1074–1080 (2012)
6. R. Karnani, M. Krishnan, R. Narayan, Biofiber-reinforced polypropylene composites. Polym. Eng. Sci. **37**, 476–483 (1997)
7. M. Noroozi, S.M. Zebarjad, Effects of multiwall carbon nanotubes on the thermal and mechanical properties of medium density polyethylene matrix nano composites produced by a mechanical milling method. J. Vinyl Add. Tech. **16**, 147–152 (2010)
8. W. Hufenbach, R. Bohm, M. Thieme, A. Winkler, E. Mäder, J. Rausch, Polypropylene/glass fiber 3D-textile reinforced composites for automotive applications. Mater. Des. **32**, 1468–1476 (2011)
9. M. Garcia, J. Hidalgo, I. Garmendia, J. Garcia-Jaca, Wood–plastics composites with better fire retardancy and durability performance. Compos. Part A—Appl. Sci. **40**, 1772–1776 (2009)
10. P. Panupakorn, E. Chaichana, P. Praserthdam, B. Jongsomjit, *Polyethylene/Clay Nanocomposites Produced* by In Situ Polymerization with Zirconocene/MAO Catalyst. Journal of Nanomaterial (2013) 9
11. G. Galgal, C. Ramesh, A. Lele, *A Rheological Study On The Kinetics Of Hybrid Formation In Polypropylene Nanocomposites*. Macromolecules, (ACS Publications, US, 2001)

12. N. Taranu, G. Oprisan, M. Budescu, A. Secu, I. Gosav, The use of glass fiber reinforced polymer composites as reinforcement for tubular concrete poles, in *Proceedings of the 11th WSEAS International Conference on Sustainability in Science Engineering*, ISBN: 978-960-474-080-2, ISSN: 1790-2769
13. K. Majeed, M. Jawaid, A. Hassan, A. Abu Bakar, H.P.S. Abdul Khalil, A.A. Salema, I. Inuwa, Potential materials for food packaging from nanoclay/natural fibers filled hybrid composites. *Mater. Des.* **46,** 391–410 (2013)
14. E.R. Degginger, M.P. Dellavecchia, A.H. Steinberg, *US 4098943 A Glass Fibers, Mineral Filler*. (Allied Chemical Corporation, Morristown)
15. J.R. Guedes, L.M. Rodrigues, D.R. Mulinari, *Mechanical Properties of Natural Fibers Reinforced Polymer Composites: Palm/Low Density Polyethylene XIV SLAP/XII CIP 2014*. (Porto de Galinhas, Brazil—1, 2014)
16. M. Asadzadeh, M.R. Khalili, R. EslamiFarsani, S. Rafizadeh, Bending properties of date palm fiber and jute fiber reinforced polymeric composite. Int. J. Adv. Des. Manuf. Technol. **5**, 59–63 (2012)
17. M. Biron, *Thermoplastics and thermoplastic composites: technical information for plastic user* (Butterworth-Heinemann publisher, Elsevier, Amsterdam, 2007)
18. Y. Xu, W. Gong, Polyisobutylene-based modifiers for glass fiber reinforced unsaturated polyesters composites. Iran. Polym. J. **21**, 91–97 (2012)
19. P. Annadurai, A.K. Mallick, D.K. Tripathy, Studies on microwave shielding materials based on ferrite- and carbon black-filled EPDM rubber in the X-band frequency. J. Appl. Polym. Sci. **83**, 145–150 (2002)
20. C.H. Hong, Y.B. Lee, J.W. Bae, J.Y. Jho, B.U. Nam, D.-H. Chang, S.-H. Yoon, K.-J. Lee, Tensile properties and stress whitening of polypropylene/polyolefin elastomer/magnesium hydroxide flame retardant composites for cable insulating application. J. Appl. Polym. Sci. **97**, 2311–2318 (2005)
21. A.B. Afzal, M.J. Akhtar, M. Nadeem, M.M. Hassan, Dielectric and impedance studies of DBSA doped polyaniline/PVC composites. Curr. Appl. Phys. **10**, 601–606 (2010)
22. K.A. Afrifah, R.A. Hickok, L.M. Matuana, Polybutene as a matrix for wood plastic composite. Compos. Sci. Technol. **70**, 167–172 (2010)
23. A. Ashori, Wood–plastic composites as promising green-composites for automotive industries. Bioresour. Technol. **99**, 4661–4667 (2008)
24. J. Li, P. Xue, W. Ding, J. Han, G. Sun, Micro-encapsulated paraffin/high-density polyethylene/wood flour composite as form-stable phase change material for thermal energy storage. Sol. Energy Mater. Sol. Cells **93**, 1761–1767 (2009)
25. M. Zampaloni, F. Pourboghrat, S.A. Yankovich, B.N. Rodgers, J. Moore, L.T. Drzal, A.K. Mohanty, M. Misra, Kenaf natural fiber reinforced polypropylene composites: a discussion on manufacturing problems and solutions. Compos. A Appl. Sci. Manuf. **38**, 1569–1580 (2007)
26. M. Wang, R. Joseph, W. Bonfield, Hydroxyapatite-polyethylene composites for bone substitution: effects of ceramic particle size and morphology. Biomaterials **19**, 2357–2366 (1998)
27. A. Bledzki, J. Gassan, Composites reinforced with cellulose based fibers. Prog. Polym. Sci. **24**, 221–274 (1999)
28. D. William, Callister (ed.), Material science and engineering: an introduction chapter 17, 522
29. S. Ahmed, F.R. Jones, A review of particulate reinforcement theories for polymer composites. J. Mater. Sci. **25**, 4933–4942 (1990)
30. H. Nitz, P. Reichert, H. Römling, R. Mülhaupt, Influence of compatibilizers on the surface hardness, water uptake and the mechanical properties of poly (propylene) wood flour composites prepared by reactive extrusion. Macromol. Mater. Eng. **276**, 51–58 (2000)
31. C.H. Hsueh, Effects of aspect ratios of ellipsoidal inclusions on elastic stress transfer of ceramic composites. J. Am. Ceram. Soc. **72**, 344–347 (1989)
32. B. Nam, S. Ko, S. Kim, D. Lee, *Weight Reduction Of Automobile Using Advanced Polypropylene Composites*. (Honam Petrochemical Corp. Daedeok Research. Inst., Daejeon, Korea)

33. D. Eiras, L.A. Pessan, Mechanical properties of polypropylene/calcium carbonate nanocomposites. Mater. Res. **12**, 517–522 (2009)
34. J. Holbery, D. Houston, *Natural-Fiber-Reinforced Polymer Composites In Automotive Applications*, vol. 58. (Springer, Berlin, 2006), pp. 80–86
35. K. Jayaraman, Manufacturing sisal-polypropylene composites with minimum fibre degradation. Compos. Sci. Technol. **63**, 367–374 (2003)
36. D. William, *Material Science and Engineering an Introduction*, 5th edn. Chapter 17, p. 523
37. R. Kumar, J.S. Dhaliwal, G.S. Kapur, Mechanical properties of modified biofiller polypropylene composites. Polym. Compos. **35**, 708–714 (2013)
38. http://info.smithersrapra.com/downloads/chapters/Engineering%20Plastics.pdf
39. C.S. Own, D. Seader, N.A. D'Souza, W. Brostow, Cowoven polypropylene/glass composites with polypropylene + polymer liquid crystal interlayers: dynamic mechanical and thermal analysis. Polym. Compos. **19**(2), 107–115 (1998)
40. M. Dewidar, M. Bakrey, A.M. Hashim, A. Abdel-Haleem, Kh Diab, Mechanical properties of polypropylene reinforced hemp fiber composite. Mater. Phys. Mech. **15**, 119–125 (2012)
41. M. Wang, L.L. Hench, W. Bonfield, Bioglass/high density polyethylene composite for soft tissue applications: preparation and evaluation. J. Biomed. Mater. Res. **42**, 577–586 (1998)
42. W. Bonfield, Composites for bone replacement. J. Biomed. Eng. **10**, 522–526 (1988)
43. W. Bonfield, M.D. Grynpas, A.E. Tully, Hydroxyapatite reinforced polyethylene—a mechanically compatible implant material for bone replacement. Biomaterials **2**, 185–186 (1981)
44. J. Huang, M. Wang, I. Rehman, J.C. Knowles, W. Bonfield, Analysis of surface structure on bioglass/polyethylene composites in-vitro. Bioceramics **8**, 389–395 (1995)
45. T. Kokubo, Bioactivity of glasses and glass–ceramics, ed. by P. Ducheyne, T. Kokubo, C.A. Van Blitterswijk, in *Bone-Bonding Biomaterials*, (Reed Healthcare Communications, Leiderdorp, 1992)
46. J.A. Juhasz, M. Kawashita, N. Miyata, T. Kokubo, T. Nakamura, S.M. Best, W. Bonfield, *Apatite-forming ability and mechanical properties of glass–ceramic A-W-polyethylene composites*, Bioceramics **14**, 437–440 (2001)
47. D.M. Bigg, *Manufacturing methods for long fiber reinforced polypropylene sheets and laminates*, ed. by J. Karger-Kocsis, in *Polypropylene: Structure, Blends and Composites.* vol. 3 (Chapman & Hall, London, 1995), pp. 263–292
48. R. Scaffaro, L. Botta, F.P.L. Mantia, Preparation and characterization of polyolefin—based nanocomposite blown films for agricultural applications. Macromol. Mater. Eng. **294**, 445–454 (2009)
49. M. Ahmad, M.U. Wahit, M.R.A. Kadir, K.Z.M. Dahlan, Mechanical, rheological, and bioactivity properties of ultra high-molecular-weight polyethylene bioactive composites containing polyethylene glycol and hydroxyapatite. *Sci. World J.* **13**, 474851 (2012)
50. M. Etcheverry, S.E. Barbosa, Glass fiber reinforced polypropylene mechanical properties enhancement by Adhesion improvement. Materials **5**, 1084–1113 (2012)
51. J.G. Gho, R.A. Garcia. US5854304-A, Epi Environmental Prod Inc (EPIE-Non-Standard)
52. J. Murphy, *Additives for Plastics*, 2nd end. (Elsevier Science Inc, New York, 2001)
53. W. Soroka, *Fundamentals of Packaging Technology*, 3rd. end, (Institute of Packaging Professionals, Naperville, IL, 2002)
54. W. Callister, *Materials Science and Engineering*, 7th edn. (Wiley, New York, 2007)
55. K. Majeed, M. Jawaid, A. Hassan, A. Abu Bakar, H.P.S. Abdul Khalil, A.A. Salema, I. Inuwa, Potential materials for food packaging from nanoclay/natural fibers filled hybrid composites. Mater. Des. **46**, 391–410 (2013)
56. Hyun Kim, Jagannath Biswas, Soonja Choe, Effects of stearic acid coating on zeolite in LDPE. LLDPE, HDPE Compos. Polym. **47**, 3981–3992 (2006)
57. P. Jakubowska, T. Sterzynski, Thermal diffusivity of polyolefin composites highly filled with calcium carbonate. Polymer **57**, 271–275 (2012)
58. H. Qin, C. Zhao, S. Zhang, G. Chen, M. Yanga, Photo-oxidative degradation of polyethylene/montmorillonite nanocomposite. Polym. Degrad. Stab. **81**, 497–500 (2003)

59. H. Cox, et al. *Nanocomposite Systems for Automotive Applications*, in Presented at 4th World Congress in Nanocomposites, EMC, San Francisco, 1–3 September 2004
60. F. Patterson, *Nanocomposites—Our Revolutionary Breakthrough*. in Presented at 4th World Congress in Nanocomposites, EMC, San Francisco, 1–3 September 2004. Through the Courtesy of M. Verbrugge, General Motors
61. S. Moritomi, W. Tsuyoshi, K. Susumu, *Polypropylene Compounds for Automotive Applications* (Sumitomo Chemical Co. Ltd, Tokyo, 2010)
62. M.M. Davoodi, S.M. Sapuan, A. Aidy, N.A. Abu Osman, A.A. Oshkour, W.A.B. Wan Abas, Development process of new bumper beam for passenger car: a review. Mater. Des. **40**, 304–313 (2012)
63. H. Yui, Polymer based composite materials. *Plastics Age* 24 (2005)
64. E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu, T.C. Chung, Polypropylene/montmorillonite nanocomposites. Rev. Synth. Routes Mater. Prop. Chem. Mater. **13**, 3516–3523 (2001)
65. http://www.nature.com/news/2008/080514/pdf/453264a.pdf
66. A. Farshidfar, V.H. Asl, H. Nazokdast, Electrical and mechanical properties of conductive carbon black/polyolefin composites mixed with carbon fiber. J. ASTM Int. 3 (2006)
67. M.Y. Koledintseva, J. Drewniak, R. DuBro, Modeling of shielding composite materials and structures for microwave frequencies. Prog. Electromagn. Res. B **15**, 197–215 (2009)
68. Z. Liu, G. Bai, Y. Huang, Y. Ma, F. Du, F. Li, T. Guo, Y. Chen, Reflection and absorption contributions to the electromagnetic interference shielding of single-walled carbon nanotube/polyurethane composites. Carbon **45**, 821–827 (2007)
69. K.H. Wong, S.J. Pickering, C.D. Rudd, Recycled carbon fibre reinforced polymer composite for electromagnetic interference shielding. Compos. A **41**, 693–702 (2010)
70. J. Feng, H. Heinz, V. Mittal, *Advances in Polyolefin Nanocomposites*. Chapter 7. Modification of inorganic filler, (Taylor group, 2010)
71. A.J. Hoffman, L. Alekseyev, S.S. Howard, K.J. Franz, D. Wasserman, V.A. Podolskiy, E.E. Narimanov, D.L. Sivco, C. Gmachl, Negative refraction in semiconductor metamaterials. Nat. Mater. **6**, 946–950 (2007)
72. P. Los, A. Lukomska, S. Kowalska, R. Jeziorska, J. Krupka, Obtaining and properties of polyolefin composites metamaterials with copper micro-and nanoflakes. Polym. Rapid Commun. **56**, 324–327 (2011)
73. H.M. Seo, J.H. Park, T.D. Dao, H.M. Jeong, Compatibility of functionalized graphene with polyethylene and its copolymers. J. Nanomater. 8 (2013)
74. S. Kalia, B.S. Kaith, I. Kaur, *Cellulose Fibers: Bio- and Nano-Polymer Composites: Green Chemistry and Technology, Polyolefin Based Natural Fiber Composite* (Springer, Heidelberg, Dordrecht, London, New York, 2011)
75. A.A.A. Aziz, S.M. Alauddin, R.M. Salleh, M. Sabet, Influence of magnesium hydroxide/aluminum tri-hydroxide particle size on polymer flame retardancy. Overview Int. J. Chem. Eng. Appl. **3**, 437–440 (2012)
76. B. Weidenfeller, M. Höfer, F.R. Schilling, Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene. *Compos. Part A: Appl. Sci. Manuf.* 35, 423–29 (2004)
77. G. Guo, G.M. Rizvi, C.B. Park, W.S. Lin, J. Appl. Polym. Sci. **91**, 621 (2004)
78. P.S. Liu, G.F. Chen. Chapter 7—Producing polymer foams. Porous Mater. Process. Appl. 345–382 (2014)
79. J.-F. Rondeau, A. Duval, H. Perrin, Inhomogeneous polypropylene/glass fibers undertray: a new broadband absorber, Faurecia Acoustic TechCenter BP 13 - ZI de Villemontry – 08, 210 Mouzan
80. K.R. Harikumar, K. Joseph, S. Thomas, Jute sack cloth reinforced polypropylene composites: mechanical and sorption studies. J. Reinf. Plast. Compos. **18**, 346–372 (1999)
81. A.K. Gupta, M. Biswal, S. Mohanty, S.K. Nayak, Mechanical, thermal degradation, and flammability studies on surface modified sisal fiber reinforced recycled polypropylene composites. Adv. Mech. Eng. **2012**, 13 (2012)

82. H. Karia, *Handbook of Polypropylene and Polypropylene Composites, Revised and Expanded*, (CRC Press, 2003) (Technology & Engineering)
83. K. Joseph, R. Dias, T. Filho, B. James, S. Thomas, L.H. de Carvalho, A review on sisal fiber reinforced polymer composites. J. Agr. Environ. Eng. **3**, 367–379 (1999)
84. http://www.google.co.in/patents/US4882208
85. A.K. Haghi, *Experimental Analysis of Geotextiles and Geofibers Composites*, (Wseas Press)
86. I.V. Arishina, T.E. Rodionova, N.G. Annenkova, A.N. Sosin, T.I. Andreeva, Investigation of the possibility of developing nanosilver-containing synthetic fibres and strands with prolonged bioactivity. Int. Polym. Sci. Technol. **39**, 55 (2012)
87. P. Brown, K. Stevens, *Nanofibers and Nanotechnology in Textiles, Chapter 13. Polyolefin Caly Nano-Composite*, (Woodhead Publishing in Textile, 2007)
88. L.J. Bastarrachea, L.A. McLandsborough, M. Peleg, J.M. Goddard, Antimicrobial N-halamine modified polyethylene: characterization, biocidal efficacy, regeneration, and stability. J. Food Sci. **79**, 887–897 (2014)
89. X. Jiang, A.M. Tafesh, J.B. Williams, H.A. Cash, K.S. Geick, *US 7582694 B2High Density Polyethylene, Quaternary Ammonium Alkyl Salt; Extrusion*. Lonza, Inc

Chapter 7
Polyolefin in Packaging and Food Industry

**Igor Novák, Anton Popelka, Zdeno Špitalský, Igor Krupa
and Sebnem Tavman**

7.1 Introduction

The commonly used food packaging polymers are polyolefins, such as low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), isotactic polypropylene (PP), and some polyethylene-based copolymers. The very low surface energies, and adhesive properties of polyolefins, which are unsuitable for many packaging purposes, have been extensively studied by Michalski et al. [1] and Novak et al. [2–6]. Packaging protects food products from unfavorable conditions, such as vapors, microorganisms, odors, and dust during distribution and storage. Packages also protect food from the loss of nutrients, functional properties, color, aroma, and taste and preserve its general appearance to meet consumers' expectations. Therefore, they should form an acceptable barrier between the food and the external environment, particularly with respect to water vapor, oxygen, and microorganisms [7] (Fig. 7.1).

The shelf life, the amount of time that the product is acceptable for use, depends on the barrier properties of the package. Packaging also enables the convenient transport of food products. The good package should provide information about the food to consumers and attract them to buy it. Food packaging is intended to protect food from contamination and preserves its quality from manufacturing to retail sales

---

I. Novák (✉) · Z. Špitalský
Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia
e-mail: Igor.Novak@savba.sk

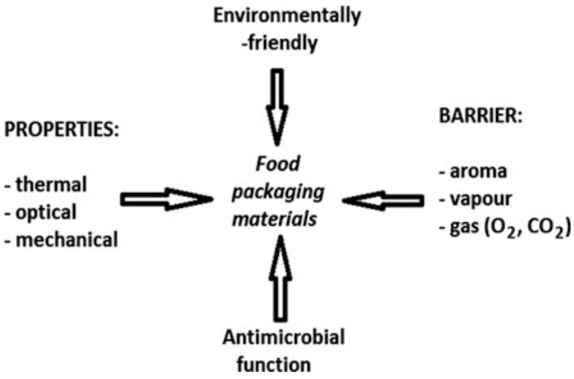
A. Popelka
Center for Advanced Materials, Qatar University, Doha, Qatar

I. Krupa
Center for Advanced Materials, QAPCO Polymer Chair, Qatar University, Doha, Qatar

S. Tavman
Ege University, Engineering Faculty, Food Engineering Department, Izmir, Turkey

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_7

Fig. 7.1 General properties required for food packaging polymers



and consumption. To be used in packaging applications, a polymer must exhibit certain properties, i.e., good mechanical strength, to allow the packaged food to withstand the rigors of handling, transportation, storage, and refrigeration.

Food packaging must also have thermal stability in thermal processing methods, such as retort and sterilization processes. Due to the complex, busy lifestyle of modern consumers, companies are aspirated to develop functional packaging systems with enhanced properties [8]. In addition to these functions, substantial product information is provided to the public to advertise and promote the product [9]. These classical functions are summarized in Fig. 7.2.

In advanced packages, these properties are enhanced by interactive elements based on chemical, physical, and/or biological processes. Intelligent packages have enhanced communication and marketing functionalities that provide dynamic feedback on the actual product quality to the consumer. In contrast, active material is adjusted for protecting and preserving the content via a process started by intrinsic and/or extrinsic factors [10]. Packaging is intended to protect foods from

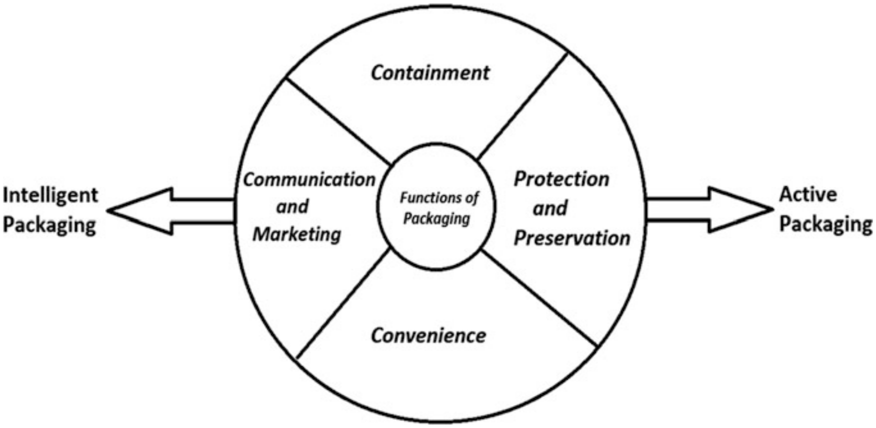


Fig. 7.2 Functions of packaging, considered those of advanced packaging systems

environmental contamination. Some of the many external variables that can adversely affect foods include oxygen, dirt, human tampering, dust, animals, insects, microorganisms, and an excess or lack of moisture. Packaging and processing are becoming increasingly integrated; for example, canning integrates packaging (the can and its contents) and a thermal preservation operation in which filling, removing air from, sealing, heating, cooling, and distributing the product must occur in a continuous process to adequately preserve the food. Polymeric materials replace the traditional materials, i.e., glass, metals, and paper, in various process industries, including the food industry [11]. The surface properties of food packaging polymers, such as the wettability, sealability, printability, uptake, glazing resistance, and adhesion to food surfaces, are of central importance to food packaging designers and engineers for the product shelf life, appearance, and quality control. The physical and chemical characteristics of polymers are similar to those of conventional materials, but the polymeric packaging materials have greater flexibility, chemical inertness, transparency, as well as low specific weights. The surfaces of polymers are mostly hydrophobic with low surface energies [12], and they do not exhibit the surface properties that are necessary in many applications. Besides that, production of multilayer polymers used for food packaging is relatively expensive. To prepare polymer foils with the necessary properties, many surface modifications are frequently used. Packaging surfaces are treated for several reasons, including functionalization, cleaning, etching, and deposition of the polymeric surface.

During functionalization process, specific functional groups are introduced onto the polymer surface. These surfaces are usually functionalized to improve their wettability, sealability, printability, glazing resistance, or adhesion to other polymers or materials without compromising the desired bulk properties of the polymer [13]. Surface modification can also be used to enhance the barrier properties of food packaging polymers and to impart antimicrobial properties. Polymer surfaces are cleaned or etched by surface modifications to remove contaminants from the surface area. The surface treatments can be used to deposit thin coatings on polymer surfaces or to sterilize them. Polymer surfaces can be modified by either chemical or physical methods. Physical methods are preferred to chemical techniques because they provide greater precision, allow for ease of process control, and are more environmentally friendly. Classical physical–chemical methods for polymer surface pre-treatment include flame; plasma modification; ultraviolet light, gamma ray, and ion-beam methods as well as corona discharge; and laser surface pre-treatment [14]. However, flame and corona treatment are limited for polymeric packaging due to hydrophobic recovery of these materials after modification and during aging.

7.2 Processing

The microbiological regulations have been used for polymeric packaging materials in food industry and represent a control point in a hazard analysis and critical control point [15]. Food packaging foils serve to preserve food quality and protect food from outside contamination and deterioration. If food packaging is not properly sterilized, the food might be further contaminated by the packaging surface, consequently resulting in health risks and economic losses [16]. Sterilization methods involving the application of dry heat, steam, ultraviolet light, and chemicals, e.g., hydrogen peroxide and ethylene oxide, can be used for food packaging foils, but also the new approaches have been tested [17]. The main drawback of these conventional sterilization methods is the liquid effluents generation. In contrast, low-temperature plasma sterilization is a safe and fast method suitable for a numerous packaging substrates. The treatment times, which are often minutes long, have limited application for food packaging mass production because longer sterilization is in terms of prices acceptable for the food packaging. The scalability of a plasma system has been used [18] for industrial purposes, and the efficiency of modification of polymeric materials in laboratory-scale system has been compared. The spore reduction kinetics for both systems suggests that the plasma array system is scalable. Muranyi and coworkers reported the use of cold plasma treatments for sterilizing polymeric foils, e.g., multilayer low-density polyethylene and polystyrene [19]. This group discovered that an increase in the relative gas humidity is essential for achieving the minimum inactivation of *Aspergillus niger* and *Bacillus subtilis* during 1-s treatments. In addition, the combination of barrier discharge plasma and ultraviolet irradiation has been described to damage the DNA of *Bacillus atrophaeus* endospores and vegetative cells. This modification method allows a short treatment time of sterilization and does not alter the packaging materials or their functionality appreciably. Another study [20] reported the effects of the position of PE sheets in the discharge, afterglow, and remote areas of the reactor on their sterilization with 13.56 MHz radio frequency O_2 plasma. The germicidal effect on *Pseudomonas aeruginosa* was smaller in these three areas at smaller exposure times, than for similar used methods. Immobilization of some bioactive compounds, such as lysozymes, niacin, glucose oxidase, vanillin, and antimicrobial peptides, in the packaging foils by the effect of cold plasma modification has been studied aiming to prepare an efficient antimicrobial packaging material [21]. Joerger et al. [22] prepared chitosan-based film containing silver using a simple modification method with corona discharge treatment. These films exhibited antimicrobial properties against *Escherichia coli* and *Listeria monocytogenes*. Various antimicrobial compounds, e.g., chitosan and triclosan, have been immobilized on polymer surface using cold plasma pre-treatment [23]. For example, triclosan and chlorhexidine were successfully immobilized on the surface of LDPE by means of acrylic acid grafted after pre-treatment of foils in barrier discharge plasma. The polymeric materials have been successfully grafted, and after antibacterial compound, immobilization met the required specifications. Triclosan immobilized samples have been more active against Gram-negative bacteria *E. coli* and Gram-positive bacteria *Staphylococcus aureus*.

Functionalization by barrier discharge plasma enables the production of very thin layers suitable for packaging production. In the case of printing on glass containers, or sealing liquid packages, materials must be processed reliably and inexpensively in the packaging industry [24]. Packaging imprints are common in the food and pharmaceutical industries, and they are protected from abrasion. Plasma modification can help achieve precise color matching, when labels are applied to jars and bottles. In addition, it prevents the inclusion of air bubbles and improves the coating adhesion and scratch resistance without damaging the packaging. Many methods have been employed to quantify the plasma modification changes influencing the printability. The contact angles are usually used to measure the surface energy as well as the wettability of polymers that are related to adhesion of printing inks [25]. Notably, the surface wettability is also determined by the interfacial energy between the solid substrate (polymer) and liquid (printing ink) [26]. This property must be considered for all practical applications. Clearly, after plasma pre-treatment, the wettability of PE with printing ink dramatically increases.

The barrier properties of food packaging materials modified by cold plasma can be enhanced. The cold plasma treatment is frequently used to modify and sterilize packages, and it can influence their mechanical and mass transfer (i.e., barrier and migration) behavior. These effects have not been widely researched, and future work should consider gas (e.g., water vapor, oxygen) permeation through the packaging substrate from the external environment into the food as well as the migration of some low molecular weight substances (LMWS, e.g., monomers, solvents, plasticizers), which must be evaluated for their toxicological properties and possibly controlled with legislation, from the packaging into the food [27]. One of the most studied applications of cold plasma-treated polymers is their application as food contact materials due to their altered barrier properties [28], which are crucial for controlling the shelf life of fresh products. In general, the use of coated foils reduces the water vapor flux by more than a factor of two. Films have the advantage of being colorless, allowing customers to see the packaged food clearly. The pre-treatment by low-temperature plasma enhances the gas permeability of PLA after cross-linking with tetramethoxysilane [29] and the hydrophobic surface coating deposition, although gas permeation can affect the quality and shelf life of foods and beverages.

The food packaging materials resulting from cold plasma processing [30] have also been studied. The low molecular weight compounds migration during modification by plasma that is important for surface sterilization and improved adhesion or printability has not been yet studied. For polyolefin-based wrap foils in the metal lids, various processing additives (i.e., plasticizers, stabilizers) might migrate from the bulk of packaging polymer in the course of storage. This migration of LMWS results in the chemical contamination of the food, and deterioration of chemical and physical properties of the polymer substrate. Some researchers [31] investigated the effects of cold plasma modification of PE films on their migration properties. After treatment with plasma in argon, migration from PE films was significantly reduced. The problem remains unresolved, despite the efforts of scientists that worked on the study food safety in terms of controlling migration of substances from packaging to thermoplastic unsolved. The previous research results show that the problem of LMWS migration can be solved, and this method of pre-treatment should be optimized to obtain the desired effect in future. Recently, dielectric barrier discharge working at atmospheric pressure and suitable for industrial production has been employed to generate plasma inside sealed packages containing bacterial samples, fresh produce, fish, and meat [32]. The decontamination of foods with in-package plasma using the polymeric package has been studied using various packaging polymers, e.g., LDPE and HDPE [33], while a significant reduction in the microbial strains on food products has been discovered. The method can easily be scaled up to continuous industrial processes preventing contamination after packaging [34]. To complete this method, it is important to know all changes that are related to cold plasma modification of the polymer packaging material. The diffusion of LMWS from the bulk of polymeric packaging material into the food and the water vapor and the permeability of oxygen should be evaluated after in-package plasma treatment for food safety reasons.

7.3 Mechanical, Physical, and Technical Requirements

Most requirements for food technology are derived from the desire to process higher quality, safer, and cheaper foodstuff. Traditional thermal processes that are used for sterilization, quality preservation, shelf-life extension, and safety enhancement have led to enormous developments in the modern food industry [35]. Shelf-stable packages produced by retort or sterile handling do not require refrigeration and are available in any grocery store. These types of packages are very favorable anywhere at any time and are easy to handle, thus profiting all from producers to consumers. The leading property of shelf-stable food packaging is to provide a microorganism barrier except for previously mentioned barrier properties, and research and development efforts have focused on creating new roles for food packaging systems, including active packaging, modified atmosphere packaging (MAP), edible films and coatings, and environmentally friendly packaging. The many new technological developments in enginery packaging have been remarkable, causing higher regulation, hygiene, health, and safety standards and to the commercial availability of new materials.

Processing and packaging equipment design must aim to improve the safety, quality, and productivity; therefore, the research of new properties appears to coincide with the development of new processes, materials, and equipment. The development of new packaging technologies necessitates new materials and packaging designs, and packaging can be expected to assume new roles when, for example, new functional packaging materials are used. The driving forces behind the research, development, and commercial applications of active packaging technologies are shelf-life extension, product quality maintenance (even quality enhancement in some cases), and safety assurance [10]. Active packaging systems extend the shelf life of food products by protecting the content of packages from pathogens due to bioterrorism and by making food processing, distribution, retail, and consumption more convenient. Several active packaging technologies that include oxygen-scavenging, carbon dioxide-absorbing, moisture-scavenging (desiccation), or antimicrobial systems have been commercialized and are currently used by the food industry.

Oxygen-scavenging systems have been produced in the form of a sachet that removes oxygen. An oxygen-free environment can protect food against oxidation, rancidity, aerobic bacteria, and mold [36]. CO_2-absorbing packaging systems protect packages against inflating due to CO_2 formation after the packaging; e.g., packaged coffee beans might produce CO_2 during storage due to non-enzymatic browning reactions. Desiccation-based moisture-scavenging systems can maintain a specific relative humidity inside the package by absorbing or releasing the moisture. Antimicrobial packaging must prevent spoilage and pathogenic microorganism growth to meet the requirements for microbial food safety, bioterrorism, and shelf-life extension. The packaging materials and in-package environments in antimicrobial packaging systems can kill or inhibit microorganisms that cause foodborne illnesses [35]. The major objective of active packaging technology development is shown in Fig. 7.3 [8]. Specifically, this field is devoted to designing functional packaging materials that release chemically or physically active substances in a specific, controlled manner [36].

Intelligent packaging has been categorized as a form of active packaging and a different type of packaging. This type of packaging incorporates intelligent functions that make food manufacturing and distribution more convenient, and its

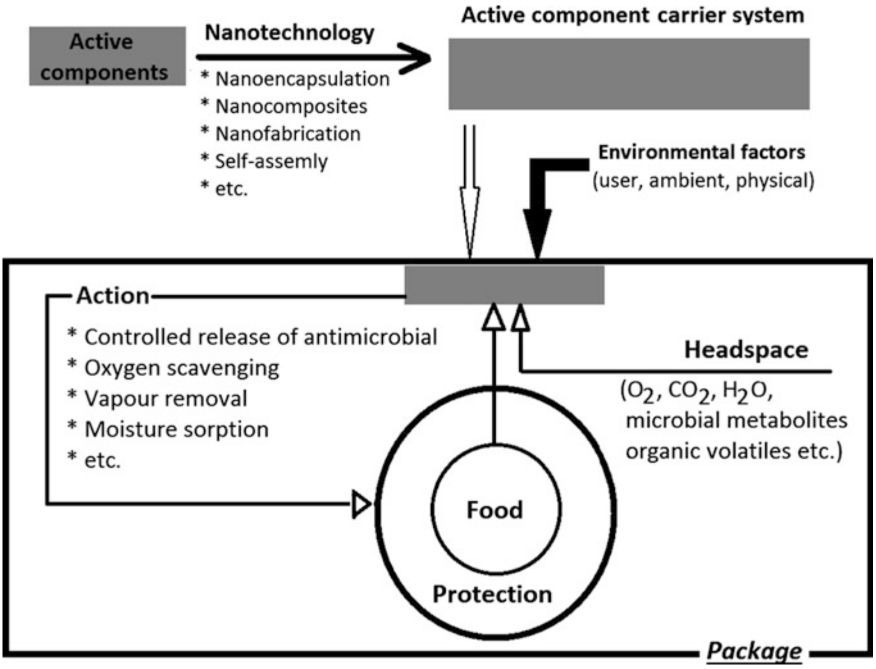


Fig. 7.3 Illustration of the active packaging concept and the nanotechnology involved

functions increasingly include improving food security and verifying its safety [37]. In contrast to active packaging, the intelligent packaging purpose is to indicate or monitor the freshness of the packaged food [38]. Intelligent food packaging differs from active food packaging in its ability to monitor the condition of the packaged food and in-package environment and to relay that information to external users and devices [10].

MAP [39] preserves the freshness of materials by controlling their biochemical metabolism and allows their breathing. Nitrogen purge, vacuum, and CO_2 injection have been used commercially for many years; however, new modified atmosphere technologies, such as inert gas (e.g., argon) flushing of fruits and vegetables, carbon monoxide injection for red meats, and high oxygen flushing of red meats, have recently been introduced. For MAP system effectiveness, optimal packaging materials with suitable gas permeability properties have to be employed. The use of MAP systems is attractive to the food industry because the demand for minimally processed fruits and vegetables, non-frozen chilled meats, ready-to-eat meals, and semi-processed bulk foods is rapidly growing. MAP significantly prolongs the shelf life of packaged food products, and in some cases, MAP products do not require any other treatment or extraordinary care during transport. In most cases, however, extension of life at shelf and quality maintenance need a multiple-hurdle technology system; e.g., combining temperature manipulation with MAP is generally necessary for maintaining the quality of packaged foods.

The pre-treatment of edible thin films or coatings is an application of active food packaging because conventional packaging systems do not include edible and biodegradable materials [40]. Edible films and coatings are multipurpose materials manufactured mainly from edible biopolymers and additives, and these films improve the quality of food products by preventing them against chemical, physical, and biological degradation. Edible films and coatings provide the easiest possibility how to enhance the physical strength of food products, decrease clustering of particles, and improve the visual and tactile features of food product surfaces [40]. They can also prevent food products against oxidation, moisture (ab/de)sorption, microbes, or other chemical interactions [41]. The standard functions of edible films and coatings are to prevent oil, gas, and water vapor migration and carry active substances such as antioxidants, antimicrobials, colors, and flavors [42]. Edible films and coatings improve the quality of food products by extending their shelf life and improving food safety.

In addition to the traditional thermal treatments for food preservation, many new thermal and nonthermal processing technologies, including irradiation, high-pressure processes, pulsed electric fields, ultraviolet (UV) treatments, and antimicrobial packaging, have been developed recently. Commercial food packaging applications have been evaluated by different agencies with some conditions. All new technologies generally call for new packaging materials and design parameters to optimize the manufacturing efficiency; e.g., irradiated packages must be chemically resistant to high energies to protect against material degradation, those that for UV treatment must transmit UV beams, and retortable pouches may refuse changes of pressure and hold seal strength at the retort temperature. New packaging materials and systems should be studied in the laboratory to guarantee their safety and no toxicity and may be verified by regulatory agencies.

Sometimes, governments might ask for new regulations and legislation in case of new processing/packaging technologies. The globalization of market means that products must adhere to global standards and comply with multiple regulations. New technologies may be tested for their effects on public health and quality, and the research outputs have to be uncovered for the public, government agencies, producers, and users. However, some criteria, such as threshold levels, allowable limits, and generally acceptable levels, are decided politically, and intervention of scientists is then confined. It is essential for all new packaging technologies to be accepted by the end users, including consumers, retailers, and producers, and to be approved by food and health regulatory agencies. Some researchers [43] identified the requirements to ensure that new active packaging technologies are financially attractive to businesses.

7.4 Mechanical, Physical, and Technical Properties

The mechanical, physical, and technical properties of polyolefins used for food packaging purposes are mainly affected by their chemical compositions. Because polyolefins comprise monomers with various atom types, their characteristics are determined by the following key factors: the arrangement, configuration, conformation, and number of molecules and atoms [44]. Polyolefins are often characterized as linear, branched, cross-linked, or network polymers based on their linearity. Because many polymer properties vary based on environmental factors and their physical characteristics, such as their linearity, molecular weight and its distribution, degree of density, crystallinity, humidity, and temperature, plastics have very practical and versatile functionality for use in food packaging systems [45]. For example, as the molecular weight of polyethylene increases, some of its properties, such as its tensile strength, impact strength, clarity, and ultimate elongation, also increase. As its density increases, all of these properties, except for the tensile strength, decrease. Changes in the morphological properties, such as the crystallinity, of a plastic packaging polymer substantially affect other properties. The following properties are considered when designing plastic packaging systems:

- Density;
- Degree of polymerization;
- Thermal properties, such as the glass transition temperature, melting temperature, crystallization temperature, enthalpy, heat expansion, and heat deformation temperature (HDT);
- Chemical resistance;
- Permeability (solubility and diffusivity);
- Physical properties, such as the friction coefficient, tensile strength, elongation, viscosity, elasticity, plasticity, and modulus; and
- Morphological properties.

In general, plastics provide the following advantages when used in food packaging:

- Very lightweight, inexpensive, and strong compared to other packaging materials;
- Good oil and chemical resistance;
- Excellent gas and water vapor barrier properties;
- Sealing property;
- Thermally stable and good electrical insulation properties;
- High processability (thermoforming, injection, and extrusion);
- Easily enhanced by the addition of other components, such as colorants, fillers, and active agents;
- Easily combined with other packaging materials; and
- Easily reused and recycled for sustainability.

7.4.1 Polyethylene

Polyethylene (PE) is a member of the polyolefin family, which also includes PP and various plastics with different molecular linearity, densities, polymerization processes, and substitution types. PE densities are relatively low with values ranging from 0.940 to 0.970 g/cm^3 for HDPE and from 0.916 to 0.940 g/cm^3 for LLDPE. Typically, these PEs not only have good processability (e.g., can be converted into bags, films, and bottles) but also exhibit an excellent water vapor barrier property, which is required for many water-sensitive food products such as dried and liquid foods. However, this type of plastic is not appropriate for easily oxidized food products due to its low oxygen barrier property. The properties of polyolefins can be significantly affected by environmental conditions and physical factors, such as the density, crystallinity, presence of free volume, polarity, humidity, and temperature [44].

LDPE is more suitable for flexible films than HDPE because it is soft, flexible, and stretchable. LDPE film and sheet applications accounted for 67 % of the total LDPE use worldwide in 2011. The majority of these applications used films instead of sheets. LDPE films were used for bakery products, frozen foods, fresh produce, meat and poultry, and confectionery products. LLDPE is produced as either a homopolymer or a copolymer with 1–10 mol% of a comonomer alkane such as butane, hexane, or octane. This plastic has better properties (e.g., mechanical properties) than LDPE at the same density. It has good clarity, heat-sealing strength, and toughness and is often used for stretch/cling films, grocery sacks, and heavy-duty shipping sacks.

In contrast, HDPE is a translucent polymerized film with higher crystallinity than LDPE, and it provides a good barrier against gas and water. The mass density of HDPE ranges between 0.93 and 0.97 g/cm^3. HDPE has a high stiffness and hardness. Ethylene-based copolymers, such as ethylene acrylic acid and ethylene methacrylic acid, and their ionomers are produced by the copolymerization of ethylene and other monomers [44]. They are generally branched forms of PE. The crystallinity and intermolecular forces of these polymers are significantly affected by the increased irregularity and polarity of their structures due to substituted groups, resulting in improved flexibility, toughness, hot tack and adhesion, heat-sealing strength, and gas barrier properties. These polymers are very often used for food products such as meats, cheeses, and snack foods and for medical products. In general, the amount of comonomer is limited to 20–25 % due to food safety issues. Ionomers (e.g., Surlyn produced by DuPont) have relatively higher processing temperatures (175–290 °C) due to their cross-linked ionic bonds and excellent elongation viscosity and pinhole resistance.

When combined with other food packaging materials, such as HDPE or foil layers, ionomers provide excellent barrier properties. Newer linear polyethylene polymers, namely metallocene polymers, emerged in the 1990s. To produce these polymers, either a single catalyst composed of positively charged metal ions and negatively charged organo-cyclic anions or a combination of catalysts is employed in the polymerization process [44]. This process has enabled the properties, such as the degree of polymerization, linearity, and configuration, of linear PE, and other polyolefin to be altered in new and significant ways. In addition, the polymer strengths, flexibilities, and crystallinities can be varied. This new type of polymer includes plastics commonly used for food packaging, such as LDPE (0.910–0.940 g/cm^3) and HDPE.

The basic types or classifications of polyethylene according to ASTM D 1248 are as follows [45]:

- Ultra-low-density polyethylene (ULDPE): polymers with densities ranging from 0.890 to 0.905 g/cm^3, that contains a comonomer;
- Very low-density polyethylene (VLDPE): polymers with densities ranging from 0.905 to 0.915 g/cm^3 that contains a comonomer;
- Linear low-density polyethylene (LLDPE): polymers with densities ranging from 0.915 to 0.935 g/cm^3 that contain a comonomer;
- LDPE: polymers with densities ranging from approximately 0.915–0.935 g/m^3;
- Medium-density polyethylene (MDPE): polymers with densities ranging from 0.926 to 0.940 g/cm^3 that might or might not contain a comonomer; and
- HDPE: polymers with densities ranging from 0.940 to 0.970 g/cm^3 that might or might not contain a comonomer.

PE represents one of the simplest food packaging polymers. PE with different densities, water vapor transmission rates, gas transmission rates, and mechanical properties, e.g., tensile strengths, is commercially available. This variety provides food manufacturers with ability to choose the optimum packaging material for their needs [45]. The surface of PE is necessary due to its low polarity and low surface energy to modify by low-temperature discharge plasma in air [3–6]. PE surfaces modified by CO_2, H_2O, and CO_2/H_2O plasma have been also characterized [46].

7.4.2 Polypropylene

PP is a general purpose polyolefin that is suitable for food packaging. The low density of PP, its low cost, high melting point, good heat sealability, as well as chemical inertness make it a suitable packaging material for different food products [45]. PP homopolymers and PP random copolymers are both available for use as food packaging materials. In general, PP is characterized by a low density, relatively low transition temperature (T_g), moderate melting temperature (T_m), and good oil and chemical resistance as shown in Table 7.1. Due to its superior properties, such as excellent low-temperature impact strength, a high heat deflection temperature (HDT), and suitable flexibility and rigidity, this polymer is often used for a variety of food products ranging from cold chain food products to heat-treated food products, including microwaveable products available in either flexible or rigid plastic packaging. Due to its poor oxygen barrier properties, PP is often combined with materials with good oxygen barrier properties, such as ethylene vinyl alcohol, nylon, or foil, in both flexible and rigid plastic packaging for oxygen-sensitive food products, such as apple products, ready-to-eat meat products, soup, baby food, ketchup, and cooked rice.

The problems in adhesion, i.e., printing, coating, and lamination of PP, are related to its low surface energy. The efficient surface modification is necessary to enhance the surface energy of PP, and mainly its polar component [2]. PP as a hydrocarbon polymer contains alternating hydrogen and methyl (CH_3) side groups on its carbon backbone. The reactivity of the PP hydrogen side groups in surface reactions depends on the nature of the C atom to which they are attached. In general, the reactivity increases in the following order: $H_{pri} < H_{sec} < H_{tert}$, where H_{pri}, H_{sec}, and H_{tert} refer to H atoms bonded to C atoms that are bonded to one, two,

Table 7.1 General properties of polyolefins and other polymers used for food packaging

Polymer	Thermal properties				Strength		Density ($g\ cm^{-3}$)
	T_m [a](°C)	T_g [b](°C)	HDT[c](°C)	CTE[d] (ppm $°C^{-1}$)	Tensile (MPa)	Compressive (MPa)	
LDPE	98–115	−25	40–44	100–220	8–32	–	0.91–0.94
LLDPE	122–124	–	–	–	13–28	–	0.92–0.94
HDPE	130	–	79	59	22	19	0.94–0.97
PMMA	–	85	79	50	48	72	1.17
PP	168–175	−20	107–121	81–100	31–41	38–55	0.89–0.92
PS	–	74–105	68–96	50–83	36–52	83–90	1.04–1.05
PVC	–	75–105	57–82	50–100	41–52	55–90	1.30–1.58
PVDC	172	−15	54–66	190	24–34	14–19	1.65–1.72
PA	–	310–365	277–360	45–56	72–118	207–276	1.36–1.43
PET	245	73	21	65	48	76	1.29

[a] Melting temperature

[b] Glass transition temperature

[c] Heat deformation temperature under a 0.455 MPa load

[d] Coefficient of linear thermal expansion

and three other C atoms, respectively. The modification of PP surface using the corona and/or barrier discharge plasma at atmospheric pressure has been extensively modeled [2, 6, 47]. The reaction mechanism of PP treatment by air plasma has been described in the literature [2, 48]. The degradation of PP during plasma treatment is due to branch scissions to form low molecular weight oxidized material, and the degradation amount decreases by ordering: $N_2 < He < Air < O_2$.

Composite materials consist of two or more phases, namely the continuous and disperse phase(s). Usually, the continuous phase consists of a polymer, and the disperse phase is filler or reinforcing material. In general, nanocomposites refer to composites consisting of a single polymer or polymer blend with (in) organic particles with a dimension lower than 0.1 μm. For example, the blending of nanoparticles such as SiO_2 has been reported [49]. As reported in the literature, the thermal stability and optical, mechanical (the stiffness, tensile strength, toughness, shear strength, delamination resistance, fatigue), and barrier properties of polymers [50] can be significantly enhanced by mixing of nanomaterials into their matrices. Figure 7.4 [8] shows the overall procedure for preparing nanocomposites and illustrates the enhanced barrier properties of these materials compared to those of a pure polymer material. The composite properties are affected by the nanoparticle dispersion in the polymer matrix. For example, with montmorillonite (MMT), the dispersed phase can adopt three different modes according to the dispersion and type of layered silicate used (native versus modified). These modes include:

(1) Tactoids—the MMT layers are not delaminated, and the final properties are almost the same to those of a microcomposite;
(2) Intercalated MMT—the macromolecule chains are penetrated between the silicate layers, what reduce their mobility; and
(3) Exfoliated MMT—the MMT layers are fully delaminated to individual layers and homogenously dispersed in the continuous polymer phase, which results in the improving the overall properties.

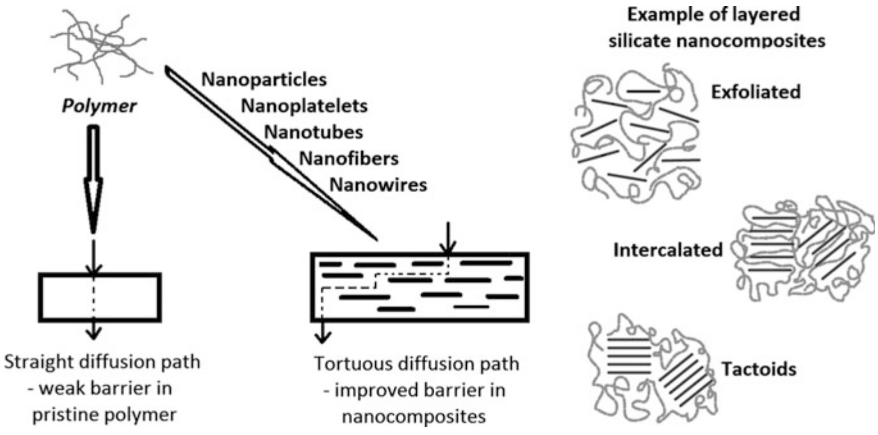


Fig. 7.4 Scheme for preparing nanocomposites and improving the barrier properties

The use of fillers, such as nanoplatelets with high surface/thickness ratios, into polymers improves their barrier properties against permeated molecules. Because these particles are impermeable or low permeable to different gases and water vapor than the polymer matrices, permeate molecules have longer diffusion paths in the composite than in the pristine polymer matrix [8] (Fig. 7.4). Consequently, the overall barrier properties of a nanocomposite against gases and vapors improve. In the case of food applications, clay/polymer composites are the most of polyolefins studied composite materials [51]. For example, Xie et al. [52] reported that the oxygen barrier properties of LDPE significantly enhanced after mixing organic MMT into the matrix.

The advantage of intelligent packaging systems is to improve the communication abilities of the package. For example, these systems can inform about the current food quality in real time instead of relying on the static “Best Before” and “Use By” dating approach [53]. This form of advanced packaging is utilizable for effectively transferring information throughout the product distribution chain via innovative communication methods, such as intelligent tags (e.g., radiofrequency identity tags, time–temperature indicators, oxygen and CO_2 sensors, and freshness indicators) [8]. The most important points of nanotechnology-based intelligent packaging systems are depicted in Fig. 7.5.

The indicator/sensor, which is manufactured by suitable nanotechnology, can interact with components inside the package (food components and headspace

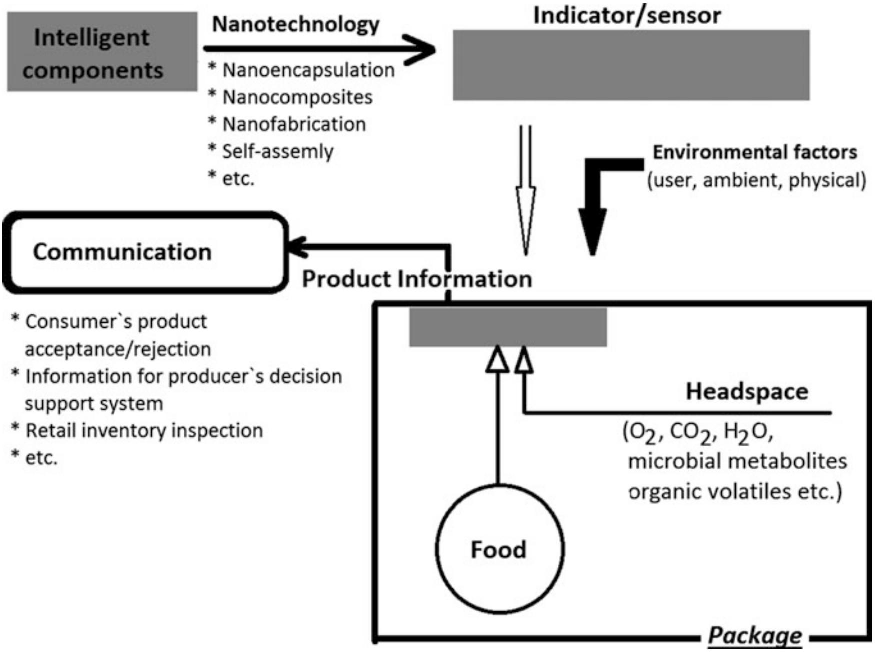


Fig. 7.5 Illustration of the intelligent packaging concept and the nanotechnology involved

species) and/or the external environment. Due to these interactions, the sensor or indicator generates a signal (e.g., visual cue, electrical signal) that correlates to the state of the food product. The generated response can be utilized not only to notify consumers about the product safety and quality but also to help producers determine what actions to take throughout the entire product distribution channel and production process and when to implement them [54].

7.5 Design Requirements

The key objective of innovative packaging design is to use the packaging as a powerful marketing tool to more effectively capture consumers' attention in the store, communicate with them, and provide the product with a competitive advantage over the other products in the marketplace [55]. The visual features, such as the package color, shape, graphemes, and typographic attributes of any text on the label, the feel of the product packaging, and the sounds it makes when the consumer interacts with it, can help convey a particular message about the likely attributes of the contents [56]. In one study, the way in which visual and auditory packaging features convey or are at least associated with the product's likely taste/flavor was investigated [57]. The idea that the different sensory features of a product's packaging can convey clues about the product's taste/flavor can be explained in terms of cross-modal correspondences. According to some researchers [58], cross-modal correspondences refer to the tendency to match various attributes and sensory dimensions across different sensory modalities. Cross-modal correspondences between tastes and other visual and non-visual sensory cues, such as colors, sounds, shapes, and even words, have been documented [59]. The typefaces on a product's packaging might also convey meaning over and above the actual semantic content of the particular words written in those typefaces. It is important to note that a product's packaging is composed of more than its visual features. For example, it has frequently been suggested that certain speech sounds convey meaning. It is then possible to suggest that by using knowledge of sound symbolism, a company might choose brand names that communicate information about the actual taste of their product [60].

The idea that people tend to match certain speech sounds to various basic tastes has also been investigated using non-speech sounds [59, 60]. To date, research in this area has primarily focused on the effects of varying one packaging feature (e.g., its shape) at a time. Thus, the interactions between the various visual and auditory features of product packaging must be investigated. Based on the fact that a product's taste can be conveyed by the sensory attributes of its packaging, we present a study designed to assess the interactions between shapes, typefaces, names, and sounds and their contributions to communicating (or being associated with) the likely taste of a hypothetical food product, which might be either sweet or sour. Based on previous studies, it is expected that rounded shapes, typefaces, and names are associated with sweetness, whereas sourness is associated with angular shapes, typefaces, and names.

According to Calder et al. [61], packaging design has become a part of brand design. In this sense, packaging has become part of the strategy used to communicate the essence of a brand to consumers. Designers and product managers should therefore capitalize on this fact by understanding how various sensory cues are involved in building brand perception. Walker et al. [62] suggested that cross-modal correspondences extend across many dimensions of experience; for example, angular shapes are related to hard surfaces or materials, high-pitched sounds, and bright stimuli. This knowledge could be used to communicate brand values, meaning, and product features via packaging design. Research on cross-modal correspondences can therefore potentially empower designers by helping them understand how well particular sensory attributes communicate certain brand and product features. In addition, these results highlight the importance of early intervention in packaging design to increase the success of product launches and reduce costs by understanding how to advertise product features and brands by the packaging in later stages of development. In the future, it would be very interesting to use predictive packaging design on the Internet and thus assess the associations of consumers in different markets.

7.6 Conclusions and Future Trends

In all fields of food science, there is an increasing interest in utilizing nanostructures for improving the performance of food products and processes. Many structures in foods are within 100 nm size range, and because of their unique physical properties, take a significant task in the delivery of nutrients or more in general, show enhanced bioactivity. By manufacturing foods using particular processing or environmental conditions, it is possible to obtain nanostructures. The small size affects their functional properties, when compared to structures with similar composition, but larger in size. In foods, these structures are usually dispersed in solution, and they are not biologically persistent, i.e., they are digested and hydrolyzed, and they do not accumulate in organs or in the environment. Because of their physical properties and especially their enhanced surface area, these structures tend to be more efficacious in encapsulating bioactive and improving texture and structures or more in general show some improved processing and nutritional functionality. The low-temperature discharge plasma treatment of polymers is used for surface sterilization of food packaging foils. The bulk and mass transport properties of discharge plasma-treated films must be explored and quantified. These properties are important for packages, and they are suitable for both respiring and non-respiring foods and also for safety product assessment. The use of discharge plasma to aid in the deposition of biologically actives and antimicrobials can help expand the emerging field of edible films and active food packaging. Future studies should focus on study of antimicrobial efficiency after their immobilization on low-temperature plasma-grafted polyolefin surfaces. The use of natural antimicrobial agents is a very promising alternative because of their appeal as natural products and consumers' preference, and because they do not conflict with regulations. For the commercialization of antimicrobial packaging, various marketing factors are involved, for example, logistics, cost, and consumer acceptance. The antimicrobial packaging systems should be manageable within current packaging-related logistic systems. Reasonable cost recovery should be promised for the commercialization of new packaging systems. Consumers' acceptance of the use of new antimicrobial packaging systems is critical. This acceptance may be related to the convenience and easiness of the use of a new system, any conflict of the new system with their culture and lifestyles, and other various reasons. The food security is a big issue in the world, and antimicrobial packaging could play a role in food security assurance, comprehensively agreed with industrial sectors, farmers, producers, wholesalers, retailers, governments, and consumers.

A following trend in food packaging technology consists from research and development of new material that exhibits significantly improved barrier properties against gases and vapors. Low-permeable materials can decrease the total amount of packaging materials required, as they are made of thin or lightweight materials with high-barrier properties. A significant trend in food packaging technology today is convenience, especially with regard to manufacturing, distribution, transportation, sales, marketing, consumption, and waste disposal. Another important trend is safety as it relates to public health and security against bioterrorism. The Foodborne illnesses and the malicious alteration of foods must be eliminated from the food chain. The food safety will become a major active food packaging application. Food packaging technologies are linked also to consumer studies. Consumers tend to seek out new materials with new functions, and new food packaging systems reflect current food processing technologies, lifestyle changes, and scientific research.

Acknowledgements The authors gratefully acknowledge the financial support of the Ministry of Education, Youth, and Sports of the Slovak Republic and Slovak Academy of Sciences, project VEGA 2/0199/14 as well as the project of Center for Applied Research of New Materials and Technology Transfer, ITMS 26240220088, supported by the Science and Research Operational Program by the European Regional Development Fund.

References

1. M.C. Michalski, S. Desobry, M.N. Pons, J. Hardy, J. Am. Oil Chem. Soc. **75**, 447–454 (1998)
2. I. Novák, V. Pollák, I. Chodák, Plasma Proc. Polym. **3**, 355–364 (2006)
3. I. Novák, A. Popelka, I. Krupa, I. Chodák, I. Janigová, T. Nedelčev, M. Špírková, A. Kleinová, Vacuum **86**, 2089–2094 (2012)
4. I. Novák, G.K. Elyashevich, I. Chodak, A.S. Olifirenko, M. Števiar, M. Špírková, N. Saprykina, E. Vlasova, A. Kleinova, Eur. Polym. J. **44**, 2702–2707 (2008)
5. I. Novák, A. Popelka, I. Chodák, J. Sedliačik, Study of adhesion and surface properties of modified polypropylene, in *Polypropylene*, ed. by F. Dogan (InTech, Rijeka, Croatia, 2012), pp. 125–160
6. I. Novák, Š. Florián, Macromol. Mater Eng. **289**, 269–274 (2004)
7. J.W. Rhim, H.W. Park, C.S. Ha, Prog. Polym. Sci. 1629–1652 (2013)

8. S. Mihindukulasuriya, L.T. Lim, Film Packag. Technol. Sci. **40**, 149–167 (2014)
9. K.L. Yam, P.T. Takhistov, J. Miltz, J Food Sci. **70**, R1–R10 (2005)
10. L.T. Lim, in *Active and Intelligent Packaging Materials*, 2nd edn. eds. by C.L. Cooney, A.E. Humprey. Comprehensive Biotechnology, vol 4, (Pergamon Press, Oxford, 2011), pp. 629–644
11. S.K. Pankaj, C. Bueno-Ferrer, N.N. Misra, V. Milosavljevic, C.P. O'Donnell, P. Bourke, K.M. Keener, P.J. Cullen, Trends Food Sci. Technol. **35**, 5–17 (2014)
12. A. Vesel, M. Mozetic, Vacuum **86**, 634–637 (2012)
13. M. Ozdemir, C.U. Yurteri, H. Sadikoglu, Food Technol. **53**, 54–58 (1999)
14. H.J. Adler, P. Fischer, A. Heller, I. Jansen, D. Kuckling, H. Komber et al., Acta Polym. **50**, 232–239 (1999)
15. J. Mittendorfer, H. Bierbaumer, F. Gratzl, E. Kellauer, Radiat. Phys. Chem. **63**, 833–836 (2002)
16. N.N. Misra, B.K. Tiwari, K.S.M.S. Raghavarao, P.J. Cullen, Food Eng. Rev. **3**, 159–170 (2011)
17. S. Lerouge, M.R. Wertheimer, L.H. Yahia, Plasmas Polym. **6**, 175–188 (2001)
18. J. Schneider, K.M. Baumgartner, J. Feichtinger, J. Kruger, P. Muranyi, A. Schulz et al., Surf. Coat. Technol. **200**, 962–968 (2005)
19. P. Muranyi, J. Wunderlich, H.C. Langowski, J. Appl. Microbiol. **109**, 1875–1885 (2010)
20. L. Yang, J. Chen, J. Gao, Y. Guo, Appl. Surf. Sci. **255**, 8960–8964 (2009)
21. M. Mastromatteo, L. Lecce, N. De Vietro, P. Favia, M.A. Del Nobile, Meat Sci. **74**, 113–130 (2011)
22. R.D. Joerger, S. Sabesan, D. Visioli, D. Urian, M.C. Joerger, Packag. Technol. Sci. **22**, 125–138 (2009)
23. A. Popelka, I. Novák, M. Lehocký, I. Chodák, J. Sedliačik, M. Gajtanská et al., Molecules **17**, 528–535 (2012)
24. M.S. Banu, Cold Int. J. Emerg. Trends Eng. Dev. **4**, 15 (2012)
25. D. Dixon, B.J. Meenan, J. Adhes. Sci. Technol. **26**, 2325–2337 (2012)
26. V. Guillard, M. Mauricio-Iglesias, N. Gontard, Crit. Rev. Food Sci. Nutr. **50**, 969–988 (2010)
27. L. Bardos, H. Barankova, Thin Solid Films **518**, 6705–6713 (2010)
28. K.T. Lee, Meat Sci. **86**, 138–150 (2010)
29. Y. Uemura, Y. Maetsuru, T. Fujita, M. Yoshida, Y. Hatate, K. Yamada, Korean J. Chem. Eng. **23**, 144–147 (2006)
30. O.B.G. Assis, J.H. Hotchkiss, Packag. Technol. Sci. **20**, 3293–3297 (2007)
31. J.L. Audic, F. Poncin-Epaillard, D. Reyx, J.C. Brosse, J. Appl. Polym. Sci. **79**, 1384–1393 (2001)
32. J. Connolly, V.P. Valdramidis, E. Byrne, K.A.G. Karatzas, P.J. Cullen et al., J. Phys. D Appl. Phys. **46**, 035401–035412 (2013)
33. N.N. Misra, D. Ziuzina, P.J. Cullen, K.M. Keener, *In American Society of Agricultural and Biological Engineers*. (Dallas, Texas, July 29–August 1, 2012), p. 121337629
34. K.M. Keener, J. Jensen, V. Valdramidis, E. Byrne, J. Connolly, J. Mosnier, et al., NATO Advanced Research Workshop: plasma for bio- decontamination, medicine and food security, Jasná, Slovakia, eds. by K. Hensel, Z. Machala, pp. 445–455 (2012)
35. J.H. Han, D.S. Lee, S.C. Min, M.S. Chung, J. Phys. Chem. C **116**, 12599–12612 (2012)
36. J.H. Han, Antimicrobial packaging materials and films, in *Novel Food packaging techniques*, ed. R. Ahvenainen (Woodhead Publ. Ltd. and CRC Press LLC, 2003) pp. 50–70
37. E.T. Rodrigues, J.H. Han, Intelligent packaging, in *Encyclopedia of Agricultural and Food Engineering*, ed. by D.R. Heldman (Marcel Dekker, New York, 2003), pp. 528–535
38. D. Restuccia, U.G. Spizzirri, O.I. Parisi, G. Cirillo, M. Curcio, F. Iemma, Food Control **21**, 1425–1435 (2010)
39. J.H. Han, Protein-based edible films and coatings carrying antimicrobial agents, in *Protein-Based Films and Coatings*, ed. by A. Gennadios (CRC Press, Boca Raton, 2002), pp. 485–499

40. B. Cuq, N. Gontard, S. Guilbert, Edible films and coatings as active layers, in *Active Food Packaging*, ed. by M. Rooney (Blackie Academic & Professional, Glasgow, 1995), pp. 111–142
41. J.J. Kester, O.R. Fennema, Food Technol. **48**, 47–59 (1986)
42. J.M. Krochta, C. De Mulder-Johnston, Food Technol. **51**, 61–74 (1997)
43. J.P. Kerry, M.N. O'Grady, S.A. Hogan, Past current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: a review. Meat Sci. **74**, 113–130 (2006)
44. Y.T. Kim, B. Min, K.W. Kim, *Innovations in Food Packaging*, Chapter 2, (Elsevier, Amsterdam, 2014), pp. 13–35
45. S.K. Pankaj, S.U. Kadam, N.N. Misra, *Trends in food packaging* (VDM Publishing House, Germany, 2011)
46. N. Medard, J.-C. Soutif, F. Poncin-Epaillard, Langmuir **18**, 2246–2253 (2002)
47. R. Dorai, M.J. Kushner, J. Phys. D Appl. Phys. **36**, 666 (2003)
48. Y. Akishev, M. Grushin, N. Dyatko, I. Kochetov, A. Napartovich, N. Trushkin et al., J. Phys. D Appl. Phys. **41**, 235203 (2008)
49. J.L. Tsai, H. Hsiao, Y.L. Cheng, J Compos. Mater. **44**, 505–524 (2010)
50. Y. Zhong, T. Poloso, M. Hetzer, D. De Kee, Polym. Eng. Sci. **47**, 797–803 (2007)
51. J.M. Lagaron, I. Cabedo, D. Cava, J.I. Feijoo, R. Gavara, E. Gimenez, Food Addit. Contam. **22**, 994–998 (2005)
52. L. Xie, X.Y. Lv, Z.J. Han, J.H. Ci, C.Q. Fang, P.G. Ren, Polym.-Plast. Technol. Eng. **51**, 1251–1257 (2012)
53. C. von Bultzingslowen, A.K. McEvoy, C. McDonagh, B.D. MacCraith, I. Klimant, C. Krause et al., Analyst **127**, 1478–1483 (2002)
54. K.L. Yam, P.T. Takhistov, J. Miltz, J. Food Sci. **70**, R1–R10 (2005)
55. A. Azzi, D. Battini, A. Persona, F. Sgarbossa, Packag. Technol. Sci. **25**, 435–456 (2012)
56. C. Spence, O. Deroy, Flavour **1**, 12 (2012)
57. C. Velasco, A. Salgado-Montejo, F. Marmolejo-Ramos, C. Spen, Food Qual. Prefer. **34**, 88–95 (2014)
58. C. Spence, A. Gallace, Food Qual. Prefer. **22**, 290–295 (2011)
59. O. Deroy, C. Spence, Cerveau Psycho **55**, 74–79 (2013)
60. R.R. Klink, Mark. Lett. **14**, 143–157 (2003)
61. B.J. Calder, S. DuPuis, Packaging and brand design. Wiley Int. Encycl. Mark. (2010). doi:10.1002/9781444316568.wiem04024
62. P. Walker, Attention, Percept. Psychophys. **74**, 1792–1809 (2012)

Chapter 8
Polyolefin Adhesion Modifications

Anton Popelka, Igor Novak and Igor Krupa

8.1 Introduction

Polyolefins exhibit excellent properties and the knowledge of their adhesion that are very important for many applications such as those in packaging, building, automobile, aeronautic, aerospace, electronics, and sport industries. Poor surface adhesion represents a serious problem in situations where other laminates, films, or metallic layers are imparted onto polyolefins. Adhesion represents the contact between two solids, for instance, in coatings, polymer blends, paints, multilayered sandwiches, adhesive joints, or composites materials. Adhesion represents a multidisciplinary topic that includes the surface chemistry, physics, polymer chemistry, rheology, mechanic analysis, and fracture analysis. Several factors negatively affect the adhesion properties of polyolefins. Generally, contaminants are responsible for a decrease of adhesion. Therefore, the removal of contaminants using chemical or physical methods is necessary. The other important factor affecting adhesion is wettability corresponding to the surface free energy. A high surface free energy is associated with high adhesion and vice versa. Moreover, the increase of the contact surface area also leads to an increase of adhesion. For the above-mentioned reasons, different techniques can be used to improve the adhesion polyolefins, such as chemical modification, UV, and flame or plasma treatment. The surface modification of polyolefin surface is necessary to improve adhesion requirements or to provide a protective surface to reduce the degradation or abrasion processes.

A. Popelka (✉)
Center for Advanced Materials (CAM), Qatar University, PO Box: 2713 Doha, Qatar
e-mail: anton.popelka@qu.edu.qa

I. Novak
Polymer Institute, Slovak Academy of Sciences, 845 41 Bratislava 45, Slovakia

I. Krupa
Center for Advanced Materials (CAM), QAPCO Chair Qatar University, PO Box: 2713
Doha, Qatar

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_8

8.2 Definition/Classification

Polyolefins belong to the most widely used class of polymers in many applications, such as in packaging, building, or transport industries. A combination of polyolefins with other materials can lead to an improvement of various properties. Many polyolefins belong among nonpolar polymers with low polarity and surface energy; these polymers excel rather poor adhesion properties with various materials [1], and therefore, these polyolefins require the improvement of their surface and adhesive properties for many applications. In practice, the modification procedure selection for the improvement of the adhesion properties of different polyolefins depends mostly on the required demands for the adhesive joints [2].

Adhesion can be divided into the (1) *intrinsic* and (2) *measured* adhesions. The first type means direct molecular forces of the attraction between the adhesive and substrate, and the second type is obtained from the measurement of the strength of an adhesive joint. Intrinsic adhesion forces across the interface are necessary for adhesion [3].

Four main theories of adhesion, namely 1. adsorption, 2. electrostatic, 3. diffusion, and 4. mechanical interlocking theories, are very well known.

1. The adsorption theory emphasizes that once the substrate and adhesive are come into direct contact, attraction forces will be between them. High bond strength is sufficient as long as the extent of the wetting is good as a result of primary bonds or secondary, such as covalent bonds, or van der Waals forces, respectively. Primary bonds are necessary for an achievement of the bond durability in an adverse environment. In this theory, macromolecules of the mobile phase (e.g., the adhesive, printing, and ink) are adsorbed on the substrate by forces (ranging from dispersion to chemical bonds).
2. The electrostatic theory indicates the electrical phenomena, for example, sparking observed during the adhesive bond destruction, considering the electrostatic charge transfer between the substrate and adhesive. This theory considers the system consisted of adhesive–substrate as analogous to a plate condenser in parallel arrangement. The energies associated with this process are generally smaller compared with energies of the adhesion fracture [4, 5]. Regarding this theory, there is a transfer of the charge between two materials joined at the interface with different band structures, and therefore, the materials are bonded by electrostatic forces. This model is applicable only for incompatible materials, such as the adhesion between a polymer and metallic surface [6].
3. The diffusion theory addresses with the diffusion of macromolecules of the mobile phase into the substrate when an interface is eliminated. In the last theory (mechanical interlocking), the mobile phase flows into the irregularities of the substrate surface and the interlocking action is present (Fig. 8.1) [7].
4. In this oldest adhesion theory, the roughness and porosity of the substrate are suitable factors as the wettability is sufficient thus far by the adhesive (Fig. 8.1a). However, the nonwetted parts are the origins of the failures (Fig. 8.1b) [8].

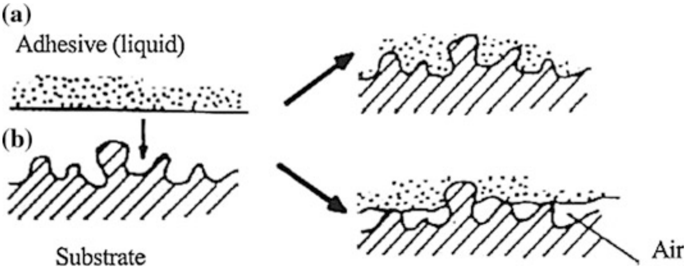


Fig. 8.1 Good wetting (**a**) and poor wetting (**b**) by mechanical interlocking [8]

8.3 Pretreatment of Polyolefin

The pretreatments used for plastics and elastomers are usually based on the different techniques. In this chapter, attention is focused on the treatment of plastic polyolefins. Over the last 50 years, many of the pretreatments have been developed to improve adhesion to polyolefins. Around 1950, the methods that were developed included treatment with flame, corona discharge, chromic acid, and chlorine gas activated by ultraviolet light. The first three methods were strongly established for the treatment of polyethylene (PE) and polypropylene (PP). Breaking down air into active species including oxygen atoms, ozone, and ions by the application of a high voltage, which involves exposing the plastic to a discharge for less than one second, represents corona discharge and remains favored for the treatment of cylindrical objects such as bottles. Chromic acid is very effective for treating three-dimensional objects, but it is phased out for environmental reasons. Chlorinated PP primers are sometimes used commercially instead of a pretreatment, e.g., they are applied to PP bumpers before painting. Many other pretreatments were examined although they have not found widespread use in the industry. These pretreatments include ammonium peroxydisulfate, organic peroxides, sodium hypochlorite, and electrochemical methods [9].

Adhesion failures that occurred in service can be very expensive to rectify. For example, poor paint adhesion to PP bumpers could involve the recall of many thousands of cars. Even when identified at the production stage, poor adhesion can be very expensive to rectify. It is not uncommon for several days' production to be lost, while an adhesion problem is being solved. When it is necessary to join two pieces of the same polyolefin, heat sealing can be used; several welding options exist, including electrofusion, ultrasonic, hot gas, hot plate, and infrared techniques. If it is necessary to join a polyolefin to another substrate, options include co-extrusion, adhesive bonding, and mechanical fastening. To achieve satisfactory adhesion when bonding with an adhesive, printing, painting, or metallizing, the polyolefin is usually necessary for pretreatment. Pretreatments of polyolefins have been the subject of a number of research and development [10–12].

8.3.1 Chemical Treatment

Generally, a chemical etch of the polyolefin to be coated represents the effective surface treatment. The chemical and physical characteristics can be transformed to enhance the wet-out or film adhesion. The chemical treatment can remove surface contamination by one or more cleaning operations. These operations can lead to a reduction of the solution contamination and ensure optimum interactions between the substrate and solution. Commonly, the surface is washed/immersed in a bath containing an acid, base, oxidizing/chlorinating, or other very active chemical agent. The control of the parts by the weight of active ingredients, solution temperature, and immersion time is required for each procedure. Some procedures excel by wide ingredient ratios range, whereas others are specific. The solution temperature is inverse to the immersion time; that means, high temperatures result in short exposures [13]. Oxidative solutions may be used to treat polyolefins, such as strong oxidizing acids can lead to the introduction of carbonyl or carboxylic acid groups on polyolefin surfaces to enhance adhesive binding. Although the surface modification can be limited only to the top surface layer by utilizing of proper contact temperatures and times, deeper surface regions can be modified in some cases [14].

Chromic acid was used for the introduction of carbonyl [15] and carboxylic acid [16] groups on the PE and PP surface. Chromic acid is the most commonly used reagent; however, for environmental reasons, its use is avoided. Even very mild treatment conditions result in the substantial oxidation of polyolefins and large increases in adhesion, as confirmed by X-ray photoelectron spectroscopy (XPS) shown in Table 8.1 [17].

Similar functionalities were introduced by an application of potassium permanganate/sulfuric acid solutions onto the PE surface [18], because sulfuric acid itself can introduce sulfonate groups on the PE substrate [19]. Adhesion methods based on the chemical ways have involved the use of strong mineral acids together with mineral oxidants or salts of strong mineral acid in aqueous solutions [20]. The use of nonchromate solutions containing sulfuric acid and either dioxide, potassium iodate, or ammonium persulfate has been also developed for treatments of different types of polyolefins for adhesive bonding applications [21]. Although later methods

Table 8.1 XPS data for polyolefins after treatment with chromic acid

Polymer	Treatment	Surface composition (at %)		
		C	O	S
LDPE	None	99.8	0.2	–
	1 min/20 °C	94.4	5.2	0.4
	6 h/70 °C	85.8	13.1	1.1
PP	None	99.8	0.2	–
	1 min/20 °C	93.4	6.3	0.3
	6 h/70 °C	94.0	5.7	0.3

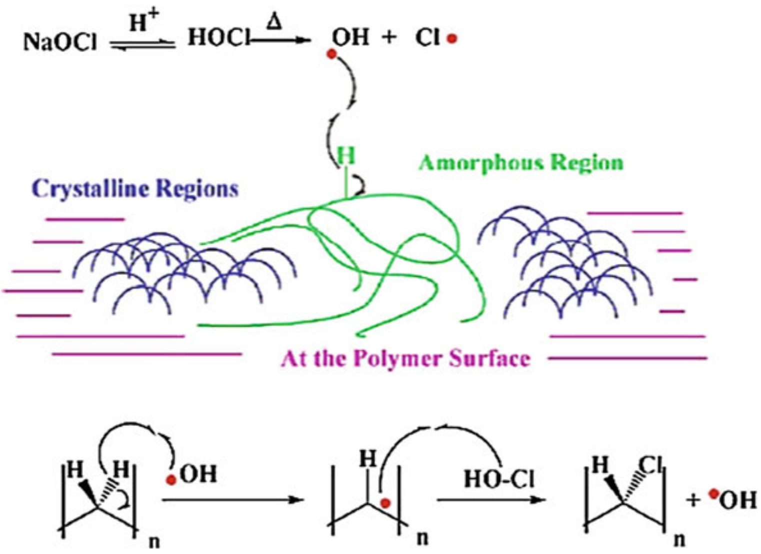


Fig. 8.2 Scheme of early hypothetical kinetic degradation model of sodium hypochlorite with subsequent reactions of released chlorine and the polymeric surface [23]

eliminated the use of the chromate, other methods based on highly toxic oxidizers have been used representing unfriendly technology, and for this reason, this method had not been used in the industrial scale. In 1997, a method was developed for unreactive polymeric materials, such as PE, using gentle adhesives after short reaction times. This technology was based on spraying or immersing the polymeric material with a dilute aqueous solution of oxidizers which were placed into a kinetically degradable state by the addition of suitable acids. Many studies regarding paint adhesion described this process as a simple resulting in improvement of substantial paintability [22]. The chlorination method of a high-density polyethylene (HDPE) surface with sodium hypochlorite was also used (Fig. 8.2). The polymeric substrate was immersed in an oxidizer-preheated solution (3–15 % aqueous sodium hypochlorite) and the acid was added to release the chlorinating species. This process made them available for the surface chlorination using the oxidizer with the kinetically degrading state [23]. Surface modification studies after the treatment process indicated resulting adhesive effects mainly as a result of the addition of chlorine atoms to the surface of the polymeric material [24].

The modification of different types of polyolefins can be performed using grafting or selected monomers in molten polyolefins using suitable organic peroxides. The synthesis of graft copolymers by the grafting of polyolefins based on molten state “onto” process was developed. Oligomers with functional groups reacted onto maleic anhydride-grafted poly(ethylene-ter-maleic anhydride-ter-methyl acrylate) [P (E-ter-MAHter-MeA)] and polypropylene (PP-g-MAH) to obtain P(E-ter-MAH-ter-MeA)-g-PMMA- and PP-g-PMMA-grafted copolymers, respectively.

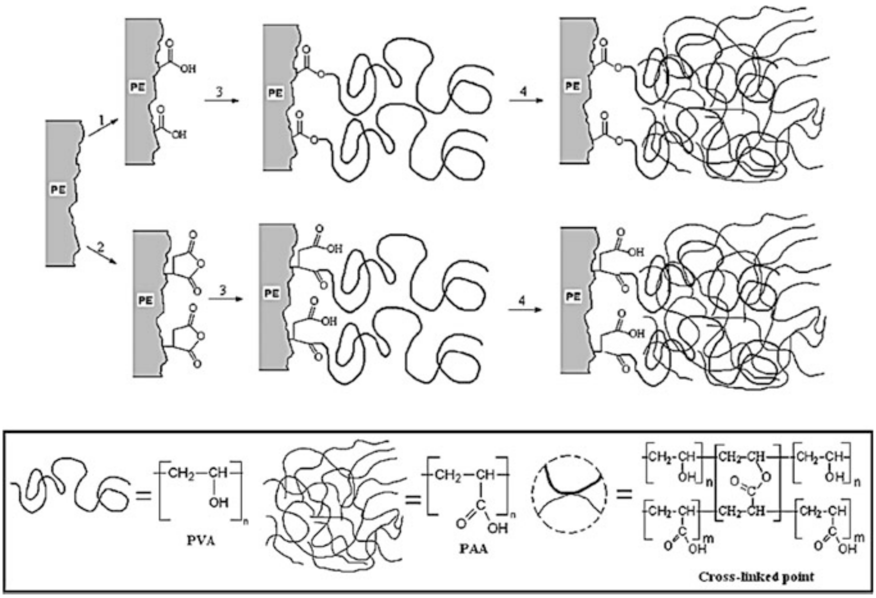


Fig. 8.3 Scheme of the chemical reactions for the PE modification [26]

The different grafting of monofunctional oligomers (aliphatic and aromatic amine, or hydroxyl functionalities) was investigated at different temperatures (180 °C and at 200 °C). The amine-terminated PMMA led to high yields in comparison with hydroxyl-terminated PMMA, whereas the grafting efficiency was very low [25].

Polymeric layers anchored on PE surface have been utilized to improve the adhesion of PE by grafting reactions. Prepared ultrathin polymer layers resulted in the permanent surface modification using covalent bonding between the polymer layers and the surface of the substrate. The procedure to prepare the anchored layers is illustrated in Fig. 8.3. The first polymer layer anchored on the substrate is responsible for the effect minimization of the polymer surface reconstruction process. The first attached layer above the PE substrate occurs melting temperature and below the melting temperature of the poly(vinyl alcohol) (PVA) coating on the PE substrate. The functionalized substrate PE in molten state allows the orientation and migration of present hydrophilic groups in the interface with the hydrophilic PVA. Moreover, the used procedure allows obtaining high conversions of the esterification process between the groups present on the substrate surface and the functional groups in coating, which resulted in a high-density anchored layer [26]. Polymer with reactive groups was used for anchoring of the second layer using the groups in the first layer. PAA was selected in this modification process due to carboxylic acid groups. In addition, PAA can form miscible blends with the PVA which was used in the first layer [27].

8.3.2 Ultraviolet Light Treatment

The interaction of photons with a polymer can result in numerous reactions, which can lead to the modification of the polymer surface [28]. The absorption of UV photons leads to electronic and/or vibrational excitation of chromophoric groups in organic materials during the interaction between UV light and polymeric materials depending on the light intensity and material properties. Polyolefins cannot be modified directly by UV light without doping with a UV-absorbing (e.g., benzophenone) molecule because the small absorption coefficient [29]. The use of a UV light can lead to an activated monomer and or the polymeric chains. Thus, UV light results in an improvement of the mechanical interlocking or monomer grafting on the polymers. The above-mentioned techniques have been successfully used to improve the interaction and compatibility of the reinforcements and polymer matrix [30]. In this preparation, the use of a photoinitiator is required to promote the monomer and surface activation. The use of polar monomers can lead to a wettability increase because of the incorporation of polar functional groups on the polymer surface [31]. Photografting can be performed in one- or two-step processes. In the one-step process, the photoinitiator and monomer are mixed together in a solvent to obtain the solution. Then, this solution is deposited onto the polymer surface. The UV radiation is responsible for an activation of the photoinitiator using the free radical formation process on the polymer surface and monomer can be interlocked successfully [32]. In the case of two-step modification process, the photoinitiator is dissolved firstly in a suitable solvent with the subsequent deposition on the polymer using UV activation. Subsequently, the monomer which was prepared in the same solvent is utilized and grafted by the UV radiation. Molecules of the photoinitiator grafted on the polymer surface are finally exchanged by monomer molecules with the same resulting effect as that in the one-step process. The one-step process is more interesting from the industrial viewpoint because the required properties can be very quickly achieved [33].

Polar monomers, such as maleic acid, acrylic acid, or vinyl acetate, can be used to obtain the hydrophilic character of nonpolar polymers. Increasing the hydrophilic character of polymers leads to an increase of the adhesive properties as well. Free radicals play the most important role in the monomer and surface activation with the subsequent monomer grafting. Therefore, photoinitiators, such as camphorquinone, hydroxyl cyclohexyl acetophenone, and butanone, are often used. Benzophenone is among the most used photoinitiators, and many studies are focused on the effect of this photoinitiator on photopolymerization processes [34, 35]. Benzophenone was successfully used to enhance the adhesion properties of PP surface by the utilization of the single-step photografting process of a methyl methacrylate for engineering applications. The detailed scheme of the activation polymer chain with benzophenone and with the subsequent bonding of methyl methacrylate monomer using UV light is shown in Fig. 8.4 [36].

Ma et al. developed the living graft polymerization consisting of two photoinduced steps [37]. Firstly, benzophenone abstracts hydrogen from the polymer

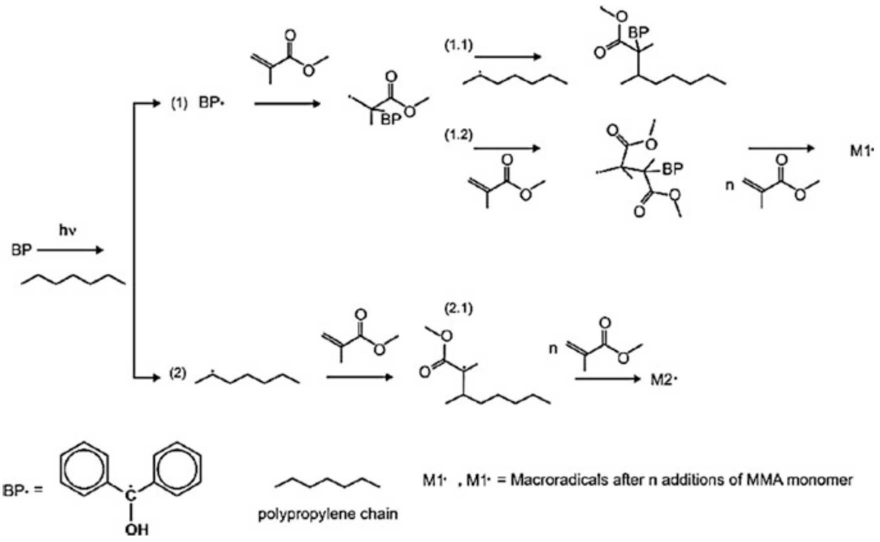


Fig. 8.4 Grafting mechanisms on polypropylene substrate and subsequent monomer grafting [36]

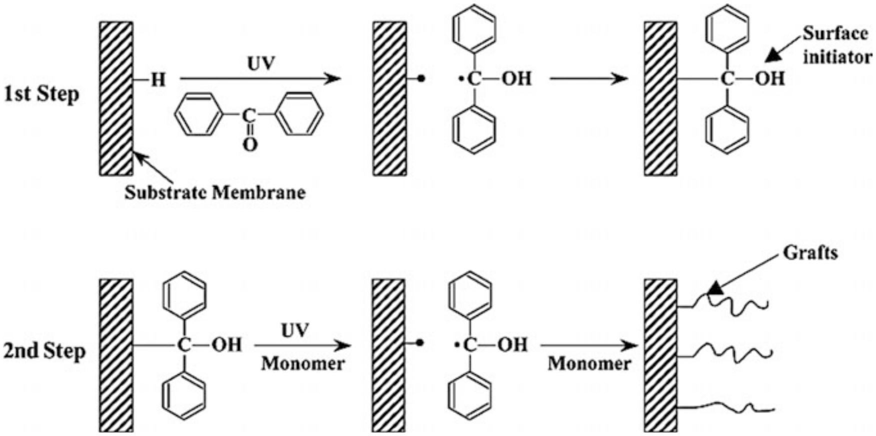


Fig. 8.5 Scheme of the photoinduced living graft polymerization [38]

substrate for the generation of surface and semipinacol radicals. These combine the formation of surface photoinitiators in the monomer solutions absence. The solutions of monomers are added onto the active substrate in the next step, and the graft polymerization under UV irradiation is initiated by the surface initiators. The graft density and chain length of created polymer can be controlled independently because the graft polymerization and initiator formation occur independently in the consecutive steps (Fig. 8.5). Moreover, this method can significantly eliminate the homopolymer formation, and branched or cross-linked polymers.

8.3.3 Flame Treatment

Flame and corona treatment belong among widely used methods for the surface activation of polyolefin surfaces [39]. The flame treatment development was proceeded together with polyolefins making them suitable adherents. Combustion ongoing during this treatment is a complex process involving many chemical reactions between a fuel (usually a hydrocarbon) and an oxidant (e.g., the oxygen in the air) leading to the heat production and light (although not always) in the flame. The chemical species migrate within the flame resulting in a subsonic wave (40–45 cm s^{-1} in case of air/hydrocarbon systems) supported by the combustion process [40, 41]. Many active radical species are created by many chemical reactions during the combustion but generally the overall process can be summarized in a few main steps, which are schematically illustrated in Fig. 8.6 [42].

Flame treatment is a suitable technique for the improvement of the surface energy of many types of polyolefins. However, it has been exploited to a minor extent in comparison with the corona treatment. Although improvements in safety conditions and in some technical aspects were observed, this approach is especially used in by industrial sector that historically lagged behind in using this treatment technique. The mechanism of free radical degradation is characteristic for the

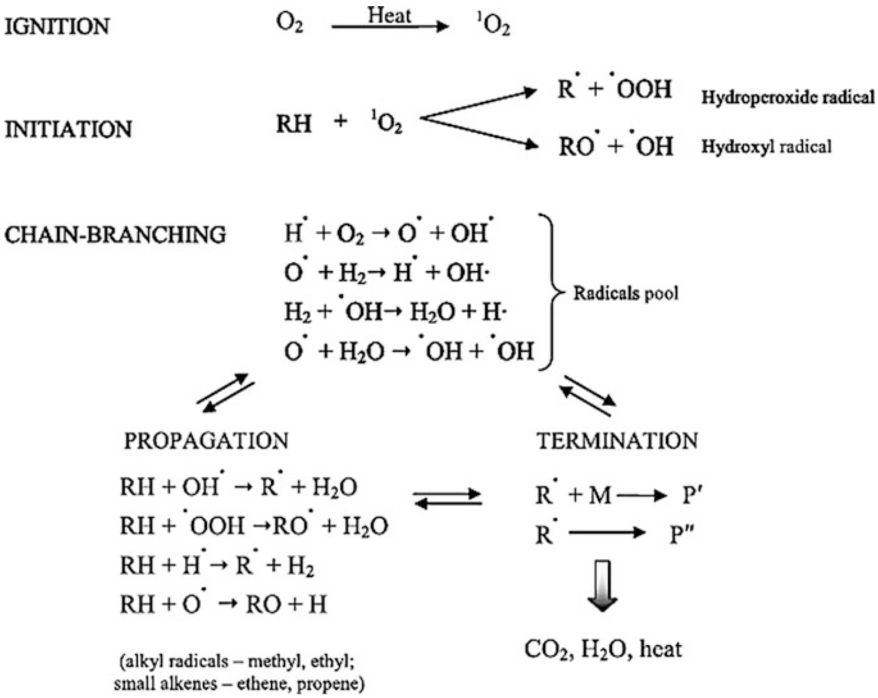


Fig. 8.6 Schematic overview of the combustion process [42]

surface activation of polyolefins by flame treatment; it occurs at the tertiary carbon in the PP chain, and in case of PE, it occurs a random attack [43]. Two main steps are present during oxidation of PP. In the first step, high temperature generated by the combustion process (~ 1700–1900 °C) leads to the breakage of the C–H links which is occurred along the polymer surface. The next step is based on the insertion of oxygen-based groups corresponding to the broken bonds resulting in the creation of new hydrophilic sites suitable for the interaction between the substrate and coating. Particularly, the oxidation process of $–CH_3$ to $–CH_2OH$ groups after the treatment was evaluated as the most relevant change in the surface chemistry influencing the wettability and adhesion properties of polyolefin surfaces [44].

In the flame treatment, the oxidation process is generally occurred by the OH• radicals. For the clarification of chemical changes in the polyolefin surface after the flame treatment, many analyzing techniques have been utilized. The increase of the oxidation level demonstrated by new formed functionalities (carbonyl, carboxyl, or hydroxyl) on polymer surface was confirmed by XPS, sometimes also called as electron spectroscopy for chemical analysis, and static secondary ion mass spectroscopy (SSIMS). It was also observed that using equal working conditions during flame treatment, more oxygen groups are incorporated into PE surface in comparison with PP surface. This phenomenon was attributed to the different domains in a semicrystalline PP than in PE. Moreover, the flame treatment affects predominantly amorphous regions rather than crystalline [45].

For the adhesion improvement of polyolefin objects with a relative large thickness, flame treatment is usually used. This method was successfully used to enhance the adhesion of PE bottles to the printing inks many years ago. Recently, the flame treatment is often used for the adhesion improvement of PP car bumpers for painting. One or more burners are used for the treatment of objects, each of which is consisted of many jets. An air–hydrocarbon gas mixture is usually added to the burners with controlled proportions. The optimal time during flame treatment using methane for an unspecified polyolefin was 0.02 s [46]. Analyses of the flame treatment of PE surface confirmed very high oxidation levels, while the thickness of oxidized layer was only 4–9 nm [47]. The use of fuel gas–oxygen flame treatment with an acetylene or propane/butane with excess oxygen leads to the oxidative surface modification. The flame treatment is predominantly suitable for handicraft applications due to low expenditures. The flame treatment time is in the range of seconds, and the distance of the flame to surface should be approximately 5–10 cm. For polyolefins such as PE and PP, care should be arranged to avoid the surface from melting [48].

The used flame treaters for treatment of polyolefin surfaces in packaging applications depend on whether the sample to be treated has a three- or two-dimensional geometry. Three prime components can be recognized in both cases. The three-dimensional treatment plant is typically consisted of following parts (Fig. 8.7a). A conveyor belt is used for a continually treatment of material, such as polyolefin objects mounted on special heat resistant holders. A cleaning equipment, such as brush-like system or a compressed air stream, commonly placed a few centimeters in front of the burners allows removing of all small particles, such

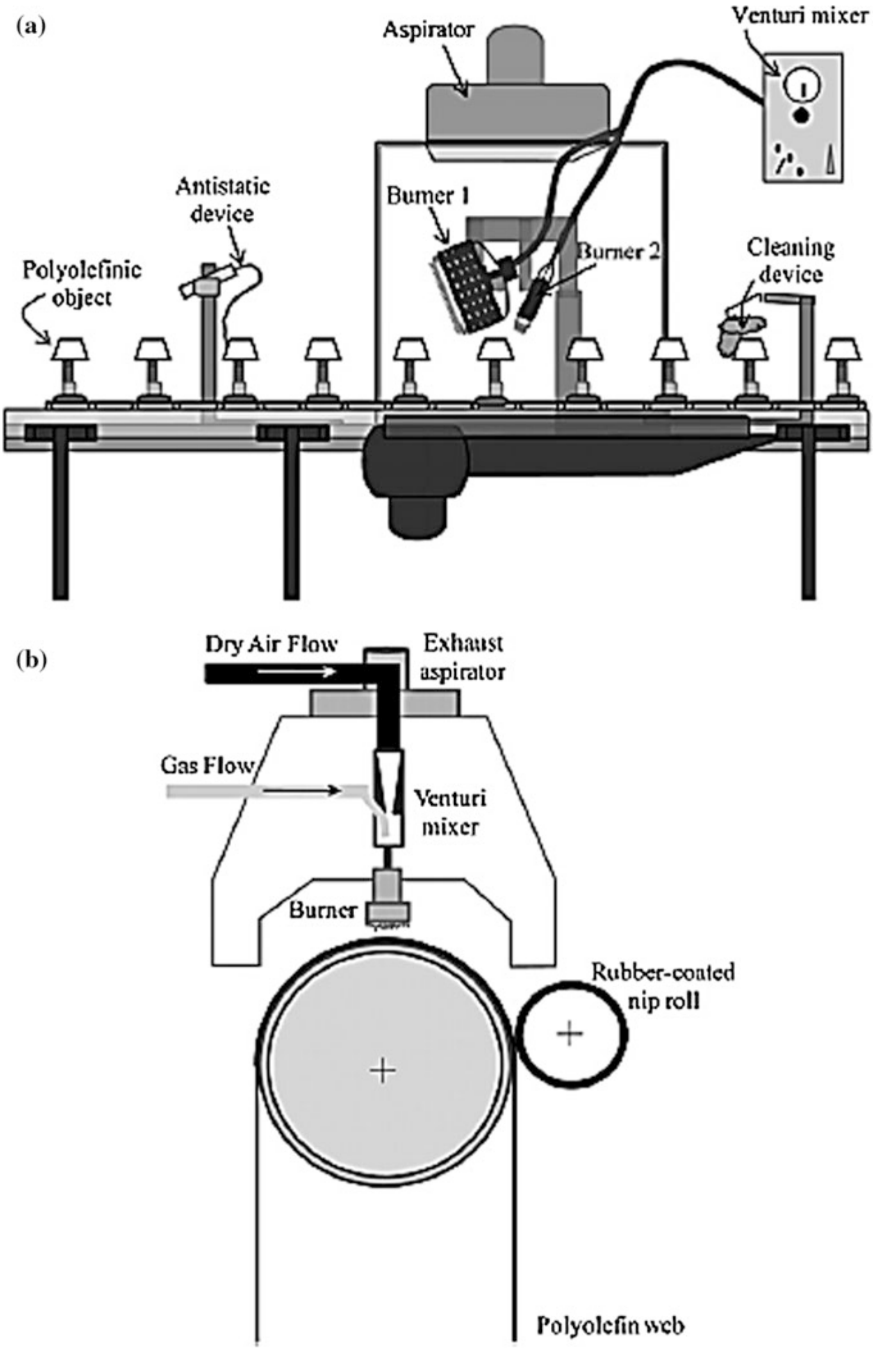


Fig. 8.7 Scheme of a flame treatment system for polyolefins: **a** three-dimensional objects and **b** flexible films [42]

as dust, negatively affecting proper flame treatment. A burner is the prime part of the treater producing the oxidizing flame. On the other side, a typical flame treatment plant for flexible films is conceived as following parts (Fig. 8.7b). A burner is suitable for the production of an appropriate flame necessary for the surface treatment of the web. A treater roll enabling rewinding of treated films is normally water-cooled and allows the prevention of any undesirable damage caused by overheating. A nip roll is part to exert a specific pressure on the film to achieve required contact between the cooled roll and web. This part is usually coated by rubber. Moreover, the function is the prevention of the bubble or blister formation, which can lead to the impeding of the right thermal exchange between the treater roll and web [42].

8.3.4 Plasma Treatment

Plasma can be generated by the application of enough energy to a gas leading to the reorganization of the electronic structure of the atoms or molecules species and to the production of excited species and ions. The energy necessary for this process can be achieved by either thermal or electrical/electromagnetic source. The energy is transmitted to the gas electrons representing the most movable charged species by the electric field. The subsequent collisions are responsible for the subsequent transmission of this energy to the neutral species. The collisions can be divided into elastic or inelastic collisions which follow probabilistic laws. Elastic collisions slightly raise their kinetic energy without changes of the internal energy of neutral species. Inelastic collisions modify the electronic structure of neutral species by enough high energy resulting in the creation of excited species or ions [49].

The plasma state represents a gaseous mixture consisted of oppositely charged particles. Plasma represents highly ionized gas obtained by high-energy radiation or an electric field. Electrons are released and heavy-charged particles are produced during these processes. Hot plasma representing near-equilibrium plasma and cold plasma or nonequilibrium plasma are two basic examples of plasma states. Hot plasma is characterized by a very high temperature of electrons and heavy particles (more than 1 MK), and the degree of ionization is almost 100 %. Cold plasma contains particles at low temperature, such as charged, neutral molecular or atomic species, while the temperature of electrons is a relatively high with a low degree of ionization (approximately 10 %). Plasma jets of rocket engines, electrical arcs, and thermonuclear reactions are typical representatives of hot plasma. On the other side, radio-frequency (RF) discharges, low-pressure direct current, and discharges in fluorescent (neon) tubes are representatives of cold plasma. Corona discharge is also cold plasma [50].

For many industrial applications of polyolefin materials that depend on adhesive bonding, surface treatment by cold plasma became preferred in industrial process. The plasma treatment is a surface modification process by which the bulk properties of the material are retained [51]. Plasma surface treatment is a very effective way to

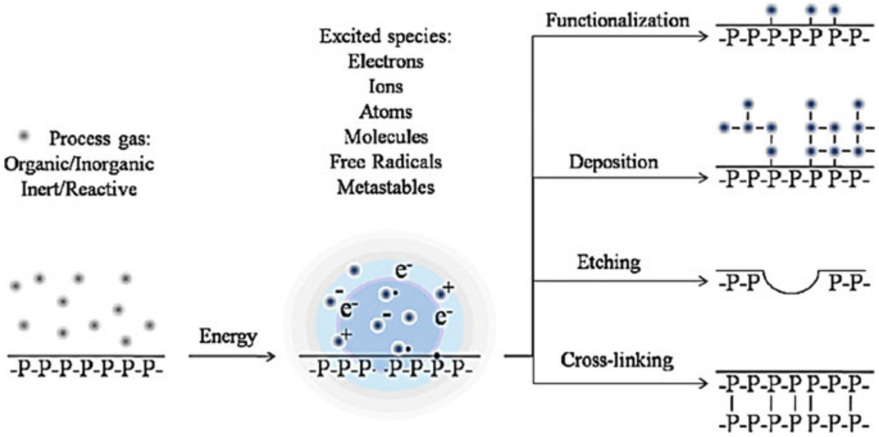


Fig. 8.8 Surface modification processes using the plasma discharge [53]

achieve the hydrophilic character of the polymer substrate surface. The plasma treatment generates radicals on the polymer surface by either scission of polymer chains (bombarding actions) or removing hydrogen in the first step. The created radicals can subsequently interact with other elements present in the used atmosphere and lead to functionalization processes, such as an incorporation of hydroxyl, carbonyl, carboxyl, and ether groups [52]. Moreover, the plasma treatment can lead to etching/ablation or cross-linking processes (Fig. 8.8) [53, 54]. The bombardment of weak bonds in polymer by high-energetic particles is responsible for the ablation process. The outermost molecular layers exposed to the plasma lead to the evaporation of small volatile fragments in this process. Multiple links between the molecular chains of polymers is characterized for the cross-linking process. The use of inert gases during the plasma process can lead to the production of cross-linked polymers or hard substrate microstructures [55].

The increase of the surface energy (wettability) can be caused by the incorporation of new polar functional groups. These groups are responsible for an enhancement of the wettability that facilitates spontaneous spreading of the adhesive or matrix resin. Moreover, the formation of these functional groups enhances covalent bonding between adhesive/resin and the substrate. This process is also characterized by the precise control of the parameters ensuring significant repeatability in industrial applications. Plasma treatment has an impact on adhesion between substrate and adhesive. The adhesive is better joined to the substrate because of the increase of the wettability and surface roughness [56, 57].

Many physical properties determine the performance of the plasma source as well as how well the plasmas are able to activate the polymer surface. The physical properties of different types of atmospheric pressure plasmas are shown in Table 8.2. In a torch, plasma densities can be extremely high, from 10^{16} to 10^{19} cm^{-3}, with average electron temperatures of 1–2 eV (1.0 eV = 11,605 K) whereby the density of neutral species is $\sim 10^{19}$ cm^{-3}. Because of the heat-sensitive

Table 8.2 Physical properties of plasma discharges

Plasma type	Working gas	V_B (kV)	n_e (cm^{-3})	T_n (K)	T_e (eV)
Corona	Air	2–20	10^9 to 10^{13}	<600	3–5
DBD	Air	2–20	10^{12} to 10^{15}	<700	1–10
RFD	Noble	0.1–0.6	10^{11} to 10^{12}	<600	1–2

V_B is the breakdown voltage, n_e is the electron density, T_n is the neutral gas temperature, T_e is the electron temperature

nature of polymer materials, a high gas temperature will damage or melt the substrate. Therefore, the neutral gas temperature of the plasma is an important parameter affecting the performance of plasmas for processing polymers and composites. In a plasma torch, the high collision rate of electrons with neutrals causes rapid heating of the gas to temperatures between 5000 and 14,000 K. These temperatures are not suitable for the treatment of polymers. Nevertheless, it is possible to blow a sufficient amount of gas through the arc such that the total gas temperature is low enough for the treatment of thermally sensitive materials. This possibility is achieved by a system that uses a rotating electrode. This electrode rapidly spins the arc in the gas, maintaining an overall neutral temperature near 600 K. Plasma streamers treat polymer substrates placed downstream. Although this system has been proven industrially for surface activation, there appears to be a lack of published information on the properties of the plasma [58–62].

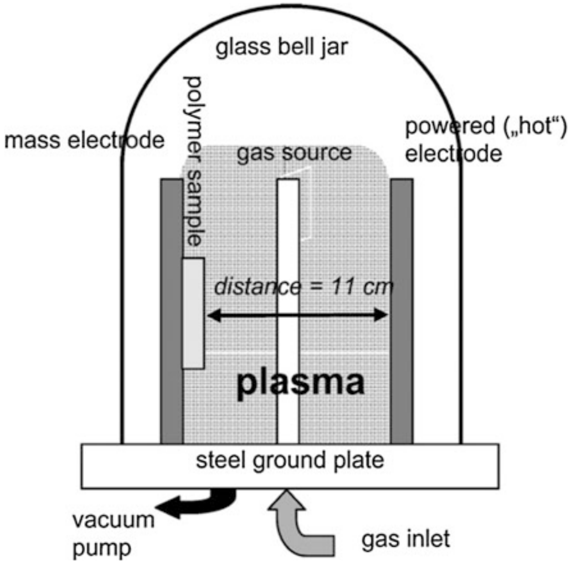
Corona and dielectric barrier discharges (DBD) operating in air atmosphere as the supply gas exhibit electron densities in the range of 10^9 to 10^{13} and 10^{12} to 10^{15} cm^{-3}, respectively, and average electron temperatures between 1 and 10 eV [63]. Corona discharge applied on polymer surfaces leads to the introduction of polar functional groups, which results in the increase of the surface energy improving the wettability of the substrate associated with adhesion characteristics. Oxidation represents the principal mechanism of the corona treatment. However, corona treatment can lead to the cross-linking of the surface regions resulting in the increase of the cohesive strength of the film. The above-mentioned mechanisms can impart improved surface properties of treated surfaces. Many other gases can be used during corona treatment process leading to the enhancement of the adhesion and wetting characteristics, while they can produce some polar functional groups and reactive species. XPS analyses confirmed that oxygen was incorporated into the surface of the treated surface in case of the use of different gases. Therefore, oxidation process plays the main role during corona treatment under different working gases to ensure sufficient adhesion [64].

Corona treatment represents the most widely used technique for the treatment of polymeric films due to very high speed of the treatment, very good efficiency, and low operating costs. PP and PE belonging to the group of polyolefins exhibit low surface energy because of the hydrophobic character, which deteriorates the wettability of inks, varnishes, or adhesives [65]. The surface tension of PP is approximately 30 mJ/m^2, while a minimum value required for printing and lamination process is generally about 37 and 42 mJ/m^2, respectively [66, 67]. The corona treatment is generated by nondestructive, continuous, and maintainable electrical discharge, when an enough high voltage is utilized between two electrodes of asymmetric shape, such as thin wire and cylinder. Air ionization is allowed by a very high electric field formed in the near region of thin wire or tip and the formed ions are driven toward the cylinder having a low electric field [68]. Negative, positive, direct, or alternating current belong among some operating settings that can be applied during corona treatment, which depend on the current in the device and active electrode polarity [69, 70]. The resulted surfaces after the corona treatment can be varied depending on the settings used during treatment [71]. The degradation effect of PP surface present after corona treatment is mainly as a result of the oxidative process [72–74] leading to the formation of oxygenated species, such as carbonyl, peroxide, esters, or carboxylic acids.

Glow discharge plasma was used by Pandiyaraj et al. [75] for the treatment of PP film surfaces, which led to the improvement of adhesion characteristics. The effect of various used working gases, mainly oxygen and nitrogen on the PP surface during the corona treatment, was studied by Carlsson and Wiles. Nitrogen derivatives were not proven on the treated surface, but the unsaturated formation was observed using the nitrogen gas. However, when the corona treatment was performed in an oxygen atmosphere, the polymer contained carbonyl and hydroxyl groups was confirmed as a result of the oxygen incorporation into the polymer surface [76]. The adhesion properties achieved after oxygen plasma treatments of polyolefin materials of different compositions were studied. Conditions during plasma treatment and the chemical composition of the treated materials strongly affected their adhesion with a polyurethane lacquer. Generally, a high content of ethylene and a low-pressure ratio of power-to-gas during the plasma process preferably lead to the formation of blocks and/or the double bonds present in the matrix suitable for good adhesion [11].

The polyolefin (PE, PP) surface functionalization using the bromoform or bromine plasma, is very selective and produces high concentrations of C–Br groups [77]. This low-pressure process is the only known way for the introduction of monosort functional groups onto polyolefin surfaces and was observed 20 years ago [78]. The detailed process using bromination technique was studied [79]. Later, the technique based on the pulsed plasma was used for the bromination of the polyolefin surfaces using bromoform and bromine as working plasma gas (vapor). Moreover, Br-containing monomers for the deposition of Br-carrying plasma polymer layers onto surfaces of polyolefins were also used [80]. The bromination (plasma halogenation) was carried out in a reactor (glass bell jar) with a steel ground plate (diode-type reactor). The sample was positioned at the mass electrode or optionally at a rotating and grounded sample holder used for the exposure of larger foils. The plasma equipment is shown schematically in Fig. 8.9. The grafting onto brominated PP foils was performed by immersing the brominated foil in tetrahydrofuran solutions of diols, glycols, or diamines and sodium metal (0.5 mol) [81].

Fig. 8.9 Scheme of the plasma reactor for PP bromination [77]



8.4 Characterization

The information about the chemical and physical characteristics is required for the adhesion of the delamination and adhering surfaces where adhesion failed during the use or due to mechanical testing. Several surface-analyzing techniques and methods were applied for the investigation of various properties related to adhesion strength and adhesion mechanisms. They include atomic force microscopy (AFM), secondary electron microscopy (SEM), XPS, time-of-flight secondary ion mass spectrometry (ToF-SIMS), attenuated total reflectance infrared spectroscopy (ATR-IR), and other techniques such as optical contact angle techniques. Many studies have investigated surface properties regarding polarity, surface energy, chemical composition, and roughness for the description and explanation of the adhesion phenomena at an interface or surface area using the above-mentioned analyzing techniques. Peel tests, pull-off tests, shear and lap tests, and scratch tests were used for direct adhesion measurements representing destructive methods measuring the force necessary for the break, delaminate, or tear the surfaces at the interface. The surface analyses and adhesion measurements using different techniques such as contact angle measurements, XPS, and ToF-SIMS represent optimum methods for the investigation of adhesion characteristics [82].

8.4.1 Surface Characterization

The information about the actual chemical composition of surfaces dominating by the nanostructured materials properties can be obtained by XPS. The travel of electrons in short distances (nanometers) in XPS can provide valuable information about the nanometer-sized structures of the materials in the near-surface region [83]. This technique can provide both quantitative and qualitative information for all elements. Bonding states together with the elemental information allow understanding the chemistry of the adhesive interface. Moreover, quantitative correlations between functional and elemental groups present in the surface area and adhesion strength or surface energy can be obtained by XPS [84].

The infrared spectroscopy can be used for analytical characterization of the chemical composition of polyolefins [85]. The study of material surfaces can be realized by Fourier transform infrared spectroscopy (FTIR), which represents one of the major analytical techniques. FTIR as rapid, noninvasive and inexpensive technique allows the quality screening. FTIR is considered as a molecular "fingerprinting" method. This method covered features of infrared spectrum from the molecular bond vibrations in the mid-infrared region (400–4000 cm^{-1}), and it is highly sensitive to the precise analyses of the chemical composition of the sample. The information about the chemical composition of various materials is provided by mid-infrared with the physical or chemical sensitivity of the absorption bands of the individual constituents. The detections of constituents in low concentrations and hardly noticeable compositional differences between multiconstituent specimens are possible by the high spectral signal-to-noise ratio, which is obtained from this modern instrumental analysis. Moreover, FTIR equipment can be equipped with some accessories, such as attenuated total reflectance (ATR). This accessory allows the analyses of solid or liquid components in a wide range (Fig. 8.10) [86]. ATR-FTIR was used for the characterization of enhanced adhesion between PE and

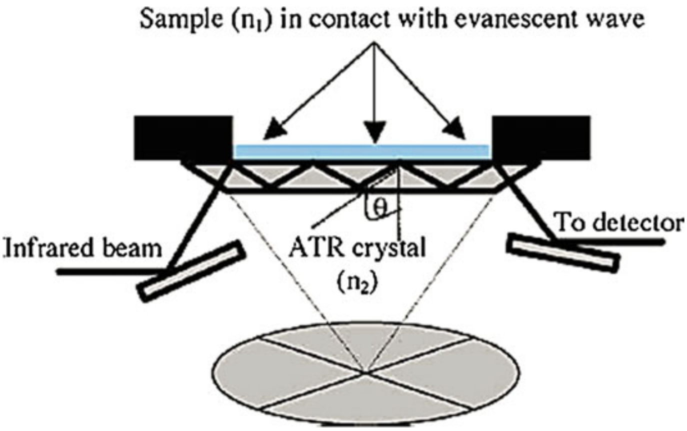


Fig. 8.10 Schematic representation of horizontal ATR system. n_1 and n_2 represent the refractive indices of the crystal and sample, respectively [86]

grafted acrylic acid (PE-g-AAc). Covalent bonds formed between carboxylic groups of grafted AA and amine groups of the hardener led to the improved adhesion [87].

ToF-SIMS is a powerful technique for the chemical characterization of the constituents in the upper monomolecular layer of various industrial materials. From the analytical viewpoint, its capability for the detection of molecular secondary ions as well as structural fragments with high sensitivity has a large potential for the evaluation of low levels of organic contamination on the sample surface, identification of the molecules, study of segregation of additives, and detection of surface functionalities and is commonly applicable to a wide variety of materials [88].

Wettability and surface energy of the investigated samples can be measured by the contact angle analysis representing a surface-sensitive technique. The main principle is the dispersion of polar and nonpolar liquids onto the sample surface, and the angle making by the liquids with the surface is recorded. More wettable surface is characterized by small contact angles with a high surface energy and also a great work of adhesion. The measurements of contact angles are involved in wettability analyses, which indicate the degree of wetting at the solid–liquid interface. High wettability is associated with small contact angles ($\theta < 90°$), while high contact angles relate to the low wettability ($\theta > 90°$) (Fig. 8.11) [89].

SEM is a fast method for obtaining detailed morphological information for different polyolefins. This method is valuable tool for the analyses of polyolefins, and it is extensively used for the analyses of failure and fracture mechanics, shape and particle size, filler dispersion, and orientation in polymer matrices [90]. A few nanometer spatial resolution and a large depth of field can be obtained by SEM, and it can work up to 100 times that of an optical microscope in some cases. From these features, information about topography of the sample surface can be obtained necessary for a deeper understanding of the interaction between the substrate and the surface treatment [91].

From the AFM measurements, the three-dimensional and force resolution can be obtained on the order of angstroms and tens of piconewtons, respectively. For this reason, this technique is suitable for the study of detailed morphology and physico-chemical properties of the investigated materials in the nanoscale which is important in the polymer-modified material surface field. Moreover, this technique can be used instead of some traditional techniques with lack for the lateral

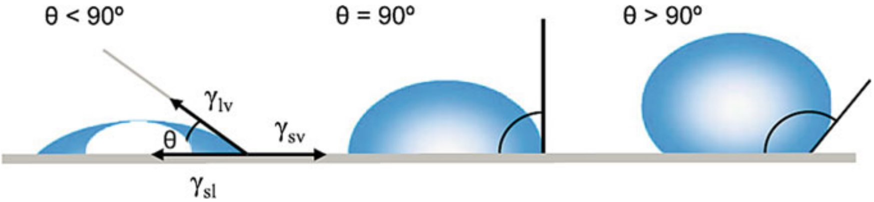


Fig. 8.11 Examples of contact angles formed on a smooth solid surface by sessile liquid drops [89]

resolution characterization in the nanometer scale necessary for the analyses of polymer nanostructures or nanopatterns, laterally inhomogeneous monolayers and submonolayers, macromolecular-sized clusters, which provide a direct analysis of polymers anchored on surfaces in different solvent conditions. Many techniques, such as a solution-based processes (e.g., spraying, spin-coating, dip-coating, and droplet-evaporation), are utilized, and subsequently, direct measurements in a good solvent are possible by AFM because it is a suitable tool for the material surface investigation modified by mono- and submono-layers [92].

8.4.2 Characterization of Adhesion

The peel test represents an outstanding type of the adhesion test. In this test, tape with adhesive is placed and subsequently pressed on the sample surface, which should be tested, such as an ink/paint layer on the substrate. A rubber cylinder applies the pressure with defined force and in a repeatable manner. In Fig. 8.12, a scheme of a 90° peel test with characterization of the bending and unbending areas is presented [93]. The study of Mahlberg et al. [94] investigated adhesion by peel tests at 90° of peeling. It was observed that the adhesion of oxygen plasma-treated PP and lignocelluloses increased. These researchers also observed that adhesion is enhanced if the substrate and film are treated by oxygen plasma. The peel strength increase of the adhesive joint of HDPE grafted with alkoxy silane using RF plasma discharge to polyacrylate was confirmed in the study of Novák et al. [95].

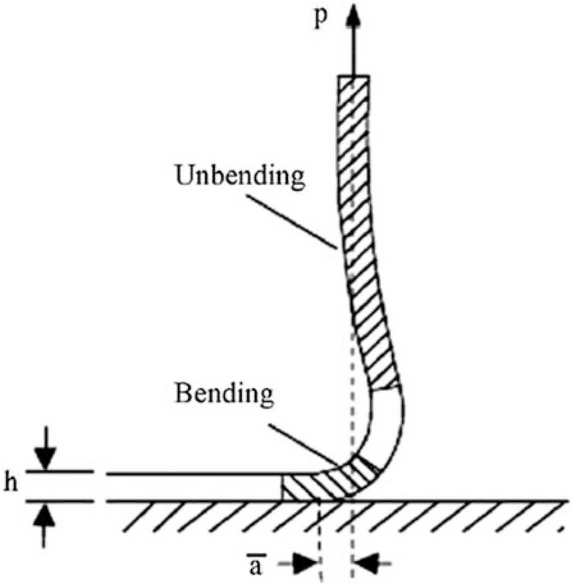


Fig. 8.12 Schematic of peel test. *P*, *h,* and $\bar{a}$ represent the applied shear force, beam depth, and beam length, respectively [93]

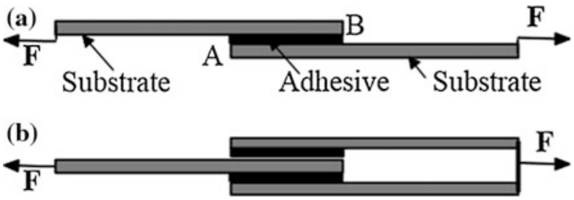
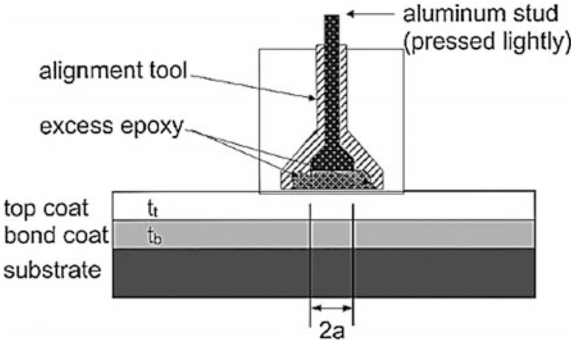


Fig. 8.13 Principles of lap shear specimens [97]

Fig. 8.14 Schematic illustration of stud with applied epoxy attached to a duplex coating [99]



Lap shear tests are close to peel tests; however, this method is more quantitative in the base. Two sheets are bonded to each other by toughened adhesives (acrylic) in the test configuration and tensile tester applies load at a rate of usually 1 mm/min [96]. The lap shear specimen represents the most utilized geometry for studies of adhesive bonding because specimens as single- or double-lap shears (Fig. 8.13a, b) are easy for the measurement [97].

Stud or butt tests representing pull-off tests used for the measurements of the adhesion characteristics between an ink/paint coating and the substrate. An adhesive is applied to the paint coating, and a metallic stud made of aluminum is glued onto the surface by the adhesive applied to the paint coating. Subsequently, the pull force is utilized perpendicular to the substrate surface with a constant rate. This measurement provides an excellent measurement of adhesion for systems, for example, for polymer–metal interfaces [98]. Figure 8.14 schematically illustrates the pull-off test schematically [99].

The scratch tests are very similar to the nanoindentation tests and can be considered side by side. In both techniques, a prime tip is used for the adhesion measurements by dragging across the measuring surface under an increasing load, which results in an indentation. Scratch and indentation tests are suitable for the analyses of the coatings and thin films [100]. Sharp diamond indenters are usually used for the adhesion and scratch resistance determination between the substrate and coating. These techniques can fail for the analyses of hard coatings on soft substrates due to no detectable failures as a result of small critical loads. Therefore, in the industrial applications, many provisional and subjective methods are performed, but the quantitative comparability is complicated with commonly used methods due to defects already occurred during application of small loads for relatively soft and ductile materials, such as plastics. For the above-mentioned reason, a tribological–mechanical test method (in macroscopic scale) can be used. This method uses hardened steel-based balls as indenters, and it can be used for both hard and soft coatings applied on different materials. Different wear and stress levels can analyze the interface of the substrate and coatings as well as mechanical and tribological behavior between the body and counterpart by varying the ball-diameter, the sliding speed, and normal contact force [101].

8.5 Applications

Polyolefins represent a substantial part of the worldwide production of the commercial polymers [102]. These polymers belong among materials with good performance and cost-effectiveness used in different applications; however, less attention is paid to their specialty applications, such as functions of the multiple performance. The shortcomings and limitations of polyolefins have originated from a lack of structure diversity and functionality compounded with the long-time challenges in the polyolefin modification. Some functional polyolefins containing flexible polar groups, which offer great mobility for polarization (hydroxylated PE or PP), have been used to form distinctive multiple-phase morphology excels hydrophobic–hydrophilic microphase separation. These materials show the potential of polyolefins in high-value, specialty applications such as high-energy and power density capacitor, ion-conducting membranes for batteries and fuel cells, or oil-superabsorbent for oil spill recovery [103]. The adhesion modification using various modification methods on the surface as well as in the mass of the polyolefins allows a new class of cost-effective and high-performance functional polyolefins to be prepared.

Recently, a noticeable increase in the application of polyolefins (LDPE, LLDPE, HDPE, isotactic PP and polyolefin copolymers) in industry was observed. This state is predominantly because of the outstanding balance between the exceptional surface properties, such as the easy processability, chemical barrier response, or surface finishing [104], which favors the growing use of polyolefin-based material, i.e., polyolefins and their composites in various applications in medicine, automotive, aerospace, electronics, and packaging. Polyolefin-based materials are in most cases combined with some other materials (polymeric or metallic), such as membranes, foams, or other polymeric films leading to the formation of laminates [105–107]. Generally, polyolefins excel great chemical inertness lading to poor adhesion and low surface energy. Various applications require the use of polyolefins with good mechanical properties and adhesion of these polymers.

Applications in the automotive industry require laminate polyolefin-based materials for the achievement of the multifunctional requirements (good chemical/mechanical properties or good surface finishing). Important efforts for various application purposes were focused on the application of different polyolefin modifications, for example, chemical [108, 109], physical [110, 111] or electrical [112, 113] modification at the improvement of the surface activity of polymers. Recently, the electrical discharge use over the gas methods (plasma treatments) was stabilized as surface treatments as useful for the modification of the topmost layers of polyolefins with remaining of the bulk properties. These methods lead to the promotion of a significant increase of the adhesive properties of polyolefins in laminates [114–116]. Some of the laminates have been prepared using a polyolefin foam with a reactive polyurethane as the adhesive and the low-density polyethylene (LDPE) film exposed to RF plasma. Glow discharge plasma generated with O_2 or in air at low-pressure represents the suitable surface treatment for the wettability and adhesive properties improvement of LDPE film used for the laminates formation with the polyolefin foam in the automotive industry. Effects of different gases used during plasma treatment process are similar since the functionalization process occurs by the oxygen-based species insertion. In addition, the plasma treatment can lead to the production of some surface etching (abrasion) responsible for the small surface roughness increase also contributing the improvement of adhesion properties. Laminates prepared from plasma-treated PE foils and the polyolefin foams excel by appropriate mechanical properties suitable for the use in technological applications. The adhesive joint has high durability once laminates are prepared. Moreover, the laminate durability under different conditions (temperature and relative humidity) was proven for automotive testing [117]. It was observed that the laminates are characterized by the good resistance under these mentioned conditions, and therefore, they are useful for the application in the automotive industry. However, a small decrease of the T-peel strength was observed because of the aging effect with more sensitivity to the temperature in comparison with the relative humidity.

The adhesives and the associated adhesion mechanisms have been investigated for more than 50 years in the aerospace and automotive industries. Recently, polyolefins were interested in the adhesion sector due to their advantageous bulk properties, good mechanical properties and low cost [118, 119]. The adhesion characteristics between the paint substrate layer and polymer are controlled by the chemical groups at the interface. The paint coating attachment to a polymer bumper is an adhesive system an example in the automotive industry. These bumpers are usually made of PP, which exhibits poor adhesive properties. Many strategies and modification methods can lead to the improvement of the adhesion properties, including an addition of adhesion promoters (chlorinated polyolefins) [120], flame treatment of the PP [121], plasma treatment of PP leading to the promotion of the polar functional groups on the surface [122], or blending with ethylene propylene rubber allowing the formation of thermoplastic polyolefins [123, 124].

Civil engineering and biomedical industries belong among other industries actively investigating the adhesion of polymers. The largest user of polymers is represented by building industry, such as polymer-based sealants and thermoplastic roofing membranes. The prime utilization of sealants is in circumstances requiring the ability to resist thermal expansion and contraction with still enough bonding to the substrate [125]. The polymer adhesion, especially for polymer composites, is still investigated by the industry.

In the last decade, the modification for the improvement of the polymer adhesion has been motivated by the increasing needs in the aerospace and automotive for better adhesion between components and applied surface coatings [126]. The manufactures should produce polymer products with enhanced surface and adhesion properties by taking advantage of the surface segregation effect. Researchers should also enhance the knowledge about polymer additives promoting adhesion properties and interactions with the segregation phenomenon. These findings can assist to manufacturers with the elimination of the needs often environmentally hazardous and expensive treatments of parts used in automotive, aircraft and space engineering, development and production [127, 128]. Investigation of polymeric materials' adhesion modification represents an important challenge in modern human medicine. Biomimetic polymeric materials promote a favorable response from cells and tissues for scaffold and implant preparation in tissue engineering and regenerative medicine. Bioinert polymers, that suppress nonspecific adhesion, that induce thrombosis and immunological responses are required for most biomedical devices and implants, such as blood- or tissue-contacting and biosensing devices. The possible mechanisms of anti-adhesion to a cell are closely associated with the design criteria for polymer-modified bioinert surfaces, which contain surface energy, electrostatic interaction, steric repulsion, hydration, and topography. The anti-adhesion polymeric materials have been considered and developed for widespread applications such as cell sheet engineering, multicellular spheroid formation, cell encapsulation, and blood-contacting devices [129, 130].

Polyolefins, such as PE and PP, are commonly used in many applications in the biomedical sector. PE and PP can achieve biocompatible and antimicrobial properties using the suitable surface treatment [131, 132]. Many modification methods of the polymer surfaces have been employed, for example, techniques based on the plasma treatment [133]. A deposition of chitosan on the plasma-pretreated PP surface provides antifungal and antibacterial properties because chitosan exhibits an efficient antimicrobial activity [134]. If PE films were modified by a multistep process using plasma discharge, carboxylic groups and antibacterial agent can be developed over the surface. Immersion of these films into the solution of chitosan leads most likely to the adherence of a chitosan monolayer on the treated film. Small concentration of chitosan was enough for the induction of antimicrobial properties to the modified material [135].

8.6 Conclusions

The adhesion properties of all types of polyolefins are not easy to explain because these properties are affected by different phenomena. Using of a single theory or mechanisms based on the physical and chemical adhesion manifestations is difficult for the description of interdisciplinary nature and diversity. There is considerable information to discuss each of the adhesion mechanisms. Therefore, it is not possible to select only the thermodynamic theory of adhesion that is the best to describe the surface free energy of the polyolefin. All mechanisms and adhesion theories are implied by the diversity of polymer systems, which are embraced in combination with research for the analyses of adhesion properties. The physical and chemical composition in the first atomic layers dictates the adhesion and some other properties of the polymer materials. This layer represents underneath layer and this subsurface partially controls the outer layers. The double bonds and cross-linked structures limit the mobility macromolecules of polyolefins in the subsurface layers, which results in the functional group stabilization on the surface. Other basic research is necessary for an examination of the polymer subsurface layer and explanation of its effect changes of the surface properties. Moreover, for the improvement of quantitative measurements of adhesion, additional investigation is required.

There is no best method that has been used for polyolefin adhesion characterization, which is used to provide an outright value for adhesion. The adhesion test majority being qualitative or results reporting obtained from the set of samples can explain these findings. Producers of polyolefins should also count with effect associated with the surface segregation for the production of the polymer products excel by enhanced surface properties. Scientists in basic research should improve the knowledge of polyolefin additives promoting adhesion and relations with the segregation effects. These findings can support the manufacturing process to obviate expensive needs and environmentally hazardous surface treatments of polyolefin products. Nondestructive analysis such as XPS and ToF-SIMS for polyolefin surfaces should be more developed for providing detailed information about their structures. The test with nondestructive effect of the test allows examination of polyolefin surface with higher accuracy. Analyses of structural information and surface energy or adhesion strength have great potential to understand their correlations. Advances have been made recently in the accurate analysis of the surface chemical compositions and surface topography (nanoindentation, AFM) having theoretical and practical potential for the adhesion of polyolefins understanding. The comparative studies with adhesion strength tests will provide the knowledge and correlations between the chemical bonding mechanism and adhesion properties. Moreover, the production of polyolefins with tailored adhesion strength can be realized using modifications/treatments that were realized in the chemical structure of their surface.

References

1. M.J. Shenton, M.C. Lovell-Hoare, G.C. Stevens, Adhesion enhancement of polymer surfaces by atmospheric plasma treatment. J. Phys. D **34**, 2754–2760 (2001)
2. I. Novák, A. Popelka, I. Chodák, J. Sedliačik, Study of adhesion and surface properties of polypropylene. In *Polypropylene 2012*, ed. by F. Dogan, InTech. pp. 1–37
3. A.J. Kinloch, in *Adhesives in Engineering* (IMechE, London, 1996)
4. D.E. Packham, Theories of fundamental adhesion. In *Handbook of Adhesion Technology*, ed. by L.F.M. da Silva, A. Öchsner, R.D. Adams (Springer, Berlin, 2011), pp. 9–38
5. S. Gorb, in *Attachment Devices of Insect Cuticle* (Kluwer, Berlin, 2002)
6. A.J. Kinloch, Review—the science of adhesion part I, surface and interfacial aspects. J. Mater. Sci. **15**, 2141–2166 (1980)
7. S. Ebnesajjad, Theories of adhesion. In *Surface Treatment of Materials for Adhesive Bonding*, 2nd edn., ed. by William Andrew (Oxford University Press, Oxford, 2014), pp. 77–91
8. S. Yang, L. Gu, R.F. Gibson, Nondestructive detection of weak joints in adhesively bonded composite structures. Compos. Struct. **51**, 63–71 (2001)
9. D.M. Brewis and I. Mathieson. Adhesion and Bonding to Polyolefins. Rapra reports, 2002
10. J.M. Lane, D.J. Hourston, Surface treatments of polyolefins. Prog. Org. Coat. **21**, 269–284 (1993)
11. A. Nihlstrand, T. Hjertberg, K. Johansson, Plasma treatment of polyolefins: influence of material composition: 2. Lacquer adhesion and locus of failure. Polymer **38**, 3591–3599 (1997)
12. J. Takahashi, A. Hotta, Adhesion enhancement of polyolefins by diamond like carbon coating and photografting polymerization. Diam. Relat. Mater. **26**, 55–59 (2012)
13. A.A. Tracton, in *Coatings Technology Fundamentals, Testing and Processing Techniques* (CRC Press, Boca Raton, 2007)
14. S. Wu, in *Polymer Interface and Adhesion* (Marcel Dekker, New York City, 1982)
15. P. Blais, D.J. Carlsson, G.W. Csullog, D.M. Wiles, Chromic acid etching of polyolefin surfaces and adhesive bonding. J. Colloid Interface Sci. **47**, 36–649 (1974)
16. S.R. Holmes-Farley, R.H. Reamey, R. Nuzzo, T.J. Mc Carthy, G.M. Whitesides, Reconstruction of the interface of oxidatively functionalized polyethylene and derivatives on heating. Langmuir **3**, 799–815 (1987)
17. D. Briggs, D.M. Brewis, M.B. Konieczo, X-ray photoelectron spectroscopy studies of polymer surfaces I: chromic acid etching of polyolefins. J. Mater. Sci. **11**, 1270–1277 (1976)
18. N. Larsson, P. Stenius, J.C. Eriksson, R. Maripuu, B. Lindberg, ESCA studies of sulfated polyethylene surfaces modified by adsorption of polyethyleneimine and colloidal silica particles. J. Colloid Interface Sci. **90**, 127–136 (1982)
19. D.A. Olsen, A.J. Osteraas, Sulfur modification of polyethylene surfaces II: modification of polyethylene surfaces with fuming sulfuric acid. J. Polym. Sci. A-1 **7**, 1921–1926 (1969)
20. V.A. Orlov, V.D. Zaitseva, V.A. Sinitsyn, E. Rostovtseva, US Patent No. 3,869,303, 1975
21. R. Rosty, S. Brook, W. Levi, US Patent No. 4,835,016, 1989
22. L.G. Beholz. US Patent No. 6,100,343, 2000
23. L.G. Beholz, C.L. Aronson, A. Zand, Adhesion modification of polyolefin surfaces with sodium hypochlorite in acidic media. Polymer **46**, 4604–4613 (2005)
24. C.L. Aronson, L.G. Beholz, B. Burland, J. Perez, in *25th Annual Meeting of the Adhesion Society (USA) and the Second World Congress on Adhesion and Related Phenomena (WCARP-II)*, Orlando, Florida; Feb 2002
25. J.J. Robin, C. Boyer, B. Boutevin, C. Loubat, Synthesis and properties of polyolefin graft copolymers by a grafting “onto” reactive process. Polymer **49**, 4519–4528 (2008)
26. R. Silva, E.C. Muniz, A.F. Rubira, Multiple hydrophilic polymer ultra-thin layers covalently anchored to polyethylene films. Polymer **49**, 4066–4075 (2008)

27. V.H. Torres, C.J.V. Rodrigues, C.C.A. Ramos, Poly(vinyl alcohol)/poly(acrylic acid) blends: miscibility studies by DSC and characterization of their thermally induced hydrogels. J. Appl. Polym. Sci. **50**, 777–792 (1993)
28. T. Lippert, Interaction of photons with polymers: from surface modification to ablation. Plasma Process. Polym. **2**, 525–546 (2005)
29. C. Vasile, in *Hanbook of polyolefins* (CRC Press, Boca Raton, 2000)
30. L. Tan, J.P. Deng, W.T. Yang, A facile approach to surface graft vinyl acetate onto polyolefin articles. Polym. Adv. Technol. **15**, 523–527 (2004)
31. T.B. Stachowiak, D.A. Mair, T.G. Holden, L.J. Lee, F. Svec, J.M. Fréchet, Hydrophilic surface modification of cyclic olefin copolymer microfluidic chips using sequential photografting. J. Sep. Sci. **30**, 1088–1093 (2007)
32. P. Lisboa, D. Gilliland, G. Ceccone, A. Valsesia, F. Rossi, Surface functionalisation of polypyrrole films using UV light induced radical activation. Appl. Surf. Sci. **252**, 4397–4401 (2006)
33. H.M. Ma, R.H. Davis, C.N. Bowman, Principal factors affecting sequential photoinduced graft polymerization. Polymer **42**, 8333–8338 (2001)
34. L.B. Kong, J.P. Deng, W.T. Yang, Detailed 1D/2D NMR analyses of benzophenone-related reaction products from a photopolymerization system of vinyl acetate and benzophenone. Macromol. Chem. Phys. **207**, 2311–2320 (2006)
35. W. Yang, B. Rånby, Bulk surface photografting process and its applications II: Principal factors affecting surface photografting. J. Appl. Polym. Sci. **62**, 545–555 (1996)
36. J. Balart, V. Fombuena, J.M. España, L. Sánchez-Nácher, R. Balart, Improvement of adhesion properties of polypropylene substrates by methyl methacrylate UV photografting surface treatment. Mater. Des. **33**, 1–10 (2012)
37. K. Kato, E. Uchida, E.-T. Kang, Y. Uyama, Y. Ikada, Polymer surface with graft chains. Prog. Polym. Sci. **28**, 209–259 (2003)
38. H. Ma, R.H. Davis, C.N. Bowman, A novel sequential photoinduced living graft polymerization. Macromolecules **33**, 331–335 (2000)
39. M. Strobel, V. Jones, C.S. Lyons, M. Ulsh, M.J. Kushner, R. Dorai, M.C. Branch, A comparison of corona-treated and flame-treated polypropylene films. Plasmas Polym. **8**, 61–95 (2003)
40. J. Warnatz, Hydrocarbon oxidation high-temperature chemistry. Pure Appl. Chem. **72**, 2101–2110 (2000)
41. I. Glassman, R. Yetter, in *Combustion* (Elsevier, Netherlands, 2008)
42. S. Farris, S. Pozzoli, P. Biagioni, L. Duó, S. Mancinelli, L. Piergiovanni, The fundamentals of flame treatment for the surface activation of polyolefin polymers—a review. Polymer **51**, 3591–3605 (2010)
43. E. Papirer, D.Y. Wu, J. Schultz, Adhesion of flame-treated polyolefins to styrene butadiene rubber. J. Adhes. Sci. Technol. **7**, 343–362 (1993)
44. F. Garbassi, E. Occhiello, F. Polato, A. Brown, Surface effect of flame treatments on polypropylene. J. Mater. Sci. **22**, 1450–1456 (1987)
45. J.G. Dillard, T.F. Cromer, C.E. Burtoff, A.J. Cosentino, R.L. Cline, G.M. Maciver, Surface properties and adhesion of flame treated sheet molded composite (SMC). J. Adhes. **26**, 181–198 (1988)
46. R.L. Ayres, D.L. Shofner, Preparing polyolefin surfaces for inks and adhesives. SPE J. **28**, 51–55 (1972)
47. D. Briggs, D.M. Brewis, M.B. Konieczko, X-ray photoelectron spectroscopy studies of polymer surfaces. J. Mater. Sci. **14**, 1344–1348 (1979)
48. W. Brockmann, P.L. Geiß, J. Klingen, B. Schröder, *Adhesive Bonding Materials, Applications and Technology* (Wiley, New York, 2009)
49. C. Tendero, Ch. Tixier, P. Tristant, J. Desmaison, P. Leprince, Atmospheric pressure plasmas: a review. Spectrochim. Acta B **61**, 2–30 (2006)
50. F.S. Denes, S. Manolache, Progress in polymer science. Prog. Polym. Sci. **29**, 815–885 (2004)

51. Q.F. Wei, Surface characterization of plasma-treated polypropylene fibers. Mater. Charact. **52**, 231–235 (2004)
52. L. Chvátalová, R. Čermák, P. Ponížil, A. Mráček, Plasma Treatment of Poly(1-butene). In *WDS'09 Proceedings of Contributed Papers Part II* (2009), pp. 264–267
53. K. Bazaka, M.V. Jacob, R.J. Crawford, E.P. Ivanova, Plasma-assisted surface modification of organic biopolymers to prevent bacterial attachment. Acta Biomater. **7**, 2015–2028 (2011)
54. P. Slepička, N. Slepičková-Kasálková, E. Stránská, L. Bačáková, V. Švorčík, Surface characterization of plasma treated polymers for applications as biocompatible carriers. Expr. Polym. Lett. **7**, 535–545 (2013)
55. K. Samanta, M. Jassal, A.K. Agrawal, Atmospheric pressure glow discharge plasma an its applications in textile. Indian J. Fibre Text. Res. **31**, 83–98 (2006)
56. R. Wolf, A.C. Sparavigna, Role of plasma surface treatments on wetting and adhesion. Engineering **2**, 397–402 (2010)
57. A. Pizzi, K.L. Mittal, *Hanbook of Adhesive Technology, Revised and Expanded* (Marcel Dekker, New York City, 2003)
58. T.S. Williams, H. Yu, R.F. Hicks, Atmospheric pressure plasma activation of polymers and composites for adhesive bonding: a critical review. Rev. Adhes. Adhes. **1**, 46–87 (2013)
59. Y.P. Raizer, in *Gas Discharge Physics* (Springer, Berlin, 1991)
60. B. Díaz-Benito, F. Velasco, Atmospheric plasma torch treatment of aluminium: improving wettability with silanes. Appl. Surf. Sci. **287**, 263–269 (2013)
61. A. Jaworek, A. Krupa, Corona discharge from a multipoint electrode in flowing air. J. Electrostat. **38**, 187–197 (1996)
62. A. Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, R.F. Hicks, The atmospheric-pressure plasma jet: a review and comparison to other plasma sources. IEEE Trans. Plasma Sci. **26**, 1685–1694 (1998)
63. J. Park, I. Henins, H.W. Herrmann, G.S. Selwyn, Gas breakdown in an atmospheric pressure radio-frequency capacitive plasma source. J. Appl. Phys. **89**, 15–19 (2001)
64. Q.C. Sun, D.D. Zhang, L.C. Wadsworth, Corona treatment on polyolefin films. Tappi J. **81**, 177–183 (1998)
65. J. Karger-Kocsis, in *Polypropylene an A–Z Reference* (Kluwer, Berlin, 1999)
66. R.S. Bisht, R. Kumar, N. Thaku, Change in surface free energy and surface resistivity of polycarbonate and polypropylene sheets after plasma exposure. Optoelectron. Adv. Mater. **4**, 144–147 (2010)
67. J.M. Farley, P. Meka, Heat sealing of semicrystalline polymer films III: effect of corona discharge treatment of LLDPE. J. Appl. Polym. Sci. **51**, 121–131 (1994)
68. J.A. Giacometti, O.N. Oliveira, Corona charging of polymer. IEEE Trans. Electr. Insul. **27**, 924–943 (1992)
69. M. Goldman, A. Goldman, R.S. Sigmond, The corona discharge, its properties and specific uses. Pure Appl. Chem. **57**, 1353–1362 (1985)
70. M.A. Salam, in *High-Voltage Engineering Theory and Practice* (Marcel Dekker, New York City, 2000)
71. D. Skalný, J. Országh, S. Matejčík, N.J. Mason, Ozone generation in positive and negative corona discharge fed by humid oxygen and carbon dioxide. Phys. Scr. **T131**, 1–3 (2008)
72. N. Sellin, J.S.C. Campos, Surface composition analysis of PP films treated by corona discharge. Mater. Res. **6**, 163–166 (2003)
73. L.A. O'Hare, S. Leadley, B. Parbhoo, Surface physicochemistry of corona-discharge-treated polypropylene films. Surf. Interface Anal. **33**, 335–342 (2002)
74. D. Zhang, Q. Sun, L.C. Wadsworth, Mechanics of corona treatment on polyolefin films. Polym. Eng. Sci. **38**, 965–970 (1998)
75. K.V. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, C. Gao, Modification of surface properties of polypropylene (PP) film using DC glow discharge air plasma. Appl. Surf. Sci. **255**, 3965–3971 (2009)
76. D.J. Carlsson, D.M. Wiles, Surface studies by attenuated total reflection spectroscopy I: corona treatment of polypropylene. Can. J. Chem. **48**, 2397–2406 (1970)

77. J. Friedrich, S. Wettmarshausen, M. Hennecke, Haloform plasma modification of polyolefin surfaces. Surf. Coat. Technol. **203**, 3647–3655 (2009)
78. J.F. Friedrich, R. Mix, R.-D. Schulze, A. Meyer-Plath, R. Joshi, S. Wettmarshausen, New plasma techniques for polymer surface modification with monotype functional groups. Plasma Process. Polym. **5**, 407–423 (2008)
79. E. Kiss, J. Samu, A. Toth, I. Bertoti, Novel ways of covalent attachment of poly (ethylene oxide) onto polyethylene: surface modification and characterization by XPS and contact angle measurements. Langmuir **12**, 1651–1657 (1996)
80. J.N. Galloway, F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P. Seitzinger, G. P. Asner, C.C. Cleveland, P.A. Green, E.A. Holland, D.M. Karl, A.F. Michaels, J.H. Porter, A.R. Townsend, C.J. Vöosmarty, Nitrogen cycles: past, present, and future. Biogeochemistry **70**, 153–226 (2004)
81. S. Wettmarshausen, H.-U. Mittmann, G. Kühn, G. Hidde, J.F. Friedrich, Plasmabromination —the selective way to monotype functionalized polymer surfaces. Plasma Process. Polym. **4**, 832–839 (2007)
82. F. Awaja, M. Gilbert, G. Kelly, B. Fox, P.J. Pigram, Adhesion of polymers. Prog. Polym. Sci. **34**, 948–968 (2009)
83. D.R. Baer, M.H. Engelhard, XPS analysis of nanostructured materials and biological surfaces. J. Electron Spectrosc. **178–179**, 415–432 (2010)
84. J.C. Vickerman, in *Surface Analysis: The Principal Techniques* (Wiley, West Sussex, 2003)
85. R.C. Asensio, M.S.A. Moya, J.M. de la Roja, M. Gómez, Analytical characterization of polymers used in conservation and restoration by ATR-FTIR spectroscopy. Anal. Bioanal. Chem. **395**, 2081–2096 (2009)
86. A. Ghauch, P.-A. Deveau, V. Jacob, P. Baussand, Use of FTIR spectroscopy coupled with ATR for the determination of atmospheric compounds. Talanta **68**, 1294–1302 (2006)
87. T. Amornsakchai, O. Doaddara, Grafting of acrylamide and acrylic acid onto polyethylene fiber for improved adhesion to epoxy resin. J. Reinf. Plast. Compos. **27**, 671–682 (2008)
88. A. Karen, N. Man, T. Shibamori, K. Takahashi, TOF-SIMS characterization of industrial materials: from silicon wafer to polymer. Appl. Surf. Sci. **203–204**, 541–546 (2003)
89. Y. Yuan, T.R. Lee, Contact angle and wetting properties. In *Surface Science Techniques*, ed. by G. Bracco, B. Holst (Springer, Berlin, 2013), pp. 3–34
90. O. Guise, C. Stroma, N. Preschilla, STEM-in-SEM method for morphology analysis of polymer systems. Polymer **52**, 1278–1285 (2011)
91. S.J.B. Reed, in *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology* (Cambridge University Press, Cambridge, 1996)
92. V. Koutsos, Atomic force microscopy and polymers on surfaces. In *Atomic Force Microscopy in Process Engineering: An introduction to AFM for Improved Processes and Products*, ed. by W. Richard Bowen, N. Hilal (Elsevier, Netherlands, 2009), pp. 225–244
93. J.G. Williams, H. Hadavinia, B. Cotterell, Anisotropic elastic and elastic–plastic bending solutions for edge constrained beams. Int. J. Solids Struct. **42**, 4927–4946 (2005)
94. R. Mahlberg, H.E.M. Niemi, F.S. Denes, R.M. Rowell, Application of AFM on the adhesion studies of oxygen-plasma-treated polypropylene and lignocellulosics. Langmuir **15**, 2985–2992 (1999)
95. I. Novák, A. Popelka, I. Krupa, I. Chodák, I. Janigová, T. Nedelčev, M. Špírková, A. Kleinová, High-density polyethylene functionalized by cold plasma and silanes. Vacuum **86**, 2089–2094 (2012)
96. R.S. Court, M.P.F. Sutcliffe, S.M. Tavakoli, Ageing of adhesively bonded joints—fracture and failure analysis using video imaging techniques. Int. J. Adhes. Adhes. **21**, 455–463 (2001)
97. J.Y. Cognard, P. Davies, B. Gineste, L. Sohier, Development of an improved adhesive test method for composite assembly design. Compos. Sci. Technol. **65**, 359–368 (2005)
98. J.M. Burkstrand, Metal-polymer interfaces: adhesion and x-ray photoemission studies. J. Appl. Phys. **52**(7), 4795–800 (1981)

99. J.G. Kohl, I.L. Singer, Pull-off behavior of epoxy bonded to silicone duplex coatings. Prog. Org. Coat. **36**, 15–20 (1999)
100. K.L. Mittal, in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings* (American Society for Testing and Materials, USA, 1976)
101. T. Sander, S. Tremmel, S. Wartzack, A modified scratch test for the mechanical characterization of scratch resistance and adhesion of thin hard coatings on soft substrates. Surf. Coat. Technol. **206**, 1873–1878 (2011)
102. M. Friedman, G. Walsh, High performance films: review of new materials and trends. Polym. Eng. Sci. **42**, 1756–1788 (2002)
103. T.C.M. Chung, Functional polyolefins for energy applications. Macromolecules 466671–6698 (2013)
104. S.S. Pesetskii, B. Jurkowski, A.I. Kuzavkov, Strength of adhesive joints from functionalized polyethylene and metals. Int. J. Adhes. Adhes. **18**, 351–358 (1998)
105. W.T. Li, R.B. Charters, B. Luther-Davies, L. Mar, Significant improvement of adhesion between gold thin films and a polymer. Appl. Surf. Sci. **233**, 227–233 (2004)
106. Y.J. Choi, M.S. Kang, S.H. Kim, J. Cho, S.H. Moon, Characterization of LDPE/polystyrene cation exchange membranes prepared by monomer sorption and UV radiation polymerization. J. Membr. Sci. **223**, 201–215 (2003)
107. J.P. Badey, E. Espuche, Y. Jugnet, B. Chabert, T.M. Duc, Influence of chemical and plasma treatments on the adhesive properties of PTFE with an epoxy resin. Int. J. Adhes. Adhes. **16**, 173–178 (1996)
108. S.J. Park, S.Y. Song, J.S. Shin, J.M. Rhee, Effect of surface oxyfluorination on the dyeability of polyethylene film. J. Colloid Interface Sci. **283**, 190–195 (2005)
109. D. Bandopadhay, A. Tarafdar, A.B. Panda, P. Pramanik, Surface modification of low-density polyethylene films by a novel solution base chemical process. J. Appl. Polym. Sci. **92**, 3046–3051 (2004)
110. S. Tajima, K. Komvopoulos, Surface modification of low-density polyethylene by inductively coupled argon. J. Phys. Chem. B **109**, 17623–17629 (2005)
111. S. Tajima, K. Komvopoulos, Effect of ion energy fluence on the topography and wettability of low-density polyethylene exposed to inductively coupled argon plasma. J. Phys. D Appl. Phys. **39**, 1084–1094 (2006)
112. V. Švorčík, K. Kolářová, P. Slepička, A. Macková, M. Novotná, V. Hnatowicz, Modification of surface properties of high and low density polyethylene by Ar plasma discharge. Polym. Degrad. Stab. **91**(6), 1219–1225 (2006)
113. I. Novak, V. Pollak, I. Chodak, Study of surface properties of polyolefins modified by corona discharge plasma. Plasma Process. Polym. **3**, 355–364 (2006)
114. E.T. Kang, K.G. Neoh, J.L. Shi, K.L. Tan, D.J. Liaw, Surface modification of polymers for adhesion enhancement. Polym. Adv. Technol. **10**, 20–29 (1999)
115. S. Bhowmik, T.K. Chaki, S. Ray, F. Hoffman, L. Dorn, Experimental investigation into the effect of DC glow discharge pretreatment of HDPE on tensile lap shear strength. Int. J. Adhes. Adhes. **24**, 461–470 (2004)
116. S. Bhowmik, H.W.W. Bonin, V.T.T. Bui, T.K. Chaki, Physicochemical and adhesion characteristics of high-density polyethylene when treated in a low-pressure plasma under different electrodes. J. Adhes. **82**, 1–18 (2006)
117. R. Sanchis, O. Fenollar, D. Garcia, L. Sanchez, R. Balart, Improved adhesion of LDPE films to polyolefin foams for automotive industry using low-pressure plasma. Int. J. Adhes. Adhes. **28**, 445–451 (2008)
118. J.P. Sargent, Durability studies for aerospace applications using peel and wedge tests. Int. J. Adhes. Adhes. **25**, 247–256 (2005)
119. J.H. Clint, Adhesion and components of solid surface energies. Colloid Interface Sci. **6**, 28–33 (2001)
120. E. Tomasetti, D. Daoust, R. Legras, P. Bertrand, P.G. Rouxhet, Diffusion of adhesion promoter (CPO) into polypropylene/ethylene–propylene (PP/EP) copolymer blends: mechanism. J. Adhes. Sci. Technol. **V15**, 1589–1600 (2001)

121. A.P. Pijpers, R.J. Meier, Adhesion behaviour of polypropylenes after flame treatment determined by XPS(ESCA) spectral analysis. J Electron Spectrosc. Relat. Phenom. **121**, 299–313 (2001)
122. M. Noeske, J. Degenhardt, S. Strudthoff, U. Lommatzsch, Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion. Int. J. Adhes. Adhes. **24**, 171–177 (2004)
123. T.L. Wong, C.M.F. Barry, S.A. Orroth, The effects of filler size on the properties of thermoplastic polyolefin blends. J. Vinyl Addit. Technol. **5**, 235–240 (1999)
124. H. Tang, D.C. Martin, Microstructural studies of interfacial deformation in painted thermoplastic polyolefins (TPOs). J. Mater. Sci. **37**, 4783–4791 (2002)
125. R.M. Paroli, K.K.Y. Liu, T.R. Simmons, Thermoplastic polyolefin roofing membranes. Constr. Technol. Update **30**, 1–4 (1999)
126. O.J. Kwon, S.S. Tang, S.W. Myung, N. Lu, H.S. Choi, Surface characteristics of polypropylene film treated by an atmospheric pressure plasma. Surf. Coat. Technol. **192**, 1–10 (2005)
127. C. Cheng, Z. Liye, R.J. Zhan, Surface modification of polymer fibres by the new atmospheric pressure cold plasma jet. Surf. Coat. Technol. **200**, 6659–6665 (2006)
128. I. Novák, V. Cecen, V. Pollák, Applications of selected multiphase systems, in *Handbook of Multiphase Systems*, 1st edn., ed. by A. Boudenne, Y. Candau, S. Thomas (Wiley, West Sussex, UK, 2011), pp. 865–920
129. L.D. Renner, D.B. Weibel, Physicochemical regulation of biofilm for-mation. MRS Bull. **36**, 347–55 (2011)
130. A. Worz, B. Berchtold, K. Moosmann, O. Prucker, J. Ruhe, Protein-resistant polymer surfaces. J. Mater. Chem. **22**, 19547–19561 (2012)
131. F. Debeaufort, J.A. Quezada-Gallo, A. Voilley, Edible films and coatings: tomorrow's packagings: a review. Crit. Rev. Food Sci. Nutr. **38**, 299–313 (1998)
132. A. Domard, M. Rinaudo, Preparation and characterization of fully deacetylated chitosan. Int. J. Biol. Macromol. **5**, 49–52 (1983)
133. F. Ferrero, R. Bongiovanni, Improving the surface properties of cellophane by air plasma treatment. Surf. Coat. Technol. **200**, 4770–4776 (2006)
134. M.Z. Elsabee, E.S. Abdou, K.S.A. Nagy, M. Eweis, Surface modification of polypropylene films by chitosan and chitosan/pectin multilayer. Carbohydr. Polym. **71**, 187–195 (2008)
135. A. Popelka, I. Novák, M. Lehocký, I. Junkar, M. Mozetič, A. Kleinová, I. Janigová, M. Šlouf, F. Bílek, I. Chodák, A new route for chitosan immobilization onto polyethylene surface. Carbohydr. Polym. **90**, 1501–1508 (2012)

Chapter 9
Polyolefins in Textiles and Nonwovens

Mabrouk Ouederni

9.1 Introduction

Polyolefins such as polyethylene (PE) and polypropylene (PP) are known for their lightweight, ease of processing, excellent chemical resistance, water repellency, and reasonable strength and tenacity. This makes them the material of choice for many textile fibers and nonwoven applications.

Polyolefins have long been used in applications such as carpets, ropes, geotextiles, hygiene nonwovens, construction, and technical textiles. This versatility is due to the wide range of technologies that have been developed by the polymer and fiber industry to convert polyolefin resins into fibers and fabrics that constitute the basis for all textile and nonwoven applications. These technologies include monofilament and multifilament spinning, staple fiber, spunbond, melt blown, and slit film.

This chapter will provide a concise summary of the main technologies and applications. Distinction will be made between PE and PP in terms of their suitability for specific fiber and nonwoven applications. Resin choice, in terms of its molecular weight and formulation, is critical not just to the final product performance but also to the type of technology used to convert the resin.

The main properties and characterization techniques used in the polyolefin textiles and nonwoven industry will be discussed, and the terminology used by the industry will also be introduced in a simple and easy-to-understand manner.

The original version of this chapter was revised: The erratum to this chapter is available at DOI 10.1007/978-3-319-25982-6_15

M. Ouederni (✉)
Head of Research and Development, QAPCO, Doha, Qatar
e-mail: MOuederni@qapco.com.qa

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_9

Finally, the chapter will discuss some recent trends in the technology development and applications of polyolefins in textiles and nonwovens.

Polyolefins are increasingly becoming an integral part of the textile and nonwoven industries. Even though they have not historically enjoyed the same fame achieved by polyester and nylon in synthetic fiber applications, polyolefins offer some unique advantages that make them essential for many textile and nonwoven applications as will be seen later in this chapter. Polypropylene, in particular, has been increasingly recognized by both industry and consumers as the fiber of choice for many applications including carpet and nonwovens. In addition to a clear cost advantage compared to other synthetic fibers, polyolefins possess a unique combination of mechanical properties, ease of processing, and low moisture absorption among other advantageous characteristics.

It will be useful for the reader to establish some basic definitions related to the topic before we proceed. The main component of the textile or nonwoven fabric is the fiber; therefore, polyolefin fiber will be defined first.

Polyolefin fiber: Also referred to as Olefin Fiber, is any fiber produced from polymers formed by addition polymerization of olefins and which contain more than 85 % polymerized ethylene, propylene or any other olefin units. This is similar to the US Federal Trade Commission's official definition that defines an olefin fiber as "A manufactured fiber in which the fiber forming substance is any long chain synthetic polymer composed of at least 85 % by weight of ethylene, propylene or other olefin units" [1].

The focus in this chapter will be on the two main polyolefin polymers, namely polyethylene (PE) and polypropylene (PP). The latter especially has established itself as a very versatile fiber with unique applications in the textile and nonwoven industry. Polyethylene, on the other hand, has not been widely used as a fiber compared to other synthetic polymers such as PET, PP, and nylon, due in part to its low melting point. This chapter will, however, discuss ultra-high molecular weight polyethylene (UHMWPE) fiber that given its success and uniqueness in the synthetic fiber industry.

9.2 Textiles

The central component of a textile fabric is the fiber, which could be natural such as cotton or wool, or synthetic such as polyester or polypropylene. Since the chapter is concerned with polyolefins, the various forms of synthetic fibers used in the textile industry will be mentioned. Fibers for the textile industry could take any of the following forms before being knitted or woven into a final textile fabric form:

- Filament: A single fiber of continuous length. It is sometimes referred to as a monofilament, but the distinction should be made with monofilaments of larger diameter which are extruded, wound on bobbins, and used in applications such as fishing line, fasteners, and paper machine clothing.

- Filament yarn: A number of continuous filaments held together by twisting or other methods.
- Filament tow: Large bundles of filament held together without twisting.
- Staple fiber: Short fibers with specific length cut from filament tow, usually packaged in bales of staple fiber before textile processing.
- Spun yarn: Staple fiber is sometimes spun for easy processing on cards and other textile machinery.
- Textured filament yarn: Filament yarn is sometimes twisted and manipulated in order to impart texture and bulk to it before it is used in a textile fabric. This step can also impart a soft hand feel to the yarn.

Fiber spinning process: Meltspinning is the common process used to make textile-type polyolefin fibers (UHMWPE is an exception due to its ultra-high molecular weight as will be seen later). The process of making continuous filament yarn consists of the following steps [2]:

- Melting the polyethylene or polypropylene polymer in an extruder and pushing it through a spinneret that consists of very tiny holes evenly distributed through the surface. A spinneret pack with polymeric filaments can be depicted in Fig. 9.1 [3].
- Solidifying the filaments exiting the spinneret by cool air and collecting them in a bundle on a rotating roll.
- Drawing the filaments between two rolls of different speeds in order to orient the molecules and increase the filament strength.
- Heat setting the filaments and collecting them on bobbins on a windup roll for further textile processing.

The process for making staple fiber is similar to the above process up until the collection of spun filaments after the spinneret. The spun bundles of fibers are collected in large spans from several parallel extruders in the form of a large tow.

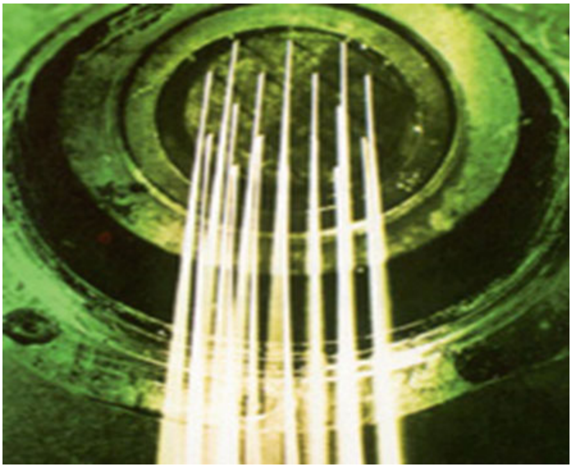


Fig. 9.1 Spinneret pack with polymer filaments exiting through the spinneret holes (*source* Fibersource.com) [3]

The tow is then taken through several steps that include surface chemical treatment, drawing to orient fibers, crimping to increase bulk, finishing, and finally cutting into several mm staple fibers (fiber length depends on subsequent process and application) and packing into bales.

9.3 Nonwovens

There are several definitions of a nonwoven, but they all revolve around the fact that it is a fabric that is different from a traditional textile fabric, a paper sheet, or a plastic film.

Unlike traditional textile fabrics which are knitted or woven from yarn, nonwovens are engineered fabric structures made directly from fibers or from webs that are made by fibers themselves. The textile institute defines a nonwoven as “a textile structure made directly from fiber rather than yarn. Fabrics are normally made from continuous filaments or from fiber webs or batts strengthened by bonding using various techniques: These include adhesive bonding, mechanical interlocking by needling or fluid jet entanglement, thermal bonding and stitch bonding” [4].

The association of the non-woven fabrics industry (INDA) defines a nonwoven as “a sheet, batt or web of natural and/or man-made fibers or filaments, excluding paper, that have not been converted into yarns, and that are bonded to each other by any of several means” [5].

Nonwovens have established themselves as a distinct and commercially very important class of materials worldwide. There are two main types of nonwovens: disposables and durable, depending on the application. Examples of disposable nonwovens include baby diapers, face masks, wet wipes, and several hygiene and medical fabrics. Durable nonwovens include filtration media, automotive fabrics, roofing fabrics, geomembranes, interlinings for clothing and shoes, and military protective garments.

They became the materials of choice for many applications in consumer, industrial, and healthcare products due to their unique combination of lightweight, open structure, filtration capability, and fluid management properties, depending on the specific application. The fabrics are very versatile in structure and appearance due to the various processes and bonding techniques used to make them. They are characterized by their basis weight, which is the number of grams per square meter, and they usually range from as low as 10 g/m^2 to as high as few thousand g/m^2 depending on the application.

Historically, nonwovens date back to thousands of years in the writings of early Greek and Chinese using wool fibers to make felted materials. But the modern nonwoven industry dates back to the 1930s when pioneering companies such as Jonson & Johnson (USA) and Freudenberg (Germany). Both companies were looking for ways to avoid spinning fibers and weaving them in order to make efficient fabric structures from cotton and rayon fibers. Johnson & Johnson introduced rayon nonwoven fabric in applications such as napkins, bedding pads, diapers, and surgical fabrics. J&J was looking for a replacement to leather and later introduced nonwoven interlinings, an application that Freudenberg NW is still leading today [4]. Other leading companies in the development of the nonwoven industry include Kimberly Clark, Proctor & Gamble, West Point, BBA Nonwovens, and Kendall. Polyolefins were later introduced as fibers of choice for many NW applications as will be seen later in this chapter.

9.3.1 Nonwoven Processing

The various types of nonwoven processes will be described in this chapter, with a special attention given to the polymer extrusion processes due to their importance for polyolefin-based nonwovens. Nonwoven processes are versatile and can be grouped under the following separate types (or a combination of them):

- Textile-based processes: Carding and aerodynamic forming can be applied to dry fibers to form nonwoven webs that are oriented and bonded by several possible methods. These processes result in what is known as dry-laid nonwovens. **Carded** and **airlaid** nonwovens are two examples of these types of processes. Garneting is also used to make nonwoven fabrics that are referred to as garneted nonwovens. These processes are flexible and unique in terms of the wide range of staple fibers that can be used and the adaptation of regular textile machinery to nonwoven processing.
- Paper-based processes: Synthetic staple fibers as well as wood pulp fibers are suspended in water and then formed into a paper-like nonwoven web on a perforated surface. The web is then bonded by interlocking the fibers by mechanical or chemical bonding techniques. Fabrics made by this type of process are known as **wet-laid** nonwovens. Such products can be made at very high speeds and are very uniform, but the process is capital-intensive.
- Polymer extrusion-based processes: Some of the most significant contributions to the nonwoven industry came from the development of the direct “polymer-to-fabric” converting processes. These processes include spun-bonding, melt-blowing, and porous film. Nonwovens made by these processes are known as **spunbond (SB)** nonwovens, **melt blown (MB)** nonwovens, and **apertured-film** nonwovens.

9.3.1.1 Spunbond Nonwovens

The SB nonwoven process was commercially developed in the 1960s in Germany by Freudenberg and later in the USA by DuPont, and it presented a significant development in the textile and nonwoven industry. Lurgi of Germany developed a commercial process that was licensed to nonwoven manufacturers around the world during the 1970s [6].

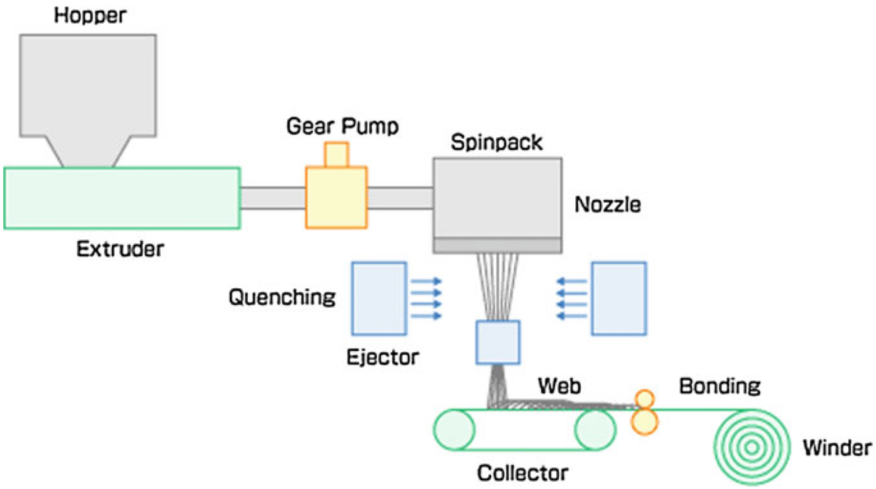


Fig. 9.2 Schematic of the spunbond (SB) nonwoven process (*source* Kasen Corporation, Japan, reproduced with permission from Kasen) [7]

The process starts with melting the polymer in an extruder and pushing it through a spinneret, similar to a regular fiber spinning process. The bundles of fibers from many spinnerets are then cooled down and stretched pneumatically or mechanically in order to orient the fibers and impart strength to them. The attenuation step reduces fiber diameter and improves fiber morphology through orientation. The fibers are then accelerated by high-velocity air stream and laid down randomly on a moving belt to form a web. The web is made even stronger by subsequent bonding which could be chemical by the use of latex or other bonding agents, or thermal by the use of thermal bonding low melting fibers and passing the web between hot rolls. The fabric is finally slit and wound on a roll that could be up to several meters wide.

There are several industrial processes available with small variations, one example is illustrated in the Kasen process chart shown in Fig. 9.2 [7].

The SB process can deliver very good strength-to-weight ratios which is very important for many consumer and industrial applications. Products made via SB range from light baby diaper and hygiene fabrics to heavy geotextile and roofing nonwovens.

9.3.1.2 Melt Blown Nonwovens (MB)

Melt blown (MB) nonwovens are also made directly from the polymer into a fabric. It was developed first at the US Naval Research Laboratories and was later improved by researchers at Exxon and 3 M and commercialized in the 1960s [5, 6].

The melt blowing process starts with melting the polymer in an extruder and passing the molten resin through an orifice. As it exits the orifice, the polymer is

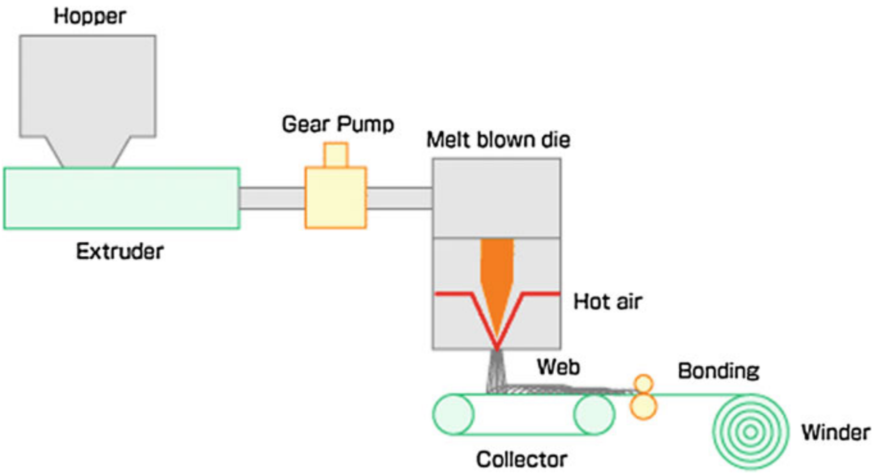


Fig. 9.3 Schematic of the melt blown (MB) nonwoven process (*source* Kasen Corporation, Japan, reproduced with permission from Kasen) [7]

blown with very high-velocity air at a temperature of about 250–500 °C. The action of the high-velocity air causes the polymer to shatter and stretch into a very fine fibrous structure made of very low-diameter fibers. The randomly oriented web of fibers is then separated from the air stream and passed through heated rolls for pressing and bonding. The web is then slit and wound in a roll. MB fabrics are known for their large surface area and extremely high number of pores per unit area, due to the fine diameter fibers, random entanglement, and close packing of fibers [8] (Fig. 9.3).

9.4 Properties of Polyolefin Fibers

Polyolefin fibers (PE and PP) are known to have good tensile strength and toughness and very good abrasion resistance, and they also have good chemical resistance, but this means that they are difficult to dye which is a drawback of polyolefin fibers. Another drawback is their low melting point which is a limitation especially for polyethylene fiber. The low melting point could also be an advantage in some nonwoven processes that use thermal bonding instead of chemical resin spray. They offer good cost-benefit for many applications. These fibers are characterized by a smooth and round cross section.

The following list summarizes some of the main properties and characteristics of polyolefin fibers:

- Lightweight: Polyolefin fibers have the lowest specific gravity of any synthetic or natural fiber.
- Ability to give good bulk, which translates into good cover properties.
- Good strength (both wet and dry) and resiliency.

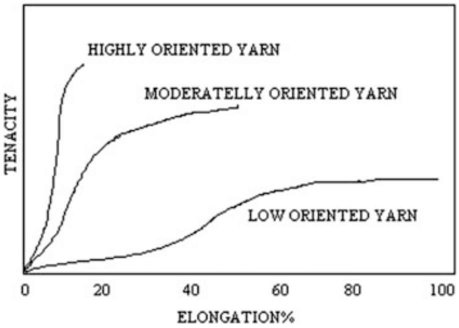


Fig. 9.4 Schematic curves showing the effect of orientation on PP fiber tenacity (*source* Reference 9)

- Good abrasion resistance.
- Very low moisture regain (close to zero).
- Quick drying ability since the fiber does not absorb moisture.
- Good chemical and stain resistance.
- Excellent thermal bonding properties (very important for nonwovens).
- Good wicking characteristics and a comfortable feel.

Polyolefin fibers, on the other hand, have some drawbacks when compared to common textile fibers such as polyester. These limitations include relatively lower resiliency, creeping due to their low glass transition temperature (T_g), poor dyeability unless treated and prepared, flammability, and poor adhesion to chemical binders such as glues and latex.

The properties of polyolefin fibers also depend on the type of process used to make them and the specific process conditions. Orientation, a common step in making synthetic fibers, results in an increased strength of polyolefin fibers by orienting the polymer chains in the drawing direction. The extent of orientation depends on the draw ratio, which is a processing condition determined by the difference in roll speeds between the first and last rolls in the fiber production line. As the chains become aligned in the drawing direction, the crystallinity increases due to an extended fibrillar morphology and as a consequence, the tensile strength (tenacity of the fiber) increases. PE and PP are semicrystalline thermoplastics with high crystallization rates. The polymers crystallize during the cooling step of the fiber-making process, but the percent crystallinity increases by subsequent steps such as drawing and heat setting. Figure 9.4 illustrates the change in strength as a result of increasing orientation [9].

9.5 Characterization and Testing of Polyolefin Fibers

Polyolefin fibers are characterized and tested using most of the common synthetic fiber techniques. It is beyond the scope of this chapter to discuss all techniques in detail. It is, however, important to mention the following properties, which are essential in understanding the identification and performance of polyolefin fibers.

Denier: It is the weight in grams of 9000 m of fiber, and it is a measure of the linear density of the fiber. For the same type of fiber, the larger the diameter, the bigger the denier. Because fibers are usually bundled in a yarn as mentioned earlier, the term total denier is used and it refers to the denier of the yarn. The term denier per filament (DPF) is a common term in the fiber industry, and it refers to the denier of a single filament (it is also equal to the total denier divided by the number of filaments in the yarn).

It is also worth noting that denier is commonly used in North America, whereas the European fiber industry prefers to use the term Tex, which is the weight in grams of 1000 m of fiber. The common unit of fiber linear density in Europe is actually the **dtex** (decitex), which is the weight in grams of 10,000 m of fiber.

Tenacity: It is the stress at which the fiber breaks, expressed in grams per denier. It is a very important property of polyolefin fibers, and it can range between 3.5 and 8 g/d (grams per denier) or 31–81 g/tex [10]. General textile use PP fibers can have a tenacity of 40.5–50 cN/dtex, whereas high tenacity yarns used in ropes and nets can have tenacities up to 81 cN/dtex [11].

Elongation to break (***Eb***): It is a measure in percent of the extent to which the fiber can stretch before breaking. Eb is derived from a stress–strain curve that can be performed on a single fiber or on a yarn, and it is measured according to standardized testing such as ASTM. The elongation to break of polyolefin fibers depends on the stretching and drawing of the fiber and on the heat setting at the end of the fiber-making process. It is a measure of the flexibility of the fiber, and producers usually try to strike a balance between tenacity and elongation as required by the specific end-use application. Extensibility is also important in order to allow the fiber to go through subsequent textile machinery and processes without breakage.

Fiber identification: There are several methods that the fiber industry uses to identify fibers and distinguish them from one another. Some of the most common methods include microscopic examination, solubility test, heating and flammability test, density, and staining techniques [10].

Microscopy test: The optical microscope is a very useful tool in fiber testing and characterization laboratories. It is easier to identify natural fibers than synthetic ones because of the similarity in synthetic fiber appearance. Shape and cross section are common characteristics to examine under the microscope. Polyolefin fibers are usually characterized by a smooth and round cross section. Microscopy is not a definite technique to distinguish between PE and PP fibers. Microscopy is effective in telling whether the fiber is a mono-component filament or a bicomponent filament where two polymers are extruded in a sheath–core configuration.

Chemical test: Solubility is a very effective test to identify fibers. Polyolefins have excellent chemical resistance to most common solvents, and they can be easily distinguished from a polyester or nylon fiber by a simple solubility test. Functional groups can also be identified using a technique such as FTIR which will help identify the fiber type.

Burn test: When in contact with an open flame, different fibers will generate different types of flame, ash, and smell. What is important in this test is the following: Does the fiber melt or burn? does the fiber shrink from the flame? What is the odor of the fumes and what kind of residue does the flame leave? Polyethylene fiber burns quickly while giving a blue flame and yellow tip, and it also drips while it burns. PE gives off a paraffin odor similar to a burning candle. Polypropylene melts and burns with a steady flame with almost no smoke and a clear melting portion. PP gives off a slightly celery odor or no odor at all. PP is characterized by a hard tan-colored residue [12].

Density test: Fiber density is an indication of the type of fiber being identified. Polyolefin fibers will float in water, which is a unique characteristic. PE fibers have a specific gravity of 0.95–0.96 g/cm^3, whereas PP fibers have a specific gravity of 0.90–0.91 g/cm^3 [10].

Stain test: This test is based on the affinity for various fibers toward different dyes. A series of dyes which have known affinity for specific fibers are prepared, and the fiber in question is immersed to check its dye pickup. The morphology of the fiber and its chemical structure determine its dyeability and hydrophilicity. Polyolefin fibers are hydrophobic, and they have very poor dyeability.

Other characterization and identification techniques: Polyolefin fibers can be characterized by numerous modern techniques ranging from thermal analysis and various spectroscopy techniques, to electron microscopy and nuclear magnetic resonance (NMR). Differential scanning calorimetry (DSC) is particularly important in determining the melting point of the fiber piece and quickly distinguishing between PE and PP. Polyethylene softens at 130 °C and melts around 140 °C, whereas polypropylene softens at 150 °C and melts around 160 °C.

Applications and use of Polyolefin Fibers

Polypropylene has the biggest share of polyolefin fiber production and consumption. Polyolefin fibers have been experiencing a 6 % growth rate representing the fastest growth in all synthetic fibers. This is due mainly to increased production capacity in developing countries as well as increased use in carpets and nonwovens in industrialized nations [13].

As it is shown in Table 9.1, PP fiber production was affected in the last few years especially due to rising propylene prices. However, as more propylene becomes available through propane dehydrogenation and other processes, and as the demand for nonwovens increases, PP fiber production is forecasted to pick up again [14, 15].

Table 9.1 PP fiber production worldwide by fiber type in 1000 tons (data compiled from Fiber Organon, USA, through reference 14 and Tecnon OrbiChem through reference 15)

Year	2000	2005	2009	2010[a]	2015[b]
Filament yarn	2600	2940	2500	–	–
Staple fiber	1200	1240	1050	–	–
Film fiber	2100	2300	2200	–	–
Total	5900	6480	5750	6000	7000

[a] Only total numbers are included in 2010 figures

[b] 2015 numbers are forecasted estimates by Tecnon OrbiChem [15]

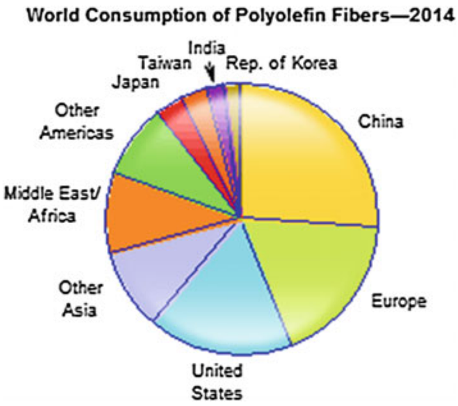


Fig. 9.5 World consumption of polyolefin fibers 2014 (*source* Reference 13)

China, the USA, and Europe still have the biggest share of world consumption of polyolefin fibers as shown in Fig. 9.5 (2014 data).

Most polyolefin fibers are used in consumer products with carpets and rugs being the largest market. This is due mainly to the ability of polypropylene to replace nylon and jute in carpets.

Polyolefin fibers, especially PP, are widely used in carpet backing, carpet face yarn, laundry bags, sportswear and sweaters, rope and cordage, hosiery, undergarments, sewing thread, and knitwear. PP slit film and monofilaments are used in ropes, agricultural nets, and flexible intermediate bulk containers. Polyolefin fibers are also used in furniture and equipment covering, outside furniture, and more recently as artificial turf.

Polypropylene film fiber is becoming of great commercial interest in many applications such as carpeting and woven sacks. It consists of an extruded film that is slit along the machine direction into narrow, fiber-like ribbons. These ribbons are then woven to make strong fabrics, nets, and sacks. Low-density polyethylene (LDPE) is sometimes blended with PP in slit film applications in order to reduce fibrillation and improve processability.

Due to the commercial significance of nonwovens for PP and gel-spun technology for PE, these two areas will now be covered in more detail.

9.6 Polypropylene in Nonwoven Applications

Nonwovens are the second largest application for polypropylene fiber after carpets. Spunbond (SB) and melt blown (MB) are the two main nonwoven processes for polypropylene. PP polymer used for nonwovens has special requirements in order to satisfy the fiber-making process. It has to be a fiber grade resin with a high melt flow rate (MFR) and a narrow molecular weight distribution (MWD). PP fibers in a SB fabric are usually in the range of 10–40 μm diameter, and their melting point of about 165 °C gives PP the advantage of being a thermal bonding fiber with a good bonding window especially when used in combination with natural or higher melting point synthetics.

Some of the main uses of PP in nonwovens include baby diapers, hygiene fabrics, wet wipes, and adult incontinence fabrics which require a soft hand. Automotive fabrics, geotextiles, disposable hospital clothing, and industrial wipes are also important PP applications.

Melt blown (MB) fibers are usually around 10 μm or less in diameter which gives them greater cover but generally weaker fabrics. Some of the main uses of PP in MB nonwovens are in filtration media, face masks, and battery separators. Recent research and development (R&D) work[1] used metallocene-catalyzed PP to make submicron diameter MB fibers [16]. The polyolefin used in this work had a narrow molecular weight distribution and an MFR greater than 1000 g/10 min, a typical range for MB nonwoven polymers.

Metallocene polymerization makes it possible to make SB and MB fibers with finer diameter which translates into softer fabrics and textile-type SB and MB nonwovens [17, 18].

The world consumes in excess of 2.5 million tons of PP in nonwovens today. According to a report by Chemicals Market Resources Inc. “Diapers, adult incontinence products, geotextile and carpets, are the end use applications expected to see rapid increase in demand in developing regions” [19].

9.7 Polyethylene in High-Strength Fiber Applications

Polyethylene is more difficult to melt blow into fine fibrous webs than polypropylene. Polyethylene is also difficult to draw because of its melt elasticity, and its low melting point is a limitation to its use in several textile and nonwoven applications. UHMWPE, however, has proven to be a very successful polymer for high-strength and low-weight fiber applications. UHMWPE usually has a molecular weight in the range of 2–6 million g/mole. It is made up of extended, fully oriented polyethylene chains which gives its outstanding strength. In fact, it is one of the world’s strongest and lightest fibers. Compared on a similar weight basis, it is 10 times stronger than steel and up to 40 % stronger than aramids. It floats on water, which gives it an advantage in many marine applications. It is chemical and water resistant and has excellent fiber-to-fiber abrasion.

UHMWPE fibers are used in applications such as marine cordage and lifting slings, police and military ballistic vests, armored vehicles, cut-resistant gloves, fishing lines, and safety clothing.

Due to its very high molecular weight and high viscosity, UHMWPE is not processed by regular meltspinning techniques. The fiber is made by the gel-spinning method that was first invented in Europe and commercialized by DSM in the 1990s. The fiber is currently made by DSM, LLC, Europe, and Honeywell Advanced Fibers & Composites, USA. The fibers are known, respectively, as Dyneema and Spectra.

---

[1] 2008 work documented in US Patent 8372292B2, granted to P. Scheerlinck and M. Ouederni Feb 2013, assigned to Johns Manville Corp., USA [16].

Table 9.2 Part of a product data sheet showing physical properties of the HT Spectra grade[a]

Product family	Spectra® fiber	Weight/unit length (denier)/(decitex)	Ultimate tensile strength (g/den)/(Gpa)	Modulus (g/den)/(Gpa)	Elongation (%)	Breaking strength (Kg)	Density (g/cc)/	Filament tow	Filament (dpf)
HT	240	267	41	1350–1650	3.1–3.5	10.0	0.97	60	4
	300	333	39.5	1200–1500	2.9–3.7	11.8	0.97	60	5
	375	417	45	1300–1700	2.9–3.6	17.2	0.97	120	3.1

source Honeywell, USA, Spectra data sheet, partial

[a] http://www.honeywell-advancedfibersandcomposites.com/products/fibers

The gel-spinning process consists of extruding a heated gel of UHMWPE through a spinneret, drawing it through air, and cooling it down in a water bath. The key in gel-spinning is to separate the molecular chains in the solvent to minimize entanglement and give the chains a chance to achieve a high degree of orientation. This high orientation gives the fiber its high tensile strength [20].

The physical properties of a spectra grade made by Honeywell are summarized in Table 9.2, showing the exceptional mechanical properties of this fiber [21].

9.8 Polyolefins in Thermal Bonding Applications

It was mentioned earlier that nonwoven fabrics need to be bonded in order to impart strength and integrity to the loose fibrous structure. Bonding could be mechanical such as needle punching, or through the action of water jets such as in hydro-entangled wet-laid nonwovens. Chemical bonding is also a common technique, and it involves spraying the fabric with latex or other adhesive chemicals and then curing the glue in an oven to bond the structure together.

Polyolefin fibers offer yet another option in bonding of nonwovens, namely thermal bonding. Thermal bonding involves the flow of low melting fibers, which are a part of the fabric construction, as the fabric passes between heated calendars. The temperature of the rolls is set higher than the melting point of the polyolefin fiber, and an amount of pressure is exerted on the web to help the polyolefin fibers melting and flow to bond the NW structure. Both PE and PP are used as thermal binders in nonwoven [22]. An innovative technology was developed by Hoechst Celanese in the 1990s that combines high melting point polyester with low melting point polyethylene (LLDPE) in a sheath–core bicomponent fiber geometry. The fiber marketed under the trade name Celbond combines the strength of polyester fiber with the low melting thermal bonding properties of polyethylene for use in airlaid, carded, and other types of hygiene and industrial nonwoven.

Thermal bonding is also environmentally friendly because it avoids the use of chemicals and solvents during the NW process. It also offer a more open structure and softer hand in hygiene and other applications compared to chemical bonding.

References

1. Man-Made Fibers Fact book, Man-made Fiber Association, 1970, p. 26
2. A. Ziabicki, *Fundamentals of Fiber Formation* (Wiley, London, 1976). ISBN 0-471-98220-2
3. Fiber Manufacturing, http://www.fibersource.com/f-tutor/techpag.html, Fibersource.com, 2013
4. Nonwovens Fabric Sampler and Technology Reference, Association of the Non-wovens Fabric Industry (INDA), USA, 1998
5. S. Batra, M. Thompson, E. Vauhn, L. Wadsworth, *INDA Nonwovens Glossary*. (Association of the Nonwovens Fabrics Industry, USA, 2002)
6. E.A. Vaughn, *Nonwovens World Factbook 1991* (Miller Freeman, San Francisco, 1990)

7. Spunbond and Melting Blown Process Charts, KASEN Corporation Japan. http://www.kasen.co.jp/English/product/line/work.html
8. L.C. Wadsworth, S.R. Malkan, A review of melting blowing technology. INB Nonwovens **2**, 46–52 (1991)
9. R. Hedge, A. Dahiya, M. Kamath. *Olefin Fiber Update*. (University of Tennessee, UTK, 2004) online article
10. H. Needles, *Textile Fibers, Dyes, Finishes and Processes* (Noyes Publications, New York, 1986)
11. H. Mohapatra, A. Chatterjee, P. Kumar, New generation application of PP fiber. Int. J. Eng. Nanotechnol. (IJAENT), **1** (2013)
12. S.C.O. Ugbolue, *Polyolefin Fibers: Industrial and Medical Applications* (Woodhead Publishing, Cambridge, 2009)
13. Polyolefin Fibers, Chemical Economics Handbook, IHS report, 2014
14. H. Koslowski, Man-made fibers for non-woven fabrics. Chem. Fibers Int. Tech. Textiles 28–29 (2010)
15. M.Y. Qin, Global fibers overview, Synth. Fibers Raw Mater. Committee Meet. APIC (2014)
16. P. Sheerlinck, M. Ouederni, Melt Blown Polymeric filtration Medium for High Efficiency Fluid Filtration, US Patent 8372292B2, Feb 2013, assigned to Johns Manville Corp., USA
17. G. Gleixner, A. Vollmar, Fibers of metallocene polyolefins. Chem. Fibers Int. **48**, 393–394 (1998)
18. M. Van Parys, PP Fiber Eng.: Latest Dev. Chem. Fibers Int. **48**, 317–322 (1998)
19. Global Polypropylene Fibers: Markets, Technologies and Trends 2014–2020. Chemical Market Resources Inc. (CMR) (2014)
20. A.J. Pennings, R.J. Van Derhooft, A.R. Postema, W. Hoogsteen, G. Ten Brinke, Hig speed gel-spinning of ultra high molecular weight polyethylene. Polym. Bull. **16**(2–3), 167–174 (1986)
21. Spectra Fiber Data Sheet, Heneywell Corporation, USA. http://www.honeywell-advancedfibersandcomposites.com/products/fibers
22. R. Dharmathikary, T. Gilmore, H. Davis, S. Batra. Thermal Bonding of Nonwoven Fabrics. Textile Prog. **26**(2), 1–37 (1995 published online Jan 2009)

Chapter 10
Biomedical Applications of Polyolefins

K.S. Joshy, Laly A. Pothen and Sabu Thomas

10.1 Introduction

In medical field, polymers find a wide variety of applications. The polymers which are used in internal devices are in continuous contact with human body. So in order to be used safely inside the body, the polymers need to meet certain requirements and regulations. The most important requirement is the biocompatibility of the polymers. They should be resistant to bodily fluids, tissues, cells and enzymes. They should be neutral to human body. The biocompatibility is in fact dependent on several factors including chemical structure of the material. The foremost consideration of a polymer to be used as a biomaterial is its biocompatible nature. That is, the polymer is to be compatible with tissues and biological fluids or more precisely it is the ability of the material which can exist in contact with blood and enzymes without undergoing degradation or provoking thrombosis, breakdown of tissues, or harmful, immune, toxicological or allergenic effects. The degradation product of polymers represents another important property of polymers for tissue engineering applications. On the basis of repeated laboratory experimentation and clinical investigation, a large number of available synthetic polymers make the selection of a suitable material for particular biomedical application. The most common

---

K.S. Joshy
Department of Chemistry, CMS College Kottayam, Kottayam, Kerala, India
e-mail: joshyk.s@gmail.com

L.A. Pothen
Department of Chemistry, Bishop Moore College, Mavelikkara, Kerala, India

K.S. Joshy · S. Thomas (✉)
International and Inter University Centre for Nanoscience and Nanotechnology,
Kottayam, Kerala, India
e-mail: sabuchathukulam@yahoo.co.uk

S. Thomas
School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_10

synthetic polymers that are considered to be biocompatible and biostable in the body are polyethylene (PE), polypropylene (PP), polyurethane (PU), polytetrafluoroethylene (PTFE), poly(viny1chloride) (PVC), polyamides (PA), poly (methylmethacrylate) (PMMA), polyacetal, polycarbonate (PC), poly(ethy1ene terephthalate) (PET), polyetheretherketone (PEEK), and polysulfone (PSU).

Among these polymers, polyolefins such as PE and PP possess a prominent position in biomedical applications. PE has the chemical formula $(CH_2CH_2)n$. It is produced by different manufacturing process and can be classified into low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), cross-linked polyethylene (XLPE) and ultra-high molecular weight polyethylene (UHMWPE). The second simplest polyolefin is PP, basically PE with a methyl side group. The properties of PP are highly dependent on the relative orientation of the side groups in the space (tacticity). Depending on the orientation of methyl side groups, PP can be classified as atactic PP (aPP), isotactic PP (iPP) and syndiotactic PP (sPP). Properties of these polymers depend on the degree of branching and length of the polymer chain. Among the many polymeric biomaterials suitable for biomedical applications, one such family currently attracting attention are polyolefins. Polyolefins are important class of commodity polymers, produced in more than 150 million metric tons per year [1]. A wide range of products are made from polyolefins ranging from fibres with superior mechanical properties to flexible packaging and moulded parts. Products made from polyolefins have increased application in recent years largely due to their low cost, good mechanical properties, light weight, durability, resistance to weathering and photodegradation as well as biological attack and hydrophobicity. Polyolefins are one of the most popular polymers in the manufacturing of biomedical field especially due to their high transparency, chemical inertness over others polymers, and tough and oil/fat resistant [2, 3].

Biocompatible polymers have been extensively used as biomaterials which are the main constituents of medical devices and also an important constituent of drug delivery systems. They have also been presented for years in pharmacy as an important candidate for the administration of drugs or pharmaceutics in the oral route. For vaccine and drug delivery, more sophisticated polymers have been developed; polymers have also been used in different parts and different functions in human body. In medical industry, polymers have a wide variety of applications. For biomedical applications, polymers should be in contact with human body, so certain requirements and regulations are needed when the polymer is safely used inside the human body. Biocompatibility is the most important property needed to be considered when a material is applied inside the body. The biocompatibility of a polymeric material not only depends on their chemical structure, but also is highly influenced by several other factors. When a polymeric medical device implanted inside the body, the body's response to the device depends on the location and movement of the material and the surrounding human environment. The material performances also depend on the microbiological effect and biofilm formation on the internal medical device. This biofilm formation initiates the biodegradation process of the polymeric material. This degradation results in the migration of additives and low-molecular weight compound that lowers the biocompatibility and stability of the polymer, which can lead to the failure of the device and/or cause health-related issues. So an awareness of different degradation processes that may occur inside the human body due to blood, tissue or biofilm interactions is very important for a polymer to be considered in medical device. A high concentration of microorganisms in the biofilm can also cause serious infections and health-related problems. Therefore, the selection of the right polymers that exhibits high stability against the previously mentioned factors is essential for biomedical applications [4, 5].

10.2 Biocompatibility

Biocompatibility of a medical device or implant is the ability of the material to perform without causing a host response, or having toxic or injurious effects. It is the basic requirement of a material implant into the body and also very crucial for the lifetime usage of the biomedical device [6–8]. The collagen tissue in the body readily encapsulates a non-biocompatible material, results in the failure of the desired function of the product, which may in turn cause serious health problems. The polarity of the polymeric material largely depends on the tissue growth. The non-polar polymers are surrounded by less tissue than polar polymers [8]. If the body's response is the rejection of a certain material, the body tries to expel it through chemical reactions by phagocytic or enzymatic activity [8, 9], resulting in the emergence of inflammations. This body's response to the implanted polymeric material is highly dependent on the form (foam, fibre, and film), shape and movement of the implant, as well as its location in the body. A smooth, rounded shape polymeric material presents less interaction and less adhesion of tissue around the material as compared to a rough-edged shape. A large surface area provided by the polymer powders gives extremely high tissue interactions compared to other forms [8]. Properties of polymeric material such as low wear resistance and mechanical stress result in the displacement of the implant in the body that causes discomfort or pain to the patient. The implant or device should be non-harmful to living tissues and no toxic substances may be formed or leached out during the implementation. The polymeric material for biomedical application must be non-toxic, non-carcinogenic, non-thrombogenic, non-inflammatory and non-immunogenic [7, 8]. The polymer that contains monomers, polymerisation catalyst, leaching additives, etc. is not suitable for biomedical application. Due to the constant blood exposure, the polymeric devices should be biocompatible to reduce the probability of clogging during the use. So the surface modification of the devices by anticoagulants such as heparin is usually preferred for improving the biocompatibility of the material [9]. The biocompatible polymers when implanted into the body should not interact with the body as a whole or the surrounding tissues. There are no material parameters or biological tests for the quantitative assessment of the biocompatibility of the polymers [10]. By definition, biocompatibility means the ability of a material to perform with an appropriate host response in a specific application. The polymer can exist in

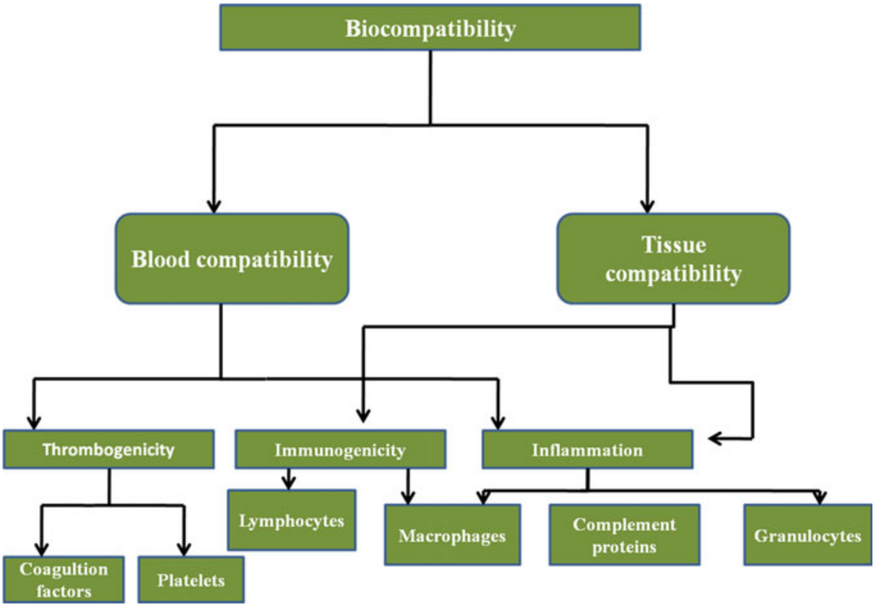


Fig. 10.1 Schematic representation of possible interactions of a material in contact with living tissue [11]

contact with blood and enzymes, as well as it will not undergo any degradation or toxicological effect. It will not cause thrombosis, breakdown of tissues, or harmful to the immune system. The biocompatible polyolefin, especially the higher molecular weight PE, shows only a minimum toxicity [7]. The biocompatibility of the polymers depends on the following factors: (a) degradation product of the polymer; (b) initial interactions with physiological components; and (c) stability of implants in the surrounding biological medium [11]. Schematic representation of possible reactions of the biomaterial in contact with human body is shown in Fig. 10.1.

10.2.1 Biocompatibility and Toxicity

Non-toxicity and biocompatibility are different terms; toxicity related to cell death. It is either systemic or local and it is generally induced by soluble products. On the other hand, biocompatibility is more related to the reactions of living tissues in contact with a solid material. Soluble products can be released by a material. It is the basic requirement of implantable materials and plays an important role throughout the lifetime of the biomedical device. If the material is not biocompatible, it is rapidly encapsulated by collagen tissue, resulting in the failure of the desired function of the product. Thus, one product is expelled by the body through phagocytic or enzymatic activity resulting in the emergence of inflammations [9, 10].

10.3 Polymers for Medical Device Applications

The medical device technology is an emerging area in recent years. According to ISO 1385 standard, the medical device is an instrument, apparatus, implant, machines, appliances, in vitro reagent or calibrator or software intended by the manufacture to be used alone or in combination with human being for specific purposes such as

- Diagnosis, monitoring and prevention of diseases;
- Diagnosis, monitoring, treatment and compensation for an injury;
- Investigation, replacement, or modification of the anatomy of a physiological process;
- Supporting or sustaining life;
- Control of conception; and
- In vitro examination of specimens derived from human body.

Table 10.1 represents the polymers which are used in medical devices. They include both synthetic non-biodegradable and biodegradable polymers. They are mainly used to produce various medical devices such as implants, drug carriers, protective packaging materials, and healthcare items [12].

Table 10.1 Common synthetic polymers used in medical devices [12]

Polymer	Medical device application
Polyethylene	Orthopaedic implants, containers, catheters, non-woven textiles
Polypropylene	Disposable items (e.g. syringes), non-woven textiles, membranes, sutures
Polyurethanes	Ligament replacements, heart valve prostheses, vascular graft prostheses, breast prosthesis, catheter, cannulae films, tubing
Polyvinylchloride	Lung bypass sets, catheters and cannulae, tubing for dialysis and endotracheal feeding
Polyethylene terephthalate	Sutures, artificial vascular grafts
Polycarbonates	Blood oxygenators, blood filters, tubing connectors, casting for dialysis membranes
Poly(methyl methacrylate)	Membranes, implants, part of bone cement and prosthetic devices
Polydimethylsiloxane	Artificial skin, joint replacement, vitreous replacement, artificial heart, breast implants, different types of catheters and cannulae
Polytetrafluoroethylene	Artificial vascular grafts, catheters (albeit rarely)
Polyether ether ketone	Tubing
Polylactide	Resorbable implants
Fluoropolymers	Prosthetic devices
Acrylics	Tubing connectors, blood set components, dental polymers, intracellular implants
Cellulosics	Heamodialysis membranes, haemofilters
Acetals	Components in asthma inhalers

Polyolefins are the main components used in prosthetic devices, hip joints and knee implants. They exhibit a high degree of biocompatibility (almost neutral), excellent chemical resistance and superior mechanical properties. The main advantage of polyolefins compared to metallic implants is the low friction coefficient and wear resistance due to their self-lubricating characteristics [13–17].

10.4 Mechanism of Degradation of Medical Polymers

Human body contains enormous number of enzymes and chemicals that are capable of attacking the implanted polymeric material, so the body itself cause degradation of the material. Depending on the chemical, mechanical and molecular interactions of the implanted polymeric material with the human body, four types of degradation of the material are generally observed [18, 19].

1. **Hydrolysis**
   Degradation of implanted polymeric material through hydrolysis is generally occurred in the case of hydrophilic polymers. The adsorbed water acts as a plasticizer, altering the physical properties of the material and resulted in dimensional instability of the device or implant [20, 21].
2. **Oxidation**
   As a result of the rejection of implanted material, peroxides are produced inside the body that causes oxidative degradation of medical polymers. The oxidative degradation of medical polymers occurs inside the human body and can be monitored in simulated environments [22, 23]. The reaction is caused by the peroxides produced by the human body against “non-accepted” implant materials through a rejection mechanism [22, 24].
3. **Enzymatic degradation**
   Enzymes play an important role in the degradation of biomaterials by catalysing their hydrolysis. They are biological catalysts, which accelerate the rate of reactions that occur in living organisms without undergoing themselves in any permanent change. Most of the reactions of cellular metabolism would not occur in the absence of enzymes. Hydrolases are the enzyme that catalyses hydrolysis reactions. pH-sensitive polymers undergo enzymatic degradation [25]. The method of quantitative histoenzymology measures the activity of enzymes in PE and PP. Aminopeptidase has very low activity on PP surface after implantation. Oxy reductase has moderately high activity on PP. Both aminopeptidase and oxy reductase have moderately high activity on PE surface during implantation [26–29].
4. **Physical degradation**
   Physical degradation of implanted polymeric material is mainly due to the interaction of the materials by means of temperature, air, light and high energy radiation [21].

10.5 Degradation of Polyolefins

Polyolefins are difficult to hydrolysis. It also inert towards enzymatic or physical degradation. Oxidative degradation is the main type of degradation observed in polyolefin. Oxidative degradation is the main type of degradation observed in polyolefin [30].

10.5.1 Oxo-biodegradation

It is a two-stage polyolefin degradation process. In the first stage, oxygen in the air reacts with the polymer results in the oxidation of carbon backbone in the polymer. This results in the formation of smaller molecular fragments. The incorporation of oxygen into the carbon chain polymer backbone results in the formation of functional groups such as carboxylic acids, ester, aldehydes and alcohols. The polymers change their behaviour from hydrophobic to hydrophilic nature and easily undergo hydrolysis. In the second stage, oxidation products undergo biodegradation by microorganisms (bacteria, fungi and algae) [30–35].

10.5.2 Photodegradation

Polyolefin products undergo photodegradation by the absorption of UV light. This is due to the unstable product formation of polyolefins during fabrication process, due to the presence of impurities like carbonyl or hydroperoxide groups [30, 31].

10.5.3 Degradation from Mechanical Stress

Mechanical stress on polyolifins causes changes in morphology of the polymer which in turn leads to the degradation of the polymer. Stress causes changes in morphology that leads to the degradation of the polymer [35, 36].

10.5.4 Processing Methods of Polyolefins

In order to transform the polymers into medical devices such as tubing, catheters and other medical items, polymers have to be processed by different techniques, such as extrusion, moulding, spinning and dip coating. Several additives are used to facilitate the processing and improve the properties of polymers. They also increase the stability of polymers during thermo-mechanical treatments. A schematic view of

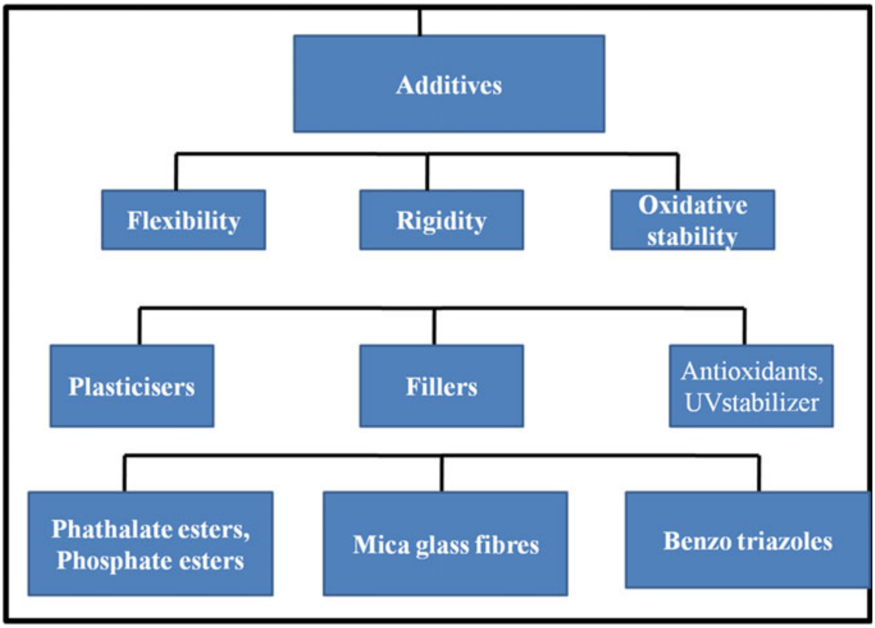


Fig. 10.2 Schematic view of different additives used to modify the properties of polymers during processing [37]

additives used during processing is shown in Fig. 10.2. For the manufacture of useful items, the addition of such products is most important [37].

10.5.5 Other Processing Methods of Polyolefins for Biomedical Applications Involves

- Solid-state mixing;
- Thermal forming;
- Solution gelation;
- Crystallization;
- In situ polymerisation;
- Compression moulding;
- Injection moulding; and
- Ball mill compounding.

Thermal forming and solid-state mixing process are easy processes to be performed. In this processing method, the filler/matrix interfacial strength is poor because only interaction between the filler and the matrix is mechanical interlocking even after chemical surface treatment is employed [38–47].

10.6 Polyolefins for Cardiovascular Applications

An important application of polyolefins is their use as a cardiovascular biomaterial. The important properties to be considered when a material is used as a cardiovascular biomaterial are (1) mechanical and physical properties such as fatigue, creep, friction, wear resistance, strength and deformation and (2) biocompatibility of the material that is compatible to the material with tissue. These characteristics can be tested by means of in vivo and in vitro experiments [48]. The first properties depend on the nature and inherent properties of biomaterial are to be considered. However, the second aspect biocompatibility is of immense interest for every cardiac implant material chosen [49]. In cardiovascular applications, both low-density polyethylene and high-density polyethylene are utilised in making tubings and housings for blood supply. They are also used in the production of blood bags. Polypropylene is used for making heart valve structures [50, 51]. *Compared with the properties of polyamides, poly esters, poly tetra fluoro ethylene and polyurethanes, polyolefins possess good strength, high hardness, rigidity and better blood compatibility that are necessary for cardiovascular applications* [52]. In order to improve the compatibility of a biomaterial used for cardiovascular applications, different strategies were adopted to modify the surface of polyolefins and other biomaterials. These surface modification techniques were classified into three major classes, namely physical immobilization of biological material, chemical modification and modification of materials using energy possessing substances such as plasma and ion implantation [53] (Fig. 10.3).

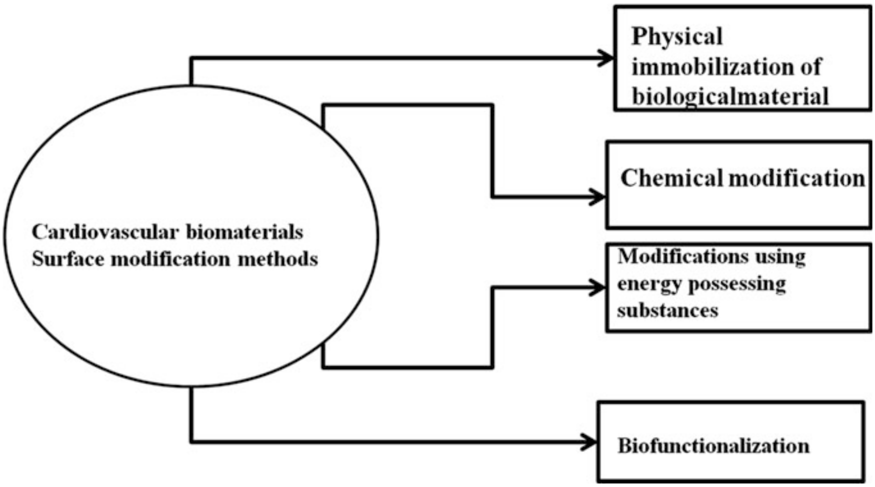


Fig. 10.3 Cardiovascular biomaterials surface modification methods [53]

10.6.1 Polyethylene

Since the 1950s, polyethylene (PE) has been applied in surgery. At that time after PE implantation, only formation of so-called granulated tissue around a polymer was found, that is a weak response of the body to the implant. PE is not widely used for the substitution of soft tissues, but it is an important substitute for bone tissues, i.e. the head of the hip bone and other elements of the pelvis bones. The wear resistance property of low pressure PE makes its application in bone tissue substitution. HDPE can be widely used in pelvic prostheses [54].

10.6.2 Polypropylene

The high chemical stability and favourable mechanical properties of PP lead to its important use in medicine. It was applied for lining the valves of artificial hearts and for ball joint prostheses in the early 1970s. PP shows a moderate response of the tissues of the living body. It is commercially available in the form of suture threads [54].

10.7 Current Biomedical Applications of Polyolefins

10.7.1 Al–Cu–Fe Quasicrystal/UHMWPE Composites as Biomaterials for Acetabular Cup Prosthetics

Anderson et al. [55] produced Al–Cu–Fe quasicrystal/UHMWPE composites as biomaterials for acetabular cup prosthetics. The usage of UHMWPE for the acetabular cup prosthetic is due to the strong and bioinert nature of UHMWPE. Quasicrystals are complex metal alloys that possess physical properties such as low thermal conductivity, low coefficients of friction, and high hardness. Compared to other rigid low aspect ratio fillers, the quasicrystal-filled polymers have improved wear properties and mechanical properties. Wear testing results from pin-on-disc wear testing showed that Al–Cu–Fe-filled UHMWPE discs had enhanced wear resistance to volume loss, as compared to unfilled UHMWPE and alumina-filled UHMWPE. The enhanced wear resistance of prepared composites is due to the high hardness, high Young's modulus and low coefficient of friction of the Al–Cu–Fe quasicrystalline filler that may increase the strength of Al–Cu–Fe/UHMWPE composites as compared to unfilled UHMWPE.

10.7.2 Bioglass/HDPE Composites for Soft Tissue Applications

In another study, Wang et al. [56] produced bioglass/high-density polyethylene composite for soft tissue applications. Bioglass composites were produced by manufacturing process consisting of blending, compounding, powdering and compression moulding. A homogeneous distribution of bioglass particles inside the polymer matrix was obtained after compounding and subsequent composite processing. The Young's modulus and micro-hardness of the composites increased with the increase in bioglass volume while the tensile strength and fracture strain decreased. Bioglass has the ability to bond with both hard and soft tissues [57, 58].

10.7.3 Bone Replacement Application of Polyolefin Composites

For medical devices particularly in tissue substitution metals, polymers and ceramics were successfully used. The development of new biomaterials has been rapidly increased for the last twenty years [59]. A bioactive and biodegradable composite is developed when a biodegradable polymer is used as matrix of the composite. When a biodegradable bone-substituting material utalised for implantation in the body, as a consequence, gradual decrease in strength and stiffness of implanted material is generally observed after the implantation. So when a material is selected for bone replacement application, it should withstand any anticipated physical load imposed by body actions without substantial dimensional changes, catastrophic fracture or failure due to impact, creep or fatigue within their expected lifetime in the body. So the best material for replacing a body tissue is the one that is similar to that of body tissue. PE is an inert material with a high degree of biocompatibility chemical resistance, tensile strength and hardness. They are also non-antigenic, non-allergenic, non-resorbable, highly stable, easy to fixate, and is available in a wide variety of preformed shapes. Polypropylene is also an inert biomaterial has good tensile strength and easy to suture. They have biologic properties similar to polyethylene. It is also used in the reconstruction of chest wall defects, either alone or sandwiched around a polymethylmethacrylate core [60, 61].

10.7.4 Polyethylene for Bioactive Bone Substitution

Bone is a natural composite of apatite-collagen. So a composite of polymer matrix containing bioactive particulate filler is a natural choice for substituting cortical bone. Bone substitutes can be easily made by using hydroxyapatite (HA) particles as the bioactive component because of its close similarity with bone apatite and its excellent bioactivity. So a composite made of HA with polymer matrix provides sufficient strength for the bone substitute. PE is widely used in orthopaedics. So a combination of PE and HA to produce a composite that mimics the structure and mechanical properties of cortical bone can be used. The high bioactivity of the composite is provided by the high volume percentage of HA which is provided by the ductile nature of PE. The good bioactivity of the composite also strengthens the bond between the implants and the surrounding tissue [62–64].

10.7.5 Polyethylene Magnetic Nanoparticle for Biomedical Applications

Polyolefin-based magnetic nanoparticles find applications in magnetic cell separations, drug delivery and diagnostics. Composites of synthetic polymers are very useful in biomedical field because they are less expensive compared to biopolymers of natural origin. In this particular application, very low-molecular weight polyethylene particles can be used. This polymer is non-hazardous and has a wax-like appearance. The synthesis of polymer-coated magnetic particle involves the ultrasound mixing of the polymer and the surface modified iron oxide in solvent. Further, non-solvent was mixed to the resultant reaction mixture which results in the formation of homogeneous emulsion with well-dispersed phase of polymers with adsorbed maghemite. Magnetic property of these composite particles is very important because these particles are aimed to be used for biomedical application. These polymer-coated magnetic particles were further coated with avidin, a strong ligand binding protein and widely used in cell separations and immunoassays [65–72].

10.7.6 Low-Temperature Plasma-Treated Ultra-High Molecular Weight PE (UHMWPE) for Biomedical Application

Surface-modified polyolefin materials are widely used in biomedical field. Low-temperature plasma-treated PE was well suited for biomedical application. UHMWPE after surface modification with low-temperature plasma is the principal material used to replace damaged cartilage in total joint arthroplasty or the surgical reconstruction of a diseased joint [73]. The UHMWPE having desirable mechanical properties and biocompatibility is used in orthopaedic implants and joint socket in bone replacement.

10.7.7 Polypropylene Monofilament for Biomedical Applications

The optimum tensile strength and low level of tissue reaction made PP as one of the widely used biostable sutures. Some of the problems usually encountered with sutures are the microbial infections on the suture site that leads to the deterioration of the wound and related complications especially where post-surgical care is not well taken up. Therefore, it is necessary to modify the PP sutures. This can be carried out in such a way that functional groups are added and where a drug may be immobilized. Once the suture is in contact with the biosystem, the drug is released from the suture and provides antimicrobial action. The grafting of other polymers on PP surface leads to considerable change in properties. The hydrogel characteristics onto PP surface for biomedical application was induced by radiation-induced graft polymerisation of monomers such as 2-hydroxyethylmethacrylate (HEMA), methacrylic acid, acrylamide and N-vinyl pyrrolidone. One of the disadvantages of grafting is the formation of homopolymers that remained occluded within the polymer matrix and its complete separation from the suture matrix could not be achieved due to the hydrogel nature of the grafting polymer, thereby the suture characteristics can greatly deteriorated. The grafting of an ionic component with the non-ionic PP matrix can add a loss in tensile strength. So in order to overcome this problem, the grafting of non-ionic monomer, acrylonitrile, onto the PP monofilament using pre-irradiation can be done. By using this method, the homopolymerisation can be minimised and phase separation of the polymer matrix can be avoided. It also provides better compatibility of the matrices. This grafted polymer matrix was subsequently hydrolysed to get carboxyl groups for subsequent antimicrobial drug immobilization. The sutures made by this grafted PP monofilament have better tensile strength and improved anti-microbial properties [74].

10.7.8 Filament Wound Flat Strip Composites

Filament wound flat strip composites of PE fibre-reinforced ethylene-butane copolymer have been used for different biomedical applications. Composites of three different matrix compositions and two winding angles were reported. The matrix composition varied with the copolymer ratio rendering the composite material softening and it is more compliant and suitable for different biomedical application [75].

10.7.9 Newly Commercially Available Polyolefin-Based Biomedical Products

A recent development in metallocene technology results in the production of cost-effective metallocene-based polyolefin and cyclo-olefin materials by the use of metallocene catalyst. Metallocenes are single-site catalysts that are used to make PE with completely different microstructures from those made with Ziegler–Natta and Phillips catalysts. This metallocene-based polyolefins have the potential to achieve better performance than existing PE and PP formulations. Cyclo-olefin material-based products give high clarity for medical applications. They have the potential to replace many of the existing speciality polymers and engineering plastics particularly for medical products which require high clarity, impact strength and ductility at low temperatures. As a result, polyolefin family took a prominent place in medical and healthcare product industries.

10.7.10 Advantages of Metallocene-Based Polyolefins

Metallocene PP, particularly s-PP, is one group of such compounds that attracted much attention. The properties of this material are similar to that of thermoplastic elastomers. Metallocene cyclo-olefin is another class that has been used in medical syringe applications. They give high clarity for solution drug prefilled syringes.

Other characteristics that make metallocene polyolefins attractive in medical industry are as follows:

- They are chemically inert and do not react with drug;
- Their narrow molecular weight distribution;
- They accommodate gamma radiation;
- They can be sterilized by steam; and
- They can be recycled and they can reduce disposal costs.

They also have some disadvantages because of their narrow molecular weight distribution, long crystallization half time and difficulties in processing techniques [76].

10.8 Future Challenges

Polyolefins are commonly found in many applications in biomedical field. Besides the advancements, there are still some drawbacks which prevent the wider use in many applications. This is mainly due to performance and cost when compared to their conventional counterparts. Studies can be focussed on the development of new in vitro environments for the degradation processes that may occur in the human body either due to body fluids or microbiological environment. Focus is on the commercialisation of currently used composites of polyolefins in medical field. The design of new material for specific applications in a traditional approach will still remain a challenging problem in the medical field.

10.9 Conclusion

The importance of polyolefins in current era has increased significantly due to their better mechanical properties, low cost and light weight. This chapter has provided an overview of the current applications of polyolefins including an overview of their properties such as biocompatibility, their interaction with body fluids, degradation of polyolefins, important additives used for strengthen the material and important processing techniques used for its formulation. Polyolefins are biocompatible and bioresorbable materials with increasing applications in the biomedical field. Applications of polyolefins include hard tissue usages such as bone substitutes, control drug delivery devices and tissue adhesives. The processing methods include spinning, dip coating and in situ polymerisation. Such state-of-the-art technologies applied to polyolefins will play a synergistic role in providing further insight and generating knowledge on the interaction between polyolefins and living tissue for a variety of biomedical applications. Thus, polyolefins have offered a very critical role in medical devices and disposable products with safety and quality of the products. They also provide flexibility to product design, manufacturing, sterility and integrity. Polyolefins offer advantages such as high-performance, low-cost medical products and are suitable for large-scale production by automation process. But still they face some limitations such as disposal of degradable products of polyolefins in human body and also the commercialisation of existing biomedical composites of polyolefins.

References

1. S.H. Teoh, Z.G. Tang, G.W. Hastings, Thermoplastic polymers in biomedical applications: structures, properties and processing, in *Handbook of Biomaterial Properties* (Springer, US, 1998), pp. 270–301
2. A. Peacock, *Handbook of Polyethylene: Structures: Properties, and Applications* (CRC Press, Cleveland, 2000)
3. S.A.S. Alariqi, A. Pratheep Kumar, B.S.M. Rao, R.P. Singh, Biodegradation of γ-sterilised biomedical polyolefins under composting and fungal culture environments. Polym. Degrad. Stab. **91**, 1105–1116 (2006)
4. P. Gupta, V. Kavita, G. Sanjay, Hydrogels: from controlled release to pH-responsive drug delivery. Drug Discovery Today **7**. 569–579 (2002)
5. G. Ponchel, I. Juan-Manuel, Specific and non-specific bioadhesive particulate systems for oral delivery to the gastrointestinal tract. Adv. Drug Deliv. Rev. **34**, 191–219 (1998)
6. D.F. Williams, On the nature of biomaterials. Biomaterials **30**, 5897–5909 (2009)
7. W.A.N. Dorland, *Dorland's Illustrated Medical Dictionary: Dorland's Illustrated Medical Dictionary* (Elsevier Health Sciences, 2011), p. 32
8. N. Akmal, A.M. Usmani, *Medical polymers and diagnostic reagents*. Environmental Science and Pollution Control Series (2000), pp. 485–514
9. C.G. Gebelein, Medical applications of polymers, in *Applied Polymer Science* (1985), pp. 535–556
10. D. Hofmann, E.C.K. Karl, L. Andreas, Knowledge-based approach towards hydrolytic degradation of polymer-based biomaterials. Adv. Mater. **21**, 3237–3245 (2009)

11. M. van Dijk, D.T. Rijkers, R.M. Liskamp, C.F. van Nostrum, W.E. Hennink, Synthesis and applications of biomedical and pharmaceutical polymers via click chemistry methodologies. Bioconjug. Chem. **20**, 2001–2016 (2009)
12. T. Galya, Antibacterial modifications of polymers by using metallic compounds, Doctoral thesis, Tomas Bata University in Zlin, Zlin, 2009
13. V. Sedlarik, Antimicrobial modifications of polymers, in *Biodegradation—Life of Science* (2013), pp. 187–204
14. G. Scott, Green polymers. Polym. Degrad. Stab. **68**, 1–7 (2000)
15. J. Guillet, D. Gilead, G. Scott, *Degradable polymers: principles and applications* (Chapman & Hall, London, UK, 1995)
16. W. Zhang, J. Junhui, Z. Yihe, Y. Qing, E.Z. Kurmaev, A. Moewes, Z. Jun, K. Paul Chu, Effects of NH_3, O_2, and N_2 co-implantation on Cu out-diffusion and antimicrobial properties of copper plasma-implanted polyethylene. Appl. Surf. Sci. **253**, 8981–8985 (2007)
17. K.J. Buschow, R.W. Cahn, M.C. Flemings, B. Ilschner, E.J. Kramer, S. Mahajan, Encyclopedia of materials. Sci. Technol. **1**, 11 (2001)
18. S. Lyu, U. Darrel, Degradability of polymers for implantable biomedical devices. Int. J. Mol. Sci. **10**, 4033–4065 (2009)
19. A. Gopferich, Mechanisms of polymer degradation and erosion. Biomaterials **17**, 103–114 (1996)
20. P. Kaali, E. Stromberg, S. Karlsson, Prevention of biofilm associated infections and degradation of polymeric materials used in biomedical applications (INTECH Open Access Publisher, 2011), pp. 513–540
21. D.M. Wiles, S. Gerald, Polyolefins with controlled environmental degradability. Polym. Degrad. Stab. **91**, 1581–1592 (2006)
22. S. Backman, B. Gunilla, J. Unn-Britt, L. Michael, M. Agneta, S. Ulla, E. Ragnhild Aune, F. Claes, K. Sigbritt, Material wear of polymeric tracheostomy tubes: a six-month study. The Laryngoscope **119**, 657–664 (2009)
23. P.E.S. Kaali, E. Stromberg, E.A. Ragnhild, C. Gyorgy, M. Dane, K. Sigbritt, Antimicrobial properties of Ag+ loaded zeolite polyester polyurethane and silicone rubber and long-term properties after exposure to in-vitro ageing. Polym. Degrad. Stab. **95**, 1456–1465 (2010)
24. J.P. Santerre, K. Woodhouse, G. Laroche, R.S. Labow, Understanding the biodegradation of polyurethanes: from classical implants to tissue engineering materials. Biomaterials **26**, 7457–7470 (2005)
25. H. Park, K. Park, W.S. Shalaby, *Biodegradable Hydrogels for Drug Delivery* (CRC Press, Cleveland, 2011)
26. E.M. Christenson, P. Sachin, M. James Anderson, H. Anne, Enzymatic degradation of poly (ether urethane) and poly (carbonate urethane) by cholesterol esterase. Biomaterials **27**, 3920–3926 (2006)
27. D.G. Duguay, R.S. Labow, J.P. Santerre, D.D. McLean, Development of a mathematical model describing the enzymatic degradation of biomedical polyurethanes. 1. Background, rationale and model formulation. Polym. Degrad. Stab. **47**, 229–249 (1995)
28. J.P. Santerre, D.G. Duguay, R.S. Labow, J.L. Brash, *Interactions of Hydrolytic Enzymes at an Aqueous—Polyurethane Interface* (1995)
29. J.P. Santerre, R.S. Labow, G.A. Adams, Enzyme-biomaterial interactions: effect of biosystems on degradation of polyurethanes. J. Biomed. Mater. Res. **27**, 97–109 (1993)
30. D.M. Wiles, S. Gerald, Polyolefins with controlled environmental degradability. Polym. Degrad. Stab. **91**, 1581–1592 (2006)
31. D. Feldman, Polymer weathering: photo-oxidation. J. Polym. Environ. **10**, 163–173 (2002)
32. E. Chiellini, A. Corti, S. Dantone, R. Baciu, Oxo-biodegradable carbon backbone polymers—oxidative degradation of polyethylene under accelerated test conditions. Polym. Degrad. Stab. **91**, 2739–2747 (2006)
33. I.I. Eyenga, W.W. Focke, L.C. Prinsloo, A.T. Tolmay, Photodegradation: a solution for the shopping bag “visual pollution” problem, in *Macromolecular Symposia* (Wiley-VCH Verlag GmbH, 2002), pp. 139–152

34. W.K. Busfield, T. Paulina, Photo-oxidative degradation of mechanically stressed polyolefins. Polym. Degrad. Stab. **51**, 185–196 (1996)
35. M. M Reddy, M. Deighton, K. Rahul, S. Gupta, S. N. Bhattacharya, R. Parthasarathy, Biodegradation of oxo-biodegradable polyethylene. J. Appl. Polym. Sci. **111**, 1426–1432 (2009)
36. A. Albertsson, S.O. Andersson, S. Karlsson, The mechanism of biodegradation of polyethylene. Polym. Degrad. Stab. **18**, 73–87 (1987)
37. D.J.P. Labarre, P. Gilles, V. Christine, *Biomedical and Pharmaceutical Polymers* (Pharmaceutical Press, London, 2011)
38. C.M. Chan, C. Chi-Leung, M.F.Y. Matthew, Electrical properties of polymer composites prepared by sintering a mixture of carbon black and ultra-high molecular weight polyethylene powder. Polym. Eng. Sci. **37**, 1127–1136 (1997)
39. W. Thongruang, C. Maurice Balik, J.S. Richard, Volume-exclusion effects in polyethylene blends filled with carbon black, graphite, or carbon fiber. J. Polym. Sci., Part B: Polym. Phys. **40**, 1013–1025 (2002)
40. S.L. Ruan, P. Gao, X.G. Yang, T.X. Yu, Toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes. Polymer **44**, 5643–5654 (2003)
41. Q. Wu, W. Xin, G. Weiping, H. Youliang, Q. Zongneng, Unusual rheological behaviors of linear PE and PE/kaolin composite. J. Appl. Polym. Sci. **80**, 2154–2161 (2001)
42. J. Tong, M. Yunhai, J. Man, Effects of the wollastonite fiber modification on the sliding wear behavior of the UHMWPE composites. Wear **255**, 734–741 (2003)
43. X.L. Xie, C.Y. Tang, Y.Y.C. Kathy, X.C. Wu, C.P. Tsui, C.Y. Cheung, Wear performance of ultrahigh molecular weight polyethylene/quartz composites. Biomaterials **24**, 1889–1896 (2003)
44. M. Hashimoto, T. Hiroaki, M. Masataka, Y. Yoshiyuki, K. Tadashi, Titanium dioxide/ultra high molecular weight polyethylene composite for bone-repairing applications: preparation and biocompatibility. Key Eng. Mater. **240**, 415–418 (2002)
45. S. Roy, S. Pal, Characterization of silane coated hollow sphere alumina-reinforced ultra high molecular weight polyethylene composite as a possible bone substitute material. Bull. Mater. Sci. **25**, 609–612 (2002)
46. J. Suwanprateeb, Binary and ternary particulated composites: UHMWPE/$CaCO_3$/HDPE. J. Appl. Polym. Sci. **75**, 1503–1513 (2000)
47. Y. Bin, K. Mayuna, Z. Dan Zhu, M. Masaru, Development of highly oriented polyethylene filled with aligned carbon nanotubes by gelation/crystallization from solutions. Macromolecules **36**, 6213–6219 (2003)
48. C.M. Agrawal, Reconstructing the human body using biomaterials. JOM **50**, 31–35 (1998)
49. M.N. Helmus, A.H. Jeffrey, Materials selection. Cardiovasc. Pathol. **2**, 53–71 (1993)
50. R.C. Eberhart, H.H. Hsiao, N. Kevin, Cardiovascular materials. MRS Bull. **16**, 50–54 (1991)
51. M. Bessler, T.A. Chuter, U.S. Patent No. 5,855,601. (U.S. Patent and Trademark Office, Washington, DC, 1999)
52. H.B. Lee, G. Khang, J.H. Lee, J.D. Bronzino, Polymeric biomaterials, in *Biomaterials: Principles and Applications* (CRC Press, Boca Raton, 2003)
53. S.K. Jaganathan, E. Supriyanto, S. Murugesan, A. Balaji, M.K. Asokan, Biomaterials in cardiovascular research: applications and clinical implications. BioMed Res. Int. **2014**, 1–12 (2014)
54. M. Mackley. C. Vasile, R. Seymour, *Handbook of Polyolefins* (Marcel Dekker, Inc., New York, 1993), ISBN 0–84247-89784, 1995, p. 176
55. B.C. Anderson, P.D. Bloom, K.G. Baikerikar, V.V. Sheares, S.K. Mallapragada, Al–Cu–Fe quasicrystal/ultra-high molecular weight polyethylene composites as biomaterials for acetabular cup prosthetics. Biomaterials **23**, 1761–1768 (2002)
56. Q. Wu, X. Wang, W. Gao, Y. Hu, Z. Qi, Unusual rheological behaviors of linear PE and PE/kaolin composite. J. Appl. Polym. Sci. **80**, 2154–2161 (2001)
57. E.S. Carlisle, M.R. Mariappan, K.D. Nelson, B.E. Thomes, R.B. Timmons, A. Constantinescu, R.C. Eberhart, P.E. Bankey, Enhancing hepatocyte adhesion by pulsed plasma deposition and polyethylene glycol coupling. Tissue Eng. **6**, 45–52 (2000)

58. J.B. Park, J.D. Bronzino, *Biomaterials: Principles and Applications* (CRC Press, Cleveland, 2002)
59. H. Balakrishnan, M.R. Husin, M.U. Wahit, M.R. Abdul, Kadir. Maleated high density polyethylene compatibilized high density polyethylene/hydroxyapatite composites for biomedical applications: properties and characterization. Polym.-Plast. Technol. Eng. **52**, 774–782 (2013)
60. A.S. Breitbart, V.J. Ablaza, Implant materials, in *Grabb and Smith's Plastic Surgery*, 5th edn. (Lippincott-Raven, Philadelphia, 1997), pp. 39–46
61. M. Wang, Developing bioactive composite materials for tissue replacement. Biomaterials **24**, 2133–2151 (2003)
62. W. Bonfield, M.D. Grynpas, A.E. Tully, J. Bowman, J. Abram, Hydroxyapatite reinforced polyethylene—a mechanically compatible implant material for bone replacement. Biomaterials **2**, 185–186 (1981)
63. M. Wang, D. Porter, Processing, characterisation, and evaluation of hydroxyapatite reinforced polyethylene. Br. Ceram. Trans. **93**, 91–95 (1994)
64. H. Liang, M.M. Savalani, Y. Zhang, K.E. Tanner, R.A. Harris, Selective laser sintering of hydroxyapatite reinforced polyethylene composites for bioactive implants and tissue scaffold development. Proc. Inst. Mech. Eng. [H] **220**, 521–531 (2006)
65. M. Senna, J. Lee, Preparation of monodispersed polystyrene microspheres uniformly coated by magnetite via heterogeneous polymerization. Colloid Polym. Sci. **273**, 76–82 (1995)
66. K. Furusawa, K. Nagashima, C. Anzai, Synthetic process to control the total size and component distribution of multilayer magnetic composite particles. Colloid Polym. Sci. **272**, 1104–1110 (1994)
67. P.A. Dresco, V.S. Zaitsev, R.J. Gambino, B. Chu, Preparation and properties of magnetite and polymer magnetite nanoparticles. Langmuir **15**, 1945–1951 (1999)
68. X. Ding, Z. Sun, W. Zhang, Y. Peng, A.S.C. Chan, P. Li, Characterization of Fe_3O_4/poly (styrene-co-N-isopropylacrylamide) magnetic particles with temperature sensitivity. Colloid Polym. Sci. **278**, 459–463 (2000)
69. F. Sauzedde, A. Elaissari, C. Pichot, Hydrophilic magnetic polymer latexes. 1. Adsorption of magnetic iron oxide nanoparticles onto various cationic latexes. Colloid Polym. Sci. **277**, 846–855 (1999)
70. J. Chatterjee, Y. Haik, C.J. Chen, Polyethylene magnetic nanoparticle: a new magnetic material for biomedical applications. J. Magn. Magn. Mater. **246**, 382–391 (2002)
71. R.S. Molday, D. Mackenzie, Immunospecific ferromagnetic iron-dextran reagents for the labeling and magnetic separation of cells. J. Immunol. Methods **52**, 353–367 (1982)
72. J. Chatterjee, Y. Haik, C.J. Chen, Size dependent magnetic properties of iron oxide nanoparticles. J. Magn. Magn. Mater. **257**, 113–118 (2003)
73. C. Klapperich, L. Pruitt, K. Komvopoulos, Chemical and biological characteristics of low-temperature plasma treated ultra-high molecular weight polyethylene for biomedical applications. J. Mater. Sci. Mater. Med. **12**, 549–556 (2001)
74. B. Gupta, R. Jain, N. Anjum, H. Singh, Preirradiation grafting of acrylonitrile onto polypropylene monofilament for biomedical applications: I. Influence of synthesis conditions. Radiat. Phys. Chem. **75**, 161–167 (2006)
75. S. Shalom, H. Harel, G. Marom, Fatigue behaviour of flat filament-wound polyethylene composites. Compos. Sci. Technol. **57**, 1423–1427 (1997)
76. M. Kutz (ed.), *Handbook of Materials Selection* (Wiley, New York, 2002)

Chapter 11
Polyolefins in Automotive Industry

Cintil Jose Chirayil, Jithin Joy, Hanna J. Maria, Igor Krupa and Sabu Thomas

11.1 Introduction

Polyolefins in automobiles have experienced a great deal of interest in the last twenty years, and their applications have been increasing with a tendency of further growth compared with other materials used in automobiles. The major advantages of polyolefin materials are their functionality, cost-effective manufacturing methods, and comparatively lower fuel consumption. In automobiles, the polymeric materials can be used in the internal and external areas, in the engine section, and in the bodywork. Polyolefin can be shaped easily, their surface can be smooth, and they are chemically resistant, lighter than metals and glass, and are also good insulators. All these good properties make the polyolefin popular in the field of automotive industry.

The demand for lightweight materials for the automobiles is gradually gaining prominence due to the continuously rising demands to reduce fuel consumption. The use of polyolefin materials in automobile applications has been increasing dramatically. Their functionality, cost-effective manufacturing methods, and comparatively lower fuel consumption are the key factors in selecting these materials compared to other materials applied in automobiles [1]. Among different polymers, polyolefin

---

C.J. Chirayil · J. Joy · H.J. Maria · S. Thomas (✉)
School of Chemical Science, Mahatma Gandhi University, Kottayam, Kerala, India
e-mail: sabuchathukulam@yahoo.co.uk

J. Joy · S. Thomas
International and Inter University Centre for Nanoscience and Nanotechnology,
Mahatma Gandhi University, Kottayam, Kerala 686560, India

I. Krupa
QAPCO Chair, Center for Advanced Materials, Qatar University,
P.O. Box: 2713, Doha, Qatar

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_11

plays the major rule. The last two decades have showed a steady growth in the quantity of polyolefin materials used by the automotive industry. This trend is driven by technological breakthroughs that extend the good properties of polyolefin.

The use of polyolefins in automobiles can reduce weight, conserve fuel, and provide comfort and safety. Polyolefins are nonaromatic and comprises only of carbon and hydrogen atoms. All polyolefins exhibit nonporous and nonpolar characteristics unless subjected to special oxidative pretreatment. The low-energy surface nature is also another inherent characteristic common to all polyolefins. Polyethylene (PE) and polypropylene (PP) are the two most important and common polyolefins widely used. This is because of their wide range of applications and low cost. Polyolefins and polyolefin-based products (composites, blends, alloys, and hybrids) are extensively used in bumpers, dashboards, and interior trim in automotive industry. In addition to these attributes, their recyclability and relative ease of processing make them very attractive. The last three decades have witnessed tremendous growth in the quantity of polyolefin materials employed by the automotive industry. Due to their excellent cost–performance ratio, low density, low weight, great weathering and abrasion resistance, and good chemical resistance, thermoplastic polyolefin finds a wide range of applications in the automotive and building industries. One of the main advantages while using polyolefins is that they can be easily processed like thermoplastics by maintaining the resilience and elastic behaviors of elastomers [2]. The demand growth of polyolefins is increasing and is continuing to increase every year. In the coming 7 years, the demand for polyolefin-like LLDPE is reported to grow by almost 6 %. The total polyolefin consumption growth is increasing as shown in Fig. 11.1 [3].

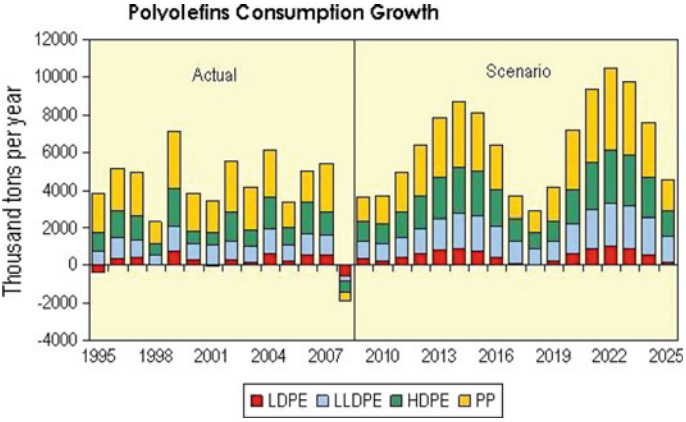


Fig. 11.1 Polyolefin consumption growth from 1995 to 2025 [3]

11.2 Polyethylenes in Automotive Industry

Because of their excellent cost–performance ratio, outstanding flexibility, low density, low weight, recycling characteristics, and great weathering resistance and good chemical resistance, PE and its composites have extensive industrial applications in the automotive and construction sectors. The main functions of PE products in automobiles are protection against high impact, absorption of noise, and vibration, as a carrier for adhesives for positioning of objects on uneven surfaces, as sound reflector in sealing, for thermal insulation etc. The use of PE also results in soft feel, smooth contour, and weight reduction. Among the different PE, ultrahigh molecular weight polyethylene (UHMWPE) is an ideal material for many wear parts in machinery and equipment as well as a superb lining in material handling systems and storage containers. This is because of its lightweight and high tensile strength. This type of PE is self-lubricating, long-wearing and possesses good break resistance, corrosion and abrasion resistance. The excellent durability and versatility of this PE make it attractive for engineers and designers in almost every industrial sector [4]. The use of this PE enhances the efficiency and productivity in automotive sector and railroad applications by its excellent nature in reducing wear and friction. They also find application in industry as gear housing, door control devices, steering angle sensors, or air bag connectors.

The excellent toughness of UHMWPE is due to the high molecular weight. But the comparatively very low density of this material compared to other class of PE-like HDPE shows the less efficient packing of the chains into the crystal structure. UHMWPE has very broad and diversified applications, because of its outstanding toughness, wear, and excellent chemical resistance. This material can safely be included in machine parts, moving parts of machines, bearings and gears, and air bag connectors. The different processing techniques used include compression molding, ram extrusion and sintering, and gel spinning technique. In the early 1960s, compression molding of UHMWPE was done by several European companies, while gel spinning was used based on the different applications (Fig. 11.2).

Another class of PE that can be subjected to abrasive or corrosive conditions is high-density polyethylene (HDPE). The high mechanical strength and good wear resistance of HDPE make it advantageous over other traditional materials. It can be used in different types of equipment and construction materials such as furniture rails and valve parts. The properties such as good wear resistance, chemical resistance, abrasion resistance, and its excellent sliding properties make suitable for replacing PP, PC, or fluoropolymers. Cross-linked PE is used in automotive industry for cold air intake systems and in filter housings (Fig. 11.2b). Cross-linked PE possesses good impact and chemical resistance, crack resistance from environmental stress, good heat deflection temperature, low flexural modulus, etc. [5].

It is interesting to note that the major portion of the PE applications is represented solely by HDPE. In 2007, the global HDPE consumption reached a volume of more than 30 million tons. This preference of HDPE over other materials is due

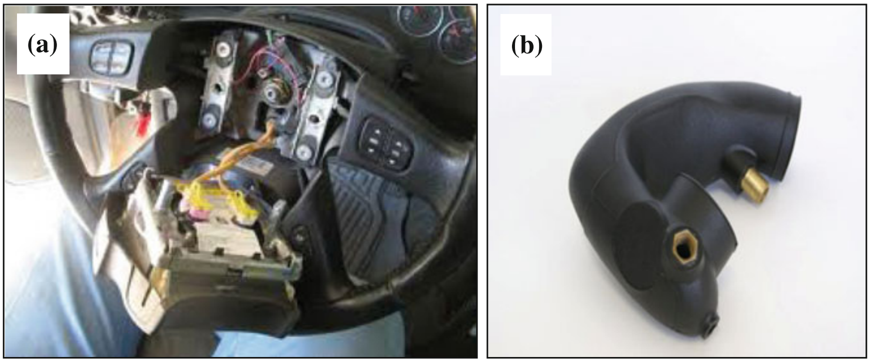


Fig. 11.2 **a** Air bag connectors (*PBT*) made of UHMWPE. **b** Cross-linked polyethylene in automotive duct [4]

to the excellent impact resistance, high tensile strength, lightweight, low moisture absorption nature, etc. Being a durable and a safer polyolefin, HDPE is favored by the pyrotechnics over steel and PVC tubes. HDPE is also used for automotive fuel tanks and pickup truck bed liners. In automotive industry, it finds use as motor oil container, portable gas cans, under-the-hood reservoirs, fuel tanks, and wire insulation. With the ever-growing research and development facilities, innovation of new products through the improvements to its processes and methodology, a lot of products could be replaced by polyolefin composites, such as interior trim and dashboard, in under-the-hood applications like heater housings, front ends, headlight housings, battery supports and structural beams, reservoirs, etc. Figure 11.3 shows various applications of PE in cars.

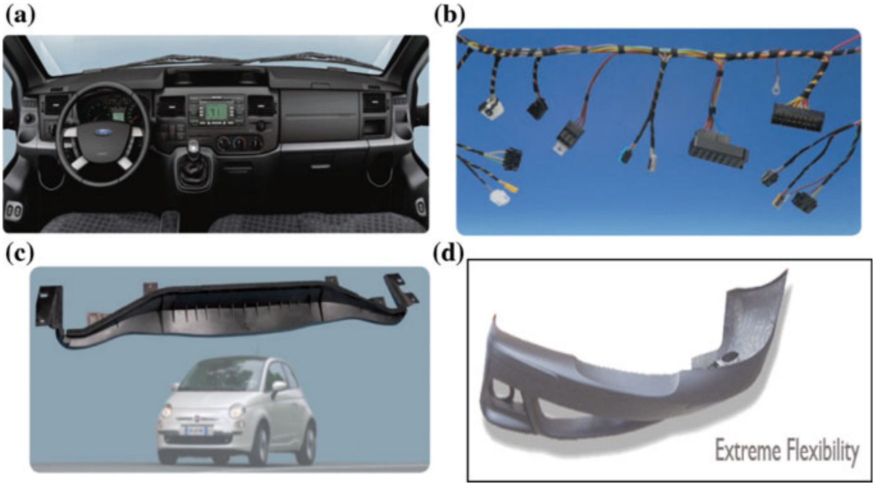


Fig. 11.3 Applications of polyethylenes in automobiles: **a** interior trim and dashboard, **b** wirings and cables, **c** external parts, and **d** bumper [6]

11.3 Polypropylenes in Automotive Industry

Polypropylene, a homopolymer polyolefin engineering plastic provides excellent chemical resistance, purity and it is the lightest of all commercial plastics. PP offers innovative solutions to many challenges that face the automotive industry today. Its low density compared to traditional materials significantly contributes to fuel economy and reduced material costs. Its excellent noise, vibration, and harshness (NVH) properties contribute to enhanced passenger comfort. Thus, PP has become the most important thermoplastic material in automobile industry. PP homopolymers, random copolymers, and impact copolymers are used in products such as automotive parts and battery cases, carpeting, electrical insulation, and fabrics.

Polypropylene nanocomposites are remarkable for their better mechanical properties, such as high tensile strength and modulus, and for their dimensional stability. They have a wide range of applications in the automotive sector [7–11]. The PP composites are used in automotive industry as battery supports, instrument panel carriers, body panel reinforcements, front-end modulus, underbody aerodynamic covers, electronic boxes, pedals and their supports, door panels and door modules, bumper beams, fender extensions, wheel covers, hub caps, and trim rings for wheels (Fig. 11.4).

For over 30 years, polyolefins are used for various types of automobile-related applications. Today PP-based materials are used to produce over 90 % of all bumper systems in Europe. A bumper system's key function is to reduce damage by absorbing kinetic energy so that the load transmitted is minimized. As a result,

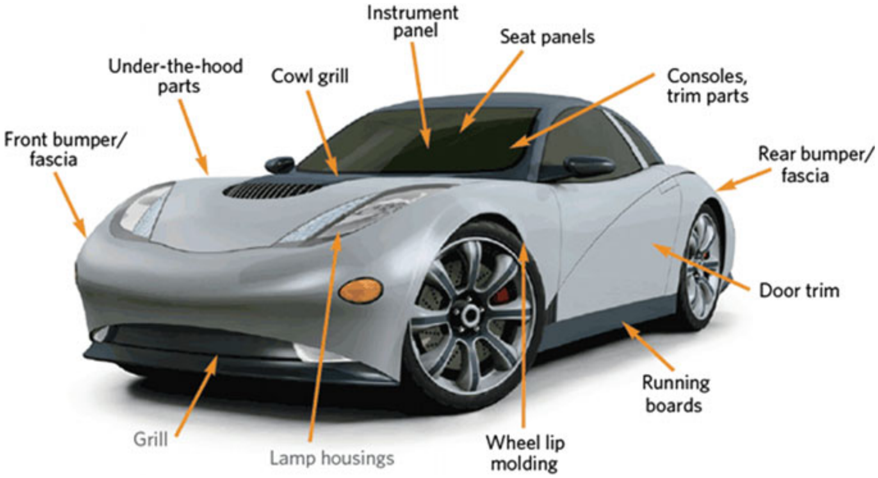


Fig. 11.4 Lightweight polypropylene automotive parts [12]

bumper systems have evolved into complex engineered systems. Bumpers form an important part of the overall 'look' of a vehicle, in addition to their safety function. They are closely integrated into bodywork with painted-in body colors and are incorporated into lighting assemblies. With the arrival of global platforms, the design and function of bumpers must often satisfy both local and international market requirements. Continuous improvements in the mechanical properties of bumper materials have enabled a progressive reduction in wall thickness. Thinner walls produce significant material savings for manufacturers, while creating lighter components that lower fuel consumption for the consumer. Making thin-walled moldings requires materials with extremely good melt flow characteristics. Although PP possesses many appropriate properties that make it a proper material, the low impact resistance, particularly at low temperature, limits its applications in certain cases. However, these properties can be improved by adding impact modifiers to PP. One of the most effective types of modifier is ethylene–propylene–diene terpolymer (EPDM) and is widely used in commercial impact PP resins. In a study by Liu and Qiu [13], the effect of a polyolefin elastomer (POE, ethylene–octene copolymer) as an impact modifier for PP was reported and also the effect of POE and HDPE in toughening PP for the application of automobile bumpers was also reported. They analyzed the effect of different POE and HDPE compositions on the mechanical properties of the blended composites. They reported that addition of POE could improve the impact strength of PP, while HDPE could improve toughness (Fig. 11.5).

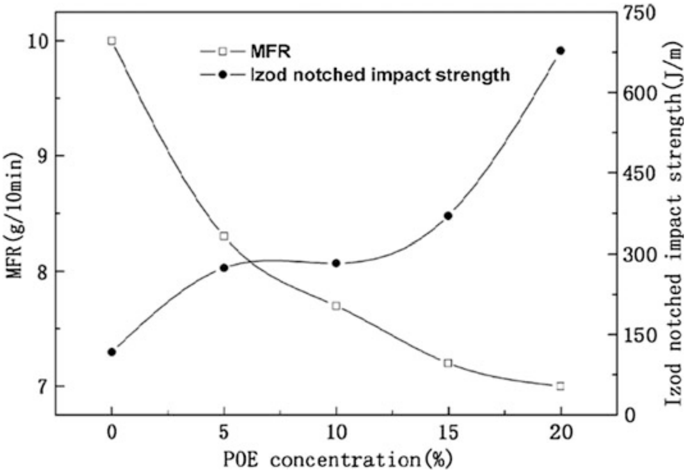


Fig. 11.5 The effect of POE concentration on melt flow rate and impact strength of the blends [13]

11.4 Polypropylene Composites for Automobile Applications

The potential use of polyolefin-based composites or nanocomposites in place of metals and high-performance engineering thermoplastics has gained wide appreciation in the area of academic and industrial research [14–21]. PPs can be processed by conventional technologies, such as injection molding and extrusion, and because of its great potential for composite and nanocomposite applications. On reinforcing PP with micro- and nanofillers, composites with high rigidity and toughness could be obtained [22]. From thermoplastic olefin–clay nanocomposites, lightweight material with good dimensional stability was developed by Montell USA and General Motors for exterior automotive applications [23]. The use of PP/clay nanocomposites by General Motors to fabricate the step-assist for two of its 2002 mid-size vans (GM's 2002 model GMC Safari and Chevrolet Astro vans) represented a major milestone in the commercialization of polymer nanocomposites technology [24]. This was one of the first attempts to commercialize polymer nanocomposite based on a 'commodity' plastic such as PP, PE, and polystyrene (PS). in automotive exterior application.

Due to their weather resistance, low density, low cost, and recycling properties, thermoplastic polyolefin blends consisting of PP and elastomer components find widespread applications in automotive and construction sectors. Liao and Tjong [25] in their work reported an elastomer-rich thermoplastic polyolefin (ETPO) resin nanocomposites in 70/30 composition of maleated styrene–ethylene–butadiene–styrene (SEBSg-MA) and PP incorporated with SiC nanoparticles (SiCp). The nanocomposite was fabricated using processing techniques such as injection molding and extrusion. From the analysis of the mechanical and thermal properties of these materials, it was found that SiCp additions lead to reduction in both tensile stiffness and strength of ETPO. However, the fracture toughness and the impact strength of ETPO nanocomposites improved on increasing the SiCp content [25]. The use of thermoplastic polyolefins (TPOs) in automotive interior and exterior applications has been increasing dramatically in applications such as instrument panel, bumper fascia, and door panels. Long-term durability and cold weather resistance are the major advantages of using TPO. Some good examples of these applications can be found on the instrument panels on 2000 Ford Focus and the 2000 Pontiac Bonneville, as well as the door panel of Mercedes-Benz E class, Porsche 986/996, and Honda Civic [26]. The use of poly(propylene) matrix composites with ethylene–propylene rubber copolymer as dispersed phase showed a dramatic loss in the mechanical performances at the end of the first-life application of bumpers [27]. Figure 11.6 shows SEM of the fractured surface of PP/EPDM composites.

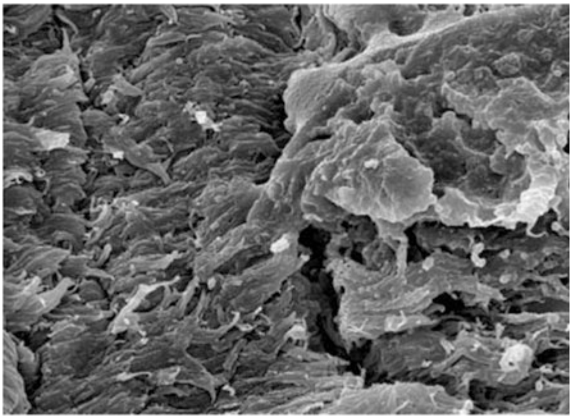


Fig. 11.6 SEM of the fractured surface of the composite (poly(propylene) matrix (*PP*) and an ethylene propylene rubber copolymer) [27]

In a recent patent by Mehbubani et al. [28], a method of construction of a nonwoven moldable material was reported. In their work, a nonwoven material was formed from natural cellulosic fibers/PP and they reported a flexural strength of about 76 N. A simplified process was developed by Du et al. [29] for fabricating polymer biocomposites using natural biobased fibers for applications in automotive interior trim substrates. Biofiber (kraft pulp fiber) and thermoplastic polymers were first wet-formed into fiber/polymer mats, and the mats were made into composites using a match-mold thermoforming process. It was found that biofiber/PP composites had comparable performance to the commercially available nonwood natural fiber/PP composite counterparts for the properties investigated such as tensile strength, flexural strength, impact resistance, heat deflection temperature, and acoustic absorption coefficients. Figure 11.7 shows the process of composite preparation that they have developed.

In another study on the correlations between EPR design and shrinkage, Potter and Grein [30] have reported a polypropylene/ethylene–propylene rubber (PP/EPR) blends for the automotive industry. They evaluated the influence of the phase morphology on the shrinkage and coefficient of linear thermal expansion (CLTE) of PP/EPR blends. Inuwa et al. [31] have reported a work on the influence of exfoliated graphite nanoplatelets on the thermal and flame-retardant studies of PE terephthalate/PP nanocomposites. They have studied the flammability, thermal properties, morphological characteristics, thermal conductivity, and arrangement of exfoliated graphite nanoplates (GNP) in the PET/PP blends as a function of concentration of GNPs. This study showed the potential of using GNPs to formulate a flame-retarded, thermally conductive polymer nanocomposite based on blends of PET/PP for applications where flame retardancy and heat dissipation in electrical components are necessary. Morphological studies showed (Figs. 11.8 and 11.9) uniform dispersion and the development of interconnected GNP sheets.

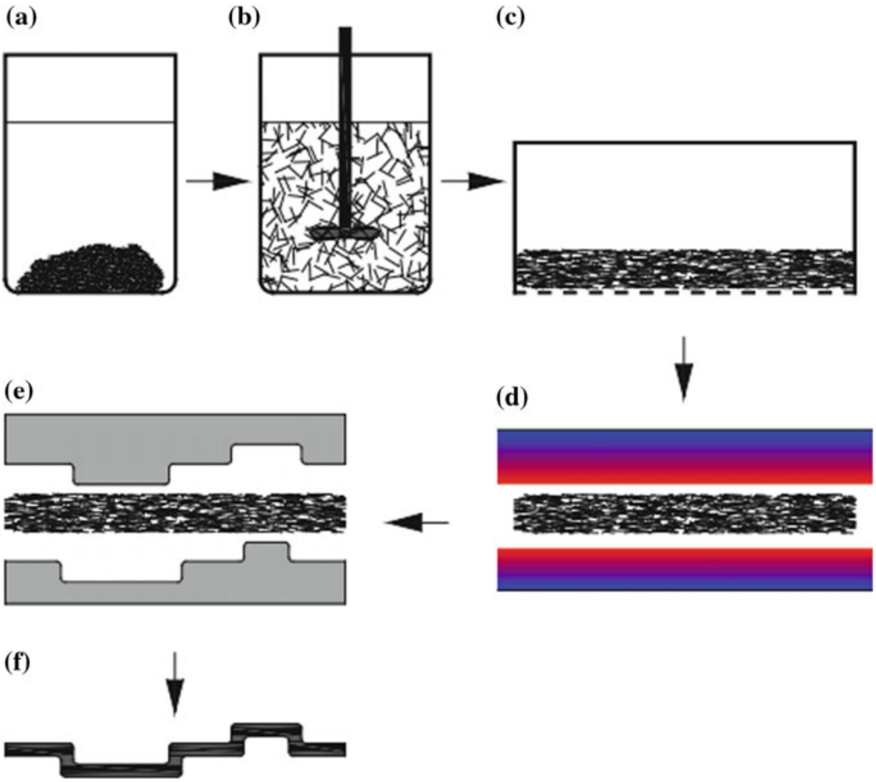


Fig. 11.7 Process of composite preparation: **a** fiber soaking, **b** disintegration and mixing with polymer fibers, **c** wet-forming, **d** heating, **e** match-mold, thermoforming, and **f** formed composite [29]

11.5 Polyolefin–Natural Fiber Composites

The demand for better fuel efficiency based on the strict governmental regulations on safety and emission has led to the wide application of composites and plastics in the automotive industry in the place of the traditionally used steels [32]. Thermoplastic materials reinforced with natural fibers have reported to have excellent mechanical properties, recycling properties, etc. [33–36]. Several natural and biorenewable fibers such as wheat, isora, soybean, kenaf, straw, jute, and sisal are used in the fiber/plastic composite industry, and the use of natural fibers as reinforcements for composite has attracted many industries [37, 38]. Compared to polymer resin, polymer biocomposites that are reinforced with natural fibers have many applications due to its ease of processing, comparatively lower cost, and excellent mechanical properties [39]. For more than a decade, European car manufacturers and suppliers have been using natural fiber-based composites with thermoplastic and thermoset matrices. These biocomposites and bionanocomposites

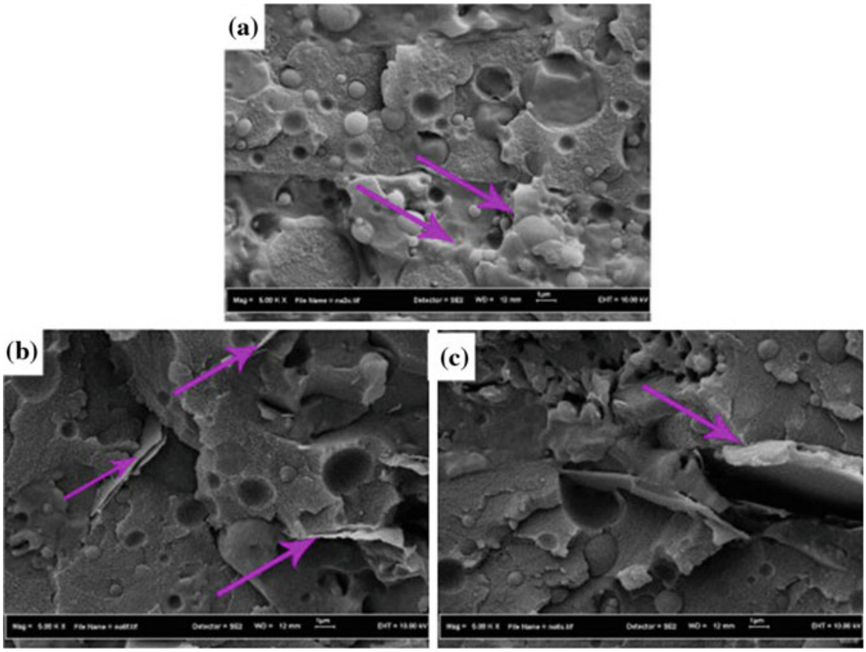


Fig. 11.8 FESEM images of nanocomposite-based polyethylene terephthalate (*PET*)/polypropylene (*PP*)/exfoliated graphite nanoplatelets (*GNP*) [*PET*/*PP*/*GNP*] nanocomposites at 3 phr showing **a** GNP0, **b** GNP3, showing the uniform dispersion of GNP3, and **c** GNP3, showing the attachment of GNP particles on the compatibilizer surface [31]

have find its applications in the interior parts of cars such as car seat backs, headliners, dashboards and package trays, and panels of the doors. Interest in natural fibers has increased worldwide because of their cost-effectiveness, low density, good thermal resistivity, and excellent mechanical properties [40, 41]. The replacement of non-natural fibers by natural fibers such as alfa, hemp, kenaf, coir, oil palm and sisal has a lot of environmental advantages which can justify their uses in many different applications. Because of their low plasticity, polyolefin–natural fiber composites present some drawbacks also [42–49]. Arrakhiz et al. [50] have reported enhancement of mechanical and thermal properties of Doum fiber–reinforced low-density polyethylene (LDPE). They compounded alkali-treated Doum fibers with LDPE matrix at different percentages and extruded as continuous strands. They reported that compared to neat polymer an enhancement of 135 % in flexural modulus at 20 wt% fiber loading, 145 % improvement in Young’s modulus at 30 wt% fiber loading, and an increase of 97 % in torsional modulus at 0.1 Hz. Thermal properties were found to show a slight decrease with increase in the addition of Doum. In another work reported by Yemele et al. [51], they have prepared HDPE composites with black spruce bark (BSB) fibers and trembling aspen bark (TAB) fibers by extrusion process. They studied the effects of hot water

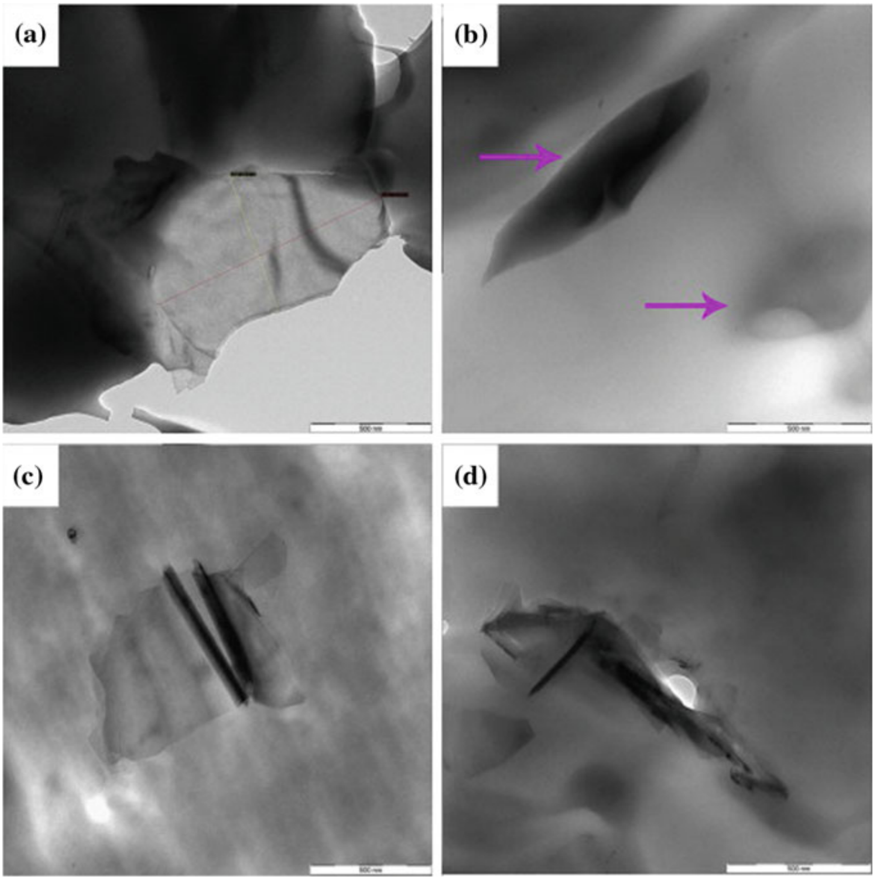


Fig. 11.9 Interconnected GNP sheets at 3 phr loading, **b** adhesion of GNP to polymer matrix promoted by SEBSg-MAH, **c** wrinkled GNP sheets, and **d** crumpled GNP sheets [31]

treatment of raw bark and the addition of coupling agent (MAPE) and lubricants (OP-100, talc) on the mechanical properties of bark/HDPE composites. It showed a significant influence of hot water treatment on the mechanical properties of composites made with both TAB and BSB. Although the toughness and strain were significantly reduced by the addition of coupling agent and lubricants, the flexural and tensile strength of bark/HDPE composites was found to be improved. Tajvidi et al. [52] reported a shift in glass transition temperatures (T_g) to a lower temperature in their work on natural fiber–PP composites. Similar results were also observed by Joseph et al. [53] for sisal–PP biocomposites.

The interfacial bonding between fiber and matrix must be optimized since it is very important for effective stress transfer. Since the fibers and matrices are chemically different, strong adhesion at the interface is required while using natural fibers as reinforcement [37]. One method is to improve compatibilization and adhesion between fiber and matrix is through physical and chemical treatment methods. Correa et al. [54] reported for wood composites with homopolymer and copolymer matrices, on varying the type of coupling agent and variable wood-flour content, good correlation between coupling efficiency and yield properties. The two main concerns while dealing with thermoplastic natural fiber composites are the processing temperature and the surface energy difference of the wood and the polymer matrix. Noble polymers reported a new PP nanocomposite, known as Forte, that is available as a cost-effective alternative to the more highly filled traditional materials, such as glass-reinforced PP, used in automotive applications. In polymer nanocomposites, the addition of very low filler loading like 3–5 wt% can bring out the same thermal and mechanical properties compared to traditional reinforcements where a higher filler loading is required. An overall increase in tensile strength and flame-retardant properties could be obtained by producing materials of lower density and higher processability [55].

Pöllänen et al. [56] reported a comparative study on the morphological, thermal, and mechanical properties of HDPE. Composites are prepared using commercial microcrystalline cellulose (MCC) and viscose fibers to improve the chemical compatibility of the fillers and the matrix. The thermal stability, the Young's modulus, and the tensile strength of the HDPE composite were found to be significantly influenced by the presence of cellulose. There was a significant improvement in mechanical properties, and the elongation at break decreased with the increase in the filler content. The presence of the PEgMA as the compatibilizer could improve the mechanical properties of the composites, and the SEM images (Fig. 11.10) revealed improved adhesion between the cellulose fillers and the HDPE matrix.

In another study by Sdrobis et al. [57], the effect of modification on cellulose pulp fibers in LDPE was reported. They used unbleached and bleached kraft cellulose pulp fibers modified with oleic acid in cold plasma conditions as reinforcements. The melt-mixed composites contain up to 10 wt% of untreated and modified cellulose pulp fibers with LDPE. They reported that interfacial adhesion between cellulose and matrix could be improved through modification and most of the properties have been improved when the modified pulp fibers were incorporated into composite matrix. Variation of complex viscosity function of angular frequency for composites is shown in Fig. 11.11.

Wood/PE composites are widely used in several fields because of their excellent properties. Liu et al. [58] used low-pressure glow discharge of air plasma to improve the adhesion properties of wood/PE composites. AFM topography of wood/PE composites treated by plasma under different discharge power is shown in Fig. 11.12. They reported that the contact angle was reduced after plasma treatment and was found to be decreased gradually with discharge power.

Because of the ever-increasing demand of biodegradable products, different approaches have been made. One such method is the use of biomass as natural biopolymer for the production of biodegradable plastics. Khalid et al. [59] have reported a work done by using cellulose derived from oil palm empty fruit bunch fiber (EFBF). The composites were prepared by blending cellulose and EFB fibers

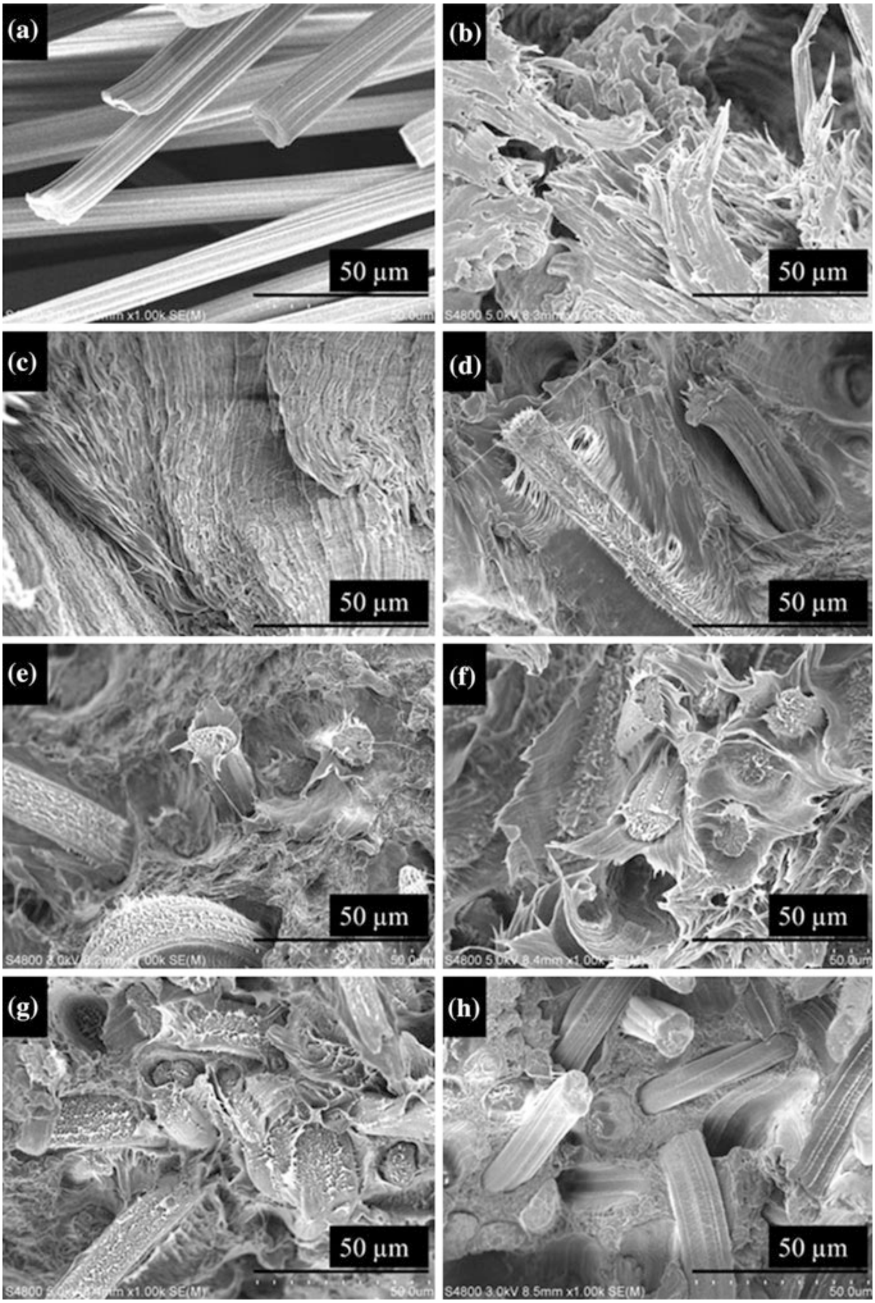
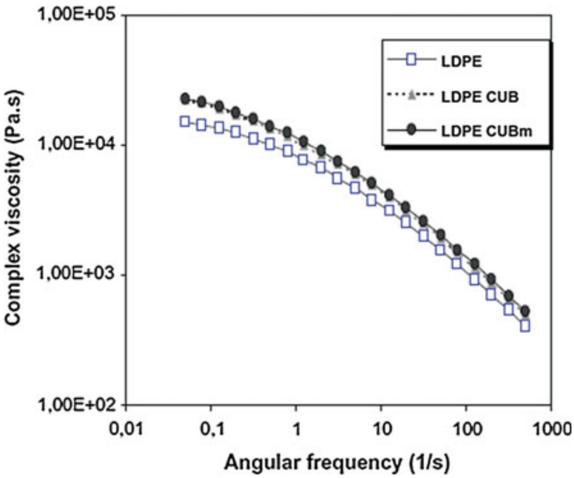


Fig. 11.10 The SEM images of **a** the viscose fibers and the fracture surfaces of **b** HDPE, **c** HDPE–PEgMA (maleic anhydride grafted-polyethylene), **d** HDPE–PEgMA–fiber (5 wt%), **e** HDPE–PEgMA–fiber (10 wt%), **f** HDPE–PEgMA–fiber (20 wt%), **g** HDPE–PEgMA–fiber (40 wt%), and **h** HDPE–fiber (40 wt%) [56]

Fig. 11.11 Variation of complex viscosity function of angular frequency for LDPE and biocomposites containing unbleached cellulose (*CUB*) and plasma modified (*CUBm*) [57]



in different ratios (up to 50 wt%) with PP. The study on the effects of cellulose and EFB fibers on the mechanical properties of the PP–cellulose and PP–EFBF composite prepared using Brabender twin-screw compounder showed that the PP–cellulose composite gave better results in comparison with PP–EFBF composite (Fig. 11.13).

11.6 Nanocomposites of Polyolefin in Automobiles, Current Opportunities, and Applications

The automotive industry can benefit from polyolefin nanocomposites in several applications, and the consumption of thermoplastics as a matrix material in nanocomposites has been increasing steadily, especially in automotive industry. The use of composite materials in the automotive industry is now commonly used and is increasing every year. Long glass fiber/thermoplastic composite systems have been used for semi-structural and engineering applications [60]. The main idea of using polymeric composite material is to decrease the overall weight of an automobile and in turn to improve its fuel efficiency. In addition, thermoplastic composites are recyclable. This characteristic is recognized as a strong driving force for future applications. Current global expectations demand for new cost-effective, high-performance, lightweight materials to replace traditional materials such as metals [61]. Nanocomposites are an emerging class of materials exhibiting excellent mechanical properties, enhanced modulus and dimensional stability, flame retardancy, improved scratch resistance, superior thermal and processing properties, and improved impact resistance, thus making them suitable to replace metals in automotive applications [62, 63]. Many automotive components have complex geometries and cannot be injection-molded efficiently. Therefore, there is a need to

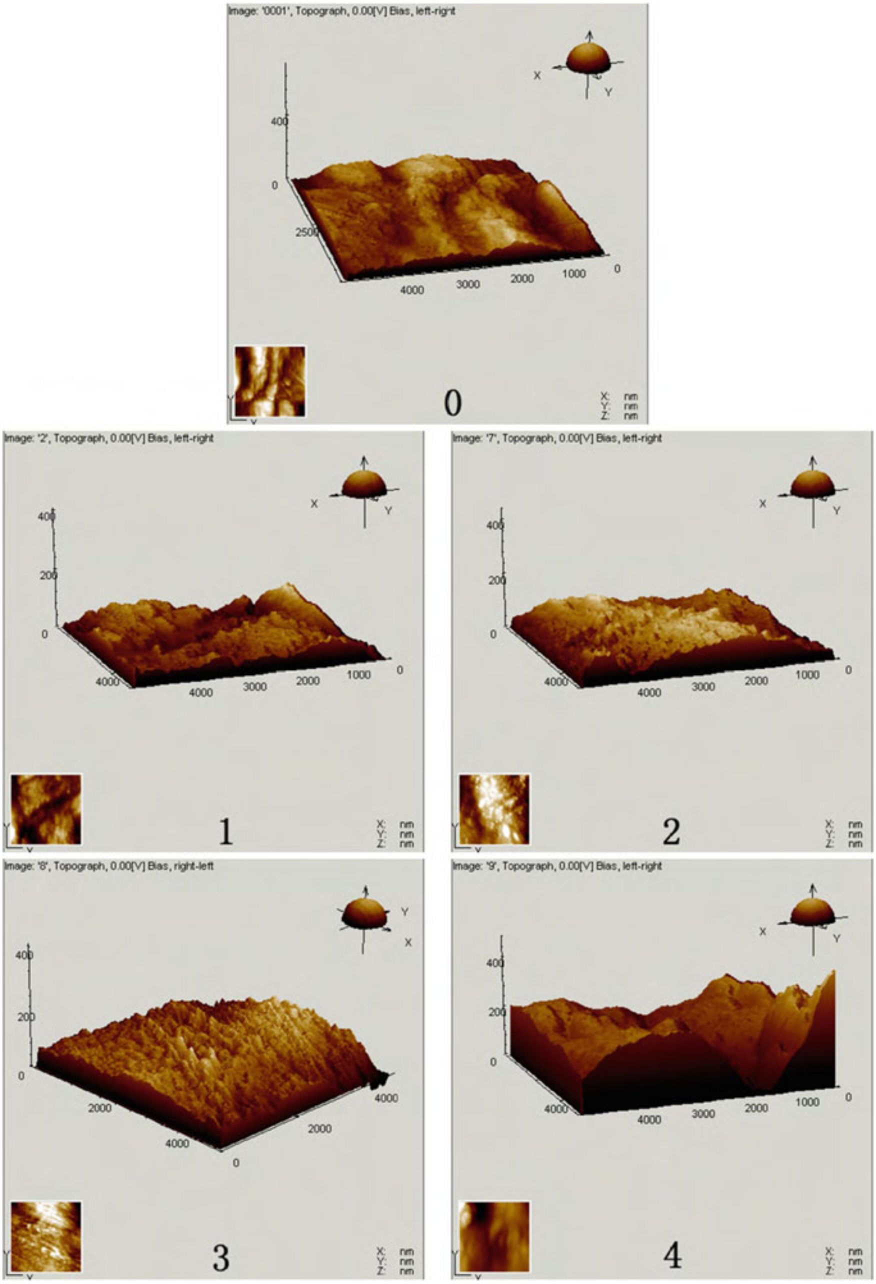


Fig. 11.12 AFM topography of plasma-treated wood/PE composite surfaces for different power (*1*) 550 W, (*2*) 650 W, (*3*) 750 W, and (*4*) 800 W [58]

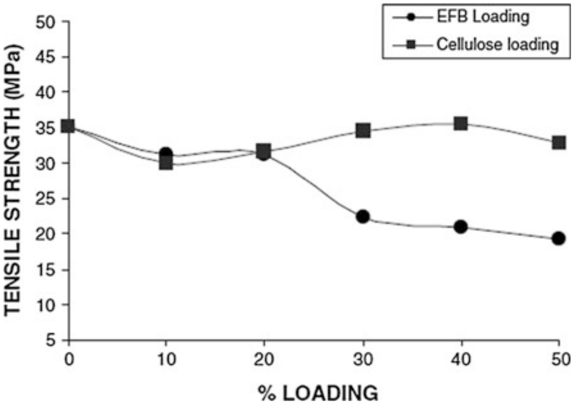


Fig. 11.13 Tensile strength of PP composites [59]

mold the components separately and join them together using a welding process [64]. There are many welding methods that can be used to join PP or TPO such as hot plate [65], vibration [66], ultrasonic [67], infrared [68], and laser. Previous studies indicated that vibration welding of TPO T-joint produced acceptable weld strength and the joint strength was not affected dramatically by the welding parameters such as amplitude, weld time, and pressure [69].

11.7 Conclusions

Polymer nanocomposites are one of the recently emerging technologies in the automotive industry, and it has drawn huge attention worldwide. Research and development in polyolefin composites is supporting the automotive industry to meet the challenges by the design and development of components and subsystems which can be used in many applications with improved properties. The usage of polyolefins in automotive applications has been increasing largely. The excellent mechanical properties, thermal properties, and good electrical and barrier properties, along with the excellent fracture toughness over thermosets, make polyolefin a perfect material for many applications. The ability to be easily joined by mechanical joining and welding techniques also makes it acceptable to the industry. The research reports, cost-effective solutions, and various techniques have been adapted to achieve this goal. Such drives include the use of specially designed nanomaterials to allow the engine to operate at higher temperature with reduced external cooling (heat removal); thus, fuel efficiency can be improved significantly.

References

1. N. Strumberger, A. Gospocic, C. Bartulic, Polymeric materials in automobiles. Promet Traffic-Traffico. **17**(3) (2005)
2. C.Z. Liao, S.C. Tjong, J. Nanomater. **9**, 3273–3279 (2010)
3. http://www.plastemart.com/upload/Literature/Global-polyethylene-PE-polypropylene-PP-polyolefins-slow%20in-2008.asp
4. J.H. Southern, R.S. Porter, The properties of polyethylene crystallized under the orientation and pressure effects of a pressure capillary viscometer. J. Appl. Polym. Sci. **14**(9), 2305–2317 (1970)
5. T. Kanamoto, A. Tsuruta, K. Tanaka, M. Takeda, R.S. Porter, On ultra-high tensile modulus by drawing single crystal mats of high molecular weight polyethylene. Polym. J. **15**(4), 327–329 (1983)
6. https://polymers.lyondellbasell.com/portal/binary/com.vignette.vps.basell.BasellFileServl
7. S. Takase, N. Shiraishi, Studies on composites from wood and polypropylenes II. J. Appl. Polym. Sci. **37**(3), 645–659 (1989)
8. J.M. Felix, P. Gatenholm, The nature of adhesion in composites of modified cellulose fibers and polypropylene. J. Appl. Polym. Sci. **42**(3), 609–620 (1991)
9. Y. Mi, X. Chen, Q. Guo, Bamboo fiber-reinforced polypropylene composites: crystallization and interfacial morphology. J. Appl. Polym. Sci. **64**(7), 1267–1273 (1997)
10. P. Mapleston, Mod. Plast. **73**, 605–732 (1999)
11. L. Jilkén, G. Mälhammar, R. Seldén, The effect of mineral fillers on impact and tensile properties of polypropylene. Polym. Test. **10**(5), 329–344 (1991)
12. http://polymer-additives.specialchem.com/centers/polyolefin-reinforcement-enter/reinforced-polyolefins-for-automotive
13. G. Liu, G. Qiu, Study on the mechanical and morphological properties of toughened polypropylene blends for automobile bumpers. Polym. Bull. **70**(3), 849–857 (2013)
14. S. Komarneni, Nanocomposites. J. Mater. Chem. **2**(12), 1219–1230 (1992)
15. L.M. Sherman, Plast. Technol. 52 (1999)
16. R. Westervelt, K. Walsh, Chem. Week (1999)
17. NIST, ATP Project Brief 97-02-0047 (1997)
18. H. Guggenbuhl, Die Weltsoche **9**, 25 (1989)
19. M.T. Takemori, Polym. Eng. Sci. **19**, 1104–1113 (1979)
20. E.P. Giannelis, Polymer layered silicate nanocomposites. Adv. Mater. **8**(1), 29–35 (1996)
21. T. Kurauchi, A. Okada, T. Nomura, T. Nishio, S. Saegusa, R. Deguchi, SAE Tech. Paper Ser. **910**, 584–599 (1991)
22. H.G. Karian, *Plastics Engineering*, vol. 51 (Marcel Dekker, New York, 1999)
23. R. Ottaviani, W. Rodgers, P. Fasulo, T. Pietrzyk, C. Buehler, *Global SPETPO Conference*, Sept 1999
24. Auto applications drive commercialization of nanocomposites. Plast. Addit. Compd. **4**, 30–33 (2002)
25. C.Z. Liao, S.C. Tjong, J. Nanomater. **9**, 3279–3341 (2010)
26. N. Kakarala, S. Shah, *SPE Automotive TPO Global Conference* (2000) , pp.147–158
27. M.P. Luda, G. Ragosta, P. Musto, D. Acierno, L. Di Maio, G. Camino, V. Nepote, Regenerative recycling of automotive polymer components: poly (propylene) based car bumpers. Macromol. Mater. Eng. **288**(8), 613–620 (2003)
28. R. Mehbubani, A. Khosroshashi, B. Taylor, S.P. Yanchek, US patent, 20140272343 A1 Publication number US20140272343 A1, US 14/216,444
29. Y. Du, Y. Ning, T. Kortschot, A. Mark, J. Mater. Sci. 2630–2639 (2014)
30. G.D. Potter, C. Grein, Borealis. Expr Polym. Lett. **8**, 282–292 (2014)
31. I.M. Inuwaa, A. Hassana, D.-Y. Wangb, S.A. Samsudina, M.K. Mohamad Haafiza, C.S.L. Wongd, M. Jawaide. doi:10.1016/j.polymdegradstab.2014.08.025

32. S. Mohanty, S.K. Verma, S.K. Nayak, Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites. Compos. Sci. Technol. **66**(3), 538–547 (2006)
33. A. Bourmaud, C. Baley, Investigations on the recycling of hemp and sisal fibre reinforced polypropylene composites. Polym. Degrad. Stab. **92**(6), 1034–1045 (2007)
34. A. Bourmaud, C. Baley, Rigidity analysis of polypropylene/vegetal fibre composites after recycling. Polym. Degrad. Stab. **94**(3), 297–305 (2009)
35. A. Bourmaud, A. Le Duigou, C. Baley, What is the technical and environmental interest in reusing a recycled polypropylene–hemp fibre composite? Polym. Degrad. Stab. **96**(10), 1732–1739 (2011)
36. A. Le Duigou, I. Pillin, A. Bourmaud, P. Davies, C. Baley, Effect of recycling on mechanical behaviour of biocompostable flax/poly (l-lactide) composites. Compos. A Appl. Sci. Manuf. **39**(9), 1471–1478 (2008)
37. J. George, M.S. Sreekala, S. Thomas, A review on interface modification and characterization of natural fiber reinforced plastic composites. Polym. Eng. Sci. **41**(9), 1471–1485 (2001)
38. D.R. Mulinari, H.J. Voorwald, M.O.H. Cioffi, M.L.C. da Silva, S.M. Luz, Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. Carbohydr. Polym. **75**(2), 317–321 (2009)
39. D.R. Mulinari, H.J. Voorwald, M.O.H. Cioffi, M.L.C. da Silva, S.M. Luz, Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. Carbohydr. Polym. **75**(2), 317–321 (2009)
40. M. Pracella, D. Chionna, I. Anguillesi, Z. Kulinski, E. Piorkowska, Functionalization, compatibilization and properties of polypropylene composites with hemp fibres. Compos. Sci. Technol. **66**(13), 2218–2230 (2006)
41. A. Bourmaud, C. Baley, Rigidity analysis of polypropylene/vegetal fibre composites after recycling. Polym. Degrad. Stab. **94**(3), 297–305 (2009)
42. S.B. Srahim, R.B. Cheikh, Influence of fibre orientation and volume fraction on the tensile properties of unidirectional Alfa-polyester composite. Compos. Sci. Technol. **67**(1), 140–147 (2007)
43. Y. Li, K.L. Pickering, R.L. Farrell, Analysis of green hemp fibre reinforced composites using bag retting and white rot fungal treatments. Ind. Crops Prod. **29**(2), 420–426 (2009)
44. S.H. Aziz, M.P. Ansell, The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites: part 1–polyester resin matrix. Compos. Sci. Technol. **64**(9), 1219–1230 (2004)
45. M.M. Haque, M. Hasan, M.S. Islam, M.E. Ali, Physico-mechanical properties of chemically treated palm and coir fiber reinforced polypropylene composites. Bioresour. Technol. **100**(20), 4903–4906 (2009)
46. H.A. Khalil, H. Ismail, H.D. Rozman, M.N. Ahmad, The effect of acetylation on interfacial shear strength between plant fibres and various matrices. Eur. Polym. J. **37**(5), 1037–1045 (2001)
47. J. Harun, K. Abdan, K. Zaman, Rheological behaviour of injection moulded oil palm empty fruit bunch fibre–polypropylene composites: Effects of electron beam processing versus maleated polypropylene. Mol. Cryst. Liq. Cryst. **484**(1), 134–500 (2008)
48. X. Lu, M.Q. Zhang, M.Z. Rong, G. Shi, G.C. Yang, Self-reinforced melt processable composites of sisal. Compos. Sci. Technol. **63**(2), 177–186 (2003)
49. A. Keller, Compounding and mechanical properties of biodegradable hemp fibre composites. Compos. Sci. Technol. **63**(9), 1307–1316 (2003)
50. F.Z. Arrakhiz, M. El Achaby, M. Malha, M.O. Bensalah, O. Fassi-Fehri, R. Bouhfid, A. Qaiss, Mechanical and thermal properties of natural fibers reinforced polymer composites: Doum/low density polyethylene. Mater. Des. **43**, 200–205 (2013)
51. M.C.N. Yemele, A. Koubaa, A. Cloutier, P. Soulounganga, T. Stevanovic, M.P. Wolcott, Effects of hot water treatment of raw bark, coupling agent, and lubricants on properties of bark/HDPE composites. Ind. Crops Prod. **42**, 50–56 (2013)

52. M. Tajvidi, R.H. Falk, J.C. Hermanson, Effect of natural fibers on thermal and mechanical properties of natural fiber polypropylene composites studied by dynamic mechanical analysis. J. Appl. Polym. Sci. **101**(6), 4341–4349 (2006)
53. P.V. Joseph, G. Mathew, K. Joseph, G. Groeninckx, S. Thomas, Dynamic mechanical properties of short sisal fibre reinforced polypropylene composites. Compos. A Appl. Sci. Manuf. **34**(3), 275–290 (2003)
54. C.A. Correa, C.A. Razzino, E. Hage, J. Thermoplast. Compos. Mater. **20**(2010), 223–239 (2007)
55. Lux Research. The Nanotech Report 2004
56. M. Pöllänen, M. Suvanto, T. Pakkanen, Cellulose reinforced high density polyethylene composites—Morphology, mechanical and thermal expansion properties. Compos. Sci. Technol. **76**, 21–28 (2013)
57. A. Sdrobis, R.N. Darie, M. Totolin, G. Cazacu, C. Vasile, Low density polyethylene composites containing cellulose pulp fibers. Compos B. **43**, 1873–1880 (2012)
58. Y. Liu, Y. Tao, X. Lv, Y. Zhang, M. Di, Study on the surface properties of wood/polyethylene composites treated under plasma. Appl. Surf. Sci. **257**, 1112–1118 (2010)
59. M. Khalid, C.T. Ratnam, T.G. Chuah, S. Ali, S.Y. Thomas, Choong a comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. Mater. Des. **29**, 173–178 (2008)
60. S. Komarnenei, J. Mater. Chem. **2**, 1219 (1992)
61. L.M. Sherman, Plast. Technol. **52**, 123–129 (1999)
62. R. Westervelt, K. Walsh, Chem. Week **24**, 84–89 (1999)
63. NIST, ATP Project Brief 97-02-0047 (1997)
64. D.A. Grewell, A. Benatar, J.B. Park, *Plastics and Composites Welding Handbook*, vol 10 (2003)
65. C.Y. Wu, A. Mokhtarzadeh, M.Y. Rhew, A. Benatar, *SPE, ANTEC 61th Annual Technical Conference* (2003)
66. C.Y. Wu, L. Trevino, *Vibration Welding of TPO, SPE, ANTEC 60th Annual Technical Conference* (2002)
67. J. Park, J. Liddy, Effect of paint over spray for vibration and ultrasonic welding processes. *SPE, ANTEC 62nd Annual Technical Conference* (2004)
68. Y.S. Chen, A. Benatar, Infrared welding of polypropylene. *SPE, ANTEC 53rd Annual Technical Conference* (1995)
69. C.Y. Wu, M. Cherdron, D.M. Douglass, Laser welding of polypropylene to thermoplastic polyolefins. *SPE, ANTEC 61th Annual Technical Conference* (2003)

Chapter 12
Polyolefins: From Thermal and Oxidative Degradation to Ignition and Burning

Jozef Rychlý and Lyda Rychlá

12.1 Introduction

Polyolefins belong to polymers that are in the pure state rather sensitive to thermal and thermo-oxidative degradation at relatively low temperatures (LT degradation), and at the same time, they are the most flammable materials when exposed to high-temperature degradation (HT degradation) or to a direct contact with the flame. The understanding of different aspects of degradation phenomenon therefore is one of the primary conditions of better application of polyolefins in many industrial fields. One should have in mind that burning of polyolefins is usually the catastrophic scenario of the HT degradation, but there exist the mechanistic boundaries dividing it from the considerably slower LT degradation.

12.2 LT Degradation

Under LT degradation, we involve all phenomena linked to degradation of polyolefins below temperature 250 °C. Under such conditions, polyolefins display different degrees of stability which depends on their chemical composition as well as on the presence of additives. Their stability is affected by:

1. Heat,
2. Oxygen,
3. Light, especially solar radiation (wavelength >300 nm),
4. High-energy radiation,

J. Rychlý (✉) · L. Rychlá
Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta,
84541 Bratislava, Slovakia
e-mail: Jozef.Rychly@savba.sk

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_12

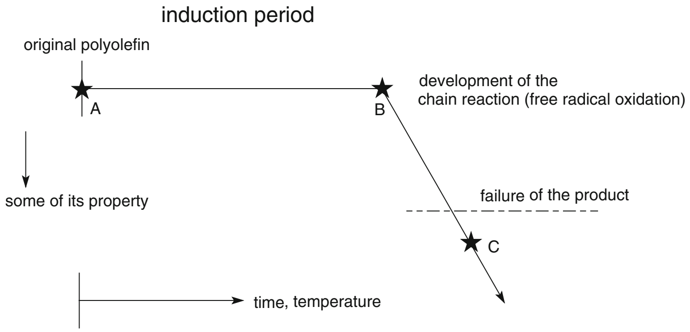
5. Mechanical stress,
6. Biological attack,
7. Liquids being in contact with polyolefin,
8. Removal of additives by bleaching and/or washing out,
9. Initial molar mass and its distribution and
10. Presence of impurities from the polyolefin synthesis.

The mode of degradation is determined by the character of the first initiating site in the polyolefin structure and is typical for conditions to which polyolefin is exposed. According to the route by which first initiating sites appear in the polyolefin, we recognize photo-degradation (photolysis), thermal degradation (thermolysis), photo-oxidation or thermo-oxidative degradations, which involve the assistance of oxygen, radiolytic and mechanochemical degradation. Polyolefins may, moreover, degrade under the effect of ozone, peroxides, acids and alkaline compounds, halogens or other aggressive compounds, under the effect of electric field, plasma and corona discharge, ultrasound, laser radiation, etc.

The items 4, 6 and 7 appear for polyolefins to be marginal, and they will not be discussed in this chapter.

The hypothetical life trajectory of the polyolefin product is depicted in Scheme 12.1. Its characteristic feature is the existence of the so-called induction period of degradation during which the material properties change insignificantly and are rather similar to those in the point A in Scheme 12.1. The time lag AB (induction period) of this interval depends on the efficiency of the polyolefin stabilization. In point B, the protection effect of polymer stabilizers is ended due to the permanent initiation attack and the product properties start to deteriorate. Point C designates the failure of the product, and its further utilization becomes impossible.

The changes which are invisible at the beginning occur in the polyolefin gradually, and in the final state, the following can appear: cracks, loss of gloss and changes in the colour, and in the case of foams, it is scrambling. The advanced stage of polymer degradation may be seen even by naked eyes as it is accompanied by the multi-cracks formation and catastrophical reduction of mechanical properties (Scheme 12.2).



Scheme 12.1 The life trajectory of the polyolefin product

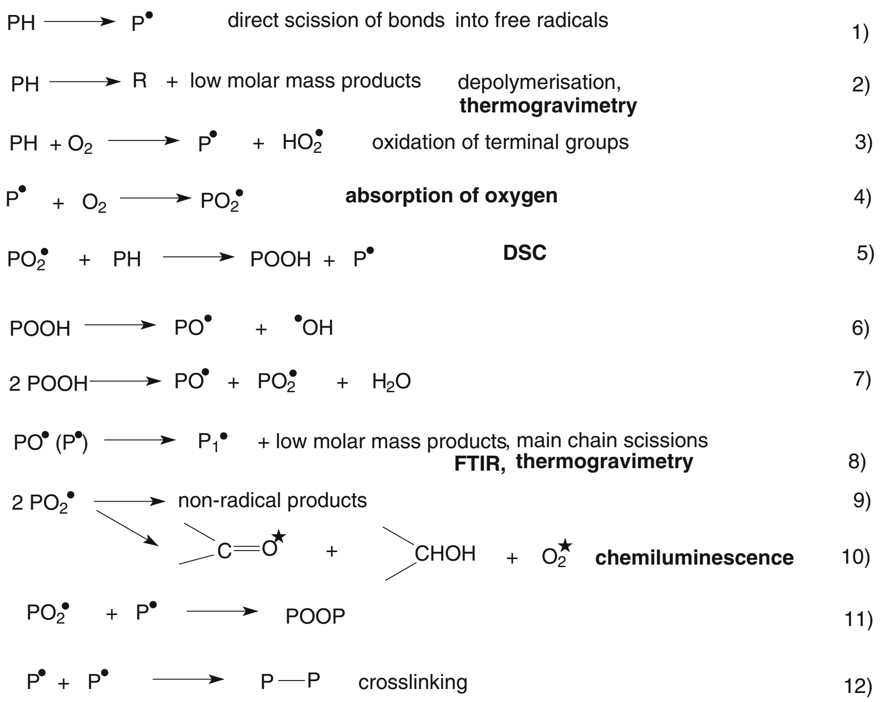
Scheme 12.2 Low-density polyethylene film (*coloured*) at advanced stage of degradation (point *C* of Scheme 12.1)

The polyolefin life trajectory is also called ageing, the term that is preferred if the long-term changes of polyolefin properties due to weathering come into the play. It may involve the participation of physical processes such as recrystallization, loss of stabilizers by bleaching and mechanically initiated embrittlement. In the older literature, the reader may encounter also the term ‘corrosion’ that was implemented from metals.

Chemical processes related to polyolefin degradation and deterioration of their properties are usually linked with either the reduction of average molar mass due to the scission of bonds in the macromolecular chain or with the increase of the molar mass due to the cross-linking while the polyolefin becomes insoluble in any solvent and brittle.

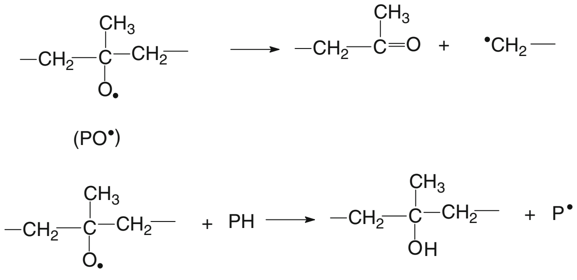
The chemical mechanism of the process may be described as the free radical reaction occurring via hydroperoxides that is described by the Bolland Gee scheme [1] adopted to polyolefins degradation (Scheme 12.3). It is represented by the complex set of elementary reactions taking place in oxidized polyolefin. Scheme 12.3 may be considered as quasi-universal approach to the kinetics and to the research methodology covering thermo-oxidative degradation of polyolefins below 250 °C. Very efficient co-factor reducing the stability of any polymer is the presence of oxygen which affects any mode of initiation. It is related with quite fast introduction of unstable O–O bonds into the polymer structure and development of free radical mechanism according to the reactions 4–12 of Scheme 12.3. According to it, free radicals (P) generated in the initiation process (reaction 1) are in the presence of oxygen converted to peroxyl radicals ($PO_2^{\cdot}$) (reaction 4) and subsequently to hydroperoxides (reaction 5). Alkoxyl radicals in reaction 8 either cleave out and the reduction of the molar mass occurs or eventually they may abstract the hydrogen atom from the substrate PH (Scheme 12.4).

Hydroperoxides as intermediate compounds initiate the chain reaction unless stabilizers (InH functioning there as the chain-breaking antioxidants or D as peroxides decomposer) interrupt it (reactions 13 and 14, Scheme 12.5).



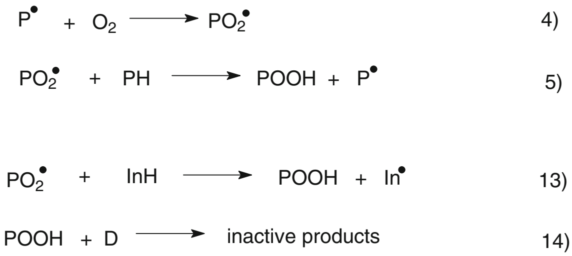
Scheme 12.3 Bolland-Gee scheme [1] for free radical mechanism of polymer oxidative degradation valid to temperatures below 250 °C

Scheme 12.4 The reaction pathway of alkoxyl radicals in degradation of polypropylene



Thermal decomposition of dialkyl peroxides, diacyl peroxides, hydroperoxides and peracids depending on the structure of the peroxidic compound occurs in a measurable rate above 60 °C. Diacyl peroxides and peracids are usually less stable than dialkyl peroxides and hydroperoxides.

Some traces of metal and metal ions may initiate the decomposition of hydroperoxides even at room temperature and contribute to the polyolefins degradation as well. The traces of metal ions are to a more or less extent present in any polyolefin from the catalyst residues and may affect the polymer oxidation and



$$P^{\bullet} + O_2 \longrightarrow PO_2^{\bullet} \qquad 4)$$

$$PO_2^{\bullet} + PH \longrightarrow POOH + P^{\bullet} \qquad 5)$$

$$PO_2^{\bullet} + InH \longrightarrow POOH + In^{\bullet} \qquad 13)$$

$$POOH + D \longrightarrow \text{inactive products} \qquad 14)$$

Scheme 12.5 Mechanistic look on polyolefins stabilization (Scheme 12.3 complemented)

subsequent degradation considerably. The sequence of efficiency of metal ions depends also on the valence state and type of its ligand and may be postulated as follows:

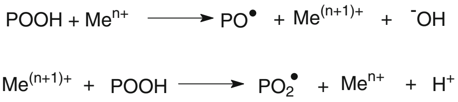
$$\text{Cu} > \text{Mn} > \text{Fe} > \text{Cr} > \text{Co} > \text{Ni}$$

This sequence correlates quite well with the reactivity of these ions in Haber-Weiss cycle of hydroperoxide decomposition (Scheme 12.6) where hydroperoxides play the role of the both oxidative or reducing agents.

The decompositions of hydroperoxides (reactions 6 and 7, Scheme 12.3) which occur as uni- or bimolecular process are the most important reactions leading to the free radical chain degradation. The bimolecular reaction takes place after some time of unimolecular initiation when a sufficiently high concentration of hydroperoxides accumulates. In the case of oxidation in a condensed system of a solid polymer with restricted diffusional mobility of respective segments, hydroperoxides may be formed around the initial initiation site and the process may have heterogeneous character. It occurs mainly if the predominating mode of initiation is bimolecular decomposition of hydroperoxides.

Reaction 8 (Scheme 12.3) representing the β-scission of alkoxyl radicals leading to the reduction of molar mass competes with transfer of free radical centre to surrounding groups and hydroxyl groups (Scheme 12.4) is formed in polyolefin which subsequently loose water, and C=C unsaturations appear randomly along the polymer chain.

Reactions 10–12 in Scheme 12.3 represent the termination of free radical sites which may have the character of cross-linking (reaction 12) and/or formation of dialkyl peroxides (reactions 10 and 11) which may act as new initiating species. The first parallel reaction in reaction 10 is typical for tertiary peroxyl radicals, while



$$POOH + Me^{n+} \longrightarrow PO^{\bullet} + Me^{(n+1)+} + {}^{-}OH$$

$$Me^{(n+1)+} + POOH \longrightarrow PO_2^{\bullet} + Me^{n+} + H^{+}$$

Scheme 12.6 Hydroperoxides decomposition in the sequence of redox reactions the second reaction for secondary (or primary) peroxyl radicals. In the latter case, the disproportionation of peroxyl radicals takes place according to the Russel's scheme, and carbonyl groups and oxygen are being formed in excited triplet and singlet states. The conversion of these excited states to the ground state occurs with a certain yield as a radiative process (chemiluminescence).

12.2.1 Instrumentation in LT Degradation

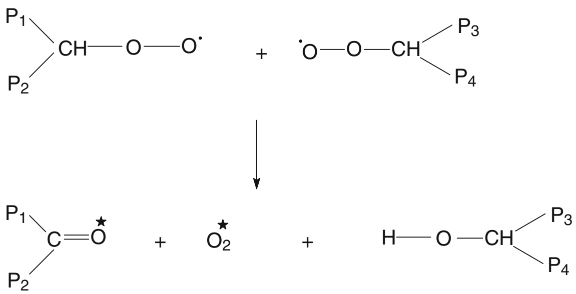
Scheme 12.3 shows to which elementary reactions of the Bolland Gee scheme the respective experimental methods of investigation of polyolefin's degradation may be assigned.

12.2.1.1 Chemiluminescence [2–14]

The light emission comes predominantly from the recombination of secondary peroxyl radicals yielding singlet oxygen, alcohol and triplet carbonyl groups (reaction 10, Schemes 12.3 and 12.7). As the rate of recombination of free radicals is directly linked with the rate of initiation of degradation, the method may yield quite representative picture of the polyolefin oxidation pattern. In the below reaction, the excited triplet ketones and singlet oxygen may be formed due to synchronously released heat (450 kJ/mol).

Figure 12.1 shows how the structure of polyolefins affects the observed patterns of chemiluminescence response in oxygen at 120 °C. As expected, the degradability decreases in the order polyisoprene > polybutadiene > polypropylene > polyethylene in correspondence with the amount of C=C double bonds and tertiary carbon atoms in the polymer structure.

The general rule exists that the polymer with higher average molar mass appears to be more stable than that with lower molar mass. This may be associated with the



Scheme 12.7 Chemiluminescence from the disproportionation of peroxyl radicals (*Asterisk* denote the corresponding excited state)

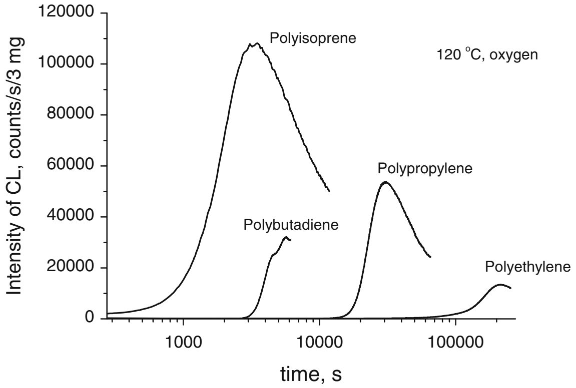


Fig. 12.1 Comparison of chemiluminescence runs from saturated and unsaturated hydrocarbon polymers having tertiary carbons (polypropylene, polyisoprene) in the main chain

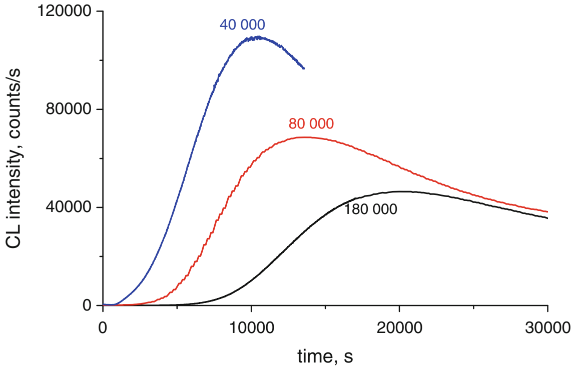


Fig. 12.2 Chemiluminescence oxidation runs at 120 °C in oxygen for polypropylene powder samples of different molar mass. The *number* against each *curve* indicates the average molar mass in g/mol

effect of increased concentration of more reactive terminal groups, which promote initiation of thermal oxidation (Fig. 12.2).

The intensity of chemiluminescence signal that is frequently used in the assessment of thermo-oxidation stability of a polymer and the kinetics of its change with time or temperature is determined by the following:

(a) The quality of the polymer, its photo-oxidation and thermo-oxidation history expressed in concentration of hydroperoxides, carbonyl groups or of other oxidized structures and terminal groups. The rate of an oxidative attack may then be related to the average molar mass and to its distribution, and to the ratio of amorphous/crystalline structures. However, polymers cannot be simply ordered according to the intensity of light emission at a given temperature.

The chemiluminescence time patterns are related to the rate of sample oxidation, but they may differ from one to the other polyolefin type.

(b) The quality of the polyolefin surface; for example, for a particular polymer, the intensity of the signal will be different for film and for powder.

(c) The temperature and concentration of oxygen in the atmosphere surrounding the oxidized sample.

(d) The extent and quality of polyolefin stabilization.

One should emphasize here that the method in non-isothermal mode is preferably used for the testing of the momentaneous degradation state of the polymer and of its position on the life trajectory line (Scheme 12.1) in dependence on the progress of polyolefin ageing.

12.2.1.2 DSC

Differential scanning calorimetry provides the complete information about the melting of polymer crystallites as well as about the position of oxidation exotherm when measurement occurs in oxygen (Fig. 12.3). With the extent of polymer stabilization, this exotherm is shifted to higher temperatures.

12.2.1.3 Thermogravimetry

In non-isothermal thermogravimetry runs, we observe the release of volatiles due to polyolefins degradation (reactions 2 and 8 of Scheme 12.3). At the same time, one may evaluate the presence of volatile low-molar mass compounds initially present in polymer, water from inorganic additives as well as the amount of residual inorganics in composite polyolefins system and finally the residual carbon being formed in cross-linking reactions. In Fig. 12.4, we see the comparison of the polyethylene and polypropylene degradation in nitrogen and in oxygen.

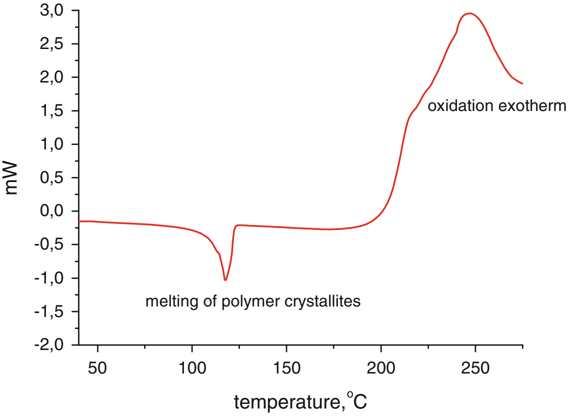


Fig. 12.3 DSC course of oxidation of polyethylene. The rate of heating 5 °C/min

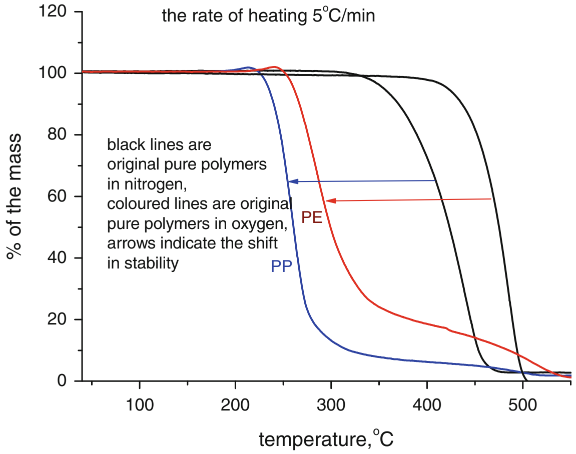


Fig. 12.4 Non-isothermal thermogravimetry records for degradation of polyethylene and polypropylene in nitrogen and in oxygen. The rate of sample heating 5 °C/min

Polyethylene is more stable than polypropylene in both atmospheres; the effect of oxygen, however, appears to be more pronounced for polyethylene.

12.2.1.4 Spectral Methods

According to the evolution of carbonyl (or hydroxyl) groups seen, e.g., by FTIR, the stability of respective polymer may well be followed in time not only at accelerated experiments but also during natural ageing. Figure 12.5 is the

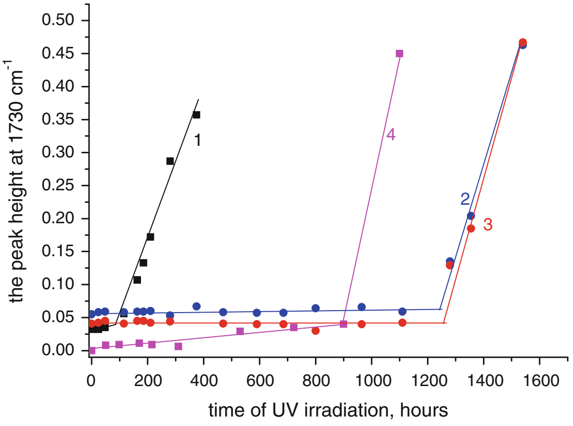
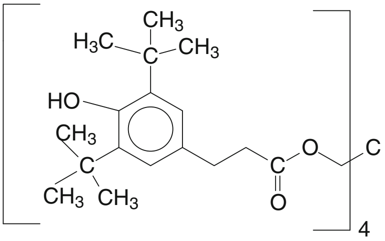
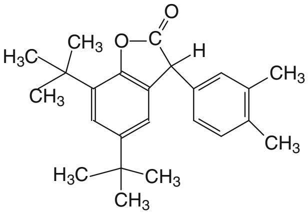


Fig. 12.5 The evolution of the intensity of the carbonyl peak (*FTIR*) at 1730 cm^{-1} during UV irradiation of polypropylene containing Irganox HP136 and Irganox 1010. The *line 1* pure PP, *line 2* 0.15 % of Irganox HP136, *line 3* 0.3 % of Irganox HP136, *line 4* 0.1 % of Irganox 1010



Scheme 12.8 Structure of Irganox 1010 having the most pronounced antioxidant efficiency



Scheme 12.9 The essential component of Irganox HP 136

demonstration of polypropylene degradation either pure or stabilized with phenolic antioxidant Irganox 1010 (Scheme 12.8) and/or Irganox HP 136 (Scheme 12.9) which is so-called captodative antioxidant of the benzofuranone series.

12.2.1.5 Analytical Determination of Peroxides or Carbonyl Groups

The determination of intermediately formed peroxides in the oxidized polyolefins by, e.g., iodometric titration was very popular at the beginning of ninetieth of the last century. As the methodology requires the precise laboratory work, declination from this trend may be noticed today and the more preferred technique is derivatization of hydroperoxides by nitrogen dioxide or sulphur dioxide with a subsequent spectroscopical determination of derivatives received.

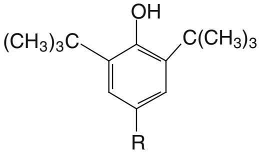
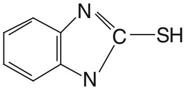
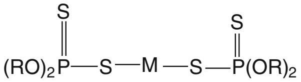
12.2.2 The Protection of Polyolefins Against LT Degradation [15–19]

Estimating the remaining service life of a polymer material for a particular application is important in modern society and industry. The practical interest represents the limiting value of some material property at which the polymer may fail such as of tensile strength, elongation at break, electrical conductivity, permeability to low-molar mass compounds and the average polymerization degree. Stabilizing additives for polymers which degrade by a free radical mechanism usually scavenge the free radicals or hydroperoxides from the system. The effect of such additives consists in reactions 13–14 of Scheme 12.5 and competes with propagation of free radicals by reactions 4–6. According to the predominance of either reaction 13 or 14, we distinguish inhibition antioxidants or *chain-breaking antioxidants* which intervene directly with the oxidation cycle scavenging alkyl or peroxyl radicals and *preventive antioxidants* which impede formation of free radicals by the non-radical decomposition of hydroperoxides.

The most widely used antioxidants are sterically hindered phenols and bisphenols; other additives are combined with phenols mostly in synergistic mixtures. The most recommended structures for stabilization of polyolefins against thermal oxidation and degradation are listed in Table 12.1.

Sterically hindered phenols are remarkably efficient in protecting saturated polymer hydrocarbons against thermal oxidation since molar fractions in the 100–1000 ppm (part per million of substrate) range which is sufficient to increase induction period by several orders of magnitude. The stabilization mechanism and the trends of structure–property relationships are generally well understood, but quantitative (kinetic) approaches of the stabilizers efficiency are scarce and often based on simplifying hypotheses that may not be always valid, for instance: the predominance of radical scavenging by the stabilizer in termination reactions, the stationary state assumption or the constancy of initiation rate (which is explicitly assumed or which derives from the steady-state assumption). It appears generally difficult to explain the very high stabilizer efficiency in the frame of such schemes where the rate of stabilizer consumption is expected to be equal (at least in a first approximation) to the initiation rate.

Table 12.1 The list of the most frequently additives used for stabilization of polyolefins against LT degradation

Secondary diarylamines	Ar NH Ar
Sterically hindered phenols (Irganox 1010, Irganox 1076)	
Nitrogen, phosphorus and sulphur containing preventive antioxidants such as mercaptobenzimidazol	
[Dialkyl (R) thiocarbamato] compounds of Sn, Ni (M) such as	 $(RO)_2\overset{S}{\overset{\Vert}{P}}{-}S{-}M{-}S{-}\overset{S}{\overset{\Vert}{P}}(OR)_2$

In connection with the search for nature friendly additives, the large interest has been devoted to so-called bio-antioxidants such as tocopherols, flavonoids and others. They are preferably used as the processing stabilizers. They perform a weaker stabilizing efficiency as, e.g., sterically hindered phenols; however, in nature, there probably exist other stabilizing mechanisms different from those already known. The good stabilizing efficiency may be, e.g., provided also by the light progress of oxidation when hydroperoxides formed convert bio-antioxidant to a more efficient stabilizing structure, the degradation is stopped, and the process subsequently repeats several times until stabilizer is consumed. It may have some analogy with highly efficient reversible processes from thermodynamics.

12.2.2.1 Synergism and Antagonism in the Effect of Stabilizers Mixtures

Synergism in the stabilizing effect of polyolefin additives is understood as the case of the polyolefin testing when the induction time of oxidation is longer than simple algebraic sum of induction times for each component used at corresponding concentrations separately. Antagonism is then the case of an opposite effect.

Several mechanisms of synergism for two different antioxidants may be put forward, namely:

(1) The additional reaction of additives in the polyolefin due to an increased temperature or light providing more efficient stabilizer. Example: aromatic amines + mercaptobenzimidazol.
(2) A redox mechanism in an oxidized polyolefin mediated by, e.g., hydroperoxides which oxidize more efficient component of the synergistic mixture that is reduced back by a less reactive component. Example: aromatic amines + phenols.
(3) Parallel effect of chain-breaking antioxidants and chelating compounds. Chelating compound deactivates traces of the transition metal ions binding them to a complex compound and converting them to less efficient initiators. The chain-breaking antioxidants decompose peroxides, and the initiation of oxidation is thus reduced. The effect of annealing of stabilized polymer sample on prolongation of its induction period may be included here, as well, whenever sterically hindered phenols, e.g., react with transition metals converting them to less efficient initiators.
(4) Interaction of scavengers of reactive free radicals and compounds which reduce the transfer reaction of an inhibitor radicals with substrate. This may occur with sterically hindered phenols or amines with compounds having the conjugated system of double C=C bonds.
(5) Synergism based on the mixture of chain-breaking antioxidant (sterically hindered phenol) and hydroperoxide decomposer (organic sulphides or phosphites).

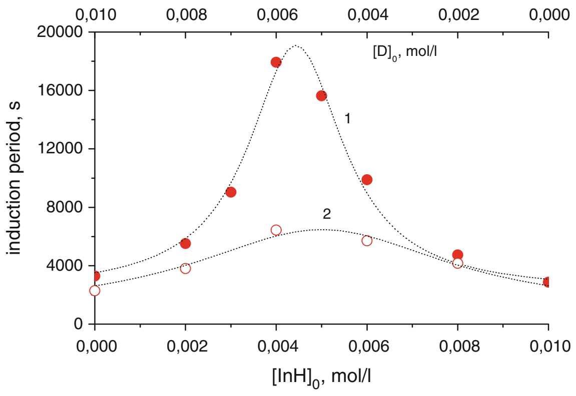


Fig. 12.6 The theoretical plot of induction time of oxidation determined for $w_i = 0$, (zero rate of initiation according to reaction 1 of Scheme 12.3) on composition of the mixture of inhibitors InH (chain-breaking antioxidant) and D (peroxide decompose) having the total sum of concentrations 0.01 mol/l. The *curve 2* below is the plot of induction times for the same values of parameters as for *line 1,* but the rate of initiation w_i due to decreased purity of the polyolefin was $w_i = 5 \times 10^{-8}$ mol/l/(the sum of the rates of reactions 1 and 3 of Scheme 12.3). The initial concentration of hydroperoxides was in both cases 0.001 mol/l

The above mechanisms may combine mutually, and the resulting effect on the polyolefin stability may be rather complex.

The search for synergistic mixtures of stabilizers that is not so vivid nowadays as earlier opens the new routes on how to increase the stability of a given polyolefin and still represents the interest among many companies. Sometimes, new properties and effects are discovered for additives already used when changing, e.g., the mode of initiation or initial purity of polyolefin. An example is shown in Fig. 12.6 where the case (5) of synergism is schematically depicted. Several times higher induction time in the presence of 1:1 molar ratio of sterically hindered phenol (chain-breaking antioxidant) and phosphite (peroxide decomposer) calculated from the theoretical scheme indicates that such an approach may be successful. The extent of a synergistic effect of polyolefin additives thus appears strongly dependent on the purity of the virgin polyolefin expressed in as low value of defect sites responsible for primary initiation as possible. Line 2 shows that the theoretical effect of the synergistic mixture of two antioxidants on thermo-oxidation stability is negligible if there occurs a relatively significant initiation of oxidation reaction in a way independent from the route taking place via hydroperoxides (reactions 1 and 3 of Scheme 12.3.

12.2.2.2 Stabilization Against UV Light

Additives which act as light filters, light absorbers and quenchers of excited states are called photo-stabilizers. Efficient stabilization against the light requires the elimination of free radicals appearing during polyolefin photolysis.

Light filters form a protective barrier between the light source and polymer molecule. They may be used as surface coatings or as pigments in the polymer bulk. Their presence may affect the rate of diffusion of oxygen through the polymer.

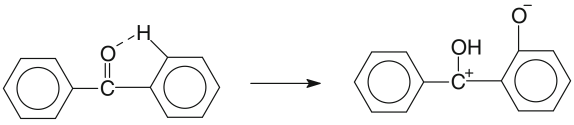
Light absorbers absorb and dissipate the energy of ultraviolet light; their effect resembles that of specific filters for the short range of wavelengths.

The *quenchers* of excited states deactivate excited states arising in the polymer system and thus inhibit direct scission of the macromolecule.

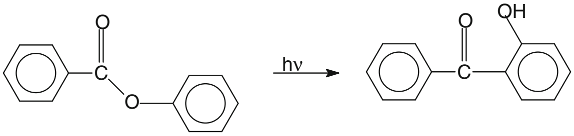
Similarly as with thermal stabilizers, the choice of a suitable photo-stabilizer for a given polymer requires a relatively good 'know-how' of the photo-oxidation process. The derivatives of 2-hydroxy-4-alkoxybenzophenone, benzotriazoles, salicylates and nickel (II) chelates, carbon black, etc., are among the most frequently used. The stabilizer should be highly light resistant; this is the case of aromatic compounds having a hydroxyl group in position 2 with respect to a particular chromophore which forms intramolecular hydrogen bond (Scheme 12.10).

The zwitterions being formed on photo-excitation of 2-hydroxybenzophenone and after the transfer of hydrogen cation to the oxygen atom of the carbonyl group, isomerize back to the original structure of the stabilizer. In the sequence of reactions, the absorbed quantum of light is transformed to heat which is harmless to polyolefin under given conditions. In benzophenone without 2-hydroxyl group, such sequence of reactions cannot occur and there are formed excited singlet and subsequently triplet states of the carbonyl group. The latter having the character of reactive alkoxy radicals that are able to abstract hydrogen from surrounding C–H bonds may develop the further degradation. Benzophenone is thus a photo-sensitizer, while 2-hydroxybenzophenone acts as a photo-stabilizer.

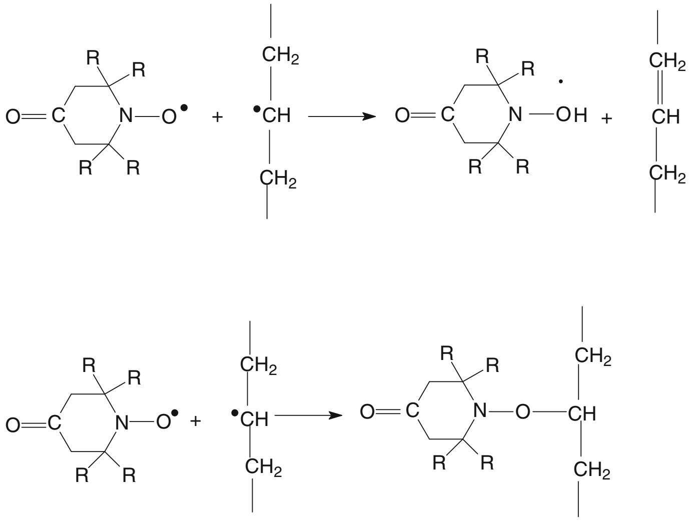
The photo-stabilizing effect of some phenyl salicylates is ascribed to the possibility of their photo-transformation to derivatives of 2-hydroxybenzophenone (Scheme 12.11).



Scheme 12.10 The 2-hydroxy benzophenone route of the dissipation of the light energy in the polyolefin structure



Scheme 12.11 The simple transformation of phenyl salicylate to 2-hydroxybenzophenone



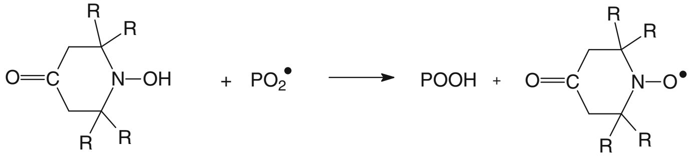
Scheme 12.12 The cycle of regeneration of HALS structure in polyolefins

Carbon black performs the combined antioxidant and light-filtering effect, and its efficiency depends significantly on particle size and on dispersion in the polymer medium. The photo-stabilizing efficiency of other pigments is usually considerably lower.

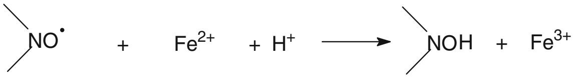
Surprisingly, high photo-stabilizing efficiency towards polyalkenes and polydienes is displayed by sterically hindered amines (HALS). It has been shown that the effect of HALS cannot be interpreted by mechanisms of quenching or absorption but by some chemical process of scavenging peroxyl or alkyl radicals. In this reaction, semistable nitroxyl radicals are regenerated periodically as seen in the following schemes (Schemes 12.12 and 12.13).

Nitroxyl radicals react with polymer alkyl radicals by disproportionation or termination mechanism, and subsequently, they are regenerated in reaction with peroxyl radicals (Scheme 12.13).

There may be, however, some additional effects. Due to its polar structure, HALS may associate with hydroperoxides and should be present at the site of an oxidative attack. The complementary stabilizing effect may follow also from the reaction of nitroxyl radicals with metal ions of low oxidation state (Scheme 12.14),



Scheme 12.13 Regeneration of nitroxyl radicals in oxidized polyolefin



Scheme 12.14 The example of elimination of lower oxidation state of transition metal

$$Fe^{2+} + POOH \rightarrow Fe^{3+} + RO\cdot + {}^{-}OH$$

Scheme 12.15 Oxidation of lower oxidation state of transition metal cation by hydroperoxides

which eliminates free radical decomposition of hydroperoxides in which the reactive alkoxyl radicals are formed (Scheme 12.15).

12.2.2.3 Captodative Compounds in the Stabilization of Polyolefin's Melt and Their Potential Application in UV and Thermo-oxidation Stabilization [23–29]

This may be exemplified, by so-called captodative lactones of the benzofuranone type that are used as the polypropylene processing stabilizers and weak antioxidants (Scheme 12.9).

Their effect is based on the efficient ability of scavenging both carbon- and oxygen-centred radicals. Today, a lot of benzofuranones with different chemical structures have been synthesized, and the combined antioxidants composed of benzofuranones and conventional stabilizers have been widely used as excellent antioxidants for polyolefins [20–24]. Lately, we have found that these compounds may act as excellent UV stabilizers (Fig. 12.7), probably due to their conversion to

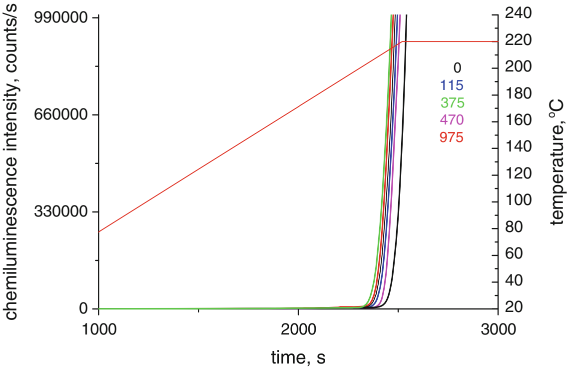
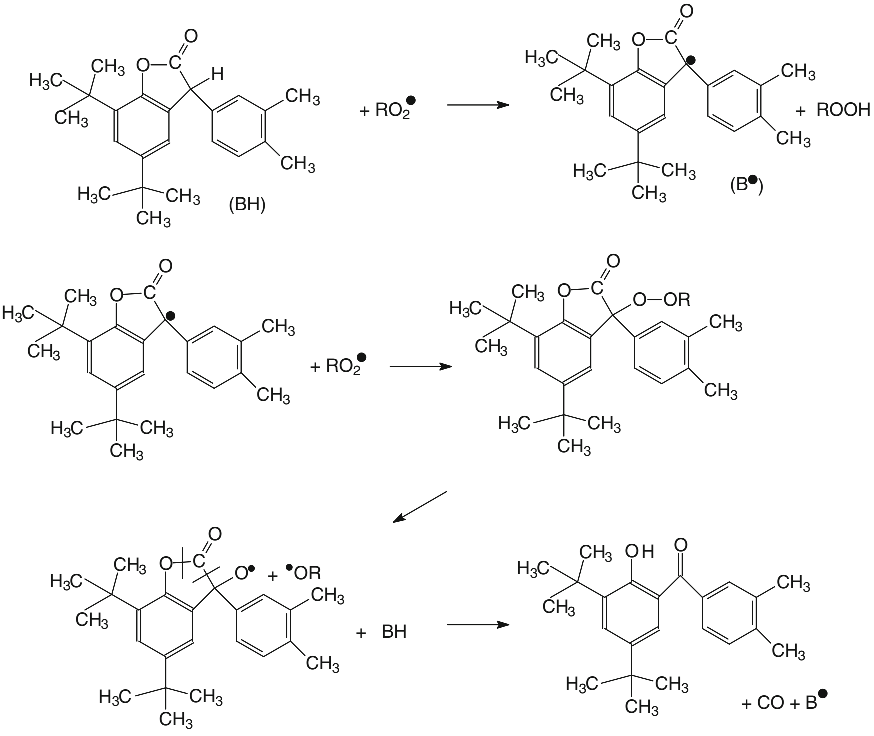


Fig. 12.7 Chemiluminescence intensity runs in oxygen (the rate of heating 5 °C/min) for polypropylene with 0.15 % wt. of Irganox HP136 irradiated in air. The *numbers* denote the time of irradiation in hours



Scheme 12.16 The sequence of radical reactions leading to 2-hydroxy benzophenone derivative, the compound with stabilizing effect against the light

2-hydroxy benzophenone derivatives (Scheme 12.16). The position of chemiluminescence intensity versus temperature on the temperature scale as the test of the momentaneous state of the polymer remains almost without change even after 1000 h of UV irradiation of polypropylene.

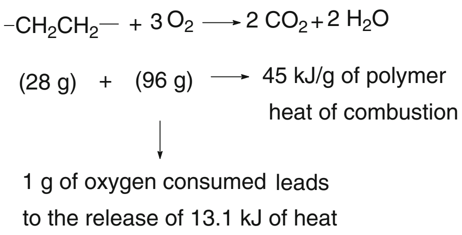
12.3 HT Degradation Leading to Ignition. Protection of Polyolefins Against Fire Risk and Accompanying Phenomena [26–41]

There is no obvious route connecting the low-temperature and high-temperature oxidation of polyolefins ending in polyolefin ignition and burning; however, it exists. One should have in mind that burning of polyolefin when compared to oxidation is a robust phenomenon where the polymer is completely destroyed leaving only some smoke and carbon residue. Their characterization, however, may serve as fingerprints of low-temperature ageing process.

In the last 20 years, there is a growing interest on the cone calorimeter measurements of burning polymers for the screening and subsequent assessment of their flammability. While the number of papers devoted to the technique steadily increases, there is still the lack of fundamental measurements describing the burning behaviour of the common polymers and particularly of polyolefins. It concerns of thermally thin samples and pure polymers. The fire science community, however, appears to be concerned with a lot of data that may be withdrawn from one cone calorimeter experiment, and its interest is focused particularly on the mutual comparison of the heat release rate curves of modified and non-modified polymer samples. We remind here that except for heat release rate and its peak, the mass loss, char yield, effective heat of combustion, time to ignition, CO and smoke formation together with deduced quantities such as FIGRA and MARHE may be received from one cone calorimeter run. The standard cone calorimeter experiment uses 10 cm × 10 cm large samples of thickness of 50 mm or less. The research on non-standard samples having initially the form of powders, granulates or even liquids, however, may contribute to better understanding of polymers combustion.

In the literature, a lot of data on the combustion of various polyolefins (industrially produced or newly synthesized) have been published in an attempt to show how the respective modification upgraded the flame performance of a given polymer. Heat release rate versus time is usually the first graph that may be encountered in the most of such assessments. It is derived from the rate of oxygen consumption as depicted in Schemes 12.17 and 12.18. Recalculating the rate of oxygen consumption to kW/m^2 of heat release rate takes into account the empirical knowledge that 1 g of oxygen consumed during burning leads to the release of 13.1 kJ of heat and calibration of the instrument taking into account the surface of the sample above which is the flame sitting.

The burning of some polyolefins may be seen in Fig. 12.8. As expected, time to ignition follows the position of non-isothermal thermogravimetry runs in nitrogen



Scheme 12.17 The principle of the heat release determination used in a cone calorimeter

$$-CH_2CH_2- + O_2 \longrightarrow 2\,C + 2\,H_2O$$

Scheme 12.18 Combustion of polyethylene under the deficiency of oxygen giving rise to only 15 kJ/g of polymer and carbon

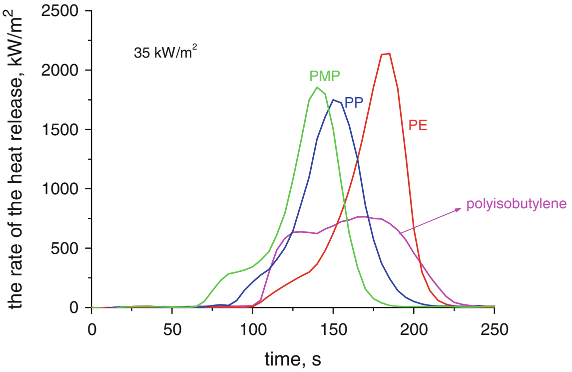


Fig. 12.8 The heat release rate for the burning of several polyolefins in cone calorimeter (*PMP* poly (4-methyl 1-pentene), *PP* polypropylene, *PE* polyethylene), the cone radiancy 35 kW m^{-2}

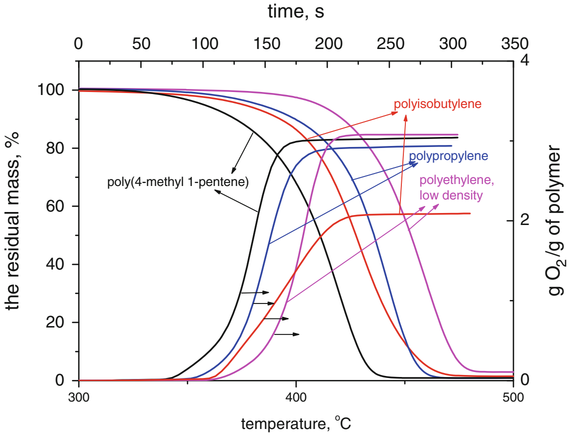


Fig. 12.9 Non-isothermal thermogravimetry of several polyolefins from the Resin Kit polymers (the rate of heating 5 °C/min), comparison with the evolution of the oxygen consumed

(Fig. 12.9). Polyisobutylene is an exception. The peak heat release rate for polyisobutylene is less than one-third of those from other polyolefins. This is probably linked with considerably larger amount of smoke being released during polyisobutylene burning. In Fig. 12.9, the amount of consumed oxygen related to 1 g of polymer may be illustrative enough.

Polyolefins examined on cone calorimetry burning were those selected from The ResinKit Company (Woonsocket, RI) (Table 12.2). The samples were supplied in the form of plates 2 mm thick, and as such, they have non-standard dimensions. The cuts from these plates having the surface 36 cm^2 were used. More information is available at www.resinkit.com.

Table 12.2 The Resin Kit polyolefins and some parameters determined from non-isothermal thermogravimetry in nitrogen and burning in cone calorimeter

Sample No.	Polymer from Resin Kit	Rate of oxygen consumption g/s/g of polymer	Peak HRR (kW/m^2)	TSR (m^2/m^2/g)	Temperature of the maximum rate of release of volatiles from TG (°C)	$k_{\text{from TG}}$ at 400 °C	E_a (J/mol)	Fraction of the main decomposition process from TG
22	Polyizobutylene *2.08*	0.0237	765	457.5	429.8	8.70E −04	222,687	0.93
24	Polyethylene (low density) *3.08*	0.072	2138	115.6	459.3	1.70E −04	241,644	0.922
25	Polyethylene (high density) *3.04*	0.0724	1864	128	465.2	1.17E −04	240,275	0.966
27	Polypropylene (homopolymer) *2.93*	0.061	1748	267.6	441.6	5.00E −04	247,457	0.954
28	Polypropylene (barium sulphate reinforced) *2.66*	0.044	1400	161.8	422	0.00117	175,513	0.632
36	Polypropylene (glass filled) *1.9*	0.028	980	149.6	440.7	5.30E −04	235,156	0.526
38	Polypropylene (flame retardant) *2.42*	0.0504	1486	223.4	432.8	9.00E −04	235,912	0.657
43	Polymethyl pentene *3.03*	0.0696	1854	174.4	419.1	0.00185	260,335	0.759

(continued)

Table 12.2 (continued)

Sample No.	Polymer from Resin Kit	Rate of oxygen consumption g/s/g of polymer	Peak HRR (kW/m^2)	TSR (m^2/ m^2/g)	Temperature of the maximum rate of release of volatiles from TG (°C)	$k_{\text{from TG}}$ at 400 °C	E_a (J/mol)	Fraction of the main decomposition process from TG
44	Polypropylene (talc reinforced) *1.73*	0.0137	538	148.8	404.3	0.0027	259,940	0.579
45	Polypropylene (calcium carbonate reinforced) *1.76*	0.0154	584	131.4	449.5	3.60E −04	229,700	0.551
49	Polyethylene (medium density) *3*	0.0391	1171	153.2	452.5	0.000263	238,855	0.965

[a] Stands for *TOC*, total oxygen consumption/g of polymer sample, *TSR* is a total smoke release, *HRR* is heat release rate, *TG* is non-isothermal thermogravimetry

12.3.1 The Evaluation of Non-isothermal Thermogravimetry Runs

Numerical evaluation of non-isothermal thermogravimetry is of interest as the polymer ignition is usually related to it. Activation energy withdrawn from single thermogravimetry run represents the scale of the polymer stability as well as its ignitability.

The formation of volatile degradation products as observed by non-isothermal thermogravimetry is a complex process. The non-isothermal thermogravimetry curve that is apparently composed of several independent processes was described by the first-order scheme, i.e. $-\frac{\mathrm{d}m}{\mathrm{d}t} = km$ where t is time, m is the actual mass of the degraded sample, and k is the rate constant of polyolefin degradation to volatile products. In a non-isothermal mode,

$$-\frac{\mathrm{d}m}{m\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right), \tag{12.1}$$

where $\beta = \frac{\mathrm{d}T}{\mathrm{d}t}$ is a linear heating rate. Here, T stands for absolute temperature, A is pre-exponential factor, and E is activation energy of degradation process. After integration, we obtain $m = m_0 \exp\left[-\frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]$, and for the process composed of j temperature-dependent components—'waves', we have

$$m = m_0 \sum_{i=1}^{j} \alpha_i \exp\left[-\frac{A_i}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_i}{RT}\right)\mathrm{d}T\right]. \tag{12.2}$$

Provided that mass changes are expressed as a percentage of the original mass, m_0, triplet of parameters α_i, A_i, E_i may be found for polypropylene (i = 1), inorganic additive (i = 2) and polymer residual mass (i = 3) decomposition by a nonlinear regression analysis program. The program was applied to the experimental mass m versus temperature T records, from the initial temperature T_0 (laboratory temperature) to a final temperature T (550 °C) of the experiment.

The essential data for polyolefins from the Resin Kit set are given in the Table 12.2.

12.3.2 Non-isothermal Thermogravimetry in Nitrogen, Time to Ignition, Oxygen Consumption and Polyolefins

Non-isothermal thermogravimetry experiments where the sample is also completely destroyed to volatiles and carbon residue have the highest potential to reveal the mutual link between degradation of polyolefin at lower temperatures and its tendency to ignition and burning.

Fig. 12.10 Non-isothermal thermogravimetry runs for additivated polypropylene

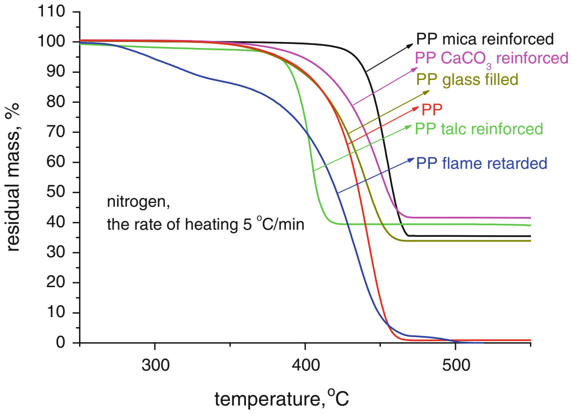


Fig. 12.11 Non-isothermal thermogravimetry of *low*-, *medium*- and *high*-density polyethylene, compared with the amount of oxygen consumed during the sample burning in cone calorimeter

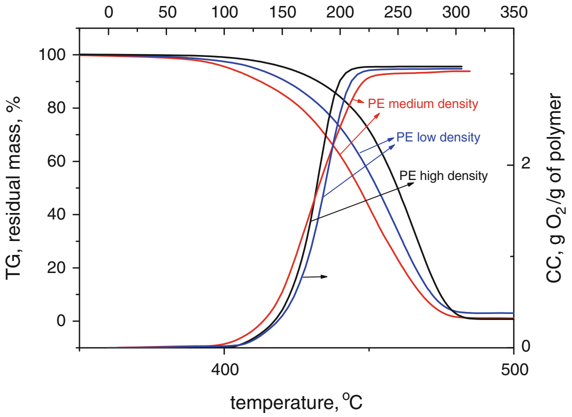


Figure 12.10 shows the release of volatiles during thermal degradation of polypropylene. Mica reinforces the polypropylene stability, while halogenated flame retardant reduces it. Both composite polymers are compared with the pure polymer. The thermal stability of low, medium and high-density polyethylenes has its linkage to the number of branches in the main polymer chain. It is of interest that the flammability expressed in the amount of oxygen consumed follows the similar tendency (Fig. 12.11).

12.3.3 Non-isothermal Thermogravimetry Runs and Polyolefins Ignitability

Flame retardants in polymers should be used in concentrations by one order of magnitude higher than the oxidation inhibitors, and their structure usually contains some weak sites generating free radicals in an additional step.

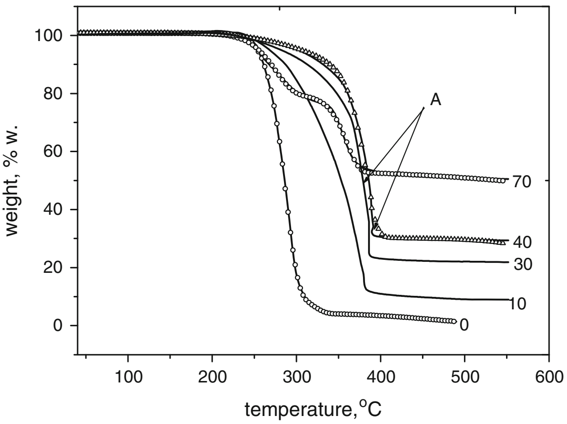


Fig. 12.12 The non-isothermal thermogravimetry runs in air for polypropylene with $Mg(OH)_2$, the rate of heating 5 °C/min. The *numbers* denote the initial concentration of $Mg(OH)_2$ in wt%. *Points* represent the examples of the fit of the non-isothermal thermogravimetry course by Eq. 12.2 from Sect. 12.3.1 for the sum of the three first-order decomposition processes ($j = 3$). *Arrows A* point to the steep slope of the experimental run

As an example of retardation of burning, we give the effect of some inorganic additives such as magnesium hydroxide and magnesium oxide that have significant reducing effect on the heat release rate from polypropylene burning (Fig. 12.12 and Table 12.2). The effect becomes very pronounced at a relatively high loading of respective admixtures. When compared with $Mg(OH)_2$ where endothermic effect due to the release of water plays an important role, MgO reduces HRR as well. It is, however, surprising that the reduction of HRR is even more distinct than that for magnesium hydroxide. This is the indication of the important role of the effect of magnesium oxide on the melt reactions during polypropylene burning.

From the limiting oxygen index (LOI) values in Table 12.3, we see a significant increase to 33 % which can be obtained at high loading of $Mg(OH)_2$ at 70 % when the polymer becomes brittle and also other mechanical properties are lost. The burning of polypropylene containing magnesium oxide and hydroxide is considerably less vigorous when compared with pure polymer even at as low loads of magnesium compound as 20 % This may be also due to the much better reflecting effect of MgO on the emissive heat from the flame than that from the metallic holder bottom. MgO remains on the bottom of the holder, and the layer of the burning material is formed above.

Provided that we mix MgO with polypropylene powder to the total weight 15 g, the time to ignition is first reduced and starts to increase slightly at higher MgO loadings (Table 12.3). When working with PP platelets containing $Mg(OH)_2$, the initial mass of which is lower than that of the mixtures of MgO with PP powder, we observe the initial increase of time to ignition; however between 40 and 50 wt% of $Mg(OH)_2$ a strong decrease was observed. It seems, therefore, that above 40 % of

Table 12.3 The main characteristics obtained from burning of polypropylene with additives ($Mg(OH)_2$ and MgO)

Sample	Gross combustion heat from calorimetric bomb (J/g)	LOI (%)	t_{ign}, s	HRR peak (kW/m^2)
Polypropylene HF322	48,270	17.5	62 61	954 971
Polypropylene, powder			37 36	1070 1022
Polypropylene + 10 % $Mg(OH)_2$	43,343	17.7	71	849
Polypropylene powder + 16.6 % MgO			22 25	409 386
Polypropylene + 20 % $Mg(OH)_2$	38,694	18.9	79	695
Polypropylene + 30 % $Mg(OH)_2$	34,289	20.1	80	544
Polypropylene powder + 33.3 % MgO			16 17	245.4 271.3
Polypropylene + 40 % $Mg(OH)_2$	29,187	21.1	78	417
Polypropylene + 50 % $Mg(OH)_2$	24,250	22.4	43	353
Polypropylene powder + 50 % MgO			15 15	176 161
Polypropylene + 60 % $Mg(OH)_2$	19,785	22.6	41	215.3
Polypropylene powder + 66.6 % MgO			16	127
Polypropylene + 70 % $Mg(OH)_2$	15,237	33.2	45	157.5
Polypropylene powder + 83.3 % MgO			19 23	82.3 75.6

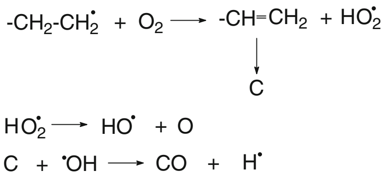
HRR is the heat release rate, *LOI* is the limiting oxygen index, t_{ign} is time to ignition, and the cone radiancy was 35 kW/m^2

$Mg(OH)_2$ there predominates the catalytic effect of magnesium compound above the effect of water release.

The gross combustion heats determined from calorimetric bomb decrease proportionally to the content of polypropylene in its blend with $Mg(OH)_2$.

12.3.4 The Appearance of Smoke in the Burning Polyolefins

It is generally valid that the more unsaturated compounds (compounds having C=C bonds) appear in HT degradation of polyolefins and the higher amount of smoke



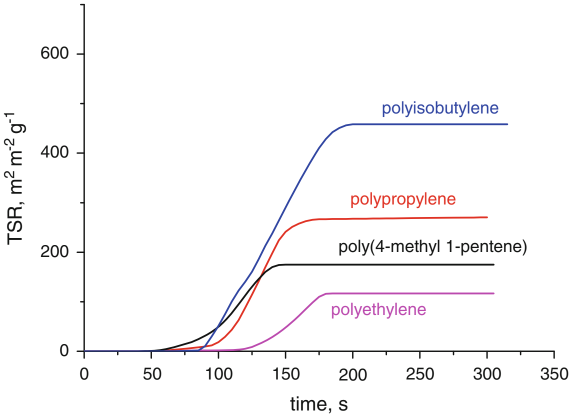
Scheme 12.19 The initial steps in the formation of carbon-rich molecules in burning of polymer

appears in their burning (Scheme 12.19). These compounds act as precursors of formation of carbon-rich particles C giving rise to the derivatives of acetylene. In the oxygen-rich flames, these smoke entities are removed by subsequent oxidation.

From the polyolefins examined (Fig. 12.13), the most heavy smokes are produced in burning of polyisobutylene, where large yield of olefinic monomer is formed during its high temperature degradation. Polyethylene belongs to polymer that produces the lowest amount of smoke when burning. Polyolefins flame retarded by brominated and other organic flame retardants gives rise also the formation of large amount of smoke.

The total smoke released during burning of polypropylene decays when increasing the content of magnesium hydroxide in polypropylene to 40 % of the weight with a certain slope (Fig. 12.14). Above this load, however, the total smoke released has a higher slope, finally achieving the value around 5 $m^2\ m^{-2}\ g^{-1}$ for the sample having 70 wt% of $Mg(OH)_2$. It appears that till 40 % of the load diluting effect of additive reducing the smoke predominates, while at higher loads the supporting mechanism of the carbon oxidation from the active magnesium oxide surface comes to play a role as well.

Fig. 12.13 The release of the smoke (*SR*) during burning of several polyolefins. The data from the cone calorimeter at the cone radiancy 35 kW m^{-2}



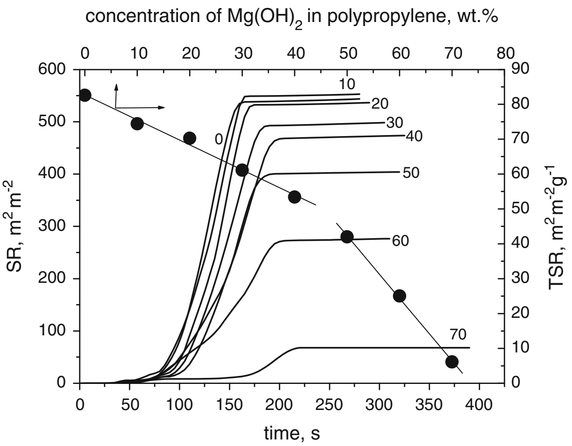


Fig. 12.14 The smoke release (*SR*) and total smoke released (*TSR*) during burning of polypropylene with $Mg(OH)_2$, the cone radiancy 35 kW/m^2. *Numbers* denote wt% of $Mg(OH)_2$

12.3.5 Mechanistic Linkage of LT and HT Degradation

In Scheme 12.20 we explain what is the main reason for the transfer of low-temperature oxidation to ignition. Provided that the reaction of addition of alkyl radical to oxygen with formation of peroxyl radicals (reaction 4) is replaced

$$-CH_2-CH_2^{\bullet} + O_2 \longrightarrow -CH_2-CH_2-O-O^{\bullet} \qquad 4)$$

$$-CH_2-CH_2^{\bullet} + O_2 \longrightarrow -CH{=}CH_2 + HO_2^{\bullet} \qquad \text{ignition} \qquad 4a)$$

$$-CH_2-CH_2^{\bullet} \longrightarrow -CH{=}CH_2 + H^{\bullet} \qquad \text{burning} \qquad 4b)$$

$$H^{\bullet} + O_2 \longrightarrow HO^{\bullet} + {}^{\bullet}O^{\bullet} \qquad \text{heat} \qquad 4c)$$

$$HO^{\bullet}\ (H^{\bullet},\ {}^{\bullet}O^{\bullet}) + HBr \longrightarrow H_2O\ (H_2, HO^{\bullet}) + {}^{\bullet}Br \qquad 4d)$$

chemical retardation

$$\text{heat} + Mg(OH)_2 \longrightarrow MgO + H_2O \qquad \text{physical retardation} \qquad 4e)$$

Scheme 12.20 The threshold of the changes of elementary oxidation processes leading to ignition and an outline of eventual retardation of burning (Scheme 12.3 complemented) by disproportionation (reaction 4a), then ignition becomes the possible alternative of the polyolefin degradation. When compared with reaction 4 which has activation energy zero, the disproportionation has activation energy several tens of kJ/mol. Increasing temperature therefore leads to the replacement of reaction 4, and hydrogen and oxygen atoms as well as hydroxyl radicals appear in the gaseous phase. The branching occurs via the reaction 4c. The retardation of the burning is based on scavenging of these reactive atoms by hydrogen bromide or antimony halogenide and/or phosphorous halogenides and on their conversion into less reactive species. Note that in the case of burning, we use the term retardation and not inhibition. Inorganic additives bring about the scavenging the reaction heat (reaction 4c) and change the character of the condensed phase reaction.

12.4 Conclusions

The possible link between low- and high-temperature degradation of polyolefins has been outlined in a mechanistic way. It is understood that at low-temperature degradation the loss of essential polyolefin properties occurs limiting; thus, any practical utilization of the product from polyolefin, the high temperature leads to its total damage. The fingerprints of stepwise changes in the polyolefin during low-temperature degradation, however, may be revealed by high temperature tests such as non-isothermal thermogravimetry and non-isothermal chemiluminescence that provide the fingerprints of the extent of the low-temperature degradation and ageing.

Acknowledgements This publication is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions. Part II supported by the Research and Development Operational Programme funded by the ERDF. The acknowledgements are also due to Grant Agency VEGA 2/0147/12, VEGA 2/0161/14, VEGA 2/0122/15 and to HUSK programme 1101/1.2.1/0209, Advanced bio-friendly polymers.

References

1. J.L. Bolland, G. Gee, Trans. Farad. Soc. **42**, 236–243 (1946)
2. G.E. Ashby, Oxyluminescence from polymers. J. Polym. Sci. **50**, 99–106 (1961)
3. R.E. Barker, J.H. Daane, P.M. Rentzepis, Thermochemiluminescence of polycarbonate and polypropylene. J. Polym. Sci. A **3**, 2033–2045 (1965)
4. A.M. Wynne, W.W. Wendlandt, The thermal light emission properties of alathon 1: effect of experimental parameters. Thermochim. Acta **14**, 61–69 (1976)
5. M.P. Schard, C.A. Russell, Oxyluminescence of polymers I: general behavior of polymers. J. Appl. Poly. Sci. **8**, 985–995 (1964)
6. L. Reich, S.S. Stivala, *Elements of Polymer Degradation*. (McGraw-Hill, New York, 1971), pp. 99, 161

7. C.H. Hsueh, W.W. Wendlandt, Effect of some experimental parameters on the oxyluminescence curves of selected materials. Thermochim. Acta **99**, 37–42 (1986)
8. W.W. Wendlandt, The oxyluminescence of polymers: a review. Thermochim. Acta **72**, 363–372 (1984)
9. C.H. Hsueh, W.W. Wendlandt, The kinetics of oxyluminescence of selected polymers. Thermochim. Acta **99**, 41–43 (1986)
10. W.W. Wendlandt, The oxyluminescence and kinetics of oxyluminescence of selected polymers. Thermochim. Acta **71**, 129–137 (1983)
11. L. Matisová-Rychlá, J. Rychlý, Inherent relations of chemiluminescence and thermooxidation of polymers. In *Advances in Chemistry, Series 249: Polymer Durability, Degradation, Stabilization and Lifetime Prediction*, ed. by R.L. Clough, N.C. Billingham, K.T. Gillen (Ameircan Chemical Society, Washington DC, 1996), p. 175
12. J. Rychlý, L. Rychlá, Chemiluminescence from polymers. In *Ageing and Stabilisation of Paper*, ed. by M. Strlič, J. Kolar (National and University Library, Ljubljana, Slovenia, 2005), pp. 71–90
13. K. Jacobsson, P. Eriksson, T. Reitberger, B. Stenberg, Chemiluminescence as a tool for polyolefin oxidation studies. In *Long Term Properties of Polyolefins, Advances in Polymer Science*, vol. 169, ed. by A.C. Albertsson (Springer, Berlin, 2004), pp. 151–176
14. L. Rychlá, J. Rychlý, New concepts in chemiluminescence at the evaluation of thermooxidative stability of polypropylene from isothermal and non-isothermal experiments. In *Polymer Analysis and Degradation* (Chap. 7), ed. by A. Jimenez, G.E. Zaikov (Nova Science Publishers, New York, 2000), p. 124
15. C. Albano, E. de Freitaz, Evaluation of the Kinetics of decomposition of polyolefin blends. Polym. Degrad. Stab. **61**, 289–295 (1989)
16. G. George, M. Celina, Homogeneous and heterogeneous oxidation of polypropylene. In *Handbook of Polymer Degradation*, ed. by S. Halim Hamid, M. Dekker (Second Edition, Inc., New York, 2000), p. 277
17. L. Zlatkevich, *Luminescence Techniques in Solid State Polymer Research* (Chap. 7). (M. Dekker, New York, 1989)
18. J. Verdu, *Oxidative Ageing of Polymers* (Wiley, Hoboken, 2012)
19. J. Pospisil, S. Nespurek, Chain-breaking stabilizers in polymers: the current status. Polym. Degrad. Stab. **49**, 99–110 (1995)
20. A. Mar'in, L. Greci, P. Dubs, Antioxidant activity of 3-aryl-benzofuran-2-one stabilizers (Irganox HP-136) in polypropylene. Polym. Degrad. Stab. **76**, 89–94 (2002)
21. A. Mar'in, L. Greci, P. Dubs, Physical behavior of 3-aryl-benzofuran-2-one (IrganoxHP-136), in polypropylene. Polym. Degrad. Stab. **78**, 3–7 (2002)
22. X. Meng, Z. Xin, X. Wang, Structure effect of benzofuranone on the antioxidant activity in polypropylene. Polym. Degrad. Stab. **95**, 2076–2081 (2010)
23. W. Voigt, R. Todesco, New approaches to the melt stabilization of polyolefins. Polym. Degrad. Stab. **77**, 397–402 (2002)
24. X. Meng, W. Gong, Z. Xin, Zi Cai, Study on the antioxidant activities of benzofuranones in melt processing of polypropylene. Polym. Degrad. Stab. **91**, 2888–2893 (2006)
25. P. Solera, New trends in polymer stabilization. J. Vinyl Addit. Technol. **4**(3), 197–210 (1998)
26. V. Babrauskas, Development of the cone calorimeter—A bench-scale heat release rate apparatus based on oxygen consumption. Fire Mater. **8**, 81–95 (1984)
27. V. Babrauskas, R.D. Peacock, Heat release rate: the single most important variable in fire hazard. Fire Saf. J. **18**, 255–272 (1992)
28. C. Huggett, Estimation of rate of heat release by means of oxygen consumption measurements. Fire Mater. **4**, 61–65 (1980)
29. V. Babrauskas, Related quantities; (a) heat of combustion and potential heat. In *Heat Release in Fires* (Chap. 8), ed. by V. Babrauskas, S.J. Grayson (E & FN Spon, Chapman & Hall, London, 1996)
30. ISO 5660-1:2002, Reaction-to-fire tests—Heat release, smoke production and mass loss rate—Part 1: heat release rate (cone calorimeter method)

31. ISO 5660-2:2002, Reaction-to-fire tests—Heat release, smoke production and mass loss rate—Part 2: smoke production rate (dynamic measurement)
32. ISO/TR 5660-3:2003, Reaction-to-fire tests—Heat release, smoke production and mass loss rate—Part 3: guidance on measurement
33. T.R. Hull, B.K. Candola, Fire retardancy of polymers: new strategies and mechanisms. Science (2009)
34. B. Schartel, Fire retardancy of polymeric materials (Chap. 15). In Uses of Fire Tests in Materials Flammability Development, 2nd edn, ed. by C.A. Wilkie, A.B. Morgan (CRC Press, New York, 2009)
35. J. Lindholm, A. Brink, M. Hupa, The influence of decreased sample size on cone calorimeter results. Fire Mater. **36**, 63–73 (2012)
36. J. Rychlý, L. Rychlá, K. Csomorová, Characterisation of materials burning by a cone calorimeter 1: pure polymers. J. Mater. Sci. Eng. **A2**, 174–182 (2012)
37. B. Schartel, T.R. Hull, Development of fire-retarded materials—interpretation of cone calorimeter data. Fire Mater. **31**, 327–354 (2007)
38. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris Jr., Flammability properties of polymer—layered silicate nanocomposites: polypropylene and polystyrene nanocomposites. Chem. Mater. **12**, 1866–1873 (2000)
39. T. Kashiwagi, E. Grulke, J. Hilding, K. Groth, R. Harris, K. Butler, J. Shields, S. Kharchenko, J. Douglas, Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. Polymer **45**, 4227–4239 (2004)
40. J. Rychly, M. Hudakova, L. Rychla, Cone calorimetry burning of thermally thin polyethylene. J. Therm. Anal. Calorim. **115**, 527–535 (2014)
41. D. Hopkins Jr., Predicting the ignition time and burning rate of thermoplastics in the cone calorimeter, Thesis, NIST-GCR-95-677, Faculty of the Graduate School of The University of Maryland, 1995

Chapter 13
Recycling of Polyolefin Materials

P.S. Sari, T. Sharika, K. Bicy and Sabu Thomas

13.1 Introduction

Polyolefins are the most extensively used category of polymers, counting polyethylene (PE) and polypropylene (PP), which take up nearly 45 % in the global market. These polymers have become the integral part of our day-to-day life because of their multiple applications. Polyolefins are the most important type of thermoplastics used all over the world in such applications as film, battery cases, automotive parts, electrical components (PP) house wares, industrial wrappings and film, gas pipes (HDPE), bags, toys, containers, pipes (LDPE), in virtue of their properties such as lightweight, durable, strong, inexpensive, high thermal and electrical insulation properties and corrosion-resistance [1–5]. The increased usage of the plastic has accelerated the waste disposal to the environment. So the plastic waste disposal is one of the important issues in this modern world. Polyolefins, the saturated hydrocarbon polymers are highly resistant to biodegradation. High consumption of plastics and the resulted inevitable production of large amount of plastic waste is one of the most discussed topics in this area. As the usage of plastics is unavoidable, the only solution for this problem is through '3R's, i.e., recycle, reuse, and reduce.

Recycling is the practice of converting the waste into an utilizable product thus decreases environmental degradation and receiving financial benefits out of waste. The process of recycling can be divided into several steps: collection, sorting, segregation, and reprocessing. Recycling offers opportunity to reduce usage of oil, carbon dioxide emissions, and the quantities of disposed waste [6]. Recycling

---

P.S. Sari (✉) · T. Sharika · K. Bicy · S. Thomas
International and Inter University Centre for Nanoscience and Nanotechnology,
Mahatma Gandhi University, Kottayam 686560, Kerala, India
e-mail: sarips1@gmail.com

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_13

technologies of polyolefin are categorized as primary (re-extrusion), secondary (mechanical), tertiary (chemical), and quaternary (energy recovery) schemes and technologies [7]. Primary recycling means processing of a recyclable material into a product without changing the characteristics and keeping them similar to those of original product. Secondary recycling involves mechanical recycling, which means the processing of plastic waste into new products that have different characteristics from those of original one. Tertiary recycling involves chemical recycling, which bring about the production of basic chemicals and fuels from plastic waste. Quaternary recycling regains the energy content of plastic waste by burning/incineration [8, 9].

The conventional approach to plastic waste management is landfilling. But that creates environmental problems of contamination of soils and groundwater by some additives and breakdown by-products in plastics, which can become constant organic pollutants [10–12]. The major drawback of landfills is that none of the material resources is recovered. The material flow is linear rather than cyclic. Primary recycling is also called re-extrusion, which is commonly applied in the processing line itself. The process involves the reintroduction of clean waste of single polymer to the extrusion cycle with the aim of producing new products of the similar material. The mechanical recycling technique generally reduced the size of scrap to a more desirable shape and form, such as pellets, flakes, or powders, depending on the source, shape, and usability. Tertiary treatment methods have put in significantly to the recycling status of plastic solid waste in recent years. Advanced thermochemical treatment methods cover a wide range of technologies and produce either fuels or petrochemical feedstock. In these days, non-catalytic thermal cracking (Pyrolysis) is getting renewed attention, owing to the fact that its added value to a crude oil barrel and its very valuable yielded products. The attainable solution to plastic solid waste, more specifically municipal solid waste (MSW), is energy recovery.

Development of new technologies and systems for the collection, sorting, and reprocessing methods of plastic wastes generated new opportunities for recycling.

The objective of this chapter is to present an overview of the recycling of polyolefin. Brief account of the various type of recycling methods and techniques starting from the separation techniques to application of the recycled material will be presented.

13.2 Separation Techniques

The first step of recycling is collection and separation from the raw waste and sorting. Normally, the raw wastes contain a variety of polymers other than papers, glass, and other contaminants. Here comes the importance of separation techniques prior to recycling. On the other hand, separation of mixed plastics comes across various problems (due to the characteristics of plastics) and represents one of the trickiest processes in the plastic waste management. Owing to the development of technology, a number of separation techniques are currently in use.

Mechanical sorting techniques have been pointed out the accepted route for separating plastic waste, which includes near-infrared sorting (NIR), triboelectrostatic separation, sink-float, and flotation [13–15]. Near Infrared (supported by hand-sorting) worked on the principle of spectroscopic identification of polymer types. It is fast and has high resolution but not applicable to black or small items, and it is expensive, surface sensitive, and lead to low material recovery [16]. Triboelectrostatic sorting based on electrostatic charge is another way for sorting polyolefins. This technique can be used only for clean, dry, and non-surface-treated polymers, and high-quality requirements of operating conditions are needed and the input materials should be a binary mix [17]. Density sorting is the cheapest and simplest technique, in which sorting is based on density. This technique can be used for any sized and colored material but needs efficient difference in density (10–40 kg/m^3). Density sorting methods are not particularly helpful in sorting, because most plastics are very close in density [18]. Flotation is a technique which worked on the basis of different surface properties of the material and sensitive to reagents, condition temperature, time, particle sizes, and roughness [19].

The technique commonly used to separate household packaging wastes is sensor-based near-infrared spectroscopy that is based on the fact that NIR spectra of different types of polymers are quite distinct. NIR is able to provide rapid and reliable identification of various polymers especially the polyolefin group, polyethylene (PE), and polypropylene (PP). However, the objects which are too small or too big are not suitable for this technology. Another drawback is its inability to detect dark polymers, like automotive parts and some of the electronics waste, since radiation is absorbed completely. In practice, for packaging polymers, around half of the total input materials end up in residuals.

Another accepted method is magnetic density separation (MDS), which is a density-based sorting technology [20]. It makes use of a liquid separation medium with a density gradient containing magnetic iron oxide particles with a size of 10–20 nm suspended in water. By applying an artificial gravity, in the form of magnetic force that varies exponentially in the vertical direction, the effective density of the liquid varies in this direction as well. Plastic particles with the same density will float in the liquid at the same level: Where the effective density is equal to their own density. On the basis of this principle, plastic mixtures segregate in many different layers and flake with the same density stay at the same vertical height. The processing time for this process is the order of a few seconds [21]. Such advantages allow MDS to be more cost-effective than other recycling techniques. Early trial separations showed that in principle, MDS can be applied to recycling of PP and PE mixtures under carefully controlled situations. Bakker succeeded in obtaining high-quality PP with a grade more than 97 % from a mixture with an initial ratio of 70:30 between PP and PE [21].

13.3 Methods of Recycling

The process of recycling plastics have mainly categorized to four primary, secondary, ternary, tertiary, and quaternary. The method of recycling can be selected depending on the nature of the plastic waste. The primary method is the re-extrusion of scrap and used directly with the virgin polymer. Secondary recycling is also known as mechanical recycling, which is widely used method for recycling of postconsumer waste, in particular municipal, plastic waste. It is the process of recovering plastic solid waste (PSW) for the reuse in manufacturing plastic products via mechanical means.

Tertiary recycling involves chemical recycling, is the process which convert plastic materials into smaller molecules, generally liquids or gases, which are suitable for use as a feedstock for the production of new petrochemicals and plastics. The chemical structure of the polymer has been altered in this process so the term chemical is used and the products of chemical recycling have proven to be useful as fuel. The technology behind its success is the depolymerization processes that can result in a very profitable and sustainable industrial scheme, providing a high product yield and minimum waste.

Pyrolysis is the treatment of plastic waste in the presence of heat under controlled temperatures without catalysts. The pyrolysis process is an advanced conversion technology, in which the hydrocarbon content of the waste is converted into a clean, high calorific value gas from a wide variety of plastic waste. The produced gas can be utilized in gas engines, electricity generation, or in boiler applications.

13.3.1 Re-Extrusion (Primary)

Primary recycling is the recycling of waste scraps which are clean, uncontaminated, and of single-type plastic. It is simple and low cost and remains the most popular process, which is mainly applicable in in-plant and fed with scrap of controlled history. This type of recycling ensures the performance level of products from waste material analogous to that of products made from virgin plastics. The recycled waste can be either mixed with virgin material to assure product quality or used as second-grade material.

13.3.2 Mechanical Recycling (Secondary)

Mechanical recycling also known as physical recycling involves operations that endeavor to get back plastic waste via mechanical processes such as grinding, washing, separating, drying, regranulating, and compounding. Thus, produced recycled material can be converted into new plastics products, often substituting virgin plastics. Only thermoplastic materials can be recycled via mechanical recycling since it involves remelting and reprocessing [9]. Mechanical recycling seems to be the most beneficial in the terms of energy efficiency and greenhouse gases emission.

Jin et al. studied the effect of mechanical recycling on rheological and thermal properties of low-density polyethylene (LDPE) by subjecting the LDPE samples to one hundred extrusion cycles [22]. The results revealed that the LDPE can be processable up to 40 extrusion cycle without any degradation. Kartalis et al. [23] reported on the recycling of LDPE/medium density polyethylene (MDPE) blend. They found that even after five successive mixings, molecular weight decreasing of PE was induced by reprocessing. The recyclability of PP composites was examined by Bahlouli et al. [24]. They studied the influence of recycling on the properties of PP-based composites (ethylene diene monomer (EPDM) PP and talc/PP) using extrusion processes. The mechanical, structural, and rheological properties of the composites were evaluated after each extrusion cycle. They found that as in the case of pure PP, the melt viscosity and mechanical properties of the composites decreases with number of processing cycle. All these changes in the composites properties were due to the changes in the structural properties of the composite during processing.

13.3.3 Chemical Recycling

In all chemical recycling processes, the solid waste is converted into smaller molecules through the formation of chemical intermediates. These intermediates are usually gases, liquids, or sometimes may be waxes or solids and are useful for the production of petrochemicals.

The decomposition of waste polymer by means of chemical substances or heat and the decomposition products are monomers or mixture of compounds [25]. In chemical recycling, monomers are produced as a result of depolymerization or other secondary valuable materials are produced by partial degradation. Energy recovery by incineration is a successful way to decrease the volume of organic materials.

Chemical recycling is also called feedstock recycling, and the method of recycling can be represented in Fig. 13.1.

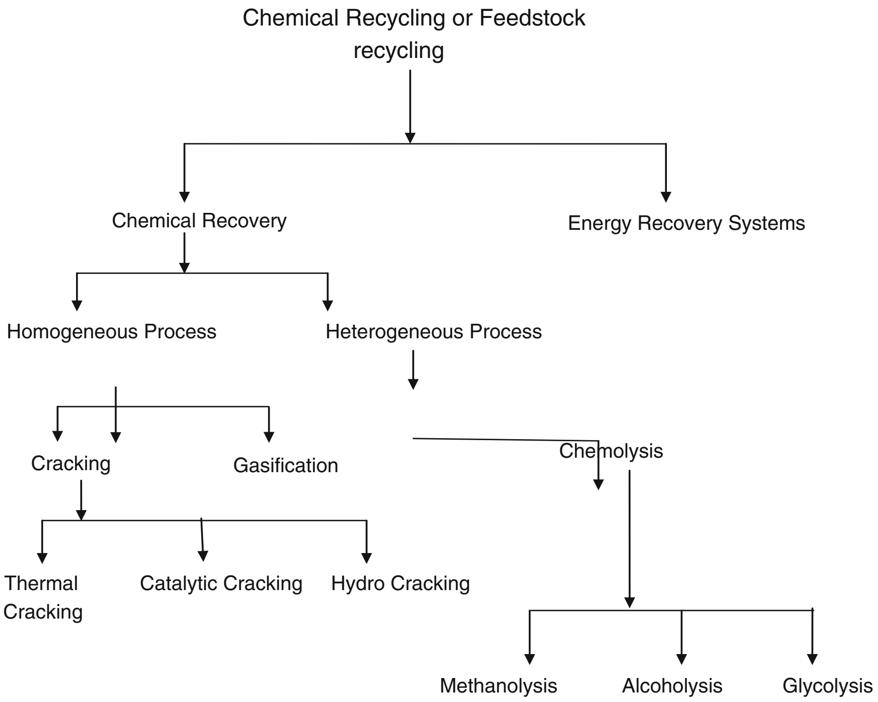


Fig. 13.1 Chemical recycling chart

13.3.3.1 Heterogeneous Process

Heterogeneous process mainly involves chemolysis/solvolysis, and it uses chemical reagents or solvents for depolymerization of the polymer into monomers. It is a secondary recycling technique; depending on the nature of polymers, a wide variety of solvents are used for the depolymerization process. Based on the nature of solvents, it is named as alcoholysis, methanolysis, glycolysis, etc.

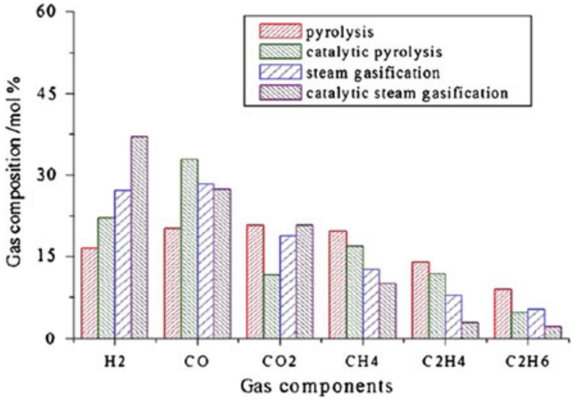
13.3.3.2 Homogeneous Process

Homogeneous process involves chemolysis or solvolysis. Here, plastics are treated with some chemicals or solvents and are depolymerized to monomers. Based on the chemicals used, it is classified as hydrolysis, methanolysis, alcoholysis, glycolysis, etc. [26].

Gasification or Partial Oxidation

Gasification is the process in which the polymer waste is subjected to direct combustion. This process superior in terms of calorific value, however, causes damage to

Fig. 13.2 Gas composition in steam gasification and pyrolysis for non-catalytic and catalytic processes [29]



the environment because of the production of toxic chemicals such as sulphur oxides, dioxins, and light hydrocarbons. Incomplete oxidation of plastics was carried out in the presence of steam or air (Oxygen), and this leads to the formation of a mixture of hydrocarbons. Yamamoto et al. described new approach of waste gasification which utilizes iron-making and steel-making technologies and smelting system, to make highly purified gases with elevated calorie value. 60–70 % efficiency in the production of hydrogen from waste polymer has been reported and is achieved through two-stage pyrolysis and incomplete oxidation process. The amount of hydrogen production can also be increased by cogasification of biomass with polymer waste; this decreases the formation of carbon monoxide. Manufacturing large volume of chemicals such as acetic acid is also possible through the oxidation of polyolefins in the presence of oxygen and nitric oxide [27].

Maoyun He et al. studied the catalytic steam gasification of PE waste, collected from municipal waste with NiO/g-Al_2O_3 as catalyst. The reaction was carried out at 700–900 °C and normal atmospheric pressure using a bed reactor. They investigated the influence of temperature on the production and composition of gas, steam decomposition, cold gas efficiency, and carbon conversion efficiency. The gas composition in steam gasification and pyrolysis for non-catalytic and catalytic processes is shown in Fig. 13.2, and the results indicated that there is a strong potential for producing syngas from waste polyethylene by a simple steam gasification process with NiO/g-Al_2O_3 as catalyst. They also studied the temperature and steam roles on the production of syngas. Results reveal that at higher temperature the higher conversion of polyethylene into syngas was take place with a significant increase of H_2 content. With temperature increasing from 700 to 900 °C, the yield of char and tar decreased while product gas yield increased. The same results observed in the presence of steam. All the studies showed that NiO/g-Al_2O_3 is an active catalyst for steam gasification of waste polyethylene; the introduction of steam can enhance the gas yield product and accelerate the conversion of polyethylene waste [29].

Cracking

There are different types of cracking used in polymer recycling. The main types are given below:

- Thermal cracking;
- Catalytic cracking; and
- Hydro cracking.

Catalytic cracking

Catalytic cracking is the cracking of heavy hydrocarbons using catalyst. The polyolefins such as PP and PE are recycled through this method. In the laboratory scale setup, these reactions are carried out in a flow reactor. There are two modes of catalytic treatment, liquid phase contact and vapor phase contact. In first case, the catalyst is in contact with molten polymers and here the catalyst reacts mainly with oligomers. In vapor phase contact, the catalyst is in contact with thermally degraded polymer [27].

In order to support cracking at lower temperatures, many types of catalytic technologies have been developed, and these reduce the energy consumption and higher conversion rates. The hydrocarbon products with higher market value are obtained by the use of specific catalyst, which has the ability to direct the reaction to the desired product [28]. Heterogeneous catalysis (solids with acid properties) has been extensively used for the cracking of heavy hydrocarbons [29]. The acid functionality of the catalyst attacks the long polymer chains, and depropagation results in high fraction of products having low molecular weight. The intermediates formed undergo rearrangement by hydrogen and carbon atoms shift. This produces isomers of high quality and can undergo cyclization. This can be achieved through intermolecular attack on the pi bond of the olefinic carbonium ion. The bifunctional catalyst consists of both acidic and metal materials. The metallic site catalyzes the hydrogenation/dehydrogenation reactions, and the isomerization is catalyzed by the acidic site. These result in the formation of branched chain hydrocarbons from long-chain hydrocarbons, cycloparaffins from straight chain paraffins, and aromatics from naphthalenes.

Various kinds of Zeolites are engaged in the catalytic cracking of hydrocarbon feedstocks, such as ZSM-5, Beta, Y, in addition to other known acid solids such as silica-alumina, alumina and clays. Various combinations of these catalysts such as SAHA/ZSM-5 and MCM-41/ZSM-5 have been also employed for the recycling of polyolefins [30].

The catalytic degradation of the polymers can be studied by a variety of catalysts. Walter Caminsky et al. studied the catalytic degradation of polypropylene using Lewis acid catalysts such as aluminum chloride and mixtures with titanium tetrachloride. These catalysts are soluble in molten polyolefin, and this helps to reduce the concentration catalyst to 0.1 or 1 % [31]. They observed that there is dramatic increase in the amount of small hydrocarbons (C_4) by the usage of these catalysts. Different conditions were used to carry out this experiment in batch reactor (PR-1) and in fluidized bed reactor (LWS-5). It is clearly revealed from the gas chromatograms (Fig. 13.3) that the products run without catalyst contain

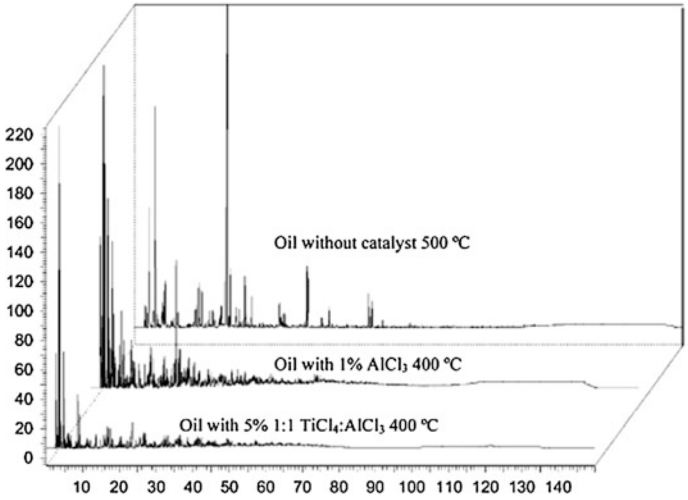


Fig. 13.3 Comparison of gas chromatograms of oil obtained with $AlCl_3$ (1) or $TiCl_4/AlCl_3$ as catalysts for the pyrolysis of polypropylene. Retention time is in minutes [31]

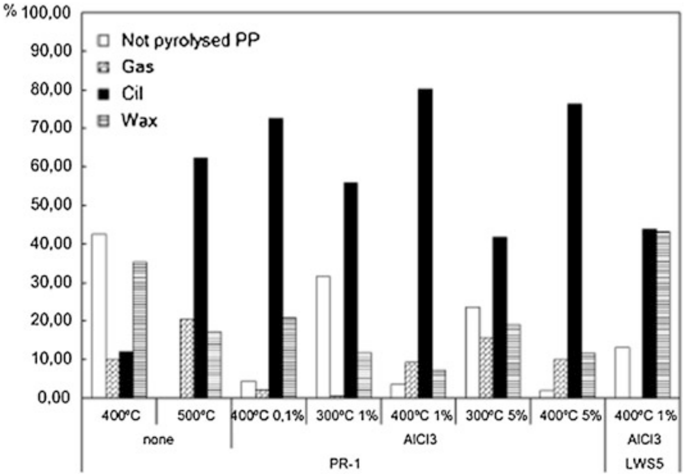


Fig. 13.4 Products' distributions (wt%) of pyrolysis of polypropylene at 300, 400, or 500 °C, $AlCl_3$ as catalyst in a batch reactor (PR-1) or in a fluidized bed process (LWS-5) [31]

long-chain hydrocarbons than those run with catalyst. It also indicates that the amount of products increases in the presence of catalyst.

The product distribution as a function of catalyst weight percentage was also studied, and it was observed that with increase in the amount of catalyst, smaller fractions were increases and also the pyrolysis temperature can be reduced to 300 °C, as shown in Fig. 13.4.

Fig. 13.5 Effect of dissolution temperature on the % recovery of polymer from model polyolefins using xylene/n-hexane and 5 % w/v sample concentration [32]

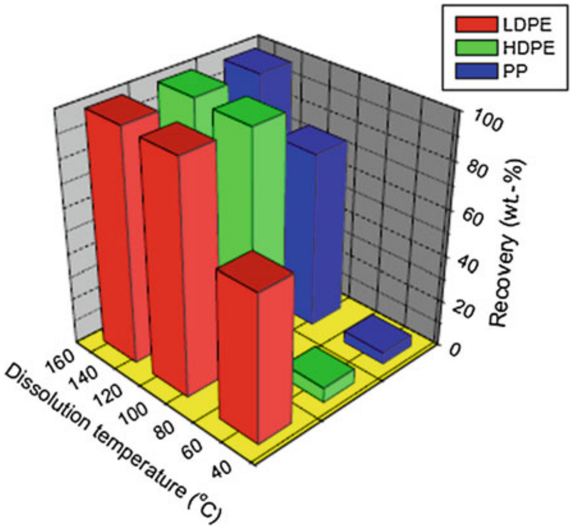
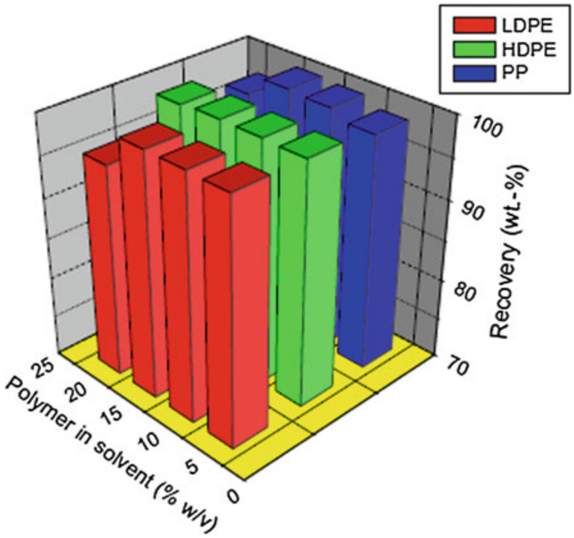


Fig. 13.6 Effect of sample concentration on the % recovery of polymer from model polyolefins using xylene/n-hexane at 140 °C



Achilias et al. [32] recycled low-density polyethylene, high-density polyethylene and polypropylene by dissolution/reprecipitation (mechanical recycling), and pyrolysis (chemical recycling) process. The quality of the recycled polymer was examined using FTIR and DSC. Figures 13.5 and 13.6 show how the dissolution temperature and initial polymer concentration affects the weight percentage recovery of HDPE, LDPE, and PP. It was observed that the polymer recovery was always high at all the experimental conditions. An increase in dissolution temperature and lower concentrations favors the polymer recovery.

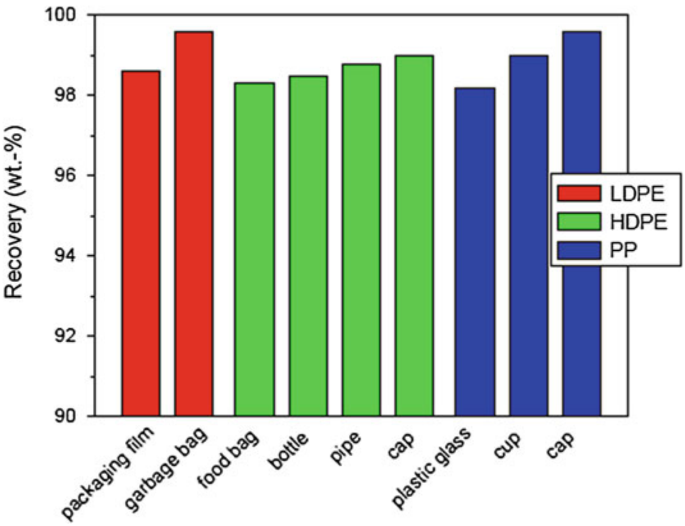


Fig. 13.7 Recovery of polyolefins from different waste plastic products by the dissolution/reprecipitation technique using xylene/n-hexane at 140 °C and 5 % w/v sample concentration [32]

Figure 13.7 shows the recovery of polyolefins (HDPE, LDPE, and PP) from several plastic waste. Very high polymer recovery was observed for all the plastic waste and proven that pure polymer can be easily recovered from plastic waste by this technique. Both solid and liquid fractions of the recovered polymer mainly consist of aliphatic hydrocarbon (a series of alkenes and alkynes) and can be recycled back into the petrochemical industry as a feedstock for the production of new plastics or refined fuels.

Rownaghi et al. [33] estimated the catalytic activity and behavior of the silica-alumina catalysts for degradation process of commercial samples of high-density polyethylene using thermogravimetric analysis. The catalyst used were silica-alumina (SiO_2:Al_2O_3 weight ratio = 10:90 and 40:60) and these mesoporous materials, in particular SiA130 and SiA180, decrease the activation energy values and it greatly influences the degradation of HDPE. The degradation of HDPE is shown in Fig. 13.8.

Shah et al. studied the role of lead sulfide on the degradation of polyethylene and it is considered that lead sulfide induces some charge on polyethylene. The unequal charge distribution of polyethylene results in the formation of carbonium ions in the polymer chain by eliminating hydrogen from the polyethylene fragments, and this leads to the fission of C–C bond and formation of lighter hydrocarbons [34]. The yield and composition of the gas, oil, and wax have been studied in terms of the temperature, time, and amount of catalyst. It was found that the catalytic pyrolysis enables 100 % efficiency and the products are liquid, wax, and gas. The char formation is very negligible in the presence of these catalysts.

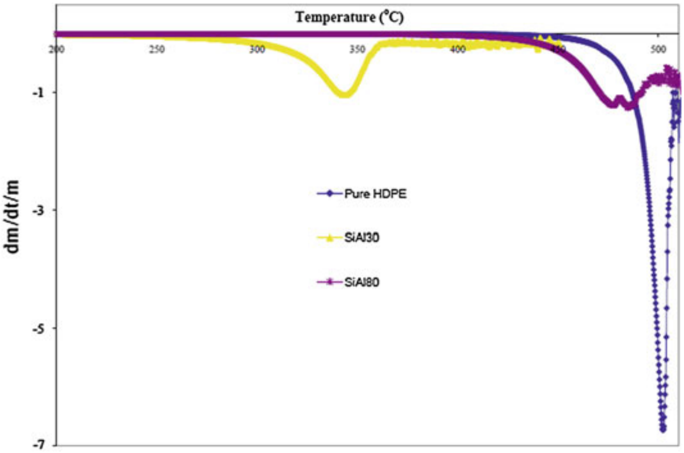


Fig. 13.8 Comparison of catalytic and non-catalytic degradation of HDPE by TGA at 5 °C/min (plastic to catalyst weight ratio, 2:1) [33]

Thermal cracking

Thermal cracking, or pyrolysis, involves the erosion of the polymeric products by heating in the absence of air or oxygen. The heating temperature range is 500–800 °C and this process leads to the formation of a carbonized char and a volatile fraction. The composition and proportion of each fraction depends on the nature of the plastic waste as well as processing conditions [35]. In thermal cracking, a portion of the species is generated from the initial degradation into secondary products because of the intramolecular and intermolecular reactions.

Hydro cracking

In hydrocracking, molecules of higher hydrocarbons (petroleum) are broken down into simpler molecules by the addition of hydrogen under high pressure and in the presence of a catalyst. In this process, high-quality gasoline is obtained from a wide range of hydrocarbons. A large number of catalysts are used in hydrocracking reactions, and these include transition metals such as Pt, Ni, Mo, Fe supported on acid solids such as amorphous silica–alumina, zeolites, alumina, and sulphated zirconia. Cracking and hydrogenation are initiated by these catalysts and results in the formation of gasoline products [36].

Venkatesh et al. studied the hydrocracking of HDPE, PP, and PS in the presence of catalysts ($Pt/ZrO_2/SO_4$ and $Ni/ZrO_2,/SO_{4)}$. They observed that sulfate-modified metal oxides having a hydrogenation metal are excellent for the hydrocracking of HDPE, PP, and PS. Hydrocracking of HDPE and PP mainly gives gasoline range branched alkenes (C_5–C_{12}), whereas PS mainly gives benzene, bicyclic compounds, and alkylated aromatics. Incorporation of non-noble metals such as Ni, which showed little activity in alkane hydrocracking at milder conditions (160 °C and 2515 kPa (cold) H_2) and high activity for polymer hydrocracking at 325 °C, indicates that activation of Ni occurs at high temperatures [37].

13.3.4 Recycling of Polyolefins via Pyrolysis

Various environmental problems are created by the wastes generated from the production, transportation, and consumptions of plastics. By considering economic, political, technological, energetic, material, and environmental dimensions, the problems created by the plastic waste can be solved [38]. Since plastic products have high calorific value utilization for their energy alone, chemical production may be an alternative option [39]. Incineration and pyrolysis are the two main processes exploring these options. In incineration, hydrocarbons are subjected to destructive process and are converted to their combustion products. During pyrolysis process, hydrocarbon may convert to other hydrocarbons, and the products may be utilized as fuel, new material, and monomer [40]. Thus Pyrolysis (or cracking) is a process where the polymeric materials are taken to chemical and thermal degradation by heating in the absence of oxygen or in an inert atmosphere such as nitrogen.

During the pyrolysis process, temperature is the most influential parameter. Depending on the feedstock being processed, pyrolysis of hydrocarbons is normally carried out at a temperature between 400 and 800 °C with or without using catalysts [41]. Dynamic (e.g., some batch reactor configurations) or isothermal (e.g., fluidized bed) heating systems can be used for the pyrolysis reactors. Among these, isothermal systems are being most frequently applied. The yields of pyrolysis process are carbonized char and volatile materials that may be separated into hydrocarbon oil/wax and non-condensable gas [42].

Depending on the range of temperatures used to destroy the plastic structure, pyrolysis processes are generally classified into low, medium, and high temperature [43]. Different pyrolysis temperature states are less than or equal to 600, 600–800 °C, and greater than 800 °C [44]. High-temperature pyrolysis processes generally enhance gaseous product and low-temperature processes enhance liquid products. An increase in the reaction temperature led to a decrease in oil production and an increase in gas production. It is due to the fact that at elevated temperatures, secondary cracking reactions convert the heavier components into gas components [45]. The products of pyrolysis can be applied as fuels and petrochemicals [44].

Usually, Polyolefin's thermal cracking at high temperatures (700 °C) produces an olefin mixture of C1–C4 gases and aromatic compounds (benzene, toluene, and xylene). Pyrolysis of polyolefins at low temperatures (400–500 °C) yields high calorific value gases, condensable hydrocarbon oils, and waxes [46].

13.3.4.1 Mechanism of Pyrolysis Process

The thermal (non-catalytic) cracking of plastics occurs by a radical mechanism. The initiating radicals are formed by the effect of heat. The instability of macromolecules under heat treatment is often due to the presence of anomalous weak links in the polymer. In these cases, low molecular weight models of the normal chain unit are much more stable than the polymer [47].

During the pyrolysis process, the following elemental reactions take places:

(a) Initiation;
(b) Formation of secondary radicals;
(c) Formation of monomers by depolymerization process;
(d) Favorable and unfavorable hydrogen transfer reactions;
(e) Intermolecular hydrogen transfer leads to formation of paraffins and dienes;
(f) Isomerization via vinyl groups; and
(g) Termination by disproportionation or recombination of radicals.

The mechanism of thermal degradation of plastics proceeds through a radical chain reaction pathway with hydrogen transfer steps. In secondary reactions, branched products were only formed as a result of the interaction between two radicals without any rearrangement reactions [48]. As a consequence, thermal cracking of polyolefins leads toward a broad distribution of hydrocarbons up to waxy products. More than 500 °C temperatures are needed to receive more oily products. In contrast, catalytic cracking takes place at lower temperatures and leads to the formation of smaller branched hydrocarbons. This catalytic cracking can potentially lower the costs and increase the yields of valuable products.

Large-scale production of oils and gases by catalytic cracking of polyolefins is a subject of growing interest in the last years. Because of this, pyrolysis (catalytic cracking) process requires less energy and produces more valuable products. By the use of catalyst, we can modify the structure of hydrocarbons produced. Compared to non-catalytic process, catalytic cracking process consumes less energy and results in the formation of more branch-chain hydrocarbons. Numerous studies have been reported in which a variety of catalysts such as zeolites, silica-alumina, mesoporous MCM-41, US-Y, and HZSM-5 solid acids and reaction conditions have been investigated. It was found that the HZSM-5 and FCC catalysts provided the best possibility to yield hydrocarbons in the boiling range of gasoline.

Catalytic cracking generally proceeds through carbenium ions, as the intermediates. When the catalyst acts as Lewis acid, these are produced by the abstraction of hydride ion from the polymer. If the catalyst acts as Bronsted acid, these carbenium ions are produced by the addition of proton to the macromolecule in the initial reaction step. Fragments formed in the first cracking reactions cracked further into lower molecular weight hydrocarbons on the active sites of the catalyst [48]. Unstable primary fragments are cracked in further leading to the idea of degradation processes which occurring within the sample.

Earlier studies show that thermal degradation of PE proceeds through free radical formation and hydrogen abstraction steps. But the thermal degradation of PS is a radical chain process and the mechanism involves initiation, transfer, and termination steps. The maximum rate of degradation can influence the production of different types of radicals [49]. The rate of radicals' formation increases with their stability; therefore, the conversion rate is higher if the radicals, which are formed during thermal volatilization, are more stable.

13.3.4.2 Factors Influencing the Pyrolysis Products

The products obtained from thermal cracking of plastics depend on the type of plastics, feeding arrangement, residence time, temperatures employed, reactor type, and condensation arrangement [42]. Reaction temperature and residence time have strong influence on the yield of pyrolysis products and the distribution of their components for plastic samples. Jude et al. conducted studies on thermal cracking of LDPE in a batch reactor resulted in the production of a broad range of hydrocarbon compounds where the yield of aromatics and aliphatics (olefins and paraffins) deeply depended on the pyrolysis temperature and residence time.

In their work, decomposition of LDPE starts at 400 °C and the optimum oil yield from LDPE was at 425 °C. The resulting oil was mainly rich in both short-chain and long-chain aliphatic hydrocarbons. However, the oils produced at 450 and 500 °C contained high ratios of compounds comparable to those found in diesel and gasoline fuels, along with higher amounts of hydrocarbon gases and char. Even at zero residence time at 450 °C, LDPE plastic sample undergoes total degradation and yields aliphatic-rich oil. Composition of oils can be altered by providing longer pyrolysis time, where aromatic and other light fractions were produced in higher concentrations. In general, LDPE pyrolysis oil has comparable high calorific value of up to 42.7 MJ/kg. In addition, due to secondary reactions, additional cracking reactions, isomerization, and aromatization, high amount of hydrocarbon gases and char was also produced [49]. The detailed composition of the hydrocarbon gas components in relation to pyrolysis temperatures and residence time is exhibited as in Figs. 13.9 and 13.10.

In their study, degradation of polystyrene starts at 350 °C, and on mixing with LDPE, liquid oil is formed even at 400 °C. Initially, degradation of PS produces viscous oil and as the residence time and temperature increased, the obvious changes occur in the formation of less viscous oil and char. The formation of up to 30 wt% of char at 500 °C was an indication of the condensation of the ring structure of the aromatic compounds at higher temperatures. They concluded that their closed batch system can be used to effectively degrade LDPE and polystyrene to produce high-grade fuel-like oils for energy production, chemical feedstock for the petroleum refinery, new industrial raw materials such as ethyl benzene and toluene in paints manufacture. Thus, this pressurized plastic pyrolysis process shows that we can obtain high-quality fuel fractions by varying some parameters such as reaction temperatures and residence times or by blending products from different reaction conditions [49].

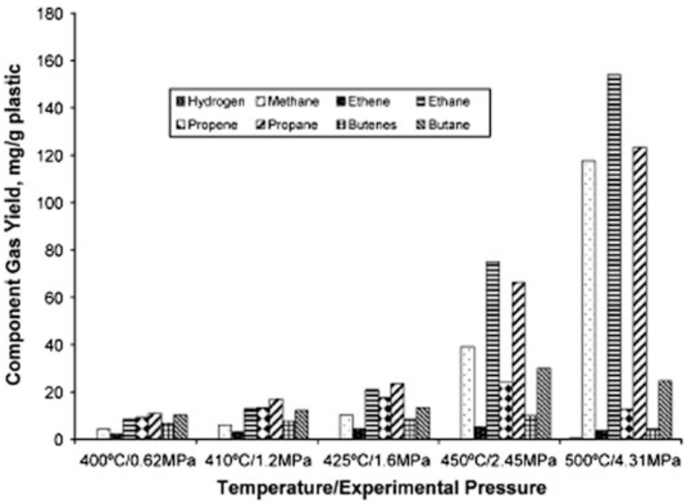


Fig. 13.9 Composition of LDPE pyrolysis gaseous product in relation to temperature [49]

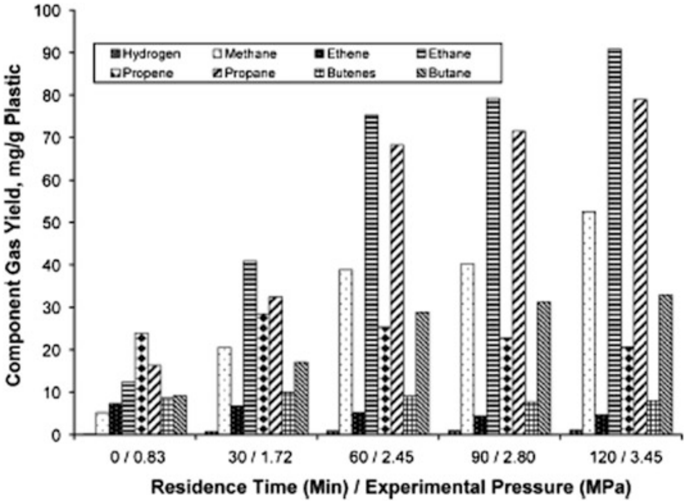


Fig. 13.10 Composition of LDPE pyrolysis gaseous product in relation to residence time [49]

Arabiourrutia et al. studied the thermal pyrolysis of three different polyolefin plastics (HDPE, LDPE and PP) in a conical spouted bed reactor. Compared to fluidized bed reactor, this technology is highly selective to waxes. This fluidized bed reactor requires low residence times and high heating rates that reduce secondary reactions and increase the yield of primary pyrolysis products (waxes). This is an efficient and great versatile technology for the valorization of polyolefinic plastic waste by pyrolysis. Solids of sticky nature that are difficult to process in fluidized bed reactors can be processed in conical spouted bed reactor. To obtain waxes, pyrolysis in spouted bed is an especially suitable technology. The pyrolysis products obtained by this technology are useful in refineries as an alternative feed in the cracking processes.

The ratio between the light and the heavy fractions of waxes significantly increases with increase in temperature. If the pyrolysis is carried out at low temperature, the resulting waxes have high molecular weight because more severe cracking is taking place only at high temperature. Furthermore, pyrolysis waxes are formed mainly by paraffin hydrocarbons, although an increasing olefinic nature has been observed at the highest temperature. At higher temperatures, the heating value of all the waxes studied is higher, and the waxes obtained by them at 600 °C have a value of 44–45 MJ/kg, which is of the same order as standard fuels. Polyolefin waxes do not have a specific melting point but they melt in a temperature range and they concluded that the lowest range corresponds in all cases to those obtained at 500 °C and, especially, to those from PP [50].

Su et al. conducted pyrolysis of fractions of waste polypropylene and polyethylene in a pyrolysis plant under different conditions. In this study, they investigate the influence of the reaction temperature (650–750 °C), the feed rate, and the kind of fluidizing medium on the product spectrum [45]. Pyrolysis of the PP fraction produced oils up to 43 wt% of the product and the amount of BTX aromatics, in the oils reached 53 wt% for the PP fraction. PE fraction produces above 60 wt% of the product and 32 wt% BTX aromatics. It was shown that the pyrolysis of PE fraction produces high amount of liquid products compared to the PP fraction. Also for both the PP and the PE fractions, if the reaction is carried out at high temperature, they obtained oil contains high amount of aromatics. Due to the intramolecular radical transfer, degradation of PP is easier than PE and it leads to higher amount of gas production. Figure 13.11 shows the influence of reaction temperature on the product distribution.

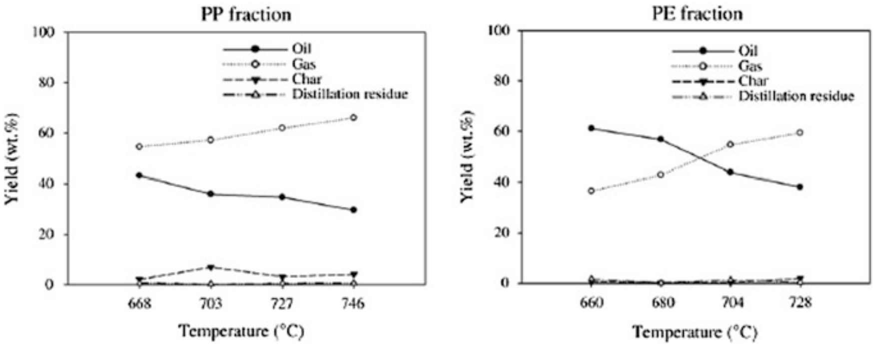


Fig. 13.11 Product distribution with respect to the reaction temperature (the *left side* of the figure shows the product distribution according to the reaction temperature with the PP fraction, and the *right* one is that with the PE fraction) [46]

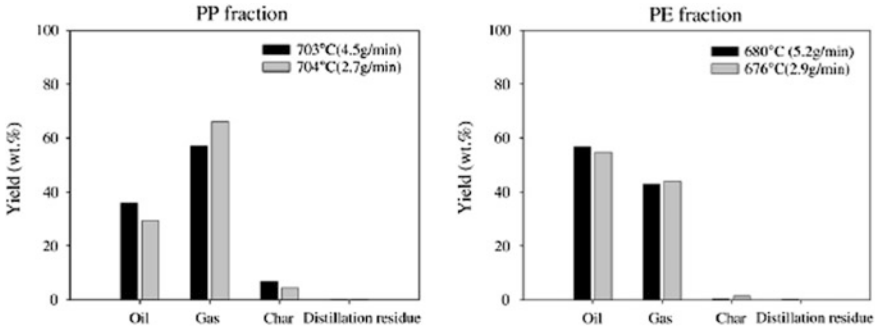


Fig. 13.12 Effect of the feed rate (the *left side* of the figure shows the product distribution according to the feed rate with the PP fraction, and the *right* one is that with the PE fraction) [46]

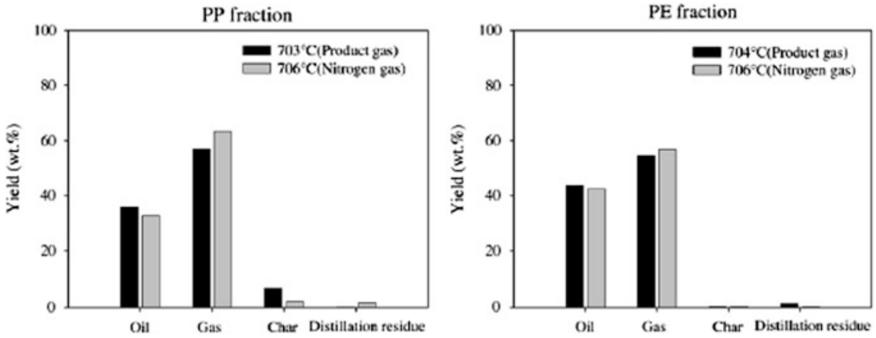


Fig. 13.13 Effect of the fluidizing medium used (the *left side* of the figure shows the product distribution according to the kind of fluidizing medium with the PP fraction, and the *right* one is that with the PE fraction) [46]

Figures 13.13 and 13.12 show the influence of the feed rate on the oil and gas yields for both the PP and the PE fractions.

It is clear that both PP and PE shows the same trend to give a higher oil yield at a higher feed rate. Because higher amount of pyrolysis vapors is produced at higher feed rate, it increases the yield of oils. Also it reduces the residence time of the pyrolysis vapors in the reactor and consequently prevented secondary cracking reactions, such as thermal cracking.

Figure 13.13 shows the effect of fluidizing medium on the product distribution. In both the cases, when the product gas was taken as a fluidizing medium the yield of oil increases. If nitrogen gas is used, it will dilute the vapors arise from pyrolysis process and prevent this vapors from certain chemical reactions that lead to the production of oil components, such as Diels–Alder reaction that takes place with dienes and alkenes. In contrast to nitrogen, if the product gas was applied, some of its components reacted with the pyrolysis vapors in the reactor to form oil components.

They concluded that pyrolysis of PP and PE fractions yields higher amount of oils by higher feed rate and selecting the gas product as the fluidizing medium.

13.3.4.3 Catalytic Pyrolysis

In many cases, catalytic cracking of polyolefins needs high amounts of catalysts; in certain cases, up to 20 wt% in relation to the polymer feedstock have to be used. It is a major problem associated with catalytic cracking process. During catalytic pyrolysis, the highly viscous polymer melt has low contact with the surface of solid catalyst. Branched hydrocarbons or aromatics are formed mainly by the influence of secondary reactions.

Kaminsky et al. investigate the effect of catalyst on the pyrolysis of polyethylene using Lewis acids and mixtures of Ziegler–Natta catalyst such as $TiCl_4$, $AlCl_3$. These catalysts are soluble in the viscous polyolefin melt and it reduces the concentration of catalyst to 0.1 or 1 %. Also the pyrolysis process temperature can be dramatically reduced by the usage of lewis acids such as $AlCl_3$ or a combination of $TiCl_4$:$AlCl_3$ as catalysts.

They were able to pyrolyze polypropylene far below 500 °C (temperature of non-catalytic experiments). Also with high amount of catalyst, polypropylene can be pyrolyze at 300 °C. Amount of light oil fraction (<C13) and gas fraction can be increased by using high amount of catalysts. But higher amounts of catalyst may cause secondary reactions and came along with decreased selectivity. By using suitable catalysts, we can decrease the processing temperature, and energy consumption of the pyrolysis. Thus, the costs of process can be reduced using the mentioned catalysts for the process [51]. Thus, by using the mentioned catalysts, it is possible to do the pyrolysis process at low temperature with low energy consumption and hence costs can also be reduced.

13.3.4.4 Microwave-Induced Pyrolysis

Tech-En Ltd.9 (Hainault, UK) developed a new process named microwave-induced pyrolysis. In this process, a microwave absorbent materials such as carbon is allowed to mix with plastics which are highly transparent to microwaves. Initially, this carbon is exposed to a microwave field, and within a few minutes, it can attain a temperature up to 1000 °C. During heating, the energy absorbed from the microwaves is transferred to the plastics that are mixed with the carbon by conduction process. This provides a very efficient energy transfer and it produces a highly reducing chemical environment. This highly reducing chemical environment has a tendency to avoid the formation of undesired hydrocarbon products that containing oxygen. During microwave-induced pyrolysis, heat distribution is higher and a better control over the heating process is possible. It is the main advantage of microwave heating than conventional heating process. Microwave radiation provides high temperatures and thus high rates of heating of plastics can be obtained

Table 13.1 Product yield (wt%) from the pyrolysis of PE reported in the literature together with the results of the present study (N.R.) (not reported) [52]

	500 °C			600 °C		
	Gas	Oil/wax	Solid	Gas	Oil/wax	Solid
Batch fluidized bed	≈7–16	N.R.	N.R.	~18–60	N.R.	N.R.
Pyroprobe 1000	2.42	97.5	N.R.	14.6	85.3	N.R.
Fixed bed	≈8–12	≈83–90	≈2–5	≈20–35	≈55–74	≈6–10
Fluidized bed	10.8	89.2	0	24.2	75.8	0
This work; microwave-induced pyrolysis	19	81	0	20.9	79.1	0

during pyrolysis. Sources of microwave radiations are highly efficient in converting electrical energy into heat (80–85 %) and also to transfer this heat to the load. Modern equipment has very high reliability and is competitive with other heating methods.

Carlos studied the performance of a novel microwave-induced pyrolysis process on the degradation of high-density polyethylene and aluminum/polymer laminates [52]. Their results showed that the new process has the same general features as other, more traditional, pyrolytic processes but with the advantage that it is able to deal with problematic wastes such as laminates. Previous researchers show that the yield of gases, liquid/waxes, and solid residue depends significantly on the process characteristics and variables, but there is a general consensus that the higher the process temperature, the higher the yield of gases.

Table 13.1 shows the results of other researchers for the degradation of PE at 500 and 600 °C along with the results obtained using the microwave-induced pyrolysis apparatus. These results show that the increase from 500 to 600 °C caused little difference in the yields of the products. They concluded that these results are contrary to most previous findings and can be explained by the configuration and the characteristics of the degradation process.

13.4 Recycling-Oriented Characterization of Polyolefin Waste

It is essential to characterize polyolefin waste before entering into the recycling process which will improve the quality of the product, even though there is no specific standard for it. To recycle polyolefin wastes, their composition has to be very well defining, taking into account their possible degradation, during initial or accidental heating treatments and UV exposure. It is well known that the properties of a polymeric material are strongly dependent on their structure, and these properties will alter if there is oxidation of the polymer occurs. Fourier transform infrared spectroscopy (FTIR) as a suitable analytical method for identifying composition of a sample containing multiple components and for monitoring the degradation of the polyolefin can be used [53]. The density distribution of the polymer types in packaging waste is the most critical parameter for polyolefin recycling by using density separation. The main purpose of defining the density distribution was to establish the correct cut density. Since the density of polyolefin is in general lower than water, the density distribution of samples is determined using a series of water–ethanol mixtures with various densities usually from 880 to 1000 kg/m^3. Hu et al. [54] have measured the distribution of wall thickness of waste plastic prior to recycling. They found that the blow molded ones had thinner walls compared to those which were injected.

Rheological characterization on thermoplastic melts measures material flow properties and provides vital information about polymer processing. Blow molding materials are expected to be more viscous than would normally be employed for the injection molding process [55]. It is also possible to separate the polymer by identifying their MFI values.

13.5 Applications of Recycled Polyolefin

The applications of recycled plastics into development of new value-added products have a lot of attention. The possibility of using plastic waste in the development of composites is very attractive, especially with respect to the large quantity of plastic waste generated daily.

Compared to virgin material, the mechanical properties are worse, mainly due to polymer contamination. Furthermore, the fluctuations in properties of post-industrial and postconsumer waste are similar. In general, the fluctuations within waste materials are high compared to virgin plastics, with post-industrial plastic waste having smaller fluctuations than postconsumer plastic waste.

There is considerable scope for the reuse of plastics used for the transport of goods, and for potential reuse or remanufacture from some plastic components in high-value consumer goods such as vehicles and electronic equipment. This is evident in an industrial scale with reuse of containers and pallets in transport.

Properties of some plastic waste are similar to those made from virgin materials, with tests indicating only a slight change in mechanical properties of recycled polyethylene [56]. Products manufactured from plastic waste are increasing and include fiber-reinforced plastic composites (FRPCs) [57]. FRPCs made with waste wood fiber/flour have also gained popularity due to the low cost of recycled wood to the manufacturers.

Ashori et al. [58] used recycled PP and HDPE as matrices for lignocellulosic fiber composite using MAPP as coupling agent. This composite has been used for board preparation. Ardanuy et al. [59] prepared recycled polypropylene-based green foams reinforced with untreated and chemically treated cellulose fibers obtained from agricultural residue. Their results showed that these foams may find potential applications as lightweight composites in different fields such as construction or automotive.

Recently, nanotechnology has been attempted to develop new application for recycled polyolefins. A variety of nanofillers such as graphene, CNTs, $CaCO_3$, SiO_2, mica, and nanoclay have been incorporated for recycling all waste polymers. The advantage of this technique enables the application of much low content of nanofillers for recycling polymers effectively. Moreover, the use of compatibilizers for recycling of polymers mainly blends and composites are more valuable. However, with the objective to a successful and economic recycling in which the recycled polymer has more acceptable characteristics, more investigations must be made on the recycling process to enhance the competitiveness in these procedures. The first step may be the improvement of interaction and interfacial adhesion in prepared nanocomposites. Compatibilizing, functionalizing, and surface modification procedures can be developed in the future works. Further, the addition of effective nanofillers includes available nanofillers or a combination of nanofillers is suggested which can provide further progress and new opportunities in these materials. It is pointed out that the addition of nanofillers to the recycled polymers can result new products with unexpected blend of enhanced properties such as low-weight, low cost materials, and ease of processing.

13.6 Conclusions

The recycling of polyolefin has great interest in the modern world. Recycling can accordingly decrease energy and material usage per unit of output and yield superior eco-efficiency. One of the key benefits of recycling plastics is to reduce the requirement for plastic production. LDPE, HDPE, and PP are the widely used polyolefin, as they found applications in our day-to-day life. This chapter discusses various recycling techniques used for polyolefin in detail; in addition to this, it also deals with various techniques for separating the polyolefin waste and the applications of recycled polyolefin. Depending on the nature of the polymer and product, suitable method for recycling can be selected. Technological advances in recycling can improve the economics in two main ways. One is by decreasing the cost of recycling by improving the productivity or efficiency and by closing the gap between the values of recycled resin and virgin resin.

In summary, recycling is one approach for postconsumed waste management of plastic goods. The importance of recycling is increasing because of economical and environmental benefits. These movements have to be continuing, but several significant challenges still exist from both technological factors and from economic or social behavior concerns relating to the collection of polymer wastes, and replacement for virgin material. The recycling of plastic waste is an effective way to improve the environmental performance of the polymer industry coupled with efforts to increase the use and specification of recycled grades as substitution of virgin plastic. Pyrolysis seems to be the most competent technique ensuing in oil and gaseous products that have great potential to use as a feedstock for the production of new polymer. Thus, it can be recycled back into the petrochemical industry. Chemical recycling technology assures the general principle of material recovery; however, it is costlier than mechanical recycling. The main disadvantage is that it is less energetically favorable as the polymer has to be depolymerized and then repolymerized.

References

1. F. Cavalieri, F. Padella, Development of composite materials by mechanochemical treatment of post-consumer plastic waste. Waste Manag. **22**(8), 913–916 (2002)
2. S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Manag. **29**(10), 2625–2643 (2009)
3. R. Dewil, K. Everaert, J. Baeyens,. The European plastic waste issue: trends and toppers in its sustainable re-use. In: *Proceedings of the 17th International Congress of Chemical and Process Engineering* (2006), pp. 27–31
4. K. Hamad, M. Kaseem, F. Deri, Recycling of waste from polymer materials: An overview of the recent works. Polym. Degrad. Stab. **98**(12), 2801–2812 (2013)
5. USEPA, Municipal solid waste in the United States: 2000 facts and figures. Executive summary. Office of solid waste management and emergency response (5305 W), EPA530-S-02-001 (2002)
6. USEPA, Municipal solid waste in the United States: 2007 facts and figures. Executive summary. Office of solid waste management and emergency response (5306P), EPA530-R-08-010, Nov, 2008. Available at: www.epa.gov
7. D.N. Beede, D.E. Bloom, Economics of the generation and management of MSW. NBER working papers 5116. National Bureau of Economic Research, Inc. (1995)
8. M.L. Mastellone, Thermal treatments of plastic wastes by means of fluidized bed reactors. Ph.D. Thesis, Department of Chemical Engineering, Second University of Naples, Italy, 1999
9. ASTMD-5033-90, Standard guide for development of ASTM standards relating to recycling and use of recycled plastics (2000)
10. N. Horvat, F.T.T. Ng, Tertiary polymer recycling: study of polyethylene thermolysis as a first step to synthetic diesel fuel. Fuel **78**(4), 459–470 (1999)
11. J. Oehlmann et al., A critical analysis of the biological impacts of plasticizers on wildlife. Philos. Trans. Roy. Soc. B Biol. Sci. **364**(1526), 2047–2062 (2009)
12. E.L. Teuten et al., Transport and release of chemicals from plastics to the environment and to wildlife. Philos. Trans. Roy. Soc. B Biol. Sci. **364**(1526), 2027–2045 (2009)
13. S. Serranti, L. Valentina et al., An innovative recycling process to obtain pure polyethylene and polypropylene from household waste. Waste Manag. **35**, 12–20 (2015)
14. G. Dodbiba et al., Sorting techniques for plastics recycling. Chin. J. Process Eng. (2006)
15. D. Froelich et al., State of the art of plastic sorting and recycling: Feedback to vehicle design. Min. Eng. **20**(9), 902–912 (2007)
16. G. Dodbiba, T. Fujita, Progress in separating plastic materials for recycling. Phys. Sep. Sci. Eng. **13**(3-4), 165–182 (2004)
17. S. Serranti, A. Gargiulo, G. Bonifazi, Classification of polyolefins from building and construction waste using NIR hyperspectral imaging system. Resour. Conserv. Recycl. **61**, 52–58 (2012)
18. G. Wu, J. Li, Z. Xu, Triboelectrostatic separation for granular plastic waste recycling: a review. Waste Manag. **33**(3), 585–597 (2013)

19. S. Karlsson, Recycled polyolefins. Material properties and means for quality determination. In: *Long Term Properties of Polyolefins* (Springer, Berlin, 2004), pp. 201–230
20. H. Shent, R.J. Pugh, E. Forssberg, A review of plastics waste recycling and the flotation of plastics. Resour. Conserv. Recycl. **25**(2), 85–109 (1999)
21. E.J. Bakker, P.C. Rem, N. Fraunholcz, Upgrading mixed polyolefin waste with magnetic density separation. Waste Manag. **29**(5), 1712–1717 (2009)
22. H. Jin et al., The effect of extensive mechanical recycling on the properties of low density polyethylene. Polym. Degrad. Stab. **97**(11), 2262–2272 (2012)
23. C.N. Kartalis, C.D. Papaspyrides, R. Pfaendner, Recycling of post-used PE packaging film using the restabilization technique. Polym. Degrad. Stab. **70**(2), 189–197 (2000)
24. A. Bourmaud, C. Baley, Rigidity analysis of polypropylene/vegetal fibre composites after recycling. Polym. Degrad. Stab. **94**(3), 297–305 (2009)
25. N. Bahlouli et al., Recycling effects on the rheological and thermomechanical properties of polypropylene-based composites. Mater. Des. **33**, 451–458 (2012)
26. D.S. Achilias et al., Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). J. Hazard. Mater. **149**(3), 536–542 (2007)
27. S. Kumar, A.K. Panda, R.K. Singh, A review on tertiary recycling of high-density polyethylene to fuel. Resour. Conserv. Recycl. **55**(11), 893–910 (2011)
28. A.A. Garforth et al., Feedstock recycling of polymer wastes. Curr. Opin. Solid State Mater. Sci. **8**(6), 419–425 (2004)
29. M. He et al., Syngas production from catalytic gasification of waste polyethylene: influence of temperature on gas yield and composition. Int. J. Hydrogen Energy **34**(3), 1342–1348 (2009)
30. J. Aguado, D.P. Serrano, Feedstock Recycling of Plastic Wastes, vol. 1. Royal society of chemistry (1999)
31. W. Kaminsky, I.-J.N. Zorriqueta, Catalytical and thermal pyrolysis of polyolefins. J. Anal. Appl. Pyroly. **79**(1), 368–374 (2007)
32. D.S. Achilias et al., Recycling techniques of polyolefins from plastic wastes. Global NEST J. **10**(1), 114–122 (2008)
33. A.A. Rownaghi, L. Tang, C. Li, Catalytic degradation of high density polyethylene using thermal gravimetric analysis
34. J. Shah, M.R. Jan, Z. Hussain, Catalytic pyrolysis of low-density polyethylene with lead sulfide into fuel oil. Poly. Degrad. Stab. **87**(2), 329–333 (2005)
35. J. Aguado, D.P. Serrano, Feedstock Recycling of Plastic Wastes, vol. 1. Royal society of chemistry (1999)
36. A.G. Buekens, H. Huang, Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. Resour. Conserv. Recycl. **23**(3), 163–181 (1998)
37. K.R. Venkatesh et al., Hydrocracking of polyolefins to liquid fuels over strong solid acid catalysts. Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. **40**, 788–788 (1995)
38. H.-J. Radusch, Future perspectives and strategies of polymer recycling. In: *Frontiers in the Science and Technology of Polymer Recycling* (Springer, Netherlands, 1998), pp. 451–467
39. A.L. Bisio, N.C. Merrieam, Technologies for polymer recovery/recycling and potential for energy savings. In: *How to Manage Plastics Waste: Technology and Market Opportunities* (1994), pp. 15–31
40. S.G. Howell, A ten year review of plastics recycling. J. Hazard. Mater. **29**(2), 143–164 (1992)
41. E. Butler, G. Devlin, K. McDonnell, Waste polyolefins to liquid fuels via pyrolysis: review of commercial state-of-the-art and recent laboratory research. Waste Biomass Valorization **2**(3), 227–255 (2011)
42. J. Scheirs, K. Walter (eds.), *Feedstock Recycling and Pyrolysis of Waste Plastics* (Wiley, 2006)
43. WRAP, The Chinese markets for recovered paper and plastics. In: *Waste and Resources Action Program* (Oxan, 2009)
44. A. Buekens, Introduction to feedstock recycling of plastics. In: *Feedstock Recycling and Pyrolysis of Waste Plastics* (2006), pp. 1–41

45. N. Kiran, E. Ekinci, C.E. Snape, Recyling of plastic wastes via pyrolysis. Resour. Conserv. Recycl. **29**(4), 273–283 (2000)
46. S.-H. Jung et al., Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. Fuel Process. Technol. **91**(3), 277–284 (2010)
47. S. Kumar, A.K. Panda, R.K. Singh, A review on tertiary recycling of high-density polyethylene to fuel. Resour. Conserv. Recycl. **55**(11), 893–910 (2011)
48. R. Bagri, P.T. Williams, Catalytic pyrolysis of polyethylene. J. Anal. Appl. Pyrol. **63**(1), 29–41 (2002)
49. J.A. Onwudili, N. Insura, P.T. Williams, Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. J. Anal. Appl. Pyrol. **86**(2), 293–303 (2009)
50. M. Arabiourrutia et al., Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. J. Anal. Appl. Pyrol. **94**, 230–237 (2012)
51. W. Kaminsky, I.-J.N. Zorriqueta, Catalytical and thermal pyrolysis of polyolefins. J. Anal. Appl. Pyrol. **79**(1), 368–374 (2007)
52. C. Ludlow-Palafox, H.A. Chase, Microwave-induced pyrolysis of plastic wastes. Ind. Eng. Chem. Res. **40**(22), 4749–4756 (2001)
53. P. Costa, et al., Study of the pyrolysis kinetics of a mixture of polyethylene, polypropylene, and polystyrene. Energy Fuels **24**(12), 6239–6247 (2010)
54. B. Hu et al., Recycling-oriented characterization of polyolefin packaging waste. Waste Manage. **33**(3), 574–584 (2013)
55. V. Goodship (ed.), ARBURG Practical Guide to Injection Moulding (iSmithers Rapra Publishing, 2004)
56. K. Jayaraman, D. Bhattacharyya, Mechanical performance of woodfibre–waste plastic composite materials. Resour. Conserv. Recycl. **41**(4), 307–319 (2004)
57. D.P. Kamdem et al., Properties of wood plastic composites made of recycled HDPE and wood flour from CCA-treated wood removed from service. Compos. Part A Appl. Sci. Manuf. **35**(3), 347–355 (2004)
58. A. Ashori, A. Nourbakhsh, Characteristics of wood–fiber plastic composites made of recycled materials. Waste Manag. **29**(4), 1291–1295 (2009)
59. M. Ardanuy, M. Antunes, J.I. Velasco, Vegetable fibres from agricultural residues as thermo-mechanical reinforcement in recycled polypropylene-based green foams. Waste Manage. **32**(2), 256–263 (2012)

Chapter 14
Oxo-biodegradable Plastics: Who They Are and to What They Serve—Present Status and Future Perspectives

Emo Chiellini and Andrea Corti

The worldwide annual consumption of polymeric materials and relevant plastic items is nowadays well above 300 million Tons, of which less than 2 million Tons is represented by polymeric materials from renewable resources. These last materials, when converted to relevant plastic manufactured goods, are identified under the ambiguous chimeric "bioplastics" terminology as evidenced in official EU documents [1, 2].

The attribute "chimeric" that we did use in identifying the "bioplastics" is due to the fact that all plastic items are "man-made" whatsoever their ultimate service life as either commodities or engineering technoplastics, or thermosetting.

Beyond the suggestive ambiguity of the terminology, it is worthwhile highlighting that the term "bioplastics" is not even comprised in the EU Technical Report relevant to the nomenclature concerning degradable and biodegradable polymeric materials and relevant plastic items [3].

The data of plastic production mentioned in the first paragraph have been detected from the histograms reported in Fig. 14.1 where (a) section is referred to the trend of the worldwide production of polymeric materials and relevant plastic items recorded since the half of the past century [4] whereas in (b) section it is reported the growing trend of the production of polymeric materials from renewable resources convertible to the relevant "bio-based" plastic items since year 2008 [5].

It is to remark that about 40 % of the worldwide production of polymeric materials is converted to relevant plastic manufactured goods intended for short service life, which under the attribute of "commodities" are meant to satisfy the needs of packaging for applications in the food and non-food segments, including also the production of single-use items (disposables) as both flexible and semiflexible, and rigid items.

E. Chiellini (✉) · A. Corti
Department of Chemistry and Industrial Chemistry, Research Unit of the Interuniversity National Consortium of Materials Science and Technology, University of Pisa, Pisa, Italy
e-mail: echiellini@instm.it; emo.chiellini@unipi.it

A. Corti
e-mail: andrea.corti@unipi.it

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_14

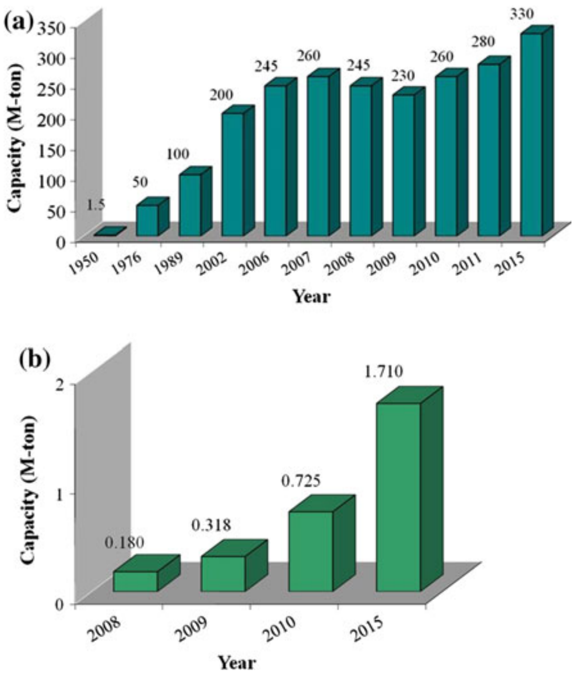


Fig. 14.1 **a** Global plastic production in 1950–2015 time frame. **b** Global production capacity of bio-based polymers in 2008–2015 time frame

Since the middle of the past century, after the various ages characterized by the use of inorganic raw materials (stone, iron, silver, and gold), we are nowadays right in the middle of the plastic age, that is based on the utilization of organic matter as raw materials susceptible to be used for the production of thermoplastic and thermosetting plastic items.

It is expected that the people have to live together for several years to come with plastic manufactures of broad use as they are nearly unsubstitutable, and permeate, with growing impact, all the types of anthropic activities which are expected to expand as a consequence of the worldwide population increase (Fig. 14.2).

This aspect, as easily understandable, implies an effective increase in the production of feed and food and hence of commodities, with all the associated risks of negative impact that may derive from their incautious release in the various environmental compartments (Fig. 14.3).

One cannot, however, ignore a serious problem relevant to the production of short-service-life plastics, mainly identifiable as commodities due to their progressive accumulation in the various environmental compartments, as not only for their incautious abandoning in the environment, but also as for the lack of an efficient capillary-organized collection of industrial and domestic waste. It cannot be also forgotten that the indicated problem is of global significance. In fact, a short-service-life plastic commodity item incautiously abandoned in a South African coastal area through free floating into marine compartments can end up on beaches of north European countries or North America [6, 7].

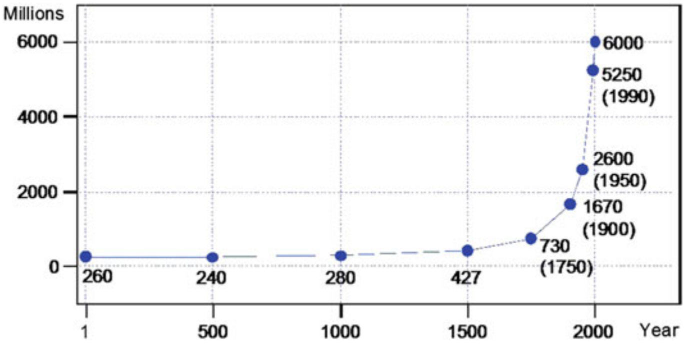


Fig. 14.2 Growth of world population

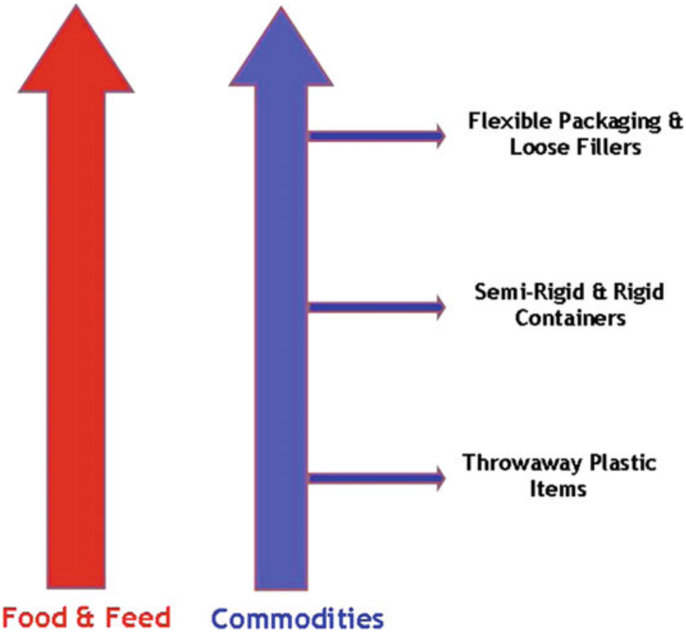


Fig. 14.3 Growing of needs versus growing of population

The plastic waste abandoned in the environment is holding a transnational citizenship, and hence, it is not easy to manage it in order to mitigate its potential deleterious effects on the environment.

The environmental accumulation of plastic waste in the last decades is simply due to the fact that the plastic commodities, as obtainable from the unsubstitutable polymeric materials based on the fossil fuel feedstock. These are consisting of full-carbon backbone macromolecules, which are characterized by degradation

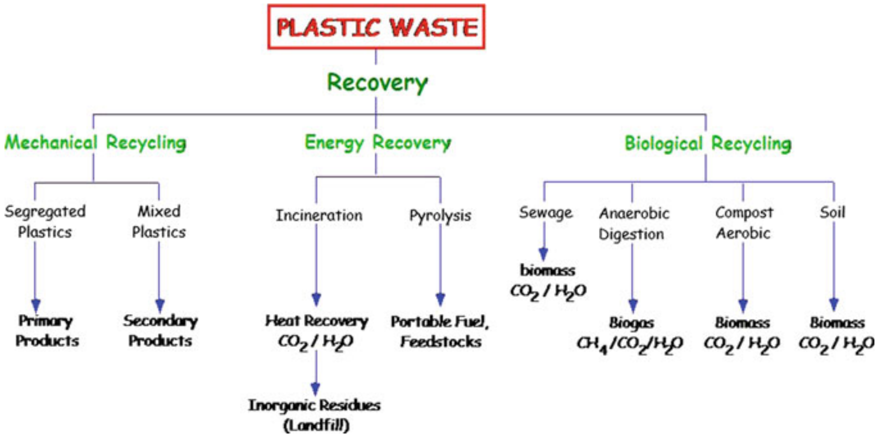


Fig. 14.4 Plastic waste management options

times and hence possibly of biodegradation in different environmental compartments, extremely long of the order of tens of decades if not of centuries [8].

Therefore, timely decisions are to be taken as aimed at promoting and approving political directives and supporting research activities focused on facing and solving the above-indicated issues by suggesting concretely viable solutions compatible with the socioeconomic development embracing effectively the worldwide global scenario of a sound plastic waste management with options as sketched in Fig. 14.4.

In this context, particular attention has to be paid to the developing countries, and countries in transition, as faced a few years ago in a program promoted and supported by the United Nation Industrial Development Organization (UNIDO) through the International Centre for Science and High Technology (ICS) established at Padriciano (Trieste, Italy) and implemented after the takeoff in year 1996 for more than a decade (Table 14.1) [9].

Even the present author (E.C.) has been pleased to contribute actively to the dissemination of the fundamental concepts relevant to the design and development of polymeric materials and relevant plastic items characterized by eco-compatibility and biodegradability under compelling suggestions on the correct management of postconsumer plastic commodities at the end of their service life.

An approach aimed at providing a viable solution to the issue of plastic accumulation in the environment has been focusing on the chimeric “bioplastics” as friendly substitutes of the commodity plastic items based on fossil fuel feedstock. In spite of the remarkable efforts spent in the design and production of plastics from renewable resources (Fig. 14.5), correctly identifiable as “bio-based” plastics, as anticipated their global production is, to be generous, extremely limited (around 0.5 %) of the worldwide plastic production based on fossil fuel feedstock.

As far as the production, consumption and management at the end of the service life of biodegradable plastics in general are concerned, from both petrochemical and

Table 14.1 Formative activity program on eco-friendly polymeric materials and biodegradable plastics promoted by ICS UNIDO in emerging and developing countries

December 1996	SPCM	Trieste, Italy	September 2002	EGM	Trieste, Italy
June 1997	TC	Alexandria, Egypt	October 2002	WSP	Bangkok, Thailand
November 1997	WSP	Pune, India	October 2002	WSP	Beijing, China
April 1998	EGM	Trieste, Italy	November 2002	WSP	Santiago, Chile
September 1998	WSP	Antalya, Turkey	July 2003	EGM	Trieste, Italy
November 1998	WSP	Campinas, Brazil	April 2004	WSP	Teheran, Iran
March 1999	WSP	Doha, Qatar	October 2004	WSP	Beijing, China
September 1999	WSP	Shanghai, China	November 2004	WSP	Kampala, Uganda
October 1999	WSP	Smolenice, Slovakia	December 2004	EGM	Trieste, Italy
March 2000	WSP	Sharjah, UAE	November 2005	WSP	San Jose, Costa Rica
September 2000	WSP	Seoul, Korea	December 2005	EGM	Trieste, Italy
November 2000	EGM	Trieste, Italy	February 2006	EGM	Trieste, Italy
June 2001	WSP	Lòdz, Poland	June 2006	WSP	Belgrade, Serbia
September 2001	WSP	Jakarta, Indonesia	December 2006	WSP	Pune, India
November 2001	WSP	Manama, Bahrain	October 2007	WSP	Beijing, China
December 2001	EGM	Trieste, Italy	March 2008	WSP	Cairo, Egypt

SPCM Scientific Planning Committee Meeting, *TC* Training Congress, *WSP* Workshop, *EGM* Expert Group Meeting

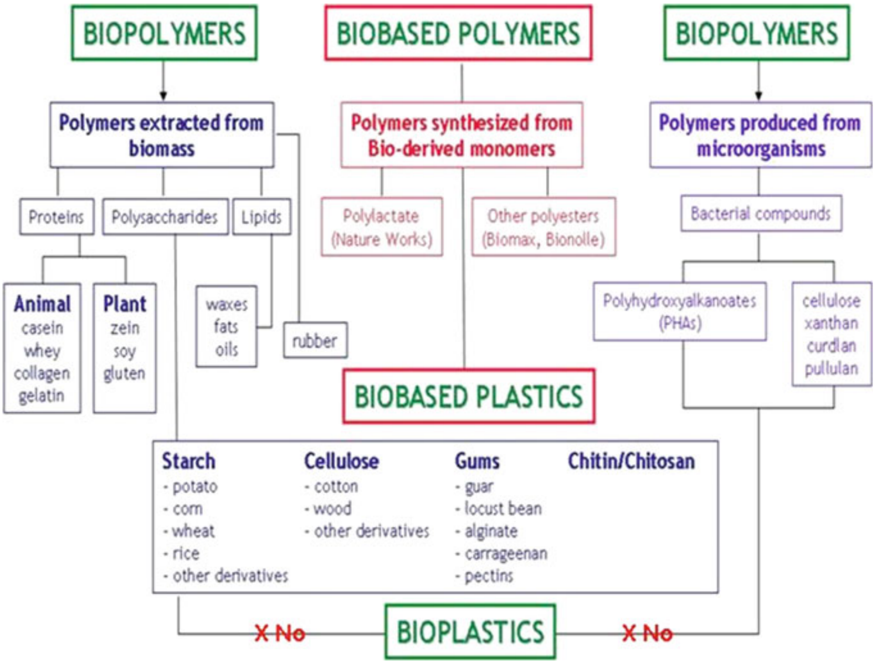


Fig. 14.5 Natural and derived polymers and relevant plastics—nomenclature

renewable resources, it is indeed worthwhile mentioning the “First International Scientific Consensus Workshop on Biodegradable Polymeric Materials and Plastics‶ [10]. That event dating back to the end of the 1980s recorded the international participation of researchers from a large number of countries, in an appreciable interdisciplinary expertise framework. The worldwide market of the biodegradable plastics from renewable resources is characterized by a productivity growth rate not commensurate, in our opinion, to the academic and industrial research investments aimed at their take-off and acquisition of reasonable quotas in the plastic commodity and disposable increasing demands.

Therefore, the outstanding recent efforts spent in industrially oriented programs aimed for the implementation of a “green chemistry” that the present authors would dare to define a reargued matter, it is not in the position to give fair answers to the growing needs for feed, food, and plastic commodities.

It is worthwhile mentioning that according to the statistic data issued by the IBAW Industrial Association, the production and consumption of “bio-based” plastics was 50 K Tons in year 2004, and two years later in spite of the rosy perspectives, only a production of 150 K Tons was recorded [11], and nowadays after a decade, it has reached a production level of one order of magnitude higher but maintaining, however, the same proportional gap with respect to the fossil fuel feedstock-based plastics [12] (Fig. 14.1).

As a case study aimed at mitigating the environmental burden caused by conventional polyethylene-based shopping bags, under this stimulus of the novel ecologist fervor born by the end of the 1980s in Italy, a decree with the force of the law was issued [13] and converted successfully in law [14], according to which a tax of 100 Italian Liras—equivalent to 5 €-cents—was charged on any conventional polyethylene (PE) shopping bag with the scope of limiting their consumption on the national territory.

Almost ten years later, that law was revoked in Italy by a decree with the force of the law issued by the Ministry of Environment [15]. The indicated legal positions gave a new input to the production of bio-based plastics as suited to cover the mercantile segments of massive consumption such as the packaging which comprises also the shopping bags.

According to the above considerations, we welcome polymeric materials and relevant plastics susceptible to be biodegraded under composting conditions, according to the Standard Norm EN 13432/02 [16] and relevant specification reported in the Norms EN 14995-06 [17] and ISO 17088 [18], provided they are derived for instance from agro-industrial waste and renewable resources that do not interfere with food and feed segments, such as agro-industrial waste, and are not intended to build up monopolies of materials and relevant manufactures against the elementary rules of commercial competitions without limiting the discretion liberty of the customers and refraining the free circulation of goods stated as safe for food contact.

It is then taken for granted that beside the biodegradable/compostable polymeric materials and relevant plastic manufactures, whatsoever the raw material used in their production, either fossil fuel feedstock or agro-industrial waste, it is necessary that plastic commodities’ massive utilization derived from fossil fuel feedstock that

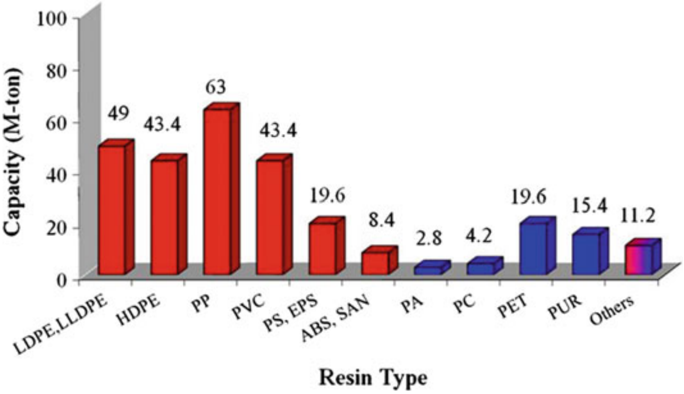


Fig. 14.6 Global plastic production in 2011 by type

continue to be produced eventually after a reengineering of their original formulations, in order to make them eco-compatible. In fact, if one makes an analytical assessment of the typology of the polymeric materials currently used for the production of massive plastic manufactured goods can realize that nowadays about 80–85 % is consisting of macromolecular components characterized by a full-carbon backbone structure (Fig. 14.6), and polyolefins are the major components of these productions.

These last materials and relevant manufactures are recalcitrant to the attack and digestion by microorganisms present in various environmental compartments, with the exception of microorganisms equipped with a genetic profile susceptible to exert a pro-oxidant activity such as those reported in Table 14.2 [20]. However, we have to take into account that due to the high molecular weight of the macromolecules, the oxidation rate of the carbon backbone in the formal average oxidation state of minus two (−2) and hence the following breakdown are extremely slow on a reasonable time frame that would refrain the accumulation in the environment.

Therefore, all the scientific and technological initiatives aimed at mimicking and hence speeding up the pro-oxidant outcome of the full-carbon backbone macromolecules, thus microorganisms can support the opening of the door to a chain breakdown to functional fragments, vulnerable to the microflora present in the different environmental compartments.

The oxo-biodegradation is then not a blasphemous attribute to be condemned like the “satanic verses,” and cannot even be set aside like a fictional word, because it is a reality to be boosted on behalf of environmental protection and freedom in competition for the production and commercialization of large consumption of plastic commodities and disposables.

The functional fragments attainable from full-carbon backbone polymeric materials as a consequence of the *tandem* action exerted by the pro-oxidant/pro-degradant additive (Fig. 14.7b), thanks to the presence of hydrophilic functional groups, become

Table 14.2 Bacteria and Yeasts capable of hydrocarbon oxidation

Bacteria	Yeast
Achromobacter	*Candida*
Acinetobacter	*Cryptococcus*
Actinomyces	*Debaryomyces*
Aeromonas	*Endomyces*
Alcaligenes	*Hansenula*
Arthrobacter	*Mycotorula*
Bacillus	*Pichia*
Beneckea	*Rhodotorula*
Brevibacterium	*Saccharomyces*
Corynebacterium	*Selenotila*
Flavobacterium	*Sporidiobolus*
Micromonospora	*Sporobolomyces*
Mycobacterium	*Torulopsis*
Nocardia	*Trichosporon*
Pseudomonas	
Spirillum	
Vibrio	

wettable, thus allowing for the attack by microbial consortia, ubiquitous in various environmental compartments, whose ultimate result is controlled safe digestion of the microbial fragments to water, carbon dioxide (and methane in semi-aerobic conditions), and cell biomass (Fig. 14.7a).

The described role of the pro-oxidant/pro-degradant additives allows us to generalize the concepts and the basic principles to support the propensity to biodegradation of polymeric materials and relevant plastic items bringing substantially all the matter to a class of materials and products identifiable as biodegradable under environmental conditions that have to be strictly defined.

In fact, the biodegradability is basically not an absolute attribute, because it is strictly connected to the environmental conditions and time frame in which the biodegradation process of either the material or the relevant products does occur.

For the sake of clarity and within the scope of substantiating and qualifying the biodegradable polymeric materials and relevant plastic items according to the key steps of the overall process, we can confine the materials and products into two classes, identifiable as “hydro-biodegradable” and “oxo-biodegradable” items, distinct for the first step of the overall process (Fig. 14.8). In both cases, the ultimate step is consisting of the microbial digestion to water, carbon dioxide, and cell biomass independent of the hydrolytic or oxidative pathways leading to the macromolecule carbon chain breakdowns.

The major difference between the two classes of polymeric materials is represented by the energetic profiles of the first step. In fact, as sketched in Fig. 14.9 the activation energy of the C–H bond that is the crucial point in the oxidative degradation step is higher than one order of magnitude with respect to the

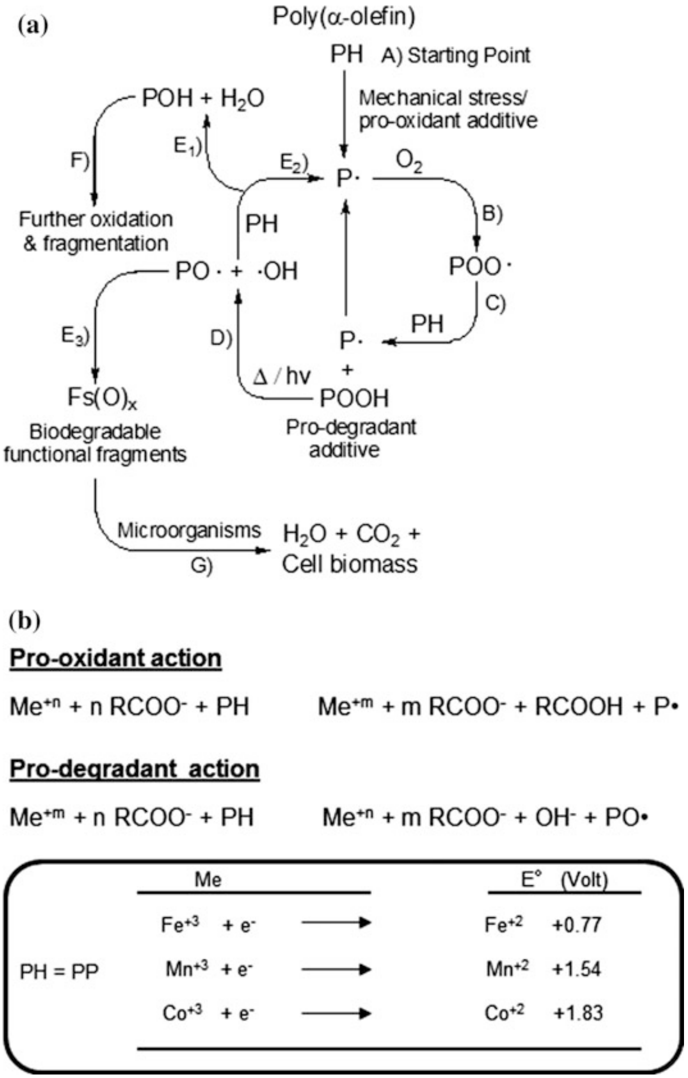


Fig. 14.7 Mechanism of oxidative degradation of full-carbon backbone polymeric materials. **a** General scheme including also the ultimate stage of biodegradation. **b** Specific transition metal salts able to promote oxidation followed by degradation of full-carbon backbone polymers in a tandem fashion action

hydrolytic step expected for the degradation of an heteropolymer such as polyesters. Therefore, in order to speed up the degradation rate of full-carbon backbone polymeric materials, a small amount of additive displaying catalytic activity in promoting the oxidation of C–H bond is needed.

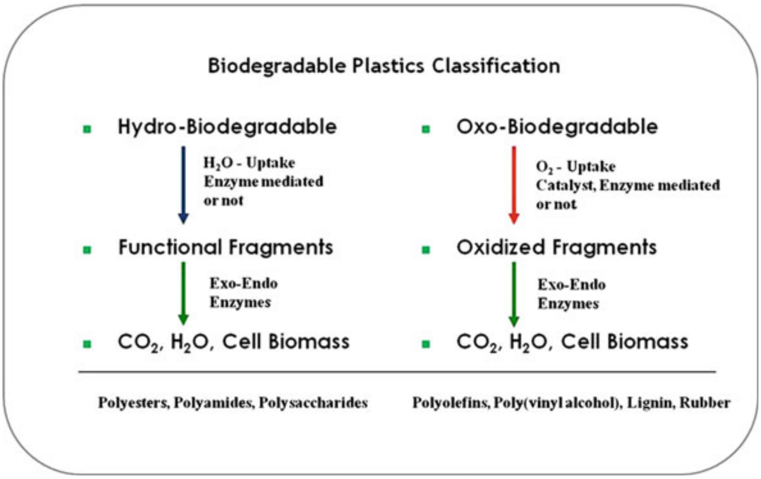


Fig. 14.8 Environmentally degradable polymers and plastics

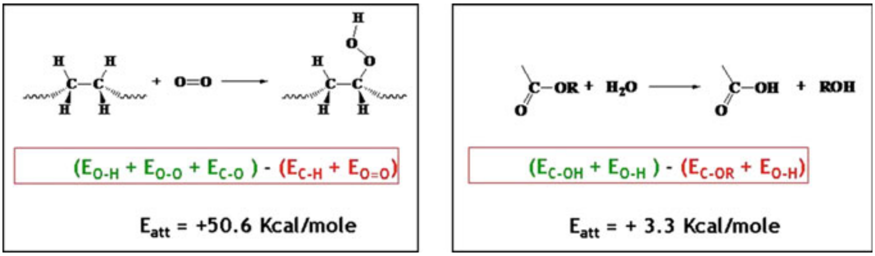


Fig. 14.9 Energetic profiles in oxo- and hydro-biodegradables' primary steps

In Fig. 14.10, a sketched representation of the effects caused by an oxo-biodegradable attack onto a low-density polyethylene (LDPE) macromolecular chain is shown. It includes at the bottom line the parameters that currently have to be monitored in order to gain undisputable experimental evidences on the various steps that start with the oxidation of the carbon backbone followed by the chain breakdown to functional fragments vulnerable by ubiquitous microorganisms in the different environmental compartments with ultimate conversion under aerobic conditions of water, carbon dioxide, and cell biomass [21–31].

It is worth mentioning that the positions taken by the unbelievers and disparagers of the oxo-biodegradable polymeric materials and plastics (OBPs) are often based on the following points:

(a) The toxicity of the pro-oxidant/pro-degradant additives due to the presence of heavy metals [absolutely false because the quoted additives are based on fatty acid salts of transition metals present as microelements in the soil and water (fresh and salty water) compartments].

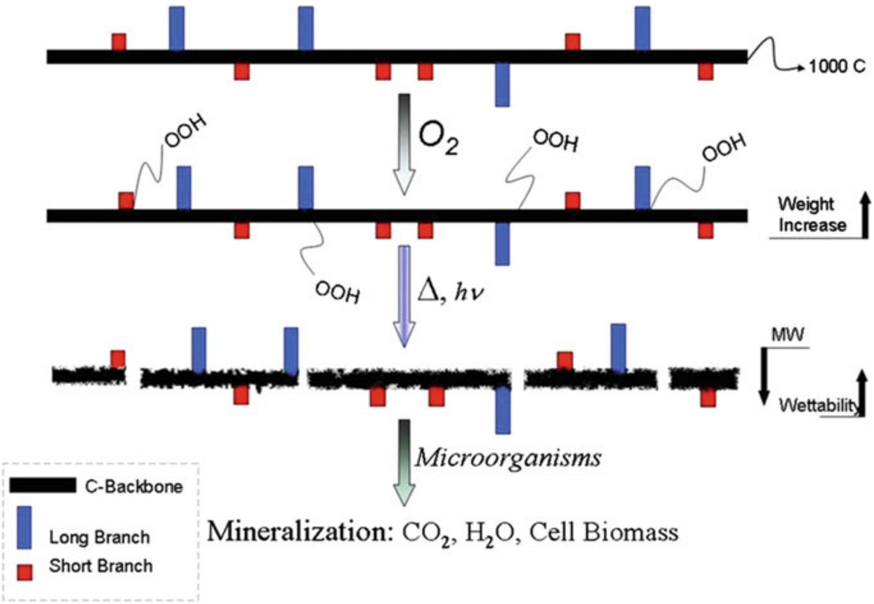


Fig. 14.10 Schematic representation of the oxo-biodegradation process of LDPE polymer chains

(b) The unsuitability of OBPs to be mechanically recycled as a second raw prime material (absolutely inconsistent, provided the recyclers do as usually a suited upgrading of the materials and manufactures submitted to a mechanical recycle).
(c) The accumulation of the oxidized fragments, derived from the first step of the process in the environment, with seriously deleterious effects on the flora and fauna present in the environmental compartments [a very debatable statement as we experimentally observed that the fragments derived from an inorganic (non-bionic step) attack can experience a further oxidative microbial attack (bionic step) in combination with the metabolic attack by the microorganisms with production of water, carbon dioxide, and biomass].

Non-comprehensive, but undebatable, evidences are reported in references [32–36].

14.1 Conclusions

OBPs based on a full-aliphatic-carbon backbone such as polyethylene (PE) and polypropylene (PP), when doped with relatively small amounts of pro-oxidant/pro-degradant additives (0.5–1 % by weight of fatty acid salts of transition metals such as Fe, Mn, or Co or their combination), become susceptible to an oxo-biodegradation process occurring at the end of their predetermined service life.

Table 14.3 List of more recent papers on oxo-biodegradable polymeric materials and relevant plastic items

M. U. de la Orden, J. M. Montes, J. M. Urreaga, A. Bento, M. R. Ribeiro, E. Pérez, M. L. Cerrada. “Thermo and photo-oxidation of functionalized metallocene high density polyethylene: Effect of hydrophilic groups”, *Polym. Degad. Stab.*, 111, 78–88 (2015)
M. E. Boscaro, E. A. De Nadai Fernandes, M. A. Bacchi, S. M. Martins-Franchetti, L. G. Cofani dos Santos, S. S. N. S. Cofani dos Santos. “Neutron activation analysis for chemical characterization of Brazilian oxo-biodegradable plastics”, *J. Radioanal. Nucl. Chem.,* 303, 421–426 (2015)
R. Vijayvargiya, A. K. S. Bhadoria, A. K. Nema. “Photo and biodegradation performance of polypropylene blended with photodegradable additive ferrocene (Part – I)”, *Int. J. Appl. Sci., Eng. Res.,* 3, 153–170 (2014)
S. K. Samal, E.G. Fernandes, A. Corti, E. Chiellini. “Bio-based Polyethylene–Lignin Composites Containing a Pro-oxidant/Pro-degradant Additive: Preparation and Characterization”, *J. Polym. Environ.,* 22, 58–68 (2014)
T. Muthukumar, A. Aravinthana, R. Dineshram, R. Venkatesan, M, Doble. “Biodegradation of Starch Blended High Density Polyethylene using Marine Bacteria Associated with Biofilm Formation and its Isolation Characterization”, *Microb. & Biochem. Technol.,* 6, 116–122 (2014)
M. Takev, P. Velev, V. Samichkov. “Physicomechanical Properties of Biodegradable Composites, Based on Polypropylene and Paper From old Newspapers”, *J. Chem. Technol. and Metall.,* 49, 363–369 (2014)
F. Masood, T. Yasin, A. Hameed. “Comparative oxo-biodegradation study of poly-3-hydroxybutyrate-co-3-hydroxyvalerate/polypropylene blend in controlled environments”, *Int. Biodeterior. Biodegrad.* 87, 1–8 (2014)
S. T. Harini, S. Padmavathi, A. Satish, B. Raj. “Food compatibility and degradation properties of pro-oxidant-loaded LLDPE film”, *J. Appl. Polym. Sci.*, 131, (2014)
M. M. Reddy, M. Misra, A. K. Mohanty. “Biodegradable Blends from Corn Gluten Meal and Poly (butylene adipate-co-terephthalate)(PBAT): Studies on the Influence of Plasticization and Destructurization on Rheology, Tensile Properties and Interfacial Interactions”, *J. Polym. Environ.*, 22, 167–175 (2014)
L. S. Montagna, A. L. Catto, M. M. de Camargo Forte, E. Chiellini, A. Corti, A. Morelli, R. M. Campomanes Santana. “Comparative assessment of degradation in aqueous medium of polypropylene films doped with metal free (experimental) and transition metal containing (commercial) pro-oxidant/pro-degradant additives after exposure to controlled UV radiation”. *Polym. Degrad. Stab.*, 120, 186–192 (2015)

That behavior is of utmost importance because it allows a consequent control of the accumulation onto the different environmental compartments of soft flexible plastic items identified as commodities eventually released in the environment as a consequence of impolite civil behavior of the end users.

In fact, depending upon the type and content of pro-oxidant/pro-degradant additives present in the doped plastic items and upon the environmental conditions recordable in the compartment where the postconsumer plastic items are either intentionally or accidentally abandoned, one can foresee what would be the reasonable time frame necessary for a safe, useful biodegradation, thus mitigating the accumulation of plastic waste in the environment.

Finally, regarding the future perspectives for the increasing production and consumption of oxo-biodegradable plastics based on full-aliphatic-carbon backbone polymeric materials, one can refer to the list of references (Table 14.3) relevant to the years 2014 and 2015 reporting on research activities ongoing in the field of products susceptible to oxidative degradation followed by production of functional fragments vulnerable to microflora present in various environmental compartments.

References

1. L. Shen, J. Haufe, M. K. Patel, Product overview and market projection of emerging bio-based plastics, PRO-BIP (2009)
2. CEN/TR 15932-2009, *Plastics-Recommendation for Terminology and Characterisation of Bioplastics*
3. CEN/TR 15351-2005, *Plastics-Guide for Vocabulary in the Field of Degradable and Biodegradable Polymers and Plastic Items*
4. www.plasticseurope.com
5. press@european-bioplastics.org
6. J.G.B. Derraik, The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. **44**, 842 (2002)
7. M.R. Gregory, Environmental implications of plastic debris in marine settings-entanglement, ingestion, smothering, hangers-o, hitch hiking and alien invasions. Philos. Trans. R. Soc. B-Biol. Sci. **364**, 2013 (2009)
8. Y. Ohtake, T. Kobayashi, H. Asabe, N. Murakami, Studies on biodegradation of LDPE: obervation of LDPE films scattered in agricultural fields or in garden soil. Polym. Degrad. Stab. **60**, 79 (1998)
9. ICS-UNIDO program on *Plastic Waste Management and Sustanaible Development*, Dec. 1996–Mar. 2008
10. S.A. Barenberg, J.L. Brash, R. Narayan, A.E. Redpath, *Degradable materials, perspectives, issues, and opportunities* (CRC Press, Boca Raton, 1990)
11. https://plasticssource.com/splasticsresource/docs/900/840.pdf, https://www.plasticseurope.org 2006
12. www.biomassmagazine.com 2009; www.Plasticculture.com 2009
13. Decreto Legge del Parlamento Italiano n. 397 del 09/09/1988 “Disposizioni urgenti in materia di smaltimento dei rifiuti”
14. Legge Ordinaria del Parlamento Italiano n. 475 del 09/11/1988 “Disposizioni urgenti in materia di smaltimento dei rifiuti industriali”, art. 1, comma 8
15. Decreto legge del Parlamento Italiano n. 22 del 05/02/1997 “Attuazione delle Direttive 91/156/CEE sui rifiuti, 91/689/CEE sui rifiuti pericolosi e 94/62/CE sugli imballaggi e sui rifiuti di imballaggio, art. 56
16. EN 13432-02, *Requirements for Packaging Recoverable Through Composting and Biodegradation*. Test scheme and evaluation criteria for the final acceptance of packaging
17. EN 14995-06, *Plastics: Evaluation of Compostability*. Test Scheme and Specifications
18. ISO 17088-08/12, *Specifications for Compostable Plastics*
19. www.cipet.gov.in, *Plastics Industry-Statistics*
20. D.T. Gibson (ed.), *Microbial Degradation of Organic Compounds* (Marcel Dekker Inc. New York, 1984)
21. E. Chiellini, Oxo-biodegradabili: realtà, non-fiction, Com. Pack **4**, 16 (2012)
22. E. Chiellini, A. Corti, G. Swift, Biodegradation of thermally-oxidized, fragmented low-density polyethylenes. Polym. Degrad. Stab. **81**, 341 (2003)
23. E. Chiellini, A. Corti, A simple method suitable to test the ultimate biodegradability of environmentally degradable polymers. Macromol. Symp. **197**, 381 (2003)

24. E. Chiellini, A. Corti, S. D'Antone, R. Baciu, Oxo-biodegradable carbon backbone polymers—oxidative degradation of polyethylene under accelerated test conditions. Polym. Degrad. Stab. **91**, 2739 (2006)
25. E. Chiellini, A. Corti, S. D'Antone, N.C. Billingham, Microbial biomass yield and turnover in soil burial biodegradation tests: carbon substrate effects. J. Polymer Environ. **15**, 169 (2007)
26. E. Chiellini, A. Corti, S. D'Antone, Oxo-biodegradable full carbon backbone polymers—biodegradation behavior of thermally oxidized polyethylene in an aqueous medium. Polym. Degrad. Stab. **92**, 1378 (2007)
27. E. Chiellini, *Environmentally Compatible Food Packaging* (CRC Press, Cambridge, 2008)
28. A. Corti, M. Sudhakar, M. Vitali, S.H. Imam, E. Chiellini, Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. Polym. Degrad. Stab. **95**, 1106 (2010)
29. E. Chiellini, A. Corti, S. D'Antone, D. Wiles, *Oxobiodegradable Polymers: Present Status and Perspectives in Handbook of Biodegradable Polymers*, eds. by Lendlein & Schroeter Eds, Wiley-VCH, Weinheim (Germany), 379 (2011)
30. E. Chiellini, A. Corti, *Developments and Future Trends for Environmentally Degradable Plastics*, eds. by P. Fornasiero, S.M. Graziani Renewable Resources and Renewable Energy: A Global Challenge, vol 91 (Taylor and Francis Group, LLC, 2011)
31. A. Corti, M. Sudhakar, E. Chiellini, Assessment of the whole environmental degradation of oxo-biodegradable linear low density polyethylene (LLDPE) films designed for mulching applications. J. Polym. Environ. **20**, 1018 (2012)
32. I. Jakubowicz, N. Yarahmadi, V. Arthurson, Kinetics of abiotic and biotic degradability of low-density polyethylene containing prodegradant additives and its effect on the growth of microbial communities. Polym. Degrad. Stab. **96**, 919 (2011)
33. S. Verstichel- Organic Waste Systems (OWS) Final Report, Ecotoxicity Tests—Cress Test. Summer Barley Plant Growth Test Earthworm, Acute Toxicity Test Daphnia, Acute Toxicity on Compost Residuals of EPI-TDPA-Study CH-3/2 (Cress Test), Study CH-3/3 (Summer barley plant growth test) Study CH-3/4 (Earthworm, acute toxicity test), Study CH-3/5 (Daphnia, acute toxicity test)
34. M. Brunet, D. Graniel, L. Cote, *Environment Department Quebec*. Evaluation of the impact of biodegradable bags on the recycling of traditional plastic bags- CRIQ File n. 640-PE35461-Final Technical Report
35. Roediger Agencies cc, Polymer Science Building Analytical Laboratory; De Beer Street, Stellenbosch 7600; 6th March 2012; "Recycling Report on d2w oxo-biodegradable Plastics"
36. I. Jakubowicz, J. Enebro, Effects of reprocessing of oxobiodegradable and non-degradable polyethylene on the durability of recycled materials. Polym. Degrad. Stab. **97**, 316 (2012)

Erratum to: Chapters 2 and 9 of Polyolefin Compounds and Materials

Mariam Al-Ali AlMa'adeed and Igor Krupa

Erratum to Chapter 2 in: M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*, Springer Series on Polymer and Composite Materials, DOI 10.1007/978-3-319-25982-6_2

An error in the production process unfortunately led to publication of this chapter prematurely, before incorporation of the final corrections. The version supplied here has been corrected and approved by the author [authors].

Erratum to Chapter 9 in: M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*, Springer Series on Polymer and Composite Materials, DOI 10.1007/978-3-319-25982-6_9

Throughout this chapter we had to correct the spelling of the expressions "melting blown", "melting spinning", "melting-blowing" and "melting". These expressions should read "meltblown", "meltspinning", "melt-blowing" and "melt".

The updated original online version for this chapters can be found at
DOI 10.1007/978-3-319-25982-6_2
DOI 10.1007/978-3-319-25982-6_9

M. Al-Ali AlMa'adeed (✉) · I. Krupa
Center for Advanced Materials, Qatar University, Doha, Qatar
e-mail: m.alali@qu.edu.qa

M. Al-Ali AlMa'adeed and I. Krupa (eds.), *Polyolefin Compounds and Materials*,
Springer Series on Polymer and Composite Materials,
DOI 10.1007/978-3-319-25982-6_15