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Scientific and Technological Comparison of Plastic Properties

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The co-authors M. Bertoldo, S. Bronco, E. Passaglia wish to dedicate the book to their guide and mentor F. Ciardelli for his 80th birthday.

F. Ciardelli wish to dedicate on his side this book to the three younger ladies co-authors, thanking them for having shared with him years of fascinating research on polymers and the burden for the preparation of the present book.

Contents

Chapter 1
Introduction

1.1 Topics and Aim of the Book

Polymers derived from fossil or renewable sources may both have, in principle, the similar application deriving from the plastic behaviour while may show differences in other properties, often relevant to the further application and final disposal, today including reuse and recycling. At present and with increasing relevance in the future, the design of a material devoted to assist the human society needs to consider, in addition to the appropriate plastic response, all the other aspects with main attention given to environmental safety and saving of resources (Kumar et al. 2014).

To be clear from the starting, while this book is mainly dedicated to relate the molecular structure of a macromolecular system, a polymer, with its plastic behaviour, cannot disregard the other properties, out of plasticity, of the selected material. It is necessary to reach the objective to provide the reader to judge the suitability of a plastic material with demand of its primary use, but with reliable knowledge about the many other requirements connected to the role in the environment (Gironi et al. 2011).

Then, while organic plastic materials of different origins are first evaluated also comparatively with regard to the response to mechanical stimuli, the additional features, mainly those connected to environmental saving, will be examined. Indeed at the end, this should allow the involved reader to acquire the instruments for the balanced sustainable selection.

We are aware of how difficult can be to reach adequately this objective due to the complexity of the subject materials always needing appropriate formulation giving molecular and structural complexity. During this process, clearly made by man, the material can lose or largely modify its original properties. In this contest, it will be easy to finally realize that the only property which cannot be modified by the successive processing is the origin; accordingly, this book, as reported in the title, will start from the origin of the component, which provides the complex final material with the plastic properties. This will be done with the further attempt to show that the successive formulation and processing to the final object sent to the market may

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completely change the environmental expectation and the philosophy that guided the primary selection.

Our teaching experience has pointed out with doubtless evidence that to be understood one has to be concise. The result cannot be obtained when talking about complex problems without neglecting in part detailed information and level of the scientific discussion. These sacrifices, not easy with specialists as we are, should be compensated by a larger number of learned people. We like to present our apology to polymer specialists which can find sometime the scientific level not adequate to their expertise, as well as to the less expert reader for many technical concepts and information necessary to maintain the rigorous connection to the reality of the presentation.

One important point is clearly related to the chemical structure of the main component which, as said, is the macromolecular system and we can indicate as the polymer. Chemistry has shown that a desired molecule can be obtained from various starting products by different routes. This brings to the first important assessment for our successive presentation*: a defined macromolecular system can be obtained either from fossil or from renewable resources.*

Thus, the polymerization with the same process of ethylene from fossil or from the biorefinery obviously provides the same polyethylene. The products obtained from the two processes, differing only in the origin of the monomer, will be identical from all viewpoints and will be then submitted to the same formulations and applications.

In addition, we know that a plastic material is a complex mixture where the polymer is only a component even if, often, quantitatively dominant and mainly responsible for the plastic behaviour. The final desired properties can be obtained with various complex mixtures where the type of polymer can be varied and the material adjusted by a different formulation to the final property. The formulation adjustment is performed by adding to the polymer appropriate amounts of various compounds which again can be from fossil or renewable origin. These additives have different reactivity and are present in several cases in some important amount. Then a second assessment is: *the optimization of the plastic behaviour of different polymers needs different additives with consequent substantially different material properties out of plasticity and origin.*

Thus, if we consider fossil-derived isotactic polypropylene and poly(lactic acid) obtained from an enantiomeric pure monomer, even if both polymers show a similar melting point, the latter needs to be plasticized for use as plastic material in the actual day life. The plasticizer will then bring new characteristics differentiating the two materials. The final plastic behaviour can be then brought at the same point for both, but the different chemical reactivity of the two polymers will suggest different applications and distinct biodegradability. The chemically very stable polypropylene will be used for long-lasting items, whereas poly(lactic acid) based materials are more suitable for short time use. The former is recyclable, the latter biodegradable.

From chemical point of view, a macromolecule derives from a reaction (polymerization) that converts a small molecule, the monomer, into a long molecule (the macromolecule). Monomer can be provided by nature or obtained from fossil oil, while the polymerization reaction can be natural (biopolymers) or man-made giving, in the latter case, synthetic polymer from renewable monomers. Then a third assessment is: *a plastic material can contain in principle as polymer component one of these three different types of polymer, derived, respectively, from fossil, from renewable monomers or renewable polymers. The main property can be the same but additives different in the three cases.*

These three assessments provide a first idea of the possibilities we have to obtain plastic materials from fossil or renewable sources and the difficulty to establish simple correlations. Such observation well reflects the fact that the plastic behaviour is not so extended in nature. The shaping of objects by moulding was not used and the plastic response we are discussing is not important in many natural systems. On the contrary, it is fundamental in modern technology.

As it will be better clarified in the following chapters, the 'perfect' plastic behaviour is operating in a well-defined range of temperatures (Rudin et al. 2013). A real plastic must show two characteristic temperatures limiting the plastic range; below the lowest one, the material becomes rigid as a glass (this temperature is indeed indicated as Glass Transition Temperature, T_g), while over the largest the material becomes a liquid. These features are related to the presence of an amorphous phase, characterized by the T_g, and a crystalline or more rigid amorphous phase with a high transition temperature. The ideal plastic material is therefore the one showing the plasticity range in the same range in which the man is exerting its activity. For general purposes, this is going approximately from the lower limit close to the earth Poles and the higher one to the equator.

Some preliminary information about the fact that nature disregarded the general use of plastics is derived from the data of Table 1.1; indeed, the T_g of biopolymers is usually over the average room temperature. From the same table, one can easily understand that polyethylene invented by man has by far the best plastic character. In addition, the nature generally provided hydrophilic polymers (biopolymers) requested by the bioprocesses and environment needs.

Table 1.1 General features of fossil and natural polymers for plastics[a]

Type of polymer	Source	Production process	Environmental properties	Application range
Nature made	Renewable	Extraction/Isolation	Biodegradable	Limited
From natural monomers	Renewable	Polymerization	Biodegradable	Limited
From synthetic monomers	Renewable	Polymerization	(a) Non-biodegradable and recyclable (b) Biodegradable	Broad, covering most of the society needs
	Fossil			

[a] Note that this very indicative table refers only to the most common polymers displaying typical plastic behaviour

From Table 1.1, the reader can also visualize that polymers from fossil origin used as plastics can be biodegradable or non-biodegradable depending on the molecular design, while plastic polymers from nature or from bio-monomers are biodegradable as polymers from hydrophilic monomers and biopolymers.

Natural life is based on water and most of the natural materials (Bharti et al. (2016)) based on macromolecules (polymers) are hydrophilic and more or less swollen by water. Often they have plastic behaviour as far as they are imbibed by water but become brittle when dried. On the other side, hydrophobic monomers from fossil resources, give hydrophobic polymers according to the extended necessity of hydrophobic materials, which was supported by the development of technology where many activities are carried out in a strictly dry environment or must be protected against water. One can argue that oil is finally a product of nature; however, oil was well underground and made available and useful thanks to the work of man. This concept will be better clarified in the successive presentation.

It is important to make clear that the property of a plastic material does not depend merely on fossil or non-fossil origin, but on the molecular structure of the chain. On the other side, it is common to call bioplastic all polymeric materials having a certain bio-character, either from the origin or from the properties. Thus, polyethylene obtained from the ethylene polymerization obtained by dehydration process of natural ethanol is called bio-polyethylene, while polyethylene indicates the same polymer prepared by polymerization of ethylene from oil. Clearly, the two monomers are chemically identical and the derived polyethylenes produced with the same polymerization procedure have the same properties and in particular are both non-biodegradable.

The world of the so-called bio-related plastics is quite complex as many aspects are involved. Indeed, one can identify:

1. Biopolymers produced by nature such as cellulose, starch, proteins and polyhydroxyalkanoates (Keshavarz et al. 2010).
2. Polymers o bio-monomers derived from natural products as, for example, poly(lactic acid) and nylon 11.
3. Polymers of non-natural monomers prepared starting from renewable sources: polyethylene obtained by polymerization of ethylene from fermentation products.
4. Biodegradable polymers of monomers from fossil origin as linear aliphatic polyesters and polyvinyl alcohol.
5. Mixed polymers such as polyurethanes prepared by combining diols from renewable sources and dissociates from fossil oil or blends of biopolymers with polymers of fossil origin.
6. Any polymer from fossil or natural sources for biomedical application.

The very complex situation is represented in the table below (Table 1.2) that does not allow an univocal classification.

It rather shows that the use of renewable materials may allow a reduction of consumption of the available resources as well as extends the versatility of plastic materials. Indeed, thanks to the basic new structures which are made available following the different possible routes, new elements have been introduced.

Table 1.2 Correlation between biodegradability and origin of different macromolecules for plastics[a]

Type	Fully fossil-based	Partially bio-based	Fully bio-based
Biodegradable	PBS (polybutylene succinate) PBSA (poly(butylene succinate-co-adipate)) PCL (polycaprolactone)	Starch blends with non-biodegradable polymers like as polyolefins PLA (poly(lactic acid)) blends	Cellulose acetate TPS (thermoplastic starch) PLA (poly(lactic acid)) PHA (polyhydroxyalkanoates) Mixtures between the above polymers
Non-biodegradable	PE (polyethylene), PP (polypropylene) and generally polyolefins PET (polyethylene terephthalate), and generally polyesters with terephthalic acid and fossil-derived diols; PA 6 (nylon 6), PA 66 (nylon 6,6); PVC (polyvinyl chloride) PUR (polyurethane resins)	PBT (polybutylene terephthalate from bio-based butane diols) PET from bio-based ethylene PVC from bio-based ethylene PUR from bio-based polyol Starch blends (with polyolefins)	Bio-based PE PA11 (nylon 11)

[a] Only a few polymer examples are reported in the table referring to the most used ones

The main consideration is therefore that the future increasing needs of highly specialized applications of the human society can conveniently profit from the availability of plastic materials with so different performances in their primary application and in their environmental impact.

Indeed, the various approaches mentioned and presently available offer the important advantage to allow saving of important non-renewable resources such as oil and natural gases while maintaining the possibility of having materials with all the properties necessary in the present technology evolution. Moreover, some of them can contribute to respect the environment with their facilitated biodegradability, which is very appreciable for short time applications as in packaging, when collection and recycling are not feasible.

All the above materials independent of origin are commercially available plastics on the market and provide a good number of opportunities to satisfy the various demands of the present society. Unfortunately, in the recent time, with the purpose to boost materials and issues on the market, by rendering them more attractive and environmentally appealing, the prefix bio was largely used to indicate polymers-based materials with some bio-character referring to origin (even if only partially from renewable resources) or to disposal at the end-of-life (biodegradable or compostable materials). In some cases, indeed, limitations and problems when producing and using bio-related plastic products were not advertised adequately and the real improvement never quantitatively evidenced. As, for example, the commonly defined bio-polyurethane are made by bio-based polyols, but their monomeric units are composed for the 50% of the content by the oil derived isocyanate, actually making the polymer only partially bio-based.

An additional important aspect often disregarded in the general customer information deals with the chemicals and additives, not always from natural sources, necessarily used by the producers in order to obtain competitive products from more or less naturally derived polymers.

The most popular bioplastic material is poly(lactic acid) (PLA) prepared by an industrial non-natural process based on the polymerization of the corresponding monomer. This last, the lactic acid, can be of natural origin. However, the actual used is produced by man at the industrial-scale through the fermentation of corn. The lactic acid is then submitted to subsequent polymerization to PLA, which is clearly carried out by the man; the routes from the polymerization process and polymer isolation use a series of chemicals with the related by-products stream to be evaluated for a correct evaluation of the environmental impact of the production of this bioplastic. Raw PLA is then mixed with various chemical additives to modulate its properties. Often petroleum-based additives are used to this purpose thus rendering not useful the main polymer biodegradability. Trends in using as much bio-based content as possible in these formulations would ensure the final product compostability. The positive last approach has brought to formulations complying with the standard of the American Society for Testing and Materials (ASTM) D6400, where the more evident feature is the biodegradability under the aerobic conditions characteristic of municipal and industrial compost facilities (compostability). On the other side for municipalities that do not have compositing facilities, PLA-based formulations should be recycled, that is, melted down and re-formed into new products, just like any other thermoplastic. But this last route is rendered more complex when dealing with easily biodegradable components.

Taking in mind these aspects, the present book is dedicated to a better understanding of the comparative features of the fossil and natural sources derived plastic polymers, to provide the users with basic information for evaluating performances—cost relation and environmental impact of materials too easily claimed as produced from nature (Faruka et al. 2012).

To reach the objective, the book describes through a series of chapters the logical evolution the role of the plastic materials in our life. The route starts from the desired property and continues in the origin of the starting material to the desired molecular structure and properties, while comparing features and behaviour of fossil and natural sources polymeric materials when subjected to solicitation from the environment during their use (Soroudi et al. 2013).

Chapter 2 is therefore devoted to discuss the origin of the plastic response, that plasticity is a property and not a material, so we should more correctly talk about materials with plastic property. In modern time technology application is running at higher speed than knowledge does and trivial names do not respect the reality. Then, even if, for practical use, the terms plastic and bioplastic are used in the everyday life, one should keep in mind that the correct full name is *materials and bio-related materials with plastic behaviour*.

The role of the polymer macromolecules and the contribution to the properties of the materials are mainly related to the molecular structure of the constituting macromolecules. This is a general important aspect described at the essential level in Chap. 3.

The monomers, the chemical reactions used by man for converting a monomer into a polymer and the process to plastic products are described in Chap. 4, which is flanked by Chap. 5 for bio-related which parallels these information for polymers having a total or partial bio-related origin.

Chapter 6 then is an attempt to provide a synthetic description of more complex multiphase materials obtained by mixing in different ways different polymers or polymers with heterogeneous material. In these cases, the distinction between fossil and renewable origin is even more difficult, and the topic arises a number of problems for the future use, problems which are reported and analysed with scientific transparency in the successive Chap. 7, where the focus is on the environmental impact of the materials described in the previous chapter and the advantages which can be realized by the opening to new plastic materials with more or less significant natural origin and properties.

Chapter 8 is finally devoted to practical and philosophic consideration on the sustainability of the so-called bioplastics and the application where they can really bring favourable effect to the Society.

Appendix

IUPAC Definitions and Statements about Bio-derived Polymers Selection of terms common to all domains and related notes that can be of interest for the book purposes (*definitions extracted from* Vert et al. (2012)).

Artificial Polymer

Man-made polymer that is not a biopolymer. Note 1: Artificial polymer should also be used in the case of chemically modified biopolymers. Note 2: Biochemists are now capable of synthesizing copies of biopolymers that should be named synthetic biopolymers to make a distinction with true biopolymers. Note 3: Genetic engineering is now capable of generating non-natural analogues of biopolymers that should be referred to as artificial biopolymers, e.g. artificial protein, artificial polynucleotide, etc.

Bio-based

Composed or derived in whole or in part of biological products issued from the biomass (including plant, animal and marine or forestry materials). Note: A bio-based polymer or polymeric device is not necessarily environmentally friendly nor biocompatible nor biodegradable, especially if it is similar to a petrol-based (oil-based) polymer.

Biocompatibility
Ability to be in contact with a living system without producing an adverse effect.

Biodegradable
Qualifier for a substance or device that undergoes biodegradation.

Biodegradation
Degradation caused by enzymatic process resulting from the action of cells.

Biodegradation (bio-related polymer)
Degradation of a polymeric item due to cell-mediated phenomena. Note 1: [*omissis*]. Note 2: In vivo, degradation resulting solely from hydrolysis by the water present in tissues and organs is not biodegradation; it must be referred to as hydrolysis or hydrolytic degradation. Note 3: Ultimate biodegradation is often used to indicate the complete transformation of organic compounds to either fully oxidized or reduced simple molecules (such as carbon dioxide/methane, nitrate/ammonium and water). It should be noted that, in case of partial biodegradation, residual products can be more harmful than the initial substance. Note 4: When biodegradation is combined with another degrading phenomenon, a term combining prefixes can be used, such as oxo-biodegradation, provided that both contributions are demonstrated. Note 5: Biodegradation should only be used when the mechanism is proved; otherwise, degradation is pertinent. Note 6: Enzymatic degradation processed abiotically in vitro is not biodegradation. Note 7: Cell-mediated chemical modification without main chain scission is not biodegradation.

Biodisintegration
Disintegration resulting from the action of cells.

Biofilm
The aggregate of microorganisms in which cells that are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS) adhere to each other and/or to a surface. Note 1: A biofilm is a fixed system that can be adapted internally to environmental conditions by its inhabitants. Note 2: The self-produced matrix of EPS, which is also referred to as slime, is a polymeric conglomeration generally composed of extracellular biopolymers in various structural forms.

Biomacromolecule
Macromolecule (including proteins, nucleic acids and polysaccharides) formed by living organisms. Note: Not to be confused with biopolymer, although this term is often used as a synonym.

Biomaterial
Material exploited in contact with living tissues, organisms or microorganisms. Note 1: The notion of exploitation includes utility for applications and for fundamental research to understand reciprocal perturbations as well. Note 2: [*omissis*]. Note 3:

This general term should not be confused with the terms biopolymer or biomacromolecule. The use of 'polymeric biomaterial' is recommended when one deals with polymer or polymer device of therapeutic or biological interest.

Biopolymer
A substance composed of one type of biomacromolecules.

Bio-related
Qualifier for actions or substances that are connected to living systems.

Degradation
The progressive loss of the performance or of the characteristics of a substance or a device. Note: The process of degradation may be specified by a prefix or an adjective preceding the term 'degradation'. For example, degradation caused by the action of water is termed 'hydrodegradation' or hydrolysis; by visible or ultraviolet light is termed 'photodegradation'; by the action of oxygen or by the combined action of light and oxygen is termed 'oxidative degradation' or 'photooxidative degradation', respectively; by the action of heat or by the combined effect of chemical agents and heat is termed 'thermal degradation' or 'thermochemical degradation', respectively; by the combined action of heat and oxygen is termed 'thermooxidative degradation'.

Degradation (bio-related polymer)
Degradation that results in desired changes in the values of in-use properties of the material because of macromolecule cleavage and molar mass decrease.

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Chapter 2
Basic Concepts for Plastic Response

2.1 Introduction and Motivation

This chapter following the general introduction is devoted to provide the reader with the basic concepts related to the understanding of the fundamental necessary properties of a polymeric material to perform as a plastic material and then to be used in the corresponding applications. The chapter main objective is to evidence the structural properties requested to a plastic material and to what extent they can be reached with differentiated molecular structures of the macromolecular chains forming the polymer. Indeed, the plastic behaviour can be found in molecularly different materials, but the precise response requested by the many specialized applications in our present style of life are obtained by a well thought analysis of relationships between detailed molecular structure and ultimate properties.

Indeed, the selection of a plastic material among the available products is determined by the requested mechanical response. This last is determined by the type of mechanical stress applied and by the working temperature. Then the suitability of a plastic polymer to be used for the production of a defined commercial item is based on the determination of its thermal and mechanical features that allow predicting its behaviour during use. Moreover, as the shape of commercial items is obtained by moulding from the melt, the properties of the molten fully liquid polymer (Rheological properties) must be known before going to an industrial production, including the information on how they are modulated by the molecular structure of the polymer.

Chapter 2 is consequently devoted to discuss in detail the physical properties that are presently considered “the bare necessities” for a polymeric material to be classified as a plastic and how they depend on the chemical structure of macromolecules. Thermal, mechanical and rheological features are described separately for sake of clarity, even if strictly interrelated.

Even if in the commercial use the term plastic is used also for some amorphous polymers, which can be shaped by melt moulding, the real plastic polymer is necessarily consisting of two phases, either physically or chemically different. Then several commercial plastics are obtained by blending two distinct polymers.

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2.2 Plastic Materials

A plastic material is a material that can be shaped in a desired form and keeps this form over time. An appreciated property of many plastic materials, so-called plastics is the "thermoplastic" behaviour that is the possibility to shape the material under a heating/cooling cycle, as it is typically done with metals, but at temperature far above the ones of the organic materials to which plastic polymers belong. Indeed, plastic polymers can be heated up until they melt or become enough soft to be shaped and the given form is thus locked just by cooling the item while the forming form is maintained.

However, in common feeling, the adjective plastic has replaced with facilitated simplicity but low scientific rigor the complex adjective "viscoelastic", which appropriately indicates that the subject materials show a balanced response between the elasticity of a solid and the viscosity of a liquid. A material is elastic if after the application of a force to it, the deformation induced is recovered to the initial shape as soon as the deforming force is removed. Typical perfect elastic materials are metals and crystals which however are so rigid that this response is valid for elongations as small as few unit percentage of the original length. Very high elastic response is shown by rubbers that under stress can become several time longer than the starting length, but this last behaviour is determined by trasversal interchain bonds rendering the material crosslinked and then not processable. On the contrary, a viscous material deforms irreversibly, and the deforming force is dissipated; there is a substantial similarity with the behaviour of a liquid that when is transferred from a bottle to a glass change its form according to the one of the bowl. Having in mind these concepts, we should also remind that a traditional material passes in a reversible way from solid to liquid at a specific temperature (melting temperature, T_m). These two physical states are both homogeneous, the former with elastic and the latter with viscous behaviour, and then one reaches the conclusion that a homogeneous traditional material cannot show any viscoelastic behaviour. However, polymers consist of very long molecules (Macromolecules) that, if the chains length exceeds a critical value, form a sort of "knots" that are named "entanglements". Entanglements playing as junction points do not allow polymer molecules flowing freely as traditional liquid molecules do. The presence of junctions allows macromolecules to recover their initial shape when deformed; the elastic behaviour is added to the viscous one. Furthermore, because of the length, chains cannot be entirely accommodated in a crystalline structure under the melting temperature, thus giving a partially crystalline product (semicrystalline), with an amorphous phase able to survive below T_m. The crystalline domains act as additional junction points for the amorphous phase below T_m. The amorphous phase of polymers will then show the behaviour of both a viscous liquid and an elastic material. However, this happens only until the temperature is not low enough to freeze all molecular movements (Glass transition temperature, T_g). In the thermal range within T_m and T_g, the viscoelastic, or polymer plastic, behaviour is a result of the contemporary existence, of the viscous amorphous and the elastic crystalline phase. The crystalline phases act as crosslinking domains for the amorphous phase giving an elastic response but when they collapse the material undergo entropy driven elongation which is partially not reversible for the lack of efficient transversal bonds.

Semicrystalline materials exhibit both viscous and elastic behaviour: they are elastic up to the yield point (which is, in a simplistic way, the moment in which crystallites are no longer bound by cohesive forces due to mechanical stress) then they deform irreversibly as liquid does. The crystalline phase acts as a crosslinking point and the significant elastic deformation is facilitated by the reversible elongation of the amorphous phase. As the deformation of the amorphous phase is governed by the entropy, the elastic response of a plastic to mechanical stress is temperature depending.

Jumping from science to everyday life, the plastic behaviour we enjoy is the one that can be detected at the temperature of the environment where we live. For stimulating the reader curiosity towards the more detailed chapters we like to remember that Nature disregarded this property, which instead becomes of primary importance in the technology revolution. Materials with extended viscoelastic (plastic) behaviour for a generalized use were man-made.

With this short conclusion, which is going to be better justified ahead, it is automatic to state that the bioplastic behaviour is not a pure invention of Nature, but results by the human work conferring the plastic behaviour to Nature derived materials. Therefore, while the origin can be in a more or less large extent from natural renewable sources, the acquisition of the useful plastic properties is a fruit of the same technology for both the so-called plastics and bioplastics.

Plastic materials were at first produced without considering disposable polymers being not a social problem in the 50–60 years. The increasing production volumes raised later on this problem. Furthermore, the man-made polymers were all effectively optimized as highly resistant to the environment exposure. While this property is outstanding with many applications, it raised some concerns for packaging characterized by short use life and rapid conversion into waste. Biodegradability became then a scientific target for research and now for production of part of plastics. While on the other side, recycling was also started with some success, saving resources was also pressing in the same directions.

The previous consideration starts the attempt of this book to clarify the duality between origin and properties as these two aspects are often used in a misleading way. On the basis of origin one apparently can easily distinguish between natural and fossil derivation, and the molecular structure and properties do not say clearly the real origin in many cases. Indeed, after the discovery of stereospecific polymerization (Giulio Natta 1954 and following years) one could find in the market, next to natural rubber, also oil derived poly(1,4-cis-isoprene) with the same molecular structure and properties of natural rubber. This was the first case in which during the lecture to celebrate the Nobel Price Award, the Professor Fregda could say that "*Nature synthesizes many stereoregular polymers, for example cellulose and rubber. This ability has so far been thought to be a monopoly of Nature operating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly.*" (From Presentation Speech by Professor A. Fredga, Member of the Nobel Committee for Chemistry of the Royal Academy of Sciences for The Nobel Prize in Chemistry 1963; MLA style:

Award ceremony speech. NobelPrize.org. Nobel Media AB 2019. Wed. 24 Apr 2019. https://www.nobelprize.org/prizes/chemistry/1963/ceremony-speech/).

Indeed the polymer synthesized (the poly(1,4-cis-isoprene)) was identical in molecular structure to that extracted from trees.

Then it may be useful to analyse accurately the following Table 2.1 for proposing a more sound classification of the bio-character of the most popular plastic materials.

Even from the limited number of examples reported in Table 2.1, it is possible to argue that the bio-character is very variable in the called bioplastics that often have some common features with plastics from fossil sources. The general trend now accepted is to call bioplastics all the plastic polymeric materials where the constituting macromolecules have one bio feature either origin, synthetic process or property, including the limiting case of two components polymer plastics, PET and polyurethanes (TPU) where one monomer, the diol, can be of natural origin, while the other component, respectively terephatalic acid and diisocyanate, is obtained from fossil products.

Actually all attempts to introduce some bio-character in plastics has to be viewed as a contribution to the reduction of the environmental impact by saving resources even if in some cases can be particularly misleading.

2.3 Measurable Fundamental Entities

The real viscoelastic (plastic) behaviour of a solid material can occur only in a limited range of temperature defined by its characteristic temperatures: the glass transition temperature, T_g, and the melting temperature, T_m. A detailed description of these parameters is out of the scope of the present book and the reader is referred to the relevant literature on the fundamentals of thermodynamic in macromolecules.

Table 2.1 Bio-characteristics of common polymers used as plastics and bioplastics

Polymer	Monomer(s)	Origin	Polymerization	Character	Biodegradable
Polyethylene (PE)	Ethylene	(a) Fossil (b) Nature	Manmade	Hydrophobic	no
Polyethylen terephthalate (PET)	Terephthalic acid Diol	Fossil Fossil or Nature	Manmade	Hydrophobic	Substantially no
Poly (lactic acid) (PLA)	Lactic acid	Nature	Manmade	Hydrophobic	yes (slow)
Poly-3-hydroxy butyrate (PHB)	3-hydroxy butyric acid	Nature	Bacteria	Hydrophobic	yes
Starch	Glucose	Nature	Nature	Hydrophilic	yes

On the other side, it is in our opinion useful at this point to have some practical information about the values of these characteristic temperatures in polymers from fossil or natural origin in relation to the available molecular structures. Providing such information is perfectly in line with the objective of the present book and helps to respond the fundamental question: *"to which extent can nature supplied plastic polymer responding to the society demand for material having plastic properties and a number of other characteristics and performances?"*

A general feature of the molecular structure having a fundamental role in determining the thermal response of the material in terms of transition temperatures is certainly the presence of structural regularity along the main chain. Homopolymers have in general regular structure along the chain formed by a sequence of identical repeating units. However, if the repeating units have a stereo-differentiation site, such as an asymmetric carbon atom, two sterically different units are possible. As the consequence the homopolymer of a prochiral or chiral monomer contains crystallisable macromolecules only in case these are stereoregular, that is contain units of a single configuration (*isotactic polymer*) or units having alternately opposite steric configuration (*syndiotactic polymer*). A random sequence of the two opposite steric configurations provides a non stereoregular (*atactic*) polymer which cannot crystallize.

In case of a prochiral monomer (having the capability to generate repeating units with carbon atoms with four different substituents) such as propylene or other vinyl monomers of general structure $CH_2 = CHR$ with R different from H, the isotactic or the syndiotactic regular crystallisable macromolecules are obtained if the catalyst used is capable of steric control. On the other side with a chiral monomer such as lactic acid, the use of a pure enantiomer as monomer provides an isotactic polymer where all chains contain repeating units of the same steric configuration as the starting monomer. The polymerization of racemic lactic acid can give rise either to a mixture of isotactic chains containing respectively all L- or D—unit chains, or a syndiotactic polymer consisting of units having alternately opposite steric configuration or an atactic polymer when the chain contains both D and L units without any regular distribution.

Polymers containing disordered (atactic) macromolecules cannot crystallize and then they have only a single characteristic temperature, the Glass Transition temperature, T_g, under which the flexible polymer becomes a rigid brittle material similar to glass. The partial crystallization occurring with regular chains gives a two phases material one amorphous and one crystalline, characterized by a T_g and a melting temperature T_m, respectively.

In the study of polymer materials, it is crucial to understand that the glass transition temperature, T_g plays a fundamental role in their behaviour and indeed in their applications. If a polymer is below its T_g, it becomes brittle; on the contrary, above the T_g, it behaves in a rubber-like manner. Thus, the T_g value governs the selection of materials by considering that, in general values of T_g well below room temperature define polymers with elastomeric behaviour (rubber) and values above room temperature qualifies polymers as rigid and tough (for instance PET and PMMA).

This behaviour has to be understood with reference to the structure of polymers that is long chains molecules or macromolecules. Such materials are characterized by a high viscosity in the liquid molten state over the T_m. By cooling the system below T_m, the crystalline state is expected to be the preferential one. However, usually owing to the length of chains, the molecular movement is slow and partially hindered thus avoiding the arrangement of the chains into a complete ordered conformation typical of the full crystalline phase. In this particular condition, the random arrangement characteristic of the liquid fraction survives, at least in small area domains. In these domains the chains behave like in very viscous liquid until the glass transition temperature T_g, at which the movements of chains are locked and the material is considered to be a solid (glass). Below this temperature, the material is rigid and easily breakable.

In polymers formed by macromolecules with a flexible chain (single bonds connect successive atoms along the backbone) the value of T_g depends on the type of side chains (short) and in some extent from the nature of the backbone atoms (Sun 2004). The T_g value increases with increasing bulkiness of the side chains and also with the occurrence of dipole formation as both factor increase the rigidity thus limiting the number of allowed conformations. Additionally, interchain interactions normally are responsible for a further increase of T_g as they provide additional limitations to conformational mobility of chains. One should conclude that the T_g is substantially a molecular property (manly affected by primary structure) even if additional contribution to its numerical values originates from interchain non-bonded interactions, with more evident effect when these lasts are strong.

The effect of the side chain structure on T_g is evident in the data reported in Table 2.2 concerning macromolecules from vinyl monomers, where the repeating units have the general formula –(CH_2-CHR)–. In case of polyolefins (number 1–6 of Table 2.2), the T_g is related to the bulkiness (volume) of the R group as dipolar interactions are lacking because of the paraffin structure. From polyethylene to polypropylene the T_g increases 65 °C by replacing –H with –CH_3, which has a 6 times larger volume. However, by replacing methyl with long linear alkyl chain T_g decreases in spite of the increasing volume due to the increase of the allowed conformations arising from the possibility of having different conformation of the side chains with comparable internal energy. This brings to larger entropy when C–C bonds free rotation is reached. Accordingly, with the replacement of the linear butyl groups with the branched isobutyl (see numbers 5 and 6 in Table 2.2), T_g becomes 50 °C larger due to the reduced numbers of allowed conformers.

The polymer reaches a larger T_g when the C-R bond becomes polarized due to the different electro affinity of the bonded atoms. Then when R = Fluorine (number 7), the T_g is equal to that of polypropylene even if the molar volume of F is one half of the methyl. Furthermore, with Chlorine (number 8), same volume as –CH_3, T_g is 100 °C higher. A different effect occurs in poly vinyl alcohol (number 9) where R = OH, which has a molar volume ½ of the methyl, but the T_g is 105 °C over that of polypropylene. This is a result of the strong interchain hydrogen bonding. Indeed, by eliminating this effect in poly(vinyl acetate) (number 10) the T_g decreases of almost 60 °C. The effect of conformational freedom on T_g is also observed in polyacrylates

Table 2.2 Structure and T_g of polymers with $–(CH_2\text{-}CHR)\text{-}$ repeating unit[a]

N	Polymer	Group-R	Volume of R ($cm^3 \cdot mol^{-1)}$	T_g (°C)
1	Polyethylene	H	3.7	−85
2	Polypropylene	CH_3	25.9	−20
3	Poly-1-butene	C_2H_5	48.1	−24
4	Poly-1-pentene	n–C_3H_7	70.3	−40
5	Poly-1-hexene	n–C_4H_9	92.5	−50
6	Poly-4-methyl-1-pentene	i–C_4H_9	92.0	29
7	Poly(vinyl fluoride)	F	12.1	−20
8	Poly(vinyl chloride)	Cl	22.1	81
9	Poly(vinyl alcohol)	OH	11.1	85
10	Poly(vinyl acetate)	$OCOCH_3$	60.1	28
11	Poly(methyl acrylate)	$COOCH_3$	60.1	6
12	Poly(ethyl acrylate)	$COOC_2H_5$	82.3	−24
13	Poly(*n*-butyl acrylate)	COO–n.C_4H_9	126.7	−55
14	Polystyrene	C_6H_5	92.3	100

[a] Data extracted from Cowie and Arrighi (2007)

as result of the increasing length of the linear alkyl substituent on the carboxylate side chain (number 11–13). Finally, when the R group is aromatic (number 14) the T_g increases remarkably because of rigidity and interchain stackings.

All linear polymers reported in Table 2.2, except for polyethylene, have an asymmetric carbon atom in the repeating unit. This means that, without steric control during the polymerization process, stereo-irregular structures are obtained, and the resulting chains cannot crystallize. As above discussed, homopolymers consisting of regular macromolecules can give rise to partial crystallization, which interests sections and not the whole macromolecule. Therefore, the single chain can be at the same time part of crystalline and amorphous domains. This feature grants a strong interconnection between the crystalline and amorphous phases and leads the elastic behaviour in the temperature range between T_g and T_m.

As for T_g, the melting temperature depends also on the molecular feature of polymers. At the melting temperature the free energy variation, $\Delta G°$, is equal to zero (Eq. 2.1),

$$\Delta G^\circ_m = \Delta H^\circ_m - T_m \Delta S^\circ_m = 0 \tag{2.1}$$

and then, the value of T_m, can be easily seen to depend on the ratio between the enthalpy ($\Delta H_m°$) and entropy ($\Delta S_m°$) changes when the polymer melts (Eq. 2.2).

$$T_m = \Delta H^\circ_m / \Delta S^\circ_m \tag{2.2}$$

Equation 2.2 clearly suggests that the melting temperature of the crystalline phase increases with the stability of the crystalline lattices and with the molecular rigidity of the polymer. However, as observed above, a large chain rigidity is accompanied by a large T_g value. Then T_m and T_g in homopolymers are not independent each other.

The examples provided in Table 2.3 gives an idea about the contribution of crystalline packing stability and conformational rigidity to the transition temperature values of various plastics. Please note that temperatures were reported in centigrade to allow a direct comparison with the living temperature range.

The data in Table 2.3 suggest that the T_g value is closely related to the chain flexibility numerically expressed with acceptable approximation by:

$$\Delta S^{\circ}_{m} / \text{ number of atoms in the repeating unit} \tag{2.3}$$

This value is very high for macromolecules where the rotation around the bonds is not hindered as in polyethylene, and decreases with the presence of steric hindrance and in the presence of heteroatoms when these last give rise to dipole moments or hydrogen bonds.

As far as the melting point is concerned this result from two different contribution, as the value of T_m in degree Kelvin is the ratio between enthalpy and entropy of melting. Then T_m increases with $\Delta H_m{}^{\circ}$ increase and decreases with $\Delta S_m{}^{\circ}$ increase.

Accordingly, both T_m and T_g increase with main chain stiffness as shown in Table 2.4.

By cooling an amorphous material from the liquid state, and by measuring the specific volume as a function of temperature, there is no sharp change in volume or enthalpy even when the system attains the corresponding T_g. Here, there is instead a change in the slope of the curve with a higher value for the liquid than for the glassy state (Fig. 2.1a). The intersection between the two straight-line segments above and below T_g defines indeed the quantity T_g. In the case of crystallizable material by cooling through its melting point, T_m, a volume shrinkage is clearly observed due to the transition of part of the material from the liquid to the more packed crystals. (Figure 2.1b). Below T_m, the specific volume, as well as the enthalpy and the density are almost constant while above the material expands as a liquid (Fig. 2.1b).

Notice that, the straight-lines below T_g for an amorphous material has slope (dV/dT) close to zero, like in solid materials below T_m. In both cases, the molecular movements are hindered because of the low internal energy or for thermodynamic reason, respectively. Above T_g the increase of temperature determines a linear increase of volume, similar to that of crystalline material above T_m, according to the liquid behaviour. In the case of two materials with the same molecular composition, one crystalline and the other amorphous, the T_m of the former is larger than the T_g of the latter and the amorphous one starts to expand during heating at lower temperature. However, if the two materials are both heated up at temperatures larger than the T_m of the crystalline one they exhibit the same specific volume (and density) as well as the same slope of the plots *vs.* temperature.

Table 2.3 Thermodynamic parameters for the thermal transitions of plastics[a]

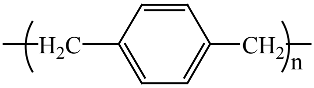
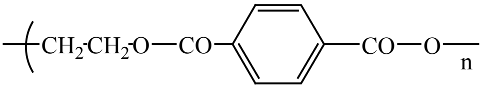
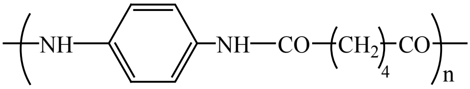
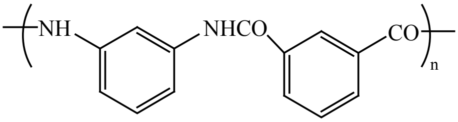
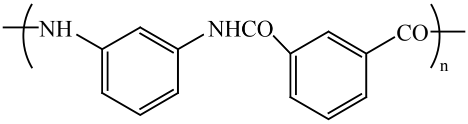
N	Polymer	Monomeric repeating unit (r.u.)	r.u.[b] MW	$\Delta H_m°$ (KJ/mol)	$\Delta S_m°$ (J/mol °C)	T_m (°C)	T_g (°C)
1	Polyethylene	$-(CH_2–CH_2)–$	28	8.2	19.8	147	−85
2	Polypropylene (isotactic)	$-(CH_2–CH(CH_3))–$	42	11.0	24.4	174	−20
3	Polystyrene (isotactic)	$-(CH_2–CH(C_6H_5))–$	104	10.0	19.3	243	100
4	Polytetrafluoroethylene	$-(CF_2–CF_2)–$	62	28.6	4.7	372	–
5	Poly (ε-caprolactone)	$-(CO–O–(CH_2)_5)–$	114	16.9	49.4	69	−60
6	Nylon-6	$-(CO–NH–(CH_2)_5)–$	113	26.0	48.8	258	45
7	Poly (L-lactic acid) (PLA) (isotactic)	$-(O–CH(CH_3)–CO)–$	72	0.7	–	164	60
8	Poly-(-(R) 3-hydroxy butyrate) (PHB) (isotactic)	$-(O–CH(CH_3)–CH_2\text{-}CO)–$	86	–	–	172	55
9	Starch[c]	$-(C_6H_{10}O_5)–$	162	–	–	–	–

[a] Data extracted from F. Ciardelli, E. Passaglia, S. Bronco Polymer and their synthesis In “Encyclopedia of Life Support Systems (EOLSS)”, EolssPublishers, Tokyo, Oxford—UK (2003)

[b] r.u. MW = repeating unit molecular weight

[c] It decomposes at about 200 °C

Table 2.4 Effect of chain stiffness on T_g and T_m[a]

	Structure	T_g (°C)	T_m (°C)
1	$-\!\left(H_2C-CH_2\right)_n\!-$	−85	+147
2	$-\!\left(H_2C-CH_2-O\right)_n\!-$	−67	+66
3		–	About +380
4		+69	+255
5	$-\!\left(NH-\left(CH_2\right)_6-NH-CO-\left(CH_2\right)_4-CO\right)_n\!-$	+57	+255
6		–	About +340
7		+273	About +362 (decomposes)
8		–	About +500

[a] Data partially extracted from Cowie and Arrighi (2007)

Both materials of Fig. 2.1 are ideal materials, one exhibiting only viscous behaviour and the other only crystalline. Examples of this last type exists only for low molecular weight materials which in very large majority give rise to a simple liquid-crystal transition at the melting temperature which is equal to the crystallization temperature. Indeed, polymers when consisting of long ordered chains can crystallize only partially and then have a T_g and a T_m of the amorphous and crystalline coexisting phases, respectively. In the range T_g-T_m they are plastic and exhibit both behaviours, the viscous response of a liquid (amorphous) and the elastic one of the crystals, therefore viscoelastic. Note that the elastic response of the crystalline polymer holds for very modest deformation (few unit percentages) and that of total

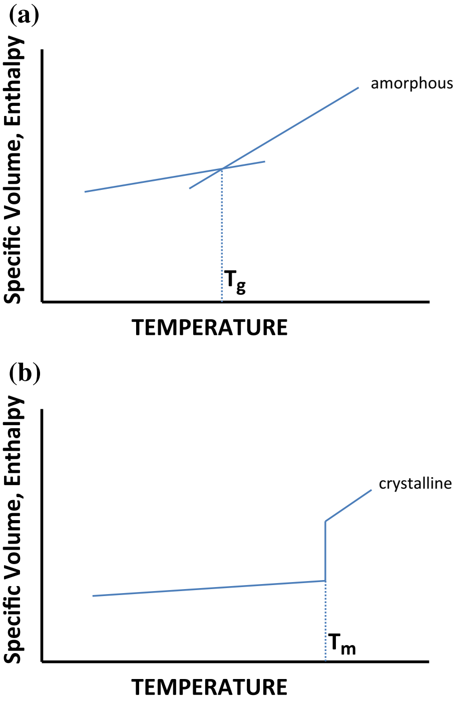


Fig. 2.1 Specific volume dependence on temperature of **a** an amorphous material and of **b** a crystalline material

amorphous material is observed only for vulcanized materials, in which junction points are introduced chemically or physically.

Notice that the term plastic is often used to indicate also fully amorphous polymers that have a single T_g with liquid behaviour over this temperature and brittle properties below the same temperature. These polymers can be shaped at temperature above T_g, by moulding and used below their T_g, but they never show a viscoelastic response as the real plastic material. A typical example is offered by amorphous polystyrene (PS) obtained industrially by free radical chain polymerization. This polymer shows a T_g over 90–100 °C and then at room temperature is rigid, but can be shaped in different items by moulding at 140–180 °C.

Indeed, to be plastic a polymeric material must have a morphology consisting of two phases, one deformable and the other that plays as junctions. This occurs in semicrystalline polymers with an amorphous phase with T_g and a crystalline phase with a T_m or when there are two amorphous phases having distinct T_{g1} lower than T_{g2}. The former material will show a plastic response in the temperature range between T_g and T_m and the latter between T_{g1} and T_{g2}.

Indeed, the real plastic behaviour requests the material to be biphasic, with an amorphous phase and a crystalline phase (Fig. 2.2) or with two immiscible, but compatibilized amorphous phases.

Two distinct T_g temperatures are observed (Table 2.5) in block copolymers and immiscible compatibilized blends of two different polymers. Clearly, in these two

Fig. 2.2 Schematic representation of the change of specific volume of a polymer with temperature T for **a** a complete amorphous sample, **b** a semicrystalline sample

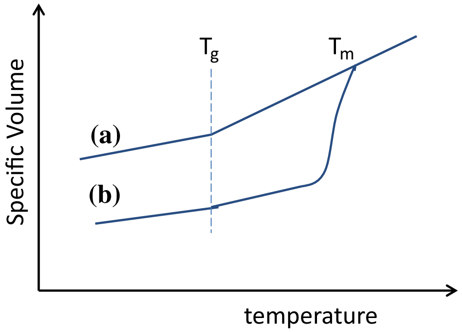


Table 2.5 T_g of a block copolymer SBS mixed with PS[a]

Sample	PS/SBS Composition (w/%)	T_{g1} (°C) (connected to polybutadiene phase of SBS chain)	T_{g2} (°C) (connected to polystyrene phase of SBS e PS chains)
1	100/0	–	116.0
2	80/20	−63	111.1
2	60/40	−60	109.1
4	40/60	−58	94.0
5	20/80	−58	90.0
6	0/100	−64	78.7

[a] Data from Buthaina A. Ibrahim and Karrer M. Kadum Morphology Studies and Mechanical Properties for PS/SBS Blends International Journal of Engineering & Technology IJET-IJENS Vol: 12 No: 03

last cases the plastic behaviour is observed in the thermal region within the two T_g values of the material.

As shown in Table 2.5 the styrene-butadiene block copolymer (SBS, sample 7) has two different T_{gs}; the lower one at −64 °C is connected to polybutadiene blocks and the higher one at 78.7 °C is connected to polystyrene blocks. Thus, sample 7 displays a noticeable elongation behaviour in the thermal range from −64 to + 78.7 °C which can be recovered when the stress is removed. However, over the PS T_g, the material flow as a liquid and is no more elastomeric. The name used for these interesting materials is therefore thermoplastic elastomer. Note that the addition of increasing amount of polystyrene homopolymer (PS), fully compatible with the polystyrene blocks of SBS, from sample 6–2, increases the higher T_g thus allowing to extend the thermoplastic elastomeric behaviour of the material up to 111.1 °C. Clearly, the lower temperature is not affected significantly, as PS is not interacting with butadiene blocks. As we shall see ahead this PS addition gives a variation of mechanical properties to a definite temperature. In other words, the material becomes stiffer. Below 78.7 °C all sample 7–2 are elastic with increasing stiffness from 7–2.

On the other side, each sample loses the viscoelastic behaviour for an almost pure viscous behaviour at temperatures over its own higher T_g.

The dependence of the specific volume of this block copolymer is represented in the Fig. 2.3. Below the lower T_{g1} the material maintains practically the same volume ($dV/dT = 0$) with temperature increase until T_{g1}. For temperature over T_{g1} and below T_{g2} the lower T_g phase undergoes an expansion with dV/dT larger than 0 with a viscous behaviour, while the material with the higher T_{g2} remain rigid. In the temperature range $T_{g1} - T_{g2}$ then we observe a substantially viscoelastic response (plastic). Over T_{g2} the material loses the elastic response and is now a viscous liquid.

The typical biphasic morphology of a block copolymer composed of two amorphous phases is sketched in Fig. 2.4 over a draw representing a picture obtained by electronic transmission microscopic analysis of a SBS copolymer. The small white spheres are the phase formed by the rigid PS segments, while the yellow background is the soft polybutadiene phase. This latter provides elasticity to the materials thanks to the presence of the junctions made of the hard PS block, which has the highest T_g. The material will then show a mechanical behaviour typical of semicrystalline polymers. Notice that, if the rigid phase is larger by volume than the soft one, the material will result as a high impact rigid product.

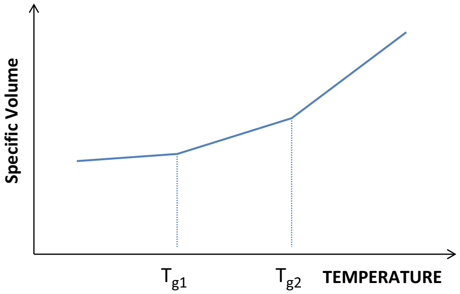


Fig. 2.3 Change of specific volume with temperature for a biphasic (amorphous-amorphous) material

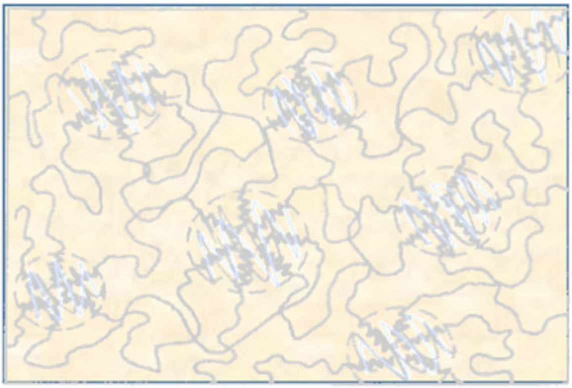


Fig. 2.4 Biphasic morphology of a block copolymer with two noncrystallizable segments. Representation of elastoplastic block copolymers, showing areas of aggregation of the glassy blocks, joined by the amorphous rubber-like chains is superimposed a draw representing a SEM image of a SBS copolymer

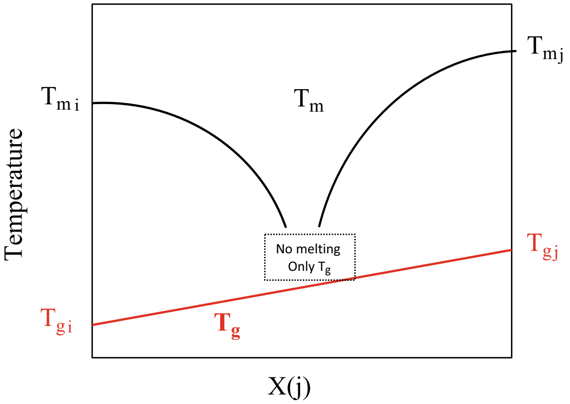


Fig. 2.5 Behaviour of transition temperatures for a random copolymer with respect to composition

From the above analysis regarding the transitions temperatures in relation to the molecular structure, it is possible to go deeper in understanding the possibility of modulation of the characteristic temperatures of polymers and then the range of applications as plastics. The Fig. 2.5 shows the variation of T_m and T_g with composition of a random copolymer of the two monomers i and j, the respective homopolymers poly-i and poly-j having respectively T_{gi}, T_{mi} and T_{gj}, T_{mj} transition temperatures.

The T_g of the copolymer assumes clearly an intermediate value between the T_{gi} and T_{gj} of the two homopolymers with a substantially linear dependence on copolymer composition. In a very preliminary, but practically useful way, the variation of T_g with composition can be described by the equation of Fox (Eq. 2.4)

$$1/T_{gij/} = W_{i/}/T_{gi/} + W_j/T_{gj/} \tag{2.4}$$

where W_i and W_j are the weight fractions of the monomers i and j in the random copolymer, respectively.

The melting temperature of the copolymer decreases exponentially from the value of the T_m of the homopolymer of the prevalent monomer in composition, according to Eq. 2.5.:

$$1/T_{mij} - 1/T_{mi} = (R/\Delta H_m)\ \ln X \tag{2.5}$$

where X is the mole fraction of the prevalent monomer in composition.

In the central region, when the two monomers are present in comparable amount the polymer is not crystallisable because of the highly disordered structure of the macromolecules and therefore there is no T_m (Fig. 2.5).

One should also remember that in addition to the above change in the transition temperatures the copolymer shows in general lower crystallinity degree than the corresponding homopolymers.

Similar modulation of the transition temperatures can be observed in compatible blends of two homopolymers as well as in mixtures of polymers with low molecu-

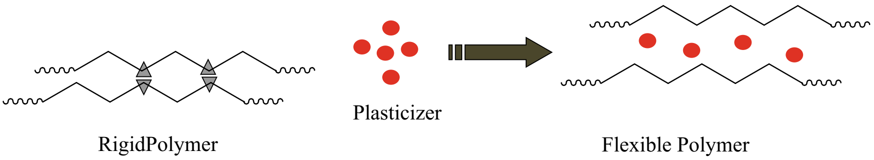


Fig. 2.6 Schematic mechanism of plasticization

lar weight compounds (plasticizers) that are typically used to reduce the T_g of the material.

This last example is really important as it accounts the plasticization concept: the use of a low molecular weight additive (plasticizer) characterized by a low T_g value to be blended (as completely miscible) with a polymer, generally grants the obtainment of a material characterized by a single T_g decreased with respect to the value in pristine polymer. Plasticization, when effective, generates: the lowering of temperature, at which substantial chain deformations occurs, the decrease of the rigidity of polymer at room temperature, the increase in the elongation at the break and in the toughness (impact strength) (see following paragraph). Plasticizers mixed at molecular level with polymer chains and, by locating in between the polymer chains, reduce the inter macromolecular forces thus increasing the freedom of polymer chains to move (Fig. 2.6). A lower temperature is thus required to stop the polymer from moving, which means lowering the T_g. Classical example of plasticizer is the bis-(2-ethylhexyl) phthalate (DOP), used to plasticize the polyvinylchloride (PVC).

2.4 Mechanical Properties

The title properties are here presented in a much-finalized way aimed at evidence some basic mechanical feature of the most intuitive mechanical properties and how they are correlated to structure at molecular level. Indeed, in the previous section dedicated to thermal properties, a picture was provided on the relationships between thermal transition of a polymer and its behavior as plastic material. Here we wish to show that within the plasticity temperature range, the material is characterized by a response to mechanical stimuli in a quantitative way determining the most suitable application (Sperling 2006).

When talking about mechanical properties, we meet words such as strength, toughness, and ductility as well as deformation (elongation) which are to be considered all mechanical properties. Their definition and correlation with structure and temperature are the subject of this section.

What is interesting to know is the behavior of a polymer material when subjected to an external stress having a certain force and application way. The *tensile* strength is measured for a material that is going to be stretched or under tension. The *compressional* strength of a polymer indicates how much it supports weight

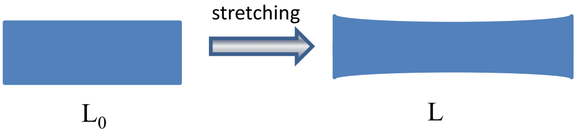


Fig. 2.7 Schematic representation of polymer sample subjected to stretching in a tensile machine

from underneath. Similarly, *flexural* strength *and torsional* strength, respectively, indicate how the material quantitatively reacts to bending or twisting deformation. Finally, the *impact* strength indicates the quantitative response of a polymer sample has suddenly beaten as with a stone or a mace.

To measure the tensile strength, the polymer sample with a shape of strip or dog-bone (Fig. 2.7) is stretched with a machine which clamps each end of the sample, then, stretches the sample. During the stretching, the machine measures the amount of force (F) that it is exerting. The *stress* that the sample is experiencing is obtained by dividing F by the cross-sectional area (A) of the sample and has clearly the physical dimensions of a pressure, units of force divided by units of area, usually N/cm^2. Stress and strength can also be measured in megapascals (MPa = 100 N/cm^2).

$$\sigma = F/A \tag{2.6}$$

By increasing the amount of force, the sample is stressed until it breaks. The stress needed to break the sample is the *tensile strength* of the material.

Similar tests can be performed for compressional or flexural strength. The corresponding strength is the stress needed to break the sample. The above tests indicate the stress a sample can support before breaking with application of a specific force, but it is not an indication of how the material has modified its form during the test. During a tensile stress test, the sample deforms by stretching, becoming longer and its deformation is called elongation. Elongation is expressed as percentage of deformation and it is the length the polymer sample after deformation (L), divided by the original length of the sample (L_0), and then multiplied by 100.

$$\frac{L}{L_0} \times 100 = \text{elongation}\,(\%) \tag{2.7}$$

Two important values are the *ultimate elongation* and the *elastic elongation*. The former indicates the amount of stretch reached just before the sample breaks. The latter is the percent elongation that is possible to attain without permanently deforming the sample. That is, the deformation can be obtained still having the sample the capability to recover back the original form once removing the stress. A reference quantity to compare how different plastics material resist deformation, is provided by the *modulus*. It is defined as the proportionality constant between stress ($\boldsymbol{\sigma}$) and elongation (L) in the range of linear dependence of the two physical quantities:

$$\sigma = \mathrm{E} \times \mathrm{L} \tag{2.8}$$

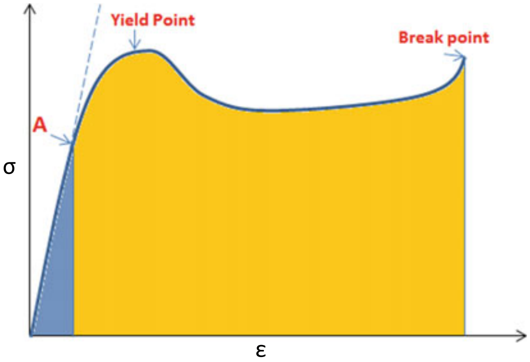


Fig. 2.8 Idealized stress-strain curve for a plastic polymer material (blue area corresponds to the energy of elastic deformation and orange area is the energy of plastic deformation)

The modulus is usually indicated with the letter E. The plot σ *vs* L is called a stress-strain curve. The height of the curve when the sample breaks is the tensile strength and the tensile modulus is the slope of this plot measured at the beginning of the plot. If the slope is abrupt, the polymer is characterized by a high tensile modulus (E), and it is able to resist stretching occurring only with low deformation. If the slope is gentle, the polymer is characterized by a low tensile modulus and it is easily deformed to high deformation. Except rare cases, real plastics do not show long linear segments of deformation, and in general, the curve appears as that in Fig. 2.8. Linear deformation occurs only up to point A. By increasing the stress force over the value corresponding to the point A, the materials starts do deform easier and easier reaching the Yield point where it deforms at constant applied stress. In the following, the deforming energy do not change abruptly but the materials continue to deform up to the Break point (Fig. 2.8). The modulus should be, and in general is, calculated in the region of linear dependence of elongation from stress. While the elongation is a pure number, the physical dimension of modulus has the same units as pressure, such as N/cm^2.

The examination of the idealized deformation curve of a plastic material when increasing stress, allows understanding the meaning of the two distinct areas before and after the A point. The area of the rectangular triangle underneath the lineal part of the stress-strain curve (covered with blue color in Fig. 2.8) gives a measure of the material *toughness*. It is the energy that can be recovered if the stress is removed and in the case the material breaks at A, it indicates the energy necessary for brittle fracture also. This occurs if the material does not undergo a further elongation after the elastic region that is from the point A to the Break point. During the elongation from points A to Break the sample becomes thinner and part of the applied energy is dissipated. The area underneath the elongation curve covered by yellow color where elongation increases without increasing stress measures the energy for though fracture.

Beyond to the Yield point the deformation is no longer elastic. Actually in the linear region below the yield stress the deformation, which always mainly regards the amorphous part, is hindered by the presence of rigid crystallites that act as physical crosslinking points. When the crystal resistance is destroyed the macromolecules flow without hindrance as a liquid, resulting in large sample deformation that includes elongation and narrowing (see Fig. 2.7). At this step, if the stress is removed the initial shape cannot be recovered.

As mentioned before, a very rigid material breaks just after the Yield point. In this case, the area underneath the total curve is not large, lacking the extended zone, and the energy that can be adsorbed by the material is low. The force (stress) necessary to break such strong material is usually large and accompanied by very small deformation. The corresponding triangle area, evidenced by blue color in the Fig. 2.8, is not large; this means that the energy for brittle fracture is also small.

A material like this is strong, can support remarkable stress, but cannot deform very much, and breaks if deformed to larger extent. It is called *brittle*.

Materials, which can undergo remarkable elongation after the Yield point, are characterized by a very different stress-strain behavior. The area underneath over the yield point is larger than the area under the linear deformation region, thus showing that they absorb much more energy before fracture with respect to brittle materials. They can absorb more energy than the samples that breaks at the yield point. These samples are therefore strong and tough at the same time and deformation allows a sample to dissipate energy. If a sample cannot deform, the energy cannot be dissipated, and the sample is broken. For most applications, it is preferred for a material to bend than to break, because bending, stretching or deforming prevents the material from breaking. So when a designing new polymer material with plastic properties, the attempt is toward reducing the strength in order to make the material tougher.

This last behavior is typical for a polymer material in the range of plasticity, that is in the interval between T_g and T_m, in case of semicrystalline polymers, and within the two amorphous phases in case of block copolymers and compatibilized blends. At temperatures below T_g in the former case or below the lower T_g in the latter case, all the materials are brittle as glass, whereas over T_m, or the higher T_g, they behave as viscous liquid.

The comparison of the typical stress-strain curves for different kinds of polymers shows that a rigid plastics (high T_g) such as polystyrene, poly (methyl methacrylate) or polycarbonate and some polyamides can resist to stress, but cannot withstand much elongation before breaking. Consequently, the area under the stress-strain curve results modest and they are strong because of the high stress resistance, but not very tough because of the low elongation. In case of these polymers the slope of the plot is very steep as the elongation before reaching the Yield point is low and the force to deform the rigid plastic is rather high meaning that the material has a high modulus. This implies that the polymer is resistant to deformation with consequent relatively low toughness thus giving a brittle material. In case of semicrystalline polymers like as polyethylene and polypropylene consisting of more flexible macromolecular backbone, the stress-strain curve shows a low resistance to deformation thus requesting a lower force to attain the Yield point with respect to the above-mentioned materials. However, the deformation is slightly larger than the one of brittle polymers, and a higher deformation before breaking is usually reached. Initial modulus is high; they resist to deformation but if enough stressed they eventually deform. The polyolefin flexible plastics are not as strong as the rigid ones, but much tougher.

It is possible to modify the stress-strain behavior of a plastic with addition of a certain amount of compatible low molecular weight molecules, which are called *plasticizers,* as previously preliminary discussed. Plasticizers render the polymer more flexible as for instance in the case of poly (vinyl chloride), PVC. In absence of plasticizers it is a rigid plastic successfully processed to produce rigid water pipes. However, by addition of a significant amount of plasticizers, PVC becomes more flexible and it is used to make soft and even inflatable items.

These considerations refer to tensile properties whereas different observations are often made when dealing with compressional properties or flexural properties. Thus, fibers have very high tensile strength and good flexural strength but usually show low compressional strength. Oriented fibers are strong when pulling in the fiber direction and weak when pulled at right angle with respect to the same direction.

From the above discussion, it appears that the mechanical response of a homopolymer depends on the chemical structure of the repeating units. However, it is necessary to remind that the material properties, including clearly mechanical properties, are also dependent on additional molecular parameters typical of macromolecules such as molecular weight, molecular weight dispersion and stereoregularity. In addition, as indicated for the thermal properties, a series of modulated molecular modifications can be used by preparing copolymers of different repeating units and controlling their distribution along the chains.

Moreover, in semicrystalline plastics the degree of crystallinity is markedly affecting mechanical response. Indeed, with increasing crystallinity the material becomes more rigid with a substantial linear increase of the modulus and reduction of elongation at break, yielding a stronger, more brittle material. The effect of crystallinity and crosslinking on mechanical properties can be evidenced by mechanical tests performed as a function of temperature. In Fig. 2.9 the tipical behaviour of three polymer materials, one amorphous, a second amorphous but crosslinked (vulcanized

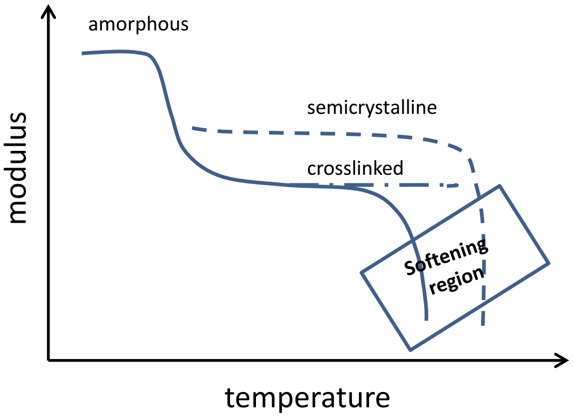


Fig. 2.9 Effect of temperature on mechanical response of amorphous, semicrystalline and crosslinked polymer

rubber) and the third a semicrystalline one, all with the same chemical composition are compared.

At low temperature all materials have comparable modulus. As the temperature approaches T_g, the two atactic amorphous polymers (linear and crosslinked) undergo a sharp decrease in modulus, while the decrement is much smaller for the semicrystalline polymer (dashed plot). By further increasing the temperature just above T_g the modulus of the amorphous noncrosslinked material decreases abruptly, the materials stop to behave like a solid and starts to flow. Notice that, the crosslinked one (dash dotted plot) after the modulus jump at T_g maintains a stable modulus. Indeed, flowing is prevented by the presence of crosslinking (inter-macromolecular bonds). The semiscrystalline polymer, not only has a larger modulus after the jump at T_g than the two amorphous materials because of the rigidity owing to crystalline phase, but also becomes a liquid only above T_m. This figure illustrates clearly that under T_g all the three polymers have high resistance to deformation, and between T_g and T_m only the semicrystalline sample has a plastic behaviour being an intimate combination of a crystalline (that provide elasticity) phase and a liquid (viscous) phase, the synergic response of the two different phases being granted by the strong interfacial adhesion due to the participation of macromolecules to both amorphous and crystal phases; if they are long enough a single macromolecule pass through different domains.

Additionally, a further broadening of the properties requested can be reached by combining in a more or less compatible extent, two polymers with different properties to get a new material with some of the properties of both or with mediated properties.

In case the two polymers are both plastics, the complex material obtained is a blend, which can show intermediate or doubled properties depending on the degree of miscibility and interface adhesion between the two more or less compatible starting homopolymers.

As an example Aranburu and Eguiazábal (2015) showed some interesting mechanical features of the blends of polypropylene (PP) and polyamide-12 (PA12) compatibilized with maleic anhydride-modified copolymer (PP-g-MA) (20% with respect to PP). In addition to the strength resistance due to the additive result of the blend components, extra effect was observed due to a nucleating effect of the PA12 for the PP crystalline phase, particularly in the case of PA12 rich blends. In addition, a slight drop in the PA12 crystallinity was observed in blends rich in PP. The synergistic effect was not observed in the non-compatibilized blends, where a larger dispersed phase size was present. The above-mentioned example clearly shows that by blending it is possible to make materials with mechanical properties ranging in a wide interval, the ultimate value depending on the blend composition.

An additional example of compatibilised blends with properties depending on the composition of two different polymers, namely PE and PET is following discussed. In this case (Fig. 2.10) both elongation at break and Izod impact strength were modulated by playing with the ratio between the two blend components.

Maleic anhydride functionalized ethylene-octene (PO-*g*-MAH) copolymers were used as compatibilizer precursors in post-consumer PET/PE blends. The composition of the non-compatibilized blend was 70% by weight of post-consumer PET and 30% by weight of post-consumer PE. The compatibilized blends were prepared by keeping

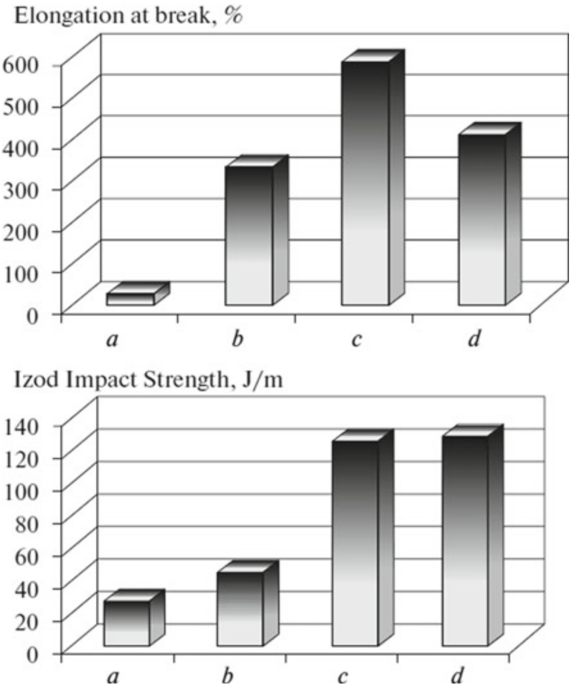


Fig. 2.10 Tensile and impact properties results about non-compatibilized PET/PE 70/30 blend (**a**) and compatibilized PET/PE/PO-g-MAH 70/20/10 blends with MAH content of 0.3 (**b**) 1.0 (**c**) and 1.5 (**d**) wt% (Reprinted by permission from Springer Nature, from Coltelli et al. 2009)

constant the ratio between the polymer components PET/PE/PO-*g*-MAH 70/20/10 and by changing the content of compatibilizer. The SEM analysis showed a dispersed-like phase morphology for all samples but the dispersed phase diameter was lower and the level of adhesion better as the anhydride content in the compatibiliser was larger.

The tensile tests showed an increase in the stiffness by increasing the amount of the MAH derived functionalities thanks to the formation of grafted PO-*g*-PET copolymer that provide chemicals bonds between the two phases of the blend. The general improvement of adhesion well explain the more ductile behavior (b and c blends) in blends with intermediate MAH content (1%). Indeed, when the PO-*g*-PET copolymer amount is too much (d blend), the material become very stiff and thus brittle. However, the biphasic morphology allows not losing Izod impact strength even in the stiff and brittle blend.

The blending approach so far described for fossil-derived polymers can be used for modulating even the mechanical properties of typical bioplastics. Tough poly (lactic acid) (PLA) and soft poly(butylene adipate-co-terephthalate) (PBAT) can be blended, for example, by conventional methods to biodegradable plastics for industrial packaging applications. Through the control of the effect of the processing at high temperature on the molecular weight distribution, morphology, and thermo-mechanical properties of both homopolymers, as well as the PLA/PBAT 75/25 (B25) blend can be tuned. Notably, the yielding PLA/PBAT mixed chains (copolymers) was observed during blending at different processing conditions in temperature (range of 150–200 °C).

As in the case of blends compatibilized with increasing amount of a third components, also in the case of increasing amounts of compatibilising copolymers formed in situ by reaction of PLA with PBAT, improved phase dispersion and increased ductility is observed. These properties are followed by a faster PLA degradation. On the other hand, if a reduced degradation rate is desired, it can be attained by promoting the formation of less copolymer. In this case, at the same PLA/PBAT ratio the materials have higher modulus, thanks to less effective dispersion of the soft phase (PBAT) into the PLA matrix (Fig. 2.11).

The latter aspects are maximized in thermoplastic composites obtained by dispersing in a plastic polymer, named continuous phase or matrix, a non-plastic material such as minerals, metals, crosslinked organic powder or fibers. These latter acts as a second insoluble dispersed phase interacting with the matrix only by interfacial adhesion. The two materials remain distinct but the interface adhesion gives them the capability to respond to mechanical stress as a single material (Thermoplastic composites).

Examples include fibers that are used as reinforcement in thermoplastic polypropylene (PP) matrix. The modulus of fiber-reinforced PP composites is usually

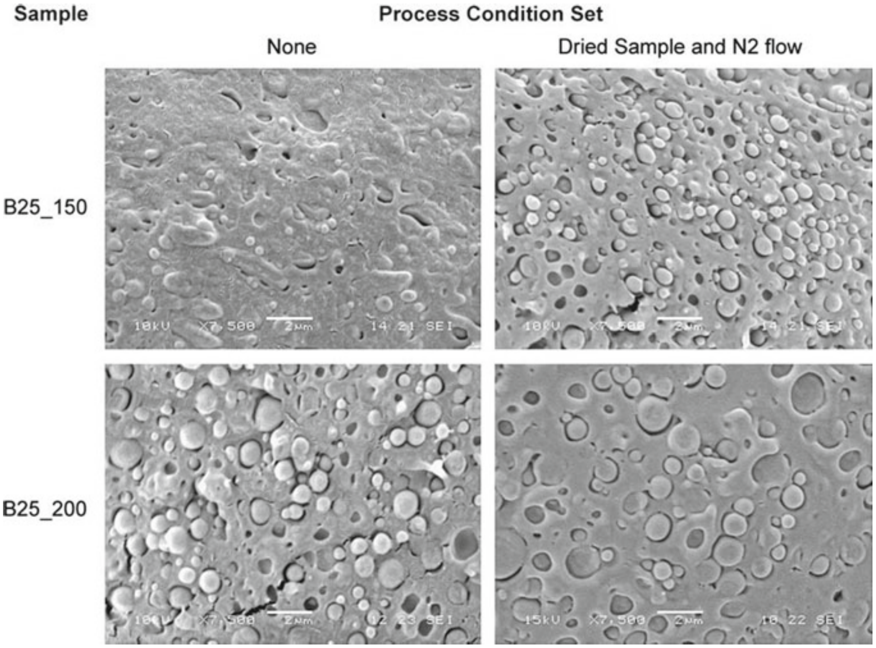


Fig. 2.11 SEM micrographs of cryogenic fractures of PLA/PBAT 75/25 (B25) blends prepared at 150 and 200°C in different conditions (bar dimension: 2 mm) (figure from Signori et al. (2009). Reprinted by permission of Elsevier)

higher than that of the matrix, however, no loss of elongation at break is observed in the case of well compatibilized formulations. To this aim fiber, treatments are often carried out to improve the adhesion between fiber and PP. In any case, the actual properties of composites are strongly affected by the mechanical properties of the dispersed phase, as well as by its surface properties, aspect ratio, size, and in the case of cellulose fibers their origin (Table 2.6).

The tensile strength of polypropylene (in the range of 20 MPa) results increased by the presence of fibres in the composite material as reported in the Table 2.7. E-glass/PP composites are characterized by better performances than that of natural fibers/PP composites. Among natural fibers/PP composites, flax fiber/PP composites have highest tensile and bending properties in agreement with the fiber's strength: among the natural ones the flax has indeed the highest tensile strength.

Table 2.6 Mechanical Properties of natural and synthetic fibres[a]

Origin	Type of fiber	Tensile strength (MPa)	Young's modulus (GPa)	Density (g/cm^3)
Natural	Flax	345–1035	27.6–45	1.43–1.52
	Silk	650–750	16	1.3–1.38
	Kenaf	930	53.0	1.5
	Sisal	511–635	9.4–15.8	1.16–1.5
	Softwood	100–170	10–50	1.4
	Hardwood	90–180	10–70	1.4
	Cotton	380–585	4.5–12.6	1.5–1.54
	Jute	393–800	13–26.5	1.3–1.45
Synthetic	E-Glass	1800	69.0–73.0	2.5
	HM carbon	2400	380	1.95
	Kevlar 49	3000	130	1.45

[a] Data from Shubhra et al. (2013)

Table 2.7 Mechanical properties of PP composites with natural and synthetic fibres[a]

Kind of fiber	Composition PP/fiber	Tensile strength (MPa)
Flax	90/10	45–50
Flax	50/50	55–60
Silk	90/10	45–50
Wood	90/10	30–40
Bamboo	90/10	30–40
Jute	80/20	40–50
E-glass	50/50	80–90

[a] Data from Shubhra et al. (2013)

2.5 Rheology and Processing Features of Plastics

In the previous sections, material properties were described with reference to the typical features necessary for a polymer to be considered plastic. The use of this material for make items to satisfy the Society needs passes through a production process. This usually consists of one or more steps where the material is molded while it is liquid or almost liquid. In the case of semicrystalline polymers, this means heating the polymers above T_m, while the amorphous part must be far above T_g, where is able to flow. The science studying the behavior of materials underflow is called Rheology. In this paragraph, some basic features of the material are therefore summarized to introduce the reader in the field of Rheology.

The determination of the rheology parameters of a polymer material is important to select the appropriate processing to form the desired objects, as well as to set the operating parameters during the transformation. For instance, based on the rheology response of a polymer it is possible to verify if it is suitable for making fibers or for being converted in a bottle by blown molding (see Chap. 4). This requests to know not only the viscosity of a materials but also how it depends on temperature and shear. Indeed, during processing liquid are forced at high speed and pressure into mold and often the liquid must stand deformation by elongation. The ability to deform without breaking is a peculiarity of polymer liquid due to the presence of long chains. Macromolecular systems in the liquid molten state cannot be considered Newtonian liquid as the viscosity depends on the shear rate. In particular, usually the viscosity decreases as the shear rate increases. This behavior is named shear-thinning and is a typical "finger-print" of long polymers. The decrease in the viscosity is observed when polymer chains are aligned in the flow direction so that flow resistance is lower and less energy is required to make the liquid flowing.

The study of rheological behavior is more properly known as rheometry, although the term rheology is frequently used. Rheology puts in relation the flow/deformation behavior of a material with its structural features (e.g., the orientation and elongation of polymer molecules), when the flow/deformation cannot be described by classical fluid mechanics.

The rheometry is performed by imposing a specific stress field or deformation to the fluid, and monitoring the resultant deformation or stress. The corresponding instruments can work in steady flow or oscillatory flow, in both shear and extension. Plastic polymers are molecular materials and the viscous response in addition to macroscopic parameters is influenced by the monomeric units structure, chains length (molecular weight) chain length distribution and branching. Additional effects are exerted by additives and fillers that are discussed ahead and are often present in practical formulations.

For instance, the addition of fillers to a neat polymer melt changes its rheological response, particularly at low shear rate value (Table 2.8) where the viscosity is higher than the one of the net LDPE due to the friction among the irregular shaped particles. Particle interactions increase the non-Newtonian range also and cause it to occur at a lower shear rate than for the unfilled polymer melt. The effect of the filler decreases

Table 2.8 Viscosity versus shear rate for unfilled and filled LDPE[a]

Shear rate $\dot{\gamma}$ (1/s)	Viscosity LDPE filled (Pa s)	Viscosity LDPE neat (Pa s)
$1E^{-4}$–$1E^{-3}$	$7 \times 10^6 - 8 \times 10^5$	1×10^4
$1E^{-3}$–0.01	$8 \times 10^5 - 9 \times 10^4$	1×10^4
0.01–1	$9 \times 10^4 - 1 \times 10^4$	$1 \times 10^4 - 8 \times 10^3$
1–1000	$1 \times 10^4 - 3 \times 10^2$	$8 \times 10^3 - 1 \times 10^2$

[a] Data from Understanding Rheology of Thermoplastic Polymers, TA Instruments, page 3, AAN013]

at high shear rate where the matrix contributions dominate. At high shear rate, the net and filled fluids have similar viscosity and the same dependence on the shear rate. The fluid behavior is dominated by the alignments of the polymer chains.

The alignments of chains occurring under shear either in net polymers or in composites affected also the final properties of the ultimate products. For instance, items obtained by processing at higher shear rate have higher stiffness but lower elongation at break than a similar items obtained at lower shear rate.

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Chapter 3
Molecular Structure Requirements

3.1 Introduction

This chapter is devoted to discuss the role of the molecular structure of the macromolecules forming the polymer in order to reach the requirements for achieving the appropriate properties necessary for plastic behaviour (Billmeyer 1984). Clearly being plastics materials formed by a molecular assembly, the isolated macromolecular structure is not the only parameter to design a final property. Then the macromolecular structure is related to the material characteristics determined by a complex relation, which depends on a series of additional parameters (Callister 2007).

The Hierarchy of Structural Order in polymers affecting the ultimate properties:

1. **Primary Structure**: Determined by the preparation method dictates the molecular arrangement of atoms in the macromolecule deriving from type and number of monomeric units, their number (molecular weight) and sequence distribution, and their stereochemistry leading to macromolecular stereoregularity. Ordered structures are referred to chains consisting of identical repeating units (one or two monomeric units).
2. **Secondary Structure**: Indicates the spatial three-dimensional disposition of the repeating units composing the macromolecular chain. An ordered secondary structure is that where the repeating units are superimposable by translation or by translation of a fixed entity and rotation around a fixed angle.
3. **Tertiary Structure**: Indicates the spatial three-dimensional disposition of a macromolecular chain consisting of blocks with various, ordered and/or disordered secondary structures.
4. **Quaternary Structure**: Describes the supramacromolecular arrangement as a combination of ordered chain blocks with the same secondary structure (leading to crystalline phase) and of different conformations (leading to the amorphous state). The combination of quaternary structures is indicated as morphology of the material.

F. Ciardelli et al., *Polymers from Fossil and Renewable Resources*,
https://doi.org/10.1007/978-3-319-94434-0_3

Thus the chapter has the objective of providing indication on how the molecular structure must be selected in order to control the above parameters. It follows from a practical viewpoint the general related concepts reported in the previous Chap. 2: the objective is to give a description of the available polymers that can be considered having plastic properties in the broad general sense accepted today. However, as it has been anticipated, the use of the plastic materials is very complex in the present society. To contribute to better understanding this concern, the focus will be on the correlation between the quantitative value of the basic entities described in Chap. 2 and the corresponding application. Again the need of both structural and functional properties will be stressed in relation to the final use to which each plastic material is directed.

The presentation includes, according to the aim of the book, both polymers from fossil source and those related to the biological word and derived from renewable sources (Gandini 2008). The molecular structure as reference parameter is clearly derived from the background of the authors, but it has to be regarded as the lecture key for a more realistic understanding of the possibility offered from man-made and nature-made polymers in solving life problems in the area of plastic materials. This brings to the evidence that final performances are clearly determined by the formulation of the basic molecular material with appropriate additives in a blend where molecular differentiation and structural complexity are combined and optimized to the applicative objective.

The present situation is, indeed, aimed to attempt the replacement of man-made polymers from fossil with bio-related polymers and polymers derived from renewable sources. Indeed, the polymer world has reached high technology level with material from fossil origin that today consists of a variety of molecular structures resulting from man-made synthetic approaches. Now the need of saving resources and reducing environmental impact requires a more extended involvement of material from renewable sources and the need of biodegradability in order to reduce waste disposal problems. Attempts in this direction are reported here after having described what man-made plastics from fossil can offer in order to have a picture of the problem at molecular and performance level.

In particular, the present world is characterized by a large number of items that are produced from a variety of plastic polymers from fossil origin for an increasing number of very basic to highly sophisticated applications. Molecular differentiation of the constituting macromolecules plays a remarkable role in addition to structural complexity of blends and composites.

While the structural complexity approach, blending, plasticization and filling can clearly be used for extending the property range of bioplastics, the molecular differentiation of the basic polymer is more limited for this last group. Indeed, only few bio-originated macromolecules, such as bacterial polyalkanoates are produced by nature and can be used as starting materials for producing plastics through the processing already established for plastics from fossil origin. Additional routes to bio-based plastics can arise from the use of monomers from natural renewable sources, which can be further converted into macromolecules according to polymerization procedures invented by man and used for traditional synthetic monomers.

Interestingly, two different situations can arise. In the former case, the monomers from natural sources are new for traditional plastic industry, even if chemically polymerizable as the ones already existing. Consequently, also the polymers obtained are new and can keep some specific properties connected to the origin from natural sources, such as, for instance, biodegradability. A typical established example is the monomer lactic acid produced from corn and converted by already known polymerization processes into a valuable biodegradable plastic material. In the latter case, the monomers from renewable sources are molecularly identical to monomers from oil and then by polymerization they provide the same identical polymer with the advantage of reducing the environmental impact. The first example of this latter class is provided by ethylene from fermentation of ethanol that can be polymerized to a broad class of polyethylene plastics with the same properties of traditional polyethylene, but saving oil resources.

In the following pages, Sect. 3.2 is then devoted to present the molecular structure and related basic properties of plastic from fossil origin that have originated many large-scale application opportunities being now a reality of the acquired style of life that cannot be given up. The creation of these plastics was made possible by man through the synthesis from oil of different monomers that are converted into plastics according to invented polymerization processes that lead to the molecular structure designed for determined ultimate applications. The successive Sect. 3.3 reports examples of various bio-related plastic materials showing improved environmental properties as derived from renewable sources and in some cases with significant biodegradability. The comparative analysis of these two groups of plastics with different origins with reference to their availability and properties is of basic relevance to help understanding how and where traditional plastics from fossil origin can be conveniently replaced by plastic from renewable sources, which are known to the general public as bioplastics.

Two successive sections of this chapter are then devoted to describe the former (plastics) and the latter (bioplastics) group, respectively. The description will be at the same time informative about structure, properties and application of the available materials in the two classes with critical comments aimed to evidence essential features connected to molecular structure differentiation in relation to the opportunities offered by man and nature.

3.2 Fossil Resources Derived Polymers

The chemical structure of most common plastic polymers from fossil origin is here described as examples for relating structure to plastic properties and consequently to number and type of uses.

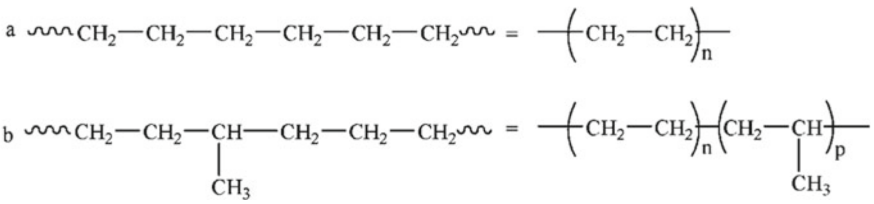
3.2.1 Polyolefins

(a) *Ethylene Polymers*

Polymers of ethylene were produced in 2018 in the impressive amount of more than 100 million tons. The original homopolymer, the polyethylene (abbreviated PE) or polyethene (IUPAC name polyethene or poly(methylene)), is actually containing in addition to the predominant dimethylene units derived from the opening of the double bond, which would bring only to –CH_2 groups, also substituted carbon atom units depending on the polymerization process. Therefore, different material properties are obtained by selecting the initiator and then the polymerization process, even if starting from the same monomer ethylene. As the consequence, the molecular structure of the constituent macromolecules of ethylene polymers is not univocally defined even if the predominant section of the chains blocks is formed by sequences of different length of methylene groups (Fig. 3.1a). The structurally regular blocks with an adequate length (more than 100 –CH_2 groups) can be organized in a regular three-dimensional arrangement giving crystalline parts with the highest melting point. However, sequences with short blocks of methylenes connected by units with short branching (Fig. 3.1b) can be also found. The accommodation of the branched units in the three-dimensional structure of crystals results in defects in the regular three-dimensional structure with lowering of the melting point. Chain portion with a high content of branches can suppress crystallinity as they cannot be organized in some regular spatial arrangement.

In the regular methylene chains, the low steric hindrance of the H-atom substituents on each backbone carbon atom generates a zig-zag planar conformation of the linear chains. Macromolecules in such conformation can be packed in a very dense crystalline structure (Fig. 3.2), thus providing a material with the highest density among ethylene polymers.

The most linear polyethylene prepared by Ziegler–Natta catalytic processes can reach high crystallinity degree (around 60–70%) and then a density of about 0.96 g/cm^3. Such ordered packed structure provides a large number of optimized hydrophobic interactions thus making energy expensive the separation of the chains to obtain a disordered system; therefore, a significant melting enthalpy is characteristic of linear polyethylene. This high enthalpy is flanked by a high entropy increase going from the rigid packed crystals to the linear individual chain, where the low



$$\text{a} \sim CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2\sim \;=\; {-}\!\left(CH_2{-}CH_2\right)_n\!{-}$$

$$\text{b} \sim CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}CH_2\sim \;=\; {-}\!\left(CH_2{-}CH_2\right)_n\!\left(CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\right)_p\!{-}$$

Fig. 3.1 Structure of long blocks in ethylene polymers

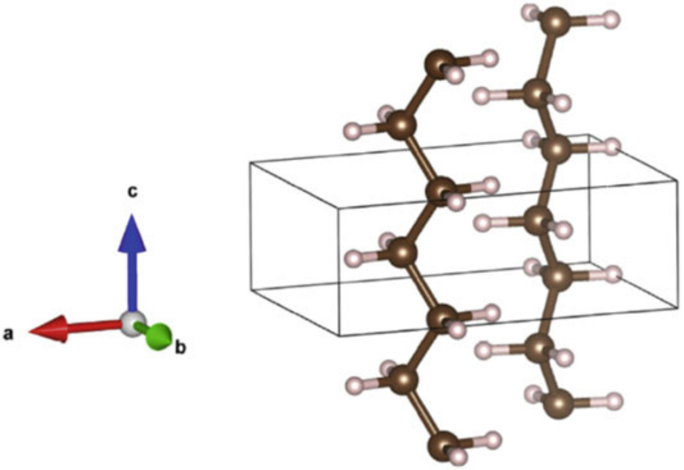


Fig. 3.2 Illustration of linear polyethylene orthorhombic crystal structure (reprinted from Olsson et al. 2017, with permission from Elsevier)

steric hindrance along the chain provides high conformational freedom and results in a T_g as low as −80 °C. Thanks to the high enthalpy, the melting point (T_m) for well-crystalline material is about 140 °C allowing polyethylene to display an ideal plastic behaviour in a very broad (220°) temperature range (that is between T_g and T_m).

Within the above plastic range, the material derived from ethylene polymerization shows a complex structure with more or less regular crystalline domains connected by chain sections that are in a random non-crystalline arrangement. The two kinds of domains cannot be separated by any method as the polymer chain is long enough to occupy different domains as reported in Fig. 3.3, which shows the complexity provided by the macromolecular structure in spite of the simple monomeric unit. The material is therefore not completely crystalline, but semicrystalline.

The homopolymerization and copolymerization of ethylene monomer (see Chap. 4) give a number of different plastics where the macromolecules are characterized by saturated aliphatic hydrocarbon structure and contain a variable amount and type of chain branching. Starting with pure ethylene two different homopolymers depending on the type of polymerization process can be obtained: catalytic polymerization provides a highly linear polymer with a high crystallinity degree and high density (high-density polyethylene, HDPE, Table 3.1); on the other side, free radical initiated polymerization, performed at high temperature and pressure, yields macromolecules with both long and short branching that reduce the extent of crystallization in packed materials and then result in low density of final polymer (low-density polyethylene LDPE, Table 3.1). The structure of the different kinds of polyethylenes is schematically reported in Fig. 3.4.

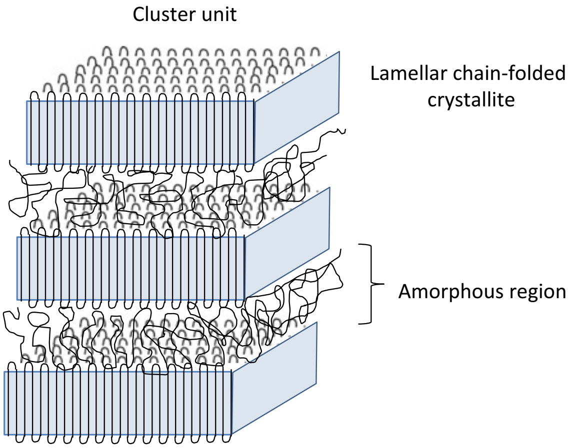


Fig. 3.3 Morphology of a typical semicrystalline polymer such as linear polyethylene

Table 3.1 Reference properties of polyethylenes with different macromolecular structures

Property	LDPE	LLDPE	HDPE
Density (g/ml)	0.92	0.92–0.94	0.94–0.96
Melting temperature (°C)	110	120–130	130–140
Tensile strength (MPa)	24	37	43

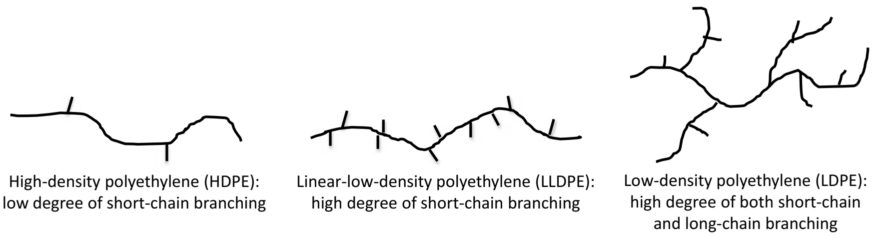


Fig. 3.4 Schematic model of the structure of polyethylenes (molecular weight distribution not included)

Low-density polymers can also be obtained by synthesizing copolymers of ethylene with 1-olefins (not more than 10% by mol) that gives rise to macromolecules with a linear backbone, but a consistent number (up to 10%) of short branching derived from the alkyl substituent of 1-olefins. These last monomers are able to reduce crystallinity and then the density with the effect to give the linear low-density polyethylene (LLDPE, Table 3.1).

When the content of the co-monomer and thus of the short branching increases up to 25–30%, the copolymer macromolecules contain very short methylene sections in the backbone that cannot crystallize. The copolymer becomes completely amorphous and loses the plastic features. Indeed, ethylene–propylene copolymers (EPM) having more than 30 to 60–65% by weight of propylene are characterized by a rubbery rather than a plastic behaviour.

An additional type of ethylene-derived polymers is the so-called ultra-high-molecular-weight polyethylene (UHMWPE) which is characterized by a very large molecular weight of several millions (from 3 to 6). As the ethylene repeating units have molecular weight 28, in this polymer, the macromolecular chains contain an average number of 100,000 units. Because of this impressive molecular weight to which very long chains correspond, the polymer is a very tough material, but the high probability of defects along the long chains results in difficulty to the three-dimensional packing and the polymer density is 0.930–0.935 g/cm^3 that is lower than the one of HDPE. The properties of UHMWPE make it useful for bottle-handling machine parts, moving parts on weaving machines, artificial joints and butchers' chopping boards. Also, it is conveniently used for articular implants in hip and knee replacements. Excellent and resistant fibres can be prepared by processing UHMWPE whose properties are competitive with those from aramids that are used in bulletproof vests.

As above illustrated, different polyethylenes are characterized by different crystallinity degree and this also affects their ultimate properties and applications.

High crystallinity is responsible for high density, good mechanical properties, high chemical stability and low solubility. For these reasons, HDPE that consists of very linear chains with a low degree of branching and consequently has a significant percentage of crystallinity making it suitable for making bottles jugs, various containers for liquids and pipes.

As mentioned above, the actual features of polyethylene depend on the polymerization process used for its preparation. For the preparation of HDPE, the polymerization process starts from pure ethylene and uses organometallic catalysts (typically titanium compounds with aluminium alkyl as co-catalyst) or Phillips-type catalysts such as chromium oxide supported on silica, which grants a low degree of branching formation. The controlled introduction of a slightly higher content of branching through the use of a minor amount (few percent units) of a substituted olefin co-monomer provides medium-density polyethylene (MDPE) with density range of 0.926–0.940 g/cm^3. MDPE can be produced by chromium/silica catalysts, Ziegler—Natta catalysts or metallocene catalysts. Thanks to the molecular defects caused once again by the higher branching degree than HDPE, MDPE has better impact and drop resistance, it is less sensitive to cuts and it has better breaking strength. Because of these characteristics it can be conveniently used for producing gas pipes, sacks, shrink and packaging films, and carrier bags. A further increase of the fraction of substituted olefins in the feed monomer and then in the macromolecules originates a further decrease in the density to 0.915–0.925 g/cm^3 (the LLDPE above mentioned). This polymer prepared by catalytic copolymerization of ethylene with small 1-olefins (1-butene, 1-hexene and 1-octene) is used predominantly in thin film production owing to the good toughness, flexibility and relative transparency.

The LDPE with density in the range of 0.910–0.940 g/cm^3 having a high degree of short- and long-chain branching (Fig. 3.4) is produced by free radical polymerization under very high pressure and temperature. The process is initiated by a species that easily forms a radical and reacts with a monomer that forms the polymer chains by successive addition to other monomers. However, the free radical on the primary carbon of the methylene at the end of the growing chain can give, with comparable probability, propagation or re-arrangement to more stable secondary and tertiary carbon atom free radicals. The disordered occurrence of these reactions is responsible for the much branched macromolecules and the low crystallinity of LDPE. The resulting plastic material is suitable for the production of both rigid containers and plastic films such as plastic bags and film wrap.

The different physical properties of the three main types of ethylene polymers, namely, HDPE, LLDEPE and LDPE, are summarized in Table 3.1.

As mentioned above, this class of polymers has generally excellent chemical resistance to strong acids and bases, as well as to weak oxidants and reducing agents thanks to paraffin structure. This resistance to liquid penetration including to water results in quite high resistance to degradation in the environment. However, after short time use they preserve almost the same original properties and can be easily recycled.

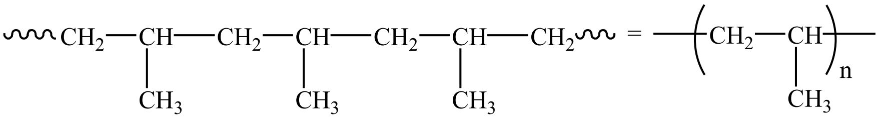
(b) *Ethylene polymers with heteroatoms*

Ethylene can also be copolymerized not only with 1-olefin (like propylene in the case of EPM family) or other small 1-olefin as in LLDPE and MDPE but also with several monomers containing heteroatoms such as vinyl acetate to give ethylene–vinyl acetate copolymer (EVA). This last is widely used in paints and to make foams in particular for shoe soles. In addition, it is hydrolyzed to yield formally the ethylene–vinyl alcohol copolymer (EVOH), which cannot be prepared by direct copolymerization of ethylene and vinyl alcohol. Several acrylates can be copolymerized also with ethylene. The copolymerization process occurs by free radical processes as the mentioned functional co-monomers would deactivate the catalytic organometallic sites. These copolymers have then a random non-regular structure and are generally amorphous; therefore, they cannot be rigorously classified as plastics. Exceptions are the copolymers with low content of co-monomers (2–3%) which have properties similar to LDPE thanks to the predominant content of ethylene units. However, the presence of the polar co-monomer and then of functional groups with heteroatoms provides a more polar nature to these polymeric materials which find use as adhesives and as compatibilizers in alloys and blends (see Chap. 4).

(c) *Propylene (PP)*

The relevant propylene homopolymer, named polypropylene or less frequently polypropene (PP), is constituted by macromolecules deriving from the head-to-tail binding of propylene molecules. These macromolecules have a linear structure of the backbone, as reported in the figure below with methyl groups as side chains attached to alternate tertiary carbon atoms (Fig. 3.5).

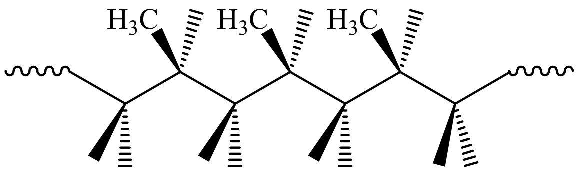
The tertiary carbon atom bearing a bonded methyl group is formally asymmetric and a regular structure can be claimed only if their absolute configuration is regularly sequenced along the chain. In the case of the regular macromolecules, they can pack together in a regular array to give a polymer with high degree of crystallinity. The only



$$\sim CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2\sim \; = \; -\!\!\left(CH_2-\underset{CH_3}{\underset{|}{CH}}\right)_n\!\!-$$

Fig. 3.5 Basic molecular structure of polypropylene (PP)

Fig. 3.6 Isotactic polypropylene in the non-real chain planar conformation



interesting material from applied viewpoint is the one formed of macromolecules containing long chain blocks where the above asymmetric carbon atoms all have the same absolute configuration (isotactic polymer: see Chap. 2 and Fig. 3.6). The process used for the industrial production of isotactic polypropylene is based on the catalytic process where the active sites have a high stereoselectivity and allow attaching propylene units in a controlled steric manner.

These macromolecules cannot assume the reality the zig-zag planar conformation reported in Fig. 3.6 that is instead typical of polyethylene. The methyl groups in the isotactic chain would stay all by the same side of the plane containing the backbone resulting in too close vicinity considering their steric dimension. The repulsion of this group is discharged by rotation of the monomeric units around the backbone carbon–carbon bonds. As a whole, the rotation of the same angle of all units lead to a helical conformation of the main chain, as shown by Natta and Corradini (1959). This conformation is found in the polypropylene crystals and leaves more empty space if compared to the planar arrangement of linear polyethylene. As the consequence, the density of isotactic polypropylene is between 0.895 and 0.92 g/cm^3, lower than that of HDPE. The less regular and less compact packing originates a lower melting enthalpy than polyethylene, but the conformational freedom, rotation of bounds along the backbone is lower thus the entropy variation during transition from crystal to melt is much lower than for linear polyethylene.

In spite of lower enthalpy, the lowering of the melting entropy provides the isotactic (or mainly isotactic) polypropylene with a melting point at around 171 °C. Notice that the commercial isotactic PP has a melting point in the range 160–166 °C due to the presence of defects in the crystals. In any case, T_m is higher than that of polyethylene. Furthermore, the T_g of PP also is higher than that of polyethylene. The range of typical plastic behaviour of isotactic polypropylene (from −10 to 160 °C) is therefore moved towards higher temperature with respect to the one of polyethylene allowing applications not accessible for polyethylene, particularly for items subjected to medium-high temperature (as for example hot water pipes). For such characteristic, it has replaced polyethylene in applications as in medical or laboratory use because it can withstand the temperature in a sterilizing autoclave. Most plastic containers for dairy products are made of polypropylene and sealed with aluminium foil (both heat-resistant materials). PP can also replace HDPE for the production of car batteries, waste bins, pharmacy bottles, cooler containers, plates and pitchers. The properties of polypropylene, as in most synthetic polymers, are depending on the molecular weight, molecular weight distribution, crystallinity degree and stereoregularity; in copolymers, it is clearly also important the type and content of co-monomer.

The industry produces three different main types of propylene polymers: the homopolymers (mostly isotactic), the random copolymers and the block copolymers with ethylene and other 1-olefins. The ethylene–propylene random copolymer with comparable amount of the two monomers (EPM) has very low or no crystallinity and is used as a rubber rather than as a plastic. The block copolymers are particularly tough and used for high-impact materials. Among the homopolymers, the syndiotactic polypropylene has a lower melting point of 130 °C and below 0 °C it becomes brittle, thus its use would be very limited and for the moment it is considered not-industrially interesting. The most commercial polypropylene is isotactic, with a significant percent of crystallinity and it is used in a wide variety of applications, such as packaging, labelling, textiles containers of various types, laboratory equipment, loudspeakers, automotive components and polymer banknotes.

An additional popular application for polypropylene is as biaxially oriented polypropylene films and sheets (BOPP), which are used to make clear bags as an excellent packaging material. In this case, a low percentage of ethylene is used as co-monomers to reduce the crystallinity and improve the transparency of films. Polypropylene is also a good starting material for the production of fibres as it costs less than most other synthetic fibres, but can give very competitive properties. It is even used as a more ecocompatible substitute of polyvinyl chloride (PVC) as insulation for electrical cables in houses, public buildings and low-ventilation tunnels as it emits less smoke and no toxic halogens when burning. However, because of larger flammability with respect to PVC flame-retardant halogen-free additives have to be inserted in the formulated.

Commercial PP is characterized by high elastic modulus, toughness, but flexible response to mechanical stresses; these features make it a very typical plastic material. The elastic modulus values ranging from 1300 to 1800 N/mm^2 are comparable to those of the more expensive acrylonitrile butadiene styrene (ABS) terpolymer and render PP useful even as engineering plastic.

Polypropylene is also used to prepare expanded foam (EPP) with very good impact characteristics due to the low stiffness that allows EPP to resume its shape after deformation. EPP is extensively used for reducing the weight of the final object and provides good impact properties. Fibres PP-based are largely employed in nonwovens for diapers or sanitary products; the empty space provided by the nonwoven structure helps in making these products to absorb water (hydrophilic) opposite to its natural hydrophobic characteristic. The nonwoven materials with the possibility to obtain fibres of very small diameters down to nanometers are used for the design and the production of filters with selected porosity for air, technical gases and liquids.

As drawback, we need to underline that the particular molecular structure with a high number of tertiary carbon atoms in the backbone makes PP liable to chain degradation or fragmentation according to a free radical mechanism during exposure to heat and UV radiation such as that present in sunlight. By ageing under these environmental stressing conditions, it shows a network of thin cracks and splits that become deeper and more severe with the exposure time. The application of PP in items for outdoor environments (automotive, gardening) needs the formulation with UV-absorbing additives; a simple example is provided by carbon black which protects the material (bumpers) against UV-activated degradation.

In addition, PP is more sensitive than polyethylene to chemical attack particularly if used in an aggressive environment, but cannot be considered biodegradable. If subjected to an extensive recycling it loses properties but this drawback can be alleviated by blending with virgin materials and specific additives.

PP is chemically similar to PE having also a saturated hydrocarbon structure. However, it is remarkable that it offers application possibility not achievable with PE. Indeed, it is a perfect plastic material in a higher temperature region than PE does, even if it loses its plastic behaviour if the temperature drops substantially below 0 °C where it becomes almost a glass. This is an additional example of the importance of a sustainable molecular differentiation to respond to the many society needs. Just to be very understandable we can conclude this comparison between these important and absolutely useful plastic materials by saying that PP is a more convenient plastic than PE in the hot Equatorial Regions, whereas the contrary holds in the Polar Regions. Clearly, both are excellent plastics in our areas with mild temperatures falling well inside the $T_g \div T_m$ range of the two polymers.

3.2.2 Polystyrenes

Styrene is a synthetic monomer from fossil origin and can be polymerized with the same processes used for aliphatic olefins. The polymerization of this monomer gives macromolecules along with alternating carbon atoms attached to a phenyl group (Fig. 3.7). These macromolecules form polystyrene (PS) and can contain up to a few thousand monomers giving a molecular weight of 100,000–400,000.

As for PP, polystyrene can have isotactic, syndiotactic and atactic structural conformation. Indeed, the carbon atoms bearing the phenyl group are formally chiral as bound to a phenyl group in addition to a hydrogen atom and two chain sections of different lengths. The macromolecules where these chiral centres have all the same

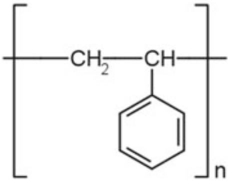


Fig. 3.7 Polystyrene molecular structure

configuration with the phenyl groups on the same side as in isotactic polypropylene (see Fig. 3.6) are also called isotactic. Isotactic polystyrene can be obtained by catalytic polymerization of styrene, but it does not have very interesting properties and therefore is not commercially produced. The syndiotactic polystyrene, in which the asymmetric backbone carbon atoms have alternate opposite configuration, is instead industrially produced by stereospecific polymerization with metallocene catalyst. This last polystyrene is highly crystalline with T_m of 270 °C and T_g at around 90 °C. Syndiotactic polystyrene has limited applications as rigid material acting as a real plastic only over 90 °C. Differently from PP, where the isotactic polymer is the only important product, among polystyrenes the atactic one is the most commercially popular material. The random sequential distribution of the asymmetric carbon atoms with opposite configuration implies a random orientation of the phenyl groups attached to the chain backbone thus preventing the chains from aligning with sufficient regularity. Therefore, it cannot achieve any crystallinity and the polymer is amorphous and characterized by only the glass transition temperature at about 90 °C and cannot be considered a typical plastic material. Non-crystalline atactic polystyrene can instead be used as a ‘solid’ at room temperature being well below its T_g of 90 °C so to behave as a rather rigid material. Close or over 90 °C atactic polystyrene flows as a viscous liquid. Therefore, its uses are for disposable plastic cutlery, dinnerware, frames, plastic model assembly kits and many other rigid objects. These items are usually produced by thermoforming (vacuum forming). It is even conveniently used for laboratory containers almost always made by injection moulding generally employed in biomedical research apparatus. A further very popular application of the subject polymer is as expanded polystyrene (EPS). The closed-cell foam obtained starting with pre-expanded polystyrene beads is rigid and tough and it is mainly used for packing material to protect items from impacts and crashes.

Polystyrene is very stable and not biodegradable in the environments. Used items must be disposed correctly at their end life. Because of its not optimal plastic properties it is often mixed with different additives or even partially cross-linked. As a result, PS items present on the market cannot be easily recycled as for polyolefins (Pan 2009). This is certainly an important concern for reducing the environmental impact of disposed plastic material.

3.2.3 Polyesters

(a) *Polyethylene terephthalate (PET)*

The most popular polyester is certainly PET with repeating units formed by the polycondensation of the diacid, terephthalic acid (IUPAC, benzene-1,4-dicarboxylic acid) and the diol ethylene glycol (IUPAC, ethane-1,2-diol) (Fig. 3.8). Clearly, the hypothetical bifunctional monomer is formed only in the polymerization system and converted into longer polyester chains.

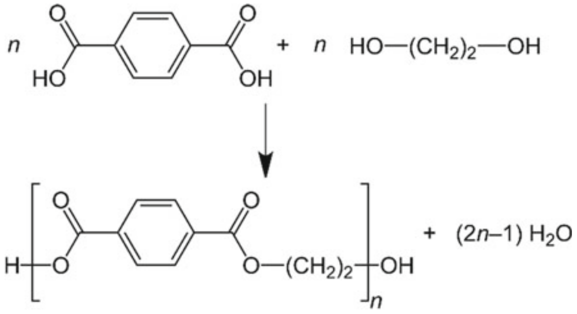


Fig. 3.8 Schematic synthesis of PET from terephthalic acid and ethylene glycol

A low molecular weight precursor of the above repeating unit is synthesized by the esterification of a terephthalic acid with two molecules of ethylene glycol to give a dihydroxy compound, the bis(2-hydroxyethyl) terephthalate. This last compound can also be prepared by transesterification reaction between ethylene glycol and dimethyl terephthalate and removal of two methanol molecules. This well-defined precursor can then be polymerized to PET through elimination of the exceeding ethylene glycol.

The molecular structure of PET is very regular as derived from alternating segments from terephthalic acid and ethylene glycol, respectively, connected by elimination of a water molecule. Thanks to this regular macromolecular structure this polymer can crystallize to give a semicrystalline material. Therefore, it is a typical plastic material in its $T_g \div T_m$ range (from about 60–70 °C to 250–260 °C). However, depending on processing and thermal history, it may exist also as an amorphous (transparent) material.

The slow cooling of the molten polymer forms a crystalline material with small crystallites dispersed in the amorphous matrix. For this reason, the semicrystalline material tends to scatter light and the polymer becomes opaque and white in most cases. The semicrystalline polymer shows mechanical properties better than the ones of polyolefins and can be used for applications where a good resistance to stress is requested. It can be used in industrial production of relatively strong and rigid objects such as bottles and sheets for structural/building application. It is used also as the carrier for magnetic tape or backing for adhesive tapes. Films and sheets of PET are characterized by significant gas and moisture barrier properties, as well as to alcohol and solvents. Accordingly, plastic bottles made from PET are widely used for water and overall carbonated drinks. Biaxially oriented PET film is useful in flexible food packaging and other applications where thermal insulation is required. Non-oriented PET sheet can be processed to form packaging trays, which can withstand both freezing and oven baking temperatures. PET-based films packing row food (meat) that can be directly introduced in a traditional oven or in a microwave to cook the food till 270 °C have been recently introduced on the market. An additional important application of PET is based on fibre drawing which is widely used in textile production. Notice that the fibre drawing produces a nearly single-crystal product.

Recycling of PET is easier and wider than in case of many other plastics because of the high value of the material and the very large use of PET for bottles.

Obviously, as many plastics, PET can be submitted conveniently to thermal incineration, being composed of carbon, hydrogen and oxygen, with only trace amounts of catalyst residues and no sulphur. Moreover, the *chemical recycling or the mechanical recycling* is particularly convenient, especially for objects such as bottles for water and beverages, which are very widespread. The chemical recycling mainly occurs by esterolysis mechanism returning to the initial raw chemicals, terephthalic acid (PTA) or dimethyl terephthalate (DMT) and ethylene glycol (EG,) and can be convenient when the final products are used as feedstock by industry. It can be cost-efficient only applying high-capacity recycling lines with size larger than 50,000 tons/year. This approach results quite limited, because of the difficulty related to keeping the working plant of this size as far as running expensive material collection/purification. Instead, the mechanical recycling is today operating in several diverse variants depending on the kinds of recycled-material feedback. The related processes are typical of small- and medium-sized industry, as the cost-efficiency requires capacities within a range of 5000–20,000 tons/year. Collected PET bottles after use may contain contaminants and the polymer can present some degradation extent occurred during the first processing and usage. Therefore, the recycled PET bottles must be submitted to washing for removing minor impurities and dirt and to be converted into pellets by extrusion of the melt material. Some of the original properties when necessary can be restored by reactive additives to repair for chain breaking, which is responsible for molecular weight decrease owing to degradation effect. Efficient sorting, separation and cleaning processes become most important for high-quality recycled polyester, but when the separation is not possible compatibilization with foreign polymer eventually present can be performed by addition of macromolecular compatibilizer. Recycling industry is mainly focused on bottles, which are easy to distinguish and separate because of shape and consistency from waste plastic routes either by automatic or by hand-sorting processes. The recycling process of post-consumer PET consists of three major activities:

(a) collection, separation and washing/cleaning of bottles from plastic wastes,
(b) production of PET-based flakes by bottles grinding,
(c) processing of flakes to provide the final products (generally obtained as pellets to be melt-processed into different items).

The intermediate product of the first section is packed with a PET content of more than 90%. The second step involves the conversion of bottles into flakes and this process can be more or less complex depending on the final PET quality of the scale required. During the third phase, the flakes of PET bottles are processed to obtain any type of product such as films, bottles, fibres or intermediates such as pellets for further melt processing.

Besides to the post-consumer polyester recycling, pre-consumer recycling processes exist: they are realized directly internally by the company as and when the polymer material scraps are reused in the same production circuit.

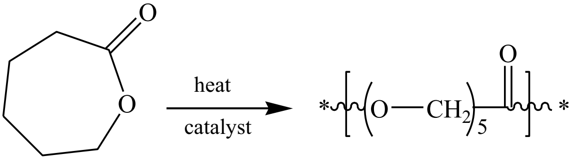


Fig. 3.9 Schematic synthesis of PCL from monomer ε-caprolactone

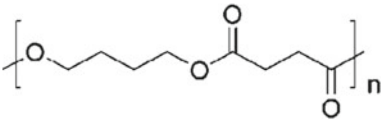


Fig. 3.10 Structure of polybutylene succinate as example

(b) *Linear aliphatic polyesters*

The man-made biodegradable polyester polycaprolactone (PCL) is a plastic material with low melting point of around 60 °C and a T_g of about −60 °C. PCL because of the low melting temperature is often used as polymeric plasticizer to improve the processing characteristics and the ultimate properties of rigid materials such as PVC (for instance, to improve its impact resistance) and starch. Thanks to this characteristic and due to the presence of the CO groups, which can act for hydrogen bonding and dipole–dipole interaction, PCL is compatible with a range of other materials, as starch thus lowering its cost and providing plastic behaviour. This sustainable and environment-friendly material is actually prepared by ring-opening polymerization of ε-caprolactone using a catalyst such as stannous octoate (Fig. 3.9). Indeed, to underline once again what we want to evidence about history and nature of polymers from fossil or renewable resources and eventually biodegradable, PCL is a biodegradable plastic but the monomer is of clear fossil origin and the catalytic process belong to those invented by man.

Learning from PCL example several linear aliphatic glycols, butanediol, hexanediol and linear aliphatic diacids such as succinic and adipic acids (Fig. 3.10) were used to obtain linear biodegradable polyesters.

Similarly, to PCL, these polymers are fully man-made and biodegradable when left in the environment. They also may have useful application properties; polybutylene succinate (PBS) (sometimes written polytetramethylene succinate, Fig. 3.10) has properties comparable to polypropylene and some grades of polyethylene (T_g= −30 °C and T_m = 120 °C) particularly for some mechanical features (strain and elongation at break). For such characteristics, PBS can be processed into films, bags, boxes and packaging for food or cosmetics under conditions and in industrial plants designed for polyolefins. Owing to its added characteristic of biodegradability PBS finds interest in agriculture for the fabrication of delayed release materials for pesticide and fertilizer as well as in other fields in which recovery and recycling of materials after use is problematic. PBS is also used in medicine as biodegradable drug encapsulation systems and for implants.

3.2.4 Polyamides

Linear polyamides, fully aliphatic or semi-aromatic, have the trivial name nylons and are very popular as can be melt-processed into significant products for several commercial applications such as fibres, moulded parts for cars, electrical equipment and films (mostly for food packaging). Nylons are first obtained either by reacting linear di-functional carboxylic acids with equal number of molecules of a linear, preferably aliphatic, diamine according to a polycondensation process. During this last process, the reaction of the carboxylic groups with amino groups forms an amide functionality that binds the two reacting molecules (e.g. PA66) (see Fig. 3.11) plus water. A similar reaction can be performed starting with aliphatic linear amino acids. A completely different process for nylon preparation starts with a lactam, obtained by cyclization of an amino acid. This last is then submitted to a process of chain polymerization started with catalysts able to open the lactam ring.

Nylon polymers are identified by a nomenclature that uses numbers corresponding to the number of carbons between acid and amine functions (including the carbon of the carboxylic acid). The successive use of cyclic and aromatic monomers required the use of letters or sets of letters. Only one number after the ‘PA’ for the so-called homopolymers obtained from an amino acid or a lactam, and two numbers or sets of letters when the nylon (PA) derives from the polycondensation of a dicarboxylic acid with a diamine. Nomenclature of copolymers consists of the same numbers for each monomer separated by slashes, as shown in the examples below:

- homopolymers:

  PA 6: $[NH-(CH_2)_5-CO]_n$ made from ε-caprolactam;

  PA 66: $[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n$ made from hexamethylenediamine and adipic acid;

  PA 612: $[NH-(CH_2)_6-NH-CO-(CH_2)_{10}-CO]_n$ is the polymer of hexamethylenediamine and hexadecanedioic acid;

- copolymers:

  PA 6/66: $[NH\text{-}(CH_2)_6-NH-CO-(CH_2)_4-CO]_n-[NH-(CH_2)_5-CO]_m$ made from ε-caprolactam, hexamethylenediamine and adipic acid;

  PA 66/610: $[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n-[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO]_m$ made from hexamethylenediamine, adipic acid and sebacic acid.

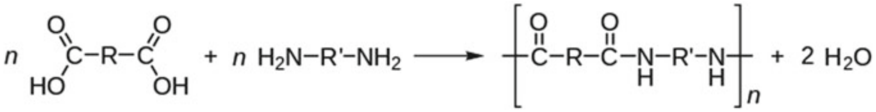


Fig. 3.11 Schematic synthesis of nylons from a dicarboxylic acid and a diamine

The prefix 'PA' or the name 'Nylon' are both used and have the same meaning.

The preparation method and the large number of available starting monomers allow to design macromolecules with a broad number of properties while maintaining the basic chemical nature of polyamide in a sort of natural inspiration derived from natural polyamides, which are obviously the proteins. Even subtle variation of the molecular structure of a monomer may be responsible for significant properties change and then solves specific application problems. As a single evident example, we can notice that the melting point of Nylon 6 (220 °C) is 45 °C lower than the melting point of Nylon 66 (265 °C) in spite of the same CO/NH/CH_2 ratio. The difference is ascribed to the different position along the chain of the NH and CO groups: perfectly alternating in Nylon 6 and with –NH–NH–CO–CO– order in Nylon 66. Other nylons include copolymerized dicarboxylic acid/diamine products that are *not* based upon the monomers listed above and some can be obtained from natural sources rather than from fossil oil. While nylons are in general fully aliphatic, some fully aromatic PA (known as 'aramids') are prepared from aromatic diacids like terephthalic acid or isophthalic acid with aromatic diamines (the renowned Kevlar and Nomex) used in protective clothing for motorcyclists and for sports activities. Linear polymers are the most useful, but it is possible to introduce branches in nylon by the condensation of dicarboxylic acids with polyamines having three or more amino groups.

3.2.5 Polycarbonates (PC)

Polymers under the name of polycarbonates are formed by carbonate links connecting hydrocarbon groups. If these last are aromatic the polymer is strong and tough, and some grades are optically transparent as the material is not able to crystallize. The most common polycarbonate is produced by the reaction of bisphenol A (BPA) (IUPAC, 4,4′-(propane-2,2-diyl) diphenol) and phosgene $COCl_2$. The scheme of the formal reaction is shown in Fig. 3.12.

Actually, the first step of the synthesis involves the reaction of bisphenol A with sodium hydroxide, to yield the disodium salt of the bisphenol A. The condensation reaction with phosgene produces sodium chloride as by-product and a chloroformate, which subsequently is attacked by another phenoxide propagating the growth of the chain by condensation reaction. The resulting polycarbonate is an amorphous material with glass transition temperature of about 147 °C that can be submitted to extrusion into tubes, rods and other profiles including multiwall.

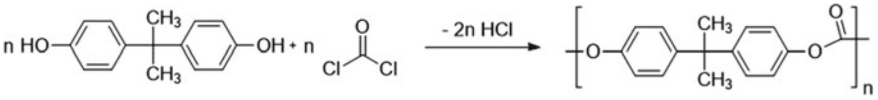


Fig. 3.12 Schematic synthesis of polycarbonate made from monomers bisphenol A and phosgene

As already evidenced for atactic polystyrene even polycarbonate is not formally a real plastic polymer as it has only a single transition temperature, the T_g, and can be used as a solid material only below the T_g itself. This last is, however, about 120 °C higher than room temperature and therefore at ambient conditions PC behaves as a very strong rigid material. In addition, the lacking of any crystalline fraction provides items with high transparency to visible light, and makes this polymer convenient for applications where transparent or electrically non-conductive parts are needed with high mechanical resistance to fracture.

3.2.6 Polyvinylchloride (PVC)

Vinyl chloride is a monomer of pure fossil origin that can be polymerized to PVC by free radical polymerization process; by opening of the double bond, it gives rise to macromolecules where the monomer units are enchained head to tail to minimize repulsion between chlorine atoms (Fig. 3.13).

No other initiator was discovered which could replace the free radical one. Because the free radical process lacks efficient stereochemical control, the Cl bearing three substituted carbon atoms is distributed randomly along the chain. This provides the polymer with an irregular structure that can be considered as atactic, even if the significant repulsion between the chlorine atoms on the last inserted unit and the incoming monomer favours the syndiotactic sequence over the isotactic sequence, and the former is present at a major extent than expected for a complete casual distribution. In spite of the presence of short syndiotactic chain segments, the polymer cannot crystallize to an amount which can be really significant for the material application. The commercially available PVC is then an amorphous polymer with T_g of about 90 °C. Then, as polystyrene and polycarbonate, PVC is not a true plastic material, but can be shaped with temperature by heating over 90 °C and then used as a solid rigid material near room temperature. Application of PVC includes also soft material obtained by using plasticizers with can derive from low or high molecular weight molecules. This molecules are characterized by a very low glass transition temperature and are compatible with the polymer. Rigid PVC is a very durable and long-lasting material also known as PVC-U (the U means ‘unplasticised’) used extensively as product/material for construction such as in window frames and cladding. Instead the flexible plasticized PVC finds use in flooring, medical products and even as a sort of synthetic leather. Because of the presence of large amount of chlorine, PVC is intrinsically

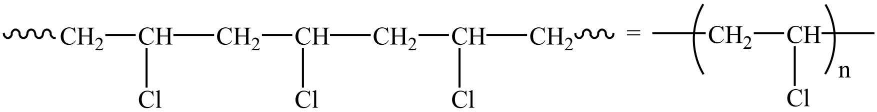

$$\sim CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2\sim = -\!\left(CH_2-\underset{Cl}{\underset{|}{CH}}\right)_n\!-$$

Fig. 3.13 Molecular structure of polyvinylchloride (PVC) fire retardant even if in some cases flame retardants can be added owing to its good compatibility with differently structured additives. All PVC-derived materials have very good electrical insulation and weatherproof properties. Over the past 15 years, it has undergone a remarkable transformation from point of view of general consideration: from being initially considered a not environment-friendly polymer to an important thermoplastic material in establishing what is called ‘a circular economy’. The PVC industry assumes a sort of role model for sustainability. This result derives from real correct technical evaluation of the concept that the sustainability of a material is achieved by inspired technology to maintain useful properties and minimizing environmental impact. To the good performances and the advantage of using as starting material chlorine derived from the kitchen salt for more than 50%, the process was made very efficient to reduce to few ppm the presence of the toxic monomer and the recycling was activated. In particular, PVC today can be recycled up to seven times without loss of performance, conserving valuable resources and raw materials. In detail, these achievements were possible as emissions of vinyl chloride monomer and dioxins during manufacturing decreased dramatically and the use of cadmium-based stabilizers was stopped. Even if plasticized PVC containing some phthalic acid derivatives is considered particularly toxic and other hazardous additives whose recycling was considered in the past a challenge and issue with particular reference to costs are involved, some interesting advances have been realized. Today the PVC is a material not only durable but fully recyclable and containing low content of carbon.

In agreement with this statement, it is of interest to the present book objective to remark that even if fully derived from fossil and invented by man PVC is not entirely derived from oil, being also produced from inorganic minerals. Indeed 57% of the polymer weight is due to chlorine, which is industrially derived from common sodium chloride and only 43% of the PVC weight is derived from hydrocarbon feedstocks. In the future, this part could be replaced with carbon derived from ethylene-originated natural resources.

3.2.7 Acrylic Polymers

This general name includes a broad number of polymeric materials obtained by polymerization of monomers containing a vinyl group to a carboxylate derivative (acrylic monomers) or a 2-propenyl group attached to the same carboxylate derivatives. Looking to the double bond type, acrylic monomers form a particular class of vinyl monomers while methacrylic monomers are vinylidenic. The corresponding polymers are usually produced by free radical polymerization and therefore the corresponding commercial homo- and copolymers are atactic and give rise to amorphous non-crystallizable materials. Some of these polymers may have T_g larger than room temperature and are used as plastics below the glass transition temperature.

For these reasons, as already discussed for PS, PC and PVC, they cannot be rigorously recognized as plastic as they lack a second transition temperature. The pres-

Table 3.2 Characteristic properties of different acrylic polymers[a]

	Polymer	R	T_g (°C)	Volume of R, $cm^{3*} mol^{-1\,(a)}$
	Polyacrylates: –CH_2–CHR–			
1	Poly(methyl acrylate)	– COOCH3	6	60.1
2	Poly(ethyl acrylate)	– $COOC_2H_5$	−24	82.3
3	Poly(propyl acrylate)	– $COOC_3H_7$	−48	102.4
4	Poly(n-butyl acrylate)	– COO*n*-C_4H_9	−55	126.7
5	Poly(i-butyl acrylate)	– COO*i*-C_4H_9	−33	119.2
6	Poly(t-butyl acrylate)	– COO*t*-C_4H_9	38	128.2
7	Poly(acrylic acid)	– COOH	106	–
8	Polyacrylonitrile	– CN	105	30.0
	Poly(methacrylates): –CH_2–C(CH_3)R–			
9	Poly(methyl methacrylate)	– $COOCH_3$	105	60.1
10	Poly(ethyl methacrylate)	– $COOC_2H_5$	66	82.3

[a] Data from Cowie and Arrighi (2007)

ence of the carbonyl functionalities attached to the double bond of these monomers generates an increased electron density on the monomer double bond that is then active for a nucleophilic attack. Typically, anions such as derivatives of metal alkyls can then start the polymerization of these monomers unless their side chain functional group does not deactivate the reaction.

The effect of molecular structure in these polymers on their thermal features can be argued by looking at the T_g values achieved when changing the monomer structure as reported in the next Table 3.2. Indeed, T_g is the property that is directly related to molecular structure more than others and the many possible molecular variations provided by human synthetic routes allow a large modulation of this property and then of the application possibility of the related polymers.

Polyacrylates and polymethacrylates differ in the structure of the side group directly bonded to the backbone. The capacity of this last group to prevent or restrict owing to steric effects the rotation of the bonds around the main chain increases with increasing steric interactions or polar groups repulsion. These restrictions, either due to steric hindrance or polarity repulsion, cause an increase of the T_g values. Thus, in polyacrylates with ester side chain, the T_g increases with the steric hindrance of the alkyl group bound to the carboxylate in the side chains, as observed when going from poly(*n*-butylacrylate) to poly(*t*-butylacrylate). If the side chain is not branched, the increase of the rotational ability of the side group with increasing chain length results in a decrease of T_g, despite the increase of Vx, as observed when comparing poly (methyl acrylate) with the polymers of ethyl, propyl and *n*-butyl acrylates. In other

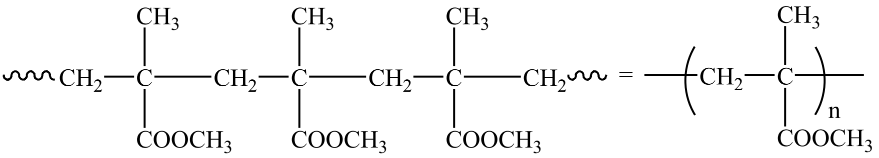


Fig. 3.14 Molecular structure of poly(methyl methacrylate) (PMMA)

polyacrylates, the dipolar interactions between the side chains increase the energy barrier of molecular motions as it appears by the T_g values of polyacrylates with side groups having specific polarity and hydrogen bond capability (i.e. polyacrylonitrile and poly (acrylic acid)). Finally, poly(methacrylate) series, where rotational restriction is strong due to the replacement of the tertiary hydrogen atom with the methyl group, shows higher T_g than the corresponding polyacrylic analogues. The remarkable increase is around 90 °C.

The most common acrylic plastic is poly(methyl methacrylate) (PMMA) (Fig. 3.14). It has several commercial names, i.e. Plexiglas, Lucite, Perspex and Crystallite depending on the company producing it, but the molecular structure is the same. Commercial PMMA is amorphous (with at T_g values of about 100 °C) highly transparent and tough at ambient temperature. It has also a good resistance to outdoor exposition and finds applications as a convenient material for airplane windshields, automobile lights and outdoor signs. As PMMA is compatible with human tissue, it can be used in the manufacture of rigid intraocular lenses that are permanently implanted in the eye.

Soft contact lenses are often made of a related polymer (copolymers obtained by polymerizing mixtures of different acrylic monomers), where the repeating units contain hydroxyl groups thus improving the hydrophilic character of the material. Methacrylate polymers are moreover extensively employed in medical and dental applications where purity and stability are critical to performance.

It is, indeed, used for bone cement to affix implants and to remodel lost bone in orthopedic surgery. Many other applications are known for PMMA and we refer the reader to commercial information.

More appropriate with the aim of this book is rather to discuss how versatile are the polymers derived from acrylic-type monomers. PMMA is mainly used for its mechanical properties, processability and stability for applications where these characteristics are of primary importance. However, it is interesting to consider the many possibilities offered for polymer properties design by this class of momomers. Indeed, acrylic and methacrylic monomers can be easily incorporated in the same macromolecules in a random distribution by free radical polymerization processes, which is largely the most used process for industrial applications. The easy polymerizability and the possibility of selecting different functionalities as the monomer double bond substituents have been largely utilized to prepare at industrial level several functional polymers for specific applications.

Some significant examples will allow elucidating this point.

The polymer of acrylic acid, CH_2=CH-COOH, can be easily prepared as a linear polymer by free radical polymerization and eventually rendered insoluble by gentle cross-linking by using in the monomers feed minor amounts of a diacrylate such as hexandiol diacrylate. The many carboxylic acid groups present as side chains can be easily salified by treatment with sodium hydroxide to give a polymeric salt very hydropylic as the salified units reach the 70% by weight of the material. When the polymer is cross-linked the polymeric salt remains solid, but it is able to absorb very large amounts of water, acting as a superabsorbent (called SAP). These materials are generally used in diapers and in sanitary napkins. Then a copolymer of an acrylic or methacrylic ester with varied amounts of acrylic acid can provide a plastic material with modulated water affinity.

On the other side, copolymers of an acrylate alkyl ester with an amino acrylate, such as 2-amino-ethyl-methacrylate can be converted into a polycation by quaternization of the side chain amino groups.

Thus, in general, the copolymerization of alkylacrylates, including MMA, with different monomers offers a flexible tool for producing a number of materials with modulated chemical and physical properties, even if, once again they have not a perfect plastic characteristic.

3.3 Bio-related Polymers from Renewable Resources

Bio-related polymers from renewable sources can have the same structure as the corresponding polymers derived from fossil or a different unique structure fully designed by nature.

The former type includes polymers with variable environmental impact and they are in general non-biodegradable, even if some are. They differ from the corresponding petrol counterpart only for the origin of the carbon and for the synthetic route adopted to produce the monomers from which the polymers are prepared. An example is the bio-polyethylene differing from the petrol-made polyethylene only for the ethylene used: the bio-ethylene is obtained by fermentation of polysaccharides (see Sect. 5.4), while the traditional ethylene is obtained by the petrol cracking process. However, the two polymers are identical and have close properties.

The latter type of bio-related polymers can be classified into two large groups based on their structure and on the synthetic procedure. One of these groups is the natural occurring polymers, the others consist mainly of biopolyesters produced by engineered microorganisms or through chemical processes capable to polymerize natural occurring monomers.

Natural occurring polymers include polysaccharides, like starches found in potatoes or wood, and proteins, such as animal-based whey or plant-derived gluten. Polysaccharides are made of glycosidic bonds, formed by reaction of hemiacetal of a saccharide and an alcohol with water loss. Proteins are made from amino acids that react to form peptide bonds, which consist of amide functional groups. An example of microorganism-made polymer is poly(hydroxybutyrate). While the most known biopolyester from renewable resources is poly(lactic acid).

Even if then the biodegradability is not the unique desired property of bio-related polymers, it is certainly one of the most attractive from the environmental viewpoint for short life material used under conditions which do not allow collection after disposal. All biodegradable polymers should be stable and durable enough for use in their particular application, but upon disposal they should easily break down as their recycling is not possible. Polymers, specifically biodegradable polymers, should not have extremely strong carbon backbones that are difficult to break. Since the degradation begins at the surface a high surface area speed-up biodegradation and allows easy access for either the chemical, light and/or organisms able to fragment the chains. The hydrophilic character, when present, can help biodegradation as it allows the water-soluble enzyme to easily get in contact with the polymer; however, if the polymer contains hydrolizable groups as ester groups in the backbone, the material can undergo biodegradation by surface enzymatic attack even if not swollen in water. Another property of bio-related, biodegradable polymers is the non-toxicity of the degradation products, which make them suitable for biomedical application. For this last-mentioned application, it is important also the capability to preserve good mechanical integrity until the material degrades, and the control rates of degradation under use conditions. It is necessary that the material does not arouse the immune response, and obviously the products of degradation also need not be toxic. These aspects are really important: the biodegradable polymers are used for the release of drugs into the body and it is really important to control the process over time, overall when the drug cannot be issued at once; in addition, the medicine has to be stable in the bottle or blister until it is ready to be taken.

In addition to medicine, biodegradable polymers are often used to reduce the volume of waste in packaging materials. In this field, there is significant effort to replace materials derived from petrochemicals with those that can be made from biodegradable components (Sasaki et al. 2003).

Examples of bio-related polymers are described below.

3.3.1 Polyethylene from Fermentation Monomer

Natural renewable resources can be used to produce the monomer ethylene by dehydration process of ethanol obtained from various feedstocks including sugar cane, sugar beet and wheat grain (see Sect. 5.4). The corresponding renewable polyethylene is successively prepared by polymerization of this ethylene from ethanol by the various industrial processes, such high-pressure free radical and catalytic (as above discussed), invented by man. The properties of the resulting polymers are identical to those of conventional polyethylenes produced by polymerization of ethylene from oil through the same processes, respectively. This holds for the physical properties for conversion into plastics products. Then one can say that in the commercial polyethylene there are no memory and evidence of the natural origin of raw material used as starting feed. It is also versatile in terms of applications and recyclable in the same chain established for conventional PE. Therefore, the bio-derived polyethylene being chemically and physically identical to traditional polyethylene does not biodegrade in the environment and must be collected and recycled. The advantages of producing and using bio-derived polyethylene are then mainly environmental. In addition to saving not renewable resources, its use can also reduce greenhouse gas emissions. Brazilian chemical group Braskem claims that by using its method of producing polyethylene starting from sugar cane ethanol captures (removes from the environment) 2.15 tons of CO_2 per ton of polyethylene produced. Annual production capacity of polyethylene from ethanol reached 200 kT in 2013. Indeed, being the process focused on the monomer, the same mature technology applied to fossil-derived ethylene can be industrially followed. Thus, high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) materials were produced from ethylene of bio-origin. The first access to the market was directed towards products for applications in rigid and flexible packaging, closures, bags and others. In January 2014, also the production of low-density polyethylene (LDPE) was effectively performed thus allowing covering additional applications in packaging and films.

3.3.2 Thermoplastic Starch (TPS)

Starch, a polysaccharide that can be used as a thermoplastic material, is one of the most abundant renewable resources known to man as the result of the biosynthesis by numerous plants. The molecular structure of starch is a polymeric carbohydrate consisting of a hydro glucose unit linked together primarily through α-D-$(1 \rightarrow 4)$ glucosidic bonds (see Sect. 5.2). The natural product is indicated as native starch, term used to describe starch in the form in which it occurs in plants such as potatoes, wheat, cassava, rice and maize. Thermoplastic starch (TPS) is the name of the commercial products mainly made of starch that exhibit thermoplastic behaviour after various man-made treatments of the native material.

Native starch, in plants, consists of granules superstructure composed of amylose and amylopectin (see Sect. 5.2). Granular starch is partially crystalline and when it is heated thermally degrades before the crystalline melting point is reached. As a result, starch cannot be melt-processed in its native form. Addition of plasticizers is necessary in order starch can exhibit thermoplastic properties when heated at elevated temperatures under shear (see Sect. 5.5) to give gelatinized starch which is then mixed with other thermoplastic additives. Granular starch can be also plasticized by blending or grafting with a soft biodegradable polymer as polycaprolactone. This allows reducing the processing temperature while maintaining the biodegradability. Materials with glycerol as the plasticizer exhibited less rigidity. Plasticized TPS has engineering properties close to those of several plastic polymers, and it can be processed as traditional oil-derived thermoplastic polymers such as by kneading, extrusion, injection moulding, compression moulding, blow moulding or heating and casting. It can also be used as matrix for composites including nanocomposites in particular with cellulose fibres and nanofibres.

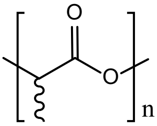
3.3.3 Poly(Lactic Acid) (PLA)

Poly (lactic acid) is derived from the monomer lactic acid that can be industrially obtained either from natural renewable resources through bacterial fermentation of sugars or from fossil resources by chemical synthesis, where acetaldehyde is the starting molecule (Jamshidian et al. 2010). Today lactic acid is produced predominantly, or almost totally, by the former microbial fermentation process. The racemic mixture of the D and L antipodes, or mixtures where the antipode L-lactic acid predominates up to 99.9%, can be industrially produced depending on the enzymatic system used in the fermentation process. At present, the industrial-scale production of D-lactic acid by fermentation is possible, but not used to a significant level.

The polymerization of lactic acid gives PLA, at present the most popular polymer derived from renewable resources. The macromolecules of PLA contain head-to-tail units derived from the formal condensation of lactic acid as indicated in Fig. 3.15.

The same repeating unit shown in Fig. 3.15 can be formally and effectively obtained by removing water before polymerization. Actually, this reaction involves the condensation of two lactic acid molecules to yield the cyclic lactide dimer. As the condensation has been performed before polymerization to obtain the lactide, the last can undergo a chain polymerization by ring opening activated with various metal catalysts in solution, in the melt or as a suspension. L-lactide, D-lactide and meso (L,D) lactide are produced from L-lactic acid and D-lactic acid. The polymerization of each of the lactide enantiomers or mixtures leads to PLAs differing in the stereochemical features. In case of these polymers, the term poly(lactide) is more appropriate and can be used instead of PLA. This last name should be used for polymers obtained by the direct condensation of lactic acid monomers. In this case, the process is carried out at less than 200 °C to avoid the formation of the lactide during the polymerization. One equivalent of water is formed for every monomer molecule added to the growing chain by condensation. The generated water causes chain hydrolysis as side reaction so that only low molecular weight chains are obtained. To overcome this drawback, the process of polycondensation is carried out in two successive steps. The first step is the above-mentioned one giving lactic acid oligomers. In the following step, the oligomers are combined to give high molecular weight polymer chain by efficient removal of the water that is formed during the condensation so to avoid chain

Fig. 3.15 Molecular structure of PLA



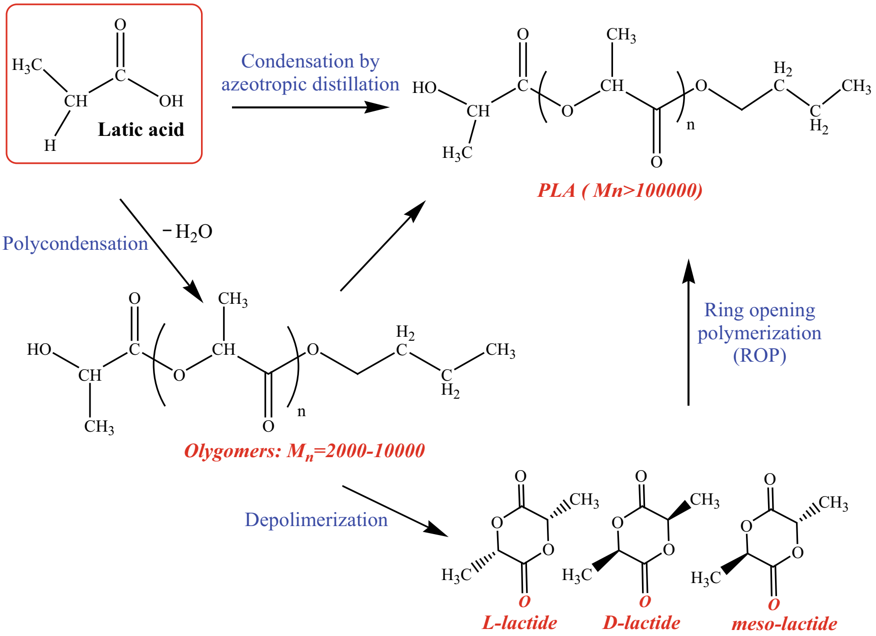


Fig. 3.16 Current production steps for PLA

hydrolyses and promoting transesterification. The above polymerization routes including lactide formation are schematically represented in Fig. 3.16.

Polymer properties are dependent on monomer stereochemistry, which is on the content and distribution along the chain of L- and D-repeating units. The polymerization of the racemic mixture of L- and D-lactides may lead in the absence of any streocontrol to the random copolymer of the two antipodes, poly-DL-lactide (PDLLA), which lacks chain stereoregularity (atactic), cannot crystallize and thus is amorphous. Interestingly, isotactic crystallizable products can be obtained even from the racemic DL-lactide in case the two enantiomers polymerize in separate chains, under steric control by the catalyst or by the growing chain. Under one of the two controlled conditions, an equimolar mixture of poly-L- and poly-D-lactic acid, both isotactic, is formed instead of the random atactic copolymer. The crystallinity is then dependent on the degree of isotactic stereoregularity, and is depending on the D/L ratio between the monomers in the feed and by the stereoselective capacity control during the polymerization reaction. When the prevalence of one antipode in the polymer units is 85–90% the polymer is semicrystalline. On the contrary, it is amorphous under this enantiomeric prevalence. The crystalline domains can assume distinct crystalline modifications, the α-, β- or γ-forms, depending on the crystallization conditions. The α-form is the most frequent and is characterized by two antiparallel chains, which in case of the L-units assume a left-handed helix conformation.

These helices are packed in a nearly hexagonal arrangement in an orthorhombic (or pseudo-orthorhombic) unit cell.

The isotactic poly(L-lactic acid) derived from the pure L antipode has about 37% of crystallinity with a melting temperature of about 173–178 °C and T_g in the range 60–65 °C. Indeed, it shows a real plastic behaviour. This kind of PLA can withstand temperatures of 110 °C, is insoluble in water being substantially hydrophobic and soluble in chlorinated solvents, hot benzene, tetrahydrofuran and dioxane.

Processing of PLA allows obtaining various items of less or more complex geometry by extrusion, injection moulding, film and sheet casting. PLA is also used as a feedstock material for 3D printers. It is widely used in packaging applications, a practice that is considered environmentally useful thanks to the biodegradability of many PLA-derived items such as many films, wrappings and containers (including bottles and cups) (Masutani et al. 2015). In 2002, FDA ruled that PLA was safe to use in all food-contact packaging materials. It has also medical applications as bio-re-absorbable material able to break down inside the body within 6 months to 2 years (as absorbable suture thread).

3.3.4 Polyhydroxyalkanoates (PHAs)

Some bacteria store carbon and energy (see Sect. 5.3) by producing linear polyesters corresponding to general structure of polyhydroxyalkanoates (PHAs) in the form of homopolymers or copolymers (Fig. 3.18). Up to 150 different monomers can be combined within this family to give materials with extremely different properties. The main known polymers belonging to this class are poly-3-hydroxybutyrate [P(3HB)], poly-3-hydroxyvalerate [P(3HV)] and their random copolymer P(3HB-*co*-3HV) whose structures are represented in Fig. 3.17.

Poly[(R)-3-hydroxybutyrate] (P3HB) has a perfectly isotactic structure with monomer units having only the (R)-configuration, and has 55–80% of crystallinity.

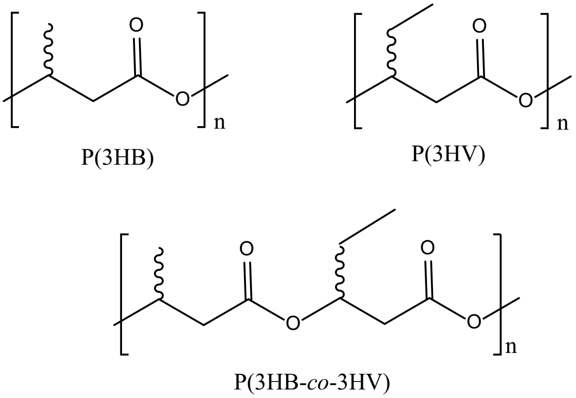


Fig. 3.17 Chemical structures of poly-3-hydroxybutyrate [P(3HB)], poly-3-hydroxyvalerate [P(3HV)] and their random copolymer P(3HB-*co*-3HV)

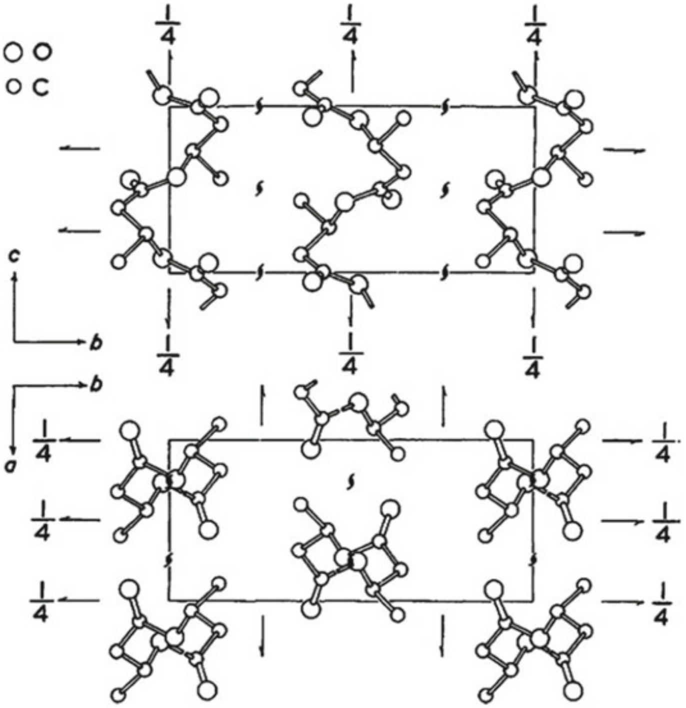


Fig. 3.18 Crystal structure of α-form P(3HB) proposed by Yokouchi et al. (Reprinted from Yokouchi et al. 1973, by permission from Elsevier)

Two crystalline modifications are observed. The α-form produced under the most common conditions is characterized by two antiparallel chains in the left-handed 2_1 helical conformation. These helices are packed in an orthorhombic unit cell with axes a = 0.576 nm, b = 1.320 nm and c (fibre axis) = 0.596 nm, according to a space group of $P2_12_12_1$ (Fig. 3.18).

The bacteria produced P(3HB) has high molecular weight with a polydispersity of around two. It is a regular plastic material with T_g at around 4 °C and T_m near 180 °C. The densities of crystalline and amorphous P(3HB) are 1.26 and 1.18 g/cm^3, respectively, larger than that of polyolefins and in the range of synthetic polyesters. On the other side, Young's modulus (3.5 GPa) and the tensile strength (43 MPa) are close to those of isotactic PP even if P(3HB) is a stiffer and more brittle plastic material than PP. Indeed, the extension to break (5%) is markedly lower than that of polypropylene (400%).

Different from other bio-related polymers and similarly to synthetic polymers, PHAs class offers many structural possibilities and then a broad variety of properties related to distinct applications. The large number of molecular structures available by feeding various bacteria families with organic chemicals of different type even if preferably of natural origin provides a first level of differentiation in structure and then in properties providing really plastic polymers. So one can expect that these materials are suitable to replace several fossil produced polymers providing non-renewable resource saving and minor environmental impact thanks to the biodegradability and the low-carbon footprint. In spite of a large number of possible polymer compositions only about 5–10 different polymers at present are of interest for industrial production. Despite many years of research, the volume of PHAs produced at industrial level is still limited. Few examples of industrial products on the market are Mirel® and Mvera® series by Metabolic, TephaFLEX® series by Thepha and EnMat® series by TianAn Biopolymer.

3.4 Structure to Fundamental Properties

This final section of the chapter is devoted to summarize and compare the relationships between structure and main properties of plastics having different molecular features, independently of their origin. In other words, this can be regarded as an attempt to evaluate how far the molecular structure of the repeating units of the macromolecule can affect the final properties and in addition how is important monomer availability and selection. In these two last aspects, the fossil way and the nature approach present distinct characteristics. For sake of clarity in this chapter, only homopolymers and the main industrially used copolymers were considered, while a very important contribution to properties versatility is certainly offered by the blending of different polymers and other products (composites).

The logical approach was then providing real examples to design a polymeric material with defined properties starting from the molecular structure either from fossil or renewable resources. In this connection, the comparison is referred to show the many different molecular structures designed by man that have assumed a practical interest to solve different needs of the everyday life. This approach was certainly the most efficient for technology results but has clear limitations for the environment.

The nature-related polymers fit in this general scheme in the applications range for which their molecular structure allows, taking in mind that the material properties start from the molecular structure, but acquire the ultimate value thanks also to the consequent organization. Moreover, one should keep in mind how the same properties can be reached with different structures (Tables 3.3, 3.4, 3.5 and 3.6).

The thermal and the mechanical features of a polymer (or copolymer) are strictly interconnected and mainly depend on the chemical structure of monomeric units (presence of heteroatoms, multiple bonds, aromatic moieties), order's degree in linking the monomeric units (head–tail, tail–tail bonds, type of co-monomer sequences), molecular weights and their dispersity. These main key aspects are obviously independent of the nature of monomeric units from fossil- or bio-derived sources. Most of the mechanical performances of a polymer and in particular the interval of temperatures for its use and processing are strictly related to its crystallinity, ranging from 0 to 80%, and T_g values. These values define the classes of thermoplastic polymers

Table 3.3 Typical properties of most used semicrystalline thermoplastic polymers

Polymer	Crystallinity (%)	Density (g/cm^3)	Tensile strength (N/mm^2)	Tensile modulus (N/mm^2)	Elongation at yield (%)	Elongation at break (%)	T of use (°C)
HDPE	65–80	0.95–0.97	19–39	13.8	18	400	−50/+120
iPP	55–70	0.90–0.91	21–37	14	6	150	−5/+130
PET	30–35	1.38	7.9	27.6	3.8	70	−10/+120
PA6	20–45	1.12/1.15	38–70	30.6	4–25	70/200	−40/+200
PVDF	About 50	1.77	30–50	23	–	>20	−30/+150
PVF (film)	–	1.4–1.7	11	26.2	–	90–250	−70/+105

Table 3.4 Typical properties of amorphous thermoplastic homopolymers

Polymer	Density (g/cm^3)	Tensile strength (N/mm^2)	Temperature of use (°C)
PC	1.20	65–70	−40/+120
PMMA	1.18	70–75	−40/+90
PS	1.05	40–65	−20/+70
PVC	1.28–1.34	40–60	−15/+60
TPU	1.10–1.18	20–50	−10/+150

Table 3.5 Typical properties of amorphous thermoplastics random copolymers

Copolymer	Density (g/cm^3)	Tensile strength (N/mm^2)	Temperature of use (°C)
ABS	1.04	38–58	−30/+95
COC	1.02	46–63	−50/+130
SAN	1.08	70–79	−20/+80

Table 3.6 Typical properties of bio-related thermoplastic polymers

Polymer	Crystallinity (%)	Density (g/cm^3)	Tensile strength (N/mm^2)	Tensile modulus (N/mm^2)	Elongation at yield (%)	Elongation at break (%)	T of use (°C)
PLLA	37	1.3	0.5	2700	1–8	1–12	−10/+120
PHB	50–70	1.25	32	2200	–	4–6	<95
PHV	–	–	–	3.7	–	10	<95
PHBV (7–20% HV)	–	–	–	–	–	10–50	<90
Starch[a]	10–40	–	3–6	–	–	10–600	0/+50

[a] Data depending on kind of starch and plasticizer used

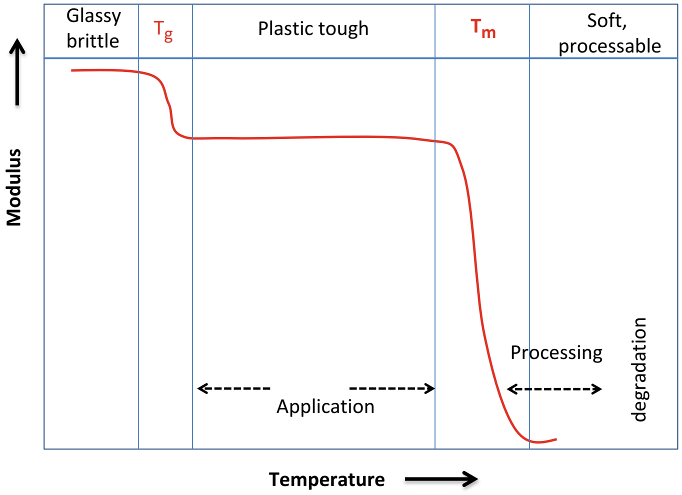
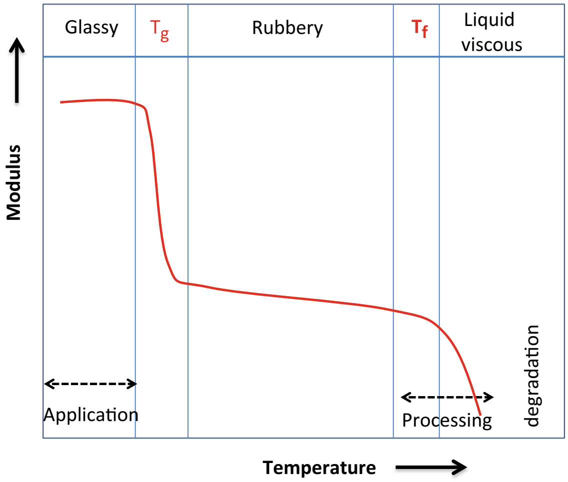


Fig. 3.19 Temperature behaviour of semicrystalline thermoplastic polymers: T_g and T_m glass transition and melting temperatures

Fig. 3.20 Temperature behaviour of amorphous thermoplastic polymers: T_g and T_f glass transition and flow temperatures, respectively



as the ones whose properties are numerically reported in Tables 3.3, 3.4, 3.5, 3.6 and in the case of the amorphous (co)polymers the crystallinity is 0 (Tables 3.4 and 3.5).

The general temperature behaviour of thermoplastic polymers, assessing the state of applications and state of processing is summarized in Fig. 3.19 and in Fig. 3.20.

A polymer can crystallize only if it has linear and regular macromolecules, even if limited crystallization can take place if a small number of branches are present (like in the case of side groups derived from vinyl monomers). Crystallization requires an orderly arrangement along the polymer chain providing the structure a high degree of symmetry.

Linear polyethylene, for example the HDPE in Table 3.3, can, in a relatively easy way, reach high levels of crystallinity up to 80% even always a certain amount of the long chain can be packed in the crystal three-dimensional order. This is possible by the planar zig-zag structure easily assumed by the polyethylene macromolecules having only hydrogen atom substituents out of the carbon atom on the backbone (see Chap. 2 and Sect. 3.2). The macromolecules therefore can assume for long section a linear ribbon form giving a high degree of order and can easily be packed into dense crystals. The small substituent volume practically cancels the steric hindrance and then the polyethylene outside of the crystals can rotate freely being extremely flexible. The rotation around carbon–carbon bonds allows the chain to assume a large number of disordered conformations with high gain in entropy with respect to the unique ordered planar zig-zag conformation. For this last reason, polyethylene is characterized by a low value of T_g thus generating a wide temperature range of use for this really important plastic commodity.

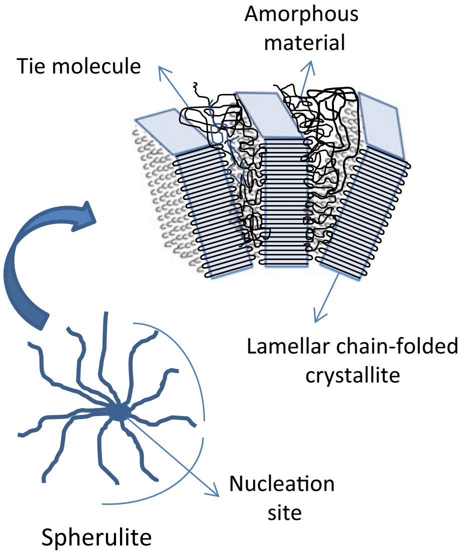
Polypropylene (PP) and polystyrene (PS) can crystallize only if the macromolecules are stereoregular: that occurs if they assume an isotactic or syndiotactic structure (see Chap. 2 and Sect. 3.2). Isotactic polypropylene (iPP, Table 3.3) is the commercially interesting materials. Its configurationally ordered primary structure allows the macromolecules to assume a regular conformation in the form of left-handed and right-handed 3/1 helices as the planar zig-zag arrangement is hindered due to steric interactions of the alternating methyl group. This helical conformation can assume an ordered supramolecular arrangement in crystal, but the packing is less dense than for polyethylene. However, the larger chain rigidity due to steric limitation to the rotations around the main chain or backbone limits the entropy variation from order to disorder thus increasing both T_m and T_g. iPP has then a plastic behaviour range narrower than that of PE, but is shifted towards higher temperatures covering an interval that PE cannot reach. Conversely, atactic PS is the only industrially produced. This polymer is un-crystallizable since the polymer chain lacks any regularity. The amorphous atactic PS has a high T_g as the dipole interactions and packing of aromatic rings reduce the chain flexibility leading to high rigidity. This polymer can then be used for various applications as solid material below the T_g. The situation is similar in other atactic homopolymers and random copolymers which all do not crystallize (Tables 3.4 and 3.5) for lack of structural order and their application is as glassy phase till close to the T_g value (Fig. 3.20).

In the hydrocarbon polymers discussed before the crystallinity is related to steric interactions which may hinder ordered structures and determine the lowest energy conformations found in the corresponding crystals. In polymers having heteroatoms and functional groups, polar interactions and hydrogen bonding favour the crystallinity because the packing in crystals brings the macromolecules closer to each other and makes possible to maximize dipole–dipole and hydrogen bonding inter-macromolecular forces.

The presence of ester linkages along the backbone of polyesters provides polar groups which certainly increases the strength of interchain interactions, but the effect on material properties is markedly affected by the type of hydrocarbon residue between two successive ester groups, that is on the whole molecular structure of the repeating unit. Accordingly, polycaprolactone where the connecting group consists of five methylene groups is finally flexible and has a lower melting with respect to PET (Table 3.3) to PLLA, and linear PHB (Table 3.6) which contains polar ester groups connected by more rigid aromatic or branched aliphatic short segments. In these polyesters, the dipole–dipole forces between the polar groups create strong interactions among the macromolecules in the crystals contributing to increased melting point and to high modulus values. PHB properties are rather close to those of iPP, and better than those of HDPE. Relaxation of the molecular rigidity can be achieved with longer alkyl groups as in PHV and with copolymers PHBV. Thus, PHV exhibit T_g values lower than PHB and below the room temperature explaining their rubbery state particularly by increasing the HV content, thus allowing plastic behaviour in lower temperature environments. PLLA having T_g higher than room temperature needs some plasticization to expand its plasticity range at the most popular room temperatures. The effect of intramolecular interactions is even more evident in the polyamides where the presence of the polar amide groups in the backbone chain originates a network of hydrogen bonds connecting different chains (see Nylon 6,6 or PA6 in Table 3.3). This strong binding among polyamide macromolecules is maximized in the crystals thus contributing to a remarkable extent to the melting enthalpy, which measures the energy necessary to remove macromolecules out the interaction distance. Once separated, the polyamide chains remain more rigid than purely hydrocarbon polymers with similar structure as the amide bond with its partial conjugation hinders free rotation around backbone, thus reducing the value of the entropy of melting. Both effects raise the melting point and the glass transition temperature with respect to polymers without strong intermolecular interactions, like polyethylene.

In addition to the above general effects, it is of interest to notice that polymers with small side chains crystallize more easily than polymers with large, pendant groups. An example is provided by poly(vinyl alcohol) (PVA) made by the hydrolysis of poly(vinyl acetate) (PVAc). Being the –OH groups rather small in volume PVA can stand in the planar zig-zag conformation independent of the configurational order of the substituted main chain carbon atoms, and therefore its crystallinity is independent on stereoregularity: this means that both atactic and stereoregular (iso- or syndiotactic) PVA can crystallize. The –OH groups in PVA also form strong interchain hydrogen bonds, increasing the melting up to 200 °C. By increasing the size of the side groups polymer encounters difficulties in folding itself along the crystal growth direction (like in the case of PVAc and PMMA, see Table 3.4). Thus, when the side groups are larger than –OH stereoregularity is needed for crystallization. Bulky side groups and branching reduce the ability and the possibility of a polymer to crystallize. For example, branched polyethylenes (LLDPE and LDPE) have a low degree of crystallinity and lower melting point than linear HDPE, because the side segment has less freedom to move and the incorporation of defects in the crystalline lattice spreads defect to the three-dimensional organization.

Fig. 3.21 Schematic picture of a polymer crystalline spherulite



The crystalline polymers have an effective incapacity to form perfect crystals as low molecular weight compounds. A crystalline basic structure is characterized by lamellae that consist of layers of folded chains. Assembling of these layers give rise to more complex larger structures named crystallites or spherulites; these are generated by lamellae growing radially in all directions and thus, generally the resulting crystalline regions are spherical (just the spherulites), unless particular thermal gradient or geometrical constraints are applied.

The thickness of a typical crystallite is in the range of 10–20 nm. For the reasons described above, polymers are arranged in partially crystalline structures, as they are semicrystalline. In between the ordered crystalline lamellae, there are disordered regions where the chains segments have assumed different spatial arrangements. The disordered regions form the amorphous phase. As the length of macromolecules in high molecular weight polymers is larger than the dimensions of the phases in a semicrystalline material, a single polymer chain may accommodate partly in a crystalline lamella, and partly in the amorphous state. Depending on the length, some polymer chains even start in one lamella and then reach another lamella, after having gone across the amorphous region (*tie molecules* in the scheme of Fig. 3.21).

Crystallinity depends on the average chain length (Fig. 3.22). Indeed, the long chains tend to be more tangled and the free energy is minimized by participating in both amorphous and crystalline phases. The resulting crystallinity is significant and the behaviour of these materials implies improved strength typical of plastics (hard/soft depending on crystallinity and thus on the chain folding/packing capability). Low molecular weight may even result in improved crystallization but the polymer material is usually weaker in strength as it is more difficult that their chains act as binders of different phase domains. Under external mechanical stimuli (stress),

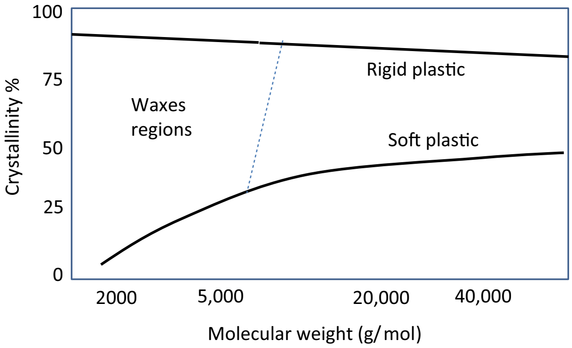


Fig. 3.22 Schematic representation of molecular weight and crystallinity effects on polymer behaviour limited to polymer/oligomer having molecular weight higher than 2000

the polymer chains can slide by each other and cause a break in the material. Therefore, an optimized balance between crystallinity and molecular weight is important for obtaining the desired mechanical response by the material.

Crystallinity has various effects, but these are interrelated with other parameters.

Crystallinity makes a material stronger (higher the tensile modulus (see Chap. 2, Fig. 2.9), but also more brittle (with low elongation at break). Indeed, a completely crystalline polymer would be too brittle and the presence of amorphous regions is necessary for toughness, that is, the ability to bend without breaking, and then what we call the plastic response in a certain range of temperature, the temperature of use (Figs. 3.22 and 2.9).

In crystallizable polymers, the crystallinity is usually induced by cooling a melt or a dilute solution below its melting point or by stretching to orient macromolecules in the stretching direction.

In the industrial production, the polymers often are cooled rapidly from the melt (see Chap. 4), and the crystallization extent is then controlled by kinetics rather than thermodynamics. These chains are entangled in the melt and may have not enough time to crystallize a high percentage; crystallinity is higher for materials cooled slowly from the melt. A typical behaviour is observed in polyesters where amorphous material from the melt can be ‘frozen into’ the solid without crystallization thanks to the kinetics control allowed by the intrinsic slow crystallization occurring in these materials. This molecular characteristic clearly holds for polyester from fossil origin and for biopolyester (especially for PLA and PHB). This behaviour is not suitable with widespread use in industrial applications, as it reduces the temperature use to that of amorphous plastics (Fig. 3.20) that is below T_g. Of consequence, prototypical polymer processing techniques such as moulding and extrusion are not possible.

Specific technological devices/designed procedures, structure modification, compounding or adding nucleating agents are therefore necessary for the conversion into valuable commercial products.

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Chapter 4
Synthesis of Polymers for Plastic Materials

4.1 Motivation

This chapter deals with the preparation of products starting with material based on plastic polymers from fossil origin (Bruckner et al. 2001). The production route of traditional plastic polymers starts from available monomers, followed by the reaction for converting them into polymers and successive processing to obtain objects. This synthetic description is considered necessary for the general objective of the book devoted to the comparison between plastics from fossil origin and from renewable sources. The description below of the various macromolecular structures that man has produced starting with fossil feedstock gives a good insight about the molecular features necessary for a plastic behaviour and for modulating plastics properties according to the application needs. Indeed, the alternative use of plastics from renewable source is first of all depending on the evaluation of real capacity of the bio-related plastics to be produced with structures granting the basic response to use. An additional concern may arise from the real possibility to provide renewable feedstocks in an adequate amount with sustainable processes not involving significant amounts of energy and of side streams producing environmental problems. Clearly, this problem arises when monomers and polymers from bio-related starting compounds with different structures than the ones traditionally used are considered as substitute of the traditional analogues from fossil sources. These new bio-related polymers may need different production processes and then arise new sustainability problems. Moreover, the bio-related polymers will be clearly submitted to the same processing technologies as the corresponding fossil products and then must be adapted to the related thermal and mechanical treatments. This problem obviously does not exist when the monomer from natural renewable sources has very similar or identical structure as in the case of ethylene from oil or from fermentation, as both will end up with not distinguishable ethylene polymers. Then this chapter has the role of describing the state of art in established plastic polymer technology as far as polymerization reactions and material processing are concerned in order to have an insight into the

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challenge encountered by monomers and polymers from renewable sources when converted in the so-called bioplastic material.

4.2 Monomers from Fossil Resources

Monomers from fossil resources can be obtained capable to undergo either chain polymerization or stepwise polymerization. Monomers used for producing plastics are bi-functional so to give rise to linear or branched macromolecules, but without cross-linking, which would originate non-thermally processable materials.

The monomer per se cannot grant polymer plastic properties, which derive from the macromolecules structure. This last and important contribution is provided by the polymerization process as discussed in the next section.

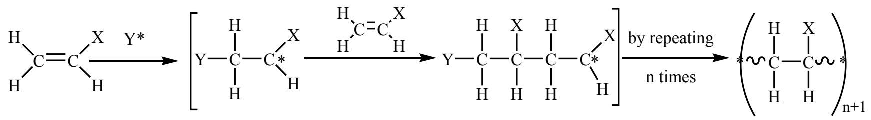
A monomer is a molecule that can be incorporated through a polymerization reaction in a macromolecule, the long molecular chain formed by connecting one monomer after the other through covalent bonds. Clearly, the monomer when becoming part of a macromolecule must undergo structural changes for forming bonds by addition or condensation reactions. The structure assumed by the monomer when part of a macromolecular chain is indicated as the 'repeating unit' (r.u.). The product of the polymerization reaction is the macromolecule, which has high molecular mass corresponding to a multiple of finite number of the repeating unit. Note that from the same monomer, macromolecules containing a different number of repeating units can be obtained, all having the same short term molecular structure, but giving different material properties.

In a picturesque simplified representation, the monomer can be designed as the precursor of the coach (monomeric unit) constituting a long train (macromolecule). A monomer must therefore have some basic requirements of being at least bi-functional for forming chemical bonds with at least two other monomer molecules, during a specific polymerization process. The polymer with plastic behaviour must be converted in the corresponding melted material by heating at a temperature over the melting point but below the decomposition temperature of the subject polymer. This is obtained only with not cross-linked chain, and therefore, the monomer for the plastic polymer is bi-functional.

For this reason, the following presentation refers only to bi-functional monomers which are submitted to polymerization reactions according to a chain or a stepwise mechanism.

The chain polymerization is generally applied to monomers that contain a reactive double bond opening up to form a chain by repeated rapid addition. The reaction is started and developed by initiators and catalysts.

The typical monomers are alkenes or substituted alkenes. The reactions are actually fast and involve the conversion of a double π-bond of the monomer to two more stable σ-bonds in the polymer chain; therefore, the polymerization reaction is usually exothermic. A general scheme illustrating the formation of a linear macromolecule from a monomer containing a double bond (bi-functional) is reported in Fig. 4.1.



Y* is an initiator or supplied energy
* may be a radical or a cation or an anion)

Fig. 4.1 Schematic representation of chain polymerization

Monomers with a carbon–carbon double bond can be polymerized by either free radical, ionic or metal-coordination methodologies. In fact, we can distinguish four polymerization procedures according to the following description.

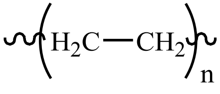
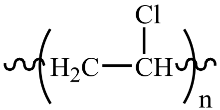
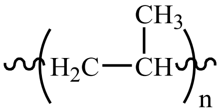
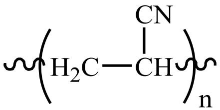
- Free radical polymerization: the initiator is a molecule generating free radicals or energy supply, and the propagating site (marked with *) is a free radical derived from the monomer.
- Cationic polymerization: the typical initiator is a protonic acid or a Lewis acid, and the propagating site (marked with *) is a carbocation.
- Anionic polymerization: the initiator is a molecule capable of generating an anion and the propagating site (marked with *) is a carbanion.
- Coordination catalytic polymerization: the initiator is a transition metal complex with, in general, an organometallic co-catalyst, and the propagating site is the catalytic complex with the monomer bearing connected the growing chain.

As a result of this polymerization, the polymer is formed of repeating units with similar structure as the monomer (without obviously the double bonds) and has a higher molecular mass (Table 4.1). The chains forming the polymer are long but not infinite and have two terminal groups derived from the initiator and from the chain termination mechanism.

The stepwise polymerization generally proceeds by the reaction between two complementary functional groups present on the same molecule (for example one amino acid or a hydroxyl acid) or formed in situ from two complementary bi-functional molecules (a diamine and a dicarboxylic acid or a diol and dicarboxylic acid). The reaction steps leading to a macromolecule can occur with loss of a small molecule (polycondensation), such as water or ammonia, but also by the addition of a functional group to a reactive unsaturated group as diol addition to diisocyanates to give polyurethanes (Table 4.2).

The examples of monomers and polymers reported in Tables 4.1 and 4.2 indicate the broad structural and chemical variability of the synthesized structures where carbon–carbon bonds, oxygen, nitrogen atoms and aromatic groups can be present in the main chain or as side groups. This in turn gives different chemical and physical properties as well as mechanical and thermal properties in assembled materials, polymer packing, going from soft to rigid plastic polymer up to fibres. Apolar/aliphatic polymers have mostly applications as soft plastics. Whereas, heteroatoms and aromatic groups give a more rigid structure, contributing to more performing plastics in

Table 4.1 Examples of monomers giving chain polymerization and the corresponding polymers

Monomer	Formula	Polymer	Trivial name	Structure of repeat unit
Ethene	$H_2C{=}CH_2$	High density poly(ethene)	High density poly(ethylene), HDPE	 $\sim\!\left(H_2C-CH_2 \right)_n\!\sim$
Chloroethene	$H_2C{=}CHCl$	Poly(chloroethene)	Poly(vinyl chloride), PVC	 $\sim\!\left(H_2C-\overset{\overset{\displaystyle Cl}{\vert}}{C}H \right)_n\!\sim$
Propene	$H_2C{=}CH-CH_3$	Poly(propene)	Poly(propylene), PP	 $\sim\!\left(H_2C-\overset{\overset{\displaystyle CH_3}{\vert}}{C}H \right)_n\!\sim$
Propenenitrile	$H_2C{=}CH-CN$	Poly(propenonitrile)	Poly(acrylonitrile), PAN	 $\sim\!\left(H_2C-\overset{\overset{\displaystyle CN}{\vert}}{C}H \right)_n\!\sim$

(continued)

Table 4.1 (continued)

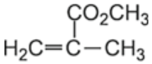
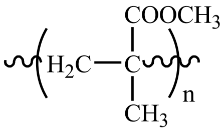
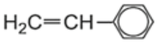
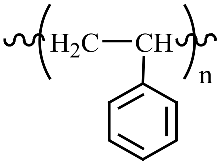
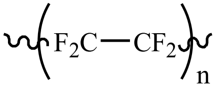
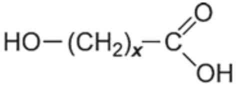
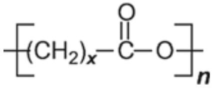
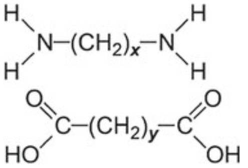
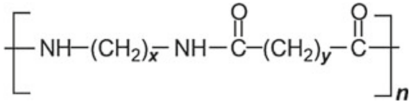
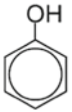
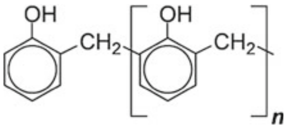
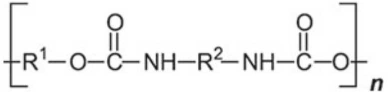
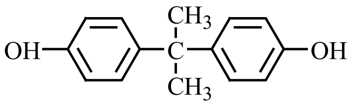
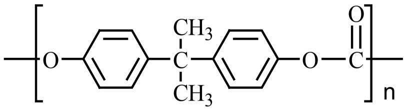
Monomer	Formula	Polymer	Trivial name	Structure of repeat unit
Methyl 2-methylpropenoate	 $H_2C{=}C(CO_2CH_3){-}CH_3$	Poly(methyl 2-methylpropenoate)	Poly(methyl methacrylate), PMMA	
Phenylethene		Poly(phenylethene)	Poly(styrene), PS	
Tetrafluoroethene	$F_2C{=}CF_2$	Poly(tetrafluoroethene)	Poly(tetrafluoroethylene), PTFE	

Table 4.2 Examples of monomers giving stepwise polymerization and the corresponding polymers

General polymer	Monomer	Polymer formula
Polyesters	 $HO-(CH_2)_x-C(=O)OH$	 $-[(CH_2)_x-C(=O)-O]_n-$
Polyamides	 $H_2N-(CH_2)_x-NH_2$ $HO(O=)C-(CH_2)_y-C(=O)OH$	 $-[NH-(CH_2)_x-NH-C(=O)-(CH_2)_y-C(=O)]_n-$
Phenol–methanal plastics	 CH_2O	
Polyurethanes	$HO–R^1–OH$ $O=C=N–R^2–N=C=O$ R1 and R2 alkyl and/or aromatic substituents	 $-[R^1-O-C(=O)-NH-R^2-NH-C(=O)-O]_n-$
Polycarbonates	 (Bisphenol A) $X_2C=O$ (X = $O–CH_3$ or Cl)	

term of applications temperature and mechanical performances and are used as rigid plastic materials or fibres (Young 1987).

4.2.1 Hydrocarbon Monomers from Oil

The viscous component necessary for plastic properties is fluid when strong interactions are lacking as in hydrocarbon macromolecules. For this reason, most common monomers polymerized for plastics are hydrocarbon molecules containing a single double bond per molecule and are made of linear chain without any cross-links. These monomers preferably contain a terminal double bond, that is a vinyl group attached to a hydrogen atom in ethylene or to alkyl or aryl groups in aliphatic and aromatic mono-olefins, respectively. These monomers have a high reactivity for surviving in the natural environment and were obtained through several man-made preparative processes starting from fossil resources. Now we are facing the real possibility to produce these monomers from renewable sources, such as fermentation, to save non-renewable resources maintaining products with exactly the same performances.

The hydrocarbon monomers used for producing the corresponding plastic materials are ethylene and monosubstituted 1-olefin, having the molecular formula reported in Fig. 4.2.

It is of interest to note that these monomers contain carbon and hydrogen only, and thanks to the reactivity of the double bond present in each olefin molecule, can be converted into macromolecules polymers, the polyolefins, by activators of the polymerization reaction. The polymerization converts the double bond in a saturated structure; thus, the resulting polymer is formed of saturated hydrocarbon macromolecules that is high molecular weight paraffins. Therefore, the polyolefins maintain the hydrophobic character of the monomer being paraffin with additional chemical inertness as the double bond disappears during the polymerization process. Due to their reactivity, olefins are not present in the major hydrocarbon sources used, such as natural gas and crude oil. Fractions of these last are then processed by steam cracking to provide petrochemicals like as olefin and diolefins (dienes) to be employed as monomers (Fig. 4.3).

Aliphatic mono-olefins (ethylene, propylene, 1-butene, etc.) are directly obtained by dehydrogenation of C2–C4 natural gas ethane, propane, and butanes, while the steam cracking of higher molecular weight saturated species present in petrol produces additional olefins and aromatics. Schematically, as shown in Fig. 4.3 a process

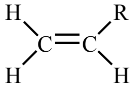


Fig. 4.2 Mono-olefins general structure

where R= H, $-CH_3$, $-C_2H_5$, and few longer alkyl group, $-C_6H_5$

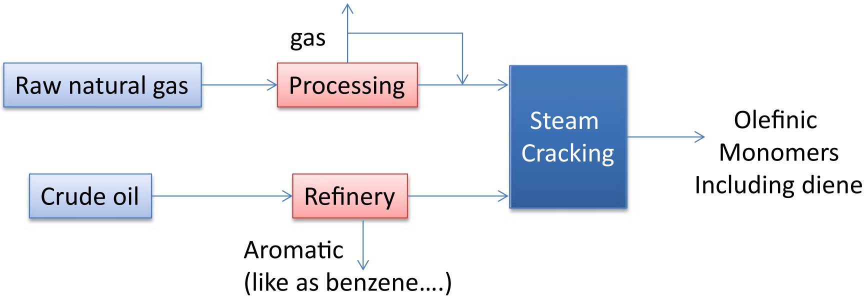


Fig. 4.3 Schematic representation of conversion of crude oil and natural gases into monomers

can be directed to produce several intermediate petrochemical feedstocks including ethylene, propylene, butenes, butadiene and benzene. The first three are, as said, very important for direct polymerization to the corresponding plastics polymers. Butadienes are interesting for producing synthetic rubber, while benzene is the basic molecule for aromatic mono-olefins.

The two most important monomers ethylene and propylene are produced in steam crackers in amount that toady are over 200 Mt overall with ethylene/propylene ratio 1.6–1.7. The plants involved in this very impressive production are very large up to as much as 1.0–1.5 Mt per year. It is evident then how difficult can be to replace in short time this remarkable production from fossil with that of the same monomers from sugar fermentation.

Even if, as mentioned before, mono-olefins do not exist in nature being too reactive, ethylene was demonstrated to be an intermediate in some fruits such as apples and pears as ripening begins but it cannot be present in the final fruit. Clearly, it would not easy to collect this ethylene in a sustainable way to feed the Industry to an acceptable level. One could argue way Nature never produced from this available monomer the corresponding polymer. The explanation could be that there was no need in nature for a filmable and processable durable plastic material with high hydrophobic character, which on the other side became very popular in the present times. The most popular aromatic mono-olefin is styrene. It is not produced directly from petrol and must be prepared according to two industrial processes starting from benzene and ethylene. The first step consists of the alkylation of benzene to ethylbenzene with ethylene under cationic catalysis and the second final step is the dehydrogenation of ethylbenzene to styrene at high temperature and in the presence of metal oxides as catalyst.

Ethylbenzene produced as reported in Fig. 4.4 can also be converted in styrene by treatment with oxygen to form the ethylbenzene hydroperoxide. This last is reacted with propylene to give propylene oxide and 1-phenylethanol, which can be successively dehydrated to styrene.

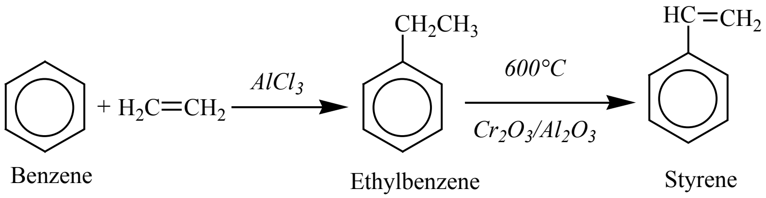


Fig. 4.4 Synthesis of styrene monomer

4.2.2 *Monomers Containing Heteroatoms*

In addition to hydrocarbon monomers providing by polymerization a number of paraffinic stable and hydrophobic plastic materials, monomers containing heteroatoms are also used to produce plastic polymers with expanded performances towards different directions. Indeed, a group of these monomers is formed by the hetero-substituted mono-olefins having the molecular structure similar to that indicated in Fig. 4.2 with the substituent R containing in general oxygen and nitrogen or a halogen atom. Typical examples are the acrylic and methacrylic monomers. In the former case, R has the structure –COOR, where R, can be alkyl or aryl, –COOH, CN or more or less substituted organic groups. Similar monomers are the methacrylic derivatives where the vinyl group of acrylates is instead a 2-propenyl group. Other used unsaturated monomers are vinyl chloride, vinylidene fluoride and tetrafluoroethylene. All the above monomers can be polymerized by chain mechanism. This last is also valid for heterocyclic compounds such as epoxides, lactones and lactams, but in these cases, the polymerization starts with ring opening instead of attack to the double bond. The resulting polymer from heterocyclic monomers clearly has heteroatoms in the macromolecules backbone.

Additional plastic polymers can also be obtained by stepwise polymerization from monomers containing two complementary functional groups, such as amino acids, hydroxy acids or by a mixture of two bi-functional compounds, with complementary functionalities such as diamine plus dicarboxylic acid or diol plus dicarboxylic acid, through a stepwise polycondensation process (Table 4.2). All these monomers are mainly produced from oil feedstocks according to various consolidated industrial processes, but some of them can also derive from renewable sources.

4.3 Polymerization Processes

4.3.1 *General Aspects*

According to the main objective of the present book, the polymerization processes are here reported in a form and in a detail aimed to provide appropriate information about the possible macromolecular structures formed when submitting a specific monomer to one of the applicable polymerization processes (Tobita 2015). Then, the following pages provide the reader with a basic knowledge about the synthetic possibility offered by the different monomers in reference to the related polymerization processes (Jenkins et al. 1996).

It is well known that polymerization processes were discovered and developed to convert monomers, which are usually in gas o liquid form, into macromolecules, which are the sub-, micro-constituents of solid polymers including plastics. These monomers are derived from feedstocks of fossil origin and were made available in huge amounts by man-developed process, which until now covered all human society requests. The type of polymerization process may be different depending on monomer general structure determining its chemical reactivity. Polymerization processes can be clearly used to produce polymers of monomers derived from renewable sources, but having the same structure as those from oil, such as ethylene from fermentation ethanol. In addition, the new bio-derived monomers, which were not obtained before in pure petrochemical production, are converted into the corresponding polymers through the mentioned polymerization processes here below described.

The polymerization is a typical man-made industrial process and its understanding, combined with the information connected to the monomer structure, is important to be fully aware of the molecular characteristics of the macromolecule constituting the derived polymeric materials.

It is fundamental to note that as the polymerization reaction consists of repeated covalent bond formation between successive monomer molecules that change their structure to that of the repeating unit either by internal electronic rearrangement in polyaddition or by eliminating small molecules in polycondensation. In case of plastic materials, the macromolecules are long linear chains derived from bi-functional monomers (see the previous section).

The final polymer product obtained from a single monomer, which originates only one type of monomeric unit, is a homopolymer but the macromolecular chains are in general not identical as they may differ in length that is in number of inserted monomeric units, as the initiation and termination reactions may not necessarily occur at the same time for all chains. The resultant molecular weight is then an average value and the dispersion (MWD) of these values is described by a curve with the maximum value corresponding to the most probable number of units per macromolecule that is equal to the number average molecular weight $\overline{M_n}$ (Eq. 4.1).

Basic definitions of the number average molecular weight $\overline{M_n}$ is reported below in Eq. (4.1):

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} = \sum n_i M_i \tag{4.1}$$

were N_i is the number of macromolecules of the i-th fraction all having molecular weight M_i and n_i is the molar fraction of the same macromolecules having molecular weight M_i The weighted average molecular weight is given by Eq. (4.2):

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \sum w_i M_i \qquad (4.2)$$

where w_i is the weight fraction of macromolecules having molecular weight $M_{i.}$

Note that the latter is usually higher than the former one.

An evaluation of the inhomogeneity of the molecular weight of the different length macromolecules is indicated by the ratio between the two above average and is named molecular weight dispersion MWD Eq. (4.3):

$$MWD = \frac{\overline{M_w}}{\overline{M_n}} \qquad (4.3)$$

In polymerization processes giving chain with different length, $\overline{M_w}$ is always greater than $\overline{M_n}$ indicating a polydispersed material; only in the case of a monodispersed material, when all chains have the same length, $\overline{M_w} = \overline{M_n}$ and MWD = 1. Indeed, MWD accounts for the molecular weight heterogeneity of a polymer.

A more complex situation arises when the monomer is not single, and a mixture of two (copolymerization) or more (multi-polymerization) is submitted to the polymerization process. In this case, two different monomeric units are generated in a relative amount depending on starting feed composition and comparative monomers reactivity towards the polymer growth reaction. The macromolecules forming the polymer can then be different also for composition (ratio between the two monomer units) and distribution of these two units along the chain. Sometimes this type of structural complexity may be encountered even starting with a single monomer, as observed for 1,3-dienes, which can originate chemically distinct monomeric units (as 1,2 or 1,4 reaction) or stereochemically distinct units (1,4 trans or 1,4 cis-diene units). The stereochemical complexity is also observed for the polymerization of prochiral monomers, monosubstituted olefins (propylene, etc.) or racemic monomers (D- and L-lactic acid).

The average length of the chain, its dispersion, as well as the content and sequence along the chain of chemically or stereochemically distinct units can be modulated by the features of the used polymerization process and related reaction conditions.

It is out of the limits of this book to discuss in detail the mechanism and the many peculiar features of all available polymerization processes. Rather here one can find a synthetic description of the polymerization reactions industrially used to produce plastic polymers and the structural features that can be achieved depending on monomer and process mechanism.

The average number of monomeric units per chain provides the number average polymerization degree, which is equal to the number average molecular weight divided by the weight of the monomeric unit. The weight fraction of monomer converted into polymer provides the polymerization yield. The two values can be independent of each other as a high average molecular weight clearly does not imply a high yield. This latter can also be reached by converting all the monomer into low molecular weight polymer. The two aspects are schematized below:

$$n\,M = m\,M_x + (n - mx)\,M \tag{4.4}$$

where m = number of formed macromolecules;

x = average polymerization degree (number of monomer units per macromolecule) defined as

$$x = \frac{\overline{M_n}}{M} \tag{4.5}$$

and $\overline{M_n}$ the number average molecular weight;

Y = percent polymerization yield is given by

$$\mathrm{Y} = (m\,x\,M/n\,M)\,100 \;=\; (m\,x/n)\,100 \tag{4.6}$$

The polymerization reactions follow two distinct kinetic mechanisms, namely, chain polymerization and stepwise polymerization.

The chain polymerization interests unsaturated monomers, such as olefin or cyclic compounds, and must be initiated by an appropriate compound, the initiator, which by reactions with the monomer produces activated species further reacting with the available monomer. The formation of a polymer from an unsaturated monomer is an example of a chain reaction, which once started is able to keep itself going if monomer is provided, while the reaction stops when the monomer is finished. Some processes can stop even in the presence of unconverted monomer; if the active species are consumed in undesired reactions. Therefore, chain polymerization reaches the maximum molecular weight allowed under the selected polymerization condition already when the monomer conversion is low. The successive progress of the reaction then is necessary to increase the polymer yield but it has very limited effect on the average chain length.

In the stepwise polymerization, the monomers combine in longer molecules one by one in successive steps. While many steps are necessary for a long chain, the monomer can disappear much earlier. In a borderline case of dimer, all the monomer would be fully converted but the polymerization degree would be only 2. We can then conclude that in the stepwise polymerization, the conversion reaches a high value when the molecular weight is low. Longer time is than necessary to reach a desired value of molecular weight, opposite to what happen in chain polymerization.

4.3.2 Chain Polymerization Processes

4.3.2.1 Free Radical Chain Polymerization

During the free radical polymerization process, it is suggested that four reactions occur and control the polymer yield and the molecular weight. The three first reactions are the initiation producing activated monomer species, the propagation responsible for the successive addition of monomer molecules to the initiated monomer and then of the chain growing, and the termination responsible for the disappearance of active species then giving termination of the growing chain and of the polymerization. These three reactions are clearly effective on the amount of polymer formed (polymerization yield), which is indicated also by the fraction of monomer converted into polymer. The molecular weight of the formed macromolecules and the average length of the chains depend on the occurrence of the additional fourth reaction, the chain transfer, which stops the macromolecule growth by transferring the activated species to a new macromolecule. This reaction has the effect of reducing the chain length and then the molecular weight but has no effect on the polymer yield. Indeed, this reaction does not reduce the number of active species and then does not affect the polymerization rate and the polymer yield, but stopping the growth of the single chain limit is molecular weight.

The combination of these reactions is described in the commonly accepted mechanism of the free radical initiated polymerization that is summarized below with reference to the above fourth reactions.

I. Initiation (the polymerization get started)

Under the impact of energy supply, the initiator is converted into reactive free radicals. Light, heat or an appropriate redox reaction can provide the energy needed for this process. Figure 4.5 describes how this can happen in case the initiator is a peroxide.

The real initiation occurs when the free radical ties a monomer molecule with formation of a new free radical, called the activated monomer (Fig. 4.6).

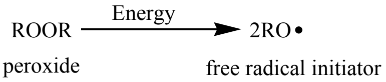
II. Propagation (polymerization continues with chain length growing)

The initiation reaction is normally instantaneous, while the chain propagation reaction needs more time to allow the polymer chain to grow. In the propagation the newly formed activated monomer attacks and attaches to the double bond of another monomer molecule, which generates the new activated monomeric unit. This addition occurs again and again to make the long polymer chain (Fig. 4.7).

The '*n*' stands for any number of monomer molecules, typically in the thousands.

III. Termination (active species are stopped)

The free radical initiated chain reaction terminates as the free radical are cancelled by side reactions. Each termination reaction stops the addition of other monomers



$$\underset{\text{peroxide}}{\text{ROOR}} \xrightarrow{\text{Energy}} \underset{\text{free radical initiator}}{2\text{RO}\bullet}$$

Fig. 4.5 Formation of primary radicals

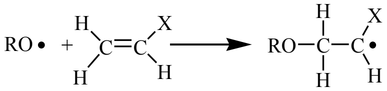


Fig. 4.6 Initiation reaction

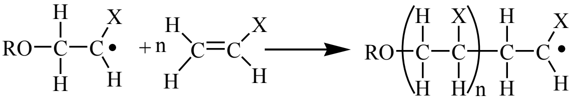


Fig. 4.7 Propagation reaction

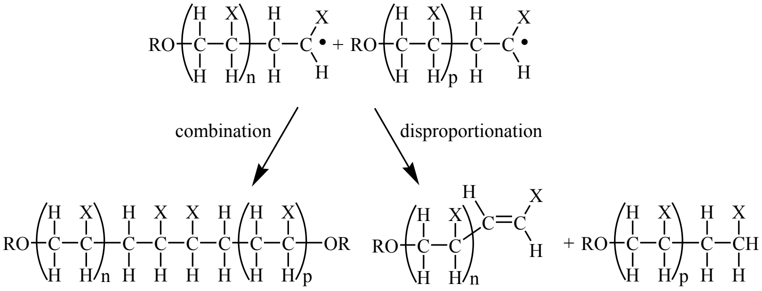


Fig. 4.8 Termination reactions

to a single chain that thus ends growing. The single termination results also in a reduction of the total concentration of free radicals and the reaction stops when these are consumed. If at this point monomer molecules are still present, the polymer yield is not complete. There are two termination mechanisms related to the encounter of free radicals at the end of two growing chains. Disproportionation occurs if the two free radicals give rise to the transfer of a hydrogen atom with formation of a saturated and one unsaturated macromolecules end group. On the other side, they may react to give a stable carbon–carbon bond between the two chain ends according to a combination process. In the former case, the length of the two terminated chains remains the same reached during the polymerization reaction, whereas in the latter case the length is the sum of the two terminated chains. The occurrence of these two processes, in addition to the termination of the reaction, affects the dispersion of the molecular weight.

The molecular description of the two termination reactions is schematically reported in Fig. 4.8.

The free radical undergoing the termination reaction can be of different origin and can be located either at the end of growing polymer chains, or in a low molecular weight molecule including the primary free radicals from the initiator. The reactants, the reaction times and the reaction conditions are important parameters determining the limitation of the termination or its direction towards preferred routes according to the various possibilities described above.

IV. Transfer (single chain stops while polymerization continues)

The transfer reaction is defined as a reaction in which a growing chain carrying the free radical end reacts with another molecule and transfers the free radical to this latter. The growth of the chain is stopped and the active specie, the free radical is

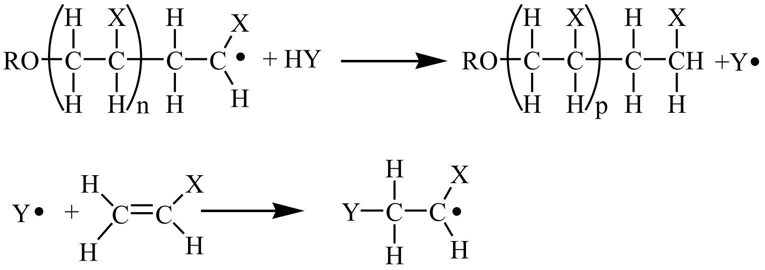


Fig. 4.9 Transfer reaction

transferred to the other molecule that can start the growth of a new chain. As the results, the chain is terminated and the macromolecule does not grow anymore. On the other side, the new free radical formed interacts with the remaining monomer and the polymerization reaction continues (Fig. 4.9).

The transfer reaction limits the polymer molecular weight but has small or no effect on the polymerization rate. In addition to the effect on the chain length, the transfer may be also responsible for branching of different length.

The occurrence of the transfer reaction in addition to the termination reactions is responsible for the formation of chains with different number of monomer units. Then the macromolecules formed by free radical chain polymerization have not all the same molecular weight and the resulting polymer has a broad distribution of the molecular weight with $MWD =$ up to 2.

For the above reasons, the physical properties of polymeric materials from a particular monomer can be varied depending on the polymer's average length, the molecular weight dispersion and the amount and type of branching.

The monomers suitable for the free radical polymerization must give rise, through the reaction with the primary radical, to an activated monomer unit bearing a relatively stable free radical. To act in this way the substituent on the monomer double bond should be capable to provide the radical stabilization while inducing on the double bond a modest or none electrons excess or deficiency to avoid the formation of charged species. These last giving electrostatic repulsion between activated monomer and incoming monomer would hinder the propagation reaction. Indeed, the activated monomer and the incoming monomer would bear a charge of the same sign as having the same substituent.

4.3.2.2 Ionic Chain Polymerization

While in the free radical chain polymerization the reaction starts when a non-electrically charged free radical interacts with the monomer to give rise to an activated free radical, in the ionic polymerization the monomer is activated under the action of a charged species that converts the monomer into a cation or an anion. This situation

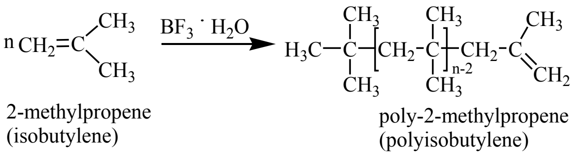


Fig. 4.10 Isobutylene polymerization

can be exemplified with reference to the X substituted ethylene monomers of Fig. 4.1. In this molecule, if X is an electron withdrawing substituent, an excess of positive charge is localized on the double bond and the polymerization can be initiated by an anion which converts the monomer in an activated monomer anion that will successively react with other monomer molecules to give a macromolecule. With an electron releasing X substituent, a negative charge excess is localized on the double bond. This monomer is then activated to a cationic monomer by the attack of a cation thus starting a cationic polymerization reaction. Cationic and anionic polymerization can also be applied to cyclic monomer bearing a site that can be subjected to cationic or anionic attack. These sites are in general related to the presence of heteroatoms either a member of the cycle or bond to a carbon atom of the cycle.

The ionic polymerization has no termination reaction as the electrostatic repulsion does not allow two growing chain ends to encounter for giving deactivated species. Therefore the whole kinetic mechanism of the ionic polymerization has only three reactions, namely, initiation, propagation and chain transfer. Clearly, the presence of transfer reactions means that one growing chain can be stopped as the active ion is removed by the transfer to another species, which can start a new chain. Therefore while the conversion monomer to polymer does not stop until there is monomer available, the molecular weight is limited by the transfer reaction. The average value of the molecular weight results at the end by the ratio between the polymerization rate and the transfer reaction rate.

Hydrogen atoms are not effective electrons donating substituent; methyl is better but still relatively weak. The simplest olefin that can be polymerized by cationic initiators is 2-methylpropene (isobutylene). Indeed, the double methyl substitution on the same carbon atom induces enough negative charging on the double bond.

The cationic polymerization of 2-methylpropene or isobutene can be performed by protic or Lewis acids such as sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water or aluminium chloride. Anhydrous conditions are necessary to avoid initiator deactivation and low temperature to limit transfer reactions. If these conditions are fulfilled a long chain polyisobutylene is formed (Fig. 4.10).

As mentioned before, ionic polymerization can also be effective for the conversion of cyclic monomers with nucleophilic character as epoxide, where the oxygen atom of the epoxy ring is subjected to the attack of cations (Fig. 4.11). Other cyclic nucleophilic monomers are cyclic sulphides, cyclic amines, small ring cycloalkanes, cyclic carbonates and also lactones and lactams.

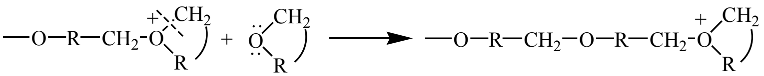


Fig. 4.11 Schematic representation of ring-opening polymerization mechanism

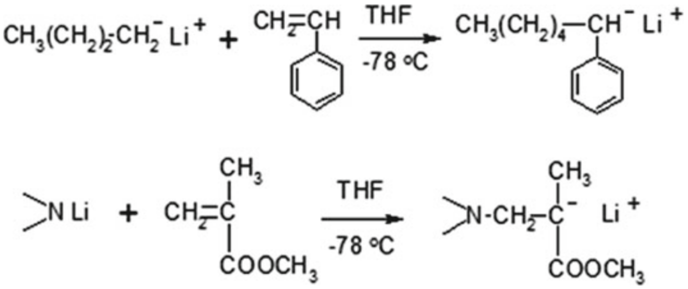


Fig. 4.12 Examples of anionic polymerization mechanisms

On the other side, if a monomer contains an electron deficient moiety, it can be subjected to nucleophilic attack by an anion to start anionic polymerization. Anionic polymerization can be efficient for unsaturated monomers having an electron deficiency on the double bond or with cyclic monomers containing an electrophilic site, such as acrylates, methacrylates, styrene and cyclic monomers such as lactams, lactones and epoxides. In these last cyclic monomers, the attack by the anion occurs on a different site in respect to what happens in the cationic initiate process (Fig. 4.12).

An important parameter in anionic polymerization is the polarity of the solvent promoting the dissociation of the active anionic growing chain end from the counterion. In polar solvents the dissociation is complete and each anion starts a chain.

In case any transfer reactions do not occur, the final number of chains is equal to the number of initiator molecules and therefore, in case of complete monomer conversion the degree of polymerization is given by Eq. (4.7):

$$\overline{x_n} = \frac{[M]_0}{[I]_0} \tag{4.7}$$

where $[M]_0$ and $[I]_0$ indicate the monomer and anionic initiator concentrations, respectively, at the zero reaction time.

4.3.2.3 Catalytic Polymerization

The most available and cheap potential monomers are the smallest olefins ethylene and propylene produced during the refining of oil and related simple processes. However, these monomers cannot polymerize by free radical or ionic polymerization under ambient conditions as the molecular structure does not allow the monomer activation and the propagation reaction to give high polymers. Ethylene polymers could be firstly obtained by ICI (Imperial Chemical Industries) in 1933 using a free radical initiator but working at relatively high temperature (200–300 °C) and extremely high monomer pressure (1.000–3.000 bar). Because of the high frequency of the transfer reaction under the drastic reaction conditions, the polyethylene formed was consisting of chains with many long and short branching. This polymer is today named low-density polyethylene (LDPE) as the branching does not allow a dense packing as expected for the linear chains.

About 20 years later, Karl Ziegler and Giulio Natta developed new catalytic processes to polymerize ethylene and propylene under extremely mild conditions, as example at room temperature and pressure. The inventive polymerization process is made possible thanks to a two components heterogeneous catalyst formed from the reaction of a transition metal derivative with an organometallic alkylating compound. The first-generation systems were prepared using $TiCl_4$ (or $TiCl_3$) with alkyl aluminium derivatives consisting of heterogeneous polymerization catalysts. A variety of transition metals as such or supported on various materials were successively employed and improved performances were obtained capable to provide very high polymer yield and to control molecular structure up to the stereochemical level. From the 80s also homogeneous catalysts were developed based on transition metal complexes bearing ligands capable to stabilize the transition metal- alkyl bond and with a spatial geometry controlling the monomer insertion stereochemistry and then the macromolecules microstructure.

The process allows the polymerization of all available 1-alkenes to obtain their copolymers. A variety of new polymers with paraffinic basic structure but with very different macromolecular structures and material properties were and are obtained. Polyolefins are today, indeed, the largest class of plastic polymers. The processes have allowed obtaining new ethylene polymers such as the very linear polymers HDPE, and many copolymers of ethylene with various 1-alkene with a good control of the density and thermomechanical properties. It is scientifically trivial, but in some way interesting to the objective of this book to remember that the application of the catalytic polymerization to the ethylene monomer obtained from renewable natural sources allows producing all the various ethylene polymers with exactly the same structures and properties as those originally obtained starting with ethylene from fossil origin.

The control of the primary structure of the formed macromolecules exerted by this catalyst class extends to stereochemistry. Thus the polymerization of the prochiral monomer propene, which gives a monomeric unit containing an asymmetric carbon atom (Fig. 4.13), is characterized by the possibility to have chains where the mentioned asymmetric carbon atom can have the same chirality (isotactic polymer) or alternate opposite chirality (syndiotactic polymer).

A third polymer of propene can also be obtained where the two configurations are randomly distributed (atactic polypropylene). The first two polymers are ordered and can crystallize to give a semicrystalline plastic material. The last is irregular and then results in an amorphous polymer. The three different chains are schematically represented in the planar zig-zag conformation just to show the stereochemical cor-

Fig. 4.13 Propene polymerization

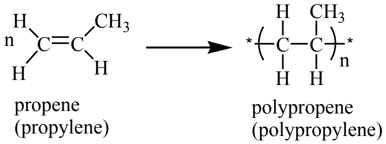
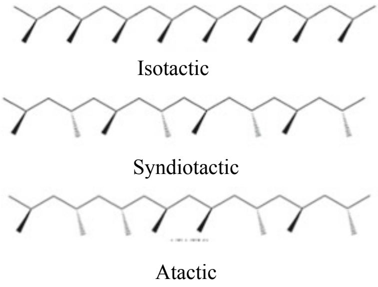


Fig. 4.14 Steric order and disorder of polypropylene macromolecules



relations along the chain (Fig. 4.14). The sketched conformation is not possible in the isotactic polymer due to the steric interaction among methyl side chain, but is observed in the syndiotactic stereoisomer where the above interaction is removed as the methyl groups are located on opposite sides of the planar zig-zag chain. Also, the atactic polymer cannot assume the indicated conformation and must rotate out of the plane when isotactic dyads are present.

From the industrial viewpoint, only the isotactic polypropylene is interesting having a range of plasticity from just below zero centigrade degree up to 160 °C with remarkable mechanical properties allowing applications as commodity but also in more advanced uses. For the industrial production heterogeneous new generation catalysts are the most used with some relevant examples reported in Table 4.3. These new catalytic systems have a very high sustainability thanks to the remarkable productivity and high stereospecificity avoiding catalyst purification and atactic polymer removal.

A large number of unsaturated monomers were indeed polymerized according to differently initiated chain mechanism. Several of them have plastic properties but differences performances thus being of interested in various applications and uses. The most successful that are produced on a large scale and are used constantly in everyday life in addition to the polyolefins are reported in Table 4.4.

4.3.3 Stepwise Polymerization

In this process different from the chain reaction one, the chains increase their length by stepwise binding of any two molecules present in the reaction mixture independent of the respective molecular weight. Indeed, the monomer and longer molecules, dimers, trimers and so on can link together at any time having two reactive terminal

Table 4.3 Typical formulations and performance of $MgCl_2$-supported Ti-based Ziegler–Natta catalyst for propylene isotactic polymerization

Internal donor	External donor	Productivity[a]	Index of isotacticity[b]	$MWD = \frac{\overline{M_w}}{\overline{M_n}}$
Aromatic monoester (e.g. ethyl benzoate)	Aromatic monoester (e.g. methyl-*p*-toluate)	0.5	>95	5–6
Aromatic diester (e.g. dibutyl-*o*-phtalate)	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	1–2	>97	5–6
2,2'-dialkyl-1,3-dimethoxypropane	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	>2	>97	3–4
Aliphatic diester (e.g. dialkyl succinate)	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	1–2	>98	>7

[a] 10^3 kg (PP) g $(Ti)^{-1}$
[b] wt% of highly isotactic PP

complementary groups. Both condensation and addition reactions can be involved in the linking between the two molecules. The former mechanism proceeds through a condensation reaction, in which a small molecule is eliminated in each step as happens in the formation of Nylon 66 from adipic acid and hexamethylene diamine (Fig. 4.15).

As all molecules have an amino and a carboxylic acid end groups, the condensation reaction can involve two molecules containing any number of monomer units. The different lengths are all present, and the average length of the macromolecules can be described by a typical Gaussian distribution whose maximum value indicates the numerically most represented chain length that is $\overline{M_n}$.This value depends on the fraction P of reacted functional groups of the monomer, which rapidly reaches values higher than 0.9. However, this is no sufficient for a useful molecular weight, which increases with time while increasing P. Values of P near to 1 are necessary to provide polymer with molecular weight enough high to have a plastic response. In case the molar ratio between the two different reacting groups is equal to 1 (this is always the cases for hetero-functional monomers as amino acids and hydroxycaboxylic acids) (Fig. 4.15), the average polymerization degree is given by (4.8):

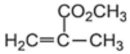
$$x = \frac{1}{(1 - P)} \tag{4.8}$$

Therefore for having $x = 50$ one needs P = 0.98.

In this case the molecular weight distribution ($\overline{M_w}$ /$\overline{M_n}$) is also controlled by P and increases with increasing P to reach the maximum value near 2.0 when P is very close to 1.

The polymerization rate is determined by the nature of the reacting groups present on the monomer and also on the molecular structure of the organic residue to which

Table 4.4 Non-hydrocarbon monomers for chain polymerization

Monomer	Formula	Polymerization	Trade name	Uses
Chloroethene (vinyl chloride)	$H_2C{=}CHCl$	Coordination Radical	Polyvinylchloride (PVC)	Piping Film, insulation Piping leatherette
Chlorotrifluoroethene	$FClC{=}CF_2$	Radical	Kel-F	Gaskets, insulation
Tetrafluoroethene	$F_2C{=}CF_2$	Radical	Teflon	Gaskets, valves Insulation, coatings
Propenenitrile (acrylonitrile)	$H_2C{=}CHCN$	Radical	Orlon Acrilan	Acrylic fibres
Methyl 2-methylpropenoate (methyl methacrylate)	 $H_2C{=}C(CO_2CH_3){-}CH_3$	Radical Anionic	Lucite Plexiglas	Coatings Moulded articles

(a) $H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow H_2N(CH_2)_6NHOC(CH_2)_4COOH + H_2O$

(b) $H_2N(CH_2)_6NH\text{-}[\text{-}OC(CH_2)_4CO\ HN(CH_2)_6NH\text{-}]_{x-1}\text{-}OC(CH_2)_4COOH$

Fig. 4.15 **a** Condensation reaction between hexamethylene diamine and adipic acid and **b** typical Nylon 66 macromolecule with x degree of polymerization (number of units per chain)

$zM_1 + pM_2 \longrightarrow$ -M1M2M2M1M2M2M2M1M1M2M2M1M1M2M1M1M1M2M2M1M1-

Fig. 4.16 Schematic representation of copolymerization reaction and the corresponding copolymer macromolecule (the reaction is not balanced, and z and p are initial numbers of M_1 and M_2, respectively)

these groups are bound. Clearly, the reaction can be accelerated by the presence of catalysts. These effects are summarized in Table 4.5 for a few selected examples.

4.3.4 Copolymerization

Copolymerization indicates a polymerization reaction starting with two different monomers giving macromolecules where two different units are incorporated in a random or controlled sequence mode and in a different molar ratio. The process then provides a useful tool for modulating material properties from the structural and functional viewpoints. Clearly similar structures can be also produced by partial post-polymerization modification of a fraction of units in a homopolymer macromolecule.

Here the possibilities are only discussed regarding the structural possibility offered by the copolymerization of two monomers, even one can easily understand that the process can be also applied, if convenient, to even complex mixtures of three or more different monomers. A typical example in this last contest is evidently offered by natural proteins.

While the term homopolymerization is used to identify the polymerization of a single monomer, the term copolymerization usually refers to the polymerization by any mechanism of a mixture of two monomers

In order to obtain a copolymer through chain polymerization is normally necessary that the process is carried out with mixture of two monomers to form polymeric products with two different structures in the polymer chain with possibly different sequential distributions. Then the product can be called copolymer if it is not a mixture of two homopolymers, but contains units of both monomers incorporated into each copolymer molecule as depicted in Fig. 4.16. Where M1 and M2 are the monomeric units formed from the two different monomers M_1 and M_2.

The composition of the copolymer is determined by the respective copolymerization rates of the two monomers in relation to their relative concentration and reactivity. The sequential distribution of the two different units along the chain can be casual (random copolymer, Fig. 4.16) as in the case reported before, in form of

Table 4.5 Kinetic constant of selected stepwise polymerizations

	Monomer 1	Monomer 2	T (°C)	Kinetic constant × 10^3 (L mol^{-1} s^{-1})
Polyester	$HO(CH_2)_{10}OH$	$HOOC(CH_2)_4COOH$	161	7.5×10^{-2}
	$HO(CH_2)_{10}OH$	$HOOC(CH_2)_4COOH$ [acid catalyst]	161	1.6
	$HO(CH_2)_6OH$	$ClOC(CH_2)_8COCl$	59	2.9
Polyamide	$H_2N(CH_2)_6NH_2$	$HOOC(CH2)_8COOH$	185	1.0
Polyurethane	m-OCN-R-NCO	$HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH$	60	0.40

Block copolymer: -M1M1M1M1M1M1M1-M2M2M2M2M2M2M2M2-

Fig. 4.17 Schematic representation of a block copolymer macromolecule

Alternating Copolymer: -M1M2M1M2M1M2M1M2M1M2M1M2-

Fig. 4.18 Schematic representation of an alternating copolymer macromolecule

$$\text{x } H_2N(CH_2)_5COOH \longrightarrow H_2N(CH_2)_5CO\text{-}[\text{-}HN(CH_2)_5CO\text{-}]\text{-}OH + (x\text{-}1)\ H_2O$$

Fig. 4.19 Polymerization reactions producing and Nylon 6

blocks (Fig. 4.17) or alternate (Fig. 4.18). These different sequences depend on the two monomer reactivity in relation to the polymerization mechanism selected. The effective formation of copolymer macromolecules is attained if the two monomers are both polymerizable with the selected type of initiator and catalyst.

The simultaneous chain polymerization of different monomers can also be carried out with mixtures of three or more monomers, referred to as multicomponent copolymerization, yielding more complex macromolecular structures, but it is not very common in plastic material.

The copolymerization reaction is important from the technological viewpoint as a sustainable tool to tailor-made plastic polymers with specifically desired properties combined in a single structural and functional material. An outstanding example is offered by the copolymers of ethylene with higher alkenes in the presence of transition metal catalyst to give the linear copolymer LLDPE with increased flexibility and lower melting point and density than the homopolymer HDPE. Also, the free radical initiated copolymerization of ethylene (E) with vinyl acetate (VA) provides the copolymer EVA combining the properties of ethylene blocks with those of the polar ester side chains.

The stepwise copolymerization needs some consideration to be well understood in relation to the concepts developed for the chain copolymerization summarized above.

Indeed the stepwise polymerization requests two complementary reactive groups that either by polycondensation or by polyaddition form links between shorter molecules present in the reaction vessel. As mentioned the two groups forming the link may be at starting present on two different molecules or on the same molecule. In the former case as for example, in the synthesis of poly(hexamethylene adipamide) [Nylon 66] the reaction is started with two distinct reactants, the diamine and the diacid, but the polymer obtained contains along the chain only one type of monomer unit derived from the alternate condensation of the two original reactants. And is therefore a homopolymer. Accordingly, Nylon 66 obtained from two reactants (Fig. 4.15b) and Nylon 6 from a single reactant (Fig. 4.19) give rise to very similar homopolymer chains.

A real copolymer with polyamide structure (Nylon) is obtained by using two heterobifunctional monomers, two amino acids, or a second diammine or diacid must be used when having the situation of homobifunctional reactants.

The particular mechanism of stepwise polymerization where reactivity towards incorporation of shorter chains into longer ones depends on the reactivity of the two linking groups and, in general, very moderately on the overall monomer structure, leads frequently to random copolymers. A segmental short block structure can be obtained by the use of macromers, which are low molecular weight polymers with two terminal reactive groups as for examples ethylene oxide oligomers. These approaches can allow the insertion in the macromolecules of part from renewable sources without substantially changes the final properties. This is the case of several diacids and diols that can replace at least in part the corresponding ones from fossil origin in the synthesis of polyamide and polyesters, respectively.

4.4 Processing to Materials

The product of the polymerization is in most cases an apparently solid material which needs fluidification to be shaped into forms useful for man activity. This fluidification process is performed with low energy consumption thanks to the relatively low melting points of organic polymers used as plastics (generally below 300 °C, which is a very low temperature as compared with the processing temperature of metals and alloys up to 550 °C and more) (Tadmor et al. 2006).

The processing of plastic material to form an object is facilitated by the remarkable reduction of the viscosity that a thermoplastic polymer shows with increasing the temperature. The original viscosity value is promptly recovered during the process of cooling (Fig. 4.20).

Once converted into a low viscosity fluid, the plastics material can be shaped in many different items by one of the following mechanical processing, the method selected being determined by the desired production (Agassant et al. 2016).

- *Extrusion*

Extrusion is a continuous industrial process for converting plastic materials from row shape (powder, pellets, and eventually milled scrap) to finished components. It consists in bringing the material in the fluid state (by heating) and in forcing it to pass continuously through a shaped profile, called extrusion head (or die), where it takes the form, and then cooling it to definitely stabilize the mould (Fig. 4.21).

First, plastic pellets are gravity fed from a hopper into a heated screw or into two co-rotating screws (Fig. 4.21). As the screw turns about its axis, it transports, melts, and pressurizes the plastic (through the degassing section). After complete melting and, in some cases, additives mixing (see the following section), the molten material is forced through a die that shapes it into a specified cross section, producing parts with a potentially wide range of lengths. The product assumes its final shape inside the die and, as a function of its different design, the final object assumes a final geometry; by considering that the extrusion is a continuous process, generally it is adopted to obtain films, profiles, laminates, tubes, pipes.

By using a slit die films with different thickness may be produced, but the most common method to extrude films is the blowing process. This process is basically the same extrusion with suitable die to provide pipe or profile apart from the die orientation which is generally vertical.

During extrusion processes, plastics are transformed from solid to liquid and back again without loss of the main properties (at least for several cycles). This is particularly effective when proper conditions to minimize degradation are adopted. Based on this feature, scrap parts can be ground and re-extruded, making the extrusion the most popular method for reducing or recycling plastic waste.

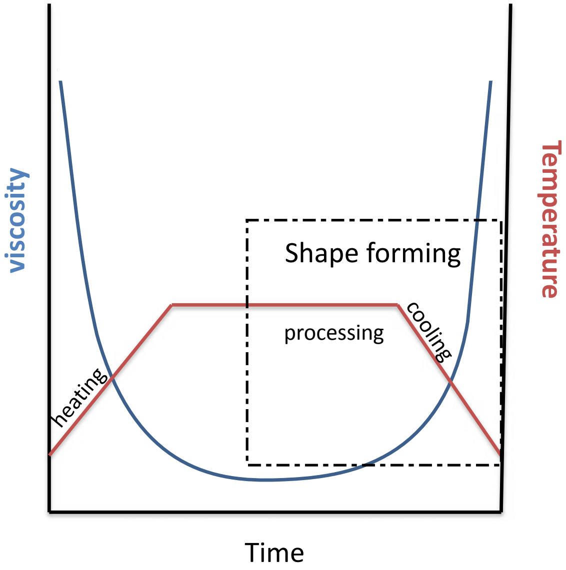
– *Injection moulding*

It is a cyclical and discontinuous process that consists in heating the material fed from a hopper of the extruder and plasticizing it; the mould is then periodically injected in a die (or mould) with the desired shape, which is then cooled to obtain the desired issue (Fig. 4.22).

The resin, in the form of granules (powders or pellets), is at first fluidized under heating, and then forced through a nozzle into the die, while kept under pressure, so as to fill the cavities and comply in a desired manner. A cooling cycle reports the material in the solid state and the formed item is expelled from the machine by an automatic extraction mechanism.

A moulding cycle lasts from several seconds to few minutes and includes the closing of the mould, the injection, the cooling of the material in the mould, opening the

Fig. 4.20 Viscosity and temperature profile vs. time during the processing of a thermoplastic polymer (dashed zone roughly indicates the range where the material is processed and assumes the desired shape)



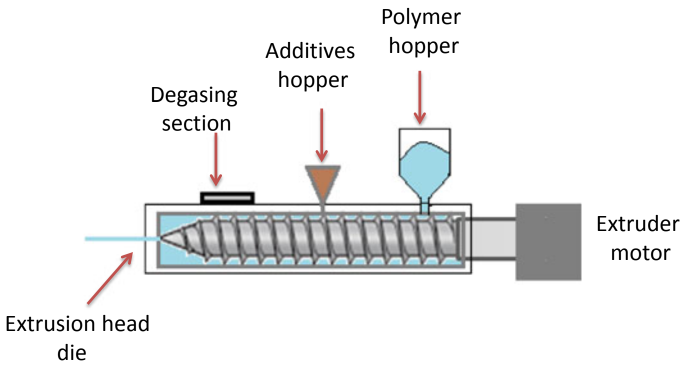


Fig. 4.21 Schematic extruder profile

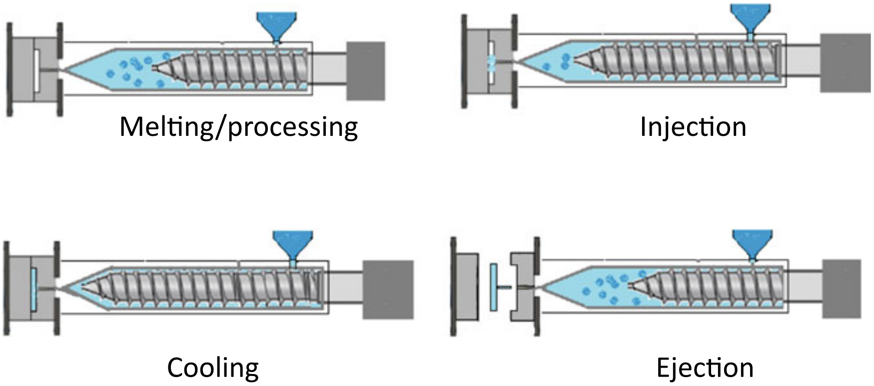


Fig. 4.22 Schematic representation of the injection moulding cycle of plastic materials to provide the desired piece by means of a mould with especially geometry

mould and the extraction of the moulded piece. The pieces unsuccessfully designed or scraps are ground and the material thus obtained is mixed with fresh polymers and additives and can be reused. A very large number of different objects are moulded with this processing methodology (ranging from parts of appliances, tools for the house, bottles and containers of various kinds) and by considering that the automatic system allows the cylinder filling a second mould during the cooling of the first, the modern machinery can be considered to work in semi-continuous cycle.

- *Blow moulding*

It is a moulding process of polymers used for manufacture opaque flasks and bottles (milk bottles, detergent bottles, containers, etc.). The most common system combines extrusion and blow moulding technologies (Fig. 4.23). Step one is the extrusion of a tube of plastic material that goes through an open mould divided in half (a); then, the

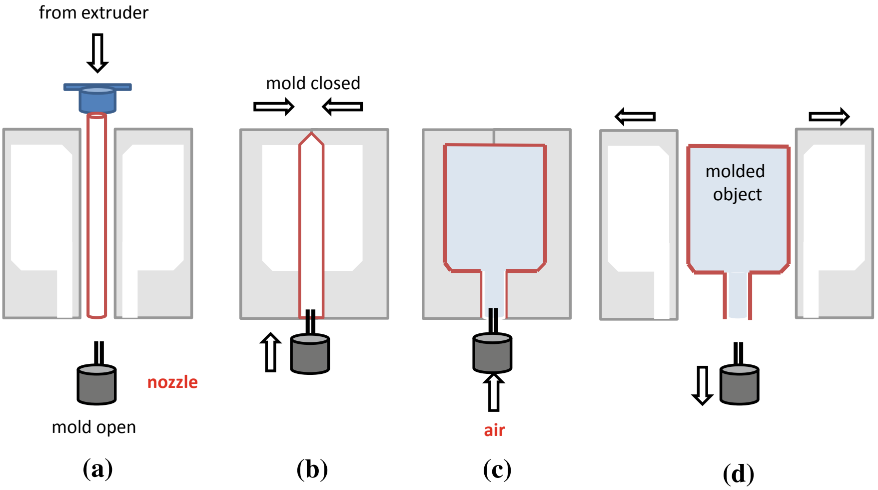
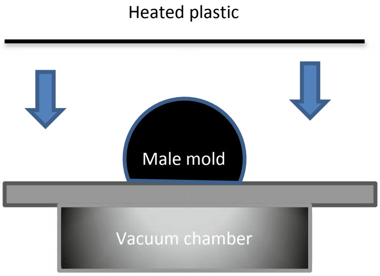


Fig. 4.23 Schematic representation of blow moulding processing of plastic materials

Fig. 4.24 Schematic representation of vacuum thermoforming technology



two cavities are closed and the polymer mould cuts the tube in one of the sections (b).

Compressed air blows from the other open section of the mould through a blow pin so that the softened polymer adheres to the wall of the mould taking the desired form and shape (c). Then the mould is cooled and the manufactured item, which is a hollow object (a bottle in Fig. 4.23), is ejected from the opened mould (d).

– *Thermoforming*

It is a fabricating process where sheet of plastics are heated up to the softening point and formed over a male or female mould. Vacuum forming and pressure forming can be used to make plastic assuming a broad and diverse shape. It is generally considered a sideline technology owing to processing taking place on materials previously extruded in the form of plates, sheets or films. The sheet, before processing, is heated in special furnaces/ovens or directly in the machine; then it is placed over a hollow mould and compressed or the vacuum allows the materials taking the form (Fig. 4.24).

Thermoformed plastics are ideally suited for automotive, consumer products, packaging, retail and display, sports and leisure, electronics, and industrial applications with particular reference to glasses, plates, interior of refrigerators, panels, small boats and even works of contemporary art.

Other less important plastic processing methodologies that deserve nomination are the calendaring, a finishing process used on cloth, paper, or plastic film/laminates; the rotational moulding a particular moulding technique dedicated almost exclusively to create hollow objects of large dimension and the sintering used in some cases for plastic powders.

– *Plastic limitations*

Plastic polymers are very convenient materials to be submitted to shaping, after thermo-conversion into the fluid state, to obtain items with features that can respond to the market demand. The shaping temperature depends on polymer melting and glass transition temperatures of the polymer as well as on the selected processing method. The selected temperature for the forming is in general higher than the polymer characteristic transition temperatures as a result of the fact that it is necessary to grant the appropriate fluidity, which should be low enough for the polymer to assume the model shape after its complete filling (see Fig. 4.20). Such requirement is particularly necessary in case of injection moulding where complicated mould has to be filled completely by the fluid materials to avoid defects in the produced item. On the other side, the temperature control is very important and must be kept well below the thermal stability limit of the polymer to avoid material degradation.

The polymer thermostability must be evaluated in advance when designing a production process. The aggressive environment by the mechanical treatment at relatively high temperature is in part released by using additives acting as plasticizer and fluidificants. Additional negative effect against the material stability during processing can derive by the chemical attack against the weakest chain sites. Molecules acting in this way should be removed before processing. A typical example is given by the water present in polymers having hydrolyzable bonds; indeed at melting temperature and over, water can hydrolyze the ester groups thus reducing the molecular weight of polyesters (Fig. 4.25) during the processing. Therefore, these polymers must be dried in advance at temperature over 100 °C to be processed.

The processing of polyesters after appropriate removal of adsorbed water allows maintaining the original chain length thus giving products with properties corresponding to those of the fed material. Practically, all organic plastics are also subjected to the free radical attack creating free radical on the chain, which can be responsible for the modification of the starting molecular structure by initiating side reactions such as degradation, branching and cross-linking. Free radical inhibitors must then be added before processing a polymer either from fossil or renewable origin.

– *Additives for processing*

Polymers need to become soft or fluids to be properly processed and this is attained by adequate increase of the working temperature.

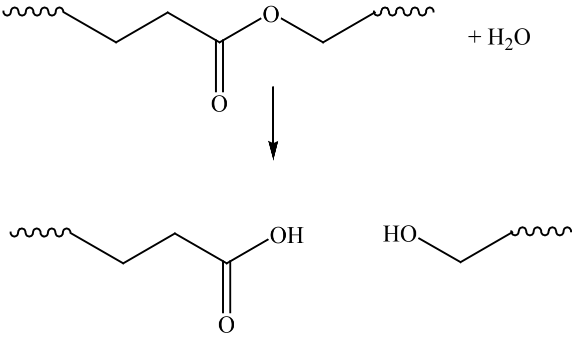


Fig. 4.25 Hydrolytic degradation of polyesters

For reaching this target it is at first necessary to operate above the glass transition temperature (T_g), in the case of amorphous polymers, and above the melting temperature (T_m) in the case of semicrystalline polymer. It is necessary that the polymer responds with a liquid behaviour in the region where the modulus exponentially decreases with small temperature variations and consequently the polymer viscosity resembling that of a viscous liquid, allowing the workability of the molten plastic. The polymer has to be structurally and chemically stable during the processing, granting the ultimate mechanical features necessary to the end products expected from those of the selected starting polymer. The bare requisite of a polymer to be used as the main material for a specific plastic object is that the degradation temperature is actually higher than the processing temperature, including attritions and shear stresses generally applied by machines. This aspect has first to take into account that plastic materials are organic molecules that are subjected to oxidation and degradation reactions with modification of the chemical structure responsible for lower quality of ultimate properties if compared to the expectation. The above undesired reactions are initiated generally by free radicals formed by thermal cracking of the weakest molecule bonds and facilitated then by the presence of substituted reactive groups that are more common in plastic materials from renewable resources than from fossil. Certainly, the best stability is observed in aromatic and paraffinic structures while the presence of functional groups acts as activator towards the degradation of the original structure.

The synthetic chemistry has developed a large number of additives to reduce the above degradative effects; listing of all of them and related efficiency is out of the aim of this book. To give the reader a first insight of the importance of the plastic industry of these polymer additives, Table 4.6 reports some information about the size of the related market of some processing additives whose use is growing.

These additives consist in different chemicals as they have to act as antioxidants, heat stabilizers, radical scavengers, plasticizers and lubricants and all these properties cannot be found in a single molecule and are more easily achieved by a mix of selected molecules. On the other side, the demand for commercial purpose considers important to extend the plastics service life by maintaining their properties. According to the relationship between the molecular structure and the degradation reactions

Table 4.6 Global market for plastic additives by type, 2010–2018 ($ Millions)[a]

Additives	2010[a]	2011[a]	2012[a]	2013[a]	2018[a]
Modifiers	21,000	22,000	23,000	24,000	30,000
Extenders	4,000	4,500	4,800	5,000	5,100
Stabilizers	10,000	11,000	11,500	12,500	15,000
Processing aids	2,000	2,100	2,200	2,200	2,500

$ Millions, roughly estimated

[a] Data from https://bccresearch.wordpress.com/category/plastics/page/2/

occurring when processing, it is evident that these man-made additives are necessary also for the good performances of bio-related polymers. The developments of eco-friendly additives also from natural resources is therefore of primary importance. Indeed these additives when the polymer is disposed and biodegraded are released in the environment.

Looking in more detail to structure and role of the above additives, it is of primary importance to correlate their structure to the stabilization against various degradative effects. Several types of phenols have been largely used for their efficient action as free radical scavengers. For outdoor applications, light and UV stabilizers which, in addition to the family based on benzotriazoles and benzophenones, includes hindered amine light stabilizers (HALS and their polymeric derivatives) and hydroxyphenyl triazines. Further specific protection requirements have promoted the preparation and addition to the main plastic materials of additives acting as biocides, flame retardants, and antimicrobial agents. Moreover, the need to modulate mechanical and physical properties was satisfied by organic and inorganic fillers, impact modifiers, antistatics, plasticizing and crystallization nucleating agents.

The modification of properties in the desired directions and the recovery of partially degraded polymers have promoted the use of reactive processing to either change or restore the main polymer structure by favouring branching and chain extension of polycondensates, adjusting the molecular weight, all effect which can act on both rheology during processing and on ultimate application properties. More specialized additives have also been introduced for specific functional applications once granted the necessary structural properties. Examples in this last direction are UV light spectrum modifiers for greenhouse films, additives for oxygen barrier in flexible food packaging films, and additives for tuning the hydrophobic/hydrophilic character.

Certainly, this basic information points out the complex formulation of plastic polymers in order to make them suitable for a predesigned application. Therefore the role of the main plastic polymer either from fossil or renewable sources must be considered by looking to the above aspects as they can indeed have an important role in deciding the best sustainability of the final product.

- *Polymer blending*

Specific desired performances of plastic materials can be reached by changing monomer structure in homopolymers, type and ratio of two different monomers in copolymers, mixing with additives with various functionalities to both homo- and copolymers. The polymer blending methodology provides an additional and very sustainable tool for producing new plastic materials and expand application properties. For having plastic properties at least one of the two polymers, the matrix must be plastics and the two different polymers must be at least partially miscible or compatible (Utracki 1995).

Indeed, this processing technology to be successful requires the possibility of compatibilization of the two blended polymers often structurally and morphologically different from each other. The chemical structure of polymers, their molecular weight and distribution, presence and nature of ends groups, melt viscosity and rheological features at the temperature used for processing may affect the compatibility even of similar polymers.

In a very few words (Chap. 6 reports a more detailed discussion of the matter), the miscibility of two polymers corresponds to the thermodynamic solubility: the two polymers are miscible when the free energy of mixing ($\Delta\text{Gmix} = \Delta\text{Hmix} - \text{T}\Delta\text{Smix}$) is negative. The entropy of mixing (ΔSmix) approximates values very close to zero when the molecules have a high molecular weight (macromolecules). The enthalpy of mixing, (ΔHmix), depends mainly on the energy variations associated with the structural changes that occur as a result of interfacial contact during the mixing and its value is strongly influenced by the degree of interaction of the polymers constituting the mixture. It has therefore miscibility between the two polymers when the enthalpy of mixing is negative.

While the miscibility has a strictly thermodynamic meaning, the compatibility is defined experimentally or based on the determination of a characteristic property of the mixture and the degree of compatibility is defined indirectly on the basis of what has performance that property. It depends on the method of analysis and the scale with which the measured property relates to the structure of the mixture. Usually, the thermal properties, with particular reference to the evaluation of glass transition temperature (T_g), morphological analyses by microscopies, the rheological properties, the mechanical properties are determined and related to the degree of compatibility.

A mixture of two components is more or less compatible depending on how much it is near or far from the miscibility condition. Obviously in a system fully compatible the polymers are completely miscible.

The compatibilization concept is closely related to the development of an appropriate morphology. There are two extreme situations, the complete phase separation (for immiscible polymers) or the formation of a homogeneous mixture at the molecular level (for fully miscible polymers); however intermediate situations are generally obtained, ranging from the formation of co-continuous morphologies to the formation of heterophasic morphologies with dispersed particles of increasing (or decreasing) size (for compatible or compatibilized polymers). The formation of a heterophasic system should not necessarily be considered an unfavourable event since many interesting properties characteristic of a single phase may be retained in

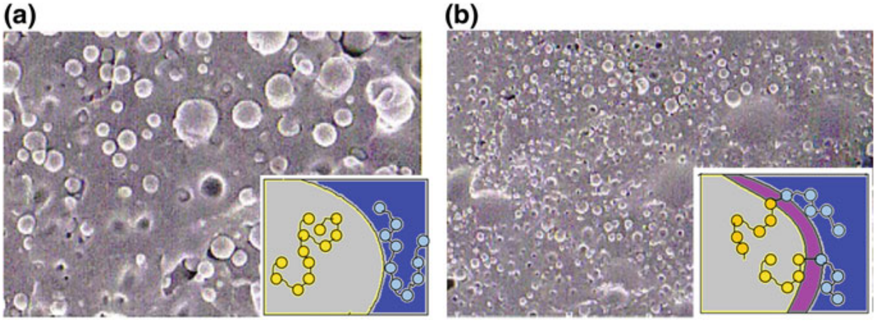


Fig. 4.26 Role of interactions at interface in the morphology development during the compatibilization procedure

the mixture while other properties are 'mediated' in accordance with the composition of the mixture. As for example by blending two amorphous polymers generating a heterophasic morphology with good adhesion at interface, the resulting polymer material is characterized by two different T_g, that are maintained (even if with different values with respect to the pristine polymers) but able to grant the plastic features at least in the temperature range between the two T_g.

There is no compatibility and thus interfacial adhesion between two polymers when they are not able to develop specific interactions whether weak or strong (Fig. 4.26a). The inter-macromolecular interactions are of two types and the total contribution comes from the energy balance of the two terms: the homo-association of two polymers AA and BB the hetero-association AB. For obtaining a morphology characterized by a stable and fine distribution of a polymer in the other, it is necessary that the interpolymer interactions of AB type are enough to form an interface, a real new polymeric phase constituted by macromolecules of A and B (Fig. 4.26b). The same effect is obtained by adding to the mixture an appropriate block copolymer or graft segments made up of identical or similar chains to the constituent polymers (A and B). In practice, it adopts the same approach used for the stabilization of emulsions and the copolymer acts as a surfactant or an emulsifier. The copolymer used is called compatibilizer or compatibilizing agent, and more rarely emulsifier or adhesion promoter.

The compatibilization of a mixture of immiscible polymers can, in principle, be obtained physically through the use of the mentioned compatibilizing agent, chemically synthesized prior to the blending/processing operations, and then added to the mixture as a non-reactive component (*physical blending*). Thanks to its chemical and molecular structure is able to be placed at the interface by reducing the interfacial tensions and promoting the adhesion between the polymer phases.

On the contrary, in the *reactive blending*, the compatibilization is achieved by chemical reactions that occur during the mixing process producing the blend. The reactions promote *in situ* formation of the real compatibilizing species, which is usually a block or graft copolymer, or the formation of cross-linked macromolecules, or also ionic associations. All these have to reduce the interfacial tension and to increase the adhesion between the phases of the two immiscible polymeric materials as in physical blending. This occurs by generally adding a polymer precursor miscible with one polymer and able to react with other macromolecules.

In the *physical blending*, it is critical that the compatibilizer exerts its action at the interface overcoming the diffusion problems associated with the different polymer viscosities. In addition, the suitable compatibilizer should be available in the market.

In the *reactive blending*, it is necessary, instead, that at least one of the two polymers has reactive functional groups capable to provide (directly at interface, in this case) the formation of the compatibilizer.

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Chapter 5
The Obtainment of Bioplastics

5.1 The Controversial Definition of Bioplastics

Under the pressure of the social requirement of a more natural style of life, many commercial products were rendered more attractive with a more or less valid superficial coverage of bio-related aspect; these products are often mixed without any scientific rule with environmentally friendly products with misleading information for the users.

The aim of this chapter is then to provide a survey of information about what we can find under the name of bioplastics and helping the reader in identifying the really biologically originated properties and how they can be modulated in the direction of more technological features typically present in fossil-originated plastics.

Indeed, it must be considered that any commercial product to be available to a large number of people needs the availability of an adequate amount of raw material and the existence of a suitable production process involving, in general, an appropriate formulation and combination with other compounds. Up till now, no natural product is ready for use in a competitive high-technology world.

The involvement of several industrial steps for the production of a polymeric material that can be classified in some way as bioplastics affects the level of natural character (Kirk et al. 1991). As already reported in the previous chapter, monomers are the starting material for polymer production; the same monomer can have both fossil and natural origin. In the latter case, the bio-monomer is converted into the corresponding polymer through a man-made polymerization process. The obtained polymer is considered here as bioplastics even if the same polymer can be obtained from the monomer with the same chemical composition but fossil origin. Therefore, the same polymer can have different origins but the same environmental impact. A typical example of this type is offered by ethylene monomer that can be obtained from

F. Ciardelli et al., *Polymers from Fossil and Renewable Resources*,
https://doi.org/10.1007/978-3-319-94434-0_5

fossil or from renewable sources. In the last case, it is called as ‘bioethylene’. Ethylene and bioethylene are identical from the molecule point of view and the corresponding polyethylenes obtained by the same man-made polymerization process cannot be distinguished in structure and properties. Nature can, however, supply directly bio-generated polymers, the biopolymers, that have to be considered real bioplastics both for their origin (completely natural) and their environmental compatibility. Then, the name bioplastics is attributed to polymer materials derived from natural monomers or polymers independently of their properties but this cannot be applied to monomers and polymers derived from fossil even if the materials are highly accepted by the environment.

These aspects deserve to be discussed in the following sections, where the various possibilities are presented separately to clarify more evidently the role of the nature and the bio-features of the produced materials for the production of the commercially classified bioplastics.

5.2 Biopolymers from Natural Resources

In this section, examples of the more relevant biopolymers are reported, polymers spontaneously produced in nature, which can assume plastic behaviour together with their availability in the world, isolation possibilities and application characteristics.

Many are the macromolecules produced in nature (Bailey 1991). Most of them belong to polysaccharide or protein classes. DNA and RNA are natural macromolecules, the importance of them in the life is well-known. Their commercial counterpart is usually extracted from microorganism, such as for instance yeast, and at present, they are investigated for possible application in sensors. However, to the best of our knowledge, they have not found yet any actual application and for this reason, they will not be considered in details in this context.

Nature produces few polyhydroxyalkanoates and few aromatic polymers also, such as lignin and the low-molecular weight shellac resin. Polyhydroxyalkanoates are very important emerging materials since they exhibit thermoplastic behaviour similar to that of the widely used man-made polyolefins. However, they will be discussed specifically in Sect. 5.3 since engineered bacteria are used at industrial level for their production. Shellac, instead, is a rare and expensive material. It is a resin secreted by the female lac bug on trees, and it is collected from thousands of years by scrapping the bark of the trees. After the coming up of synthetic polymers, its use has been limited quite only to restoring ancient furniture and thus will not be considered longer here.

Lignin represents the second polymer on the Earth and the only large-volume renewable feedstock of aromatics. It is found in all vascular plants where it has a support function. It can be described as a cross-linked polymer of substituted phenols. Its aromatic nature and the presence of many cross-linkings make it a rigid polymer providing the structural stability to plants (Heinze 2008). Because of its chemical structure, lignin is insoluble, it has a very high-glass transition temperature and it

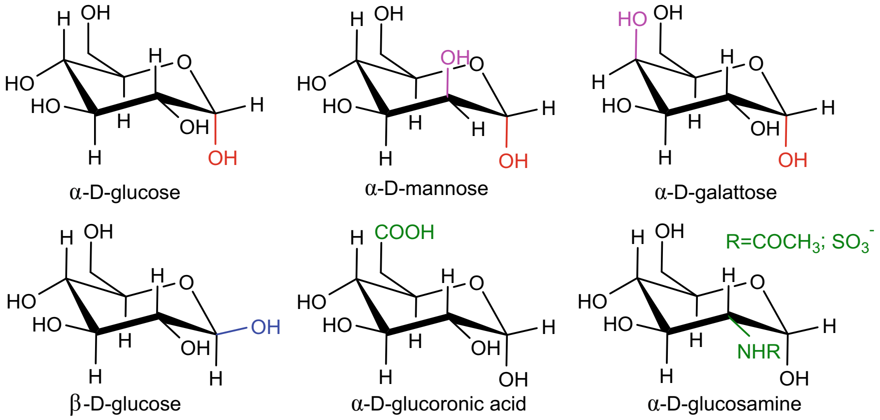


Fig. 5.1 Principal repetitive units of polysaccharides

does not melt, being amorphous. For all these reasons, it cannot be extracted and used in its native status and up till now, it has been exploited in the past only as an energy source by burning. At present, it is widely investigated as a possible renewable source of low-molecular weight aromatic chemicals since it is a very abundant by-product of the paper industry and biorefinery. In any case, it is not used or studied as polymer and thus it is not relevant for the topic of this paragraph.

Natural polymers of practical interest, in fact, are restricted to few polysaccharides and proteins, with the former being much more important than the latter. In fact, polysaccharides represent 75% of the annual biomass production (around 170 billion tons). They play key roles in nature basically for their structural function (cellulose, pectin in plants and chitin in animals), elasticity regulation in the connective tissue of animals (anionic polysaccharides such as glycosaminoglycans), energy storage function (starch and glycogen), control of the migration of water and cations from and to the cells. Other anionic polysaccharides (alginates, carragenans and pectates) act as an extracellular matrix in plants.

From a chemical point of view, polysaccharides are chains composed of monosaccharide units (Fig. 5.1) bound together by glycosidic linkages (Fig. 5.2). These last are formed between the hemiacetal or hemiketal group of a monosaccharide and any hydroxyl group of another monomer (Fig. 5.2). In addition to the hydroxyl groups, the repetitive units can carry other functionalities such as carboxylic groups (i.e. glucuronic, mannuronic and galacturonic acids), sulphate groups (i.e. chondroitin 4-sulphate, chondroitin 6-sulphate and dermatan sulphate) and amine or acetylamide groups (Fig. 5.1). Moreover, polysaccharides may be composed of a single type of glycosyl unit (homoglycans), as in the case of glucans (i.e. cellulose, starch, glycogen, dextran, …), or from two–six different glycosyl units (heteroglycans) in the form of alternating copolymers (carragenans, glycosaminoglycans) or block copolymers (alginates).

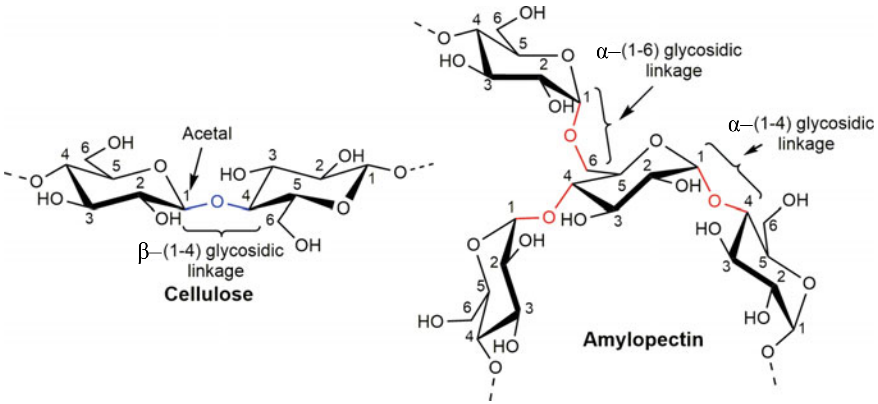


Fig. 5.2 Glycoside linkages in cellulose and amylopectin

The number of bonds for each repeating unit influences the structure of the polysaccharide, since it can bring to linear or branched chains and the position of glycoside bonds influences the polysaccharide structures in terms of the possible chain conformations. Since the cyclic aliphatic units are relatively rigid, the flexibility of the polymer is essential due to the possible rotation of the monomers around the glycoside bonds. From a structural point of view, polymer chains can be linear (such as cellulose, dextran, amylose) or branched (such as amylopectin, glycogen) and branches can be made of single monomeric units, as for scleroglucans and some galactomannans, or they can be extended, as for amylopectin and glycogen (Fig. 5.2). The conformation of polysaccharide chains and the spatial organization are influenced by the configuration of the carbon atoms, particularly the C-1 (α or β). For example, β(1-4) glucan chains correspond to extended linear structures (stripes), while a large helicoidal structure is originated by α(1-4) connected chains. Hydrogen bonds play a key role in the stabilization of polysaccharide chain conformations and supramolecular structures creating stable intra- and intermolecular interactions. The conformation of polysaccharides suggests their biochemical function, since stripe-like polysaccharides have structural and protective functions (i.e. cellulose), while polysaccharides with storage function (i.e. starch) have a large helicoidal structure that facilitates the enzymes accessibility.

In any case, in spite of the wide variety of possible monomers and structures, the polysaccharides of practical interest are only few with cellulose and starch being the most important.

Among the natural polymers, cellulose is the most abundant on the Earth (Klemm et al. 2001). It has support function in all plants including the ones where there is not lignin. Dry softwood and hardwood are made up to 40–45% cellulose, and are the most important source of cellulose for paper fabrication. The second economical source of industrial cellulose is cotton that is made up to 95% cellulose. Moreover, cellulose can be found in all vegetables and fruits (Table 5.1) and it is produced

Table 5.1 Chemical composition of some typical cellulose-containing natural materials[a]

Natural source	Main components (%)			
	Cellulose	Hemicelluloses	Lignin	Others
Cotton	95	2	1	0.4
Hemp	70–80	10–22	6	2–3
Agave	73–78	4–14	11–17	2–4
Ramie	76	17	1	6
Flax and Jute	63–71	12–21	2–13	2–13
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25–29	25–31	1–5
Kenaf	36	21	18	2
Bagasse and grain stubbes	35–45	25–50	15–35	5–10
Coconut fibre	32–43	10–20	43–49	4

[a] Data from Klemm, D.; Schmauder, H.-P.; Heinze, T., Cellulose. In Biopolymers, Steinbüchel, A.; Hofrichter, M. Volume 6 of the series Biopolymers, Viley-VCH 2001

by unicellular plankton or algae in the oceans by the same carbon dioxide fixation process that is found in photosynthesis of land plants.

The formation of β(1-4)-glycosidic bonds between D-anhydroglucopyranose units gives the linear high-molecular weight homopolymer of cellulose (Fig. 5.2). The polymerization degree (DP) depends on the origin and ranges from 1000 to 14,000, with corresponding average molecular weights (M_n) from 162 to 2268 kDa. Whatever the source, in nature, cellulose is found in hierarchical organized fibre structures composing the primary cell wall (Fig. 5.3). Indeed, living structures are usually made of several or often many components. Accordingly, cellulose-containing materials include other chemical components such as hemicellulose, lignin, pectin, salts in different percentage ratios as summarized in Table 5.1. The best situation is found in cotton fibre sources that are made up to 95% of cellulose (Table 5.1).

As mentioned above, cellulose is mostly included in fibres constituting the plant cell wall. These fibres are composed of twisted microfibril boundless that are aligned in the fibre direction (Fig. 5.3). Whereas, microfibers are 15–18 nm thickness hierarchic structures composed of elementary fibrils, which are made by the macromolecular chains of cellulose in highly ordered regions (i.e. crystalline), alternate with disordered domains (i.e. amorphous). Crystalline cellulose occurs in several polymorphs or allomorphs. Moon et al. gives in their review, a detailed description of cellulose and of the cellulose crystalline structure.

The hierarchical structure of cellulose is stabilized by intra- and intermolecular hydrogen bonds between hydroxyl groups. The resulting network provides stiffness to the straight chains and promotes the aggregation into the crystalline structures of cellulose.

As mentioned above, in these ordered structures, cellulose is usually accompanied by other chemical components and separation processes are usually required to get

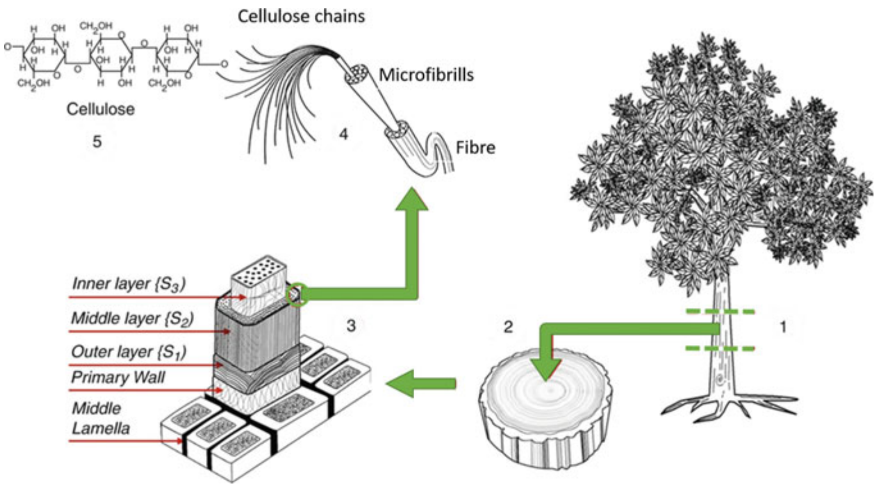


Fig. 5.3 Structure of cellulose fibre as it occurs in a plant cell wall. Adapted by permission from Springer: Springer Berlin Heidelberg, Electrospun Cellulose Composite Nanofibers. In Handbook of Polymer Nanocomposites. Processing, Performance and Application: Volume C: Polymer Nanocomposites of Cellulose Nanoparticles by Abdul Khalil, H. P. S.; Davoudpour, Y.; Bhat, A. H.; Rosamah, E.; Tahir, P. M.; Pandey, J. K.; Takagi, H.; Nakagaito, A. N.; Kim, H.-J., COPYRIGHT Springer Nature (2015)

pure cellulose. In the case of wood, two processes are currently used: the sulphite and the prehydrolysis Kraft pulping. Cellulose with purity larger than 97% is obtained by processing under high pressure in the presence of chemicals to separate lignin and hemicelluloses. Figure 5.4 shows the scheme of a typical Kraft sulphate process.

The pulp produced in the Kraft process is typically used to fabricate high-quality paper. In general, the term pulp is referred to wood or other lignocellulosic materials that have been physically and/or chemically broken down such that (more or less) discrete fibres are liberated and can be dispersed in water.

The purity, molecular weight and structure of cellulose affect its properties and the corresponding actual applications. In general, the high-molecular regularity and order result in high crystallinity degree providing stiffness and rigidity. On the other hand, the presence of amorphous domains provides flexibility. Crystalline cellulose has a negligible accessibility to water and chemicals: chemical attack can occur only on amorphous domains and on crystal surface. This results in a high inertness to chemicals and in a scarce solubility: cellulose can be solubilized only in solvents with strong ability to interrupt hydrogen bonds such as ionic liquid or binary mixtures (Biermann 1996) like electrolytes in strongly dipolar aprotic solvents (LiCl in N,N-dimethyl acetamide, in N-methyl-2-pyrrolidone, or in 1,3-dimethyl-2-imidazolidinone). This highly stable structure prevents cellulose from melting and it degrades first. In other words, cellulose does not exhibit thermoplastic behaviour. Traditional methods to process cellulose are based on chemical derivatization such as in the Celophane® process that is based on the transformation of cellulose in cel-

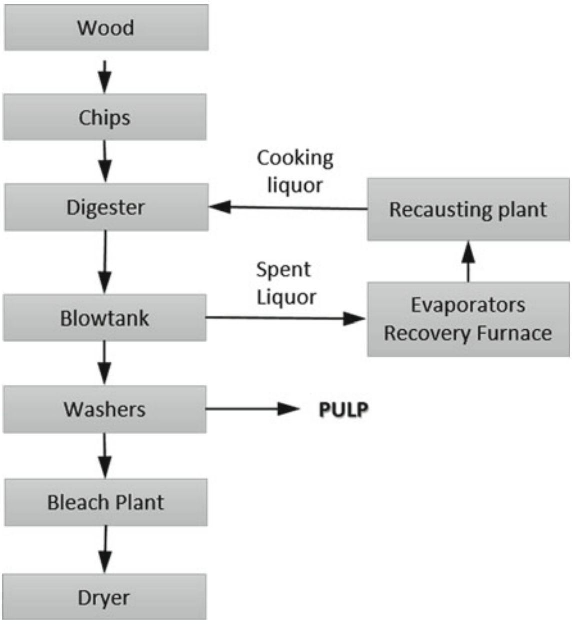


Fig. 5.4 Scheme of Kraft pulping process

Table 5.2 Properties of native starch granules[a]

Granule properties	Potato[a]	Maize[a]	Wheat[a]	Tapioca[a]	Peas[b]	Rice[c]
Diameter (µm)	5–100	3–26	1–40	4–35	2–40	3–9
Lipid (%w/w)	0.05	0.60	0.15	0.10	n.a.	–
Protein (%w/w)	0.06	0.35	0.40	0.10	0.6	n.a.
Phosphorus (%w/w)	0.08	0.02	0.06	0.01	n.a.	0.06
Amylose (%w/w)	–	–	–	–	33–49	5–28
Amylopectin (%)	21	28	28	17	–	–
Degree of polymerization (DP_n)						
Amylose	3000	800	800	3000	1300	1000
Amylopectin $\times 10^6$	2	2	2	2	80	9
Peak Viscosity (mPa s)	3000	600	300	1000	Not present	
Swelling ability at 95 °C (%)	1153	24	21	71	20	23–30

[a] Data from (a) Ellis et al. (1998). (b) Ratnayake, W. S.; Hoover, R.; Warkentin, T., Pea Starch: Composition, Structure and Properties—A Review. Starch - Stärke 2002, 54, 217–234. (c) Singh, N.; Singh, J.; Kaur, L.; Singh Sodhi, N.; Singh Gill, B., Morphological, thermal and rheological properties of starches from different botanical sources. Food Chem 2003, 81, 219–231. And references cited therein

lulose xanthate by reaction with carbon disulphide, and on the regeneration back of cellulose as semicrystalline material by extruding xanthate in NaOH solution.

On the other hand, many derivatives of cellulose such as cellulose acetate, nitrocellulose, cellulose ethers exhibit thermoplastic behaviour: the conversion of the –OH groups into other functionality reduces the chains regularity, the crystallinity degree and the chain stiffness.

After cellulose, starch is the most available polysaccharide (BeMiller et al. 2009). It is relevant to human and animal diet. It has many uses in non-food applications also, in particular as a sizing agent in papermaking, textile, as chemical (e.g. adhesives, starch-based plastics) and as a pharmaceutical excipient. Its industrial, non-food use is growing in production volume particularly for the preparation of starch-based plastics.

Actually, starch is not a single polymer. It occurs in plants as a multi-scale granular structure composed mainly of amylose and amylopectin. Granules size is in the micrometre range even if the exact value, as well as the granule shape, depending on the botanical origin (Table 5.2).

Amylose makes up about 20–30% of the starch granule (Fig. 5.5); the remainder consists of the branched amylopectin. The linear and branched polymers are arranged to give alternate lamellae of crystalline and amorphous regions, with branches included in the amorphous one. Lamellae are 9 nm thick with a spherical morphology and form concentric multilayers within the granule with a total thickness of a few hundreds of nanometres. These well-arranged multilayers are periodically alternate with full amorphous zones of comparable thickness composed of amylopectin and amylose in poorly regular arrangements. One repeat on this scale is known as a ‘growth ring’.

As in the case of cellulose, starch granules are not made only of pure amylose and amylopectin but proteins, enzymes, amino acids, nucleic acids and lipids are included. Their proportion depends on the plant of origin and impacts on the extractability of starch (Table 5.1). Accordingly, the botanical origin of starch affects starch production processes including costs (Purves et al. 2015). In general, starches from maize, wheat, barley, sorghum, potato, sweet potatoes, cassava and pea can be extracted via two methods (dry and wet). Isolation of starch from tubers (potato, cassava and tapioca) is relatively easy and cheap due to the simple structure of tuber tissue and the low protein and fat contents. Isolation from cereals is more difficult and expensive because starch is included only in the endosperm of kernel. Germ and pericarp that are rich in fats, proteins and fibres, respectively, need to be removed. In the case of tubers, after sieving, washing and eventually peeling, roots are crushed in the presence of water to give a slurry containing both the starch granules and the other minor components (proteins, non-starch polysaccharides, amino acids, salts). Starch granules and high-molecular weight compounds are separated by sedimentation or filtration from the smaller components. Purification from non-starch polysaccharides and soluble proteins can be eventually performed by centrifugation and countercurrent washing, respectively. After these stages, a highly pure starch powder can be obtained simply by drying.

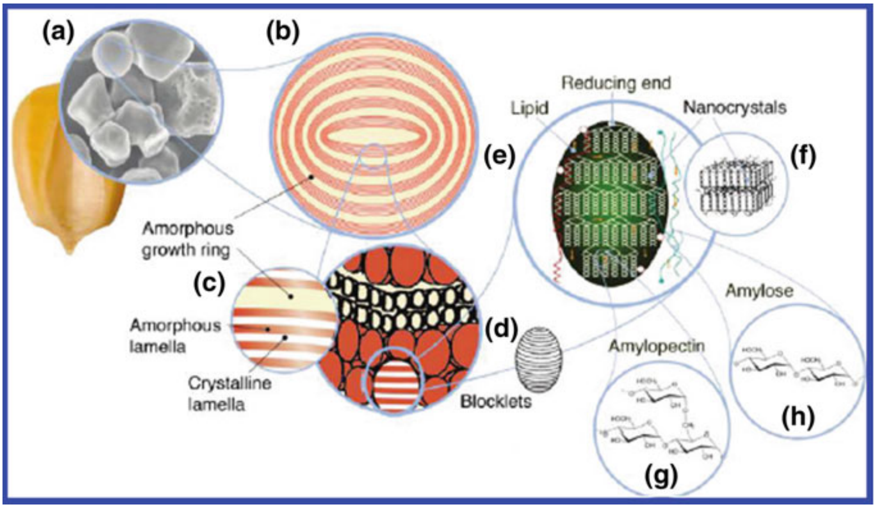


Fig. 5.5 Starch multi-scale structure: **a** starch granules from normal maize (30 μm), **b** amorphous and semicrystalline growth rings (120–500 nm), **c** amorphous and crystalline lamellae (9 nm), magnified details of the semicrystalline growth ring, **d** blocklets (20–50 nm) constituting a unit of the growth rings, **e** amylopectin double helixes forming the crystalline lamellae of the blocklets, **f** nanocrystals: other representation of the crystalline lamellae called starch nanocrystals when separated by acid hydrolysis, **g** amylopectin's molecular structure and **h** amylose's molecular structure (0.1–1 nm). Reprinted with permission from Le Corre et al. (2010) Copyright (2019) American Chemical Society. The figure was made by combining Fig. 1 from Tang, H.; Mitsunaga, T.; Kawamura, Y., 2006. Molecular arrangement in blocklets and starch granule architecture. Carbohydrate Polymers 63:555–560 and Fig. 11 from Gallant, D. J.; Bouchet, B.; Baldwin, P. M., 1997. Microscopy of starch: evidence of a new level of granule organization. Carbohydrate Polymers, 32:177–191. Copyright (2019), with permission from Elsevier

Potatoes are the major source of starch only in cold countries, such as, for instance, the Netherlands. The major source of starch in the world is maize (also named corn) (Table 5.3) and starch is extracted, mainly by wet milling process. This process was optimized over 150 years to extract not only starch but also the other vaporizable components of the corn kernel. The process begins by steepening the kernels in a dilute sulphur dioxide solution into large tanks (steep tanks). The resulting softened kernels are then processed to obtain the germ and a starch–gluten slurry. The former is thus processed to obtain oil and the fibre. The latter fraction is sent to centrifugal separators where the two main components are separated based on their different density, lower for gluten and higher for starch. The starch is then washed and dried or modified and dried.

The transformation of starch including its extraction and possible modification as well as the physical properties relevant for application and use are largely dependent on the structural organization of the granule in amorphous and crystalline domains, even if strongly affected by the presence of water. When native starch granules are

Table 5.3 Main starch crops in the world

Crops	World production in 2013 (P tons)[a]
Maize	1020
Rice (Paddy)	74.1
Wheat	71.6
Potatoes	37.6
Cassava	27.7
Bananas	10.7
Yams	0.631
Sorghum	0.623

[a] $P = \text{peta} = 10^{15}$

left to stand in water, they undergo limited reversible swelling at room temperature. On heating at a temperature in the 58–78 °C range, depending on the starch origin, the granules begin to swell irreversibly. This phenomenon is called gelatinization and the temperature at which it starts to occur is named as gelatinization temperature. The gelatinization proceeds with the disorganization of granular structure by breaking of H-bonds inside the granule. Some properties like as swelling degree, melting temperature, birefringence, soluble fraction and viscosity in water are irreversibly changed. Solubilization occurs by leaching of amylose and amylopectin from the granules. The relative amount of the two polysaccharides that can be solubilized depends on the origin of the starch and on the heat–shear conditions used.

Generally, on cooling a polymer solution, chain rigidity gradually increases and phase separation between solvent and polymer occurs. The exclusion of water from starch is accompanied by a decrease in the granule swelling and in the recovery of molecular order. The ordering called ‘retrogradation’ is a recrystallization process occurring after the crystalline order lose during gelatinization. As a whole, gelatinization and retrodegradation can be seen as an annealing process promoted by the solvent in which the crystalline order is initially destroyed thanks to the ability of water to interact by hydrogen bonds with the hydroxyl groups of starch.

Interactions of water with starch occur strongly during the early stages of sorption when molecules diffuse as isolate species. Because of the interaction with water, intermolecular bonds between starch units becomes weaker resulting in an increase in the distance between starch chains and then in a higher mobility of the macromolecular chains. Both these effects indicate the role as plasticizer of water on starch at a molecular level and are accompanied by a decrease in the T_g values. At high water content, clusters of water molecules form with strong and well-oriented intramolecular hydrogen bonds among them. At this stage, water exhibits typical liquid-like properties and forms weaker bonds with starch. T_g value of dry starch is in the 225–235 °C range; it decreases with moisture sorption and level off below 0 °C at water content above 30%. Under this condition water forms a separate phase outside the granules. The plasticization effect of water is due to its ability to enter into the very rigid hydrogen bonds network of the dry starch and to interrupt the networks by replacing some hydrogen bonds either intra-chains and interchains, the former between neighbouring repeating units and the latter between closed chains.

Polyols, such as sugars and alditols, including glycerol and ethylene glycol have also the capacity to plasticize starch as well. Several thermoplastic materials based on starch and formulate with polyols have been patented. They are produced by using conventional techniques employed for commodity plastics, such as extrusion, compression moulding, injection and blow moulding (see Sect. 4.3.5). The key step is the destructurization of starch under extrusion condition in the presence of plasticizers. In fact, with water as plasticizer, starch destructures under extrusion at water content lower than 20%, while for gelatinization water must be in excess (>30%). The final properties of processed starch depend on the starch type, as well as on the processing parameters such as temperature, shear, cooling regime and amount of plasticizers. On the other hand, mechanical properties of extruded starch depend on the plasticization degree: the fracture mechanism changes from a rapid, brittle fracture at plasticizer content below 8% to slow, plastic fracture (tearing) with content close to 20% (Bastioli 1998).

Commercial thermoplastic starch usually includes destructurized starch in mixture with plasticizers and polymers. For instance, thermoplastic starches commercialized by Novon are blends with various hydrophilic polymers, such as ethylene–vinyl alcohol copolymers (EVOH). Hydrophobic polymers and additives, such as plasticizers and lubricants, could also be included. Mater-Bi® is the trade name of the formulations produced by Novamont that are typically comprised of at least 60% starch. Other natural additives and hydrophilic, biodegradable synthetic polymers are included in the blends forming interpenetrated or semi-interpenetrated structures at the molecular level. The resulting ultimate properties are comparable to the ones of low- and high-density PE.

Others nature-made polymers of practical interest are fibre proteins such as collagen, silk and keratin. None of this exhibit thermoplastic behaviour, or in their native status or after extraction. In order to become thermoplastic, they need to be processed like cellulose (in the case of fibre proteins) or starch. They must be destructurized and plasticized to assume thermoplastic behaviour.

5.3 Bioplastics in Engineered Systems

The concept of Metabolic Engineering was introduced over 20 years ago from Bailey. The metabolism of an organism is modified by genetic engineering. More recently, the concept has undergone a transformation and actually, metabolic engineering is not only used for improving the production of native metabolites but also for producing any desired molecule. It usually involves the optimization or modification of biochemical pathways already existing by the introduction of new pathway components, most commonly in bacteria, yeast or plants. The goal is the exploitation of these organisms in a cost-effective production at the industrial level of valuable substances. In this field, the recent increase in the variety of molecules produced from engineered cellular and the growing of commercial interest in bio-based polymers and plastics with a particular interest in products with improved functionalities and obtained with sustainable and environmental-friendly synthetic approaches can be combined.

From a general point of view, biopolymers can be synthesized from monomers produced in vivo and then polymerized in vitro. Alternative and very appealing approaches produce the polymer directly by the microbe. Both methods allow a diversification of the final product by using a simplified production scheme with respect to traditional industrial methods with the control in molecular weight. During the last two decades, the knowledge on genes, proteins and metabolites are improved, the costs of oligonucleotides synthesis are decreased and much more precise techniques for investigating the metabolism inside the cells have been developed. For this reason, the target of metabolic engineering is actually the possibility of manipulating the entire cell instead the perturbation of single pathways to. New approaches are now considered including the possibility of controlling the gene expression and modulating the regulatory networks throughout the cell. Traditional methods instead were simply based on deleting and/or over-expressing endogenous genes with eventual introduction also of heterologous genes.

In addition to monomers (see Sect. 5.2), the use of the microbial cell factories for the production of full-length polymers is attracting the interest of the scientific community. The most significant example of bioplastic produced in engineered system is poly(hydroxyalkanoates) as showed is below in Fig. 5.6.

It is already known that some bacteria are able to accumulate polyhydroxyalkanoates (PHAs), in the presence of an excess of carbon source and under nutrient-limited conditions. PHAs are intrinsically biocompatible and biodegradable. Others example of polymers produced microbially are, cellulose and spider silk others. Cellulose can be bio-synthesized by cyanobacteria *Synechococcus leopoliensis* constitutes, e.g. a feedstock of CO_2, because it can be easily digested by cellulose due to its non-crystalline structure. Silk proteins with an optimized molecular weight were expressed in *E. coli* by inducing the glycine production in the cell.

Even if some monomeric constituents can be produced by microbial fermentation (such as lactic acid) and used in chemical synthesis of the corresponding bio-based polyesters, PHAs and their polythioester analogues (see the general chemical structures in Fig. 5.7) are the only relevant examples of polymers produced and accumulated in vivo and whose structure can be manipulated by metabolic engineering. The host enzyme, which is present in the cell, affects the monomeric composition and as a consequence, the polymer properties by supplying the PHA-synthase and hydroxyacil-CoA thioester precursors involved in the metabolic pathway.

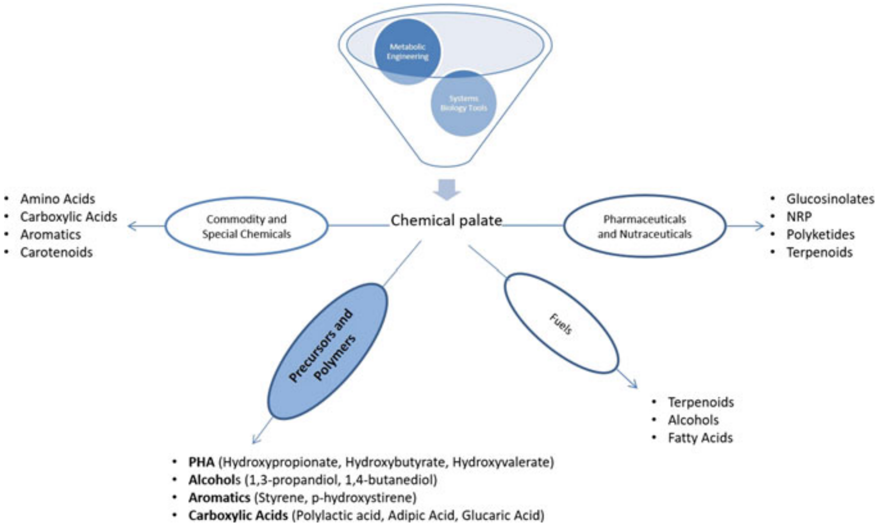
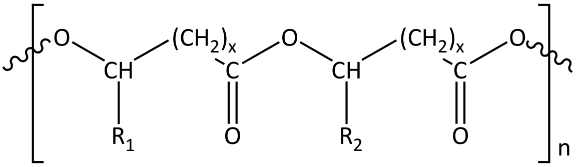


Fig. 5.6 The main classes of polymers produced in engineered systems

Fig. 5.7 General structure of polyhydroxyalkanoates



R_1, R_2 = alkyl groups C1-C13
X = 1 - 4
n = 100 - 30.000

From the pioneeristic studies in the 1920s of Maurice Lemoigne with the discovery of poly(3-hydroxybutyrate) (PHB), as a product of accumulation in *Bacillus megaterium*, many others polyhydroxyalkanoates with different chemical structure (PHA, Fig. 5.7) have been reported to form in a wide range of organisms (e.g. *Psedomonas* sp., *Bacillus* sp. and *Methylobacterium* sp.). Some of them are homopolymers of a *R*-hydroxyalkanoic acid (HA) while others are copolymers based on two or more HAs.

PHB plays the role of intracellular reserve for carbon and energy in bacteria similarly to starch and glycogen in plants and animals. At the beginning of the scientific investigation, 3-hydroxybytyrate unit was believed to be the only hydroxyalkanoate (HA) constituent of the microbial reserve polymer. Instead, up to now approximately, 125 different HAs are known to be present as building blocks in a more general class of polymers named as polyhydroxyalkanoates (PHA).

The growing interest in these polymers derives from their rapid degradation (3–9 months) under both aerobic, with the development of carbon dioxide and water, and anaerobic conditions, with the development of methane. They are degraded without the need of any special environmental set-up by different kinds of microorganisms. In particular, they degrade in the see and ocean also.

Gram-positive and Gram-negative bacteria from *Necator*, *Cupriavidus*, *Ralstonia*, *Pseudomonas*, *Aeromonas*, *Bacillus*, *Alcaligenes*, *Enterobacter*, *Rhodobacte*r and some cyanobacteria and halophiles can naturally synthesize polyhydroxyalkanoic acids as insoluble inclusions accumulated in the cytoplasm and playing the role of storage compounds, if carbon is in excess, especially if other essential nutrients, such as nitrogen or phosphorus, are in limited amount. However, *Azobacter vinelandii UWD*, *Azobacter eutrophus*, *Azobacter latus* and a *mutant Azobacter vinelandii* are able to biosynthesize PHAs under non-limiting conditions. The type of microorganisms, the availability of low cost of carbon source, culture conditions, growth rate, polymer yield from the substrate affect the final composition of PHA and its properties. Renewable resources such as starch, cellulose, hemicellulose, sucrose, triglycerides, wheat, sub-products such as glycerol, rice bran, molasses, whey, organic acids, fossil resources such as methane, mineral oil, lignin and wastes such as wastewaters and palm oil mill represent suitable substrates for bacteria in PHAs production at lab scale. The choice of the substrates is one of the weaknesses of the production because it largely affects the PHA production costs. Only a few kinds of bacteria are able to be used for industrial low-volume scale production of low-cost materials, but with high-value biomedical application for their versatility and biocompatibility, such as *Azotobacter vinelandii*, *C. Necator*, *Methylobacterium organophillum*, *A. latus*, *Protomonas extorquens*, *Pseudomonas olovorans*, *recombinant E. Coli and Paracoccus denitrificans*.

The classification of PHAs is based on the number of the carbon atoms in the monomer units and split them into two main groups. PHAs with a short-chain length of C2–C5 atoms (scl-PHAs) are brittle, stiff and have high crystallinity content. The increase in the chain length of the monomer from C4 to C14 (mcl-PHAs) produces an increase in flexibility and melting point and a decrease in crystallinity degree and tensile strength. There are also some examples of PHA-copolymers synthesized from a combination of short-chain and medium-chain monomers (e.g. P(3HB-*co*-4HB), P(3HB-*co*-3HV), P(3HB-*co*-3HHx)).

The chemical structure of the monomers (i.e. molecular weight, presence and structure of branches, presence or heteroatoms) and the distance between the ester linkages largely affect all the properties of PHAs. The nature of the microorganism, the culture conditions and carbon source determines the type of monomer incorporated during the polymerization. The type of microorganisms with their activity, fermentation conditions, state of inoculum, the nature of the medium composition and the type of processing are used to affect the molecular weight of PHAs. The $\overline{M_w}$ values of *mcl*-PHAs moved in the range 60,000–412,000 independently by the presence of both saturated and unsaturated pendant groups and $\overline{M_n}$ between 40,000 and 231,000. They are generally lower than the values of scl-PHAs. The polydispersity ranges between 1.6 and 4.4 and it is higher with unsaturated monomers.

All PHAs are semicrystalline polymers. In the case of *mcl*-PHAs, the values of T_g are in the range from −25 to 65 °C and T_m from 42 to 65 °C (Table 3.6). The T_g value decreases with the increase in the average length of the pendant group. A higher degree of crystallization is observed only in the case of higher T_m values. A different crystalline packaging can be due to the presence of odd or even numbered monomers. A layer-like order arrangement involves both the backbone and the side chains and the structural regularity of the repeating units affects the crystallinity degree and promotes the formation of lamellar crystals. For this reason, a low crystallinity degree is the consequence of large and irregular pendant side groups. PHAs are enantiomerically pure (all in *D*(-) configuration) and their isotactic and syndiotactic sequences help the crystallization process (see Sect. 3.4).

PHAs with medium-chain length show elastomeric behaviour thanks to the presence of crystalline domains acting as physical cross-links. The properties are completely different for the ones of short-chain length PHAs. On the other hand, an increase in the toughness and in the flexibility, measured as elongation at break and a decrease of the stiffness, measured as Young's modulus (Table 3.6) can be obtained with the presence of a comonomer into the polymer backbone.

The most important issue towards the industrial use of PHAs on a large scale is the high production costs because of the microorganism cost. In alternative, the use of a microorganism's population selected from the variety already present in wastewater was proposed. This methodology resulted in an enhanced PHA-producing capacity and in the reduction of expensive feedstock use, with respect to the traditional pure culture bacterial fermentation. The consequence is a reduction not only of the production costs but also of the environmental impact of the whole process. Examples of wastewaters used at lab scale are from the paper mill and food industries. The effectiveness of mixed microbial cultures (MMCs) production processes is based on the selection and enrichment of the PHA-accumulating microorganisms and a maximum PHA content of 89% of dry cell weight is obtained. MMCs can be exposed to biomass for repeated periods of feasts under aerobic, anaerobic and/or anoxic (a total depletion in the level of oxygen) dynamic feed conditions to enrich them with PHA-storing bacteria.

In-silico genomic studies have also allowed the investigation of bacterial strains able to produce at the same time H_2 and PHB polymers under dark fermentative conditions. It was found that a single isolated bacterial suffers from the risk to be contaminated because a rapid increase in the amount of contaminants can take place with the elimination of the original culture. Instead, the use of a mixture of well-defined bacterial cultures with different and high metabolic activities can help to solve this aspect and to enlarge the operative physiological conditions. The use of biowastes as feed represents a promising possibility to produce H_2 and PHB in a sustainable manner. At the same time, the immobilization of the bacterial cultures on natural, high biocompatible and biocompatible substrates such as coconut coir, groundnut shells or banana sleeves allows solving the difficulties to retain a large population of free-floating bacteria in a continuous culture mode.

Recently, the production of novel biopolymers in plants represented a challenge to provide renewable sources of materials of industrial interests from agriculture. Plants cells play the role of miniature factories because they produce biochemicals and materials necessary for their growth, reproduction, defence and for monitoring and interacting with their environment. Cellulose, lignin, starch and hemicelluloses are materials traditionally produced from plants and used by humans for their lives. It is known from ancient times that the production of natural rubber is from *Hevea brasiliensis* or Para rubber tree. Anyway, the addition of genes encoding enzyme activities can convert the endogenous plant metabolite to a polymeric structure. PHAs, collagen, silk, elastin and cyanophycin are produced *in planta* with this strategy.

As previously reported, the industrial PHA production by microorganisms must overcome the disadvantages of the high production costs. Therefore, the use of pure cheaper carbon sources instead of glucose or sucrose is of real interest. In this direction, glycerol, which is a coproduct, produced in large scale, of many industrial processes such as in the production of biodiesel, represents an interesting solution. In particular, some studies showed that some bacteria and archaea strains are able to produce PHB oligomers in the presence of glycerol. In particular, it was demonstrated that glycerol by-product from biodiesel production can be used as a liquid phase in the cultivation of osmophilic organism in the presence of hydrolysates from meat and bone meal (free from prions of bovine spongiform encephalopathy) that acts as sources of nitrogen and phosphorus.

5.4 Monomers from Nature and Their Polymerization Derivatives

Several molecules with the suitable structure to be converted into macromolecules by man-made polymerization processes can be obtained either during natural processes (lactic acid) or by synthetic routes using bio raw materials (ethylene from bioethanol).

Renewable resources constitute an extremely rich and varied array of molecules. Most of them have more than one functional group and therefore, under the definition of polymerizable monomers, they are suitable building blocks to prepare long polymeric chains. However, in spite of the huge variety, only a limited number of them have found practical applications. Among these, we can mention monoterpenes from Pinewood that found applications mainly as adhesive components and spray adjuvant in the form of low-molecular-weight hydrocarbon-like resins. Rosin, also known as colophony, is the term commonly used for the non-volatile residue obtained after the distillation of conifer tree resins. It is mainly composed of aromatic acids. It looks like a semitransparent and brittle solid. Pine trees (*Pinus genus*) is the most important source of rosin. In spite of the broad variety, often-natural molecules are available in low amount or are difficult to recover in pure form, since they are

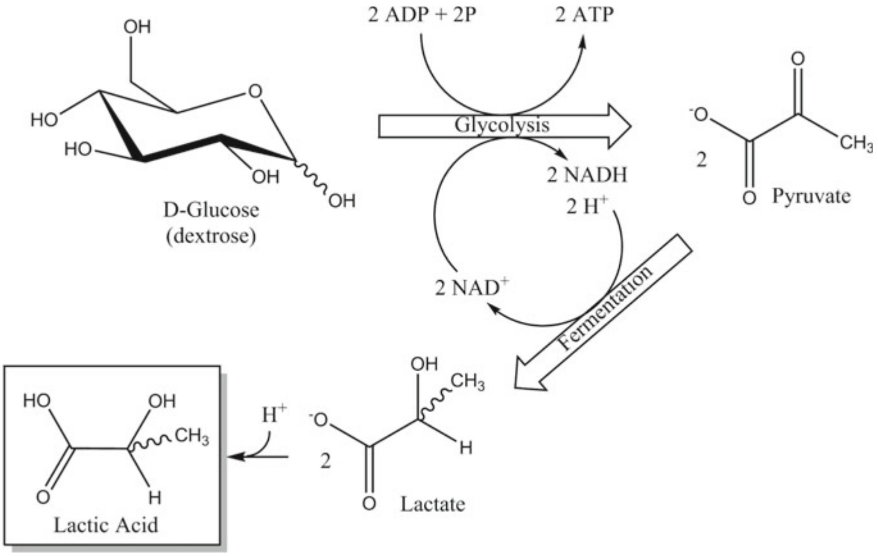


Fig. 5.8 Biosynthesis of Lactic Acid from dextrose

included in complex biological systems. A representative example is provided by lactic acid, the monomer of polylactic acid (PLA). It is the well-known by-product of muscles when they work under anaerobic conditions producing energy from glucose. It is responsible for the fatigue disease since it accumulates in muscles after intensive work. Like other chemicals, it is a naturally occurring molecule, but to be available in large amounts, it must be produced through industrial process. In this case, its natural origin is preserved by using renewable resources as raw material for its production. Actually, lactic acid has been produced on large scale from maize by NatureWorks since 2001 in Nebraska (USA). At present, it is produced by many other companies around the world. The process adopted by NatureWorks starts with the extraction of starch from maize and the separation from the other components of the kernel (proteins, fats, fibres, ash and water). A wet milling process is adopted (see Sect. 5.2) and the extracted starch is then hydrolysed to D-glucose (dextrose) in the presence of an enzyme, in the second process stage. The resulting sugar solution is transferred to a fermentation process where lactate is produced by fermentation with a microbial inoculum under anoxic condition (Fig. 5.8). Calcium hydroxide is used to control the pH during the fermentation and to achieve high conversion. Finally, a pure lactic acid monomer is obtained by acidification with sulphuric acid, filtration-off of the precipitated by-products (mostly $CaSO_4$) and evaporation of water from the solution.

The industrial process of lactic acid production is a multistep process based on the transformation of an agriculture crop into a chemical by using biological and chemical processes (Fig. 5.9). This is what typical occurs in a modern biorefinery,

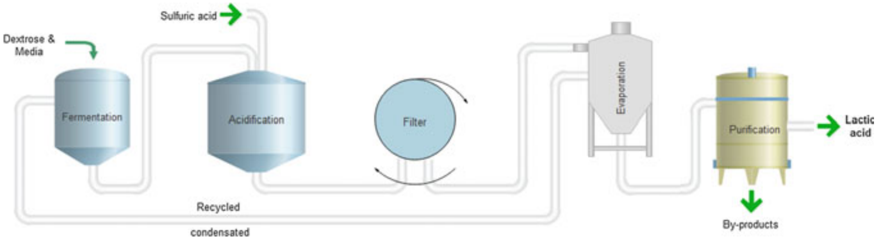


Fig. 5.9 Lactic acid production process

even if this last is usually more complex integrating several processes of biomass conversion to produce not only fuels and chemicals but also power energy and heat.

In other words, the biorefinery must be considered quite similar to today's petroleum refinery, which produces multiple fuels and products from petroleum; the main difference being the starting raw materials. By obtaining multiple products, a biorefinery gives values to and takes advantage of the different components that are present in biomass and their intermediates. The inherent value of biomass feedstock can thus be fully exploited and promoted. A biorefinery typically produces chemical or nutraceutical products in low-volume but high-value, fuel and commodity chemicals in high-volume and low-value such as biodiesel and bioethanol, respectively (see also alcohol fuel). The latter being used as raw materials for the production of many others derived chemicals such as for instance monomers for polymer and solvents. In biorefinery electricity, the heat needed for the process is usually obtained by combustion of the produced fuel through combined heat and power (CHP) technology. Exceeding energy is usually sold as electricity to the local utility. A typical example of this sort is the production of ethylene as high-value derivative of ethanol, the primary product of the biorefinery (bioethanol). Ethylene is the monomer, which produces any polymer belonging to the well-known commodity thermoplastic polyethylene family.

Ethanol is currently produced from different kinds of renewable raw materials, including starch, cellulose, hemicellulose and lignin-containing crops. In particular, first-generation processes used food-competing raw materials such as maize, while the most recent second-generation process is based on non-food crops and agriculture by-products, which are composed mainly of cellulose and hemicellulose. Third-generation processes use agriculture or urban organic wastes. The most part of plants operating while this book is in preparation produce ethanol mainly from sugar, cellulose or starch, with the last two being both sugar polymers (see Sect. 5.2). The first step of all processes have the aim to get sugars from the raw crops and the operative conditions adopted in each of these steps depend on raw material and on the used technology. In Brazil, for instance, sugarcane is mostly used as a substrate to

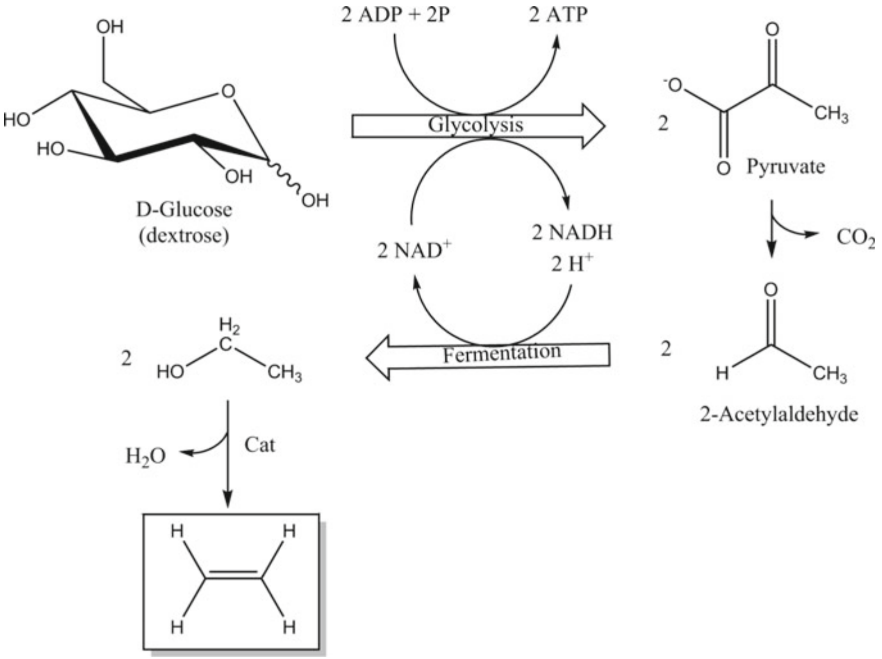


Fig. 5.10 Synthesis of ethylene from ethanol, which is obtained by biosynthesys from dextrose

get ethanol. Sugarcane is pressed to obtain the sugarcane juice. This is separated by filtration from the solid fibrous residuum named as cane bagasse. The juice is clarified and concentrated at first by water evaporation to promote sucrose crystallization and then centrifugated. The obtained sucrose-saturated viscous phase is called as cane molasses. It is made of 45–60% sucrose, 5–20% glucose plus a low amount of fructose. Sugarcane juice, molasses or a combination of them are used as fermentation substrates for ethanol production. In fermentation, the first reaction is usually the glycolysis to pyruvate (Fig. 5.10), then depending on the used bacteria and on the process conditions different products can be obtained by the true fermentation step. In most of the actual operating plans, ethanol is the target product since it can be used as fuel and chemical raw material, as well.

To be used as fuel, crude ethanol must be purified, in particular, it must be extracted from the aqueous fermentation broth. This is typically the most energy demanding and thus cost-effective part of the plant, since ethanol distill as azeotrope with water and further purification steps are need to get dry ethanol. This cost can be compensated if it can be used as a reagent to obtain other chemicals with high value. The Brazilian petrochemical company, Braskem is producing ethylene from bioethanol and then polyethylene, the first bio-PE certified in the world. Ethylene is obtained by dehydration in the presence of a suitable catalyst (Fig. 5.10).

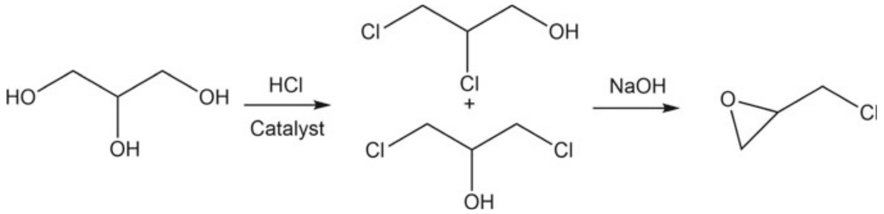


Fig. 5.11 Epichlorihydrin synthesis from glycerol

The two examples so far mentioned (lactic acid and ethylene production) are both based on sugar fermentation platforms. An alternative platform for monomer production is based on the use of fatty acids as raw materials. In fact, glycerol is becoming available at a low price on the market since it is a by-product in biodiesel production. Glycerol is an interesting raw material for the production of monomers with even carbons, which are difficult to obtain from petrol. Among these 1,3-propandiol, which can be used to prepare polyesters and polyurethanes, as well as epichlorohydrin. This last is mostly converted into epoxide monomers, and acrolein, which is an intermediate for the preparation of acrylic monomers. The first two examples are already operating on pilot plant by DuPont and Solvay, respectively. A process for the production of acrolein from glycerol on gas phase has been patented by Arkema and developed at pilot scale. However, the industrial scale-up has not been carried out up to now because of economic reason. In fact, the price for the production of acrolein from petrol is still lower than the production from glycerol. Other companies are also developing others alternative processes for the production of acrolein or acrylic acid from biomass.

Epichlorohydrin produced by Solvay and commercialized as Epicerol® is obtained in a two-step process. In the first step, glycerine is reacted with hydrochloric acid to give dichloropropanol, an intermediate product. The second step is the dehydrochlorination of the product, which produces epichlorohydrin (Fig. 5.11). Different from the others mentioned examples, this process does not differ from traditional petrol-based process except for the origin of the starting reagent.

5.5 Bioplastic Formulation and Processing

The above classes of polymers are then going to end products for commercial use through a procedure similar to one of the fossil-derived polymers, which implies the use of additives to modulate their performances according to the market request. Biodegradable polymers, particularly those from renewable resources, allow solving the low sustainability of long-lasting polymers on short-lived applications and the difficulties to find accurate and economically viable outlets of traditional materials by taking also into account the negative environmental balance of the material recycling.

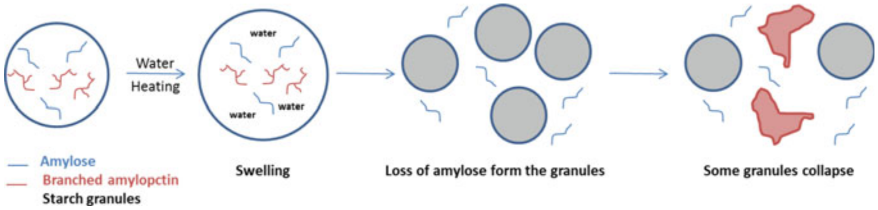


Fig. 5.12 Gelatinization of starch

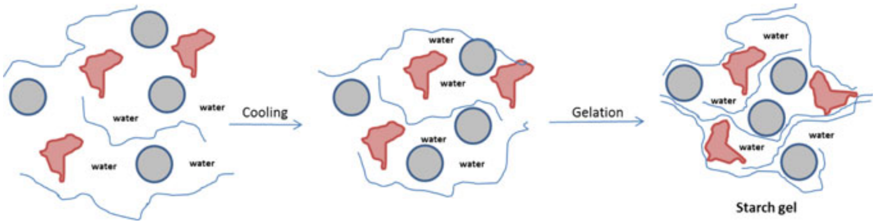


Fig. 5.13 Gelation of starch

Polysaccharides represent the most abundant family of agro-polymers, with cellulose, starch and chitin as the main actors. Their use can contribute to preserve petrol resources replacing fossil resources-based polymers for some applications, e.g. packaging, agricultural, biomedical uses.

In this class of polymers, starch is an important material, because it represents the main storage supply in botanical resources. It is available in large amounts at the raw state and can be easily processed and transformed for many industrial applications. For this reason, its processability is described in detail in this paragraph.

With the only exception of the use as a filler in reinforced plastics, native starch is typically modified by chemical or physical approaches and converted into thermoplastic polymer and then processed in the melt. The treatment of starch at high temperature in the presence of large amount of water causes the denaturation of the granular organization through the gelatinization process (Fig. 5.12).

Gelation (Fig. 5.13) step follows the gelatinization and the process concludes with the retrogradation of the starch gel.

During this process, starch forms a sort of paste and most of the intermacromolecular hydrogen bonds are destroyed. The melting and glass transition temperature of starch decrease as a consequence of the transformation. Different products for different applications can be obtained by playing with the process condition such as water content and thermomechanical inputs. In order to split the value of the melting temperature and the degradation temperature of starch, chemicals with boiling temperature higher than the processing one are used as plasticizer, i.e. glycerol, sorbitol, polyethylene glycol urea and high molecular weight amines. Water can play both the role of destructuring agent and plasticizer.

The disruption of native starch granules by the combination of thermal, mechanical, destructuring agents and plasticizers is generally carried out by extrusion processes. They can be carried out in one or two steps. In one-step process, a twin extruder is fed with starch granules and then water and plasticizer are added along the barrel. Exceeding water is eliminated. At the end of the process, starch is completely destructured and melted. In two-step processes, first, starch granules are mixed at dry state with the plasticizer, and then the mixture is heated up to allow the diffusion of the plasticizer into the granules. After that, water is added and the blend is introduced in the extruder. Along the barrel, starch is destructured, plasticized, melted and partially depolymerized. In any case, a homogeneous molten state is obtained. Plasticized starch shows strong modifications of the chemical–physical properties with respect to the native one. In particular, during plasticization, the crystallin phase decreases and modifies. Two kinds of crystallinity can be obtained: residual crystallinity from native starch and processing-induced crystallinity. The latter is influenced by the process parameters such as temperature, screw geometry and speed, plasticizer kind and content. Crystals form by fast recrystallization of amylose into single-helical structures even if co-crystallization of amylose and amylopectin is also proposed. The process is indicated to occurs mainly during extrusion even if recrystallization during ageing has been documented with some plasticizers. The presence of water affects some properties of plasticized starch, in particular, the mechanical ones that result to depend on the sorption–desorption of moisture with the environment. This equilibrium is affected by the presence of other plasticizers. Glycerol, e.g. can be differently linked to the polysaccharide chains as a consequence of the humidity content and total amount of the plasticizers. In the presence of moisture excess, a phase separation occurs with the formation of a multiphase system with rich and poor plasticizer domain. The ratio between water and plasticizer influence also the mechanical properties and permeability of plasticized starch. Anyway, the water permeability results higher because of the polar character of the material even if the oxygen permeability is lower than in other polyesters.

Similarly, water plays an important role in the denaturation of biological macromolecules such as proteins. It was shown that water does not play just the role of solvent, but it also takes part in the structure of biological polymers affecting their properties. Indeed, some water molecules are strongly bonded to proteins by hydrogen linkages, the exact amount depending on the chemical composition of the protein as well as on its spatial organization. Fibrillar macromolecules, such as collagen, with their larger exposed surface, have large amount of bonded water. On the contrary, globular proteins having highly ordered and compact structure with molecular mass less than about 30 kDa have lower amount of bonded water. The polypeptide chain is packed into well-defined conformations, which is determined by the sequence of the polar and apolar groups along the chain that is defined by its primary structure (i.e. the sequence of amino acid residues). The original conformation and the corresponding biological function is lost if proteins are submitted to severe conditions (e.g. high temperature, high pressure, high acidity, or high concentration of denaturants) promoting unfolding and denaturation. The denaturation process occurs in a short temperature range with extensive heat absorption. It is a highly cooperative process involving a high number of contacts between nonpolar groups in the protein. The overall surface area of the nonpolar groups has to be rearranged and exposed to water upon globular protein unfolding. Significantly different is the unfolding of fibrillar proteins. Collagen represents an extreme example of this group with a very large exposed surface area per unit volume. The macromolecular chain of collagen is highly flexible and assumes the form of a random coil in aqueous solution. However, three chains of collagen can associate forming a stable rope-like poly-l-prolyl superhelix able to provide biological tissues with mechanical stress resistance over long distances. A feature of collagen is the loss of its regular rigid structure with the increase in the temperature above a critical value (above 40 °C) at which the chains are separated into three independent random coils. It is important to note that collagens obtained from different sources do not differ essentially in their structural organization but differ significantly in their thermal stability; this last depending on the imino acid content. Indeed, the number of possible conformations depends inversely on the amount of pyrrolidine ring in the chain. Thermal studies have demonstrated that, in contrast to globular proteins, there are no apolar groups in the collagen triple helix that might be exposed to water upon its unfolding, because hydroxyproline is in the third (Y) position of the triplet repeat. As a consequence, hydroxyl groups of prolines are able to interact with the water molecules that surround the collagen superhelix and form an extensive cooperative network of water hydrogen bonding. This extended network is suggested to be responsible for the very large enthalpy of collagen 'melting', which is much larger than the enthalpy of globular protein denaturation.

Similarly, to the process of synthetic macromolecules, extrusion of proteins must be performed after denaturation (often named melting for analogy with crystalline polymers) and far above the glass transition temperature so that the macromolecule chain mobility is high enough to allow chain flowing and eventually mixing with other components. However, temperature during extrusion must be kept below a limit value to avoid thermal-activated reactions, such as degradation with the formation of volatile compounds. For this reason, proteins can be processed only if their denaturation temperature is significantly below their degradation temperature. As previously reported, water is the most effective plasticizer agents for proteins: by increasing the moisture content from 0 to 20% w/w the denaturation temperature of proteins decreases from 200 to 80 °C. Extrusion of protein-based thermoplastics requires the following steps: protein chains denaturation, disassociation, unravel and alignment that are possible only if the chains are enough mobile and can form new molecular interactions on cooling. Even if proteins are considered as amorphous structures plasticized by water, some aspects related to the native protein structure (ordered regions, such as α-helices and β-sheets) and thermal behaviour (endothermic events) correlate with the behaviour of semicrystalline materials. A series of transitions must be taken into account: at the glass transition, the amorphous regions become mobile, at the melting temperature, the crystalline regions melt, at the degradation temperature the polymer chains thermally decompose.

As in polysaccharides, plasticizers with two or more hydroxyl groups such as glycerol, sorbitol, and di-, tri- or mono ethylene glycol are added to proteins in combination with or instead of water for thermoplastic applications. The presence of a second plasticizer with water in protein mixture allows avoiding the increase in the T_g value and brittleness as the moisture content decreases. During extrusion, mechanical stress promotes protein de-aggregation, while heating promotes aggregation by hydrophobic interactions (physical cross-linking) and stabilization of the aggregated structures by disulphide bonds, reducing melt flow. Processing temperature is, therefore, an important parameter to control protein/protein association. Furthermore, degradation of the protein can occur because of the increase in the residence time, torque, and pressure. For protein processability, plasticizers as well as others additives such as thermal stabilizer and disulphide bonding inhibitors are need to reduce macromolecular associations during extrusion and to achieve a thermoplastic behaviour. On the contrary, an extensive cross-linking (>10%), can result in the formation of a thermoset material (an extended cross-linked material that can not be processed again). It is important to point out that the behaviour of natural polymers is difficult to generalize and differences can be observed because of the difference in composition that always exist even among polymers belonging to the same class but of different origin. Covalent cross-links are not the only inhibiting factor for the thermoplastic behaviour. Actually, the hydrophobic interactions have to be overcome and sometime this drawback can be negligible. For instance, in the case of water-insoluble and hydrophobic proteins, such as zein, amphiphilic molecules, such as sodium dodecyl sulphate, are need to enable thermoplastic processing. Ionic surfactants give electrostatic as well as hydrophobic interactions leading to the dissociation of protein chains. On the other hand, hydrophobic plasticizers usually give non-homogeneous and non-compatible blends with a reduction in water absorption. Indeed, the proteins ability to interact with water is not only influenced by covalent cross-linking and chain arrangement but also by the chemical additives.

Based on the possible ways to transform a natural polymer in a thermoplastic material, the most common bio-based and biodegradable polymers are classified into the following four categories depending on the synthetic route used to prepare them:

- Natural polymers: They are usually obtained by extraction from biomass, in particular from agro-resources and include mainly polysaccharides and proteins both from animals (whey, collagen) and plants (zein, soya and gluten) (see Sect. 5.3);
- polymers obtained by microbial production, e.g. poly(hydroxyalkanoates) (PHAs) (see Sect. 5.4);
- polymers made by man using monomers obtained from agro-resources, e.g. polylactic acid (PLA) (see Sect. 5.5);
- biodegradable polymers whose monomers are obtained by chemical synthesis from fossil resources, e.g. poly(ε-caprolactone) (PCL).

Actually, starch and PLA biopolymers are the most interesting since they are produced on an industrial scale and thus are commercially available in relatively large amounts. Furthermore, they have an interesting balance of properties. In particular, PLA shows excellent transparency and relatively good water resistance. The high stiffness can be reduced to obtain flexible films by the addition of plasticizers. However, oxygen barrier decreases as a consequence.

Natural polymers have excellent oxygen barrier under dry conditions. However, they are usually too much stiff and difficult to process by using conventional equipment. These drawbacks can be overcome by taking advantage of their strong water sensitivity that allows biopolymer processing in the presence of moisture acting as a plasticizer. On the other hand, oxygen barrier properties can be recovered after processing by material drying. All biopolymers with commercial interest show excellent gas barrier properties in their optimum formulations, even if the large amount of plasticizers, necessary to get materials properties adequate for processing have a detrimental effect.

Polyhydroxyalkanoates show very high water barrier properties and they can be used in multilayer systems in combination with other natural polymers. However, all these materials usually suffer from relatively high production cost, and their commercial interest remains in competition with conventional thermoplastic materials. An innovative trend in polymer science with high practical interest is the addition of natural additives in bioplastic formulations. This approach is promising for food-packaging applications and allows the reduction or elimination of some of the main food spoilage causes, such as rancidity, colour loss/change, nutrient losses, dehydration, microbial proliferation, senescence, gas build-up and off-odour. Natural extracts from plants, essential oils or agricultural waste products can show antimicrobial activity against different pathogenic and spoilage microorganisms, including Gram-negative and Gram-positive bacteria and moulds. Examples are extracts of blueberry on the growth of *Listeria monocytogenes* and *Salmonella Enteritidis*, grape seed extracts against major food pathogens like *Salmonella Typhimurium*, *Escherichia coli* (*E. coli*), a green tea extract against *Staphylococcus* and some Gram-negative bacteria, such as *E. coli* or *Salmonella*. The use of natural extracts or their original compounds (including low-molecular-weight phenolic acids, tannins, proanthocyanidins, flavonoids, such as anthocyanins or flavonols) is growing. Disadvantages are their high volatile; to overcome this drawback, they are incorporated into the packaging materials as additives to be released to food by migration. With this purpose, several natural extracts have been incorporated into different types of biopolymers that were used in the development of antimicrobial active films. The addition of citrus extract to gelatine and methylcellulose gives films with no For instance, odour and negligible water solubility. polycaprolactone (PCL)/Alginate films containing three natural extracts from rosemary and Asian and Italian essential oils were developed and they showed good activity in controlling/inhibiting the growth of foodborne pathogens in fresh-cut vegetable. Active materials can be obtained also by incorporating lemon, propolis extracts and olive leaves as a source of polyphenols on PLA, and PCL films. The processing temperature must be selected below the temperature at which degradation of the polymer matrix starts as well as below the volatilization and degradation temperatures of the active compounds. Furthermore, the hydrophobic/hydrophilic nature of active compounds may affect in a positive or negative way, respectively, the water vapour permeability, the water solubility, and the biodegradation rates. The incorporation of natural extracts, such as rosmarinic acid, showed their potential capability to control food pathogens with no significant modifications on tensile strength. The presence of additives in the polymer matrices allows their release during long periods of time from preparation, storage and distribution, resulting in the extended shelf life with spoilage decrease and maintenance of nutritional quality of foods. FAO (2013).

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Chapter 6
Hybrid Materials and Systems

6.1 Introduction

Plastics were invented based on homopolymers, which are polymers consisting of macromolecules characterized by uniform chemical structure along the main chain, the successive investigation and related discovery demonstrated that the plastics behaviour could be reached with more complex systems in term of molecular structure and composition. Then, as already described in previous chapters, macromolecules based on two different monomers could offer a possibility for designing plastics with a broader spectrum of properties (Flory 1953). In these cases, the molecular heterogeneity introduced in the macromolecule by the incorporation of two monomers was generally flanked by a substantial homogeneous morphology and then the presence of a single phase. These copolymers were indeed produced by creating chemical bonds between different monomers, thus suffering from the limitations that the two co-monomers should be structurally similar while requesting the copolymerization reaction, which involves expert handling and not negligible realization cost.

The possibility of obtaining plastics material by mixing two or more components appeared, therefore, very attractive and is today largely used. Indeed, this route is relatively low cost, with moderate processing conditions and starting from cheap components. It offers a large number of possibilities and unexpected performances are being applied also for very different materials (Utracki et al. 2014). A possible problem is offered in these last hybrid materials by the limited compatibility, interfacial adhesion, of the components with different nature. Special compatibilizers, macromeolecules with adhesive properties towards both components were then prepared and provide a very important contribution to extend plastic properties to very complex mixtures. These last include blends of two different polymers, thanks to the adhesive interface provided by the polymer compatibilizers that bring their original functional properties whereas respond as a unique material to mechanical stimuli. The concept and the application were extended to plastics loaded with heterogeneous

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materials, where the role of the dispersion and of interface interactions play an even more determining role. This holds for both micro- and nanocomposites.

6.2 Chemical Modification of Molecular Structure. Compatibilizers

The main objective of chemical modification of polymers is to impart new properties not own of specific plastic commodities by insertion of functionalities (as short and/or long side chains) tailored as a function of the target property. Apolar and hydrophobic polymers are chemically modified by insertion of polar and hydrophilic side groups, while more polar polymers are rendered more hydrophobic by anchoring or coupling with alkylic chains/functionalities. This real and general description is based on the main structural features of plastic commodities, without taking into account the purpose of the process that deals with the compatibilizer preparation and, indeed, it has to be addressed to each specific application.

First, a compatibilizer is any substance used to stabilize blends of immiscible polymers. Polymer compatibilizers are used to promote interfacial adhesion between pair of polymers that are otherwise incompatible. Compatibilizers can be used in polymeric composites as well to guarantee the adhesion at the interface of the polymer matrix and dispersed particles. They are usually block or brushed copolymers (physically added or formed in situ during a reactive compatibilization process) composed of structurally different macromolecular chains. Each part of the compatibilizer (one block or the backbone and the other block or grafts) is compatible with one of the phases and thus the compatibilizer tends to concentrate at the interface. In this way, they are able to decrease the interfacial energy, thus allowing finer dispersion and mutual interactions between the incompatible pairs (see Sect. 6.3). In some cases, they are even stated as coupling agents: this refers generally to chemicals improving the interfacial interactions in composites between mineral fillers (micro- and nanostructured) and polymers; coupling agents reduce the coalescence tendency of filler particles, thus improving their accessibility to polymer molecules generating well-dispersed composites or hybrids, depending on the final size of filler (see Sect. 6.3). Coupling agents usually react with the filler surface and have at least one side group able to react or interact with the polymer matrix.

It appears evident that any kind of modification should be tailored on the basis of the final use of the compatibilizer or coupling agent, meaning that the chemical nature of the main structure and the eventual presence of functionalities onto the components of blends and composites steer the modification process. In addition, it is necessary to underline that, particularly for polymer blends, the compatibilizer is often formed by in situ reaction, generating blocks or brushes acting as a stabilizer. Therefore, both compatibilizers and coupling agents can be generally assessed as polymers having one side compatible with a polymer component and specific functionalities able to

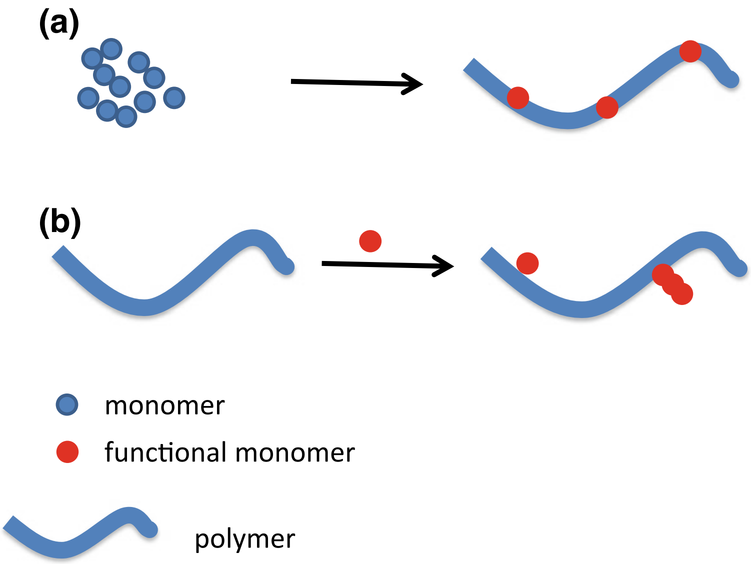

Fig. 6.1 Insertion of functionalities onto polymers by **a** (co)polymerization and **b** post-reactor modification approaches

react or interact with polymer's and filler's functional groups that constitute the other component of the blend or composite (Sugimoto et al. 2014).

The chemical modification can be accomplished by using two fundamental approaches: (a) copolymerization or (b) post modification. In the copolymerization, insertion of a specific functionality is made directly during the synthesis of the macromolecule (Fig. 6.1a) and it involves the polymer chains building up by meeting specific structural/functional requirements. Modifications made through a post-reactor reaction approach (Fig. 6.1b) means that a reaction ensuing the polymerization is getting ready to reach the target.

Both the modification methodologies have been employed having advantages and drawbacks depending on the kind of polymers and polymerization strategies. Obviously, it is possible to operate onto the synthesis of man-made polymers, but in the case of natural and natural-made polymers only the latter approach can be addressed. In addition, by considering that the synthetic strategies of most man-made commodities involve the use of chemicals (the catalysts) that are not always compatible with the new functionalities and that the supply chains of these plastics are well assessed at industrial level with productions on the market since 70 years, generally the post-reactor modification approach is preferred (Jawaid et al. 2016). This is particularly advantageous when the modification process is simple and friendly in terms of environmental impact and costs.

To covalently "anchor" a molecule (or a macromolecule) onto a polymer substrate, it is necessary that the polymer reacts with a (macro)reagent or being specifically

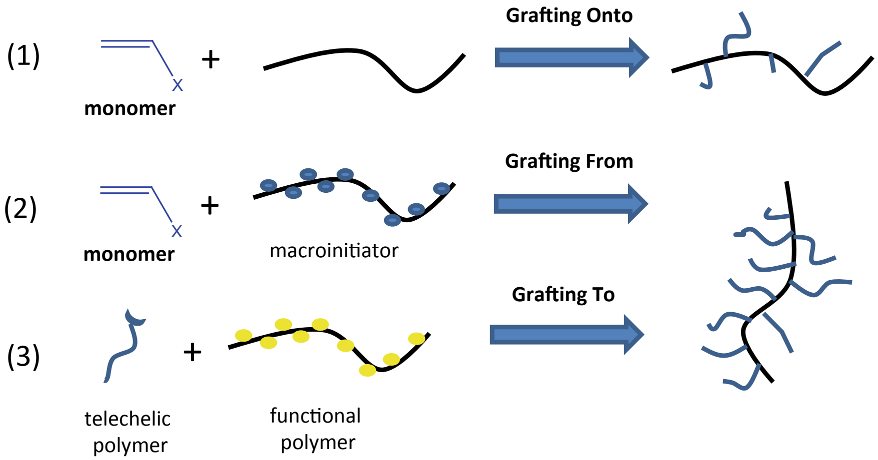

Fig. 6.2 Synthetic strategies to functionalize polymers by post-reactor modification approaches

activated; three main post-reactor modification strategies can be described among the "*grafting methodologies*" depending on the specific reactivity of polymers and monomers (Fig. 6.2). All they can provide macromolecules with grafted short functionalities (as side groups) or polymer brushes.

The example (1) in Fig. 6.2 refers to the functionalization reaction that occurs with the insertion of a low number of functionalities (less than 5% wt) as monomeric units or oligomers. This strategy is widely used to provide plastics with new polar moieties, while preserving the main structural, thermal and mechanical features.

The reaction is adopted with the aim to improve some properties, which are not own of specific plastic commodities such as for example compatibility, adhesion, paintability, dyeability of the olefin-based polymers and it occurs by the insertion of carboxylic functionalities (anhydrides, esters, acids). In fact, the completely lacking of any functional groups does not allow these hydrocarbon polymers to be useful in coating/adhesion applications, like in the case of their use as compatibilizers or coupling agents. The "*grafting onto*" procedure (applied to molten polymers or onto surfaces) is a well-assessed strategy and the resulting functionalized polyolefins are used in daily issues for rigid and flexible packaging, as components of home or industrial pipes, sound-proofed composites for building, in automotive parts as, for example, in engines as improvers for lubricants or in blending for tyres (Hu et al. 2013). Functionalized materials are used also as primers, or adhesion promoters for coating applications.

The chemical inertness of polyolefins constraints to "activate" their reactivity by using radical processes, meaning that the macromolecular places for the insertion of the monomer bearing the specific functionalities are macroradicals (P species in Fig. 6.3). These are generated by H-abstraction from the polymer backbone by using peroxide or irradiation at different wavelengths (UV-light, γ-rays), and by exposure to plasma ion beams. The grafting takes place by addition of the formed macroradical

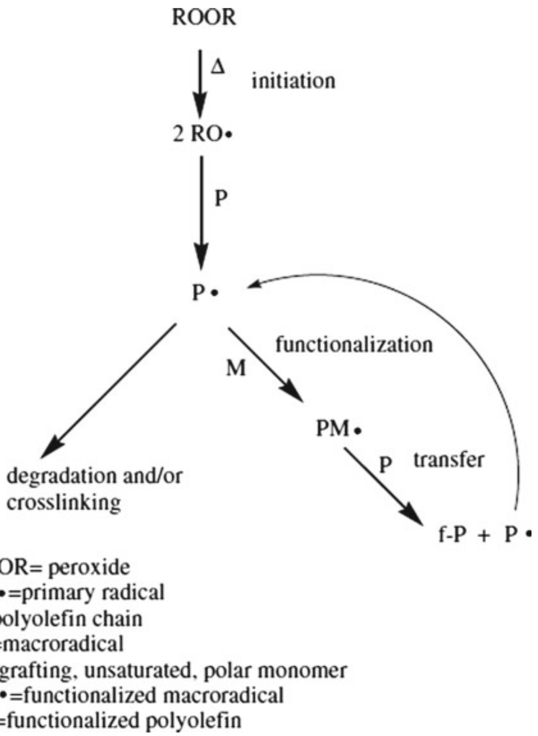

Fig. 6.3 Schematic simplified mechanism of polyolefin grafting; figure from Passaglia et al. (2014) Wiley & Sons Reprinted with permission

to the double bond of the unsaturated monomer, most likely maleic anhydride (MA) and its derivatives which are used even at industrial level (Fig. 6.3).

Therefore, this process, particularly when carried out with polymers in their molten state and thus at high temperature, is not completely selective and, depending on their structure, the macroradicals undergo to side and collateral reactions, mainly breaking by chain scission and cross-linking by macroradicals coupling. In particular, while cross-linking effects own of polyethylene-based plastics can be controlled by optimizing the reagents ratios (meaning generally by employing low content of radical initiator) the polypropylene (PP) functionalization carried out in the melt was proved to be affected by extensive degradation, due to the intrinsic instability of the formed tertiary macroradicals undergoing to chain scission (Fig. 6.3). These effects can be partially controlled by using molecules acting as macroradical stabilizers that are called co-agents. In particular, recent reviews on the topic pointed out the possibility to use a variety of co-agents that are all characterized by the presence of aromatic or heteroaromatic moieties able to grant resonance-stabilized structures of the macroradicals. These results definitely stated the proposed mechanism, justifying the preservation of molecular weight and the grafting level values (or functionalization degrees) trend.

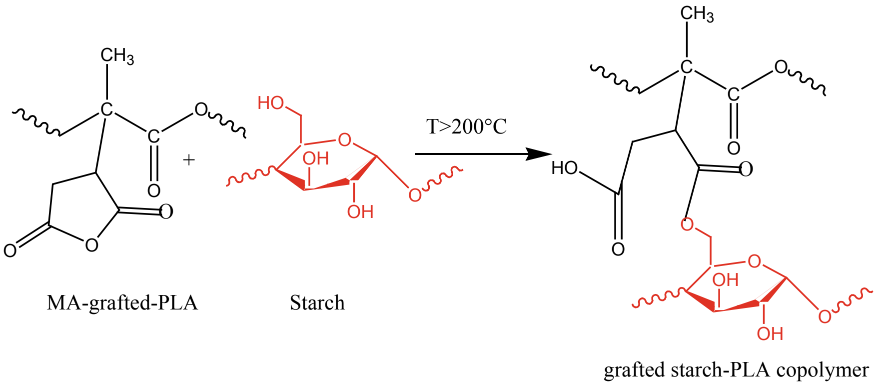

Fig. 6.4 In situ reactive processing product of MA-grafted-PLA and starch

Among man-made plastics, polyesters such as the aromatic PET, which is produced currently mainly from fossil oil, the biodegradable PBS, PLA, PBAT and polyamides such as PA6 and PA11, have been all successfully modified with this technology. Reactive side groups (once again by grafting maleic anhydride and its derivative or glycidyl methacrylate), capable to establish effective interactions with different substrates (organic and inorganic or metal) or to subject to successive reactions, have been successfully inserted. Recently some bioplastics have been used in blending with natural-made polymers, such as cellulose, starch, lignin derivatives to provide biobased mixtures aimed at improving the mechanical features of natural polymer phase. For this purpose, as an example, PLA grafted with maleic anhydride (MA-grafted-PLA) was used for the compatibilization of the blend obtained by mixing PLA and starch, because MA can react with the hydroxyl groups of starch as shown in Fig. 6.4. The grafted starch–PLA copolymer is then proved to act as a compatibilizer for the starch/PLA blends.

The "*grafting onto*" is, moreover, a useful tool to insert reactive groups used for anchoring dyes, antioxidants, antibiotics and so on by covalent bonds to macromolecular structures. The methodology is, indeed, suitable to impart, respectively, light responsiveness to polymeric materials or simply to avoid the leaching/migration of specific active molecules.

By using functional monomers capable to homopropagate in the adopted conditions, the grafting (by *free radical polymerization*) generates grafts or brushes with different lengths. This approach generally uses acrylic monomers (like in the case of acrylic acid) that are able to grow starting from backbone macroradicals. The monomer reacts with any macroradicals generated as reported in Fig. 6.3 and propagates as new polymer chains growing bounded to the backbone. The propagation of the branch continues following the mechanism already reported in Fig. 6.3, until termination that can occur either by the addition of two growing chains or by a disproportionation step generating two polymer chains that are terminated by saturated and unsaturated terminals, respectively. The methodology, well-known for fossil-

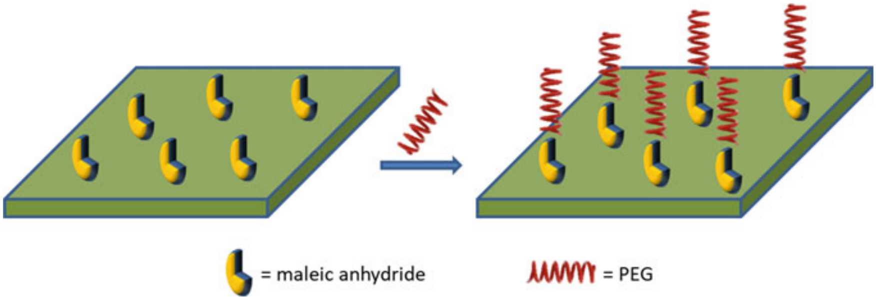

Fig. 6.5 Surface functionalization of plastic with maleic anhydride followed by grafting to with PEG

derived plastics to obtain resins for wastewater treatment, membranes for separation and fuel cell, has been also applied to natural polymers (as followed reported).

Although free radical grafting is one of the most used and versatile methods to provide a grafted derivative, it is an extremely complicated process. First of all, the presence of synthetic polymer that is not covalently bonded to the substrate cannot be completely avoided, thus resulting in problems in the purification and accurate characterization of the grafted product. For these reasons, numerous methods have been developed to increase control over the macroradical formation specificity.

The "*grafting onto*" is a useful tool to design multilayered polymer architectures by employing "*grafting from*" and "*grafting to*" approaches, (Fig. 6.2 (2) and (3)). The generation of a functional polymer ((2) Fig. 6.2) can, indeed, allow bioconjugation capability for drug delivery or biomedical/pharmaceutical applications or, more important in relation to the aim of this paragraph, to design copolymers fitting structural requirements for compatibilization effects. In fact, often, especially if the starting polymer substrate is among polyolefins, the grafting is used to "anchor" a reactive group suitable for *grafting from* or *grafting to* approaches and then to provide functional polymer/substrate or macroinitiators. As an example, polyolefin substrates (once again grafted with MA) were used for reacting with end-groups of PEG (Fig. 6.5) to get materials constituted by a polyolefin substrate with anchored PEG brushes; these copolymers were used to design devices for drug delivery. Similar approaches have been used to design materials with antifouling characteristics.

With the "*grafting to*" approach, it is possible to synthesize the side chains independently. The reaction mechanism is chosen in relation to the monomer structure, and the oligomer/polymer obtained is characterized before the coupling. This step-by-step approach can provide very complex architectures such as comb copolymers with side chains of different compositions. However, grafting degree is often achieved in low amount and an excess of side chains is necessary to achieve a high yield at the end of the grafting reaction; in addition, purification is necessary and it is not an easy procedure when it is necessary to remove the unreacted side chains. These factors point out the need for highly efficient kind of reactions such as "click-type" coupling reactions.

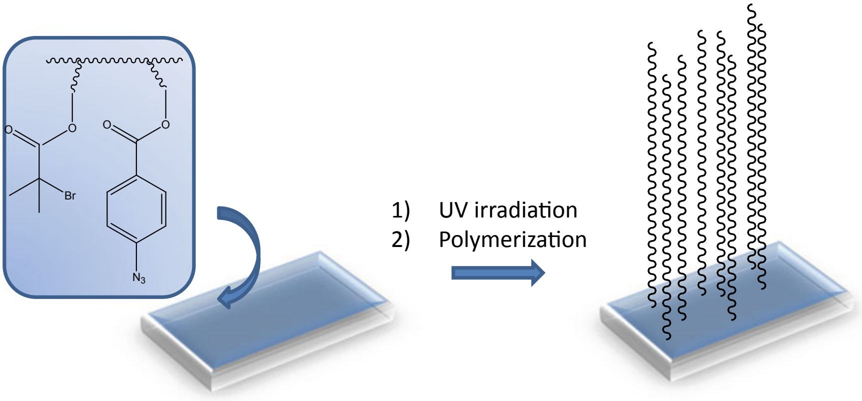

Fig. 6.6 Schematic representation of combining *grafting to* and *grafting from* approaches to provide a polymeric substrate coated with well-defined polymer chains

As for example, random copolymer has been prepared with both phenyl azide groups and ATRP-initiating sites as side chains and filmed on PET as polymer substrate by spin-casting. The copolymer was then immobilized on the substrate by UV light irradiation which promotes the reaction of the azide groups. At this point, by the surface-initiated atom transfer radical polymerization, a polymer brush is obtained because of the presence of the initiator-immobilized polymeric substrate. This strategy combining *grafting to* and *grafting from* approaches provided a polymeric substrate coated with well-defined polymer chains (Fig. 6.6).

In fact, one of the major advantages of "*grafting from*" approach is that the side chains can grow by overcoming the problems related to steric hindrance issues and usually enables to obtain high grafting density. The polymer chains, in this case, have to be functionalized with molecules able to act as initiators. Polymers (PP and PE) functionalized with MA was reacted to anchor alkoxyamine of TEMPO derivative by obtaining macroinitiators for Nitroxide-Mediated Polymerization (NMP) that can be used to grow PS brushes (Abbasian et al. 2013). Very similar macroinitiators have been obtained by nitroxide radical coupling (NRC) reaction of TEMPO derivatives to provide alkoxyamines used to build PS brushes (Fig. 6.7).

Other synthetic strategies aimed at converting a polyolefin or a polyester or a polyamide substrate into a macroinitiator to build polymer brushes have been described, all referring to ATRP approaches (as in the case reported in Fig. 6.6). These are generally multi-step procedures, where the first step is the macroinitiator formation by chemical modification (even grafting) of any functionality that can be converted into the ATRP initiator. Thereafter, the growing of acrylate- or methacrylate-based grafts starting from the modified surface takes place generating more or less complex structure/architecture. Bromination or UV irradiation in the presence of a CuBr/ CuBr2 based catalyst for ATRP and acrylic monomers are compelling examples of the first step. It appears evident that this is a versatile method

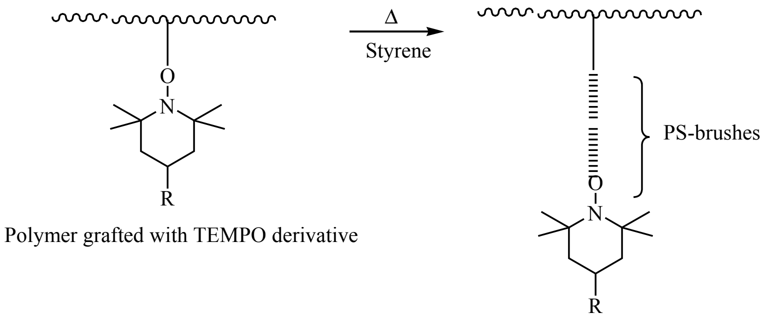

Fig. 6.7 Polymer macroinitiators obtained by TEMPO derivatives grafting and used to graft PS brushes

to assemble macromolecular structures with a variety of targeted properties not only addressed to compatible features; substrates for drug delivery, biomimetic surfaces, membrane for fuel cells. Nevertheless, these synthetic strategies are particularly interesting for obtaining functional polymers that can be used in designing structurally tailored copolymers acting as interfacial stabilizers for blends between polyolefins and polystyrene- or polyacrylate-based materials and even with natural polymers, like as polysaccharides.

These latter polymers are instead generally modified and functionalized by taking advantages from the functionalities naturally occurring in these substrates. Of course, the hydroxyls groups are the most obvious site of chemical modification that has been used for over a century, but also other functionalities such as acetamido groups (chitin) or carboxylic groups (hyaluronic acid) have been widely exploited. The most common modification strategies included direct substitution reactions (esterification or etherification), but also hydrolysis, controlled oxidation, polymer brushes growth.

Among the most abundant polysaccharides (cellulose, chitin and starch) the extensive research on cellulose modification has achieved a high degree of advances and the number of functional groups that have been attached to its backbone is enormous. Between the cellulose derivatives, some ethers and esters such as methyl-, carboxymethyl-, ethyl-, hydroxyalkyl ethers, or cellulose acetate and nitrate, are well known since decades and are still commercially relevant. Analogous considerations can be applied to starch and the kinds of its derivatives. Some starch derivatives have well-established importance in various application fields: starch ethers (neutral and cationic) such as hydroxyethyl-, hydroxypropyl-, diethylaminoethyl-, 2-hydroxy-3-(trimethylamino)propyl-starch, or starch esters like acetates, succinates and starch sodium phosphate monoesters are currently used in the food industry or in papermaking. The same industrial fields are also exploiting other starch derivatives such as oxidized starch, carrying carboxyl and carbonyl groups, or partly hydrolyzed starch (dextrins and acid-modified starch).

Chitin is relatively abundant but the interest in its chemical modification is relatively recent owing probably to its insolubility in the most common organic solvents.

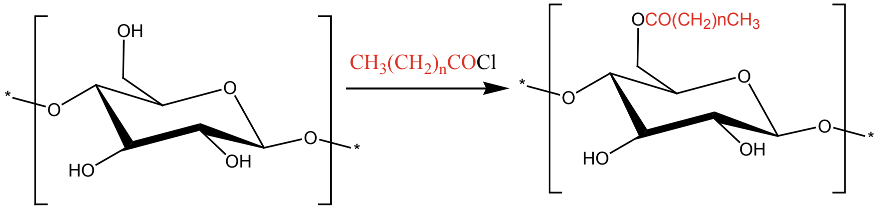

Fig. 6.8 Example of synthetic route to amphiphilic cellulose derivatives

However, the simple modification of chitin by hydrolysis of acetamido groups to free $-NH_2$ bring to a much more versatile material (chitosan), which is one of the most promising materials having potential applications in biomaterials, pharmaceuticals, cosmetics, metal ion sequestration, agriculture and food treatment. Research concerning the functionalization of chitosan tremendously increased during recent years and it represents an effective example of how controlled modifications can be used to prepare polysaccharides derivatives with well-defined structures for functional applications. Hydrolysis of the main chain, deacetylation, acylation, Schiff base formation, N-phthaloylation, tosylation, alkylation, reductive amination, O-/N-carboxyalkylation, etc. have been all employed.

All these functionalization possibilities are owing to the need to render more soluble and processable polysaccharides or to improve their thermo-mechanical behaviour. Among the possible functionalization of polysaccharides, the growing interest towards the production of hydrophobically modified derivatives is justified by their application as modifiers, emulsion stabilizers, compatibilizers and as surface modifiers of nanoparticles.

Despite the highly crystalline and extremely insoluble structure of cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, 2-sulfoethyl cellulose, cellulose sulphate, etc., examples of water-soluble cellulose derivatives have been reacted to be modified with hydrophobic long side-chain such as alkyl or acyl halides, long-chain alkyl epoxy compounds, etc. Generally, water-soluble derivatives are modified with hydrophobic moieties under heterogeneous conditions and low substitution degrees (DS) are usually obtained (Fig. 6.8).

The modification of polysaccharides can be successfully realized by using some long-chain fatty acids such as hexanoic acid, decanoic acid, linoleic acid, linolenic acid, palmitic acid, stearic acid and oleic acid.

These materials like as hydrophobically modified starch exhibit properties important for many applications and overall can act as emulsions stabilizers as in the example reported in Fig. 6.9.

Even lauric, palmitic and stearic acids under mild reaction conditions have been used in the esterification of a water-soluble semisynthetic polysaccharide such as the hydroxyethyl starch (HES) by using dicyclohexyl carbodiimide (DCC) and dimethylaminopyridine (DMAP). Micelles of 20–30 nm and polymeric vesicles of 250-350 nm have been obtained by the aqueous self-assembly of the modified polymer that might find use as a drug carrier.

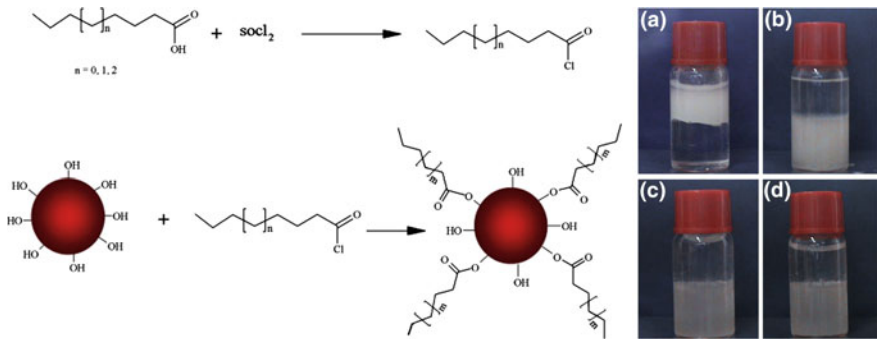

Fig. 6.9 Esterification reaction of starch nanocrystals and wettability tests of **a** unmodified starch nanocrystals in distilled water **b** octanoyl starch nanoparticles **c** nonanoyl starch nanoparticles **d** decanoyl starch nanoparticles in chloroform, (from Namazi and Dadkhah (2010). Reprinted with permission by Elsevier)

As evidenced in many parts of this book, according to the end use or specific needs, tailor-made graft copolymers can be synthesized using specific polymerization or functionalization methods. This is of great interest for polysaccharides, polypeptides, polynucleic acid, which belong to our renewable resources but generally do not show the properties necessary for many structural and functional applications and, in addition, do not exhibit plastic behaviour. As for example, generally the design of copolymers architecture has been used to improve different features like as the dimensional stability, the resistance to abrasion and wear, the wrinkle recovery, the oil and water repellency, the elasticity, the thermal resistance and the resistance to microbiological attack of cellulose-based materials, while some compatibile effects are generally recognized to amphiphilic nature/behaviour of these complex structures.

Well-known examples of "*grafting to*" polysaccharides are the ones applied to the modification of cellulose fibres, mainly for applications in the textile industry or fibre reinforced composites. In this case, condensation and addition reactions are employed owing to the nucleophilic character of hydroxyl groups. Typical reactions involve species containing methylol groups (–CH_2OH), isocyanates, triazine coupling agents, organosilanes and anhydridic derivatives.

Some of the reactions considered above are also used in the field of starch-based bioplastics to increase the compatibility between starch and different synthetic polymers (mainly biodegradable polyesters such as poly(lactic acid) and poly(caprolactone)) in polymer blends (see Sect. 6.3). For instance, diisocyanates, maleic anhydride, dioctyl maleate and epoxides are able to increase the interfacial interaction between the hydrophilic and the hydrophobic counterparts in blends, generating in situ graft copolymers between, for instance, starch and the synthetic polyolefins. Copolymers can be generated by grafting acrylic monomers where the free radicals on the backbone can be formed once again by chemical initiators, irradiation with ultraviolet light, gamma rays and by exposure to plasma ion beams by

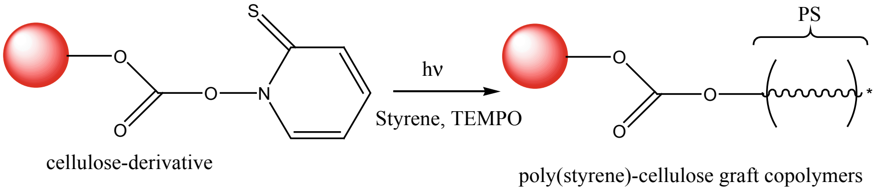

Fig. 6.10 NMP-mediated controlled radical grafting from cellulose derivative

taking advantages from the huge amount of functionalities (mainly –OH groups) already present in their main structure. The general mechanism of "*grafting onto*" involves the formation of –O$^{\cdot}$ radicals (formed by chemicals or radiation) starting from –OH functionalities and proceeds with unsaturated monomer additions like as reported in Fig. 6.3 for the substrate cellulose, whose products are generally used to improve the mechanical resistance of the final material or to impart completely new properties out the main purpose of this chapter.

The recent advances in the theme of "*grafting from*" by controlled radical methodologies have been applied to polysaccharide grafting also. Cellulose grafting was realized by NMP and the analogous approach was used for hydroxypropyl cellulose. For this derivative, a TEMPO mono-adduct was obtained by photolysis of the N-hydroxypyridine-2-thione carbonate derivative, and by heating in the presence of styrene poly(styrene)–cellulose graft copolymers were obtained (Fig. 6.10). An increase in grafted polymeric chains length was obtained with increasing the polymerization time with a polydispersity of the grafted poly(styrene) in the 1.3–1.5 range.

Anyway, among all of the living radical polymerization techniques, ATRP is the most used for the modification of polysaccharides; in particular, it has been used to change the surface properties of cellulose and cellulose derivatives. After the transformation of molecules bearing hydroxyl groups into ATRP initiators the application of ATRP for the grafting of monomers on cellulose at ambient temperature has been extensively reported. As an example, 2-bromoisobutyryl bromide was used for modifying hydroxyl groups of cellulose to form initiators at the surface. PMA-grafted paper was formed by grafting methyl acrylate (MA) from the surface and the resulting excellent hydrophobicity. In a successive step, 2-hydroxyethyl methacrylate (HEMA) was grafted onto PMA to form a second layer and generating a more hydrophilic surface and proving that the hydrophilic/hydrophobic feature of the cellulose surface can be tuned using such modification approach.

6.3 Blends

The concept of polymer blend does not depend on the origin of polymers and can be equally applied to man- and natural-made polymers (Goh 2014). Indeed, a polymer blend is simply a mixture of two or more polymers or copolymers in which the content of every component is above 2% by weight. The term polymer blend does not apply to a mixture of a polymer with a low molecular weight additive such as plasticizer or others. Blend properties differ from those of the neat constituents and can be modulated in a wide range according to the type of the components and their respective content. It is a common and reasonable rule that the blend properties result in an intermediation between that of the components even if the prediction of the ultimate value is much more complex than in mixtures of low molecular weight compounds. From a practical viewpoint and in a very general meaning, the term blend indicates that the two mixed polymers interact in such a way that the mixing is thermodynamically favoured or at least the repulsion energy, if the materials are different, is lower than the energy gain connected with the entropy increase. This means that the value of the free energy of mixing, ΔG_m, is given by

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{6.1}$$

respects the following:

$$\Delta G_m < 0 \text{ and } \left(\frac{\partial^2(\Delta G_m)}{\partial \phi_i^2}\right)_{T,p} > 0 \tag{6.2}$$

where ϕ is the volume fraction of one of the components. ΔS_m is the entropy factor related to the disorder or randomness resulting by the mixing of two different materials. The entropy of the blending process is always positive and, therefore provides a contribution favouring the miscibility. However, in case of blends of high molecular weight polymers, the entropy contribution is small due to the low conformational freedom of the monomer units connected in the macromolecule backbone. Therefore, for an adequate negative value of the free energy of blending, the enthalpy of mixing (ΔH_m) must be negative. However, ΔH_m can be either positive (endothermic) or negative (exothermic): the miscibility is becoming possible only in the former case. Strong specific interactions between the blend components such as hydrogen bonding, dipole–dipole, and ionic interactions are, therefore, necessary to reach this result. For this reason, two polyolefins, such as polyethylene and polypropylene are immiscible as the interactions between the two different types of macromolecules are weak or zero due to the high hydrophobic character of the materials having both paraffin natures. The situation is different with polymers containing polar groups that can give rise to favourable interactions and then can result in negative enthalpy of mixing. Biopolymers are often polar, as, for instance, chitosan, starch, and several proteins. They are then miscible with complementary polar and hydrophilic polymers, such as poly(ethylene oxide) (PEO), poly(N-vinylpyrrolidone), poly(N-methyl-N-vinylacetamide), poly(2-ethyl-2-oxazoline), or poly(2-methyl-2-oxazoline).

In case of blends of two non-polar polymers interactions between different macromolecules are similar to those between similar macromolecules and therefore $\Delta H_m \approx 0$. In this case, both the terms, the free volume and the specific interac-

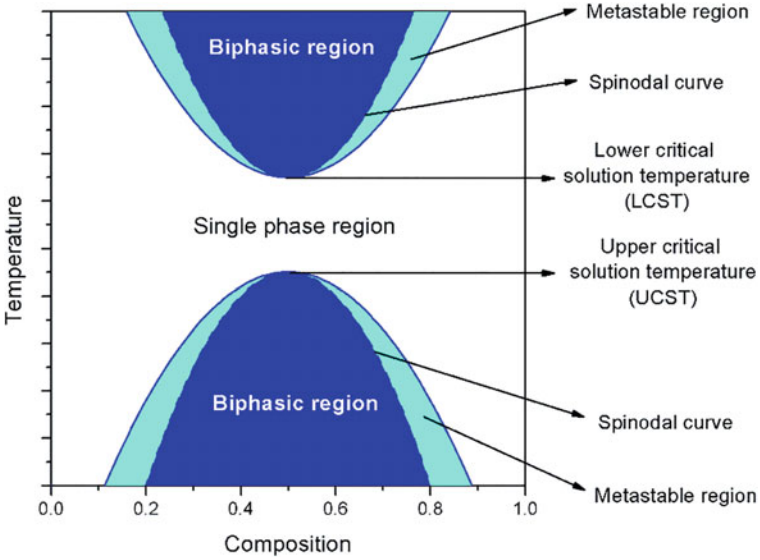

Fig. 6.11 Temperature-composition phase diagram for a binary polymer blend showing the different regions

tions, can be not considered, and the Flory–Huggins equation (Eq. 6.3) gives the free energy of the mixing of the two polymers (polymer 1 and polymer 2).

$$\Delta G_m = RT\left(\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_1 + \chi_{12}\phi_1\phi_2\right) \tag{6.3}$$

where ΔG_m is the free energy change, ϕ the volume fraction, N the number of chain segments and χ the Flory–Huggins interaction parameter. The first two terms on the right side of Eq. (6.3) are related to the entropy of mixing while the third term corresponds to the energy of mixing of two polymers with infinite molar mass, for which the two entropic contribution terms are negligible; then if the mixed polymers have high molecular weight the system miscibility depends on the value of the enthalpy of mixing, being possible only if the last is negative. The free energy values calculated by Eq. (6.3) with variation of the temperature, allow drawing a phase diagram in which three different regions with different degrees of miscibility (Fig. 6.11) can be recognized.

Figure 6.11 shows clearly the role of temperature in determining the miscibility of two polymers when blended. The shape of the diagram obviously changes depending on the interaction parameter characterizing each pair of polymers.

If two polymers mix at low temperature without phase separation and then they separate on heating, the pair is characterized by a lower critical solution temperature (LCST). On the contrary, if the phases remain separate at ordinary temperature and mix to form a single phase at a higher temperature, the corresponding blend has upper critical solution temperature (UCST) behaviour (as shown in Fig. 6.11). At the critical point or temperature, the product of entropy of mixing and absolute temperature must be balanced by the heat of mixing.

If the polymer blend under conditions corresponding to the miscibility area of the phase diagram is submitted to conditions corresponding to the non-miscibility, phase separation takes place (spinodal phase separation). The thermodynamic condition for spinodal phase separation is given by the Eq. (6.4).

$$\left(\frac{\partial^3(\Delta G_m)}{\partial \phi_i^3}\right)_{T,p} = 0 \tag{6.4}$$

It has been observed that the spinodal separation usually gives rise to interconnected domains (co-continuity) both in the minor and major phases, which favor the synergism of properties, as, for example, modulus and impact strength. Determination of conditions for co-continuity is, therefore, important to understand. The occurring of strong interactions, typically involving complementary polar groups, between the two blend components requests a modification of Eq. (6.3), which gives the free energy of mixing of two polymers with weak non-specific interactions. The modification is based on additional term ΔG/RT of the free energy of mixing that represents this favourable thermodynamic contribution. Consequently, Eq. (6.3) assumes the extended form reported in Eq. (6.5):

$$\frac{\Delta G_m}{RT} = \left(\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_1 + \chi_{12}\phi_1\phi_2\right) + \frac{\Delta G}{RT} \tag{6.5}$$

The terms within the brackets on the right side of Eq. (6.5) correspond to the whole right side part of Eq. (6.3), while the added term ΔG/RT gives the specific interactions that contribute to the increase of the free energy of mixing. In the case of the corresponding blends, a critical value of the miscibility can be calculated in the whole composition range though Eq. (6.6).

$$\left(\frac{\partial^2(\Delta G/RT)}{\partial \phi_i^2}\right) = \left(\frac{\partial^3(\Delta G/RT)}{\partial \phi_i^3}\right) = 0 \tag{6.6}$$

The former Eq. is reported to lead to the following expression (6.7) for the Flory–Huggins interaction parameter (χ):

$$\chi_{cri} = \frac{1}{2}\left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right)^2 \tag{6.7}$$

The experimental determination of χ is possible with the inverse gas chromatography and solvent diffusion or by the determination of the blend glass transition temperature (T_g) with reference to the same temperatures of the mixed polymers. Indeed, it was demonstrated that miscible blends obeys the Fox Eq. (6.8) over the entire composition range:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{6.8}$$

where w_1 and w_2 are the weight fraction of the two polymers, T_{g1} and T_{g2} the respective glass transition temperatures and T_g the glass transition temperature of the blend.

Depending on the validity of the above equations, the blend may present distinguished characteristics. A first important distinction is based on the classification of a blend as miscible or immiscible. Former blends are substantially homogeneous even if an ideal homogeneity is practically impossible to reach in real cases. Substantially, in these blends, in each point a very close molecular composition is found and the individual polymer properties are markedly changed. In the latter case, the immiscible blend has the characteristics of heterogeneous material, and at least two different phases survive, where the characteristic properties of each polymer component can be evidenced. Clearly, positive interactions at the interface must exist to keep the two phases well connected (Coleman et al. 1990).

Examples of miscible blends are provided by the systems poly(styrene)/poly(2,6-dimethyl-1,4-phenylene ether) (PS/PPE), poly(styrene-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA) and poly(3-hydroxybutyrate)/poly(methyl methacrylate) (PHB/PMMA) but only in a certain composition range. Much larger is the number of heterogeneous blends; among these the most common are poly(propylene)/poly(ethylene) (PP/PE), poly(propylene)/poly(styrene) (PP/PS), thermoplastic starch/poly(butylene adipate-*co*-terephthalate) (TPS/PBAT), poly(lactic acid)/poly(3-hydroxybutyrate) (PLA/PHB) and several others. The type of blend is dependent on respective molecular structure and therefore can be independent on fossil or natural origin as well. The mentioned examples indeed included pairs of two man-made polymers, (PS/PPE, SAN/PMMA, PP/PE, PP/PS), pairs of a biopolymer with a man-made polymer (PHB/PMMA, TPS/PBAT) and a pair of two bio-related polymers (PLA/PHB). In general miscible polymer blends form one-phase material whose properties are averaged over the component properties in the full compositional range (Fig. 6.12).

The blend poly(styrene)/poly (2,6-dimethyl-1,4-phenylene ether) (PS/PPE) provides a very evident example of a miscible blend, present in the market in different compositions since 1965. These blends have glass transition temperature regularly increasing with the PPE content following very well the prediction from the Fox law. PPE is about three times more expensive than PS and the use of PS/PPE blends as a replacement for PS is justified only when higher heat distortion temperature (HDT) and/or impact strength is required.

Gazzano et al. (2012) reported that also bacterial poly(3-hydroxybutyrate) (PHB) and the tributyrate cellulose derivative (CTB) are fully miscible over the whole composition range. While the previously considered PS/PPE blend derives from two amorphous non-stereoregular homopolymers, PHB and CTB are stereoregular polymers that are able to crystallize and then their domain can be semicrystalline even in the blend. Therefore, a crystalline phase from one or the other component may be present in the blend depending on the composition. According to theory,

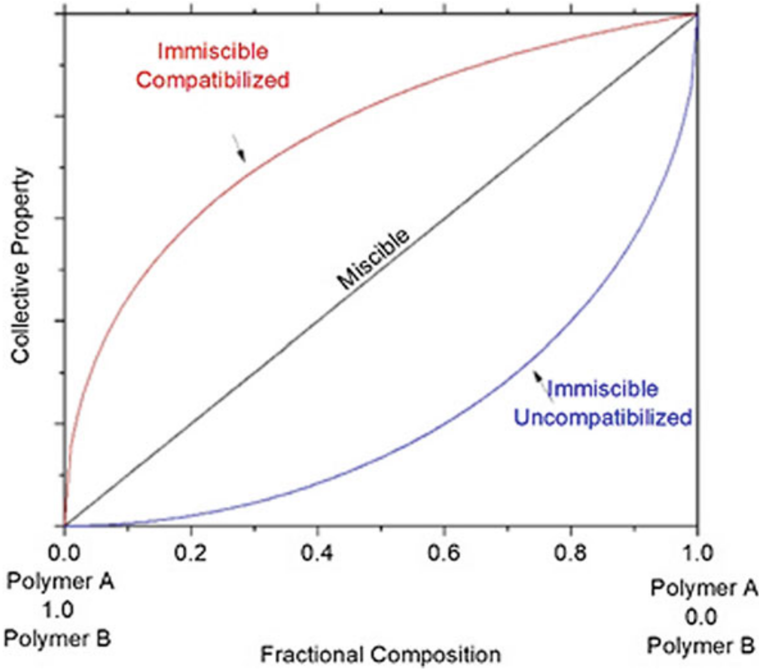

Fig. 6.12 Variation of polymer blend properties as component concentration changes

PHB crystallinity is observed in blends containing 40 % w/w or more PHB itself. When PHB is less than 40% and the CTB content becomes then larger than 60% crystallization of the latter is detected. The melting temperature and the crystallinity degree of the PHB phase depend on the blend composition: at high PHB content, the values decrease with respect to neat PHB reaching a minimum at PHB/CTB 40/60. Then CTB crystallizes with increasing melting point and crystallinity degree up to the values of the pure component at CTB 100%.

If the two blended polymers are not compatible, we deal with immiscible blends, where both the crystalline phase and amorphous phase are separate. The continuous phase contributes to the main properties and the dispersed phase adds additional properties such as toughness, where the stress is transferred from the continuous phase to the dispersed phase. In general, the interaction between the different polymer phases determines the interphase compatibility, which strongly affects the properties of a heterogeneous polymer blend (Fig. 6.12). The interface between the polymer phases in a polymer blend is characterized by the interfacial tension, which approaches zero when the components are miscible. Large interfacial tension leads to phase separation, and in general increased particle size and coalescence may occur; which, in turn, decreases mechanical properties. Additives able to reduce the interfacial tension are then used, and are named compatibilizers (Sect. 6.2). Compatibilizers can be produced separately or in loco by reactive compatibilization. Further possible strategies for compatibilization are the co-crystallization of two phases or the in situ immobilization of one phase (dynamic vulcanization). Dynamic vulcanization is today largely used to stabilize polyolefin heterophase mixtures by submitting to the vulcanization process (cross-linking) the mixture itself where the more reactive component gives a dispersed phase in the thermoplastic matrix provided by the other blend component less sensitive to the cross-linking reaction. The cross-linked phase can no longer evolve towards the thermodynamic equilibrium state and affects the finally thermoplastic materials with improved impact properties. On the other side, if the two miscible plastic polymers or two immiscible polymers are blended with compatibilization, a mixed more or less homogeneous phase can be formed with a balanced combination of properties derived from each polymer. An example of the former type is provided by blending of a thermoplastic polyamide with good thermo-mechanical properties with a cross-linkable elastomer to yield, a rubber-toughened polyamide. Examples of the latter situation are offered by blending miscible polystyrene and polyphenylene oxide (PPO) to modulate monotonically the final structural properties. In addition to the main structural properties, additional features modulated by the blending are heat distortion temperature, solvent or water resistance, dimensional tolerance, higher flow, recycling of post-use materials, and lower cost.

The blending procedure has been also largely used to extend the performances and application of bio-derived plastic materials (Yua et al. 2006). A typical example is offered by the starch blending with hydrophobic polymers to achieve water resistance and improved mechanical performances. Starch is indeed cheaper than other biopolymers, readily available and renewable. In plastic starch (TPS), granules have been plasticized under heating to allow classical processing of plastic polymers such as injection moulding and extrusion (Sec. 5.5). Glycerol, water and urea and several organic amides were employed as plasticizers. Also, hydrophilic polymers containing hydroxyl groups, such as poly(vinyl alcohol), copolymers of ethylene and partially hydrolyzed vinyl acetate were blended with starch to obtain plasticized materials. The water plasticized can be blended as an aqueous emulsion, with natural rubber latex, poly(vinyl acetate) and other synthetic polymer lattices. However, starch blends can be also produced by melting. Alternatively, starch can be gelatinized in a first single screw extruder and then fed into a twin-screw extruder, which processes the other component. Most frequently biodegradable polyesters as for the first commercial example of the fully biodegradable polyester/starch blend was produced by Novamont (Mater-Bi® Z), and many others examples have been produced later.

The blending of starch with the hydrophobic PLA with coupling agents such as methylene diphenyl diisocyanate (MDI) or functionalized PLA bearing reactive groups such as maleic anhydride is necessary.

Commercial biodegradable polymer blends are also obtained by combinations of PLA with different synthetic biodegradable polyesters such as the poly(butylene succinate-*co*-adipate) (PBAT) and the poly(butylene succinate) (PBS). This last polymer improves the toughness and punctures resistance. Thus, the 70/30 (% w/w) PLA/PBSA blend shows a 5-fold higher tensile elongation to break and about a

Table 6.1 Some commercial biodegradable polyester blends

Blend components	Commercial grade	Melting point (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Water permeability
Starch, PCL	Mater-by-Z	65	31	185	800	High
PLA, PBAT	EcoVio-F	110–140	35	750	300	High
Starch, PLA, PBSA	Bionolle Starcla	93	20	690	–	High

25-fold increase of tensile toughness. These effects are reciprocal and the too soft PBAT, when blended with PLA, shows improved stiffness and strength while lower cost while retaining biodegradability and compostability. Examples of commercial biodegradable polyester blends are reported in Table 6.1, which shows that the processability and properties are comparable to LDPE.

6.4 Composites and Nanocomposites

As described in the former paragraph, blends are mixtures of two or more high molecular weight polymers. The term “polymer composites” is instead used for indicating materials based on an organic polymer component acting as the continuous matrix and at least one additive of different chemical and physical type that interact with the matrix only at the interface with the consequent modification of the final performances of the material if compared to the neat matrix. As the additive remains in the form of dispersed phase being incompatible, the properties’ improvement depends markedly on the interaction surface area and then on the dimension of the dispersed phase particles (Sarath et al. 2014). In polymer composites, this size is of the order of microns whereas in polymer nanocomposites at least one of the component particles or fibres/films has to size between 5 and 100 nm. Clearly, to maintain plastic behaviour the composites must be prepared with thermoplastic polymers as the matrix and the amount of filler must not be below the limit for the plastic behaviour of the final product. This goal is easier to reach with nanocomposites as the smaller size particle allows reaching the requested interphase surface with a much smaller amount of dispersed phase with respect to traditional composites. Both plastic polymers from fossil or natural origin are used as binders (matrices) both in the production of polymer composite materials (PCM) and polymer nanocomposites (PNC). The production of PCMs and PNCs with a thermoplastic matrix is carried out mainly during the melt processing of the matrix by adding the dispersed phase component or a masterbatch of this last previously prepared. Note that both PCM and PNC can be produced with a thermoset polymer matrix (materials that when heated and/or in the presence of a curing agent lose the ability to transform into a viscous-flow state) but this is clearly out of the interest of the present book.

The use of a plastic polymer matrix is more and more researched to improve the sustainability of composites, which, on the other side, allows replacing some traditional materials with increased sustainability. Indeed, the disposal of thermoset polymer composites creates very complex environmental problems and it is not simple to handle safely. The use of thermoplastic matrix offers the advantage of reprocessing and then recycling thus reducing waste disposal. Moreover, the separation matrix-dispersed phase is technically possible and can be used when convenient with much less difficulty than for a cross-linked material. Nanocomposites offer in principle fewer problematics in this context standing the very small amount of filler. But even in this case, the recycling is preferable to disposal as the possible degradation or biodegradation of the matrix can leave in free in the environment nanosized particles with their health problems for humans.

Clearly, the main objective of preparing composite materials consisting of at least two phases is the occurring of synergistic effects to obtain a material of different properties than the components. Among the properties to be improved from polymer to composites or nanocomposites, one can find both structural and functional properties. Micro fillers, and particularly fibres, are normally used to attain mechanical properties not typical of thermoplastic polymers. Indeed, composites are often produced to replace metals or ceramics having comparable performances and lighter weight (minor density). Often elevated thermo-mechanical performances are required for materials granting good durability in time even under aggressive conditions. As mentioned before the composite material is usually composed of two components, matrix and filler. The former is clearly a polymer and in our case a thermoplastic polymer. Evidently, often the required durability of the matrix excludes biodegradable polymers and therefore in these composites plastic polymer obtained from renewable sources can be used, provided their structure grants the same durability as the synthetic analogues from fossil origin, called also reinforcement. In traditional composites, the most used filler was derived from glass and is mainly glass fibres. More recently, this was replaced with common natural fibres. The origin of the fibres determines the classification into plant fibres and animal fibres, which can be processed at low cost and are biodegradable. They can allow producing low-weight composites and higher resistance during the process because they can bend rather than fracture and break. The matrix holds and transfers the loads along the reinforced matrix and the reinforcing material (usually fibres) and this determines the overall basic properties. Often a third component, in minor quantity, can be added to improve the dispersion of the reinforcing phase. Disadvantages occur anyway from their poor compatibility with long-lasting hydrophobic polymers, low thermal resistance and high flammability. The compatibilizer is then added to increase interactions between matrix and filler necessary for material cohesion and homogeneity, and then its processing properties and strength. In reinforced composite, the dispersed phase is made by particles with rigidity and hardness greater than the matrix. Matrix and filler act synergically in the transfer of the external load. The reinforcement is shown for a filler content higher than 20%.

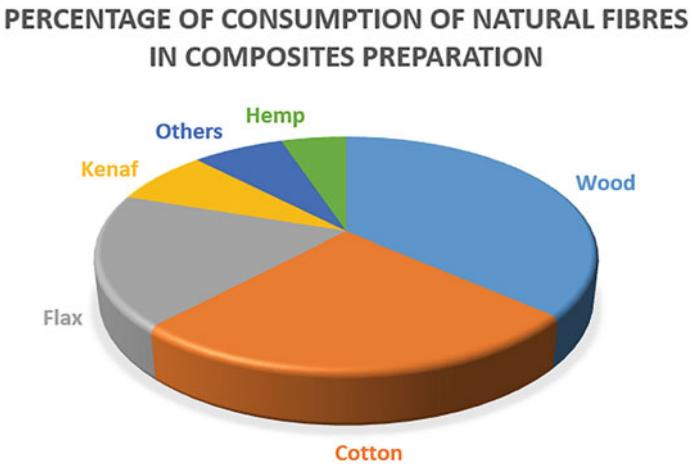

Fig. 6.13 Relative consumption of natural fibres in composites preparation (data from www.news.biobased.eu)

The increased sensitivity towards environment preservation has stimulated the search for efficient solutions to produce new biocomposites in which at least one component is biodegradable or derives from renewable sources. As already mentioned, the attempt could be focused either on the polymer matrix or on the dispersed fillers and finally in both. These three distinct aspects lead to different opportunities and handling problematic with reference to the saving of resources and to final environmental impact. The advantages of biodegradability, reduced carbon emission, sustainable waste management and a positive balance between supply and demand of products from renewable sources have been already discussed in the previous chapters and are also reconsidered in the following chapters. As far as composites are concerned, the characteristic aspects refer here to the filler from renewable sources. Fibres from renewable resources are becoming more popular in the production volume and of application fields (Fig. 6.13). Indeed, the use of natural fibres in composites was shown in several cases to cover both the gap in the properties between bio-derived and fossil-derived polymers. Today, the replacement of synthetic fibres with natural fibres characterized by similar stiffness is becoming a reality in specific applications (Saba et al. 2016).

A comparison of natural fibres properties with those of synthetic fibres is reported in Table 6.2.

The most common molecular components of natural fibres are cellulose, hemicellulose and lignin. These bioorganic products have poor thermal stability compared to mostly inorganic synthetic fibres and this affects the organoleptic and mechanical properties of the derived biocomposites. To overcome this challenge, relatively low melting thermoplastic matrices such as polyolefins, and polyesters are preferentially used. For completely biodegradable composites, a low melting biopolymer should then be used. Interphase interactions affect the properties of biocomposites as for

Table 6.2 Comparison of properties between synthetic and plant fibres

Properties		Carbon fibres	Glass fibres	Plant fibres
Technical	Density (g cm^{-3})	Low (1.70–2.20)	High (2.50–2.70)	Low (~ 1.35–1.55)
	Tensile stiffnes (GPa)	High (150–500)	Moderate (70–85)	Moderate (~ 30–80)
	Tensile strength (GPa)	High (1.3–6.3)	Moderate (2.0–3.7)	Low (~ 0.4–1.5)
	Tensile failure strain (%)	Low (0.3–2.2)	High (2.5–5.3)	Low (~ 1.4-3.2)
	Specific tensile stiffness (GPa/g cm^{-3})	High (68–290)	Low (27–34)	Moderate (~ 20–60)
	Specific tensile strength (GPa/g cm^{-3})	High (0.3–3.7)	Moderate (0.7–1.5)	Moderate (~ 0.3–1.1)
	Abrasive to machine	Yes	Yes	No
Ecological	Energy consumption/kg of raw fibre (MJ)	High (> 130)	Moderate (30–50)	Low (4–15)
	Renewable resource	No	No	Yes
	Recyclable	Partly	Partly	Yes
	Biodegradable	No	No	Yes
	Hazardous/toxic (upon inhalation)	Yes	Yes	No
Economical	Annual Global production (tonnes)	55,000	4,000,000	31,000,000
	Distribution of fibres for Fibre Reinforced Products in EU	Low (15,000)	Wide (600,000)	Moderate (~ 60,000)
	Cost of raw fibre (£/kg)	High (> 120)	Low (~ 1.3–2.0)	Low (~ 0.5–1.5)

Data from Shah (2013)

traditional composites. When the selected pair, matrix plus fibres, do not provide the necessary favourable interactions a modification is necessary, such as surface chemical modification, graft copolymerization, physical treatment or mercerization. Natural fibres are characterized by the large content of –OH groups on the surface, which is then hydrophilic and poorly compatible with hydrophobic matrices such as polyolefins or poly(lactic acid). The treatment with soda (mercerization) of plant fibres allows to converts the native crystalline cellulose-I in the much more thermodynamic stable cellulose-II (Fig. 6.14). Because of this conversion, the surface of the fibres becomes much more polar and rougher with an increase of the wettability and of the possibility of chemical interaction, which can help in some systems.

Compatibility and surface interaction energy between polar fibres and polymer matrix can be made more favourable by appropriate modification of the polymer matrix. This is done more conveniently by using a polymer compatibilizer that contains both polar and non-polar groups, positioned at the interface and acts as an adhesive between fibres and matrix. Polyolefins bearing a small amount of grafted maleic anhydride act efficiently in this way (see sec. 6.2). Indeed, the anhydride functionalities can react with the hydroxyl groups of the natural fibres with the formation of links with the fibre surface, while the hydrophobic long unsubstituted chain sec-

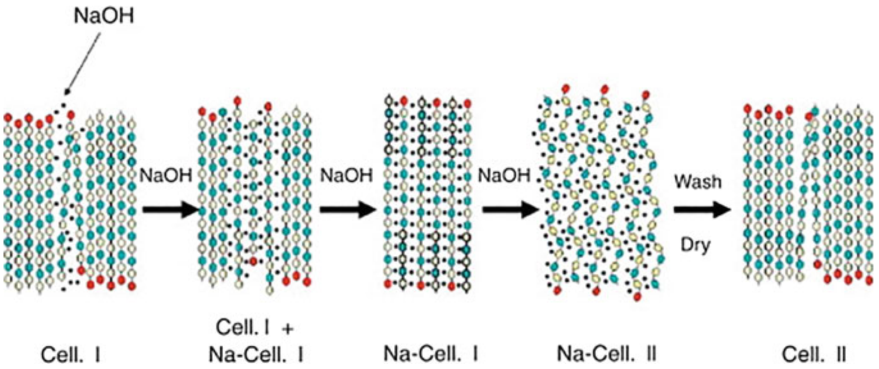

Fig. 6.14 Mercerization process of cellulose (figure from "Structure and Engineering of Celluloses", Pages 25–116, Serge Pérez, Daniel Samain in Chemical Structure Analysis Advances in Carbohydrate Chemistry and Biochemistry: Volume 56, Elsevier Science Publishing Co Inc,, Ed. Derek Horton, 2010; reprinted with permission

Table 6.3 Typically reported mechanical properties of different fibre-reinforced products

Manufacturing technique	Reinforced form	Composite	Fibre content (%)	Tensile modulus (GPa)	Tensile strength (MPa)	Specific tensile strenght (MPa/gcm^{-3})
Injection moulding	Short fibre-3D random	Flax/PP	30 wt	1.7	27	26
		Hemp/PP	30 wt	1.5	30	29
		E/glass/PP	30 wt	2.2	49	35
Compression moulding	Short fibre-2D random	Flax/PP	40 v	8.8	57	52
		Jute/PP	30 v	3.7	22	26
		E/glass/PP	22 v	6.2	89	59
Compression moulding	Long fibre unidirectional	Flax/pp	43 v	26.9	251	220
		Hemp/PP	42 v	21.1	215	185
		E/glass/PP	35 v	26.5	700	461

Data from Shah (2013)

tions provide a good connection to the hydrophobic matrix. Composites based on polypropylene and wood flour added with small amounts of maleic anhydride–modified polyolefin shows a larger modulus and lower loss factor than unmodified PP. The properties of the composites can be also affected by the possibility of the fibres to be preferentially aligned, as the transverse moduli of raw anisotropic fibres is an order of magnitude lower than the axial moduli. The orientation and organization of the fibres inside the polymer matrix and then the mechanical properties of the composite may be appreciably affected by the process used in the composite production. As reported in Table 6.3 for the polypropylene matrix with different types of fibres.

The natural fibres are also important in the preparation of fully bio-based composite from bio-derived or biodegradable polymers. The most studied bio-derived polymers for this last purpose are PLA and PHB. Challenges to be solved for the for-

Table 6.4 Natural-made Nanocomposites

Nanofiller	Macromolecules	Nanocomposite
$CaCO_3$ + $Ca_{10}(PO_4)_6(OH)_2$	Collagen (protein)	Bones
$CaCO_3$	Proteins + peptidies	Shells, Egg Shells
$CaCO_3$	Glycoproteins	Spines
$CaCO_3$	Polysaccharides, Proteins	Insects cuticle

mer polymer are the low heat distortion (~ 60 °C) and limited melt strength, while the latter application is limited by the brittle nature. The use of PLA and PHB matrices for fully bio-derived composites still requires, therefore, some matrix modification of the plastic properties.

A further problem with natural fibres is given by the variability of the tensile properties of the fibres also for the same type of materials from the same harvesting. Structural variation is related to crystallinity, composition and porosity connected to different growth conditions. The fibre diameter cannot be accurately controlled and largely depends on the mechanical collection procedure with the possibility of production of defects on the surface. The presence of these defects is responsible for fibre breakage during processing and then of varied ultimate properties of the biocomposite (Fortea-Verdejo et al. 2017).

The hydrophilic character of the highly hydroxylated natural fibres is responsible for their poor moisture resistance and in turn for poor mechanical properties. Absorbed water acts as a plasticizer and interferes with adhesion bonds at the polymer–fibre interface. This effect may need a protection of the biocomposite against water absorption by appropriate hydrophobic additives. This once again shows how difficult can be to use fully bio-derived materials with well-defined properties.

A different situation arises in nanocomposites where the dispersed phase is usually present in an extent of few units percent or less. The size reduction from micro to nano is responsible for the enormous increase in the filler surface area and then of the interface. This last, where the filler modifies the matrix to give the specific ultimate properties, becomes predominant even with a small amount of filler. Indeed, by reducing the particle diameter from 1 micron to 10 nm, the surface increase from 1 to 1 million (six orders of magnitude).

Materials with this unique structure allowing to combining performances of a macromolecular system with an extremely small particle of a mineral filler to improve up to an extraordinary extent the mechanical properties were well known to Nature, particularly in the human and animal word. Some typical examples are referred in Table 6.4.

In the examples of Table 6.4, Nature clearly used biopolymers as matrix and minerals as fillers, the objective being toward mechanical properties.

Following this concept at the end of the past century, Toyota produced plastic polymer nanocomposites with improved thermo-mechanical properties with a polyamide

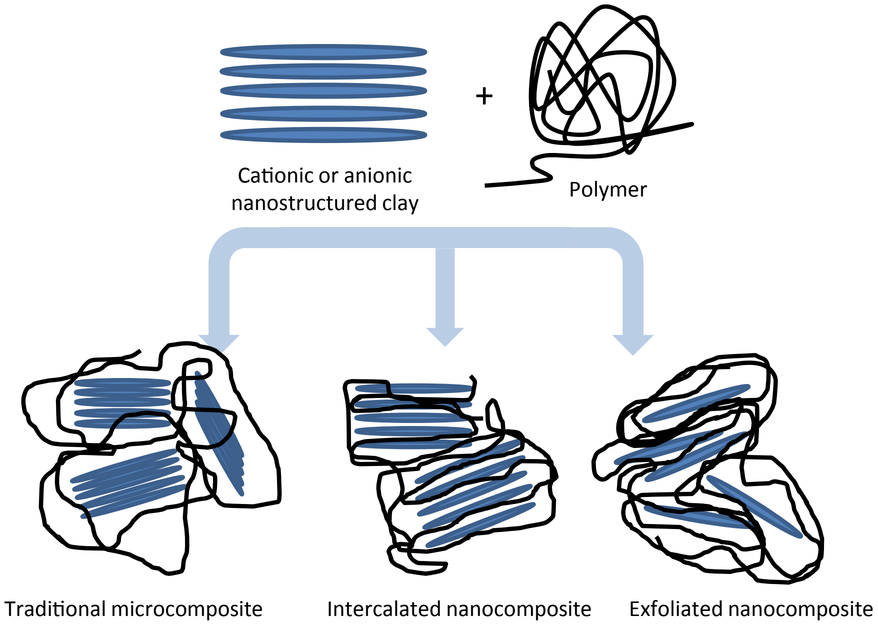

Fig. 6.15 Classification of morphologies for polymer–clay composites

matrix and minor amounts of lamella alumosilicate exfoliated to nanosized layers. These clay materials (montmorillonite, bentonite, mica, saponite and hectorite) in nano-dimensions provided heat resistant and flame retardant properties to polymers as well the thermal barrier property of the composite. The resulting plastic nanocomposite had improved toughening features thanks to the plate structure, high surface to volume and strength to weight ratio of the exfoliated clays.

Additional thermoplastic nanocomposites were successively investigated to provide different plastic polymers with functional properties such as thermal and electroconductivity and optoelectronic properties. In man-made nanocomposites, three different types of nanofillers were used: 1D-linear (monodimensional), e.g. carbon nanotubes; 2D (bidimensional-layered), e.g. montmorillonite and 0D (zero-dimensional—spherical powder), e.g. metal or silica nanoparticles.

The preparation of nanocomposites can be performed by the traditional processing methods used for plastic polymers, such as by mixing the nanofiller with the molten state polymer matrix or by in situ polymerization or solvent method.

Nanomaterials based on polymer matrix and inorganic or organic nanofillers are prepared in general with a content between 5 and 10 % w/w of nanofiller having a high aspect ratio (more than 1000), high surface area (more than 750 m^2/g) and higher modulus values (176 GPa). Depending on the materials used and the dispersion process either intercalated or exfoliated nanocomposite morphologies can be obtained (Fig. 6.15).

Nanotubes or nanofibers are particles of linear structure and can help to obtain specific and remarkable mechanical properties for demanding structural applications.

Nanofillers characterized by electron delocalization such as carbon nanotubes and graphene layers in addition to improve mechanical performance can supply electrical properties to the nanostructured materials based on plastic polymers such as polyolefins, polyvinyl alcohol, polymethyl methacrylate and polycarbonate and others.

The nanofiller POSSs (Polyhedral Oligomeric Silsequioxanes) with general formula $(RSiO_{1.5})_n$, where R can be hydrogen atom, alkyl or aryl groups and n can range between 6 and 12 are also used. With polyolefins, epoxy resins, polyimides, polyamides, polycarbonates and poly(vinyl chloride) POSSs improve the flow rate and the thermal stability.

The combination of two kinds of fillers has been recently developed. An example is the addition of nanoclay in plant fibre composites to compensate the lack of compactness derived by the internal gaps among the filaments of the helical-like structure. A small quantity (1 % w/w) of nanoclay in plant composite allows the improvement of the impact and flexural properties.

In addition, the improvement of dimensional stability and of processing easiness has a positive effect on dynamical–mechanical and tensile and flexural strength properties. The improvement is more evident if bonding interaction occurs between the matrix and nanoclay.

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Chapter 7
Environmental Impact

7.1 Plastics and Bioplastics Versus Environment

We should be well aware that human activity is not favourable to maintain an intact environment. In this sense, both plastics and bioplastics production and use are responsible for a certain environmental impact. The complete understanding of the respective effects is not trivial and a clear unique conclusion is not possible at present. Indeed, several conflicting aspects were and are currently reported in the pertinent literature and the debate is still rather open. For this reason, it was considered useful to report the various points here to provide a broad but, complete as far as possible, imagine of the conceptual situation. The discussion is often not very scientific but useful. After this relatively long presentation, the successive subchapters will attempt to provide some technical analysis on the role of modern technology to give a valid response.

The accumulation and fragmentation of plastics deriving from the increased use and often not correct disposal after use has produced an evident impact on the surface of our planet. The plastic's production at world scale began in the 1940s stimulating the society development to the present status thanks to the wide range of unique properties. Nowadays several hundred million tons of plastics are produced per year worldwide. The amount of plastic processed and transformed in the first 10 years of this century will be similar to the total production in the entire last century. Most products in plastic are characterized by a very long life and are potentially useful over decades. On the contrary, often these materials are as single-use items going to the garbage dump within a year, where they can persist for centuries. Furthermore, for some plastics, there is evidence that the same chemical features that make them so versatile might harm people and the environment. The production and disposal contribute both to increase the environmental impact connected to the plastic use. Indeed, the plastics industry claims that their products are safe having been tested for decades not only by the industry, but also by government agencies in an independent way. All the chemicals components used in plastics including the additives are and have been singularly tested in advance, as for any other industrial product. However,

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successive investigation showed that some chemicals can affect reproduction and development in animal studies.

One typical example regarding the environmental impact of plastics comes, in particular, on the widespread use of plastic in goods packaging (Ezeoha et al. 2013). In particular, plastic bags have been introduced about 50 years ago and have gained an increasing popularity by consumers and retailers. The number of plastic bags used in the world per year is estimated to be 500 billion thanks to the low-cost, lightweight and excellent mechanical and prospective properties providing a very convenient and safe use. For a long time these bags were usually discarded as waste after a single use. It is also believed that after their entry into the environment, plastic bags can persist up to 1000 years being not affected by sunlight and/or attached by microorganisms. They do not degrade and hence pose a disposal challenge. An additional impact is derived by the fact that most users discarded the bags in the environment, thanks to the lack of any adequate control. Littering plastic bag over time causes environmental pollution, while those not correctly disposed of contribute to the deterioration of natural beauty and may be responsible for the casual death of domestic and wild animals. Public regulation such as levies and taxes on the production and use of plastic bags have not been as such effective, without planning efficient waste management and making known the negative impact of plastic bags if abandoned and the benefits of their proper disposal.

In addition, it is important to report on the information and thinking related to the risk of release in the environment of chemicals from plastics and the effect on wildlife. It is generally believed that polymers, and then plastics, are to be considered biochemically inert because of the large molecular size that prevents penetration through the cell membrane. However, this may not hold for additives often based on smaller molecules (for instance, MW < 1000), unconverted monomers, catalyst residues and oligomers. In addition, the plastics porosity allows the absorption of affine chemicals from the environment and these remain in the plastic's waste acting as a source of contaminants. Absorption may occur both during use or after improper discard such as, for instance, in the marine environment. The extent and type of uptake vary among plastics and is affected by the ambient conditions such as temperature and ultraviolet radiation. The environmental impact of discarded plastics should not be underestimated, in particular, if the production, usage and disposal are not properly managed (Tueten et al. 2009). Among of plastics disposal, inadvertent release, magnification and transport of contaminants should also be taken into proper consideration.

It is well-known how plastics with their properties benefit society as far as human health in spite of the environmental concerns, the long-term pollution and even the possibility to affect the endocrine. Indeed, being cost-effective and considered inert, polymers are used in many health applications, such as disposable syringes, latex gloves, dialysis tubes and intravenous bags as well as sterile packaging for medical instruments. Disposable plastic items are chosen by healthcare workers because of their long-cited convenience, the patient safety and the time savings. The fact that the sterilization step can be avoided after use for disposable items is the most relevant advantage. In the early years of 1980, the widespread use of disposable syringes allowed a decrease in the risk of transmitting blood-borne infections such as human immunodeficiency virus (HIV) and hepatitis through injections from used needles. The same applies for the other disposable items that are now ubiquitous to hospitals, such as intravenous bags and tubing. These are used in different applications such as drug delivery, treatment of dehydrated patients through fluid replacement, transfusion of blood and correction of electrolyte imbalances as quickly as possible (North et al. 2013).

Absorbable sutures are realized in polymers with tuned biodegradable properties over differing time periods depending on patient need. In this way, they must be not surgically removed after implantation, and the number of procedures the patient must undergo are reduced. Similarly, plastics are used in tissue scaffolds that can be designed to biodegrade in the needed time.

However, the contact with the human body continuously increases due to the extended widespread exposure to plastics constituents and contaminants. Although plastics components do not have significant bioaccumulation potential (except when accidentally ingested and becoming entrapped in the gastrointestinal system), the balance between constant uptake, metabolism and excretion allows the achievement of the steady-state concentration of plastics' components in the human body. Unfortunately, in today's plastics-enabled society, despite the huge literature on the matter, no adequate investigation can be found to study the effects from low-level exposures to plastic constituents. Concerns with human health originate by the absence of chemical bonds between additives and plastics in which they are incorporated, leading to leach out risk. For instance, several studies carried out on rodent and human allow to correlate the exposure to bis(2-ethylhexyl)phthalate (DEHP), a common additive for PVC, and harmful health effects, including influences on the female and male reproductive systems, increased waist circumference and insulin resistance. The 'cocktail effect', i.e. the fact that environmental exposure occurs in cumulative, also must be further studied. In any case, results so far described give sufficient details to the governmental agencies to take action even if more is being done and negative health effects are already listed.

The extent of health effects of human exposure to plastics constituents is as of yet uncertain. Indeed, the topic is made complex by the wide variety not only of plastics but also of formulation, which makes hard to identify all the possible constituents of plastics, some being present at very low concentration and thus to correlate any side effects on health to a particular substance. On the other hand, the issue of plastic waste has been obvious and problematic for some time and demands action. The selection of a proper end-of-life destination for plastic products should be related to the previous use of the item taking into account the suitability of the selected disposal/recycling procedure to avoid or minimize the possible impact on the environment. For instance, after medical use, potentially infectious risk exists and incineration must be preferred over alternative destinations even if this method is not readily associated with sustainability. However, this disposal route has a number of benefits, including the prevention of disease transmission, a reduction of waste in volume and mass, recovery of at least some of the energy used to produce these materials. Obviously, incineration should be performed under appropriate conditions, in particular, if chlorinates species are included in the waste to avoid the release in air of carcinogenic toxins such as dioxins. Also, the residue of the incineration process, the ashes contain toxic metals if present in the waste and then they must be controlled and disposed properly.

In addition to healthcare applications, another major use of plastic is in disposable products, in particular in food packaging and disposable dishes because plastics are both inexpensive and lightweight. These applications account for 50% of the annual plastic production. In this case, a different post-use disposal can be envisaged. Indeed, these materials can be recycled if disposed and collected properly and in some cases, the items can be reused allowing significant savings of energy and starting material resources. Obviously, this procedure is more effective and convenient from an economic and environmental point of view if durable plastics are used. It is thus clear that different possible routes benefit from using different kinds of plastics and that the life cycle considerations must be integrated into all processes and consumption decisions to handle the great amount of information needed to drive the right solution.

In case of large volume applications, if reuse is not possible, biodegradable options in order to reduce plastic waste without compromising human health or the environment, should be conveniently regarded.

Increasing the availability of biodegradable plastics, which can be made from renewable sources, is indicated as a possible solution to reduce environmental problems. Biodegradability occurs when the material is degraded under the action of microorganisms such as bacteria, fungi and algae Compostable plastics instead undergo degradation by biological processes without yielding not visible or toxic residues. To obtain the corresponding specification, these plastic materials must satisfy the specification indicated by the progressive evolution of knowledge and the evolution of requirements for packaging materials to be certified and commercialized as compostable. A polymer can be certified if it biodegrades at a similar rate as other naturally occurring compostable materials. Whereas, compostability standards are unique to the United States, different national and international standards exist in others countries. In any case, testing occurs at ~58 °C and ~60% relative humidity at the same conditions of composting facilities and these conditions are not the ones in marine or water conditions. Hence, compostability does not correspond with compliance with the environment if plastics are not properly disposed. Biodegradable plastics are fairly new and designed to look and behave like traditional plastics. Even if the former may contaminate composting feedstock, biodegradable plastics may enter into recycling streams. In any case, the quality of both compost and recycled plastics is decreased. Some bioplastics can be recycled a limited number of times, but certainly cannot be mixed with long-lasting plastics from fossil origin systems (Kumar et al. 2017).

Indeed, biodegradable plastics offers a solution to waste management issues, especially in the case of disposable packaging that cannot be easily separated from organic waste in catering or from agricultural applications. However, currently, production capacity for plastics from renewable sources is still limited, far lower (<1%) than the ones of fossil-based plastic. Most of these materials do not degrade quickly in natural habitats, and at the same time, some degradable oil-based polymers could disintegrate into small pieces that are not in themselves any more degradable than conventional plastic. To avoid environmental risks, it is recommended to improve the studies on biological mechanisms and in particular on the influence of the plastic additives as well as degradation products and in particular, low-dose chronic exposures. On the other hand, in order to reduce the need for limited world sources, both industry and society need to investigate and find solutions at the end-of-life of items, including plastics, as raw materials rather than waste. Plastic waste can be reduced by educating consumers to prefer products with a low environmental impact based on life cycle analyses. Simple communication strategy must be developed to this aim. For example, if the product was made of mostly recycled materials, used minimal packaging and could be easily recycled, it would be identified in the market with a green dot. On the contrary, if it is included in an excessive large packaging made of virgin materials, it would get a red dot.

In any case, it must be remembered that a simple solution to solve some environmental problems in particular energy saving is the application of production process and the use of plastics in a responsible way (Schulze et al. 2017). For example, the use of light packaging in PET for beverages reduces energy consumption by 52% and greenhouse gas emissions by 55% with respect to the use of heaviest glass or metal. And, solar water heaters containing plastics can provide up to two-thirds of a household's annual hot water demand, reducing energy consumption.

The widespread utility of plastics is proven by the enormous quantity (300 tons) produced in the world annually, half of which is for disposable applications. These products are discarded within a year of their purchase and the major options for their disposal are landfilling, incineration, recycling and biodegradation. However, the former requires space and disperses chemical constituents as well as the energy contained in plastic. On the other side, incineration allows energy recovery but fumes may contain contaminants. Durable plastics can be recycled, but difficulties exist with the collection and sorting, particularly in case of post-consumer plastics. Biodegradable plastics prevent long-term environmental pollution and the biodegradation products can enrich the soil of carbon. However, accumulation may occur if the biodegradation is too slow. Furthermore, biodegradable plastics are harmful if included in waste for recycling by the contamination and disruption of the current recycling stream as not easily distinguishable from oil-derived plastics.

At the time of this book, writing solutions to these problems seems to be only market-, volume- and use-dependent. Plastics designed for durability and low volume applications may still rely on fossil fuel, whereas high-volume uses for consumer products will have to be realized from renewable material stocks. It must be distinguished applications for which recovering and recycling is possible, such as beverage bottles for which non-biodegradable recyclable plastics should be used and applications for which the reuse and the recycle is not possible; for those plastics, it is desired a programmed rapid environmental decay (i.e. biodegradability). This strategy could prevent irreparable environmental damage from disposable plastic products. The benefits of plastics in specialized cases like electronic and public health could, on the contrary, be maintained and maximized.

Disposal of plastics in landfills must be the ultimate solution because it is unsustainable; it steals land resources to other uses of higher societal value such as, for instance, food production. Incineration produces carbon dioxide, a greenhouse gas as well as other pollutants, depending on the burning composition. In theory, recycling is the best solution, but numerous practical challenges exist: in particular, proper and accurate sorting of plastics still represent a strong limitation. The competition between recycled plastic and virgin one is still unbalanced because of the current low price of oil and the low quality (in some cases) of the latter. Furthermore, it must be remarked that a significant amount of disposable articles will bypass programmed disposal and enter the environment, thereby resulting in widespread, long-term pollution. This drawback does not apply for biodegradable plastics. Furthermore, the use of biodegradable plastics can reduce the carbon footprint, pollution risks, and greenhouse gas emissions; however, this is true only if these alternatives are made from renewable resources using renewable energy. However, as just pointed out separating biodegradable from potentially recyclable polymers is a challenge to both consumers and centralized refuse-sorting operations.

The disposal of plastics in landfills implies the loss of material and of the energy stored in plastics, thus wasting the advantage of the use of light plastics instead of heavy glass and metal in different applications. A high weight entails a high energy cost for transport with the consumption of fossil fuels and greenhouse gas emission. In addition, landfills, if not properly designed and managed, can pollute drinking water resources in the case of rupture of the protective liners that separates the landfill from the soil. Long-term risk of contamination of soil and groundwater with plastics' components is due also to low leak over time.

Clearly, the recycling may be considered as the best option for partial recovery of both the material and energy used in the production process, but not all plastics can be recycled (Wei et al. 2017). In addition, plastics are often recovered as mixtures and must be effectively sorted. Another issue is the low quality of the post-consumer plastics because of the common presence of contaminants including different kinds of plastics. In fact, recycled plastics cannot have the same quality as virgin polymers because no perfect separation and sorting process exist and the contamination of raw materials by impurities derived from the use damages the production of recycled products. The quality of recycled plastic decreases with each recycling cycle preventing its use in the same application it was initially used and must be addressed to lower value applications. Therefore, in spite of the low cost of recycling, the still low price of oil makes virgin plastic price competitive. This will be true at least up to the rise of oil price or landfill disposal cost.

The above considerations, even if partially and relatively conceptual, show clearly that the problem of the environmental impact derived from the extremely extended, but highly useful use of thermoplastic materials is far to be solved. Problematic issues extend far beyond the replacement of disposable plastics with bioplastics, which is in general more biodegradable and compostable. A complete rethinking is necessary for the way in which plastics are presently used today. Indeed, several problems derive primarily from the excessive use of plastics for short-term packaging application. On the other side, applications exist where the long duration outweighs any benefit from the easy degradation. Evidence of differences come out if polymers are used in applications that need limited quantities and provide significant benefits—such as polymers for electronics and medical care—and if polymers are used in large quantities with limited properties as in simply convenience items, such as plastic bags and beverage bottles.

The current human society is in the ‘age of plastics’ that has been produced from fossil oil. Part of these materials can be conveniently replaced by bioplastics but this replacement is not fully possible because of different performances. Also for bioplastics, the problem of the adequate availability of starting material and productive processes still exists. A real alternative to conventional, petroleum-based plastics must truly reduce environment pollution deriving from inappropriate disposal but also other adverse effects of traditional plastics such as any other unwanted effect due to human exposure in plastics manufacturing and use. For instance, developments would be largely appreciated aimed at large volume consumption of greenhouse gases to drive the sustainable production. For the production of bio-related and biodegradable plastics, this would represent a significant starting point to limit the competition of the plastics industry with food supply chain in the world.

The correct approach to protect the environment against the improper use of plastics should first eliminate the uses of plastics. In this way, it is possible to reduce waste and disposal needs, together with the reduction of harmful health effects that can be associated with the production process and some product features. The situation is also dependent on the evaluation of the duration of use life in order to select non-biodegradable materials for applications requiring long-term life and the biodegradable in case of expected short-term applications. Production of disposable items with a programmed, short life span from biodegradable polymers would certainly help to realize a more sustainable use of thermoplastic materials without compromising the quality of life of current and future generations as far as the progress of technology and healthy environment.

7.2 Materials from Oil and Renewable Sources

Traditional plastics that still are the great majority (more than 95%) of the plastic material used in the word were and are produced from oil and natural gas. The refining of these organic materials provides in addition to fuel for energy production and transportation also adequate feedstock of organic molecules that are the starting base for the industrial petrol chemistry. A variable amount, around 5%wt of this feedstock is used by man to produce macromolecules and among them, the macromolecules, suitable for producing thermoplastic materials, are included. These were shaped into a huge number of different products capable to satisfy the sophisticated requests of a world becoming every day more demanding for the quality of life.

The main drawbacks related to plastics from fossil origin are in most cases the lack of biodegradability and the use of non-renewable sources. Clearly, the former becomes a problem only when the plastics are dispersed in the environment or not properly disposed. In any case, it is related to the application for some of which it is necessary. The latter aspect is, instead, a general problem for all the organic chemicals used by man and it is not necessarily related to biodegradability.

There is no doubt that the environment and the human society would benefit from the use of feedstock from renewable origin. Many possibilities exist to recover starting materials for plastics production from resources different from oil and gas. No one has the dimension in the availability of oil and several routes must be investigated.

Biomass mainly from vegetal is the main reference, but other routes are and will be possible. For instance, current research is interested to solve some of the challenges and limitations of biodegradable plastics that are currently produced mainly from starch. For example, a method was recently reported to allow the catalytic synthesis of biodegradable polymers from carbon dioxide and carbon monoxide in the presence of metal complexes. This development represents a potential solution to two different problems: a gas, widely available and unwanted in atmosphere because it is responsible of the greenhouse effect, is used as raw material; at the same time the production process does not need any raw materials competing with animals and the human food supply chain, as occurs for other products on the market (i.e. thermoplastic starch and PLA). This method is now being commercialized to produce epoxy resins containing bisphenol A (BPA) and used to coat metal cans inside. If this coating is fully adopted 180 million metric tons of carbon dioxide emissions annually would be sequestered.

As plastic production facilities take steps towards the use of safer plastics and reductions in overall consumption of polymers, this approach, aimed at the environment preservation without affecting the quality of life, can be prosecuted by using more and more feedstock from renewable resources, simplifying preparative processes, improving the reuse in view of the circular economy.

However, the real origin of ecocompatible plastics is not so well defined. Here, one can examine the present situation and collect correct information about renewability. Indeed, in bioplastics all carbons should be derived from renewable feedstocks, and this is valid even if they are not biodegradable. On the other side, bio-based plastics can contain not only renewable but also fossil fuel-based carbon. As a consequence, the percentage of bio-based ingredients in bio-based product as the biodegradation conditions can vary. Because the CO_2 fixation occurs via photosynthesis, bio-based materials include all plant and animal mass. While fossil carbon derives from large unified original materials with very common properties and is developed according to well-defined industrial processes and products, natural feedstocks have different origins including (only as examples) corn, potatoes, rice, tapioca, palm fibre, wood cellulose, wheat fibre and bagasse. A biodegradable plastic should be completely converted into H_2O and CO_2 (mineralized) by microorganisms. Notice that some biodegradable products can degrade in municipal or commercial composting facilities, others in home composting or in aquatic and roadside environments. In some cases, items made of biodegradable plastic cannot biodegrade at all or degrade too slowly in uncontrolled conditions. This means that usually, the possibility that a material biodegrade depends on specific properties of the object and of the environment, and generalization is usually not possible. For this reason, testing and labelling are using refer to specific analysis conditions.

According to the present regulations accepted and applied in many countries, the certification as biodegradable compostable materials requires that: 1. The disposed material disintegrates rapidly during the composting process giving small particles; 2. biodegrades quickly under the composting conditions; 3. properties of the final compost are not affected; 4. heavy metals are present in amount lower than the critical value.

From the above remarks, one can evidence that bioplastics have some benefits over petroplastics in particular if they come from renewable sources. However, their massive and regular production still need a solution. In general, it is important that they have opened a way towards more sustainable plastics connected to the green economy.

The shift of the production of energy and of chemicals towards renewable sources could prevent plastics production problems expected as consequence of some oil crisis and could give a contribution to relieve, hence, the growing interest of the public opinions towards the global warming problem, which is responsible for a increasing demand for sustainable 'green' products. Also, it is necessary to notice a continuous increase of more or less clear environmental legislation and regulations for stimulating the diffusion of environmentally friendly products identified by a low carbon footprint. The objective is clearly an attempt to save natural resources such as oil, gas, potable water, clean air, fertile soil, rare metals, minerals and biodiversity. However, the definition 'green' does not identify uniquely biomaterial and biotechnology as many existing polymers and polymerization processes can be considered environmentally acceptable because they fit with the requirement of modern green chemistry.

A significant example is provided by polyethylene and polypropylene production processes that cover around half of the total amount of polymer production; they allow very high polymer productivity under really mild conditions and with an extremely low content of by-products/waste. Indeed, highly active catalysts supported on silica or magnesium salts are used to polymerize propylene and ethylene without solvent and in gas phase and in liquid pool processes without by-product formation and without the need for waste disposition. The catalysts are characterized by extremely high catalyst activity, and as a consequence, the toxicity risks are negligible because very small amount of catalyst residue remains in the polymer (Fig. 7.1). Moreover, polypropylene is very effectively recycled at temperatures around 230 °C in remoulding processes. In addition, polypropylene backbone can be easily cleaved at temperatures above 400 °C and hydrocarbon feedstocks can be produced by chain scission. The obtained 'oil' can be reused for producing ethylene monomer or as a source of energy. Under these circumstances, polyolefins industrial production meets the demands of sustainable development, as the resources are preserved for the future. In addition, the technology currently used to obtain polyolefins allows the production of granules directly in the reactor, by limiting the consumption of energy in pelletizing melt extrusion step (Fig. 7.1). The same technology allows fine design and achievement of different polymer properties by a proper selection

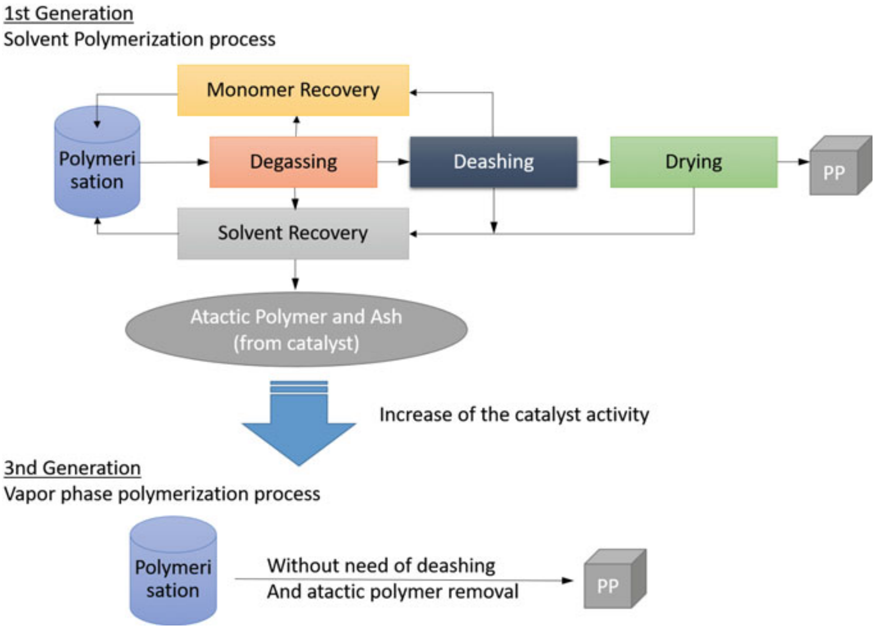


Fig. 7.1 Evolution of the polypropylene production process as a consequence of the improvement of the catalyst performance

of the catalyst and process conditions to obtain materials with different properties for different applications. Furthermore, the technology can be easily switched from fossil resources to bio-based feedstocks in polyolefin manufacturing to satisfy the demands of green chemistry. However, polyolefin technology allows an effective and sustainable use of oil and gas, especially in comparison with their use in energy production. Furthermore, there is no need for significant amount of water; there is almost no waste production and low energy requirement that on the contrary of almost all biotechnology processes.

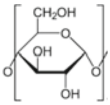
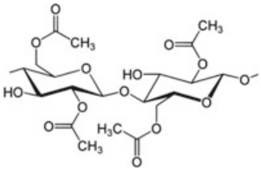
It is becoming much more clear that ‘bio’ does not automatically means ‘green’. Positive environmental effects concerning the use of biofuels and petroplastics are listed in the following Table 7.1. The table reports a qualitative comparison of the favourable properties of plastic material from natural or fossil sources. It can be easily argued that both not only can be useful depending on the application and one replacing the other when convenient reducing the global environmental impact. The useful features can be balanced or partial in polymers that are derived from the combination of natural and man-made processes and fossil raw materials.

According to the non-easy and complex problem of the classification of bioplastics, Fig. 7.2 gives an idea of the relative performances of the most common environmentally friendly thermoplastic materials: the green and blue parts are refered to the bioplastics. By looking at Table 7.2, where the molecular structure of the

Table 7.1 Main environmentally useful features of plastics materials from natural or fossil source

Feature	Bioplastic materials	Plastics from fossil
Source	Renewable	Non-renewable
Production process	Under evolution	Mature
Carbon dioxide emission	Low	High
Number of molecular structure	Limited	Very large
Biodegradability	Partial to total	Very limited
Recycling	Difficult or impossible	Possible and efficient
Toxicity and health Hazard	Limited	Significant to high
Competition versus food production	Generally significant	None
Water interaction	Hydrophilic in general	Mostly hydrophobic

Table 7.2 Molecular structure of common bioplastics and their origin

Acronym	Name	Molecular structure of monomer units	Origin
PCL	Polycaprolactone	$–CO–(CH_2)_5–O–$	Fossil
PBS	Poly(butylene succinate)	$–CO–CH_2–CH_2–CO–O–(CH_2)_4–$	Fossil and BIO
PES	Poly(ethylene succinate)	$–O–CH_2–CH_2–O–CO–CH_2–CH_2–CO–$	Fossil
PLA	Polylactic acid	$–CO–CH(CH_3)–O–$	BIO[a]
Starch	Starch		BIO
PHB	Polyhydroxybutyrate	$–CO–CH_2–CH(CH_3)–O–$	BIO
AcC	Cellulose acetate		BIO[b]
PE	Polyethylene (bio)	$–CH_2–CH_2–$	BIO[a]
NY-11	Nylon 11	$–CO–(CH_2)_{10}–NH–$	Fossil

[a] Biomonomer and man-made polymer

[b] Man-modified natural polymer

respective monomer units is reported, it can be understood how difficult is to relate the molecular structure to the behaviour in the environment. In addition, the ultimate properties encountered by the consumer during use and disposal are rendered more complex by the fact that the present plastic products, either from fossil or renewable origin, are a mixture of polymers with different molecular weights, sometimes with different structure and contain additives and fillers.

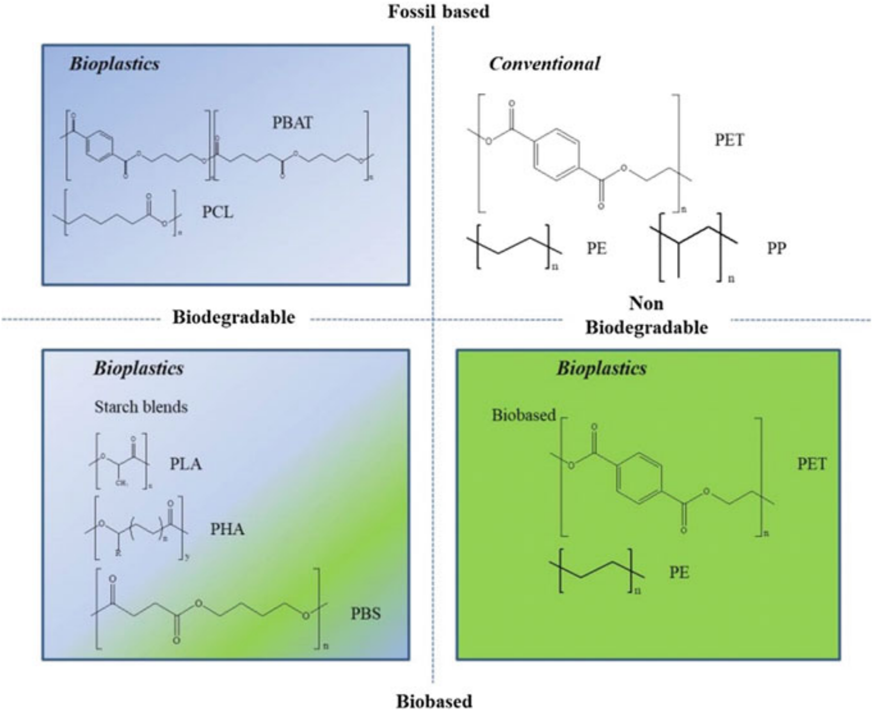


Fig. 7.2 Common bioplastics and bio-based plastics

7.3 Production Processes

Production processes were described in the previous chapters while, here, a comparison will be carried out with the aim to evidence that the preparative process is a typical man-made activity independent of the starting material. In general, synthetic polymers are produced by polymerization while bio-related plastics can be derived from already existing biopolymers or by polymerization of monomers with bio-origin (see Chap. 5). In the latter case, polymerization processes are necessary and these last resemble very closely those already used by industry. Moreover, some bio-derived monomers can be molecularly identical to monomers derived from fossil as in the case of bioethylene. The obtained polymers have finally the same structure and properties, independently of natural or fossil origin of the monomer.

Therefore, in the future, we are going to face distinct situations originated by the possibility to respond to society requests according to different routes. The choice is not trivial as a series of distinct favourable and unfavourable aspects combine in a complex way to determine the best compatibility with respect to the environmental impact.

The possibility of different routes offers clear advantages and is the result of our technology growth, but the decision must more and more be made with real knowledge of the problem in a global approach and in relation to the circular economy. Saving resources is certainly important, but one should consider that the largest consumption of oil is not in material production but in fuel for electric and mechanical energy. Thus, the displacement of the energy production to non-oil sources will allow fossil being used for chemicals and synthetic materials to satisfy all human needs.

Natural gas, crude oil and petroleum products have been exploited mainly for energy production since the beginning of their use. In the EU, energy is still obtained mainly from crude oil and its derived products. The primary production of crude oil picked in 1999 at 165.8 Mtoe (toe = tonne of oil equivalent), then progressively decreased to 64.5 Mtoe in 2014 where it almost stayed in the past years. United Kingdom (45.6 Mtoe) was the top oil producers in the EU-28 in 2016, followed by Denmark (7.0 Mtoe), Italy (3.8 Mtoe) and Romania (3.8 Mtoe). The largest European non-EU crude oil producers are Norway with a production of 80 Mtoe in 2016.

The amount of fossil fuels, especially oil derivatives used to produce electricity, is slowly decreasing and several of the oil-fired plants already existing are fed with mainly fuel oil and gas/diesel oil and are kept only as a power reserve. In 2016, the quantities of crude oil used to produce electricity was a quarter of the amount used in 1990. In the 2011–2016 period, energy consumption of petroleum products has globally quoted below the 1990s level. The three most important products throughout the 1990–2016 period are gas/diesel oil, gasoline and kerosene-type jet fuel (listed in order of significance), although each of them showing different evolution schemes.

EU report about the consumption of petroleum production in 2016 indicated that the transport sector was by far the main consumer with road transport being the maximum one (47.8%). Non-energy purposes consumption was 13.9% in 2016 and was the second after road transport. It includes the chemical industry as use of oil products to produce monomers for plastics as well as additives and components for paints, home and personal care products, bitumen for road surfaces, lubricants for many purposes, etc. The transport sector is becoming much more independent from the use of oil due to the use of liquid biofuels. Nevertheless, the dependency is still large with a value for oil still above 93.8% with an amount of renewable fuels of 3.8% in 2016.

The detailed consumption of fuels in transport significantly changed over the 1990–2016 period: the most used in 1990–1998 period was gasoline while latter, it was progressively substituted by gas/diesel oil. Kerosene jet fuel consumption increased constantly over the whole period due to the increased use of this transportation sector.

Crude oil and petroleum products have the highest share of energy consumption in EU as well as on all the developed countries. Several policy initiatives are under discussion or application concerning the security aspects of energy supplies as well as environmental and climate aspects of oil production and consumption. Among the latter, there is the Paris Agreement of 2015 to combat climate change that entered in force in 2016. To achieve the agreement goal of keeping the temperature rise in the actual century below 2 °C, several strategies are needed. In the past year's structural changes in the economy decreased the demand of fossil oil for a more efficient use of oil products and the progressive substitution in transport with biofuels or electricity. Chemical industry, in general, and specifically industry for plastics production need carbon-containing feedstocks, and more conveniently, with flexible molecular structure and a certain number of atoms. On the other side, a great amount of energy presently is produced mostly from oil and natural gas so dramatically reducing convenient available sources for chemicals necessary for the future human life. So, it would really very wise to save carbon feedstocks (oil and natural gas) for chemical applications by obtaining energy from different sources.

Thanks to renewable feedstocks derived from forestry and agriculture, several industrial processes were recently developed both for energy and chemicals production. The question can then be raised if vegetal feedstocks products have to be used as an alternative to fossil feedstock for producing chemicals or energy. In both cases, one would positively face the saving of important non-renewable fossil materials. The comparative evaluation must be based on various aspects some of which depending also on geographical and social aspects.

The energy production is increasingly directed to the development of processes where the staring feed is based on any type of biomass, including waste. New processes and plants are proposed having efficient thermal balance and adequate eco-friendship. Bioplastic materials or products can be defined as compostable only if the rules EN.

13432 or EN 14995 are satisfied according to the technical criteria used in industrial composting plants (humidity, aeration, temperature). The organic matter, which can contain biodegradable and compostable plastic products are converted into CO_2, water and biomass during the process. Compost is used as a soil improver and can, in part, also replace mineral fertilizers. However, with respect to the about 300 Mtons of plastic produced annually, biodegradable and compostable plastics can only play at the moment a marginal role in the biowaste stream, because they represent about 1 per cent. The market demand for bioplastic according to the data of the European Bioplastics and Novo Institute is predicted to increase. In 2018, the global production capacity of bioplastics was 2.11 million tonnes and it is predicted to grow to 2.62 million tonnes in 2023 with an increase by 24% (Table 7.3). These predictions are less optimistic than the one of 2017 when a growth by 50% in 5 years was foreseen. However, the last values are still such that it is to predict that bioplastic will remains only a very little part of plastics production in the next decade (see Fig. 7.3).

Table 7.3 Global production capacity (green) and forecast (orange) of bioplastics (*source* http://www.european-bioplastics.org/market/. Joined data from 2017 and 2018 reports)

	2017	2018	2019	2020	2021	2022	2023
	(× 1,000 tonnes)						
Biodegradable	885	912	994	1026	1026	1113	1288
Non-biodegradable	1175	1200	1200	1190	1179	1244	1328
Global production	2060	2112	2194	2216	2205	2357	2616

The production of bioplastics is still too low to appreciate from the point of view of resource saving (Biron 2017), but it can be interesting to analyse the real sustainability of the existing processes from the environmental viewpoint. The main contribution to this last aspect is probably represented by biodegradable polymers that serve to solve disposal problems in some well-defined applications. Agro-polymers (starch, chitin, protein) and biopolyesters (polyhydroxyalkanoates, polylactic acid, etc.) represent the main families of biodegradable polymers (Avérous 2011).

For the former group, an illuminating example for the real material characteristics is offered by biodegradable plastic packaging film consisting in a mixture of cassava starch, polyvinyl alcohol (acts as an adhesive and thickening agent), talc powder (lubricant), glycerine (colourless, odourless, viscous liquid with a high boiling point used as plasticizer), urea (used as crossing link agent) and water. The film was further studied for various physico-chemical changes and its effect on food during storage; the results suggested comparative properties of the film with the conventional polymers. The production process is relatively complex (Fig. 7.3) consisting of several treatments and additivities use, and this must be considered in the LCA evaluation of the product together with its good application and environmental properties.

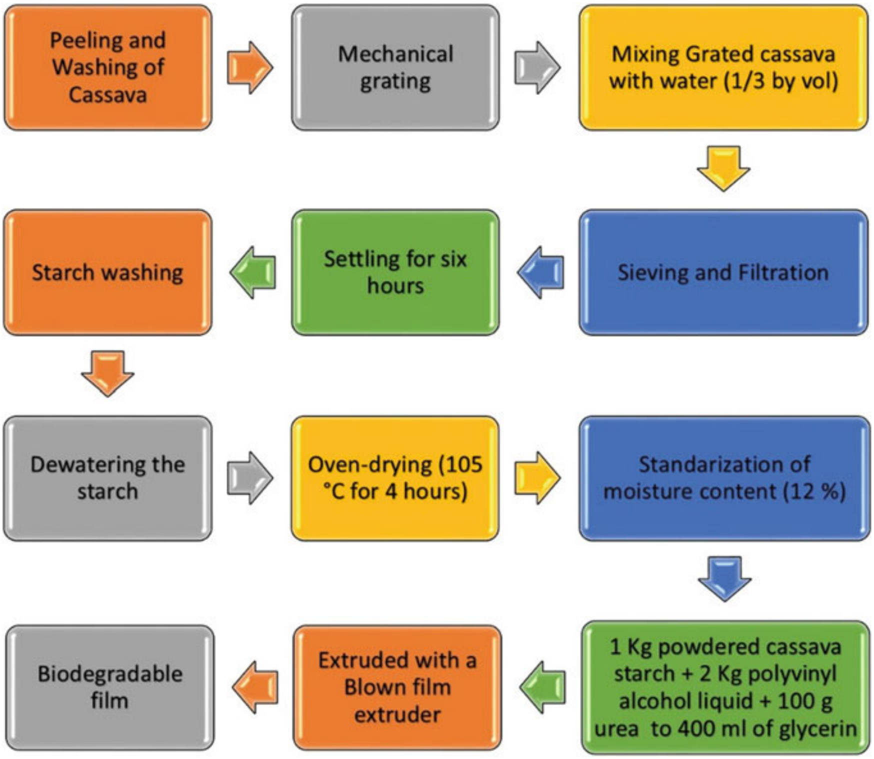


Fig. 7.3 Production process scheme of cassava starch film

Biodegradable films can also be derived from chitosan, a polymer extracted from chitin of crustacean and insect exoskeletons having a chemical structure similar to cellulose. The material is not simply a polysaccharide and significant man-made technology is necessary to obtain functional properties. Indeed, the final film must be formulated as above described for starch-based films.

Among biodegradable polymers, the most successful are the polyesters from renewable sources polyalkanoates and poly(lactic acid).

Poly(hydroxyalkanoate) or PHA were produced from genetically engineered corn developed by Monsanto. The grain corn is harvested in a conventional manner, and the polymer is extracted from the corn stover (i.e. residues such as stalks, leaves and cobs), which would be otherwise left on the field. Four different hypothetical PHA extraction processes were tested and differed in the energy source used for polymer extraction and compounding. The results were compared to polyethylene (PE) production processes. The first process involves burning of the residual biomass (primarily cellulose) remaining after the polymer was extracted from the stover. In the three other processes, the use of conventional energy sources of coal, oil, and natural gas was investigated. This study indicates that an integrated system, wherein biomass energy from corn stover provides energy for polymer processing, would result in a better greenhouse gas profile for PHA than for PE. However, plant-based PHA production using fossil fuel sources provides no greenhouse gas advantage over PE. These results are based on a 'cradle-to-pellet' modelling. Since now, the PHA end-of-life was not quantitatively studied due to complex issues surrounding the actual destination of post-consumer PHA. The PHA production starting from the raw material sugarcane and integrated into a sugar and ethanol factory is realized on semi-industrial scale in Brazil. This integration makes it possible to achieve an economically competitive production price for the biopolyester when compared to other PHA production processes on a larger scale. This cost reduction is enabled by an efficient utilization of by-products of the sugarcane plant, especially the lignocellulosic waste bagasse, and by the utilization of additional in-house waste streams for the biopolymer isolation from bacterial cells. In this process, bagasse is burned for the generation of steam and electrical energy required for several process steps in PHA production. Further, the price advantage to be obtained is due to the availability of sucrose in high quantities used as substrate. Together with the combustion of the sucrose stemming ethanol as a 'first generation biofuel', CO_2 emitted from the production plant can be fixed again via photosynthetic in sugarcane. As a result, the carbon balance results nearby zero.

Polylactic acid (PLA) is the plastic biopolymer having the highest market share and can be converted into different items by standard processing methods such as injection moulding and extrusion. The large scale production of PLA bioplastic is currently limited by the still high price of the raw material, if compared with nowadays commodity plastics such as polyolefins. Furthermore, the lack of widespread composting infrastructure in the market is another reason containing the commercial use of PLA in spite of its potentiality, in particular in packaging. The 2016 global market for lactic acid was 100,000 ton, more than 75% in the food packaging application.

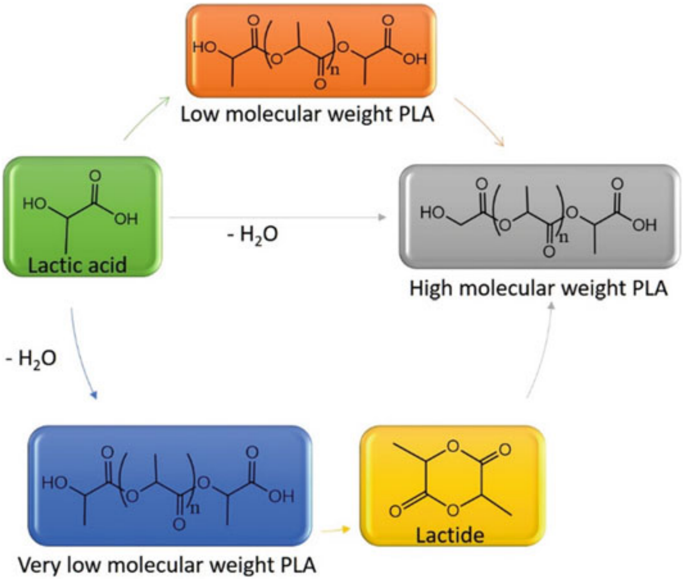


Fig. 7.4 General scheme of lactic acid and PLA preparation

The monomer can be used in the direct polymerization by condensation resulting in polymers with low molecular weight or it can be used to produce the dimer lactide. This latter is then used as an intermediate compound to yield PLA with higher molecular weight (Fig. 7.4).

General production process for PLA is much more complex and includes the production of both the monomer and the polymer (Fig. 7.5). It starts from the bacteria fermentation of the sugar from plants, mainly corn, to obtain lactic acid. Sugars play as a carbon source for the bacteria strain. In addition, a nitrogen source (yeast extract, peptides), and mineral elements are needed (Fig. 7.5). Once obtained, the L-and D-lactic acid monomers and converted into the intermediate lactide which is purified and used in the production of long macromolecular chains, the PLA. The final properties of PLA can be tuned by modifying the ratio and sequence of L-and D-lactic acid units in the developed polymer. The composition 90% L-lactide and 10% racemic L-D-lactide mixture is used for most of the commercial packaging applications. This material can be melt processed and oriented further, giving commercial products that are relatively cheap compared to other bioplastics available in the market. As a result, the present bioplastic market of the world is almost dominated by PLA packaging and most of the research efforts are oriented towards the development of PLA blended with other material to further extend its properties to different applications need. Indeed, the impact strength and thermal properties of PLA are not sufficient for many applications. Accordingly, the recent trends in research are focused on the improvement of the mechanical properties of PLA while still maintaining the biodegradability to achieve the maximum benefits.

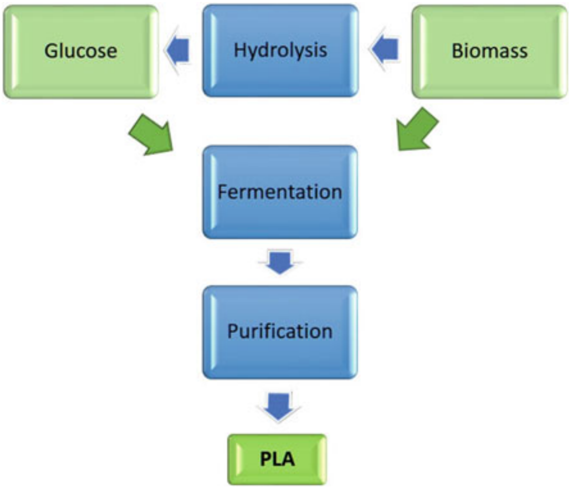


Fig. 7.5 Scheme of PLA production starting from biomass

7.4 Consumer Use

Plastic materials are presently playing a determining role in our everyday life and it is not likely that this will be reduced in the future. Rather one can expect that with the increasing of world population and sophistication of the main style of life the demand for plastic-based materials with designed performances will become larger and larger. Then there is no doubt that similar to what happens for any new product promoted by man, the consequent impact on nature will be affected and increased, unless the problem is not adequately approached from the regulation and technical viewpoints (Mülhaupt 2012).

In the previous sections of this chapter, we have reported a not exhaustive but very indicative description about the state of art of the present knowledge of the negative aspects that the use of plastic has on our environment and the partial relief that may derive from the use of bio-based and in particular biodegradable plastics. Also, it appears how the solutions are only partial and the real advantage can be significant if used properly. To this aim, the participation of the final consumer is absolutely necessary. Present consumer is becoming more and more sensitive to environmental and health consequences of the technology without renouncing to it. The only way to reach real progress and better protection is with transparent information by mass media and producers on one side and appropriate education of the users on the other.

The dispersion of plastic items after use by the not respectful people and particularly during use under the effect of the stresses deriving from the application is well documented and there is now a very general concern. An additional claim deals with the fact that at least fossil-derived plastics contribute to the exploitation of the world resources, even if this specific concern should be reconsidered in comparison with the many times larger consumption of oil and natural gas for energy production and transportation.

In any case, one does not need to be an expert to understand that all the above impact and exploitation of nature would benefit from a reduced consumption of plastics in various fields of application. Clearly, the exploitation of this last proposal needs the solution of a series of scientific and technologic aspects. At present, however, we have already at hand, at more or less extended development, two available effective instruments, namely bio-based plastics and plastic recycling. Both contribute to save non-renewable resources, while the biodegradable plastics help to short the permanence in the environment of abandoned plastic residues, recycling optimizes the use of resources of whatever origin by increasing the number of times each material is restored in the production cycle and reused.

The user in principle may not distinguish between natural and fossil origin of the plastic encountered in the everyday life and will be happy with any material having the desired ultimate properties. But he is becoming more sensitive to the environmental aspects and certainly his role is determining to reduce the use of resources and the waste production by recycling and selection of the most appropriate material for any specific application by taking into account not only the technical properties but also the ecology aspect.

7.5 Disposal, Recycling, Biodegradation

Even if not all the world countries are really keen on or sensitized to plastic waste impact on the environment, it is undoubted that plastics are seriously harming several ecosystems with reference in particular to the Oceans. The recent EU waste framework directive sets out that waste should be dealt with in accordance with the Waste Hierarchy with legislation aiming to move waste management up the waste hierarchy. The Waste Hierarchy concerns to all materials and goods produced in the world and it is reported in Fig. 7.6 by indicating the target that is the ‘prevention’ instead of ‘disposal’ in landfill, which has to be considered as the least favoured option. Nowadays, this last is the most applied ‘solution’ to plastic waste treatment, while plastic goods should be designed for easy end of life management.

In particular, by looking at the different options ranging from the most favoured to the least one, we can approach the problems by

(1) Prevention—Reducing resource use in manufacture, ensuring products last for a long time and using less hazardous material. To reach this goal, the amount of plastic must be reduced (for example, the film thickness), particularly in packaging, or by substituting conventional plastic with other materials (biodegradable plastics).
(2) Preparing for reuse—Repairing, cleaning, refurbishing and checking. Soaps containers and beverage bottles can be reused. This can be achieved by designing the products to be reused by facilitating the dismantling of products and replacement of parts. For instance, bottle labels could be designed to be easily

Fig. 7.6 Waste hierarchy

removed. This could involve also standardizing of parts across manufacturers to facilitate disassembly and remanufacturing.

(3) Recycling—Among the large variety of plastics availabile, some of which can be easily recycled, for example, polyethylene and polyethylene terephthalate (PET). These should be preferred. Furthermore, mixed polymer materials are usually more difficult to be recycled than pure one. Therefore, fewer types of plastics and colours have to be preferred. For example, some plastic water bottles are coloured and for this reason, they are difficult to be recycled since undefined colour results. The process would be simpler if all bottles were clear. Disassembling the constituent parts of complex products such as appliances can foster plastic recycling, while it can be promoted by the use of smart materials such as magnetic one, or materials able to change their shape and properties under an electric field.

(4) Other recovery—Incineration with energy recovery, gasification and pyrolysis, which produces fuel as the last option when the previous one is not possible. Indeed, the large amount of energy included in plastic can be recovered in waste-to-energy plants.

(5) Disposal—Landfill and incineration without energy recovery. In the case of biodegradable plastics, nervertheless, their low persistence in the environment than traditional plastics, they need specific and suitable end-of-life treatment.

At present, the most suitable approaches to plastic disposal for limiting the environmental impact are based on the production of biodegradable bio-based plastics and on recycling the non-biodegradable.

7.5.1 Biodegradation

Fossil or biorigin of plastics is not directly related to the biodegradability as can simply be derived from examining commercially available bio-based plastics. Indeed, polycaprolactone (PCL) and poly(vinyl alcohol) (PVOH) are petroleum based, while poly(hydroxybutyrate) (PHB), poly(lactic acid) (PLA) and starch blends are obtained from renewable resources but all are biodegradable because of the degradative actions of the microorganisms. On the other hand, polyethylene (PE) and Nylon 11 (NY11), despite the possibility to be produced from biomass or renewable resources, they are non-biodegradable. Acetyl cellulose (AcC), a polymer obtained by modification of the natural cellulose, is either biodegradable or non-biodegradable, depending on the degree of modification (acetylation). Indeed, AcCs with a low acetylation can be degraded, while those with high substitution ratios are non-biodegradable.

Biodegradable plastics offer a promising solution to the environmental problem of the world pollution by plastics and microplastics. Some people believe they are a general solution to all problems connected with plastics with few deepens into the situation and driven just by the idea that biodegradable plastics are environmental-friendly. Indeed, the use of renewable feedstocks for the production of biodegradable plastics allows a reduction of greenhouse gas emissions.

Chemical and physical properties of plastics have a significant influence on their biodegradability. The kinds and strength of forces among macromolecular chains affect the accessibility of polymers, their reactivity and then their eventual biodegradability. Enzymes able to degrade proteins and enzyme present in the intestinal tract are often able to degrade plastic. For instance, Proteinase K and PLA-degrading enzyme from Amycolatopsis sp. can degrade both PLA and silk fibroin. Aliphatic polyesters such as cutin, suberin and esteroid in the natural environment and animal digestive tract can be hydrolyzed by enzymes such as lipase and esterase similarly to the action on fatty acid esters and triglycerides.

However, the biodegradation rate depends either on the chemical structure but also on the physical properties of the material and on the size and shape of the plastic object. Indeed, it depends on the accessibility of the plastic structure to microorganisms. This means that not only the first order structure, namely the chemical composition and structure of the polymer, but also the organization and packing in high-ordered structures of the polymer chains play an important role in determining the biodegradation rate or in other words, the biodegradation process. Furthermore, it is worth to mention that the biodegradation processes of polymers are influenced by surface features (surface area, hydrophilic, hydrophobic properties), the first-order structures (chemical structure, molecular weight and molecular weight distribution), the high-order structures (crystallinity degree and crystal structure) as well as the derived physical properties (glass transition temperature, melting temperature and elasticity).

Polyesters with side chains, in particular with hydrophobic ones, are usually less biodegradable than those without. Biodegradability depends also on the molecular weight, as this affects many physical properties of the polymer. Usually, the increase of the molecular weight of the polymer decreases its degradability. For instance, PCL with $M_n > 4{,}000$ Da was reported to be degraded slower by Rhizopus delemar lipase (endo-cleavage type) than similar polymer with lower M_n. Moreover, crystallinity degree increase often negatively affects the biodegradability rate, because enzymes mainly attack the more accessible amorphous domains of a polymer. The molecules in the amorphous region are less dense and loosely packed, and thus make it more susceptible to degradation. On the contrary, the crystalline parts of the polymers are difficult to access and are more resistant to the attack. This has been reported for PLA but also for other semicrystalline polymers such as PBS and PHA.

Biodegradability correlates also with the melting temperature (T_m): the higher the Tm is, the lower the biodegradation of the polymer results. In general, T_m is described by the following formula:

$$T_m = \Delta H_m / \Delta S_m \tag{7.1}$$

where ΔH_m and ΔS_m are the change of enthalpy and entropy in melting, respectively. It is well-known (see Chap. 3) that ΔH_m mainly reflects the force of the interactions among polymer chains and ΔSm the movement freedom of the chain corresponding to the flexibility of the polymer molecule. Therefore, T_m reflects the ratio between the interaction forces and the flexibility of the molecules. In this sense, a higher Tm means a lower flexibility and a higher energy of interaction between chains, which turn into a decreased accessibility for biodegradation.

Two aliphatic polyesters [PLA, PHA and others with ester bond (–CO–O–)] are used as biodegradable plastics, because they are susceptive to the action of lipolytic enzymes and microbial degradation. This does not hold where the presence of interchain hydrogen bonds for polyurethanes and polymamides is responsible for high Tm values. These high (T_m)s values of polyurethane and polyamide (nylon) combine with better performances of these classes of plastic material necessary for advanced modern application are on the other side responsible for more compact structures hindering biodegradative reactions promoted by microorganism. However, one should also take into account that the high-performing plastic products are for application with long durability in sometime aggressive environment. As a consequence for polyamides and polyurethanes, durability is more important than biodegradation.

Polycaprolactone (PCL) is a biodegradable polyester produced by chemically man-made methods from a monomer, which, at least at present, is obtained only from oil. It occurs as semicrystalline material with melting point (T_m) of 60 °C and glass transition temperature (T_g) of −60 °C. PCL can be degraded by many microorganisms of various ecosystems under both aerobic and anaerobic conditions. In particular, even high-molecular weight PCL can be degraded in only 12 days by Penicillium sp. strain 26-1 (ATCC 36507), a microorganism isolated from soil. A faster degradation (6 days) was reported by incubation at 50 °C in the presence of Aspergillus sp. strain ST-01 also from soil.

Poly(butylene succinate) (PBS) and poly(ethylene succinate) (PES) are aliphatic polyesters synthesized from dicarboxylic acids (e.g. succinic and adipic acid) and glycols (e.g. ethylene glycol and 1,4-butanediol). The monomers can be also obtained at present either from fossil oil or renewable resources (vegetables). They have melting points of 112–114 °C and 103–106 °C, respectively, and mechanical properties comparable to polyethylene (PE). In the environment, there are many PBS degrading microorganisms even if their ratio to the total microorganisms is lower than for PCL. Microorganisms degrading PBS such as Amycolatopsis sp. HT-6 usually degrades PCL also. Other thermophilic actinomycetes from Japan Culture of Microorganisms (JCM) are reported to degrade PBS: Microbispora rosea, Excellospora japonica and E. viridilutea. Among these, M. rosea was observed to degrade 50% (w/v) of PBS film after 8 days of cultivation in liquid medium.

The aliphatic poly(3-hydroxybutyrate)s (PHB) are polymers produced by many bacteria under different carbon source feeds. They can be biodegraded by many microorganisms in both aerobic and anaerobic environments including in the sea, without forming any toxic products. This property makes PHB, as well as other PHA polymers very promising for reducing the marine pollution and the use of this class of polymers is expected to grow faster in the near future.

On the contrary, PLA the widest used and cheapest biodegradable polymer currently on the market, can be degraded by lower number of microorganisms than PHB does. Furthermore, microorganisms degrading PLA are not widely distributed in any environment. For instance, the degradation of PLA in soil is slow and takes a long time to start and PLA is not degraded in marine conditions (the degradation is so slow to be considered negligible!).

A practical strategy to reduce product cost while preserving or modulating the good biodegradation rate is to prepare blends of biodegradable polymers. Indeed, less expensive and less biodegradable polymers could be incorporated with others to improve their biodegradability while reducing the total cost. In any case, the biodegradability of the prepared blends must be verified. The formation of miscible blends especially with non-biodegradable polymers can slow down or even inhibit the degradation of all the blend components, including the one that is biodegradable when isolated. For instance, PCL degradability drops off remarkably when blended with polystyrene (PS) or poly(ethylene terephthalate) (PET) while it is retained with LDPE and PP and only partially decreased with nylon.

PHB has been blended with non-biodegradable and biodegradable polymers showing good biodegradability. Indeed, either immiscible blends of PHB with PCL and poly(butylene acrylate) (PBA) as well as miscible blends with poly(vinyl acetate) (PVAc) shows weight loss decrease in the presence of enzyme depolymerase from Alcaligenes feacalis T1 depending linearly on the amount of PBA, PVAc or PCL, thus indicating the preservation of the PHB biodegradability in all blends.

A typical blend component used to reduce material cost is starch. It offers several other benefits in addition to the low cost such as renewability, biodegradability and available year round. Starch is used either after gelatinization or chemical modification and generally blends with PCL exhibit a high degree of biodegradation.

PCL/granular starch blends are produced world around by using starches from different origins such as cassava, sago, corn, etc.… Whatever the source, the tensile strength and the elongation at break of the blends decrease as the starch content increase. However, in general, the tensile strength is poor while elongation is relatively good. The biodegradation of blends in the presence of lipase is faster as the starch content increase. This behaviour has been attributed to the increase in the surface area of PCL after blending with starch, thereby rendering it more susceptible to biodegradation.

Starch is also blended with PLA to reduce the cost and improve the biodegradability of the latter. On the other hand, PLA can tune the mechanical properties of the blend. However, the hydrophilic features of starch not allow the interaction with hydrophobic polyesters resulting in unfavourable qualities of the blends. For this reason, several methodologies have been proposed and developed helping to solve the problem of incompatibility of starch and synthetic polymer blends. These approaches generally involve the use of chemically modified plastic components as compatibilizer, (see Chap. 6) and the biodegradability of the resulting compatibilized blends depends on the accessibility of the blend phases to the degrading microorganisms and enzymes.

7.5.2 Recycling

Recycling can be considered as the opposite approach versus biodegradation for disposal of plastics waste. Indeed, the recycling requests long-lasting duration and survival to use and exposure of the starting properties, whereas biodegradation implies a short material life. Just to clarify this concept, let us examine the situation with plastics bottles by considering if the presently used bioplastic bottles can contaminate the PET recycling programmes. Several beverage containers made from biodegradable plastic polymers are already in the market and are not easy to be distinguished from the non-biodegradable PET bottles and the labelling of the two types of bottles could be indeed convenient. Intermediate situation may occur with PLA, claimed as both recyclable and compostable as independent technical studies indicate PLA is not a recycling contaminate. However, when mixed with PET, for instance, PLA at concentrations above 0.1% (1,000 ppm) only results in hazing and colour effects on the PET. In any case, currently PLA is not yet a contaminant in PET recycling because of the limited market share. However, it is necessary to consider how bioplastics can affect recycling of conventional plastic sand inform the consumers so they can learn how to promote recycling or compost products. These questions need to be addressed quickly as the recycling community is already handling items from bioplastics, particularly beverage containers.

The problem remains open and, at present, it is reasonable to evaluate the recycling validity and its environmental effect limited to non-biodegradable plastics either from fossil origin or bio-based.

The most valuable non-degradable polymer which was submitted to extensive recycling is certainly PET. The virgin PET is widely used for the production of fibres, films and bottles for water and other beverages (especially carbonated drinks). It is used also to produce packaging products because of its combination of unique physical, mechanical, and permeability properties, as well as the good processability. As an engineering plastic, it is characterized by excellent high-temperature properties, creep and solvent resistance with respect to others. From the recycling point of view, it is a particularly fortunate case because it is easy to separate from other city waste and allows the recovery at a good quality and purity level, and at acceptable cost when properly assisted by the education of citizens and regulation. The recovery of PET flakes with an adequate purity for mechanical recycling requires a complex treatment, composed of many steps (washing, grinding, flotation, etc.). These operations give a product, PET flakes but with possible lower cost. The process aimed at upgrading the recycled polymer is often requested. Therefore the success of PET recycling depends on the possibility of developing strategies leading to materials and products with high technical value, by following an upcycling.

Different recycling methods are potentially available for post-consumer PET. These include the recovery of the energy stored in the material through thermovalorization and the production of feedstocks, for chemical or fuel industry, through controlled degradation processes. Solvolysis allows the recovery of the monomers and oligomers to be used in the synthesis of various polyesters. PET pyrolysis at 700 °C under inert gas allows the recovery of molecules such as benzene or toluene, which can be used in the petrochemical industry. Moreover, the conversion of PET to a mixture of gases, such as H_2 and CO (gasification), can occur in inert gas flow in the range 500–1000 °C in the presence of catalysts based on NiO and $Ca(OH)_2$. The effective application of this conversion process requires, however, very high plant costs because of the presence of solvents or by-products, which may also originate environmental problems.

The thermomechanical reprocessing of recovered post-use PET is the simplest and most largely adopted and cheapest recycling method as it requires the use of conventional processing plants. The resulting pellets from post-use PET flakes can be used to produce new containers, bottles or thermoformed items. The preparation of blends and composites (with fibres or inorganic fillers) is also often used. During the use and in particular during the reprocessing, PET undergoes hydrolysis, thermal or thermooxidative reactions requiring the control of molecular weight as a critical and essential point. Chain extenders, that is polyfunctional molecules, able to react with PET terminal groups, thus determining the increase of average molecular weight, are necessarily employed. Blends of post-consumer PET with polyolefin is also used to obtain tough materials. In this case, the use of compatibilizers such as copolymers or functionalized polymers is fundamental in order to prepare engineering materials with good mechanical performance from post-consumer immiscible polymers, avoiding a down cycling approach.

The plastic recycling process starts with the separation of the various items by their compositions. the seven different plastic recycling symbols are summarized in Table 7.4. They are typically shown on the bottoms of plastic containers. The recycling mill sorts the used plastics by these symbols. In additional separation based on the colour can be added. Then plastics are chopped up into small pieces and chunks. These pieces are then washed to remove debris like paper labels, residue from what was inside the plastic, dirt, dust and other small contaminants.

Table 7.4 Resins codes allowing sorting and recycling

Plastic polymer	Identification number	Symbol on item
Polyethylene terephthalate (PET)	1	♳
High-density polyethylene (HDPE)	2	♴
Polyvinylchloride (PVC)	3	♵
Low-density polyethylene (LDPE)	4	♶
Polypropylene (PP)	5	♷
Polystyrene (PS)	6	♸
Not specified	7	♹

The cleaned plastic pieces are melted down and compressed into tiny pellets called nurdles that can be reprocessed and designed into new and completely different products. Recycled plastic is generally used to create different plastic items of its former self. Some undesiderable chemicals such as dyes used in creating the raw plastic can be present and cause an entire batch of potential recycling material to be wasted. Additionally, the recycling is quite limited; the actual amount of plastics being returned for reuse are roughly 10% of what is used as virgin. In any case, even if the whole produced plastic is recycled, the need for virgin plastic would not be cancelled. However, plastic recycling can and does reduce the total consumption of resources since each plastic unit is used many times before been discarded.

The most commonly recycled plastics are the following:

(1) Poly(ethylene terephthalate) (PET) used in bottles of soft drink and water in salad dressing bottles in peanut butter jars and in packaging films because of its excellent clarity, strength, toughness, and barrier to gas and moisture.
(2) High-Density Polyethylene (HDPE) used in rigid bottles and containers for milk, juice, and water and in soft bags for trash and retail thanks to its excellent stiffness, strength, toughness, resistance to moisture and permeability to gas.
(3) Low-Density Polyethylene (LDPE) used in frozen food bags and freezable bottles because of its good processability, strength, toughness, flexibility, good heat sealability and barrier to moisture.
(4) Polyvinyl Chloride (PVC) used in juice bottles, cling films, and piping because of its excellent versatility, clarity, ease of bending, strength and toughness.

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Chapter 8
Response of Society and Market

8.1 Society and Plastics

Plastic polymers have benefited the human society and heavily contributed to our improved style of life from several viewpoints. Indeed the easy processable, light and low-cost structural plastics and the possibility of combining them in materials with functional and thermomechanical properties have allowed a rapid growth for easy and large-scale production with advanced performances in all fields from building and construction, electronics, packaging and transportation industries as well as to the activities addressed to the biomedical assistance for human health. No doubt that this trend will continue and will certainly be assisted and promoted by developing new strategies to produce plastic polymers from renewable sources when this is sustainable.

Packaging sector is the industry that has the greatest consumption of plastic, thanks to the versatility of the material able to respond to different needs. Depending on the degree of protection necessary to preserve the shape and properties of the packaged object (also perishable, such as food), the plastic used can be rigid and tough or if the packaging must be convenient to goods transportation one can choose a more flexible plastic or a combination of the two packages. The packs can have any shape, size and colour. Plastic packaging helps also to keep people healthy in a number of ways. It is used for medical facilities, to store a variety of solid and liquid goods of regular home use.

Plastic (and more generally polymers) plays a significant role in the building and construction industry. In fact, the construction industry is the second largest consumer of polymers used in items such as pipes and valves. These goods have superior resistance to corrosion with respect to traditional materials (generally provided by metals and alloys) and can be used for fresh water (cold and hot), but even for oil and in some cases for saltwater. In addition, some decorative and attractive elements including bathroom units, floors, pipes fittings, plumbing fixtures, insulating panels, banisters, windows, doors, gratings and glasses are increasingly designed by using thermoplastic polymers. Polymers are the main components of paints for exterior

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and interior (Ali et al. 2013). Made of plastic is the garden furniture such as tool sheds (recently produced also in composites with cement and wood fibres), toys for children, tables, chairs, deckchairs, armchairs, lamps, pergolas and canopies. With this regards, it is important to mention that polymers and plastics are generally less expensive, even if the cost of such furniture is strictly depending on the design. Thanks to thermal and insulating properties, plastic is ideal for use in house wiring generally passing corrugated pipes in walls or floors.

Plastic is nowadays widely used in domestic environments, especially for small appliances such as food processors, microwave ovens, toasters, mixers, coffee makers, irons, vacuum cleaners, small mixers, razors and hairdryers. Plastic foams are used in refrigerators for insulation, while the interior is made of plastic that is durable and easy to clean. In dishwashers, dishware racks and water diffusion blades are made of plastic. The use of these plastic elements in the listed electric households makes these last particularly durable and allows saving energy considerably. Also, plastic allows making smaller computers possible by allocating all of the electronics necessary within a dust-free and well-insulated environment where miniaturization was possible thanks to the use of plastic.

Evolution of modern transportation was also markedly supported by plastic materials thanks to the toughness, resistance to corrosion, durability, lightweight and easy dyeing. In particular, in the use in automobile, plastic and polymers saved million barrels of petrol owing to weight decrease of passenger cars.

Likewise, in the field of public transport, with particular reference to aircraft, trains and buses, the increasing use of polymers and plastic (seats, engine parts, wiring, roofing/interior and exterior panels, floors, windows and portholes) has made these mass transport tools cheaper and even lighter. This results in improved aerodynamics, which leads to better fuel efficiency and performance and generates a reduction of fuel consumption. Plastic can be used in part of helicopters because rigid and durable, but even flexible enough to withstand the vibrations.

Plastic and more generally polymers have entered powerfully as the main materials in all consumer goods used in sports activities: from motorcycles to bicycles (for outdoor or gym), canoes, skateboards, skis, gymnastic equipment, tennis rackets, sports clothing with particular reference to increasingly performing and engineered shoes. The plastic, in addition to being used for everyday objects or almost, has found advanced applications in radar systems because it allows the passage of waves and in some aerospace technological applications as, for example, in apparatus of space shuttles (such as the ablative shields necessary for re-entry).

The above helpful applications were first realized with polymer produced from fossil and mostly characterized by long durability (Pereira et al. 2013). In the absence of rules and control about disposal this has created problem to the environment as dismissed items, if freely abandoned in the environment, can withstand for long time producing mostly an aesthetic pollution which can also become dangerous. Clearly, this is a very moderate problem for more durable and higher cost items but is typically a problem for packaging, which is by the way the largest application field.

An approach to relief this problem comes from biodegradable plastics, which can be disposed in the environment and disappear in much shorter time than traditional plastic does. Clearly, these products cannot be used for practically all the other uses summarized above.

The biodegradability has also attracted the attention towards plastic from natural and then renewable sources thus helping to save oil and introduce more natural technology.

As discussed in this chapter, the term bioplastic includes today a series of polymeric materials where a significant weight part derives from renewable sources, but the final properties are not necessarily different from those of the analogues from fossil sources. Rather, apart the biodegradability necessary in some applications (agriculture, biomedical material and some very short-term packaging) the objective is to reach comparative properties. In this framework, the modern idea of circular economy, which claims recycling to zero waste, and the availability of raw materials in the necessary quantity put forward additional concepts in evaluating the comparative use of plastics and bioplastics.

8.2 Available Raw Materials

From the previous introductory section, it may result that today, and particularly in the future, the most relevant property for sustainability and then low environmental impact can be identified in the origin from renewable sources, whereas properties such as biodegradability will be requested only for some short-term application and when the collection for recycling is not possible. Indeed, the scheme below provides a synthetic but clear picture of the relationships between raw starting materials and final product related to plastics and bioplastics. It appears that the origin is clearly different but the functional properties, biodegradability taken as reference, are not strictly related to the origin. Therefore, one can say that on one side similar structures and properties can be reached from both renewable and fossil organic compounds, while the final application remains open to both. Conceptually, bioplastics allow saving resources, as the used raw materials are renewable. On the other side, fossil raw materials are not regenerable and it is necessary to consider the recycling a very efficient way of saving resources for long life materials of the latter type.

In an integrated view of sustainable materials displaying plastic behaviour, it is today possible to tell that in principle man is capable to produce the large variety of molecules for any distinct properties from different types of raw materials either from fossil or renewable sources (Fig. 8.1). For this purpose, the fossil oil and its refining supply a number of hydrocarbon compounds as convenient starting feed for chemical synthesis of monomers, which are then converted in a number of plastics by industrial polymerization processes. On the other side, nature with its cycles is constantly producing renewable organic molecules: some of them are already in form of biopolymers and can be converted into bioplastics by formulation, others are building block to be used by man for preparing either new plastics or the same

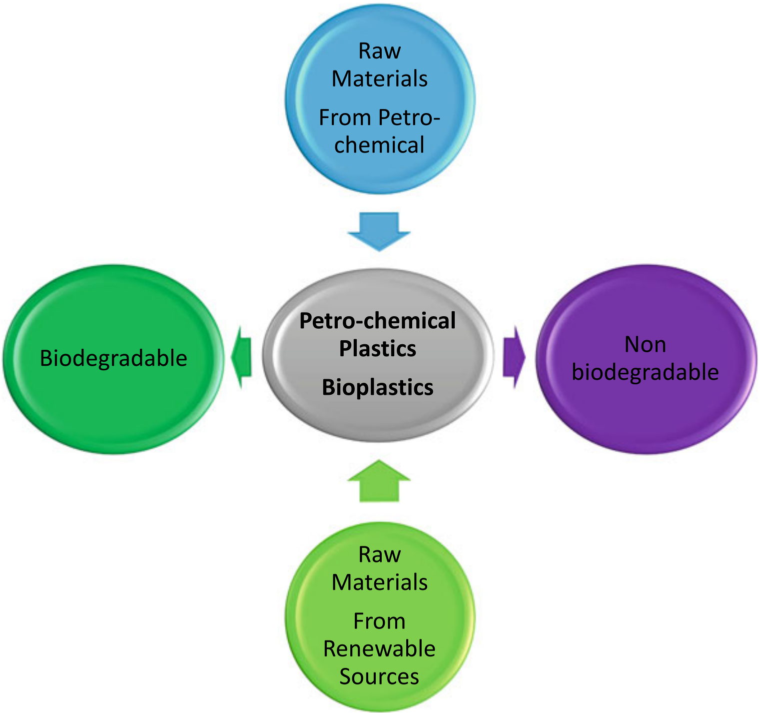

Fig. 8.1 Different origin and property comparison of bioplastics and plastics

plastics as those from fossil origin. Plastic materials both obtained by formulation containing nature-made biopolymers and by polymerization of monomers from bio-raw materials are classified as bioplastics. Raw materials from any origin are not only used for making plastics, but suffer from strong competition by other applications. It is necessary to note that oil and natural gas come from ancient organic materials compressed under heating over geological time and are not renewable in a human time scale; its reserves are roughly estimated at around 130–200 billion tons, which can increase to 500–600 billion tons with oil sands (for the moment not extracted for technological and economic issues). By considering that the consumption is currently around 3–5 billion tons per year, reserves wear out in approximately 30 years for oil and 100 years if technology will be able to recover oil form sand. Even if oil consumption for plastics polymerization, formulation and processing is in the order of some percent of the global oil consumption, in the general context of consumption related to human activities, it actually suggests to find alternative sources for the synthesis of plastics in order to have a beneficial effect on the future availability of this fraction of oil that could be used for different applications and thus by replacing crude-oil-sourced polymers with non-fossil materials.

It is well known that agricultural potential on the Earth is limited by the competition with food crops. Therefore, raw materials should be selected among agricultural, urban or industrial waste or secondary products from food and/or agricultural industries (biomass) or carbon dioxide known to be 'greenhouse gases' which could be conveniently converted into chemicals useful for the plastic industry. The conversion processes of these raw materials into bio-monomers and bio-blocks to replace those of petrochemical derivation can follow microbial, chemical, mechanical or genetic methods. At the end of the process, i.e. after conventional polymerization, finished products are similar to the raw materials or plastics based on petroleum. Renewable sources are the most promising solution if the so-called renewal period is of the order of one or a few years, exceptionally of several tens of years as it happens for wood. Biomass (especially waste from the food industries), but also agricultural products not dedicated to the food industry (such as wood) are generally rich in chemicals, monomers, oligomers and polymers. As such, they can be a promising natural resource for polymers, reinforcements and additives for direct use or after physical, chemical or microbial treatments.

Monomers and polymers from renewable sources, bio-based building blocks, are now subject of activity of several chemical industries even if the quantitative availability is far below that necessary to replace the raw material request at present satisfied by fossil sources. There is no well-identified process that can provide a uniform supply to chemical industry and in particular polymer industry. In addition, the polymerization processes provide for a significant chemical differentiation of the building blocks necessary for the production of materials with the standard properties and performances required by the market. The above biomasses used as renewable resources already foresee a very significant differentiation in the chemical substances that can be extracted both from plants and in general from agricultural products or by-products and this aspect should be taken into serious consideration in future developments of the chemical industry and polymers. The aforementioned differentiation in materials from renewable resources is confirmed by recent progress in the sector.

Some examples are given below to comment and inform about the natural resource building blocks used at present for the production of bio-related plastic materials to provide evidences about the possibility offered to the human society for producing useful materials without consuming fossil resources. At the same, we mention the presently available synthetic routes leading to bio-related polymers for plastics while the already formed bioplastics derived from nature were reported in Chap. 5, even if more details and information outside the purpose of this book can be found in the literature cited at the end of the present chapter (Ali et al. 2013; Chen 2014; Kang and Lee 2015; Park et al. 2017; Pereira et al. 2013; Raj et al. 2008; Scarlat et al. 2015; Wagner 2014).

8.2.1 Monomers from Alcohols

Fermentation of sugars from renewable sources can be directed towards ethanol which can be easily converted to ethylene, thus providing a way to produce by conventional polymerization bio-originated polyethylene. The ethylene derived from the

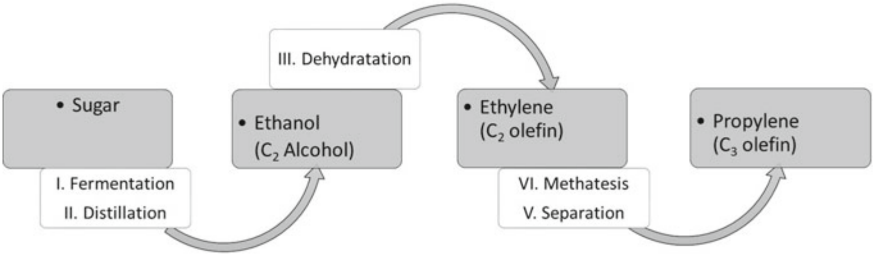

Fig. 8.2 General processes scheme of ethylene and propylene preparation from sugars

fermentation of biomaterials can be converted by metathesis to propylene, according to scheme shown in Fig. 8.2.

Again, the propylene produced according to this process can be also polymerized to isotactic polypropylene. This process, already described from another viewpoint in Chap. 5, is here mentioned for having a complete coverage. Industrially, PE from sugar cane ethanol is produced since September 2010 by Braskem in Brasil which is world leader with an annual capacity of 200 KTons. Total Petrochemicals, IFP Energies Nouvelles (IFPEN) and Axens announced an alliance to develop a new technology for the production of ethylene by dehydration of ethanol. Dow and Mitsui also have an ethanol-to-ethylene plant and a polymerization plant. Clearly, both ethylene and propylene obtained accordingly can be converted into the corresponding homopolymers as well as in the useful copolymers by the same catalytic processes used for the same monomers derived from fossil oil. This route therefore does not produce an alternative material to two important polymers, polyethylene and polypropylene from fossil, but rather the production of the same polymers from renewable sources.

8.2.2 Monomers and Building Blocks from Diols and Polyols

Fermentation of renewable biomaterials can be directed towards various diols through a fermentation enzyme assisted route as described in the very general scheme reported in Fig. 8.3.

Microbial-based 1,3-propanediol can now be produced with a method competitive with traditional technologies utilized to obtain this compound from fossil 1,3-propanediol. This allows replacing to an important extent the same compound from fossil origin in the manufacture of polymers with plastic properties such as polyesters and polyurethanes. The biotechnological route passes through glycerol produced by cleavage of natural fats, which is available in large amount as waste in the biodiesel production. The process is based on the conversion to 1.3-propanediol by the microbic action of *Citrobacter*, *Klebsiella*, *Lactobacillus*, *Enterobacter* and *Clostridium* strains.

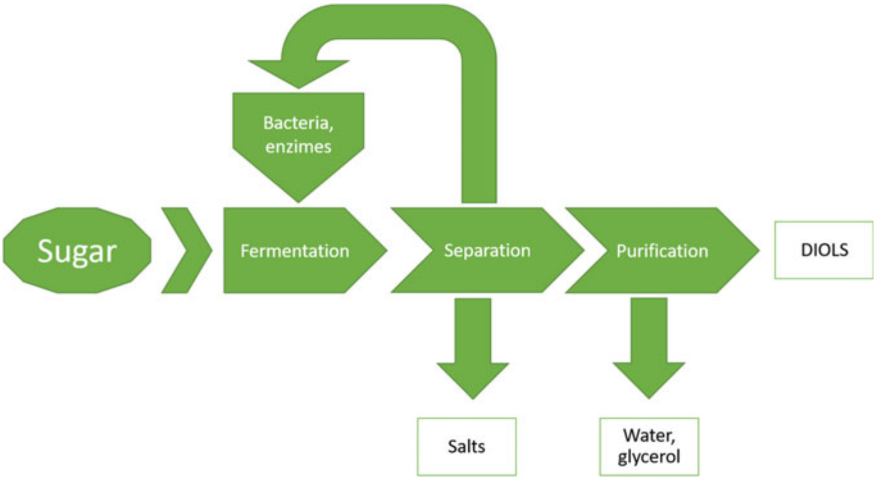

Fig. 8.3 General scheme of diols production via fermentation of natural products

An additional industrially relevant diol is 1,4-butanediol (BDO). The BDO production is an emblematic example of how the future of chemistry should evolve, not only because it will use renewable raw materials and especially genetically modified enzymes but also because it is currently one of the chemical products synthesized from all the raw materials possible alternatives to oil. Now Genomatica has developed a commercial bioprocess for the production of BDO from dextrose. The sustainable bioprocess was successful and was developed by selecting a strain of *Escherichia coli*; the results have led to such a high level of performance that an integrated technological platform has been developed providing for the engineering of the enzyme, and of the metabolic process of the organism, as well as for the development of an effective fermentation and recovery processes downstream. This allows to use biogenerated BDO instead of the same compound from fossil; BDO is one of the key building blocks to make polyurethane and co-polyester. The major uses of BDO are in the production of polybutylene terephthalate and polyurethane fibres and intermediates such as γ-butyrolactone (GBL) and tetrahydrofuran (THF). THF is used as raw material for the synthesis of polytetramethylene ether glycol (PTMEG), monomer to produce elastomers based on polyurethanes and polyurethane fibres. Furthermore, in small part THF is used also as a solvent in the production of PVC. Recently, low molecular weight polytetrahydrofuran (PolyTHF) has been produced by BASF and goes out on the market for application as elastic fibres.

Moreover, other natural polyols or vegetable oil polyols, often generated by glycerol fermentation can lead to polyurethane foams, thermoplastic polyurethanes, polyurethane elastomers and unsaturated polyesters; all being considered partially bio-derived polymers or plastics.

8.2.3 Lactic Acid and PLA

Lactic acid is the monomer used for the production of the corresponding plastic polymers under the name of polylactic acids (PLA) already mentioned in the present book. The synthesis of this acid monomer can be performed either by chemical synthesis routes or by fermentative production routes. The former produces the racemic 1 to 1 mixture of D- and L-lactic acid while the latter fermentative production allows the generation of optically pure D- or L-lactic acid when the appropriate microorganism is selected. Almost all lactic acid is today produced by the fermentative route, starting in general from corn-derived dextrin. Two processes are generally used, namely, the homofermentative route converting a hexose molecule into two lactic acid molecules, or the heterofermentative process which gives one mole of lactate from one mole of glucose as well as CO_2 and acetic acid or ethanol. Some basic information are given in Table 8.1.

The fermentation starts, indeed, from cheap renewable raw materials, but suffers from low productivity due to long conversion times and low active cell concentrations. The fermentation procedures using high cell densities or cell recycling have been recently shown to achieve high lactic acid productivity. Additional improvement comes from the integrated-membrane fermentation reactor, a system able to reduce the supplied raw material need. Several different substrates, apart from pure sugars and food crops, can be used for lactic acid production with advances in process engineering as reported in Table 8.1.

Also, lignocellulosic, starch biomasses, dairy by-products, agro-industrial and food wastes, glycerol and algal biomass can be used for the fermentative production of lactic acid. Commercial fermentation takes place in batches, with process conditions that provide a pH of around 6, temperatures of 40 °C and a low concentration of oxygen. The addition of calcium carbonate or calcium, magnesium and sodium hydroxides to the broth neutralizes the solution giving the corresponding lactate salt, which is soluble in the reaction mixture whatever the counterion. The fermentation broth is then filtered to remove bacterial cells and other insoluble impurities. The purification takes place through separation techniques such as ultra- and nanofiltration, electrodialysis or ion-exchange processes. The major problem associated with efficient lactic acid fermentation is related to the end-product inhibition. The removal

Table 8.1 Lactic acid from bacteria-assisted homofermentative and heterofermentative process

Materials and results	Homofermentative process	Heterofermentative process
Starting feed	Hexose, Pentose	Hexose, Pentose
Bacteria	Lactococcus, Streptococcus, Pediococcus, Enterococcus	Leuconostoc, Oenococcus, some Lactobacillus species
Products	Lactic acid (good purity)	Lactic acid, ethanol, acetic acid, and carbon dioxide
Industrial meaning	Sustainable thanks to high selectivity	Problems of monomer purification

of formed lactic acid during fermentation has resulted in a 50-fold enhancement in cell concentrations with dialysis membranes. Lactic acid derived from fermentation can be obtained almost entirely in the form of the isomer L. From lactic acid, the polymer can be produced by polycondensation with azeotropic condensation which does not require the use of external agents for the elevation of the molecular weight. The method requires a high aprotic solvent, temperature around 130 °C and reaction time of 30–40 h.

As reported in other sections of this book (Sec. 5.4), the PLA can also be obtained from the dimeric lactide by ring-opening chain polymerization with the assistance of catalyst.

8.2.4 Polyamides

Polyamides have this name as their macromolecules are formed formally by condensation of a carboxylic acid with an amino group to give an amido group through the elimination of a water molecule. The amido group, –CO–NH–, formed is part of the macromolecule backbone and interconnects monomeric units of which is part. The same functionality, called peptide group, is present in the biopolymers proteins, which, however, are not usually named polyamides. Indeed, the presence of a significant number of intra- and interchain hydrogen bonding in proteins do not allow a useful plastic behaviour. On the contrary, this is rather very typical in synthetic polyamides thanks to the significant separation between successive amido groups by long flexible aliphatic chains as for example, in nylon-6 where a linear chain of five methylene groups separates two successive amido groups.

One of the industrial route to produce plastic polyamides is based on the condensation of a diamine with a dicarboxylic acid as in the pioneer case of nylon 66 derived from hexane-1,6-dioic acid (adipic acid) and hexamethylene diamine, both from fossil origin.

Attempts to produce bio-derived polyamides were therefore based on the preparation of building blocks from renewable natural sources for finally obtaining the same plastic polyamides as from fossil, but saving resources. Accordingly, bio-polyamides are synthesized from two or more dicarboxylic acids and diamines. Triglycerides and the derived long-chain unsaturated acids present in vegetable oils can be converted into suitable bifunctional diacids which in combination with aliphatic diamines can be used for the production of polyamides by polycondensation processes. In this contest, raw castor oil is hydrolyzed to give ricinoleic acid, which is then converted to sebacic (1,10-decandioic) acid by reaction with alkaline hydroxide at high temperature. 1,12-dodecanedioic is prepared from oxidation process of lauric acid catalyzed by yeast strain. These partially bio-derived plastic polyamides are an industrial reality, such as polyamide 6.10 Ultramid® balance (by BASF) based about 60% on the renewable raw material sebacic acid. Also, diamines are derived from renewable sources for the production of bio-polyamide; indeed, pentamethylenediamine and tetramethylenediamine are naturally occurring substances produced by microbial biosynthesis by decarboxylation of the amino acid lysine and ornithine.

Interestingly, aminobutyric acid is originated from biomass fermentation and its polymer, unlike the other polyamides, is fully biodegradable by bacteria isolated from activated sludge.

8.2.5 Acrylic Polymers

Starting once again with glycerol, which is a largely diffused natural product and apparently one of the most used as raw source for different building blocks or monomers, it is possible to produce a precursor of acrylic acid today coming mostly from fossil. This precursor is actually the 3-hydroxypropionic acid (3HP), and can be obtained from glycerol according to the pathway reported in Fig. 8.4 (Raj et al. 2008). The successive dehydration produces the target monomer.

The bio-based acrylic acid has been proposed for use in the manufacture of superabsorbent polymers (SAP) used mainly in diapers (for baby or for adults) and other hygiene products. Clearly, there is a significant and impressive aspect towards the replacement of acrylic acid produced by oxidation of propylene derived from the refining of crude oil with acrylic acid from renewable resources, but we must emphasize that the monomer molecule and the polymer is the same with its advantages and disadvantages; the only difference being the origin which does not affect the ultimate properties. In any case, as acrylic acid is largely used even in copolymeric products, the developing and commercializing renewable acrylic acid is important as the present industrial production mainly depends on fossil fuel resources. Some recent non-positive economic evaluations have suggested to stop this route.

The most popular acrylic derivative with application in plastics products is certainly the poly (methyl methacrylate) (PMMA), which at the time of this book preparation is exclusively produced from fossil. Indeed, there are no sustainable routes to its obtainment from naturally occurring raw materials. When this happens, the recourse to natural sources implies a change of the polymer structure. In case of PMMA, a very interesting approach to reduce the environmental impact of the material from fossil has been achieved by blending PMMA with a compatible biopolymer, and in this case the PLA. The resultant blend features are lower processing temperatures, greater melt flow properties and reduced carbon footprint, as up to 25% PLA is added. It is

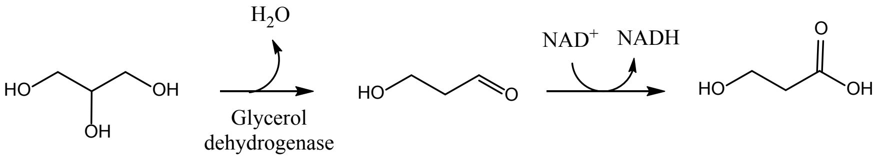

Fig. 8.4 Preparation of 3-hydroxypropionic acid from glycerol promoted by enzymes

important to stress that the blend material maintains the good and requested property characteristics of neat PMMA. Clearly, the new blends are not exactly the same also from plastic viewpoint as indeed PMMA is an amorphous material with T_g close to 90–100 °C, PLA can be amorphous with lower Tg at around 60 °C, while the possible presence of a crystalline phase would imply a melting point of 160 °C. Thus, the morphology and thermal behaviour of the blend must be controlled for appropriate application.

8.2.6 Other Bio-derived Building Blocks for Plastic Polymers

This section has the purpose to introduce a very significant aspect of the structure to property relationship in plastic polymers which can be profitable for reducing the environmental impact of these materials.

This aspect is alternative to the obvious approach based on the development of a preparative route for the obtainment from natural resources of a monomer or polymer presently from fossil. In this case, nothing changes in the properties and use of the final material with the additional positive result of saving resources. This complete substitution is not always possible and the approach for saving resources towards improved bio-derivation can be achieved by a partial substitution of the material with building blocks from nature or by compatible blending of a fossil polymer with a bio-derived polymer (as above described in the case of PMMA).

An additional example about the possibility of this chemical differentiation related to naturally derived molecules is provided by succinic acid as a versatile starting material. Figure 8.5 shows several useful molecules which can be prepared from this acid, in turn, obtained from renewable plant sugars. The succinic acid production in nature was extensively studied and related to several enzymes, namely, PEP carboxykinase, malate dehydrogenase malic enzyme, fumarase and fumarate reductase. Theoretically, 1 mol of CO_2 is required to form 1 mol of succinic acid.

Succinic acid from natural resources, according to the concept to replace polymer building blocks, contributes to greener polymers as reducing the use of non-renewable sources. A significant example is provided by poly(butylene succinate) (PBS), which is prepared by condensation of succinic acid with 1,4-butanediol. Both starting molecules can be now obtained from natural sources. The polymer PBS is clearly a synthetic material invented by man, but thanks to recent efforts it can now be fully produced with starting materials of bio-origin. Furthermore, thanks to its molecular structure it is also biodegradable. Therefore, PBS presents an illuminating case of clever combination of the inventive technology with the use of natural resources. It is not a biopolymer, but certainly a bio-derived synthetic polymer with good properties with respect to performances, application and environmental impact. Then it is used successfully in biodegradable packaging films and disposable cutlery and its market is expected to increase with the green succinic acid process improvement. Also, it is predictable and partially already done that the bio-derived succinic acid can help to reduce the carbon footprint of commercial polyesters, polyols and

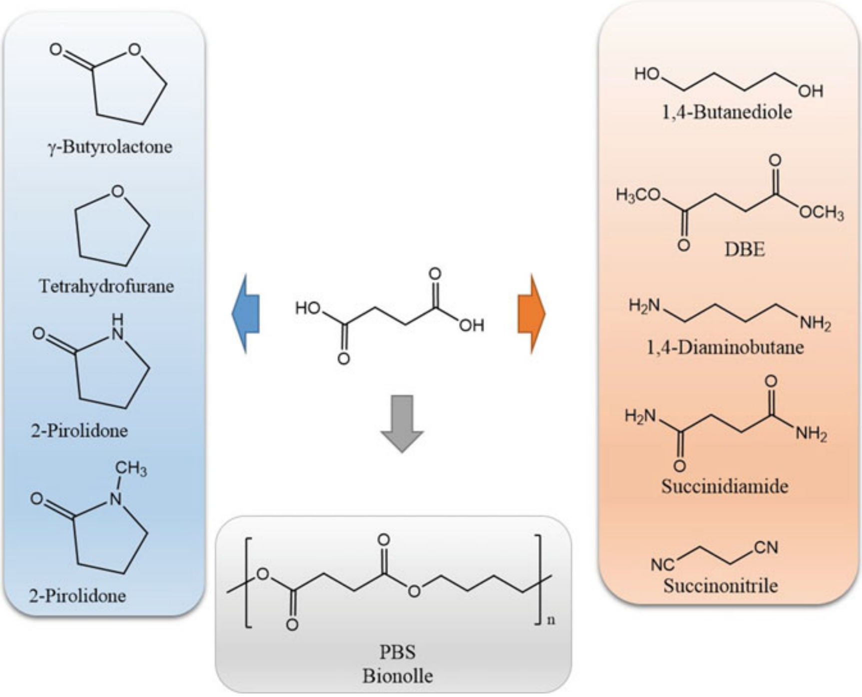

Fig. 8.5 Various building blocks obtainable from succinic acid

polyurethanes currently produced from succinic acid obtained from fossil sources. Also, succinic acid allows the production of bio-chemicals like pyrrolidones which, in addition to be used also as green solvents and eco-friendly chemicals, is the base molecule for the preparation of vinyl pyrrolidone that is converted successively in a useful water-soluble polymer. Figure 8.5 shows that succinic acid is certainly very useful and versatile for use as a building block in a variety of bio-derived polymers, with the same or innovative structure with respect to analogues from fossil. All molecules shown in that figure and derived from succinic acid can be replaced by the same molecules of bio-origin when starting their preparation with succinic acid from natural sources. Bacterial strain and glycerin or glucose are the feedstock for the production of succinic acid that many, more or less bio-oriented, companies are today worldwide exploring and realizing to expand the market of succinic acid starting from a variety of biomaterials from plants.

In the search of new processes for the production of building blocks from natural sources, there are several issues to be considered if the objective is to replace already existing plastic polymers derived from fossil and with a well-acquired market share. These issues regard the availability of raw material, the processes for the industrial production of the useful molecules and their polymer and the ultimate properties of the prepared polymers.

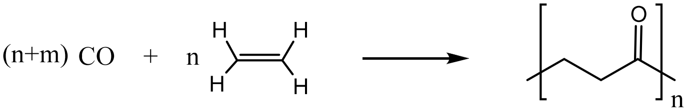

Fig. 8.6 Copolymerization of carbon monoxide with ethylene to the corresponding alternating copolymer with polyketone structure

As far as availability and collection of raw material are concerned, the situation is made complex by the fact that starting plants derive from different types of agricultural productions and thus have different composition. The useful properties are present in different components that need to be separated and, in general, the transportation of the material to be used as feed in the industrial plant is necessary. Indeed, these feed materials are more differentiated and less treatable than oil and this implies a sort of molecular differentiation already at this level. The sustainable large-scale production of bio-derived building blocks for the chemical industry and the related market of plastic polymer is strongly dependent on a solution of this challenge. The processing of raw materials to products can certainly profit of the many advanced technologies discovered and applied by man for the conversion of oil in monomers and their polymers, even if some significant changes will be necessary as a much lower recourse to vapour phase is expected. Polymers with their complex structure and possibility to obtain similar properties from different molecular system may alleviate the above problems. Also, we have seen how sometimes the bio-derived building block has the same exact structure of the material from fossil. Polyesters as seen above, and also polyols and polyurethanes with properties comparable to those of petroleum-based analogues have been prepared from vegetable oils and their derivatives. However, building blocks from vegetable oils and their derivatives still face technical and/or cost barriers and the varied composition makes difficult to obtain polyols with consistent properties. Better collection and selection of starting materials from vegetable oils could allow the use of single components with more homogeneous structures and consistent ultimate properties.

The last mentioned challenges encountered when using fully renewable carbon sources are markedly overcome in case of use, as starting materials, of carbon monoxide (CO) and dioxide (CO_2), that are abundant by-products of human activity. These C1 molecules clearly can be converted into useful products only if man-made processes are used. The first example was provided by the production of linear polyketones from CO or polycarbonates.

Homopolymerization of carbon monoxide was not obtained yet, but CO can be efficiently copolymerized with alkenes to alternating copolymers where the CO is incorporated in the macromolecule backbone. The copolymerization of ethylene with carbon monoxide in the presence of palladium catalyst proceeds as depicted in Fig. 8.6.

New polymers with different physical and chemical properties can also be obtained by a proper selection of a mixture of alkenes. Indeed, the same catalyst used for ethylene and carbon monoxide copolymerization can be used for higher monoalkenes,

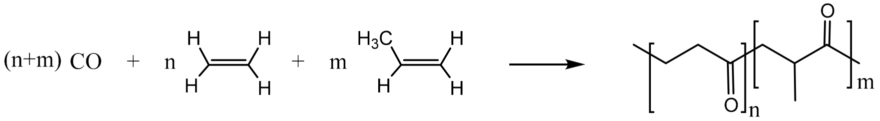

Fig. 8.7 Synthesis of ethylene, propylene terpolymer–polyketone

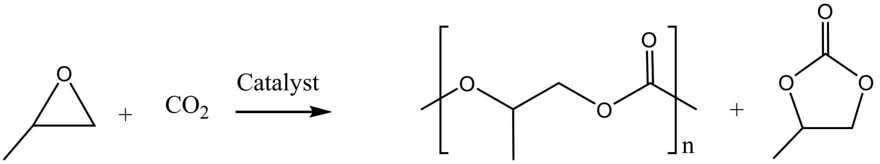

Fig. 8.8 Copolymerization of carbon dioxide with epoxides

also olefins. The property variation achieved by molecular differentiation can be approached also by terpolymerization starting with CO and two different olefins (Fig. 8.7). The introduction of structural disorder in the terpolymer allows modulating the thermomechanical ultimate properties of the produced polyketones.

The presence of carbonyl groups in 1–3 position along the macromolecular chains is responsible for strong intermolecular attractive interactions among polymer chains. As a consequence, the melting point and heat of fusion of polyketones are much higher than those of the corresponding polyolefins. Thus, poly(ethylene ketone) has melting point 290 °C, higher than linear polyethylene where the CO backbone groups are replaced by methylene groups. Polyketones have therefore higher tensile and impact strength than polyolefins; they also have remarkable abrasion resistance, very low water absorption, high barrier properties against fuel and oxygen, and good chemical resistance. Therefore, polyketones can be considered among high-performance engineering plastics. From the environmental viewpoint, the incorporation of CO in the alternate copolymer with ethylene indicates a saving of nonrenewable resources of 55% if ethylene from fossil is used and of 100% if ethylene from sugar fermentation is selected. Clearly, the polymer cannot be considered a biopolymer and it is not biodegradable, but certainly offers an interesting route to high-performing plastic material partially or totally derived from vegetables.

The same concept applied for olefin-CO copolymers was used by Novomer which developed a process for the production of polypropylene carbonate (PPC) by copolymerization of propylene oxide with CO or CO_2. Polypropylene carbonate can be produced from propylene oxide, and carbon dioxide in the presence of various metal catalyst as reported in Fig. 8.8.

Again, the structure of the macromolecules originated from the formation of monomeric units derived by alternating combination of carbon dioxide with opened epoxy group. Therefore, each monomeric unit incorporates a molecule of CO_2. Being propylene oxide also produced by fermentation, the final polycarbonate could be obtained totally from renewable sources. The same reaction can be applied to a number of different epoxides including various natural derivative products such as epoxidized soya bean oil, thus making the process significantly effective towards green plastic polymers.

8.3 Ultimate Properties for Distinct Applications

The main question to which this book is attempting to provide not an answer but just some partial understanding is: 'How far can bioplastics replace plastics from fossil origin?' Even if apparently all what is Bio is better than what is from Fossil, the examples and considerations reported in the previous chapters have certainly indicated that the answer to the above question is very complicated by the concurrence of many factors making impossible to provide a simple Yes or a simple No.

The main aspects to be considered in approaching the problem are technical on one side and economical on the other side. Both are time depending and can vary very rapidly in our times with the technology evolution becoming to grow asymptotically and difficult to control.

In this section of the chapter, we try to give some insights basing our consideration on the application performances of plastics and bioplastics where the only homogeneous and definite distinction is connected to the different origin.

According to the considerations reported in the previous chapters and the generally accepted definition, the term bioplastic applies to those materials with plastic behaviour that are derived from renewable natural sources. Then plastics from fossil and bioplastics can show similar properties and even the same molecular structure. The only distinct ultimate property is the biodegradability.

The present consciousness of the necessity to preserve the environment and its resources clearly would recommend saving, as far as possible, oil and natural gas and using material from renewable sources. This concept is much more effective in the case of energy production, but its validity certainly extends to all chemicals including plastics. The question that this section intends to approach is if the requested ultimate properties for plastics playing significant role in our life can be reached with feedstock from renewable sources, mainly vegetal.

This question is easily answered in case of bioplastics consisting of macromolecules with the same structure as the corresponding plastics from oil. The clear example is offered by the bio-polyethylene that is obtained by the same polymerization process as traditional polyethylene. In the former case, the monomer ethylene is obtained from bio-fermentation and in the latter case from oil, but the polymers are or at least should be identical as well as their final properties and applications. Accordingly, green polyethylene (PE) and green polypropylene (PP) claim, as understandable, full similarity, on all basic points summarized below and a remarkable contribution to preserve the environment.

- The production process is the same, for equipment, as for oil-based PE and PP.
- The polymer has similar properties to oil-based PE and PP, respectively.
- The polymers are also recyclable.
- The two polymers from fermentation reduce the greenhouse effect. It is possible to calculate that bio-derived PE helps to catch and commander 2.5 tons of CO_2 for each ton produced and 2.3 tons of CO_2 for each ton of bio-derived PP.

This example suggests that the easy way would be producing from renewable sources the same macromolecules for plastics as those presently used, at least those demonstrated to be safe during use and recyclable. The new property to be introduced would be biodegradability when this cannot be avoided, as indeed it may be argued that recycling is more conservative and safe than degradation in the environment. Biodegradability is in any case an important additional property to consider and this requests development of new structures with respect to traditional plastics, which are presently considered to be too much long living; these good properties being converted into a drawback by the bad human use and incapacity to the correct disposal after use.

With these considerations in mind one should recall that nature is producing several important macromolecules such as polysaccharides, bacterial polyesters and proteins but their properties are far to be similar to traditional plastics and in addition to the not easy and not eco-friendly separation need additives to reach the requested ultimate properties. These additives must also be biodegradable and biocompatible to maintain this distinct feature. In general, these biopolymers are too rigid for providing viscoelastic response at room temperature and need the addition of significant amount of plasticizers to lower the T_g to the useful value, as in the case of starch. Others are not easy to be processed as traditional plastics, due to the unfavourable relation of thermostability to melting temperature.

As already reported in this book, several chemical building blocks are now industrially produced from renewable sources. Then it is predictable that a sufficient molecular differentiation can be reached also starting from renewable resources and, in principle, all useful and safe plastics can be in the future prepared without using fossil feedstock as an important contribution to saving natural resources and lowering the carbon footprint.

It seems reasonable that rather than looking to completely new structures from bio-origin having the marked requested properties, it is more convenient to approach the problem by replacing the fossil-derived plastics with bioplastics with the same or similar structure. This approach can also allow introducing better ecocompatibility and including biodegradability when strictly necessary, without excessive detriment of the ultimate properties.

Examples in this direction, in addition to the already mentioned PE and PP, are certainly available and have reached the market. One of such examples is provided by the so-called bio-PET (bio-polyethylene terephthalate) produced from plant-based ethylene glycol rather than petroleum-based ethylene glycol. In this way, while the 70% weight provided by therephtalic acid remains of fossil origin, 30% of the weight coming from ethylene glycol is from renewable sources. The ethylene glycol used in bio-PET is produced from agricultural activities and includes molasses, hay and bagasse. Bio-PET is used to make a number of useful industrial products such as drinking water and soda bottles. Products made from bio-PET have the same molecular structure as traditional and then the same ultimate properties. Bio-PET is widely accepted especially in the European and American markets and trusted by leading global drink manufacturers such as Coca-Cola (Japan). These products as the traditional ones must be submitted to strict measures in scrutinizing the production processes and quality control of products to ensure that they meet quality and consumer safety standards. This has earned bio-PET various accreditations from leading global organizations such as the Japan Food and Drug Association.

The same route was also applied by several industrial producers for very common plastics such as polyamides (nylon) and polyurethanes.

8.4 Market Evaluation and Future Developments

There is no doubt that the increased concern for the preservation of the environment has reached the market thus promoting the utilization of renewable vegetal resources to ensure the consumption of carbon dioxide instead of the emission of CO_2. This aspect is so important that one can also propose some price increase simply with this justification. Also, the consumer is ready to accept to a certain extent higher cost and lower performances if this is presented as the result of a more environmentally sustainable production route. These performances decay is evidently acceptable only for applications characterized by a low technology profile and where they do not arise any risk. An additional limitation may arise from the availability of raw material and the competition between application of crops for plastic polymers rather than for food.

The above very real consideration make rather complex to evaluate the real possibility of replacing traditional plastic materials from fossil with bio-derived material. The recourse to natural raw material also implies a revision of global market as the differentiation occurs not only during processing and synthesis as in traditional chemical Industry, but already from the supply of raw material. Indeed, this last may be derived from different nature renewable products and then request different method of isolation and collection (Scarlat et al. 2015).

Worldwide attempts have pointed out that the consumption data broadly vary with sources, and the continuous technology evolution towards safer products independently of origin. Similarly, the larger sensitivity of the population to post-consume recycling of plastics which is becoming every day more effective in the concept of a circular economy may request to reduce material degradability. Production capacity of bio-derived plastic polymer could be not adequate to the market request for real difficulty of collecting starting material and the probability of increasing production cost to an extent that could hinder the diffusion in the market. According to market studies carried out by several international institutions, the consumption of bio-derived plastic polymer is expected to increase in the future (Table 8.2), but forecasts are variable in a rather broad range for the existence of the uncertainties indicated above.

Looking inside the numerical data in Table 8.2 it is interesting to evidence how different plastic polymers more or less bio-derived are requested by the market. According to European Bioplastics Society, the percentage is shown in Table 8.3 where the data were elaborated taking also into account the different bio-based content of different bio-derived plastics (Table 8.3), calculated by the following formula:

Table 8.2 Global consumption of bioplastics from 2017 to 2022

Year	Consumption (million tons)	% Biodegradable of total consumption
2017	2.05	42.8
2018	2.09	43.5
2019	2.14	44.2
2020	2.19	45.5
2021	2.25	45.9
2022	2.44	44.5

Data source www.europeanbioplastics.org

Table 8.3 2018 market shares of main bioplastics with the reachable bio-based carbon content

Type	Consumption as percentage of 2.05 Mtons (used in 2017)	Bio-based content %
Bio-PET + PTT	28.6	25.0
Bio-PE	10.2	100.0
PLA	11.1	100.0
Starch derivatives	19.7	Up to 85%
Others Biodegradable polyesters	12.7	Up to 50%
Bio-PA	12.5	Up to 50%
PHA	1.6	100%
Others	3.6	ND

$$\text{Bio-based content} = \text{Amount of bio-based Carbon}/(\text{Amount of Bio-based Carbon} + \text{Amount of Fossil Carbon}) \times 100$$

An additional important analysis for a better understanding of the market potentiality of bio-based plastic polymers comes from the analysis of the Greenblue Organization that reports data about the differentiated market interest towards bio-derived and biodegradable plastic polymers also with reference to the related applications (Table 8.4).

The data of Table 8.4 demonstrate the market sensitivity to bio-derived properties. Thus, the biodegradability is not always appreciated, but depends on the application and seems to show a decreasing interest with years.

Increasing regulations and bans against fossil-derived and non-biodegradable plastic bags and other single-use plastic items promoted by Western Europe Countries are contributing to a significant extent to increase the demand for biodegradable plastics. According to new analysis from market research consultancy like IHS Markit, increased market value larger than 50% from 2018 to 2023 is expected in Europe.

Table 8.4 Time evolution of biodegradable and non-biodegradable plastic polymers consumption in different applications

Year	Biodegradable polymer, %				Non-biodegradable polymer, %			
	Non-packaging	Flexible packaging	Rigid packaging	Total	Non-packaging	Flexible packaging	Rigid packaging	Total
2015	11.7	15.7	23.4	**50.8**	5.7	8.4	35.1	**49.2**
2020	8.5	6.0	11.5	**26.0**	9.2	3.2	61.6	**74.0**

Data from www.greenblue.org

However, these evaluations are keen to be changed depending on the very variable analysis of the environmental impact made by experts and institutions, which may influence remarkably the public opinion (Wagner 2014). An example is provided by the regulations concerning food packaging, disposable tableware and bags sector which traditionally are the largest end-use segment. In this sector, some modern trend would recommend to avoid single use as multiple use reduces waste volume collection and may result to be more compatible with circular economy. In this case, biodegradability can be less important or better avoided. On the other side, the gradual expansion of composting infrastructure and the extended use of organic waste for energy production could act in the opposite direction.

The above data offer clear evidence that the prevalent interest for bio-derived plastic polymers was born from the need to avoid the long-lasting life of packaging dispersed in the environment by non-educated people and the lack of any sensitivity to recycling possibilities. We may argue that the situation is partially changed and while there is a strong interest in producing plastic materials from renewable sources, the biodegradability is not the only driving property. Rather the future attention may be more and more focused on producing from non-fossil sources plastic material having similar properties to the traditional ones (Chen 2014). Some examples were encountered already in the previous pages of the present book with monomers and building blocks from plants having the same or close molecular structure of the correspondent from oil. Also, the use of additional products from nature may provide a useful molecular differentiation more compatible with the environment thus making science and technology developed by man to work arm in arm.

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Epilogue-A Current Consideration

We like to add this current comment at the conclusion of our contribution fully aware of the fact that Science and Technology of plastics will continue its evolution independently of the fossil or natural origin.

Indeed, we hope to have reported convincing indications in favour of our objective of giving an up to date picture of the features of plastic behaviour material produced by man, starting with molecules derived from renewable and fossil sources, as well as of the structure allowing to reach the desired performances.

Let us state once again that both the so called “plastics” and “bioplastics”, more properly plastic materials of fossil or natural origin, exist thanks to the inventive capacity and work of man. Indeed a large number of scientists and engineers have provided the human kind of very useful material possessing a property, thermo-mechanical plasticity, not common at all in nature. The human Society still continues to ask for plastic material with useful final properties depending on the specific application but in all cases has recently added the important request of low environmental impact. This last is not simply determined by the fossil or renewable origin but is the result of a complex analysis based on the Life Cycle Assessment (LCA). The reasonable approach is then to reach the desired property with the friendliest plastic material responding correctly to the application demand.

Then while it is obviously convenient to select a plastic material on the basis of the optimized relation property/environment impact, the saving of original sources must be rewarded. As shown in the various chapters of the present book this is presently not possible for all types of applications and necessary performances and cannot be always reached in a sustainable way by starting with polymers from renewable sources. So when it is necessary to use not degradable polymers from fossil, the saving of resources should be reached by an appropriate recycling. All these aspects are certainly the objective of the circular economy and better rational automation of industrial production, presently promoted with important efforts.

In any case, the ongoing shifting of many chemical platforms from oil-based to bio originated materials will enable in a near future preparing almost any man-made plastic from renewable resources. At that time plastic materials should be

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distinguished only by properties, e.g. biodegradable, biocompatible, etc. and production route, e.g. natural or man-made polymers, while the distinction between the raw material origin is expected to progressively disappear.

In the present time, while facing the continue evolution of the technology towards future sustainability, we should consider positively the availability of plastic materials produced for our welfare from both fossil and renewable sources and profit of both depending on the case. So the availability and difference between "plastics" and "bioplastics" can be satisfactorily accepted with the same expression used when thinking to the presence in our World of two distinct human genders, men and women, and bid "*long live difference*".

The authors with their best Wishes.

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