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Recent Developments in Plastic Recycling

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Editors are honored to dedicate this book to their parents

Preface

In modern society, the use of plastics in every sector has increased at a rapid pace from toys to advanced military aircraft. This is because of their versatility, lightweight, low cost, and easy processing. However, the reusability and recyclability of the plastics is not even 10%. This has caused serious concern to the environment, and adversely affects humans, fishes, birds, and animals. Many studies reported the presence of micro and nano plastic particles in animals, fishes, and birds. The situation is alarming. Therefore, recycling or reusing plastics is very important not only for the survival of mankind but for all living species.

In the past decade, research on the recycling of plastics has been increased and this caused an upsurge in the number of papers published. However, only a few books are available in the area of plastic recycling. Therefore, it is important to edit a reference book on *Recent Developments in Plastic Recycling*. The book covers all the important topics related to plastic recycling and hopefully will provide a solution to the problem of plastic waste. The invaluable information present in this book will benefit students, researchers, plastic manufactures, government policymakers, and general public.

In this book, we covered various topics of plastic recycling such as detailed introduction to the recycling of various plastics, recent developments and challenges for recovery and recycling of waste plastics, Recycling of engineering plastics PC, HIPS, ABS, and PA, their blends and composites, Waste Rubbers into Value-Added Products, Thermosetting Plastics, Marine Plastic Debris, Synthetic fiber reinforced plastics, Recycled thermoplastics: textile fiber production, scientific and recent commercial developments, Rheological behavior of recycled plastics, blends, and composites, Thermal Analysis of Recycled Plastics, Mechanical Properties of Recycled Plastics, Plastics into Advance Carbon Nanomaterials and Their Application in Energy Storage System, Plastic wastes to fuels and chemicals, Food Packaging Plastics: Identification & Recycling and Applications and future of recycling and recycled plastics.

The editors are thankful to all the authors for their chapters. The editors also thank the publisher for their guidance and support.

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Introduction to Recycling

Bupe G. Mwanza

Abstract Recycling continues to contribute to the sustainable management of plastic solid wastes (PSWs) and it's among the important approaches currently used for reducing the impacts of PSWs in the plastic industry. It provides opportunities for reducing quantities of wastes disposed, oil usage and carbon dioxide emissions. Further, opportunities in form of job creation, global warming reduction, reduction of virgin material consumption, reduction in landfill contamination etc. It also presents demerits such as being costly, contamination, littering, pollution etc. The chapter outlines the concept of recycling with particular attention to plastics. It discusses the two strategies of recycling: open-loop recycling and closed-loop recycling. These strategies are compared and the difference is that, open-loop recycling provides an opportunity for new product development while closed-loop is confined to the original products. Different recycling processes such as primary recycling, secondary (mechanical) recycling, tertiary recycling and energy recovery are discussed by focussing on the processes, merits and demerits. Recycling is contributing to the sustainable management of wastes and, because of advances in technologies and systems for segregating, collecting and reprocessing of recyclable wastes, it is rapidly expanding. It is creating new opportunities for integration with industries, communities and the governments.

Keywords Recycling · Plastics · Strategies · Processes · Merits · Demerits

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1 Understanding Recycling

To support the survival and wellbeing of mankind, various technologies and systems have been invented. These technologies and systems have focused on several aspects of survival. One sector in which these technologies and systems, have contributed massively is the manufacturing sector. This sector has produced many products that continue to excite mankind as well as present opportunities for innovation. Nevertheless, among the many industries that exist in the manufacturing sector is the recycling industry. This industry continues to contribute to many goals for achieving sustainability and circular economy. As a result of numerous benefits and challenges associated with recycling, it is important to provide a detailed overview on recycling with particular interest to the plastic industry.

Recycling involves activities in which unwanted/or waste materials are reused for the reproduction of new products. Coelho (2011) affirms that, recycling reintroduces unwanted materials and/or energy back into the production system. The unwanted materials reintroduced into the production system can be plastics, metals, papers etc. The materials used in the recycling activities are substitutes for virgin materials that would have been obtained from scarce natural resources such as petroleum, trees, coal and many others. From the sustainability angle, there are many benefits associated to recycling other than virgin material substitution. Al-Salem et al. (2009) adds that, recycling is important for various causes including oil preservation, minimization of greenhouse gas (GHG) emissions, energy preservation etc. Recycling is a cardinal element in the waste management (WM) hierarchy where it sits as the third strategy on the 3Rs "Reduce, Reuse and Recycle."

1.1 Recycling Strategies

Many studies on recycling processes have been conducted. Ragaert et al. (2017) conducted an extensive review on the recent strategies for polymer recycling through chemical and mechanical processes. The study also established the relationship between recycling and design while emphasizing the function of design from recycling perspective. Maris et al. (2018) reviewed the strategies for compatibilizing blends of mixed thermoplastic wastes. The study confirmed mechanical recycling as the most economical, ecological and energetic option for managing plastic wastes. Al-Salem et al. (2009a) affirms mechanical recycling as the most common process for recycling plastic wastes and it includes collecting, sorting, washing and grinding. It is worth noting that, mechanical recycling is not the only recycling process in the plastic industry. A number of processes including chemical recycling has emerged as a result of the drawbacks experienced in mechanical recycling (Kumar et al. 2011; Angyal et al. 2007). These recycling processes are discussed in more detail later.

From the circular economy perspective, categorization of recycled materials is based on the product manufactured from the secondary raw materials (Ragaert et al.

2017). The two terms that focus on material to product processes are "closed-loop" and "open-loop" recycling. These two terms are most important for making an objective division on the new product manufactured. Thus, the terms are subjected to labels such as "up-cycling" and "down-cycling," indicating an added value to the process of recycling (Ragaert et al. 2017).

1.1.1 Closed-Loop Recycling

This term is most applicable to many PET packaging products such as water bottles. Under this process, recycled plastics are utilized to manufacture similar products they were originally recovered from. The new product is manufactured entirely from recycled plastics or in some cases a mixture of recycled plastic is produced with its virgin counterpart. The type of dilution allows continuation of the recycling and recovering cycles.

1.1.2 Open-Loop Recycling

Examples of products recycled using this process include textile fibers from manufactured bottle-PET. Recycled plastics are utilized to manufacture a different product from the originally recovered one. The application does not imply the new product is of less value than the original one.

1.2 Types of Recycling Processes

The disposal of plastic solid wastes (PSWs) has become a critical global environmental problem (Environmental Impact of Polymers 2014). Despite this, large quantities of PSWs continue to be generated and introduced into the environment through disposal and production processes and this has continued the accumulation in the ecosystems across the oceans and globe (Ivleva et al. 2017). Given the serious environmental, economic and social challenges caused by PSWs, several decrees and regulatory guidelines focusing on the recovery of PSWs have been imposed by many authorities of different countries. Coupled with these guidelines and decrees, many methods of recycling PSWs that depend on sources of plastics, polymer type and package design have been developed. The difference in the recycling processes presents some challenges and hence some studies have been conducted to explain the sequential steps involved (Hopewell et al. 2009). However, the first study concerning the classification of recycling techniques was conducted by Clift (1997). Further, the classification has been standardized into four categories by the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM). Many studies have applied this classification (Al-Salem et al. 2010; Saiter et al. 2011; Brems et al. 2012; Ignatyey et al. 2014).

1.2.1 Primary Recycling

This recycling process reintroduces pre-consumer residues i.e. (scrap, single polymer edges, parts etc.) into the extrusion cycle in order to manufacture products of the same material (Maris et al. 2018). This is the best recycling method for plastics because of its merits on less energy consumption and fewer resources while more retain on fossil fuels. This recycling method is referred to as the closed-loop recycling strategy because of its ability to reuse products in their original structure (Grigore 2017). Primary recycling presents advantages such as; simplicity and low cost. Nevertheless, scraps of PSWs must be from a single waste source and pure (Bartolome et al. 2012). The existence of low number of cycles for each material is a major disadvantage of primary recycling (Singh et al. 2017; Francis 2016). Further, different materials and polymers cannot be recycled (Park and Kim 2014).

1.2.2 Secondary Recycling

Secondary recycling also referred to as mechanical recycling involves operations that recover PSWs through mechanical processes. This process substitutes recycled materials for virgin polymers or a portion of virgin polymers in the new manufactured plastic products. However, mechanical recycling has a demerit of deteriorating the properties of recyclable materials and hence degrading the polymers. Occurrence of low molecular weight compounds and heterogeneity of plastic wastes is another disadvantage.

Grigore (2017) asserts that, secondary recycling represents a physical methodology in which recovered PSWs are transformed through cleaning and drying, sizing, agglomeration, extrusion and manufacturing. Transformed PSWs can be combined with virgin materials for excellent results. However, it is challenging to recycle PSWs or wastes that are complex and contaminated. Therefore, wastes are cleaned to remove contaminates and it is a first process.

Mechanical recycling is utilised as a profit oriented process (Al-Salem et al. 2009) with products of different shapes being manufactured. Examples of products manufactured through mechanical recycling include; grocery bags, windows and pipes (Al-Salem et al. 2009). Companies in developing continue to utilise this process because of the merits it presents (Mwanza 2018). Nevertheless, drawbacks to mechanical recycling can be, the presence of impurities, complexity of PSWs, mechanical stress and poor quality of recycled wastes (Tshifularo and Patnaik 2020). The quality of the manufactured product is compromised through processes of waste preparation, cleaning and separation (Park and Kim 2014). Waste deterioration, unbalanced shapes and sizes of PSWs and dissimilar colours influence the complexity of mechanical recycling. Upasani et al. (2012) adds that, products stored in PET bottles speed contamination and deterioration. In addition, life cycle of recycled polymers influence the quality.

1.2.3 Tertiary Recycling

This process is also referred to as chemical recycling and involves processes that chemically produce small molecules from polymer chains that are later used as feedstock in the manufacture of fuels (Kunwar et al. 2016; Lopez et al. 2017; Mohanraj et al. 2017); other chemicals (Serrano et al. 2012) and new polymers (Kwan and Takada 2017). Globally, many chemical processes exist, gasification, hydrocracking, pyrolysis, depolymerisation, methanolysis and aminolysis (Nikles and Farahat 2005; Genta et al. 2005; Pingale et al. 2010; López-Fonseca et al. 2010; Fukushima et al. 2013). It is a paramount process for manufacturing food packaging products (Patterson 2000).

Chemical recycling is a sustainable recycling method (Tshifularo and Patnaik 2020) and will continue to be used without difficulties in the future (Wang et al. 2009). Its purpose is to achieve higher rates of the monomer with reduced reaction time (Al-Sabagh et al. 2016). The presence of depolymerizing agents, monomers and resin synthesis are some of the advantages presented in chemical recycling. The process of recycling PET is grouped into methanolysis, glycolysis and hydrolysis.

PET producers recycle using Methanolysis and PET is reduced using methanol at higher pressure and temperature. The pressure is between 2 and 4 MPa and temperature between 180 and 280° (Paszum and Spychaj 1997). Its drawbacks include; high cost, high temperature and pressure (Shukla et al. 2009).

Glycolysis begins by crushing the PSWs into flakes and these are cleaned to remove contaminants. The dried flakes are then extruded into desired products. In other cases, virgin PET is blended with the flakes for quality improvement (Tshifularo and Patnaik 2020). Glycolysis is also used to recycle PET bottle wastes under pressurised reactor kept between 238 and 242°.

Hydrolysis process involves the reaction of PET with water in an alkaline, acid or neutral environment resulting into total depolymerisation into its monomers (Grigore 2017). It is not a preferred method for manufacturing virgin PET for packaging food because of high cost. High temperatures of between 200 and 250° and pressures of between 1.4 and 2 MPa are the major disadvantage of hydrolysis recycling. Ghaemy and Mossaddegh (2005) adds that, pollution and corrosion related problems are another set of disadvantage. Compared to glycolysis and methanolysis, it is slow.

1.2.4 Quaternary Recycling

This term is also referred to as energy recovery. It involves the incineration of PSWs and recovery of energy via the generation of heat and/or electricity. In developed economies such as the European Union (EU), energy recovery is the most used recovery method for post-user PSWs (Plastics Europe 2016). It is an appropriate process for application in instances where mechanical recycling cannot be applied as a result of separation difficulties, excessive contamination or deterioration of polymer properties. The high caloric value in PSWs makes them a suitable source for energy production.

In a report by Bartolome et al. (2012), the amount of chemical energy present in PSWs is recovered through incineration. This shows that, in any burning process of PSWs, energy is present and can be recovered. However, the amount present in burning is much lower compared to an incineration process. Quaternary is the best recycling option for complex to collect and segregate waste as well as harmful and toxic wastes.

The drawbacks of quaternary process is the poisonous air generated that is harmful to human health (Park and Kim 2014). As a result of the inability to produce another product from a recycled materials, quaternary does not fully fit in the recycling definition (Tshifularo and Patnaik 2020).

1.3 Merits and Demerits of Recycling

Recycling as a strategy of waste management and number 3 in ranking on the waste management hierarchy has changed the ways in which humanity deals with wastes. It is interesting to indicate that, recycling has existed as far as the 1800 (Bradbury 2017) and the process has continued to grow globally. The growth and innovations in recycling has come with advantages and disadvantages. A study by Hopewell et al. (2009) discusses the opportunities and challenges found in plastic recycling but still points out that, recycling is one of the vital options available for minimising the environmental impacts caused by plastics. Further, the plastic industry is represented dynamically by recycling.

1.3.1 Merits of Recycling

Recycling has enabled producers to create a wide range of products from clothing to furniture to kitchen utensils. It provides a platform for giving new life to valuable materials and hence closing the loop. It has expanded rapidly and provides several merits to the recycling industry and the society at large. The following are some of the benefits of recycling.

Reduction of landfill contamination

Majority of the manufactured plastics are non-biodegradable and cause a lot of harm to the environment. Recycling of plastics and other materials enables to reduce the contamination to the environment. The contamination takes long but its effects have lasting implications to the environment and all the living things.

Diversion of waste materials into other recovery streams

It is not certain that the operation efficiency of a recycling program will be at 100% for society to benefit. Major metropolitan cities continue to generate huge tonnes of wastes per annual and with diversion of 50% by least recycling technologies, an extensive amount would be reusable and return to the markets.

Reduction of raw material consumption

Establishment of recycling programs costs more but it contributes to less consumption of virgin materials. For example, plastics are manufactured from petrochemicals which are produced from fossil gas and oil and 4% of annual petroleum is converted into plastics (British Plastics Federation 2008). This is not sustainable consumption considering that, majority of the plastics are manufactured into post-consumer products with a short life cycle. Hopewell et al. (2009) mentions that recycling provides opportunities to reduce oil usage hence virgin material consumption reduction.

Ability to work as an open and a closed loop system

Recycling can be implemented as a closed and open loop system. Products can be transformed into different products. For example, transforming a plastic bottle into a refuse bag (open-loop system). For closed loop systems, products are transformed into the same products. For example, aluminium cans transformed into aluminium cans.

Reduction of pollution levels

It is possible to reduce the amount of air pollution by 70% through a recycling program. For example, 1.5 tons of CO_2-e per ton of recycled PET is given as a net benefit in greenhouse gas emissions (Department of environment and Conservation 2005). LCA studies have also shown that, recycling contributes to the reduction in emissions (Patel et al. 2000). 100% recycled PET has the ability to reduce life-cycle emissions from 446 to 327 g CO_2 per bottle compared to 100% virgin PET (WRAP 2008). This shows that, recycling reduces the threat of environment impacts.

Creation of educational opportunities

Availability of knowledge on recycling is a driver to community participation in recycling programs. Mwanza (2018) shows that, lack of information on recycling prevents communities from participating. Therefore, creation of recycling programs is an opportunity to provide knowledge and education. Informing communities on waste recycling contributes to sustainable management of waste and households can be taught how to reduce disposal and focus on recovery.

Profitability of recycling programs

Depending on the size of a city, significant profits can be obtained from a recycling program. For example, $90 per bin per year can be created and this depends on the effectiveness of the recycling program.

Creation of jobs

In developing economies, majority of the PSWs is recovered by the informal waste sector. The livelihood the informal waste sector get from recovering has contributed to sustainable recovery and management of PSWs. Therefore, the existing of recycling processes has contributed to job creation in the recycling industry.

Minimization of global warming

When the wastes disposed at landfills are combusted, emissions in the form of greenhouse gases are generated and these contribute to climate change and global warming. Therefore, the diversion of wastes for recycling minimizes the environment impacts caused by wastes. The process of recycling generates less greenhouses compared to landfilling since the amount of fossil fuels burnt less.

1.3.2 Demerits of Recycling

According to (Tshifularo and Patnaik 2020), the demerits presented in new products manufactured from recycled plastics have poor thermal and mechanical properties and lower melting viscosity. The presence of contaminants and reduced molecular weight of the recycled wastes is caused by degenerated mechanical and physical properties of the recycled wastes and this is another demerit of recycling. Besides these demerits presented in recycled plastics, a number of demerits on recycling exist such as.

Recycling is costly compared to landfilling

Other than the costs of constructing recycling plants, purchasing of required recycling equipment and machinery, and educating locals on available recycling programs and seminars, it is costly to recycle compared to landfill. Statistics published on Credit Donkey show that the cost of recycling prevent communities to recycle. Mwanza (2018) shows that, costs associated with waste recovery, logistics, and production and labour are obstacles to recycling in developing economies. However, Mwanza (2018) also shows that, comparative of recycling cost to landfilling is slowly promoting recycling. The cost of landfilling a ton is around \$28 compared to \$147 a ton to recycle. Further, landfill management is less costly than managing a recycling facility.

Communities lack of compliance to recycling programs

Lack of compliance by communities presents demerits of recycling. Communities desire to recycle but lack the understanding of rules for wastes to include in the curb. This creates a lot of problems for recycling programs. Mwanza (2018) shows that, lack of information on PSWs recycling prevents communities to participate in recycling. Despite most recyclable products having recycling symbols, compliance from communities is still very low because most of them do not understand these symbols and therefore end up mixing these recyclable wastes.

Unhygienic and unsafe recycling sites

Majority of recycling sites are unhygienic and unsafe because a location where waste piles is a conductive environment for debris to form. Workers and waste collectors face several toxins at collection points and landfills. Workers are exposure to chemicals, fluids, and microbial agents and every collection point creates a possible health related problem.

Problems created by contaminants

The presence of any contaminant has high possibilities of damaging the entire batch prepared for recycling. It is a big challenge in the recycling industry despite specific rules been established for wastes.

Litter creation by waste collectors

In developing economies, major of waste collectors are in the informal sector. This sector does not have adequate capacity in terms of waste collection equipment and vehicles. This challenge has continued to create problems of littering after waste recovery. Scenes of this kind are observed neighborhoods despite waste management trucks with hydraulic arm to lift the container been used.

Non-durability of recycled products

The durability is always questioned and majority of the products manufactured products cannot be compared to those manufactured from virgin materials. Quality is always an issue in recycled products.

Energy Consumption and Pollution

Throughout the life of a product, energy is required. During recycling, energy is consumed from transportation of waste from collection points, during sorting, cleaning and manufacturing. In all these processes energy is consumed. Further, wastes in form of pollutants are created. The vehicles used in the transportation processes create pollution. Chemicals pollutants from the waste materials are harmful to the environment.

1.4 Recent Developments

Globally, the innovations, manufacturing and usage of plastics continues to increase exponentially annually, resulting in continuous increase in disposed end-of-life plastics in dumpsites, landfills and natural environments. Although recycling is ranked third on the waste management hierarchy, it has become an extremely important ecological and economic issue because of the merits it presents such as; low cost of energy, reduction of pollution and preservation of virgin materials. The desire to reduce the amount of plastics on the environment is growing from developed to developing economies and this has seen many legislations on plastics coming up. However, the relatively low costs of landfilling is proving to be an obstacle to the expansion of recycling especially in developing economies. Nevertheless, the drive for circular economy and political pressure has resulted in the creation of strict legislations focused on reduction of PSWs landfilling.

The majority of PSWs generated comes from post-consumer products because of their short life-cycle compared to pre-consumer products. Majority of plastic materials is manufactured as post-consumer products such as packaging products. The short life-cycle of plastic packaging products entails continuous demand for virgin materials. However, with the efforts to educate the public on sustainable resource utilisation, several legislations and systems have been devised to make inappropriate disposal costly and recycling more feasible, if possible mandatory. More and more wastes are been channelled into sustainable routes either through buy-back strategies or reduced recycling quotas. From these changes, recycling has increased and continues to increase globally.

Recycling approaches focus on; mechanical recycling, chemical recycling and energy recovery. Mechanical recycling is the most promising strategy from the environmental and economic aspects. However, if sorting is not conducted because of economic or technical constraints, recovered PSWs will constitute of different polymers and this presents a challenge to mechanically recycle. Thus, the drive for waste segregation is growing because for any recycling strategy to sustainably work, wastes should be segregated appropriately. Segregation of wastes results in reduced process time and hence reduced production costs. Chemical recycling through monomer recycling and pyrolysis are technologies that are showing a lot of potential in the recycling industry. Therefore, the recycling industry should invest in research that can provide feasible implementation plans for these technologies. Mechanical recycling as an established business in many developed economies is profitable and can generate new polymer with minimum investment. It is a comparatively an advantageous route to polymer manufacturing and can be used to recycle many polymers. For example, mechanically recycling LDPE and HDPE has the potential to generate the largest profit by 2030 (Hydrocarbon processing 2019). As a result of the demerits found in mechanical recycling such as quality deterioration and residue build-ups, chemical recycling through pyrolysis provides an optimal value treatment option while monomer recycling provides the highest recycling profitability levels.

Contextual development of recycling systems has the potential to improve recycling rates. The focus should be to design systems and deploy appropriate technologies that fit contexts. For example, most emerging economies lack waste sorting infrastructure and therefore, the wastes recovered is a small percent of the waste flow. An assessment of wastes generated and collected should be the starting point. Once these waste management capabilities are established, waste segregation strategies should follow. When this is achieved, pyrolysis of mixed PSWs can be the most efficient option.

By 2030, plastics reuse could increase to 50% of its production (Hydrocarbon processing 2019) assuming enforcement of regulatory frameworks and adjustments in the oil prices. The regulatory frameworks should be supported by industry stakeholders and consumers. To achieve a 50% reuse in plastics, capital investments is required.

The demand for plastics will continue to grow worldwide and it is imperative to establish effective systems for managing PSWs. Development of sustainable paths for quadrupling the amount of PSWs being reused and recycled should be focused on. The pathways will demand alignment of regulators and behaviors from major stakeholders such as consumer goods and society. Establishing partnerships will enable players to access the required technologies or secure access to the feedstock supply-chains. Collaborating with research institutions and creating long term agreements with private waste companies, landfill sites, municipalities and the communities will improve the supply-chain management of feedstock. For contextual supply-chain management of feedstock, integration of the informal sector into formalized systems will work for most developing economies.

1.5 Conclusion

Based on the reviewed literature, recycling is a vital element within the waste management hierarchy and will continue to contribute to sustainable development of the global. The different recycling strategies present a number of merits and demerits. These merits and demerits have enabled the recycling of different types of PSWs. As innovations and technological advancement continue to emerge, improvements within the recycling space continue to advance. This advancement in technology through research is needed by the recycling companies because the plastic manufacturing industry is not waiting for recycling technology to advance before they design and manufacture new products.

Integration of the required stakeholders, regulation enforcement, knowledge and awareness on recycling and systems development are needed for successful implementation of recycling programs but should be contextually aligned. Societal integration in the recycling process is necessary because waste is generated from all aspects of life i.e. workplaces and households. Lastly, the different strategies for recycling PSWs are not 100% sustainable but are contributing to resolving the PSWs problems.

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Recovery and Recycling of Polymeric and Plastic Materials

Ravindra Prajapati, Kirtika Kohli, Samir K. Maity, and Brajendra K. Sharma

Abstract The use of plastic materials is increasing worldwide because of their durability, cost-effectiveness, and light weight. This uncontrolled usage of plastic materials is creating severe disposal and environmental problems. This chapter includes recent and conventional practices for the recovery and recycling of plastic wastes. Brief classifications on the origin of plastic waste, such as thermoplastic, thermosetting, and elastomers, are specified. The sorting of plastic wastes plays a significant role in the overall performance of any recycling method. Various direct and indirect sorting methods are discussed along with their features and limitations. Recycling methods of plastic wastes are mainly classified as primary, secondary, tertiary, and quaternary. Detailed literature analysis including the advantages and technical challenges of each recycling method is discussed. A comprehensive investigation of the literature showed that new and innovative recycling approaches for plastic waste, particularly the scientific and technical inventions in tertiary recycling, present problems that impact their practicality in the industrial and manufacturing sectors. Currently, the recycling of highly contaminated plastic wastes from medical and e-waste are creating new challenges for the recovery and recycling sectors.

Keywords Plastic waste recycling · Sorting technologies · Near-infrared hyperspectral imaging (NIR-HSI) · Laser-induced breakdown spectroscopy · Technical challenges

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1 Introduction

The plastic industry is one of the developed industries derived from non-renewable fossil fuels. In the past few decades, progress in this industry has reached a remarkable level. Currently, plastic material is a better option than wood, glass, or metal because of its light weight, durability, and cost. Plastics are used in many applications such as household appliances, disposable medical equipment, automotive parts, packaging, construction, bags, containers, mulches, coatings, electronics, greenhouses, and aerospace components. Therefore, the presence of a large amount of plastics in municipal solid waste (MSW) is obvious.

Plastic waste production and disposal have a great impact on the MSW management by incineration and landfilling. Plastic incineration causes the emission of gases and the generation of toxic residues (mainly containing lead and cadmium) (Curlee and Das 1991). Plastic waste mainly goes into landfills and is released into the environment. These wastes, especially plastic packaging, end up in rivers and oceans and are a major threat to aquatic environments. The literature studies suggest that more than 88 kilotons of plastic wastes end up in seawaters yearly (Jambeck et al. 2015). Due to the ongoing global health crisis because of COVID-19, the global plastic packaging market size is projected to reach USD 1 trillion with a CAGR of more than 5.5%. This will ultimately put extra pressure on regular waste management practices. Between 1950 and 2015, 6300 million tons of plastic waste was generated and among these, 12% was incinerated, 9% was recycled, and 80% ended up in landfills or in the open environment.

The best way to control the plastic waste management problem is to recycle wastes and produce either recycled materials or useful materials of high value. The major advantages of plastic waste recycling are:

1. Plastic waste recycling leads to a reduction in land and marine pollution; it also significantly reduces CO_2 emissions in the environment.
2. Plastic waste recycling makes countries more resource independent and decreases their dependency on non-renewable sources such as oils and natural gas.
3. Developing recycling technologies will create more jobs, which will foster local growth.
4. By setting up systems for plastic waste recycling, local industries recover and value-added products emerge from the recycled materials.

Certainly not all plastic types can be recycled. Polypropylene (PP), high-density polyethylene (HDPE), and polyethylene terephthalate (PET) can be recycled easily; however, the recycling rate of low-density polyethylene (LDPE) is lower due to difficulties in sorting plastics in mixed waste streams. The remaining plastics such as polystyrene (PS) and polyvinyl chloride (PVC) are almost never recycled. The recycling of household plastic wastes and mixed waste streams is particularly difficult as these are highly contaminated. Thus, technologies are needed to sort plastics. Manual sorting technologies are challenging, inefficient, and time-consuming. Therefore, automatic sorting technologies using advanced techniques are required (Becker et al. 2017; Serranti et al. 2011). Innovative sorting technologies using robots help to sort materials with higher yields and efficiency. The artificial intelligence used by sorting robots showed an improved ability to recognize plastic wastes. Also, consumers need to take responsibility to sort their waste properly. The sorting guidelines in place directly impact the quality of streams for recycling. Public authorities need to make guidelines for the sorting of household wastes.

Plastic recycling methods are classified into four parts, from primary to quaternary recycling (Hopewell et al. 2009). The primary or closed-loop recycling method includes the processes in which products like the original plastic are produced. This method can process post-consumer plastics of known origin. Secondary or mechanical recycling can treat plastic materials to produce products that can be used in different forms. The polymers are sorted, ground, washed, and extruded by mechanical means in both primary and secondary recycling methods. These processing techniques lead to varying degrees of polymer degradation which limits their applications for plastic waste recycling at a large scale. Tertiary or chemical recycling uses hydrolysis, solvolysis, thermal and catalytic cracking, gasification, or plasma pyrolysis processes to recover the hydrocarbons in the form of fuels or chemicals, depending on the process configuration. Although this recycling technique produces high-value products, still, it is not implemented on an industrial scale very widely. This process requires high-energy inputs. However, if chemical-conversion processes can produce pure monomers, then they can truly aid in reducing dependence on non-renewable resources. Quaternary recycling includes incineration of the plastic polymers for energy recovery. The energy is recovered in the form of heat, and this process releases hazardous gases in the environment and produces large amount of toxic residues.

The overall efficiency of the plastic waste recycling methods depends on the sorting techniques involved. In fact, different plastics possess different physiochemical properties; therefore, different recycling methods are used. For example, plastics from mixed waste streams needs to be sorted first and contaminants need to be removed because these contaminants lead to the production of unwanted depolymerization reactions. This reaction will ultimately decrease the efficiency of plastic recycling methods. Therefore, fruitful and focused research work is needed not only to reduce and recycle plastic waste but also to find ways to separate it from the rest of the solid wastes. This will be the best way to minimize the technical, environmental, economic, and social impacts associated with plastic waste recycling.

This chapter focuses on different sorting technologies and recycling methods for treating plastic wastes. In addition, technical challenges associated with these techniques are discussed along with future directions.

2 Types of Plastic Wastes

There are several types of developed and commercially available polymers for global applications. Polymer materials are typically catalogued into three types: thermoplastics (also known as “plastics”), thermosets, and elastomers. Table 1 summarizes the types of plastics and their applications. In the thermoplastics type, cross-linking between the polymer chains is not present. Thermoplastics melt upon heating and reversibly become hard when cooling. Polyethylene (PE), PP, PS, and PVC are commonly used thermoplastics that can be recycled. Thermosets are a class of polymers that become hard and infusible upon heating. This type is composed of semi-fluid, small molecular mass units in which a three-dimensional (3D) network of bonds are formed by cross-linking between the polymeric chains. Polyurethanes (PU) and epoxy resins are mainly included in thermosets, and these cannot be recycled. Elastomers are amorphous polymers that have high-degree elasticity. Vulcanization in the elastomers is responsible for the high cross-linked molecular structure. For the recycling process, the capex required for the prior devulcanization process is high; therefore, elastomers have comparatively low recycling rates. The most common elastomers are natural rubber, isoprene rubber, crum rubber, and ethylene propylene rubber. The recycling of elastomers is a difficult process because of cross linking. Therefore, to overcome this problem, thermoplastic elastomers (TPEs) were developed. TPEs have good recyclability and re-moldability properties along with their elasticity and mechanical strength (Naskar and Babu 2014).

Plastic wastes are also classified as municipal and industrial wastes based on their origin. Among these, a major portion of plastic wastes is contributed by municipal wastes. Sources of municipal plastic wastes arise from household items such as foodstuff dishes, one time-use cups, packaging items, compact discs (CD), cassette boxes, fridge liners, cutlery, peddling cups, drainage pipes, sanitation pipes, electronic equipment cases, cushioning fluffs, thermal filling foams, etc.; wires and cable; automobile wrecking; agricultural wastes (fertilizer bags, films, feed bags, and covers for hays, silage, etc.). Therefore, municipal wastes are a mixture of PE, PP, PS, PVC, PET, etc., meaning that this waste has all kinds of polymers, recyclable and non-recyclable. To recycle municipal wastes, sorting and separation of plastics from extra domestic wastes is a necessary step. The most commonly used technique is mechanical separation. For example, in the wet separation technique, mixed plastics can be separated based on their density. Plastics such as PS and PVC have a density greater than water, while PE and PP which have a density inferior to water can be separated. Waste separation at the domestic site is better, and wastes can be segregated into three parts: (i) combustible materials like cloths, newspaper, pantry waste, and timber; (ii) incombustibles such as glass, metallics, and porcelains; and (iii) plastics. In addition, a large amount of plastic waste is also generated as a by-product in industries and farming activities. Industrial plastic wastes (IPWs) are sometimes also called primary wastes. These mainly consist of plastics from demolition and construction companies, electrical and electronics industries, and automotive industry spare parts. IPWs are satisfactorily cleaned and free from impurity and

Table 1 List of different types (thermoplastic, thermoset, and elastomer) of polymeric materials and their applications

Polymer	Applications
Thermoplastic polymers	
Polystyrene (PS)	Disposable cutlery and cups, transparent toys, transparent office objects (rulers, pens, etc.), components of appliances and electronics. In expanded form, it is used in food packaging and acoustic/thermal insulation
Polyvinyl chloride (PVC)	Packaging of food, cosmetics, and medicines, tubes and fittings, coatings, automotive parts, medical apparatuses (blood and serum bags, endotracheal tubes, cardiovascular catheters, etc.)
Polypropylene (PP) isotactic	Films for food packaging, transparent bags, components of automotive and appliances
High density polyethylene (HDPE)	Buckets, toys, bottles, tubes, automotive parts, wire and cable insulation
Low density polyethylene (LDPE)	Packaging films, trays and containers for food, plastic bags
Polyethylene terephthalate (PET)	Food packaging, beverage bottles, fibers for the textile industry, wires
Polyamides (PA)	Fibers for the textile industry, ropes, toothbrushes, technical parts of vehicles, gears
Polylactic acid (PLA)	Medical implants, decomposable packaging material, food packaging, hygiene products
Polyurethane (PU) thermoplastics	Internal parts of cars, fibers for the textile industry, medical devices
Polytretra fluro ethylene (PTFE)	Gasketing, belting, pump and valve packing, cable insulation, insulation of motors, generators, transformers, and coils
Polymethylmethacryalate (PMMA)	Transparent tiles and windows, lanterns of vehicles, eyeglasses and contact lenses, optical equipment
Thermoset polymers	
Polyester	Craftwork, adhesive, technical yarns, manufacturing of fiberglass reinforced plastic
Polyurethane (PU)	Flexible and rigid foams, building insulation, automotive components, coatings and adhesives, thermal insulation in refrigerators and freezers
Silicon	Medical and kitchen utensils, thermal and electrical insulation, coatings
Urea-formaldehyde	Wood adhesive, manufacturing of plywood, plugs, sockets, switches, pan handles, and tableware, textile finishing

(continued)

Table 1 (continued)

Polymer	Applications
Phenol-formaldehyde (PFR)	Circuit boards, composites with fiberglass clothes, manufacturing of plywood, electrical insulation, coatings, and adhesives. Furthermore, production of laminates, pan cables, billiard balls, telephone handsets, home appliances, shells and others (known worldwide as "Bakelite," thermoset obtained after curing these resins)
Epoxy	Composite materials, coatings, adhesives, potting, encapsulation
Melamine-formaldehyde	Laminate flooring, erase boards, appliance housings, stove hardware, kitchen utensils (known worldwide as "Formica," thermoset obtained after curing of this resin)
Elastomer polymers	
Ethylene propylene rubber (EPR)	Insulation of high-voltage cables, automotive seals, radiators
Chlorosulfonated polyethylene (CSPE)	Shoe soles, hoses, tubes, tank linings
Styrene butadiene rubber (SBR)	Beltings, hoses, pneumatic tires, sealing
Natural rubber (NR)	Tires, conveyor belts, gloves, shoes, blankets
Isoprene rubber (IR)	Bearings, tires, shoes, gloves, rubber bands
Ethylene propylene diene monomer rubber (EPDM)	Sealing and insulation in general
Acrylonitrile butadiene rubber (ABR)	Fuel tanks and gasoline hoses
SR	Gaskets, seals, surgical and prosthetic devices, wire and cable insulation, sealing, and encapsulation
Crum rubber (CR)	Industrial hoses, diving clothes, electric insulation and belts, shoe heels, wire and cable coatings
Chloropolyethylene (CPE)	Cable jacket, medical gloves and clothes, fibers

are accessible in large amounts. Municipal and industrial wastes are heterogeneous and homogeneous in nature, respectively. Remolding and repalletization were found to be effective and simple for homogenous plastic waste recycling. However, for heterogeneous plastic wastes, chemical recycling processes are required.

3 Sorting of Plastic Wastes

Plastic recycling is more difficult because of the presence of a mixture of polymers in the waste streams. Plastic materials lose their characteristics because of contaminants present in the waste streams and the aging process in each period of their life series (Ragaert et al. 2017). Therefore, the major obstacle to plastic waste recycling is the availability of capable and precise waste sorting technologies. The sorting plays an important role in recycling and recovery of plastics. Waste sorting technologies are required to:

1. Detect contaminants present in plastics and their technical problems during reprocessing.
2. Improve the efficiency of the separation processes.
3. Recognize the different polymer mixtures to select an appropriate recycling process.
4. Select the additives to reprocess plastics, based on their additive composition.

Manual sorting is the most widely used method, which is effective depending on the identification of plastic constituents. However, it is a challenging, tedious, and time-consuming process. In the following sections, the different methods used to sort plastic waste will be discussed more elaborately.

‘

3.1 Spectroscopic Methods

The detection of plastics based on the chemical composition is a crucial step to develop an innovative waste sorting technology. The most used technique is densimetric (float-sink) separation in which plastic materials are separated based on their densities (Pongstabodee et al. 2008). The less dense materials float and heavier ones sink to the bottom. This method is conducted by the dissolution of mixed plastics in suitable solvents.

The use of several spectroscopic methods such as Fourier transform infrared (FT-IR) spectroscopy (Guidelli et al. 2011; Verleye et al. 2001), Raman spectroscopy (Tsuchida et al. 2009), laser-induced breakdown spectroscopy (LIBS), and hyperspectral imaging methods (Serranti et al. 2011) are also reported for detecting plastic materials. FT-IR is a simple, robust, efficient, flexible, and non-destructive technique to distinguish plastic polymers. This technique is based on infrared absorption bands that represent the unique chemical functionalities present in the materials. For instance, LDPE showed a unique band at 1377 cm^{-1} due to CH_3 bending deformations that is not present in HDPE. In this technique, dominant vibrational modes present in the polymers are detected. However, unique identification is challenging due to the weak spectral features. Therefore, the techniques such as near-infrared (NIR) (12,800–4000 cm^{-1}) and mid-infrared (MIR) (4000–600 cm^{-1}) are investigated (Becker et al. 2017). These techniques can record unique vibrational overtones that are mainly observed in plastics such as PS and PVC. NIR analysis gives information about the molecular structure of the plastics and helps to classify them. NIR and MIR techniques are used mainly in the waste industry to recover high-value materials from waste streams.

NIR spectroscopy uses differences in the wavelengths of infrared (IR) light that are reflected by polymers having different chemical structures. The reflected wavelengths depend on the covalent bonds present in polymers. NIR spectroscopy is also used with hyperspectral imaging (HSI) cameras (Serranti et al. 2011) that generate 3D pictures of polymer scarps on a conveyor. The detected scarps are then expelled in two or three altered collecting trays based on their chemical behavior (Fig. 1). The HSI technique can be used for qualitative analysis such as principal component analysis (PCA). NIR spectroscopy has many benefits for detecting and sorting plastic resins; however, this method is not suitable for identification of black-colored or dark-colored plastics.

In the MIR spectral region (4000–600 cm^{-1}), plastic materials show additional vibrational modes spectra such as rocking, deformation, and twisting, depending on the molecular structure of the analyzed samples (Becker et al. 2017). The various functional groups such as O–H, N–H and O–C showed unique spectrums in the range of 2500–600 cm^{-1} (fingerprint region). The main advantage of this spectroscopy is that it can also analyze dark-colored polymers.

Raman spectroscopy is also used to differentiate between different plastic types because of its spectral range that is well beyond the fingerprint region, its high signal-to-noise ratio, high sensitivity, and better reproducibility. This technique can be used at the industrial level where a massive amount of sorting is required. Raman spectroscopy has advantages over the FT-IR and NIR techniques, including (i) no

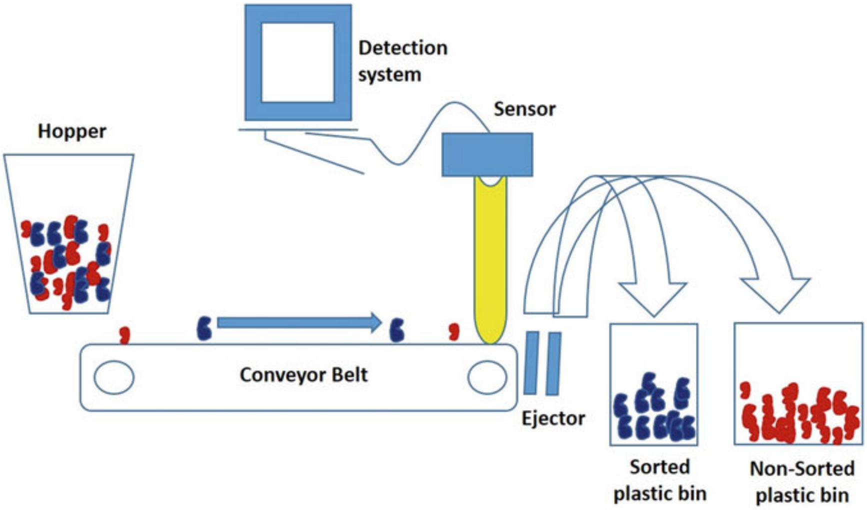

Fig. 1 Principle of near-infrared hyperspectral imaging (NIR-HSI) sorting technology (Serranti et al. 2011). Copyright permission Elsevier, License number 5014220891135

reference signal is obligatory and (ii) contamination of water and CO_2 from the air or on the surface has less of an influence. The mixtures of plastics such as PE/PP, PA/PTFE, and ternary polymer blends and their spatial structures can also be recognized by means of Raman spectroscopic analysis. The effect of fillers and additives on phase separation can also be investigated.

LIB spectroscopy (Noll et al. 2008) uses high-power laser pulse for identification of metallic wastes. LIB spectroscopy provides high-dimensional spectrometric determination for analyzing plastics, metal alloys, and treated wood wastes (Solo-Gabriele et al. 2004; Grzegorzek et al. 2011). The main components of an LBS system are a solid-phase neodymium (Nd)-fixed on yttrium aluminum garnet laser, a charge coupled device (CCD) spectral range spectrometer, and a data analysis processing unit. In the first step, the laser is focused on the bulk waste, leading to cutting out of waste that generates plasma plumes. The cutter portion emits radiations that are captured by the CCD spectrometer. This technique states and discriminates the characteristics of atomic emission streaks and can quickly analyze bulk waste and then detect constituent materials.

Use of the small-angle X-ray scattering technique is also reported in the literature (Jong and Dalmijin 2012; Mesina et al. 2007). It is a powerful technique used to determine the side chains of plastics by diffraction at small angles. The molecular weight of plastics in dilute solutions can be determined by light scattering analysis.

Recently, electronic devices have been used increasingly in our day-to-day lives, as the number of devices per user grows, and product life cycles decrease. Therefore, the amount of waste electrical and electronic equipment (WEEE) plastics is increasing significantly. These materials are more complex, containing co-polymers and composites added to improve the functional properties. These also contain a more intricate set of flame-retardant additives such as ABS-PC, ABS-PMMA or HIPS-PPE. This makes the use of plastic densimetric methods difficult. Beside these challenges, WEEE plastic materials and End-of-Life Vehicles (ELV) are black for photoaging reasons. Carbon black absorbs NIR rays, so NIR-HSI techniques also have a limited use for sorting electronic wastes (Beigbeder et al. 2013). Thus, innovative sorting technologies are required for electronic wastes.

3.2 Automated Sorting Systems

Automatic sorting systems are designed to distinguish plastics like PVC, PET, PS, and PP with ease and identify cellulose-based materials such as cards, paper, wood, cardboards, and natural fibers. Automated waste sorting techniques are classified into two types (i) direct sorting and (ii) indirect sorting. The direct sorting method depends on material properties such as density, electrical conductivity, and magnetic susceptibility by applying exterior fields like gravity, eddy current, and magnets individually (Gaustad et al. 2012; Svoboda 2004). On the contrary, in the indirect sorting method, sensors are used to detect the existence and location of materials in wastes. For this process, automated machines and robots are generally used to sort the identified materials.

Process of automatic sorting of MSW: In the first step, pre-treatment is conducted using disc screen, shredder, screw press, and magnetic techniques. Following the pre-treatment, dry waste is recovered and then subjected to a shredding process or comminution. Further, the ferrous materials are sorted by magnetic drum techniques. Non-ferrous metals are sorted using indirect sorting methods such as X-rays, eddy current, optical sort, LIBS, and hyperspectral imaging.

Comminution techniques: In comminution practices, loose waste solid is pulverized into even-sized particles by utilizing forces that are generated by pressure, cutting, impact, or abrasion (Bonifazi and Serranti 2012). Tools such as rotating drums, ring mills, alligator shears, hammer mills, swing hammer shredders, and impact crushers are used for this process.

Table 2 lists a summary of the different direct and indirect sorting technologies and details of the materials that can be sorted. These sorting technologies are explained in detail in the following sections.

Table 2 List of different types of direct and indirect sorting techniques

Sorting technique		Materials						
		Organic waste	Ferrous metal	Non-ferrous metals	Plastic	Paper	Glass	Wood
Direct sorting	Screw-press	√						
	Disc-screen	√						
	Shredder magnet	√	√		√			
	Magnetic drum		√					
	Magnetic head pulley		√					
	Magnetic cross belt		√					
	Eddy current			√				
	MDS			√	√			
	Froth flotation				√			
	Triboelectrostatic			√	√			
	Hydrocyclone				√			
	Air-separator				√	√		
In-direct sorting	Eddy current			√				
	LIBS			√	√			√
	X-ray sorting			√	√			√
	Optical sorting			√	√	√	√	
	Spectral sorting			√	√		√	

MDS = Magnetic density separation and LIBS = Laser-induced breakdown spectroscopy

3.2.1 Direct Sorting

In direct sorting, pre-treatment techniques such as magnetic drum, screw press, magnetic head pulley, disc screen, or shredder are used along with a magnet, magnetic crossbelt, eddy current, froth flotation, magnetic density separation (MDS), tribo-electrostatic separation, hydrocyclone, or air separator.

(i) In a screw press, waste materials (organic) are squeezed through narrow slits; thus, lenient and wet portions can be separated from plastic, paper, wood, and metal (Jank et al. 2015). (ii) In the disc procedure, rotating discs are used in which small and heavy waste portions are dropped in among discs, though large and light portions are transported to the edge of discs (Jank et al. 2015). (iii) The shredder along with a magnet is used for sorting paper and carbon-based fractions from MSW. (iv) The magnetic drum and magnetic head pulley techniques separate ferrous portions from non-ferrous and other mixed wastes based on the magnetic susceptibility of wastes (Svoboda and Fujita 2003; Bonifazi and Serranti 2012). (v) The rotary drum type separators are used in the eddy current technique, and the rotary drum is in-line by neodymium iron boron (NdFeB) with alternating north and south magnets. This technique has a low operating cost and highly pure products can be recovered. (vi) Magnetic liquids such as ferrofluid are used in MDS techniques as a separation medium. (vii) The froth flotation technique practices the phenomenon of hydrophobicity of plastic materials for separation. To use this technique, first waste materials are shredded into small particles using the comminution technique (Wang et al. 2015) and then mixed with water. This technique is mainly used for separating plastics from aquatic waste mixtures. (viii) The physical phenomenon, i.e., “contact electrification” or “frictional electrification” are used in the triboelectrostatic separation technique (Lowell and Ross-Innes 1980). (ix) The centrifugal forces are used for density separation in the hydrocyclone technique. This is mainly used for the separation of materials such as acrylonitrile butadiene styrene (ABS), PE, PVC, and HIPS (Al-Salem et al. 2009). (x) An air separator is mainly used for the retrieval of lighter non-metallic materials like foam, polymers, rubber, and fibers after applying techniques such as magnetic sorting and eddy current technologies. In an air separator, a compressed air nozzle is used (Bonifazi and Serranti 2012).

3.2.2 Indirect Sorting

In this sorting technique, sensors are used to identify recyclable materials in the bulk waste and then segregation is performed using various actuators. The techniques such as eddy current-based sorting, LIBS, optical-based sorting, X-ray-based sorting, and spectral imaging-based sorting (summarized in Table 3) are included in indirect sorting technologies.

(i) In eddy current-based sorting, electromagnetic sensors (EMS) are used to detect non-ferrous metal fractions depending on the electrical conductivity and magnetic permeability of the sample (Kutila et al. 2005; Mesina et al. 2003). (ii) The LIBS system uses high-power lasers for the detection of metallic wastes. In this system,

Table 3 Summary of indirect automated sorting techniques

Techniques	Types of materials recovered	Types of sensors	Process features	Limitations
Eddy current based sorting	Non-ferrous metal fractions	–	Based on electrical conductivity of the materials	–
LIBS technique	HDPE, LDPE, PP, PS, PET, PVC, CCA treated wood, Aluminum (Al) alloys	Nd:YAG laser, CMOS and CCD spectrometer	Detect components based on spectral characteristics	Sensitive to surface contamination Significant fluctuation in signal intensity
X-ray based sorting technique	Cu, Cast and wrought Al, Mg	DE-XRT detector, line scan, EMS	Materials are detected based on the atomic density of material	Issuing in classifying between cast and wrought Al
Optical-based sorting technologies				
Optical sorting method	Al, Zn, Cu, SS, Al, Br, Ni	3D imaging camera, linear laser, optical CCD	Material color, shape, and size detected	Inductive sensors are sensitive to distance changes Process becomes difficult when complex shapes of materials are there
Ultraviolet (UV)-based sorting	Lead glass, ceramic glass, borosilicate glass	UV sensor	Technique is based on monochromatic properties of materials	Identification of non-transparent or low transparent impurities is difficult
Spectral-based imaging techniques				
Spectroscopic based techniques	PE, PP, PET, PLA, PS, HDPE, LDPE	NIR, MIS, VIS spectrometers	Detect color (red, green, blue) and spectral signature	–

(continued)

Table 3 (continued)

Techniques	Types of materials recovered	Types of sensors	Process features	Limitations
Hyperspectral imaging (HSI)	Al, SS, Cu, Brass, Pb	Spectral CCD camera	Detect color properties of materials and spectral signature	HSI technique is unable to distinguish SS if it has similar spectral characteristics with other non-ferrous metals

LIBS = laser-induced breakdown spectroscopy; PE = polyethylene; HDPE = high density polyethylene; LDPE = low density polyethylene; PP = polypropylene; PS = polystyrene; PET = polyethylene terephthalate; PVC = polyvinyl chloride; Al = aluminum; SS = stainless steel; Cu = copper; Pb = lead; Mg = magnesium; Nd :YAG= neodymium-doped yttrium aluminum garnet; CMOS = complementary metal oxide semiconductor; EMS = electromagnetic sensors; NIR = near-infrared; MIR = mid-infrared; VIS = visible spectroscopy; and CCD = charge-coupled devices segregation of waste materials is done at a comparatively higher speed and volume compared to the eddy current method. However, for LIBS system waste, the sample to be used should be free from paints, lubricants, and oxide layers (Gesing et al. 2008). (iii) The camera-built sensors are used for the identification of waste portions in the optical sorting technique (Rahman and Bakker 2012). In general, the optical sorting technique uses multivariate analysis that comprises an amalgamation of a weight-meter and 3D shape detection camera fixed laterally on the conveyor system. A 3D imaging camera, web camera, optical CCD, linear laser, line scan camera, and ultraviolet are mainly used as sensors in this technique. Non-ferrous metals such as wrought Al, Mg, and cast Al with a sorting efficiency of 85% can be recovered with this technique (Koyanaka and Kobayashi 2011). The efficiency of this technique is not disturbed by surface impurities such as oil, dust, and paint. The hybrid techniques use a combination of an inductive sensor array and color vision to detect metals like zinc, brass, aluminum, copper, and stainless steel (Kutila et al. 2005). The UV sorting procedure is utilized to differentiate between opaque and special glasses (lead glass, ceramic glass, and borosilicate glass) from assorted glass wastes (Huber et al. 2014). The UV technique is independent of the shape and color of the glass specimen. (iv) The X-ray transmission type of indirect sorting is relatively fast and captures X-ray images within a few milliseconds by using a high-intensity X-ray beam. This technique provides data about the atomic density of the material tested. With this technique, copper, chromium, and arsenic were detected with 91, 97, and 98% efficiency, respectively (Hasan et al. 2011).

(v) The spectral imaging-based sorting technique utilizes both spectral reflectance measurement and image processing technologies. This technique uses various methods such as NIR, VIS (visual image spectroscopy), and HSI. In spectroscopic-based technologies like NIR, MIR, and Raman, light is illuminated on the plastic waste sample. Then an exclusive set of wavelengths of light is reflected because of the interaction between light and the tested sample. The reflected wavelength is different for different plastics, and these wavelengths are detected by various sensors such as NIR, MIR, and Raman. Further, processing units are used to sort out the desired material. VIS reflectance spectroscopy was used to detect PP plastic in mixed waste by Safavi et al. (2010). The HSI-based technique is used to classify the polyolefins (PP and PE) from mixed waste with high purity in the NIR region (Serranti et al. 2012).

Among all the discussed automated sorting techniques, the eddy current technique is the most widely used for segregation of metal waste fractions. The spectral- and optical-based techniques have shown improved performance with better coverage of material variations.

For more clarity, an example of a post-consumer, plastic materials sorting system is described as follows. Tsuchida et al. (2009) demonstrated a plastic sorting arrangement using the Raman spectroscopic identification technique, as shown in Fig. 2. In this system, post-consumer plastics were first shredded and added into a preprocess line for removal of wires, metals, labels, and other contaminants. The plastic materials were then moved under a spectrometer using a conveyor. In the final step, an air gun was intended to sort the plastic materials.

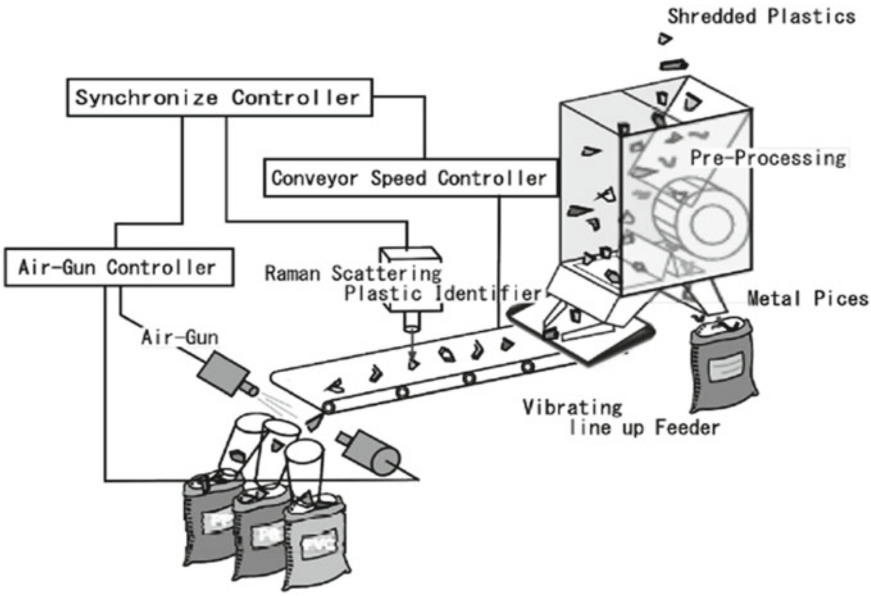

Fig. 2 Plastic sorting system with Raman spectroscopy (Tsuchida et al. 2009). Copyright permission Elsevier, License number 5014230074103

3.3 Technical Challenges and Possible Solutions for Sorting Technologies

The most widely used process, manual sorting, depends on the identification of plastic constituents, but it is tedious and time-consuming. On the contrary, the use of automated waste sorting systems is not very common, and these systems are mainly designed for source-segregated wastes. Segregation at the source sites is not commonly practiced because of the very inadequate door-to-door collection and absence of enthusiasm in consumers. Due to this, collected wastes are in an assorted form and discarded in landfills. Then the waste sorting is done manually. In this process, workers are exposed to pathogenic and toxic contaminants. Thus, there is a need to provide automatic tools to the workers to improve the safety and efficiency and specially to eradicate toxic pollutants.

There is a need to grow cheap and persistent computerized waste sorting machinery for cracking waste management problems. Automatic handling of MSW is very challenging because of the mixed nature of the wastes. To mitigate this challenge, researchers need to consider the use of multi-sensor type of systems and find ways to increase the recovery rate. The main technical challenge is the physical integration of more than one sensor in the sorting systems. Hence, sensors should be combined in the system in such a way that cross sensitivity is diminished, and the prototype should be modest.

In addition, an energy-competent computerized robotic system needs to be developed to recover recyclable fractions from landfill sites. These systems must be operated for extended stages, which need long-term self-sufficiency.

The strength of the automated systems could be amended by extending the variety of operating conditions for different robot sub-systems. The major technical challenge for enhancing the robustness is the effect of adverse environmental conditions, such as moisture, dust, wind, and soft terrain, while segregating recyclable portions from MSW in a landfill.

4 Recycling of Plastic Wastes

Plastic recycling is a process of recovering plastic wastes or scraps and reusing the solid for valuable products. The useful products can be either similar or different in forms from virgin plastic. The recovery and recycling of plastics is not a novel methodology. After increasing the rate of production and consumption of plastics every year, many researchers started studying the various types of plastic recovery and recycling processes. Table 4 lists the various plastic waste recycling methods.

Plastics are non-biodegradable; therefore, they cannot be simply converted to the natural carbon cycle. Thus, the life span of plastic wastes ends at waste disposal sites (Luo et al. 2007). The methods for plastic waste disposal are landfilling, incineration, chemical recycling, and material recycling. The largest portion of solid and plastic wastes are landfilled. However, waste disposal to the landfill is highly undesirable because of legislative pressure and the meager biodegradability of packaging polymers (Garforth et al. 2004). Hence, alternative recycling methods need to be explored.

Table 4 List of plastic recycling methods and their applicability for different types of plastics

Type of recycle	Methods/process	Applicable to type of plastic
Primary	Mechanical/closed-loop recycling	Pure thermoplastic polymer
Secondary	Mechanical recycle/downgrading	Mixture of thermoplastic and thermosetting elastomers
Tertiary	Chemical/feedstock recycling	Mixture of thermoplastic and thermosetting polymers
Quaternary	Energy recovery/valorization	Contaminated mixture of various plastics

4.1 Types of Plastic Waste Recycling Methods

The recovery and recycling of plastic wastes is broadly divided into four parts as described in detail in the following sub-sections.

4.1.1 Primary Recycling

Primary recycling is also called closed-loop recycling. It is a simple and easy process except for the sorted and cleaned collection of plastic wastes. Primary recycling involves the reprocessing of in-house scrap and industrial residual materials. The industrial residual materials are produced in a plastic manufacturing process such as extrusion and molding. The quality and properties of primary recyclate are similar to regular virgin plastic. Recycled material is either mixed with virgin material or used as a second-grade material. The adaption of the primary recycling process reduces waste production from industries to a great extent. A well-known example of a primary recycling process is PET recovered from postconsumer bottles and used in the production of new bottles (Grigore 2017).

4.1.2 Secondary Recycling

Secondary recycling is also recognized as mechanical recycling. It is one of the most widely used recycling processes because of its cost-effectiveness. This recycling process includes a collective set of different pretreatment and separation steps. Plastic wastes obtained from different sources have different pretreatment preferences (Al-Salem et al. 2009). In general, the following major steps are considered.

1. *Polymer waste separation and sorting*: The separation and sorting of polymer waste can be carried out simultaneously and step by step. The collection of polymeric material from MSW is part of the separation process, whereas in the sorting process, polymeric waste is segregated based on its type, density, color, and physical properties. The sorting technologies described in Sect. 3 are mainly used.
2. *Milling and grinding*: In this step, the well-sorted polymeric waste is fragmented into small parts using rotary mills and grinders. After this process, plastics are transformed into powder, granules, and fragments.
3. *Washing and cleaning*: The plastic material obtained from the separation process is still somewhat contaminated. Therefore, plastic waste is washed with different solvents based on their impurities. For instance, these wastes are washed with water in the cyclones. For the further removal of other impurities, chemical washing is carried out using surfactants and alkaline solvents.
4. *Drying*: After the washing process, drying of the plastic waste is an important step. The plastic material containing PA and polyester are susceptible to a hydrolysis reaction that leads to degradation of the plastic.

5. *Agglutination*: After the drying process, plastic waste and binder are mixed, and the homogenization of additives and pigments is carried out. In this process, volume reduction of plastic waste takes place.
6. *Reprocessing*: In this final step, plastic residue is transformed into polymer pellets of different shapes. This process is performed by extrusion or molding techniques. The recyclate plastics are packaged and transported to manufacturing factories for the production of new products.

The order of these steps depends on the MSW that needs to be processed and the desired product materials.

Advantages and Disadvantages of Secondary Recycling

The advantages associated with mechanical recycling are the comparatively lower capex, much less operational complexity, and the capability of existing machines to be used to recycle virgin and recyclate plastics.

The reclaim plastic used for mechanical recycling or secondary recycling contains a large amount of contaminants and other plastic mixtures. The presence of other polymer mixtures creates phase separation; consequently, a compatibility issue arises. The dyes and inks present in plastics restrict the homogeneity of the recyclates. For an efficient large-scale recycling of the plastics, proper segregation and separation from contaminates is highly desirable. Along with a contamination problem in the secondary recycling, the thermochemical degradation of plastic materials is also a major challenge. The over-degradation can limit the number of cycles during reprocessing of the plastic materials.

Products such as packaging materials, grocery bags, shutters, and pipes can be made from recyclates that are obtained by mechanical recycling. But there are always limitations in using recyclate plastic to make food packaging materials. Safety regulations standardize the contamination level in the recyclate plastic.

Initially, primary and secondary recycling were applicable only to thermoplastic plastics. Recently though, mechanical/secondary recycling is also popular for elastomers. The cross-linked rubbers can also be thermo-mechanically recycled after the devulcanization process.

4.1.3 Tertiary Recycling

Tertiary recycling is also identified as chemical or feedstock recycling. This is the most advanced type of recycling technology. In this kind of recycling, plastic waste constituents are changed into smaller molecules, known as chemical intermediates, by using thermal or chemical treatments. The smaller molecules are generally liquids or gases and sometimes solids or waxes. These molecules are used as a raw material or feedstock to produce new plastic and petrochemical materials. That is why it is called feedstock recycling.

Chemical recycling is a reverse process in which long-chain plastic polymers are broken down into monomer units and feedstock by the depolymerization and degradation process. The feedstock obtained after chemical recycling can be used to make comparatively less valuable products based on the level of impurities. Chemical recycling is not restricted to a single type of plastic materials. The mixture of plastic materials can be used in chemical recycling, but for better quality of the final product, sorting and separation technologies are also adopted in the process. Chemical recycling is a better alternative than mechanical recycling of thermosets, fibers, and cross-linked elastomers.

Table 5 describes the mechanisms and significance of different chemical recycling methods. The different methods used for chemical recycling are bio-chemical degradation, chemolysis/solvolysis, gasification or partial oxidation, and cracking. Among these, chemolysis and bio-chemical degradation are considered chemical routes, and gasification and cracking are thermal routes. Biological degradation is a simple and less energy-consuming process, but it has limitations for synthetic plastics. The rate

Table 5 Mechanisms and significance of various methods of chemical recycling of plastic wastes

Sr. No	Process	Mechanism	Significance
1	Biological degradation	In this process, plastic and polymer chains are fragmented into smaller monomers in the presence of fungi, bacteria or other microorganisms	Simple and eco-friendly process; Cost effective process
2	Chemolysis	In this depolymerization process, long chain polymers are broken into monomers by glycolysis, hydrolysis, aminolysis using water and alcohols	More suitable for condensation polymers than addition polymers; The quality of obtained product is good
3	Pyrolysis	Plastic materials are cracked into hydrocarbons and soot residue in the absence of air using high temperature and low pressure	Less operation complexity; Applicable to mixture of polymers
4	Hydrocracking	Hydrocracking is a process in which cracking takes place at high hydrogen pressure and high temperature. Supported catalysts are generally used for hydrocracking	Good selectivity of lighter range hydrocarbons
5	Microwave-assisted pyrolysis	In this recycling process, microwave is used as an energy source for the breaking of the plastics	It can also apply to composite materials

of biological degradation is very slow for the high-molecular-weight hydrophobic plastic materials.

Chemolysis

In this process, plastics are chemically treated using chemical agents to break down into monomers. Different processes such as hydrolysis, alcoholysis, methanolysis and glycolysis, are included in chemical recycling.

Hydrolysis

In the hydrolysis process, plastics are treated with water to recover the original raw materials. Hydrolysable polymers like polyesters, polyureas, polyamides (PA), PU, and PC are resistant to hydrolysis. Hydrolysis of PU foams is of great interest because they have a very low density, i.e., 30 kg m^{-3}, and thus take up considerable space. With this process, high product yields can be obtained. For instance, 90% amine and 100% polyethers can be recovered. The separated materials can be either reprocessed directly or mixed with virgin plastics. The quantity of waste generated is reduced (Ullmann 2003a).

Alcoholysis

PU can be depolymerized by the alcoholysis method to recover a polyhydroxy alcohol and small urethane fragments. This is an example of a transesterification reaction. If a diol is used as an alcohol, then a urethane fragment with terminal hydroxyl groups can be obtained. The recovered polyhydroxy alcohol can be used to make PU foams by treating with isocyanates (Ullmann 2003b).

Sub- and Super- critical Solvents

Plastic depolymerization reactions in sub- and super-critical fluids like water and alcohols are also investigated for the chemical recycling process. For instance, monomers such as terephthalic acid (TPA) and ethylene glycol (EG) were obtained by the solvolysis of PET in supercritical water (Al-Sabagh et al. 2016). The hydrolysis of PU in water produces polyol and diamine. In the presence of sub- and super-critical solvents, polymer decomposition proceeds rapidly, and therefore, highly selective products can be obtained.

Methanolysis and Glycolysis

The polymer degradation in the existence of methanol and glycols is known as methanolysis and glycolysis, respectively. The methanolysis of PET using methanol at a 180–280 °C temperature and 2–4 MPa pressure produces mainly dimethyl terephthalate (DMT) and EG (Scheirs 1998). The glycolysis of PET in the presence of EG produced a chemical, BHET (Chen and Chen 1999). The selectivity depends on the reaction temperature, reaction pressure, catalyst, and EG concentration.

Gasification or Partial Oxidation

Gasification or partial oxidation is a well-known process where hydrocarbon containing materials such as plastic or petroleum residues are converted into syngas ($CO + H_2$) in the presence of oxygen. Product quantity and quality are dependent on the polymer type used. Hydrogen production with 60–70% yield is reported by using a two-stage process: pyrolysis followed by partial oxidation. Co-gasification of plastic wastes and biomass is also reported, and an increase in hydrogen yield and decrease in carbon oxide is observed.

Plasma gasification is a method in which plasma torches generate an electric arc via passage of an electric current via a gas. Plasma is created through plasma torches by heating gas (mainly air) to a very high temperature (approx. 3900 °C). In this process, high temperatures 1500 and 5000 °C are used with a very short residence time. On injecting plasma in carbonaceous solids, they are heated and volatile matter is produced and cracked to release CO, H_2, CH_4, C_2H_2, and other hydrocarbons. Therefore, plasma technology can be used to produce gaseous fuels. Syngas was produced from waste rubber by using thermal plasma (Huang and Tang 2007). In the near future, plasma gasification can be a very attractive option to reduce greenhouse gas such as CO_2 emission. In this plasma gasification, the energy source is non-fossil fuel based and hence, CO_2 emission is much less.

Cracking

Cracking is a process that includes depolymerization of the plastic materials into smaller hydrocarbons. Thermal cracking, catalytic cracking, and hydrocracking are the processes that are used to depolymerize plastic waste.

Thermal Cracking/Pyrolysis

This type of cracking is also known as pyrolysis. In thermal cracking, depolymerization of plastic materials is performed by heating without oxygen at temperatures between 550 and 800 °C. The products obtained are a volatile fraction and carbonized char. The volatile portion can be divided into condensable hydrocarbon oil and a high heating value non-condensable gas. Product composition and yields depend on the nature of the plastic waste and the reaction parameters used. Reactor design also plays a crucial role, and various types of reactors such as a batch reactor, fixed-bed reactor, fluidized bed reactor, and screw kiln reactor have been used. The main features of the thermal cracking process are:

1. A high yield of C_1 and C_2 hydrocarbons in a gaseous product can be obtained.

2. The selectivity of gasoline is very poor.
3. Less branched olefins are formed and a small amount of diolefins can be made at a high temperature.
4. Gas and coke yields are very high.

Catalytic Cracking

In catalytic cracking, pyrolysis is performed in the presence of a catalyst to improve the quantity and quality of the desired products. Mainly solid acid and bifunctional catalysts are used. With added solid acid catalysts, the molecular weight of the main polymer chains is minimized by consecutive attacks by acid sites on the catalysts. This leads to an increase in yields of low molecular weight products. In addition, the carbonium ion intermediates formed in the catalytic reactions may undergo rearrangement reactions to produce high-quality isomers. The bifunctional catalysts contain both acidic and metal active sites. The metallic sites help to catalyze hydrogenation or dehydrogenation reactions, whereas the acidic sites catalyze the isomerization reactions. These catalysts can enhance the isomerizations of straight-chain paraffins to branched-chain paraffins and promote the dehydrogenation of naphthenes to aromatics and dehydrocyclization of straight-chain paraffins into cycloparaffins. All these catalytic reactions help to increase the octane number in the resulting hydrocarbon oils. The main features of catalytic cracking are:

1. Low reaction rates and reaction temperatures are used.
2. Gaseous products with more C_3 and C_4 hydrocarbons.
3. Gasoline selectivity is high with more C_5–C_{11} hydrocarbons.
4. The product oil composition and yields can be controlled by using suitable catalysts.
5. The catalysts used are expensive.
6. Naphthene dehydrogenation and olefin cyclization reactions produce more aromatics.

Hydrocracking

In the hydrocracking process, the larger molecules are cracked into smaller molecules (mainly naphtha or kerosene) in the presence of high hydrogen pressure and catalysts. Typical reaction conditions used are 250–400 °C and 3–10 MPa hydrogen pressure. Hydrocracking is mainly conducted to produce high-quality gasoline using various feeds such as PE, PP, PET, PS, PVC, mixed plastics, and co-pyrolysis of plastics with biomass/coal/VGO/scrap tires. The catalysts mainly include supports such as alumina, silica-alumina, sulfated zirconia, and zeolites and transition metals like Mo, Pt, Fe, and Ni. These catalysts possess functionalities of both cracking and hydrogenation.

Plasma-Assisted Pyrolysis

Recently, PE depolymerization was performed using plasma technology (Guddeti et al. 2000). The major advantages of plasma pyrolysis over conventional pyrolysis are that plasma provides a high temperature and high energy for the reaction.

All the previously discussed chemical recycling methods can be effectively used for contaminated and mixtures of plastic wastes. Also, the purity and selectivity of the recycled product are good. However, limitations associated with this recycling technique include the high capex of chemical recycling instruments; expensive catalyst systems; energy-intensive processes; and time-consuming development of an efficient catalyst.

4.1.4 Quaternary Recycling

Quaternary recycling mainly includes the incineration of plastic waste to produce energy in the form of heat, steam, and electricity. This recycling process can treat a mixture of plastic wastes containing huge amounts of contaminants. This process is effective compared to other recycling processes. It is a suitable process for medical wastes, cross-linked polymers, and thermosets. In this energy recovery process, the chemical energy of plastics is transformed into electrical and thermal energy. The incineration of high calorific plastic waste is carried out to produce a huge amount of energy. Since in this method only the inherent energy of plastic waste is used, the most contaminated waste plastic can be used without extensive sorting of used plastic.

Thermoplastic and thermosetting plastics are a high-yielding energy resource. For instance, burning 1 ton of organic waste, approximately 2501 kcal kg^{-1} of heating oil could be saved (Maraghi 1993). The energy recovered depends on the type of plastics used. The energy recovered from PE, PP, PS, phenol–formaldehyde, PVC, and PU is 18720, 18343, 16082, 13179, 7516, and 7014 kcal kg^{-1}, respectively. In a general sense, the average energy contained in plastic is around 10000 kcal kg^{-1}.

There is also a disadvantage of this energy recovery system from plastic waste. During the process, plastics release polyaromatic hydrocarbons (PAHs), soot, pollutant gases, and particulates, and hence, recovering energy from plastic is not suitable at a large scale. Also, various environmental regulation-related concerns are associated with this type of recycling process. There are various modifications that are suggested for the minimization of the emission of gases and particulates such as an addition of ammonia in the incineration chamber, cooling of the flue gas, neutralization by an acid, and adsorption using activated carbon.

The following methods generated during quaternary recycling are examined in the literature to minimize pollutants and particulates in emissions. *Wet scrubbing*: Gaseous oxides are simultaneously removed by various adsorbents such as NH_4OH, $Ca(OH)_2$, NaOH, $Mg(OH)_2$, and Na_2SO_3.

1. *Selective catalytic reduction (SCR)*: Nitrogen oxides present in the flue gas are chemically converted into nitrogen gas using reducing agents such as urea, ammonia, and hydrocarbons.
2. *Adsorption*: Nitrogen and sulfur oxides are adsorbed on the surface of adsorbent materials such as alumina, activated carbon, and coke. The metal modified adsorbents showed better catalytic activity.
3. *Non-thermal plasma methods*: Nitrogen oxides are selectively removed by dielectric barrier, pulsed corona, and radio frequency discharges.
4. *Electron beam*: Nitrogen and sulfur oxides are converted into chemicals in the presence of ammonia using irradiation of an electron beam.
5. *Electrochemical method*: In this method, nitrogen oxides are converted into molecular nitrogen by electrochemical redox reactions. Hydrogen acts as an anode and oxygen acts as a cathode for the electrochemical reaction.

4.2 Technical Challenges for Plastic Wastes Recycling

Worldwide, the production of plastics far exceeds plastic recycling. The recycling of plastics is hindered by many factors.

1. *Additives*: Several additives are used extensively to improve the properties of plastic materials, but they increase the chemical complexities of the final plastic material. Antistatic agents, antiblocking agents, antioxidants, antifogging agents, colorants, flame retardants, blowing agents, impact modifiers, coupling agents, plasticizers, and viscosity depressants are a few examples of additives. Their presence has been reported to create problems in plastic recycling. Some additives present in one plastic material can degrade other plastics. For example, recycled ABS can degrade PC during the recycling process.
2. *Compatibility*: Plastic material is composed of different chemical units. Therefore, most polymers are immiscible to each other. For example, some coatings and adhesives are made of thermoset materials that make recycling problematic.
3. *Contamination*: Different types of contamination are present in the recycled plastic based on their usage and sources. Contamination can be from dirt, oils, resins, food items, adhesives, glasses, metals, silica, etc. The presence of these contaminants affects the efficiency and productivity of the recycling process.
4. *Discoloring*: Often, some plastics are discolored due to the degradation of monomers. This mainly occurs because of the presence of some additives.

5 Conclusions and Future Perspectives

This chapter contributes to the sorting technologies for plastic wastes and recycling techniques used for plastic solid waste management. The recycling of household plastic wastes and mixed waste streams is challenging as these are highly contaminated. Thus, technologies are needed to sort plastics automatically using advanced techniques. The automatic sensor-based sorting technologies such as eddy current-based sorting, LIBS, X-ray-based sorting, optical-based sorting, and spectral imaging-based sorting are highly attractive for the fruitful use of plastic wastes. These methods should be coupled with artificial intelligence so that the process becomes more efficient. This will not only improve the efficiency of the process, but also provide higher yields. Most importantly, these techniques will help in reducing the exposure of manual labors to the contaminants, during sorting of plastic waste. Despite a lot of reported research work, the use of automatic waste sorting technologies is not very common worldwide. Still, there is a need to develop energy-efficient, low cost, simple, safe, and pervasive automatic waste sorting systems. These systems should be designed in such a way that they can be operated for extended periods and under adverse environmental conditions. Also, consumers need to take the responsibility to sort their waste properly. The sorting guidelines in place directly impact the quality of waste streams for recycling. Public authorities need to make guidelines for sorting of household wastes.

The best way to deal with plastic waste disposal is to recycle it. Recycled plastic and useful products obtained from plastic waste will contribute to environmental sustainability and reduce global warming to some extent. Primary and secondary recycling of plastic wastes involves thermal treatments like “melt-and-remold”, while tertiary or chemical recycling techniques include thermal and chemical cracking of plastics into fuels and chemicals. Recycling technologies can only be successful when the appropriate infrastructures and collection systems are implemented. Chemical recycling techniques are gaining momentum for use at the large scale and are being adopted in various countries. This method can easily produce a substitute for fossil fuels as an alternate source of energy. The design of catalytic systems for the chemical recycling of plastics is highly desirable. The catalytic system should work even under mild conditions and have the capacity to produce highly selective compounds. These help to produce high-value products on an industrial scale. In addition, the recycling methods should be designed in such a way that the method must be superior economically and ecologically. The designed method would also manage hazardous plastic wastes and emit negligible or a low amount of pollutants. All these efforts have set the future trends in plastic recycling as an industry.

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Recycling of the Engineering Plastics PC, HIPS, ABS and PA, Their Blends and Composites

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Abstract This chapter focuses on the chemical recycling of engineering plastics while providing a comprehensive presentation of all current recycling methods that have been applied for their management. Firstly, a classification of plastics according to their performance properties, takes place; along with an adequate definition and examples for each class. Then, the most representative and frequently used engineering plastics are reviewed, such as ABS, HIPS, PC, PA, their blends and composites, as well as their properties that make them special and extremely useful in demanding applications. Due to their wide use, the volume of end-of-life engineering plastics increases, which necessitates their environmentally friendly disposal. Thus, special attention is given to the recycling techniques that can be applied to the waste engineering plastics. All the disposal methods that have been used over the last decade including landfilling, primary recycling, energy recovery, mechanical recycling, and chemical recycling are fully described; emphasis is given though on the latter technique, which is presented in detail, due to its advantages over other methods in terms of the plethora of products produced.

Keywords Polymer wastes · Engineering plastics · Catalytic pyrolysis · Chemical recycling

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1 Introduction

Plastics undeniably have a vital role in everyday life, since plastic parts can be found in almost every application, from food containers to aerospace applications the diversity of plastics' applications is very wide (Fig. 1). Among other plastic categories the engineering polymers are gaining a great share of the market nowadays. The term "engineering plastics" refers to polymeric materials that present superior mechanical and thermal properties, such as increased toughness, strength and heat resistance, in comparison with the commonly used commodity plastics. The superiority of their physical properties and the operating temperatures has also enhanced their use over traditional engineering materials, such as metals. Due to their improved performance, engineering plastics can be used in demanding and load-bearing applications, including automotive, electric and electronic equipment, etc. Representative examples of engineering plastics are poly(acrylonitrile–butadiene–styrene) (ABS), polycarbonates (PC), high impact polystyrene (HIPS), nylon or polyamide (PA) and others (Shrivastava 2018; Crawford and Martin 2020).

The advantages they offer resulted in an increase of their consumption, which however led to a rise in the amount of their waste; especially those that come

Fig. 1 Plastics' applications

from electric and electronic equipment. The increase of plastic waste in combination with their non-biodegradability urged the development of environmentally friendly approaches for their management. So, attention was paid to collection, treatment, and recycling of engineering plastics at the end of their life. However, finding and applying environmentally friendly methods for their disposal is quite difficult, since not only many and different types of polymers are used; but also, various additives are inserted into them, with the aim of improving further their properties (Tarantili et al. 2010; Buekens and Yang 2014; Crawford and Martin 2020; Charitopoulou et al. 2020).

The challenges encountered in post-consumed plastics' handling and recycling are many (Fig. 2). Namely, the existence of different types of polymers (perhaps of unknown composition), polymeric blends or composites, multilayered structures with sometimes others than polymeric materials, as well as the presence of additives, are some of the issues that have to be solved during recycling. The methods that have been applied over the last decade for engineering plastics' handling are landfilling, primary recycling, energy recovery, mechanical recycling and chemical recycling. Landfilling is undesirable, since it is related to environmental pollution issues. The group of Ragaert et al. (2017) has recently reviewed methods for the mechanical and chemical recycling of plastic wastes. Among the other recycling and recovery methods, chemical recycling seems to be the most preferable choice (Yang et al. 2013; Charitopoulou et al. 2020). Pyrolysis, which belongs in chemical recycling techniques, is an environmentally friendly method, where secondary valuable materials can be received, monomers can be recovered and the liquid pyrolysis-fraction may be used as fuel for energy production (Achilias et al. 2012). So, it is regarded as the most promising method for the recycling of waste engineering plastics and that's why research is focused on it.

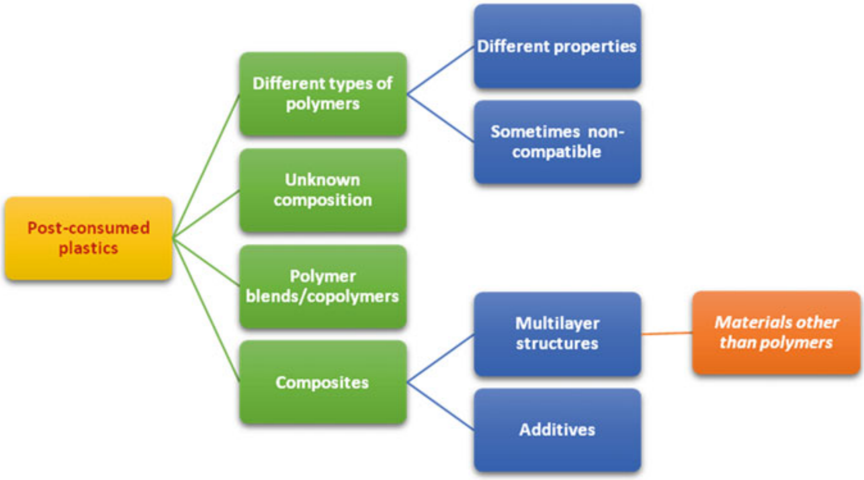


Fig. 2 Challenges in post-consumed plastics' recycling

Another aspect of the issue that we ought to illuminate is the statistics regarding the socio-economic practices on plastics recycling. In Europe, there are approximately 3,000 companies dealing with the mechanical recycling, and approximately 100 companies that receive mechanically processed recycled plastics (pellets and flakes). Only 13% is directly integrated into end products, which are mostly low-value floor coverings, grilles and plant pots (Ignatyev et al. 2014). According to the Institute for Prospective Technological Studies of the European Commission, there is an annual capacity in the EU of 5 million tons for mechanical recycling and only 50,000 tons for chemical recycling. The existing consumption in Europe cannot fulfill even half of the demand for reused polymers. In Europe, the market of recyclates is certainly not yet mature: a more intensive and efficient interaction is needed between recycling businesses and end-product producers. A dramatic increase in the demand for plastics (especially for food packaging, construction, agriculture and nonwoven hygiene products) and a great availability of end-of-life streams in Europe should become essential assets for the companies. Intensification and optimization of recycling can also decrease the dependence on oil-based raw materials (Ignatyev et al. 2014).

This chapter offers a critical review of the recycling methods that are applied, during mainly the last decade, onto engineering plastics, such as PC, ABS, HIPS, PA, as well as their blends and composites. Emphasis is given on chemical recycling methods and specifically on thermal and catalytic pyrolysis process. Below, the state-of-the-art of the thermochemical recycling of engineering plastics will be presented, along with suggestions on how to treat them properly, in case they comprise toxic additives that require extra attention.

2 Classification of Plastics

Polymeric products are present in every aspect of our daily lives; from kitchen equipment (dishes, storage containers, etc.) to automotive and buildings' construction or industrial uses. So, plastics inevitably play a major role in people's life and as a result their consumption has increased over the years (Fig. 3). All these plastic products often consist of different types of polymers. One classification of plastic materials based on their performance properties and their market share (Fig. 4) divide them as commodity, engineering or specialty plastics (Kahlen et al. 2010).

Commodity plastics known as *plastics of general purpose* are the dominant class in volume terms, since their annual consumption accounts for ~80% of the total plastics consumption (Shrivastava 2018). They offer many advantages including low density, high flexibility, good transparency, ease of mouldability or low-cost (Crawford and Martin 2020). Although they are found in very high volumes, commodity plastics are mainly used in less demanding applications (if compared to engineering plastics) such as packaging, toys, clothing, transportation, food containers etc. because of their

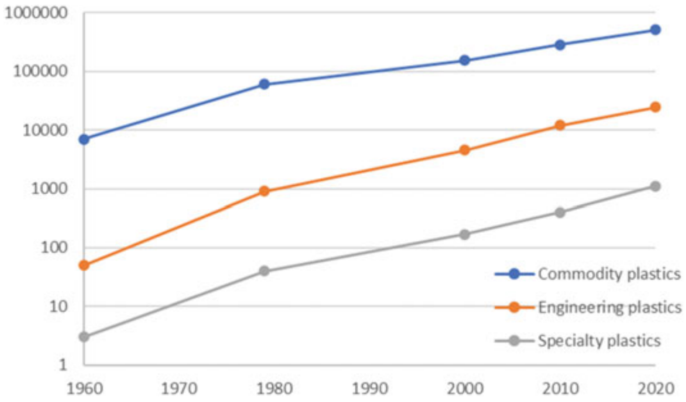


Fig. 3 World plastics' consumption over the years (data from Pardos Marketing 2020)

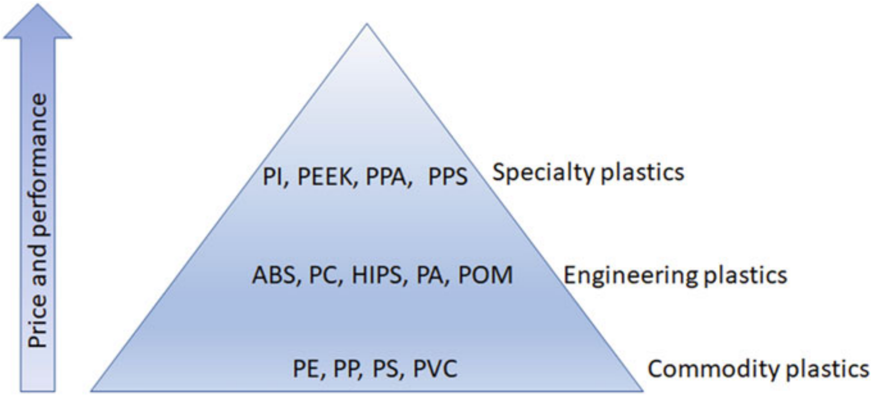


Fig. 4 Representative examples of plastics classified according to their performance properties (Kahlen et al. 2010; Crawford and Martin 2020)

moderate properties (e.g. relatively low mechanical properties). The most representative commodity plastics are polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET) (Hudson 1994; Shrivastava 2018; Crawford and Martin 2020).

Engineering plastics include polymeric materials with superior mechanical and thermal properties, such as heat resistance, impact strength, rigidity, chemical stability, flame retardancy, in a wide range of conditions compared to the widely used commodity plastics (Foy 1969; Tarantili et al. 2010; Shrivastava 2018). The term engineering plastics emerged when they gradually replaced, because of their physical properties and the operating temperature ranges, the traditional engineering materials such as wood, metals or ceramics in various applications (Crawford 2003; Melton et al. 2011; Shrivastava 2018). When they are properly formulated, they can be shaped into mechanically functional, semi-precision parts or structural components; which means that they will continue working even after being subjected to mechanical stress, vibration and hostile conditions (Peters and Arisman 2000; Melton et al. 2011). So, their premium properties, in contrast to commodity plastics, enable their use in more demanding and load-bearing applications such as in transportation, medicine, automotive market, building constructions, electrical and electronic equipment (EEE) and aircraft/aerospace (Foy 1969; Peters and Arisman 2000; Crawford 2003; Tarantili et al. 2010; Mittal 2015).

Specialty plastics, known as high-performance or advanced engineering plastics, are polymers with even higher performance (e.g. higher chemical resistance and heat stability) than the conventional engineering plastics (Crawford and Martin 2020). They exhibit useful mechanical properties at temperatures greater than 150 °C. However, due to their relatively high selling price their consumption is limited compared to the conventional engineering polymers (Parker et al. 2012). Some examples of the specialty plastics are: polyarylethersulfone (PAES), polyimide (PI), polyphthalamide (PPA), poly(phenylene sulfide) (PPS), poly(ether ether ketone) (PEEK), etc. (Kahlen et al. 2010).

2.1 General Characteristics of Engineering Plastics

Engineering plastics mainly refer to thermoplastic materials instead of thermosets; some of the most representative and widely occurring are ABS, HIPS, PC, PA (Tarantili et al. 2010), as well as their blends and composites. Their properties can be divided into appearance, mechanical, electrical and thermal properties; and are briefly described in this section. The appearance properties concern plastics' colour, gloss, haze and possible yellowness (which is related to plastics' degradation); and always tests are conducted for their quantification. These properties can often be noticed even by consumers, since a change in a material's appearance, for instance fading or yellowing, may be obvious (Mc Keen 2019).

As for the mechanical properties, most of them are affected by parameters, such as temperature, strain, humidity etc. (Mc Keen 2019). Among mechanical properties, impact strength, which has to do with plastic's ability to withstand impact forces, is a significant one. It is not an inherent property but a quantitative measure of material's ability to absorb impact energy; and it is influenced by parameters such as geometry, environmental conditions, etc. Other main mechanical properties are creep and fatigue. They are considered as long-term properties and they have to do with material's behavior after being exposed to long-term static loads and to long-term fluctuating loads respectively. The fundamental characteristic and property of the plastics that should be taken into account when are used in constructions is modulus. Specifically, despite the fact that metals can withstand an applied load for a long time—modulus can be regarded as constant; plastics are not able to do the same since their modulus will decrease with time; thus, when a product is designed modulus has to be relevant to the time scale of the loading (Crawford 2003).

Likewise, the electrical properties of engineering plastics are not constant with time, for instance, a polymer’s dielectric strength (the electric strength that an insulating material can withstand) decreases when time and temperature increase. Apart from dielectric strength, other crucial electrical properties are volume resistivity, surface resistivity, arc resistance, dissipation factor and dielectric constant. Generally, plastics are considered as electrical insulators, that insulation make them irreplaceable in various applications. Nevertheless, nowadays, the development of electrically conducting plastics seems also possible, either by coating, using a conductive coating such as carbon or metals, or by compounding, using fillers, e.g. brass, aluminum or steel, which are incorporated into the plastic (Crawford 2003; Crawford and Martin 2020). As for the thermal properties, heat-deflection temperature, which is a measure of polymer’s resistance to distortion under a given load at elevated temperatures, is a very important one. The melt flow index has to do with the measure of the ease of flow of the melt for a thermoplastic material (Mc Keen 2019). Other thermal properties that need to be defined and depend on various factors, such as temperature and structural variations, include coefficient of linear thermal expansion, thermal conductivity, as well as specific heat.

Most of the plastics’ properties are strongly dependent on temperature changes, fact owed to their molecular structure. For instance, when materials are heated, their molecules receive extra energy which increases their relative movement and make them more flexible. On the other hand, when materials are cooled down, their molecular mobility is decreased and turning them into stiffer (Crawford and Martin 2020). As a result, the melting temperature, crystallization temperature as well as glass transition temperature of plastics are vitally important and can be easily measured applying the DSC technique. Glass transition temperature (T_g) is the temperature, below which plastics are hard and rigid and their physical properties change in a manner similar to those of crystalline state where their molecules have limited relative mobility; whereas, above T_g plastics are flexible and behave like rubbery materials (Mc Keen 2019; Crawford and Martin 2020). Taking into account plastics’ dependence on temperature, it is of paramount importance to know the temperature range within each polymer can operate. For instance, PC’s maximum operating temperature is 110 °C, whereas for ABS it is 70 °C, while when plastics are reinforced with either glass or carbon fibers these working temperatures can be increased (Crawford and Martin 2020).

Another property of paramount importance is that of flammability; which isn’t an inherent property of the polymer, since it depends on various parameters and conditions. Furthermore, smoke-emission rate, flame spread, self-extinguish ability and so on, are also crucial characteristics that should be taken into consideration when designing a product (Crawford 2003). One other interesting characteristic of engineering plastics is their corrosion resistance. Generally, although plastics’ chemical resistance to, for instance, acids, solvents etc. varies from plastic to plastic, they are prone to chemical attacks and finally to degradation. Also, weathering plays a key-role, as far as the performance of plastics used in exterior applications regards. Weathering has to do with plastic’s exposure to ultraviolet (UV) radiation, which can sometimes be coupled with water absorption. Both UV radiation and water absorption affect various polymers' properties, from visual ones such as colour or haze till mechanical properties, such as strength or flexibility. Sometimes, the effects may lead to materials failure during plastics' normal use; consequently, attention should be paid to appearance changes, such as colour losses, which is usually indicative of weathering effects on plastics (Crawford 2003; Mc Keen 2019; Crawford and Martin 2020).

2.2 *Properties and Applications of the Most Representative Engineering Polymers: ABS, PC, HIPS, PA*

ABS is a very common thermoplastic material that can be easily molded. It is made by copolymerizing styrene and acrylonitrile in the presence of butadiene (Fig. 5); and in this way it combines strength and rigidity of the first two monomers with toughness, which is a characteristic of butadiene rubber. It is a tough, hard plastic with a relatively high modulus, good dimensional stability, low water absorption and good wear resistance. In comparison with nylon or acetals ABS is cheaper. However, ABS is vulnerable to exposure to chlorinated solvents, esters, ketones, acids and alkalis. Its properties can be modified and improved by changing the proportions of the mentioned monomers (styrene, acrylonitrile, butadiene). The final properties are also affected by the conditions under which the material was processed to the final product. The aging characteristics of ABS materials are influenced by the polybutadiene content and, more often than not, antioxidants are added. ABS can be used for the production of light, rigid, molded products and so it finds various applications, as in the production of pipes, automotive parts, wheel covers, helmets, consumer electronics goods, toys, sporting goods etc. (Crawford 2003; Mc Keen 2019; Crawford and Martin 2020).

PCs of numerous bisphenols have been studied, with the most commercial ones derived from bisphenol-A (BPA). BPA-based PC (Fig. 6) is an amorphous engineering polymer with a T_g ~50 °C and is characterized by outstanding toughness,

Fig. 5 Monomers of ABS

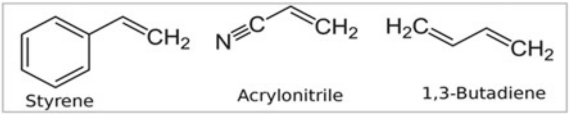
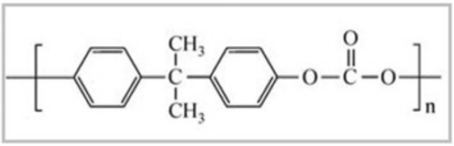


Fig. 6 Structural units of PC



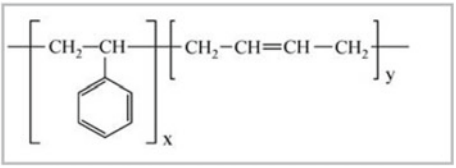


Fig. 7 Structural units of HIPS

glass-like transparency and clarity, excellent outdoor weathering resistance (which enables its exterior use), good heat resistance and good creep resistance, excellent electrical properties, as well as intrinsic flame retardancy. Nevertheless, it is vulnerable to chemical attack by alkaline solutions and hydrocarbon solvents. Due to its great properties, PC finds plenty applications in building, data storage (e.g. CDs, DVDs and Blu-ray discs), eye glasses, camera parts, LCD/LED screens, mobile phone cases and covers, light covers, automotive headlamp lenses etc. (Crawford 2003; Melton et al. 2011; Mc Keen 2019; Crawford and Martin 2020).

Polystyrene (PS) is another common thermoplastic material which can be available in a wide range of grades and impact strengths, although it is naturally a brittle material. Two common forms of PS are the general-purpose PS (GP-PS) and high impact PS (HIPS). The latter (Fig. 7) is produced when polybutadiene rubber is inserted in PS' matrix, resulting in a great reduction of polymer's brittleness and in an increased toughness. High impact grades usually consist of 6–12% of elastomer. Elastomers are inserted into the polymer's matrix with the aim of improving its impact resistance and deformation before fracture (Massey 2007; Mc Keen 2019; Crawford and Martin 2020). Polystyrene may be available in an expanded form too. Unmodified HIPS properties are affected more than those of GP-PS, when they are used in exterior applications. Specifically, solar radiation, mainly at the UV end of the spectrum, along with oxygen lead to material's embrittlement and yellowing. These changes take place mainly in the butadiene elastomer part. To overcome these difficulties, additives, such as UV stabilizers, are added in order to improve material's performance and prevent its yellowing and brittleness that could be caused because of prolonged exposure of unmodified HIPS to sunlight (Vouvoudi et al., 2017). According to the above mentioned, HIPS has greater physical performance than pure PS. This makes HIPS one of the most demanded plastics that can be used in various applications, including refrigeration accessories, small appliances, electric lawn and garden equipment, toys, remote controls, sterile applications, such as labware and medical equipment (Massey 2003, 2005, 2007; Mc Keen 2019).

Nylon or polyamides (PA) (Fig. 8) were the first commercial engineering thermoplastics due to their premium properties; since they could be tough and stiff, with

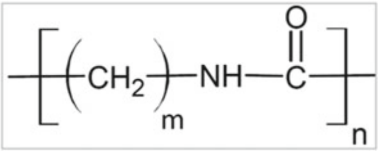


Fig. 8 Structural units of aliphatic PA

better performance in comparison to metals in some cases (Melton et al. 2011). Apart from high toughness PA also present high wear resistance, low coefficient of friction, excellent chemical resistance and low dimensional stability, because of their high-water absorption (Crawford 2003). The fact that all PA tend to absorb moisture should be taken in account when designing a product; since moisture affects not only dimensional stability but other properties as well. With the aim of overcoming this problem, glass reinforcement takes place most of the times (Crawford and Martin 2020). There are many types of nylon as nylon-6, nylon-11, nylon-12, nylon-6,6. The numeric suffixes refer to the number of carbon atoms present in the molecular structures of the amine and acid, respectively (Mc Keen 2019). Due to their unique properties PA can be used in mechanical bearing and gear applications, in automotive, in electrical and electronic equipment, in fibers (Melton et al. 2011; Crawford and Martin 2020).

2.3 Properties and Applications of Composites and Blends

Beginning with a fundamental term, a miscible polymeric **blend** consists of two or more homopolymers and appears itself homogenous down to the macromolecular level, in which the domain size is comparable to the macromolecular dimension. It is noteworthy that homogeneity at fine level is necessary for overall performance, but some degree of micro-heterogeneity is usually expected, thus blend preserves the individual properties of respective polymer components. This means, that the properties ruling the individuals may affect their blend as well. Commercial interest in blend system involves both the concepts of property combination and cost dilution. Nowadays, the majority of engineering, industrial, household, electrical, automotive, plastic parts are constructed by blends, which find themselves as waste too when their usage is over (Alston et al. 2011).

On the other hand, the incorporation of inorganic particles like silicates, glass, clays, oxides, complexes, minerals, carbon in polymer phase in various shapes, volumes or sizes makes them totally immiscible to the matrix and creates the polymeric **composite** materials. The interaction forces between the two phases are physical and may be strengthened when a coupling agent is intervened. The composite material results to be seriously reinforced in mechanical, thermal, chemical terms and more affordable in financial terms. The matrix and the filler maintain plenty of their properties separately in major terms. As previously, the application of polymeric composite materials is tremendous in all kind of fields (Mittal 2015; Crawford 2020).

3 Recycling of Engineering Plastics, Composites and Blends

The engineering plastics, considered as the fastest growing segment of the plastics industry (Melton et al. 2011), result in large volumes of waste, especially waste of electric and electronic equipment (WEEE), generated every year by the disposal of goods from these applications. Also, since plastics are resistant to environmental degradation and they are not biodegradable materials, they can remain in the environment for many years after their end of life. So, the development of recycling techniques and strategies for environmentally friendly disposal of plastic waste is necessary but challenging too (Tarantili et al. 2010; Crawford and Martin 2020). Those practices and efforts are dated back to 1990 but eventually recently have become widely-known and vastly adopted by citizens of developed countries.

The main obstacles concerning engineering plastics' recycling are the fact that they consist of various, different types of polymers and that there are many, often toxic, additives (such as UV and thermal stabilizers, flame retardants, colorants, plasticizers, fillers, reinforcing glass, carbon fibers) that are incorporated in them (Buekens and Yang 2014; Charitopoulou et al. 2020; Crawford and Martin 2020). At present, the methods applied for engineering plastics' disposal in line with the broader framework for plastic recycling (Fig. 9) are landfilling, primary recycling (recycling without quality losses), mechanical/solvent-based or secondary recycling, chemical/feedstock or tertiary recycling and energy recovery or quaternary recycling (Achilias et al. 2012; Wagner et al. 2019).

During landfilling large expanses of soil are covered with waste and polluted, due to contaminants' leaching; and since plastics are non-biodegradable materials many years are required for their natural degradation. Apart from the ground pollution, the

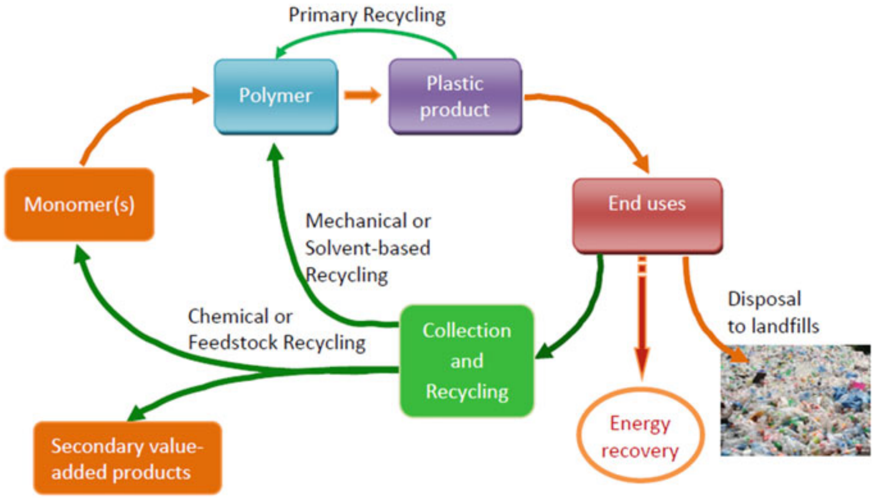


Fig. 9 Disposal techniques applied to engineering plastics (Achilias et al. 2012)

groundwater can also be contaminated, resulting in huge environmental pollution (Nnorom and Osibanjo 2008; Anuar Sharuddin et al. 2016). As a result, landfilling has become an undesirable disposal method and researchers' interest is many years now attracted by recycling methods for engineering plastic waste safe handling. Landfilling rates are very uneven across Europe; in countries where landfill bans are in effect (e.g. Belgium, Netherlands, Germany, Denmark, Switzerland, Austria and Sweden) less than 10% of plastic waste is landfilled, in other countries, such as Spain and Greece, a surprising amount of over 50% of all plastic waste still finds its way to landfill (Ragaert et al. 2017).

However, before their recycling, engineering plastics have to undergo some preprocessing steps, which involve manual dismantling, and mechanical treatments. There should take place sorting and dismantling of the plastic waste in order to separate the reusable parts and then mechanical particle size reduction follows (Khaliq et al. 2014; Marra et al. 2018; Maisel et al. 2020).

3.1 Primary Recycling

Primary recycling is the direct reuse of the uncontaminated discarded polymers into new products without loss of properties. In most cases, primary recycling is conducted by the manufacturer itself for internal industrial waste and it is often termed "closed-loop recycling", also known as re-extrusion. During this method the plastic process scrap is re-introduced in the heating cycle of the processing line in order to increase the production. However, only plastic scrap with similar characteristics to the original products can be used. It's a simple and low-cost method; but it can only be applied to clean (or semi-clean) uncontaminated single-type waste (Al-Salem et al. 2010, 2017; Achilias et al. 2012). The latter requirement limits its applicability.

3.2 Mechanical Recycling

Mechanical or secondary recycling is a technique in which engineering plastics are reprocessed through mechanical means to form new products, with nearly the same or lower performance in comparison to the initial products. It is applied to homogeneous plastics, so heterogeneous plastic waste needs to be separated and sorted before mechanical recycling takes place. Several sorting techniques have been employed including: manual sorting by trained operators, flotation (or float-sink separation), a density-based separation technique, melt filtration, tribo-electric (electrostatic) separation, froth flotation, magnetic density separation, X-ray detection and use of FT-NIR (Fourier Transform Near Infrared), which is one of the most widely used techniques for the automated sorting of plastics (Ragaert et al. 2017).

In this category the solvent-based recycling falls too, where specific solvents are used to dissolve the polymer of interest and further recover it using a re-precipitation technique. This method can be applied to multilayer structures also.

Mechanical recycling is employed worldwide and in a large scale for industrial use. Its main drawbacks are the fact that during every cycle the product's properties are deteriorated (Achilias et al. 2012). Specifically, their mechanical properties are usually reduced due to a decrease in the molecular weight owing to chain scissions. This can take place either by increased temperatures and prolonged times (thermo-mechanical degradation) during re-melting or the existence of even low amounts of foreign substances such as water. Thus, each polymer can endure only a specific number of reprocessing cycles. The latter explains the reason why mechanical recycling is also known as downgrading or downcycling (Rahimi and García 2017).

An additional challenge in the mechanical recycling is the existence of mixed plastic wastes (containing polymer blends). Different polymer types have different melting points and processing temperatures. When reprocessing these mixtures, usually the processing temperature is set to the highest melting component, which often leads to overheating and possible degradation of the lower melting components resulting in reduced final properties (Ragaert et al. 2017).

The mechanical recycling of engineering plastics is further complicated by the presence of certain brominated flame-retardants like pentabrominated diphenyl ethers (PBDE) or decabrominated diphenyl ethers (DBDE) which have been banned as additives for new products. It is thus very important to identify if flame-retardants are incorporated in plastics; since in case that they are present during mechanical recycling, toxic substances, such as dioxins or furans, may be formed (Yang et al. 2013; Ma et al. 2016; Charitopoulou et al. 2020).

3.3 Chemical Recycling

Chemical recycling is also known as tertiary or feedstock recycling. During this, engineering plastic wastes are converted into lower molecular weight products (such as monomers, secondary valuable chemicals and fuels) through chemical reactions (Fig. 10). Chemical recycling includes various techniques such as hydrolysis, glycolysis, thermolysis etc. It is considered as an environmentally friendly and economically feasible approach, taking into account that the recovery and exploitation of monomers or useful chemicals is possible in this way (Yang et al. 2013; Ma et al. 2016; Sahin and Kirim 2018). Although this method is mainly studied on laboratory scale since large amounts of energy are consumed (Rahimi and García 2017), it has attracted researchers' interest due to the plenty advantages it offers (Ma et al. 2016); and for this reason, the next section presents in detail all current techniques of chemical recycling that can be applied to engineering plastics.

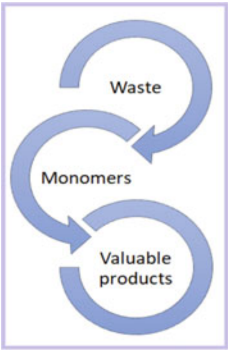


Fig. 10 Conversion of waste into monomers and secondary valuable products via chemical recycling

3.4 Energy Recovery by Incineration

Energy recovery or quaternary recycling is a method in which plastic waste is incinerated in order to take advantage of the high energy value of polymers. The aim of incineration is to recover the plastics' energy content in the form of heat and electricity. In many countries in Europe, it is the most common method of utilizing discarded plastics since it can be used especially for processing of mixed and heavily contaminated wastes, which cannot be recycled easily and/or economically by any other method (Ignatyev et al. 2014). The energy content of typical plastics including polyolefins is nonetheless comparable with heating oil. Nevertheless, attention is needed during this method, since if incomplete incineration of plastics occurs toxic substances (dioxins, polychlorinated biphenyls, and furans—PBDD/Fs) may be released into the atmosphere (Achilias et al. 2012; Yang et al. 2013; Ma et al. 2016).

4 Chemical Recycling of Engineering Plastics: PC, HIPS, ABS

During chemical recycling, engineering plastic materials are converted into smaller molecules that can be used as feedstock for the production of new chemical products. This method has more advantages (Fig. 11) in comparison with primary recycling, mechanical recycling and energy recovery), such as the fact that it can be applied to heterogeneous and contaminated polymers with only a limited pretreatment prior to it having required. Many engineering polymers seem to be advantageous for such recycling method; for instance polyamides: nylon-6 and nylon-6,6 can be efficiently depolymerized so as to produce monomers that can be either used as feedstock or for monomer recycling (Al-Salem et al. 2009).

Chemical recycling comprises two main routes (Fig. 12) solvolysis and thermolysis. During solvolysis, polymers are dissolved in a solvent and are treated with or

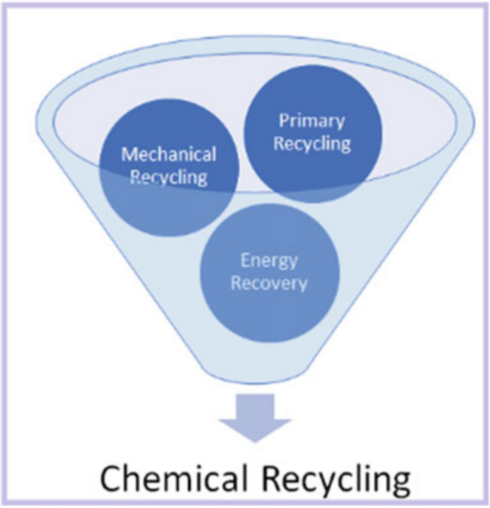


Fig. 11 Chemical recycling vs other recycling techniques

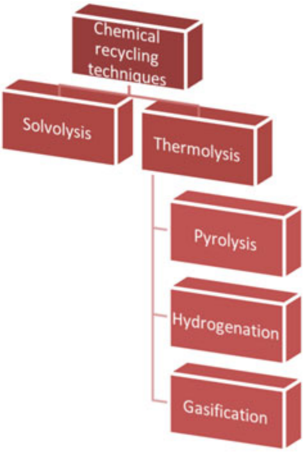


Fig. 12 Chemical recycling techniques

without catalysts and initiators. It can also be used as a pretreatment prior to thermo-chemical processes such as pyrolysis. During thermolysis, polymers are heated in an inert atmosphere (e.g. N_2 atmosphere) in the absence of air, oxygen or vacuum. It consists of various processes including (thermal and catalytic) pyrolysis, gasification and hydrogenation (Vinu et al. 2016; Sahin and Kirim 2018).

During pyrolysis thermal cracking of polymers occurs in an inert atmosphere at high temperatures. Many pyrolysis studies have been carried out applying different temperatures (from 300 to 900 °C); and it was found that usually the optimum pyrolysis temperatures for plastic waste were between 500 and 550 °C. Moreover, different heating rates varying from 4 to 25 °C/min as well as different retention times for pyrolysis process were examined, with the goal of optimizing the process (Zhao et al. 2011; Velghe et al. 2011; Chen et al. 2014; Miandad et al. 2016). Pyrolysis can take place in the absence (thermal pyrolysis) or presence of catalysts (catalytic pyrolysis). During pyrolysis, engineering plastic waste is converted into liquids, gases and solid residues (chars) (Vinu et al. 2016; Sahin and Kirim 2018). Pyrolysis of engineering plastics occurs through the following mechanisms (Sahin and Kirim 2018; Yang 2020):

- Depolymerization: where polymers are consecutively broken down into their monomers from the end groups
- Random chain-scission: where the chain of the polymer (e.g. PA) breaks down randomly and later leads to fragments with irregular length and different carbon numbers
- Chain-stripping: side groups or reactive substitutes on the polymer chain are eliminated
- Cross-linking: evolution of a chain network in the presence of heat, with cyclization or cross-linking reactions occur; generally, it appears at thermosetting polymers

During hydrogenation or hydrocracking large hydrocarbon molecules are converted into lower molecular weight products. The whole process occurs in hydrogen atmosphere, high pressure (approximately 100 atm) and at moderate temperatures between 150 and 400 °C (Sahin and Kirim 2018).

During gasification partial oxidation or indirect combustion of polymers at high temperatures (up to1600 °C) and in the presence of oxygen occurs. It leads to the formation of two main products: CO and H_2. This mix of gas can be used either in order to run a gas engine or to be finally converted into hydrocarbon fuels via the Fischer–Tropsch process. More often than not, deriving condensable liquids or petrochemicals as the main products is the desirable goal. Since this pyrolysis is favoured over gasification, in case of gasification multiple steps are needed in order to obtain liquid products (Vinu et al. 2016; Sahin and Kirim 2018).

4.1 Pyrolysis of Engineering Plastics

Generally, pyrolysis seems to be one of the best choices as regards engineering plastic waste recycling. Some of its plenty advantages include the both material and energy recovery from polymer waste, considering that only ~10% of the energy content of waste is consumed for its conversion into valuable hydrocarbon products (Brebu et al. 2004; Liu et al. 2016). Also, in case that flame retardants are incorporated in plastic waste, through pyrolysis the formation of toxic substances, such as dioxins and furans, may be suppressed, since it is performed in the absence of oxygen (Liu et al. 2016).

Pyrolysis process and especially the quality of pyrolysis products and their distribution, strongly depend on various parameters including temperature, heating rate, residence time, operating pressure, the presence/absence of catalysts etc. Pyrolysis temperature is considered as one of the most crucial parameters; since when high temperatures (>500 °C) are applied, the formation of gases and chars is favoured, whereas when lower temperatures (between 300 and 500 °C) are applied the liquids are enhanced (Charitopoulou et al. 2020). The presence/absence of catalysts plays a vital role in the whole pyrolysis process and the products distribution too. The conventional (or non-catalytic) pyrolysis, contrary to catalytic pyrolysis does not promote the cracking reactions abetted by the catalyst; thus, there is high potential for obtaining liquids with better quality and commercial value, at lower temperatures and times in comparison with thermal pyrolysis (Panda et al. 2010).

4.1.1 Conventional Pyrolysis of Engineering Plastics

Non-catalytic pyrolysis of a number of engineering polymers has been reported in literature, where different temperatures, residence time and others were applied. One of the most studied polymers is HIPS, whose degradation follows the random chain-scission mechanism. According to Ojha and Vinu (2015), it yields styrene (monomer) as the major pyrolysis product, along with styrene dimer (such as 1,2-diphenylpropane, 1,10-diphenyl-1,3-butadiene, etc.), trimer and in less grade other aromatic compounds. When slow pyrolysis conditions are applied, the formation of styrene monomer, dimers and trimers increases with time. In another study (Antonakou et al. 2014) pyrolysis of HIPS and PC took place at 600 °C and the products formed were in accordance with the previous study; since they found that HIPS pyrolysis resulted in the formation of single ring aromatic compounds (mainly toluene, styrene) and few aromatic compounds with two rings (mainly styrene dimer). As for PC, after its pyrolysis, phenolic compounds were detected, including single ring phenolic compounds (such as phenol, 4-methylphenoland 4-ethylphenol, 4-isopropyl and isopropenyl phenols) and phenolic compounds with two rings (which include the monomer (phenol, 4,40-bis(1-methylethylidene)).

From the results of this investigation (Antonakou et al. 2014) it is important to highlight that the distribution of pyrolysis products is dramatically affected by the nature of the polymer that is being pyrolysed. For instance, in case of PC the total gas yield was higher than that in case of HIPS. Also, as it was mentioned, there were noticed differences in the liquid fraction too. Particularly, the liquid fraction obtained after PC's pyrolysis consisted mainly of phenols, whereas that of HIPS was rich in aromatic hydrocarbons. As a result, apart from pyrolysis temperature whose effect was presented before, the polymers' type strongly affects the products' distribution as well. The latter observation leads to the conclusion that it may be beneficial to pyrolyze engineering plastics after a first separation of the kinds of polymers participating.

Likewise, pyrolysis of PA leads to the formation of other types of products; a wide range of N-containing compounds (such as amines, amides and nitriles), CO_2, unsaturated and cyclic hydrocarbons. For instance, pyrolysis of nylon-6 produces mainly ε-caprolactam, acyclic amides, CO_2, nitriles, whereas pyrolysis of nylon-6,6 is more complex. In the latter case the products obtained consist of N-containing compounds

Table 1 Major pyrolysis products of HIPS, PC, PA and ABS

Polymer	Major pyrolysis products
HIPS	Styrene, styrene dimers (diphenylpropane), trimers, toluene and other aromatic hydrocarbons
PC	Phenolic compounds with one aromatic ring (4-methylphenol, 4-ethylphenol, 4-isopropylphenol and 4-isopropenylphenol) and phenolic compounds with two rings
PA	N-containing compounds (amines, amides and nitriles), CO_2, unsaturated and cyclic hydrocarbons
ABS	acrylonitrile, acetonitrile, toluene, ethylbenzene, styrene, α-methylstyrene

mostly, CO_2, cyclopentanone and many unsaturated and cyclic hydrocarbons of low molecular mass (Bozi and Blazso 2009).

Additionally, pyrolysis of ABS leads to the formation of various other products. Brebu et al. (2000) examined the pyrolysis of ABS applying different pyrolysis temperatures, found that plenty products were obtained, including acrylonitrile, acetonitrile, toluene, ethylbenzene, styrene, isopropyl benzene, α-methylstyrene and others. They underlined the importance of the temperature in which the degradation occurs, since it significantly affects the rate of the evolution/transformation of compounds along with the amount and the quality of the derived pyrolysis oils. Furthermore, they found that by changing the atmosphere (*e.g.* N_2 dynamic atmosphere) or the residence time the products of ABS degradation were greatly affected.

In most cases the derived pyrolysis products are comprised high added-value chemicals (aromatic hydrocarbons, phenols, etc.) that can act as feedstock in petrochemical industries. So, judging by the products obtained, pyrolysis can indeed be considered as an environmentally friendly and sustainable method. In Table 1 some of the major products derived after thermal pyrolysis of the mentioned engineering polymers are shown. Nevertheless, one representative category of additives found in polymers is that of flame retardants and especially, brominated flame retardants (the most commonly used of the kind) which can lead to the production of various, toxic brominated substances in the liquid fraction obtained by pyrolysis. This is undesirable since in this way the liquid fraction cannot be reused.

In such cases pretreatment steps, before or during pyrolysis, are of great importance in order to gain bromine-free products; and have been well studied. One of the most common pretreatments used prior to thermal pyrolysis for identification and removal of (brominated) flame retardants is solvent extraction. Usually, it takes place through *soxhlet* extraction, which is a popular method due to its low cost, despite the fact that large amounts of solvents and much time are required (Covaci et al. 2003; Vilaplana et al. 2009). Apart from the typical *soxhlet* extraction, many advanced solvent extraction techniques have been developed over the years. Some of them are supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), ultrasonic assisted extraction (UAE) and microwave-assisted extraction (MAE), which demand shorter time and lower volumes of solvents (Vilaplana et al. 2009). To overcome the mentioned difficulties when plastics are flame retarded and in order to obtain high-quality oils, researchers (Bhaskar et al. 2007; Ma et al. 2019) have also examined other approaches, such as two-step pyrolysis of plastic waste. Their results indicate that pyrolysis steps can affect the obtained products and in that way, by controlling pyrolysis parameters, the formation of brominated hydrocarbons can be minimized.

Co-pyrolysis is also a worth mentioning process, in which two or more materials are pyrolyzed together with a view of improving the quality and quantity of the liquid fraction without the use of catalysts or solvents. What makes this process worth referring is the fact that it takes advantage of the synergistic effect of different materials (for instance polymers) which can react together during pyrolysis, resulting in a reduction of the total volume of waste (Abnisa and Wan Daud 2014). This method is used for the reduction of bromine (in case that brominated flame retardants are present in plastics) in the liquid pyrolysis fraction too. For instance, Ma et al. (2015) examined co-pyrolysis of HIPS, which contained brominated flame retardants, in the presence of PP to investigate the latter's effect on the bromine reduction. They found that the presence of PP enhanced the reduction of bromine, affected positively the products distribution and in the meanwhile more waste (PP) was treated.

4.1.2 Catalytic Pyrolysis of Engineering Plastics

For catalytic pyrolysis specifically, lower temperatures and shorter times are needed and as a result less energy is consumed during the process. Furthermore, the quality of the derived pyrolysis products is greatly improved, since the selectivity is enhanced and the formation of undesirable products is limited (Aguado et al. 2006). Due to the advantages they offer, various catalysts have been examined for pyrolysis of engineering plastics, including silica-alumina, zeolites (HZSM-5, zeolite-Y, HUSY etc.), mesoporous catalysts (MCM-41), metal based catalysts, fluid catalytic cracking (FCC) catalysts and minerals (Ma et al. 2016; Vinu et al. 2016). In Table 2 some of the most widely examined catalysts for each engineering polymer are presented. Moreover, various reactor types including batch, flow, fixed bed and tubular, autoclave reactors have been used in laboratory and in large scale experiments (Buekens and Huang 1998; Sahin and Kirim 2018).

Table 2 Most commonly used catalysts for pyrolysis of HIPS, PC, PA and ABS

Polymer	Commonly used catalysts
HIPS	Zeolites: HZSM-5, Hβ, HY, iron oxide–loaded HY zeolite, iron oxide–loaded natural zeolite; mesoporous: all-silica MCM-41 and active Al_2O_3 etc.
PC	Zeolites: HY, HZSM-5, iron oxide–loaded HY-zeolite and iron oxide–loaded ZSM-5 etc.
PA	Zeolites: HZSM-5, Hβ and HY etc.
ABS	Zeolites: HZSM-5, Hβ, HY, iron oxide–loaded HY zeolite and iron oxide–loaded ZSM-5 etc.

Among the mentioned catalysts, zeolites are the most widely used, since they promote the formation of aromatics, during catalytic pyrolysis of N-containing polymers such as ABS and PA (Vinu et al. 2016). Of course, their properties vary depending on the zeolite type. For instance, HZSM-5 catalysts enhance the formation of olefins (original monomers) while Hβ and HY catalysts favour the production of middle distillates (Castaño et al. 2011). Generally speaking, the catalysts' properties affect the selectivity and distribution of pyrolysis products. Some of the most crucial properties of catalysts are the total specific surface area, the micropore area, the pore diameter and the pore size distribution, the acidity or basicity and the ratio Si/Al for zeolite type catalysts (Vinu et al. 2016). Since more often than not, engineering plastics contain flame retardants, in this paragraph of the chapter, some examples of catalysts that were examined not only for favouring valuable products but also for reducing undesirable too, there are presented.

In a recent work (Ma et al. 2017) three zeolites (HY, Hβ and HZSM-5) as well as two mesoporous (all-silica MCM-41 and active Al_2O_3) catalysts were investigated for their effect on products distribution, after pyrolysis of HIPS that comprised brominated flame retardants. Pyrolysis was held in a fixed bed reactor at 410 °C. They found that in the presence of the examined catalysts, the main pyrolysis products were aromatic compounds (toluene, styrene etc.) which are valuable chemicals; and moreover, that the presence of the catalysts enhanced the debromination of the liquid fraction. Wu et al. (2015) examined small-scale two-stage pyrolysis and catalytic reforming of flame retarded HIPS at 500 °C and they used four zeolites: natural zeolite, iron oxide–loaded natural zeolite, HY zeolite and iron oxide–loaded HY zeolite. They observed that the liquid fraction mainly consisted of phenolic compounds (toluene, ethylbenzene, styrene etc.) which are valuable products and that all catalysts contributed to the reduction of bromine in the oils obtained.

Areeprasert and Khaobang (2018) studied pyrolysis and catalytic reforming of a polymer blend (ABS/PC) at 500 °C, using conventional catalysts: Y-zeolite, ZSM-5, iron oxide–loaded Y-zeolite and iron oxide–loaded ZSM-5, and some alternative green catalysts: biochar, electronic waste char, iron oxide–loaded biochar and iron oxide–loaded electronic waste char. They found that all catalysts increased the single-ring hydrocarbon products of the liquid fraction and enhanced its debromination. In addition, they concluded that the green–renewable catalysts could be a promising choice for removing bromine from the liquid fraction. Ma et al. (2018) investigated pyrolysis-catalytic upgrading of flame retarded ABS. The process took place in a two-stage fixed bed reactor and the examined catalysts were HZSM-5 and Fe/ZSM-5. Both catalysts had high catalytic cracking activities that led to an increased yield of oil and to a reduction of the bromine in the liquid fraction, which contained aromatic compounds, such as toluene, ethylbenzene, styrene etc. From the results obtained they concluded that Fe/ZSM-5 catalyst significantly promoted the formation of styrene monomer and dimer derivatives, and in the meanwhile, exhibited effective debromination performance.

4.2 Other Thermo-Chemical Recycling Methods

Other thermo-chemical recycling methods used for plastics recycling include (Ragaert et al. 2017):

- Hydrocracking or hydropyrolysis: The main difference of this method in comparison to pyrolysis is the addition of H_2. The process takes place at elevated hydrogen pressures, nearly 70 atm and temperature ranging from 375 to 400 °C.
- Gasification: This is a process where almost every feed composed of organic material is converted into a gaseous mixture containing mainly CO_2, CO, H_2 and CH_4. The mixture of carbon monoxide and hydrogen is the so-called Syngas. The process requires an oxidation agent, usually a mixture of steam and pure oxygen or air. Syngas may be further transformed to CH_3OH via a catalytic process.

4.3 Treatment of Polymeric Blends or Composite Materials

A very important issue regarding the effective recycling of plastics has to do with how clean the plastics stream is. Meaning that reprocessing of mixed polymer waste or polymer composites poses quite a few challenges. The removal of metal, glass or paper parts of items can happen in the first step for a better waste management. Only manufacturing waste (10% of total waste) is mainly formed of a single material and since they are not contaminated (or less purified) with other materials, its recycling is easier. Typically, these wastes are reintroduced into production lines (secondary recycling).

In case waste is easily manageable (consists of mix or blends of polymers in macroscopic or microscopic scale) what follows is the direct transformation of the mixture without prior sorting, in order to reduce the volume of waste. Despite the chemical nature of the two components of the blend being theoretically similar/close, the processing may significantly change both the structure (e.g. from linear to branched polymer) and the composition (e.g. introduction of unsaturations or moieties) that can prevent the formation of a homogeneous material afterwards. For example, the tensile properties of ABS/r-ABS blends decreased during the first reprocessing, even by adding the smallest amount of r-ABS (La Mantia and Scaffaro 2014). This is why current trends in purchasing polymers in market impose the labeling “r-” in name. Another example for blends is the r-PC/r-ABS blends which may also include PMMA as a third component, it was found to have a dramatic effect on the morphology (La Mantia and Scaffaro 2014).

On the other hand, when microscopic mixtures or intimately connected (soldered, interpenetration) units occur, the separation of constituents is difficult or even impossible, requiring complicated operations. In that category the organic matrix composites belong eventually. The most representative example is the waste from the automotive industry where thermoplastics are found along with polymer mix, fibers, fillers and multilayer composite materials (Sabău 2018).

Sorting of waste is done according to the basic polymeric material. The following steps are (a) Shredding (size reduction), (b) Separation of metals, (c) Spraying (washing waste) (d) repeat of some stages if necessary. The target is to achieve high degrees of purity in feedstock and advanced technological processes to improve the quality, productivity and competitiveness of industrial products.

The thermochemical recycling in that category of feedstock may, also, be divided into three main categories:

Pyrolysis: This process consists of the thermal degradation of organic materials between 400 and 800 °C. The mater in the absence of O_2 decomposes, producing gases (hydrocarbons, NH_3, HCl) up to 50%, plus 25–40% of oils and the lasting residues.

Hydrogenation: The material is processed in a H_2 atmosphere at 300 to 500 °C and pressures of 100 to 400 bar, to yield 65–90% oils, 10–20% gases and up to 20% of solid residues.

Cracking: The material is heated at 400 to 600 °C, and at pressures slightly above atmospheric, to produce oligomeric waxy liquids suitable for further catalytic cracking. The gases formed are used to fuel the process itself (Pinto and Rossi 2003).

5 Conclusion and Future Perspective

The present text briefly presents all categories of thermoplastics: commodity, engineering and specialty plastics, depending on their performance properties and their market share. Emphasis though is given on engineering polymers, their blends and composites, due to their superior properties that are fully described. Some of the most representative engineering plastics including ABS, PC, HIPS, PA are mentioned, along with their properties and their applications, such as automotive applications, electrical and electronic goods, toys, sporting applications, etc. However, since they find many applications, because of their premium properties, there has been a rise in volumes of end-of-life engineering plastics. Consequently, finding environmentally friendly and sustainable ways for their recycling is of paramount importance, but very difficult too. The main difficulty as regards their recycling lies in the fact that they contain different types of plastics and many, often toxic, additives (such as flame retardants which are very common additives).

All the current methods for engineering plastic waste's disposal: landfilling, primary recycling, energy recovery, mechanical recycling and chemical recycling are discussed in this chapter. Chemical recycling is thoroughly presented, since it offers more advantages in comparison to the other mentioned techniques, and has attracted a lot of attention over the last decade. Pyrolysis is a chemical recycling technique during which plastic waste is converted into valuable products that can be further used as fuels or feedstock for industries. It can take place in the absence (thermal) or presence of catalysts (catalytic). Both methods are investigated and various studies on pyrolysis of engineering plastics, along with their derived products are presented. Furthermore, since the quality of pyrolysis products and their distribution depends on various parameters such as pyrolysis temperature and others, they are also analyzed here. Last but not least, taking into account the fact that engineering plastics usually comprise flame retardants (mainly brominated ones), pretreatment processes (such as solvent extraction) or co-pyrolysis are described too. Development of recycling technologies should be coupled with research on the combination of both the most effective and environmentally benign developments.

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Recycling of Waste Rubbers into Value-Added Products

Sandeep Pandey, Manoj Karakoti, Gaurav Tatrari, Sunil Dhali, Satish Chandra Sati, and Nanda Gopal Sahoo

Abstract Rubbers and plastics are the widely used polymeric materials for various kinds of applications such as automobiles, packaging, constructions, material handling, sports and toys etc. Because of long durability and ease of manufacturing rubbers and plastics are vigorously used in last decades. However, long term durability of these materials becomes a serious issue for the environment and treated as hazardous waste polymeric materials at the end of their life. Still these polymeric materials, showed the extensive critical problems due to unfruitful management. Among these, rubber waste is exponentially increase in past few year because of revolutionary changes in automobile industry and dependency of human over the automobile. To overcome this issue, land filling and combustion are the most employed traditional methods used for the disposing and treatment of rubber waste, respectively. Although, these methods showed several disadvantages such as evolution of toxic gases, dust, fumes and water pollution etc. Hence, the whole world is looking out for some of the best promising solutions to utilize these polymeric waste materials into value added products. In this regard, recycling and upcycling of rubber waste into value added products such as thermoplastic elastomers (TPE), value added fuels, additive materials for construction and carbon nanomaterials. Upcycling of waste rubbers into TPE showed one of the methods to get the value added products, however the incompatibility and immiscibility of the rubber based additives in polymer matrix show poor mechanical performance. On the other hand, upcycling of waste rubbers into value added fuels and carbon nanomaterials showed a potential remediation process for a wealthy management of rubber waste, while another way of recycling use of rubber waste in construction materials. Although whatever be recycling and upcycling process were suggested by various researchers, still a deep insight is urgently needed in order to confront the upcoming challenges of

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the rubber waste. Thus, the present chapter describes the detailed recycling and upcycling processes, challenges and future recommendations regarding the management of the rubber waste.

Keywords Waste Rubbers · Recycling techniques · Pyrolysis · Nanocarbon · Value-added products

1 Introduction

Today, almost all the automobile, construction, packaging and sports industries are depends upon the polymeric materials due to their ease of manufacturing, durability and cost effectiveness. Among, various kinds of polymeric materials, rubber has gained significant attraction due to ease of manufacturing, durability and elastomeric properties. Because of the elastomeric properties, rubber has the capability of reversible deformation, which is again considerably influenced by the nature of rubber. The chemical and physical properties of the rubber based materials have decided its elastomeric properties and consequently type of applications of the rubber. Apparently, there are 25 kinds of rubber materials are present including natural rubber, silicone, styrene-butadiene rubber (SBR), fluorocarbon rubber, ethylene-propylene-diene monomer (EPDM) rubber, nitrile-butadiene rubber, polyurethane and so on. These rubbers are widely used in various types of end products such as seals, gaskets, sports goods, diaphragms and tubes etc. (Fazli and Rodrigue 2020). Tire industries are the one of the most dominant sector of the rubber based goods which covers more than 65% part of the total rubber industries (Marín-Genescà et al. 2020). Generally, car tyres composed 42–48% of rubber, 24–28% carbon black, 12–16% metal, 4–6% textiles and about 9–12% additives (Rajan et al. 2006; Akiba and Hashim 1997; Sienkiewicz et al. 2012). However, the quality of the rubber based materials in various kinds of tires also decides the application of the rubber in different kind of automobile industries, which in turn of it depends upon the process of vulcanization and types of stabilisers, anti-oxidants and anti-ozonants (Ramarad et al. 2015; Karger-Kocsis et al. 2013; Ikeda et al. 2018). The addition of various kinds of fillers, antioxidants and curating agents enhances the life of the tires by increasing the resisting power from photochemical decomposition, biodegradation and temperature based degradation. Although, high quality rubbers gives various fruitful products to tire and automobile industries, but the end life of these products becomes a serious and alarming situation due their non-biodegradable nature (Fukumori et al. 2002). Thus, the management of waste rubbers has become challenging issue due to the large quantity of the rubber based products and scrap tires. According to the global estimates, only 3–15% rubber waste is recycled at the end of its life cycle, while 5–23% waste rubber were reused for the development of new products with improved properties. An approximate 25–60% waste rubber were used for energy recovery and about 20–30% waste rubber were sent for worst option of landfill or stockpiled (Forrest 2014). Figure 1 is showed the pictorial representation

Fig. 1 Picture depicted waste rubber landfill (Reprint with the permission of IJSBE 2015) (Rashad et al. 2016)

of the current situation of the tyre waste stacks and also exhibited is alarming situation. Although the accurate data regarding the handling of rubber waste is difficult to find, but the current situation is showed that various efforts has been made in order to confront the problem of waste rubbers. However, the nature and properties of the rubber based goods also defined the end use of the rubber waste i.e. the microstructural composition of the rubber also decide the end use of the rubber based goods. The most common rubber materials are used in the rubber industries are briefly discussed in the next section.

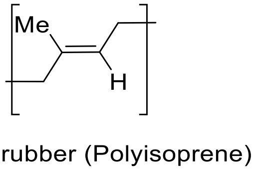


Fig. 2 Chemical structure of natural rubber

1.1 Commonly Used Rubber Materials

1.1.1 Natural Rubber (NR)

Natural rubber (NR) is one of most commonly used rubber in rubber industries. It is basically originated form a vegetable origin *Hevea brasiliensis*. Chemically natural rubber is a kind of biopolymer with the chemical formula of cis-1, 4-polyisoprene which is basically formed by the monomer unit of isoprene. NR possessed high elastic properties (Tg ~ −70 °C), which makes it a viable for various applications of tyres, gloves, sports goods and erasers etc. Because of highly flexible structural properties, NR can be easily elongated reversibly in under high deformation, although the rubber industries always followed the process of vulcanization for NR to get a highly rigid 3D network of rubbers, so that NR based goods can be used for soft to hard applications. However, due to very poor stability in the presence of oxygen and ozone, the direct implementation of NR becomes difficult and hence addition of fillers and other stabilizers were introduced (Niyogi 2007; Mente et al. 2016; Massey 2006) (Fig. 2).

1.1.2 Styrene-Butadiene Rubber (SBR)

The chemical backbone of SBR consist the copolymers of styrene and butadiene. The preparation of the SBR was mainly done by free radical copolymerization method in presence of emulsions and anionic copolymerization method in presence of various kinds of solvent system. The properties of the SBR mainly depend upon the styrene content and the skeleton of the polymeric chains. Generally, SBR is mostly vulcanized under various kinds of sulfur agents. Because of low mechanical strength of SBR, various reinforcing fillers were introduced within the matrix of the SBR. SBR is regarded as one of the most commonly used rubber for various kinds of automobile applications. Because of its high thermal stability, abrasion strength and high resistance ability against the crack formation, SBR is showed its high potential for tyre industries (Wypych 2016; Massey 2006) (Fig 3).

Fig. 3 Chemical structure of SBR

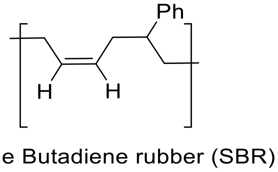
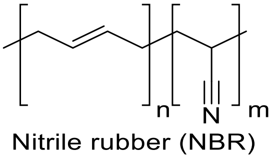


Fig. 4 Chemical structure of NBR



1.1.3 Nitrile-Butadiene Rubber (NBR)

Basically, the chemical backbone of the NBR is consists acrylonitrile and butadiene units as well as synthesized by their radical copolymerization at low temperature range of 5–30 °C. The structure of NBR is generally depends upon the method of preparation and the branching molecules as well as temperature of copolymerization process. Further, the glass transition temperature (Tg) of the NBR is basically depend upon content of acrylonitrile within the NBR. NBR is generally showed low tensile strength because of low crystallization rate under stress, although it showed very high resistance power towards to the non-polar solvents, oils and various kinds of motor fuels. Because of its high resistance power towards various oils and fuels, NBR is widely used for the oil transport equipments, sealing tubes and other similar oils resistive appliances (Massey 2006) (Fig. 4).

1.1.4 Polyurathane (PU)

Polyurathane is regarded as another widely used rubber which is explored in variety of automotive and electric industries. PU is generally synthesized by polyaddition of polyols and diisocynates. Depending of the types of monomers for the synthesized, different kinds of PU can be obtained with varying properties. Because of high tensile strength, good abrasion, low friction coefficient and high resistive power towards the oxygen and ozone. Thus, PU is widely used in electric lines, flexible connections, and automotive industries (Akindoyo et al. 2020) (Fig. 5).

1.1.5 Ethylene-Propylene-Diene Monomer (EPDM)

EPDM is regarded as one of the most versatile used synthetic rubber used for the application of sealing materials. Chemically, EPDM is regarded as a terpolymer with having ethylene, propylene and non-conjugated diene units, where non conjugated

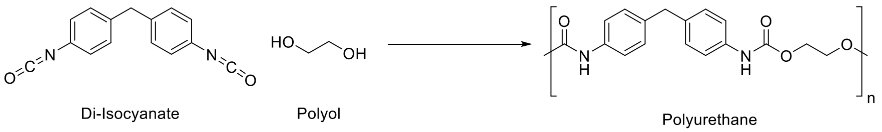
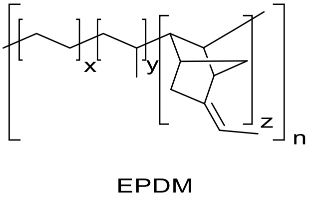


Fig. 5 General route of the synthesis of polyurethane (PU)

Fig. 6 Chemical structure of EPDM



diene is generally attached with a residual unsaturated side chain. Comparatively, EPDM is showed better resistive power towards the oxygen and ozone than the NR and SBR because the presence of unsaturated side chain. However, the properties of the EPDM depend upon the content of ethylene and propylene unit within the matrix of EPDM. Because of the high resistive properties towards the oxygen and ozone upto 150 °C, EPDM is widely used for the high temperature sealing applications. Figure 6 is showed the chemical structure of EPDM (Massey 2006; Morton 2013; Mitra et al. 2009; Milani and Milani 2011, 2012).

1.1.6 Silicone Rubber

Silicone rubber is mainly used for the application of tubing for the safe transportation of the ozone. Silicone rubber is showed very high stability over the wide range of temperatures i.e. −7 to 250 °C. Basically silicone rubber is also known as siloxanes and generally prepared by the hydrolysis and condensation of dimethyldichlorosilane in the acidic medium, while some other routes are demonstrated the acid or base catalytic preparation via ring opening polymerization of cyclotetrasiloxane. The backbone of silicone rubber consist the chain of silicon and oxygen atoms as shown in Fig. 6. Further, silicone rubber is also used for various kinds of medical applications due to its highly biocompatible nature and hence regarded as ideal material for medical implants and other kind of medical devices which are directly associated with human beings (Niyogi 2007; Morton 2013; Percec et al. 1989) (Fig. 7).

Although, the natural and synthetic rubbers are showed variety of applications, but still management of rubber waste has become a great challenge across the world due to the vast amount rubber goods are used. Although various recycling techniques have been demonstrated, but only few of them are capable to work in ground level. In the next section we will discusses about the different kinds of the recycling techniques which are for the rubber and polymer based waste materials.

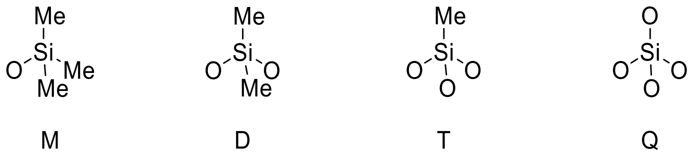


Fig. 7 Different kinds of polysiloxanes showing the various types of chemical skeletons (M represents trimethylsiloxychlorosilanes (Me_2SiO), D represents Me_2SiO_2, T represents Me_2SiO_3, Q represents SiO_4)

2 Various Recycling Techniques

The recycling technology was came into existence in early 1980, when several European nations are targeted towards recycling of carbonic polymers viz rubbers and plastics etc. (Kim and Pal 2010; Epro statistics 2018). The recycling process is regarded as the process of recovering of materials with or without significant change in its chemical structure (Schonmayr 2017). There are four types of recycling technologies which are mainly based on the methodological processing and qualitative production of value added products (Fig. 8).

2.1 Primary Recycling

The recycling of singular polymers having possession near to original material is called primary recycling or re-extrusion also known as closed loop technique (Kumar

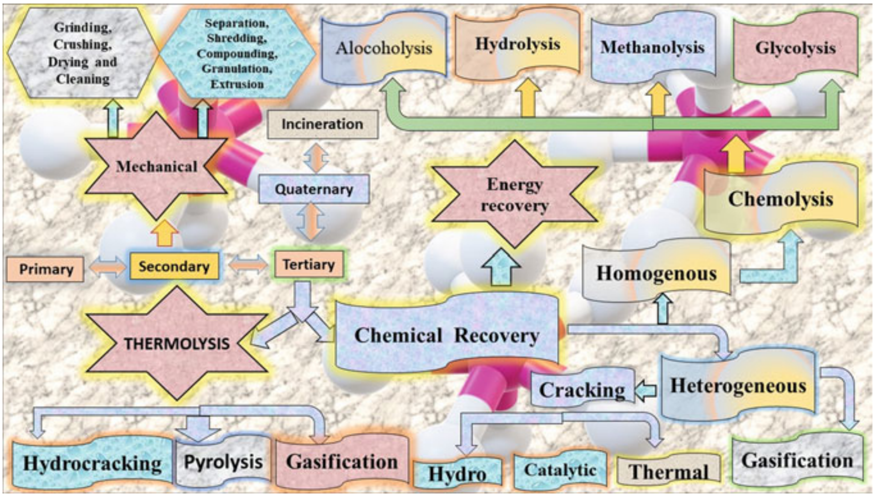


Fig. 8 Different kinds of rubber recycling technologies

et al. 2011; Al-Salem et el. 2009; Sadat-Shojai and Bakhshandeh 2011). Usually the process is done by cleaning and mechanically removing the contaminations. The primary recycling sometime may provide better materials than the virgin one, the technique often regarded as primitive or traditional way to recycle the polymers (Sadat-Shojai and Bakhshandeh 2011). However, the process is quite popular in industries due to its simplicity and conversion rate to virgin products. The procedure includes comparative molding through injection and mechanical recycling, although the procedure may fluctuate for the production of qualitative products (Barlow 2008).

2.2 Secondary Recycling

The processing of materials into less demanding products through mechanical way of recycling is called secondary recycling technique (Kumar et al. 2011). The processing of secondary recycling is involves cutting, grinding, mechanical separation and floating separation technique for separation of polymeric flakes (Aznar et al. 2006; SubsTech 2006), Further, the rubbers or polymers are processed to form granulates, then washing and drying are step needs to be followed in order to make appropriate purifications. The obtained products sometimes may be sold by the addition of some sort of pigments or additives. Whereas, the singular polymeric materials were processed for the formation of pellets through extrusion before final product is achieved (Kumar et al. 2011; Al Salem et al. 2009). The secondary recycling technique is include different procedures i.e. screw extrusion, injection molding and blow molding etc.

2.3 Screw Extrusion

The rubber polymers, plastic waste, leather and agricultural waste including food waste can be processed through extrusion method (Mikulionok and Radchenko 2012). However, currently double and single screw extruders are available in the market particularly for recycling according to the nature of precursors (Hopewell et al. 2009). The extruders with mutable shapes, sizes and operative procedures are available (Frame 1994). In this procedure the polymeric form can be converted into its new structure by heating up to its melting point. Briefly, the precursor material placed into barrel container, then heating is required up to its melting point, further allowed to process through a die with distinct dimensions to make final product as per the shape of die. The instrument mainly is consists of tools such as hopper, cylindrical barrel, screw, die head and motor. Hopper is used to barrel the materials under gravity, usually the barrel is aligned to heaters for the optimization of different temperatures. As heating is processed, screw is used to process the substance into die. The parameters such as length of barrel and speed of screw are important aspects for appropriate processing as well as for qualitative production. Too low and too high speed of screw can cause multiple effects on the recycling process, it will either over melt the polymer or it will not form completely (Sombatsompop and Panapoy 2000). Multiple heating zones are responsible for steady rise in the temperature of polymer. The process is fairly important for the uniform mixing of the material.

2.4 Tertiary Recycling

The tertiary recycling process is comprised of energy sustainability as the major involvement. The process regenerates all precursors from which the processing materials are made. The methodologies followed in tertiary recycling techniques are pyrolysis, cracking, gasification and chemolysis. These processes followed the basic principle of de-polymerization of polymer into its monomers. In essence, thermal recycling and chemical recycling are the two major techniques available. The depolymerization process can be done through solvents via solvolysis and through heating via thermolysis, however if the thermolysis process is done in the absence of air is called pyrolysis. While if done in precise atmosphere it is called gasification, similar degradation approach in presence of glycogens or ethylene glycols is called glycolysis, whereas in catalytic presence of methanol it is known as methanolysis (Kumar et al. 2011).

2.5 Quaternary Recycling

The quaternary recycling is most authenticated process to recycle polymeric products into their monomeric structural forms. The quaternary recycling is also known as energy recovery process which goes through incineration and other similar approach (Scott 2000). The process projects are involves in volumetric reduction of the waste materials (Kumar et al. 2011). Further, the obtained crude oils from such method is processed many time to get extremely high calorific value of the oil which is comparable to traditional fossil fuels i.e. petroleum and diesel (Dirks 1996). Hence, above conversation is draw very sensible line and explains why? not to use waste landfill sites as the solutions of environmental rubbers polymer pollution (Singh et al. 2017). Actually the necessity is to resolve the matter with appropriate scientific recycling techniques.

3 Applications of the WTR Recycling

3.1 Waste Rubber as an Alternative Source for Traditional Fuels and Chemicals

The waste rubber especially the waste tyre pyrolysis at 45–250 °C which leads to the complex mixture of crude oils that might contains aromatic, aliphatic and polar functional groups or heteroatoms. Significantly, reported and identified content from the pyrolysis of tyre waste are includes chemicals such as benzene, Toluene, xylene, limonene and styrene (Williams 2013). The obtained oil from pyrolysis of tyre waste is usually consists of various aromatic hydrocarbons and their derivative incorporated with heteroatoms, thus become quite difficult to outcast them from the crude mixture. Nearly, every researcher has utilized GC–MS and FT-IR techniques as the toolkit for the identification and analysis of compounds presence in such waste. The FT-IR can only determine the functional moieties of any materials on the other hand GC–MS is visualizes nature and type of compound present, but still more than half of the compounds are remained anonymous (Miandad et al. 2018). The oil is obtained from pyrolysis of waste rubbers or tyre cannot be directly used as the fuel in combustion processed as it consists sulfur's content, which may cause corrosive outcomes by the production of sulfur dioxide. A recently study is showed that the efficiency of formic acid having pH 4.0 and hydrogen peroxide with 25 vol% for the removal of sulfur from crude oil (Bunthid et al. 2010). They have reported 70% removal in the sulfur content due to absorption over the surface of carbonic material. Initially, the obtained oil was categorized into low oil with having the boiling point of 45–205 °C, middle oil with having the boiling point of 205–300 °C and heavy oil with having the boiling point over 300 °C. The low oils have reported with higher octane number thus could be used for combustion process after hydro refining and reforming. While the other fuels can be used directly as fuel added to petroleum refineries or its quality can be improved using the different organic catalysts. The pyrolysis of tyre has been done by one of the researchers group and compared the obtained fuel with diesel; they have concluded that these fuels can replace the diesel in smaller engines (Islam and Nahian 2016). Thus the pyrolysis of rubbers or waste tyre can be very suitable option for futuristic solution of waste rubbers problem which can easily help and regain its cost value through production of valuable fuels. Along with this, the obtained fuel can also serve as a good source of chemicals production, which will add more value into rubber's pyrolysis (Williams 2013).

3.2 Pyro-Gas

The pyrolysis also leads some of the combustible gases as the byproducts along with fuels and char. While, the heating value of pyrolytic gas is around 2900 J/g, as the waste tire obtained gases are usually consist of mixture of several olefins, carbon oxides, hydrogen, small amount of sulphur and nitrogen compounds (Czajczyńska et al. 2017). From all of them, hydrogen is acts as the most efficient and excellent replacement for traditional fossil fuels, mainly due it has high energy density as well as it is carbon-free energy and almost zero emission of greenhouse gases (Srilatha et al. 2017). Lately, several research groups are exploring the mass production of hydrogen from waste tires that can act as excellent replacement of fossil fuels (Lerner et al. 2012, Zhang et al. 2015). Recently, a group of researchers have reported the synthesis of carbon nanotubes along with hydrogen gas from waste tires by using Ni/Al_2O_3 as the catalyst for the two step pyrolysis in a fixed bed reactor (Zhang and Williams 2016).Thus, the bulk scale industrial production of hydrogen gas by utilizing waste tyre rubber as the useful precursor which can be deal with universal waste tyre problems.

3.3 Ground Tire Rubber Recycling for Insulator Applications

The recycling of the rubbers sometimes becomes difficult to handle because of their complex chemical and physical properties. For instance, vulcanized form of the rubbers is showed the difficulty in recycling due to their crosslink structures (Cañavate et al. 2010), hence the vulcanized form of the rubbers is need to special attention for effective recycling. In this regard, recently attention has been driven towards the use of the waste tyres into polymeric matrix as filler material to enhance their chemical and physical properties. This way of utilization of the waste rubbers as ground tyre rubbers (GTRs) not only reduces the foot-print of the rubber waste, but it also significantly reduced the cost of the final products. In this process, firstly, waste rubber materials are shredded (ground) into very fine particles, generally in micrometer size and then mixed with the different kind of polymers, virgin rubbers, automotive components, sports goods and several other applications (Rodgers and Waddell 2011; Behnood and Olek 2017). Especially, thermoplastic blends with GTR showed huge sustainability and cost effective preparation methods (Cañavate et al. 2011; Liu 2000; Orrit-Prat et al. 2011). However, still there is a huge challenge to mix these GTRs with polymers with uniformity due to compatibility issues. It is reported that compatibility issues are arose significantly when the amount of mixing of GTRs in polymeric blends enhances more than 20% (Colom et al. 2007; Mujal-Rosas et al. 2011, 2014). Recently, demonstration of the utilization of the GTR for the application of the insulator as per the Spanish UNE standards was reported by a group of researchers (Genesca et al. 2020). This group have mixed the GTR having a particle size of 200 μm with the matrixes of polyvinyl chloride (PVC), ethylene vinylacetate (EVA) copolymer, polypropylene (PP), high-density polyethylene (HDPE), polyamide 6 (PA 6), acrylonitrile butadiene-styrene (ABS) and polystyrene (PS). Five specimens of for every selected polymer were prepared in different amount (0, 5, 10, 20, 40, 50 and 70%) of GTR and blended within a Brabender mixing machine for 4 min at various temperatures. Finally, the polymer/GTR blends were prepared in film form by using a hot plate press with a pressure of 100 KN at various temperatures. The whole test was carried as per the standard ASTM-D0638-V standards. After the preparation of the blends, electrical properties of the polymer/GTR blends were investigated by determining the conductivity, loss factor (Tg δ) and electrical resistivity. Results obtained after the investigation are showed that mixing of the GTR with the selected polymer exhibits a good insulating properties as UNE and IEC standards. Further, results demonstrated by this group are showed that the insulating properties of the polymer/GTR blend decreased significantly with high content of GTR > 10%. For low content of GTR i.e. (5–10%), electrical insulating properties showed sufficient value of the electrical insulation for the use of the different kinds of electrical insulation applications. Further, among all polymer/GTR blends, EVA-GTR is showed promising insulating properties (Table 1).

Table 1 The summarized electrical properties and analyzed applications for the selected polymer blend

Components analyzed	Electrical criterion	Mechanical criterion	Application standard	Polymer + GTR suitability
Insulation for electrical shepherds	Conductivity $<10^{-12}$ S/cm, T_g δ $< 10^4$	Tensile strength: 12.5 MPa, elongation at break: 300%	ITC-BT-39, 22, 23, 24 UNE-EN 60,335-2-76 IEC 60,335-2-76	EVA + 10%
Spacer for power lines	Resistivity: $>5.5 \times 10^5$ Ω cm	Minimum tensile strength: 17.2 MPa Minimum elongation at break: 300%	IEC 61,854	EVA + 20%
Universal electrical cable joint	Resistivity: $>10^{12}$ Ω cm	Tensile strength: 12.5 MPa Elongation at break: 400%	IEC 60,840 UNE HD 628	EVA + 10%
Filler for electrical applications	Resistivity: $>10^{12}$ Ω cm	Tensile strength: 12.5 MPa Elongation at break: 350%	UNE 53 602; UNE 53 510; UNE-HD 632; UNE-EN 60,811-4-1	EVA + 10%
Trays and pipes for electrical cables	Resistivity: $>10^{12}$ Ω cm	Elongation at break: 80 ± 10% Tensile strength: 15 MPa	UNE EN 61,537 UNE EN 50,085-1: IEC 61,537 (EN 61,537)	PP + 10% EVA + 10%
Footwear for work use (insulating) Insulating: High electrical resistance	Resistivity: $>10^6$ Ω cm $>10^9$ Ω cm	Tensile strength >10–12 MPa Elongation at break > 450%	UNE-EN ISO 20,345/6/7:2005 UNE 53,510	EVA + 10%

3.4 Nanocarbons from Tyre Waste

Several researches have been conducted regarding the upcycling of waste tyres rubbers (WTRs) into value added products. Among the variety of value added products from WTRs, synthesis of the nanocarbons has shown tremendous interest among researchers due to their invincible properties and applications. In this regard, pyrolysis approach has refocused by the researchers in which the development of the nanocarbons was done in presence of the several catalytic systems. The pyrolysis of the WTRs in the temperature range of 400–600 °C in the oxygen free medium forms oil, gas and carbon char (Kordoghli et al. 2017) in which the produced oil can be used in various kinds of automobile and other similar industries, while the gas thus produced can be used to run the pyrolysis plants. The carbon char is another value added product which was generally used as source of the solid fuel, carbon black or sometimes upgraded in the form of activated carbon (Williams 2013). However, despite of the tremendous applications of the carbon derived from WTRs, still limited research were done on the re-establishment of the carbon value from WTRs. The nano-allotropic forms of the carbon such as carbon nanotubes, graphene nanosheets, nanocarbons and other similar forms are showed tremendous interest among researchers in the recent two decades (Mittal et al. 2015; Vilatela and Eder 2012). These materials are possesses extraordinary electrical and mechanical properties, high surface area, high transparency, unique 1D, 2D and 3D dimensions, porosity and many other high value added properties, because of which today most of the material scientist are working in the field of carbon nanomaterials. Today these materials are widely used for the development of the highly efficient supercapacitors, batteries, solar cells, fuel cells and for many other fields (Zhang et al. 2019; Lee et al. 2018; Cui and Maruyama 2019; Chou et al. 2014; Fang et al. 2019). In the year of 2004, synthesis of carbon nano particles were done by pyrolysis method (Ding and Olesik 2004), while another research is showed the synthesis of carbon nano particle through microwave plasma catalytic chemical vapor deposition (CVD) technique in which iron (Fe) and nickel (Ni) were used as a bimetallic catalytic system (Yu et al. 2002). Electrolysis process for the synthesis of the carbon nanoparticles was also reported in which electrolysis process was performed by using carbon electrode in molten alkali halide salts (Hsu et al. 1996). Various approaches have been done in order to synthesize variety of the nanocarbons from different kinds of sources; pyrolysis approach is still regarded as one of the best method for the mass scale production from carbon based precursor materials. Several research groups have been reported the synthesis of nanocarbon from WTRs by slow pyrolysis technique over a temperature of 900 °C (Jang et al. 2002; Cormia et al. 1962; Mileva et al. 2012; Cuesta et al. 1998; Sing 1985; Nieto-Márquez et al. 2011; 2009a, b, 2010). Recently, fast pyrolysis of the WTRs was demonstrated to synthesize carbon nanoparticles (CNPs) with a sustainable approach (Maroufi et al. 2017). Fast pyrolysis of the WTRs was carried in the temperature range of the 1550 °C at the time period of 5 s–20 min. The CNPs thus produced were reported about 30–40 nm in diameters as analyzed by FESEM images (Fig. 9).

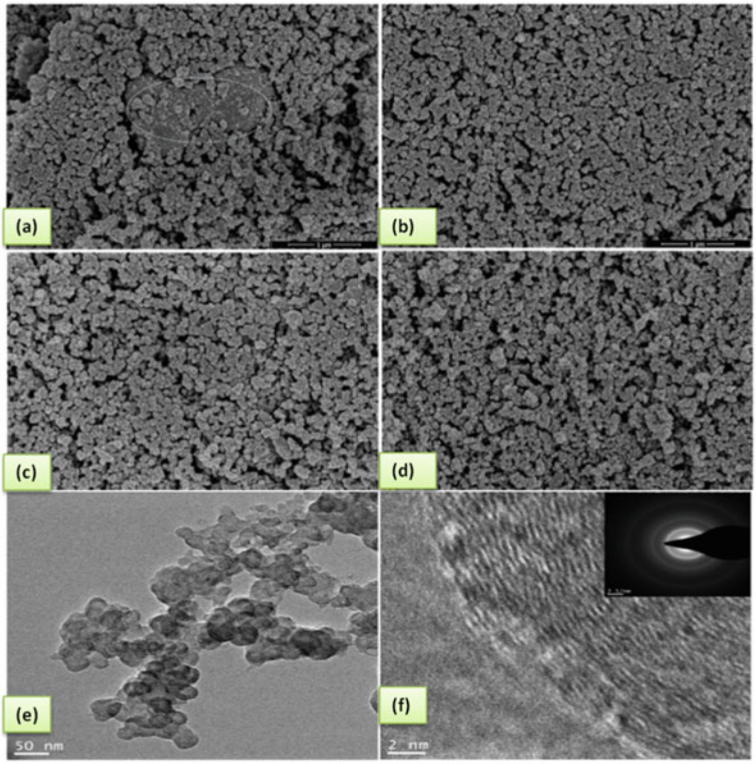


Fig. 9 FESEM images **a**–**d** and TEM images **e**–**f** of the rubber derived CNPs at the temperature of 1550 °C, where FESEM images is captured for the sample processed at **a** 5 s, **b** 5 min, **c** 10 min, and **d** 20 min. Reprint with the permission of Elsevier 2017 (Maroufi et al. 2017)

The fast process depicted in this work was reported as sustainable process, as this process lower downs the production of the toxic gases. The only drawback associated with this process is the demand of the high temperature which consumes high amount of the energy, but as the process depicted time saving and environmentally friendly technique, the process can be adapted for the mass scale production of the CNPs from WTRs. Another work on the nanocarbon was also showed by a group of researchers, where they reported the synthesis of CNTs from scrap tyres by using CVD techniques (Yang et al. 2012). This work demonstrated the use of the cobalt based catalytic system for the growth of the CNTs. The SEM and TEM images of the CVD processed scrap tyres over the catalytic system are showed that the obtained product mainly exist in the form of CNTs, although they have not mentioned the average length and diameter of thus obtained CNTs from scrap tyres (Fig. 10).

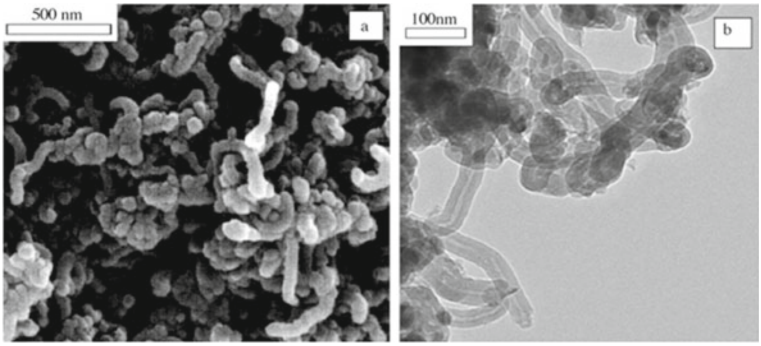


Fig. 10 **a** SEM image of scrap tyre derived CNTs and **b** TEM image of scrap tyre derived CNTs. Reprint with the permission of Elsevier 2012 (Yang et al. 2012)

3.5 Waste Rubbers to Supercapacitors

Renovated recycling of waste tyre or rubbers to respective valuable products initially came into existence as relative solution for the global energy crisis. In this regard, a group of researchers have utilized the crushed and chopped waste tyres as the precursor to get activated carbon (AC), where potassium carbonate (K_2CO_3) was used as the material activator (Bello et al. 2018). Five samples were prepared for the activation with variable weight ratio of the material. Further, they have done mechanical mixing of K_2CO_3 powder with each sample before processing into tube furnace for pyrolysis. The horizontal tube furnace was used for the processing of material at 800 °C, while creating inert atmosphere by passage of nitrogen for 1 h. The obtained material was further washed until they get completely neutral pH of material. The activated carbon appeared with excellent mesoporous structural framework having surface area of 147–385 $m^2\ g^{-1}$. AC was further utilized as the active material to fabricated electrode for supercapacitor device that displayed excellent discharge capacity of 50 $mAh\ g^{-1}$ at 0.25 Ag^{-1}. Redox electrolyte 1 M $K_3Fe(CN)_6$–1 M HNO_3 was mediated as electrolytic medium to get specific capacitance from respective device that showed corresponding specific capacitance of 140 $F\ g^{-1}$ at 0.25 $A\ g^{-1}$, while the energy efficiency of retained around 70% for 1000 cycles. Another group of researchers were derived carbon onion from tyre waste, further incorporated the carbon onion with sulfur doped polyaniline (PANI) nanotubes ornamented with self-designed hierarchical $Ni(OH)_2$ sponge for supercapacitors application (Bhaumik et al. 2020). The designed architecture of mesoporous $Ni(OH)_2$ over PANI nanotubes and carbon onions produced exceptional composite with excellent electrochemical potential for supercapacitors. Briefly, the fabrication process starts with development of slurry by the homogenous mixing of tyre derived carbon material with PANI, $Ni(OH)_2$, carbon black and the binder polyvinylidene fluoride (PVDF) in weight ratio of 80:15:5 while anhydrous N-methyl-2-pyrrolidone (NMP) acts as the solvent. Further they have coated the obtained slurry over nickel foam in mass of 3 to 7 mg and overnight oven drying at 60 °C for the fabrication of electrodes. They have used 3 M KOH as the electrolyte and the porous Whatman filter paper as the separator. Thus fabricated device is showed excellent specific capacitance of 622 F g^{-1} at 2 A g^{-1} along with extraordinary retention capacity of 97% over 10,000 cycles. The device delivered huge energy and power density of 70 Wh kg^{-1} and 136 kW kg^{-1}, respectively. The extraordinary cyclic stability may be due to corresponds the synergetic binding of nano sponge $Ni(OH)_2$ with PANI nanotubes on carbon onion's surface, which stabilizing the volume changes upon cycling. The work is depicted that of waste tyre derived carbon onions as excellent the value added product for supercapacitor application. Similarly, synthesis of hierarchical and porous carbon from scrap rubber for methane storage and supercapacitor electrodes were also reported (Li et al. 2020). They have used KOH as the activator for the activation followed by pyrolysis approach. In brief, waste rubber scrap was heated upto 1000 °C under inert atmosphere with heating rate of 5 °C /min for 1 h. The obtained materials were grinded and mixed with KOH in 4:1 ratio. Further, the materials were allowed to activate by KOH under inert atmosphere for 2.5 h at different temperatures viz. 650, 750, 850 and 950 °C in pyrolysis furnace. Finally, for the removal of metallic impurities the carbonic material was washed by 1 M HCl solution followed by double distilled water until the pH of removed liquid became neutral. The temperature variation is tailors the structure and morphology of the obtained activated carbon which excel the input for high performance energy and methane storage. The electrode device was fabricated by preparing the slurry of activated carbon, polyvinylidine fluoride (PVDF) and carbon black in the ratio of 85:10:5 while using N-methyl 2-pyrrolidone (NMP) as the solvent. The slurry of thus prepared material was casted over nickel foam having surface area of 1cm^2. The mass loading of 3–4 mg/cm^2 was allowed for electrodes fabrication and further they were oven dried at 105 °C for next 12 h under 10 MPa. Fabricated device was exhibited excellent specific capacitance of 167.7 F/g at 0.5 A/g, while the storage capacity of 110.39 F/g was obtained for the sample having highest surface area along with micro porous structure. The obtained hierarchical and porous activated carbon based fabricated electrode unveiled decent rate capacitance retention of 86% with 40 times increase in charge/discharge current density (Li et al. 2020). One of the groups of researchers have treated rubber wood waste with H_3PO_4, NaOH and further used the obtained material as supercapacitors electrode material (Thubsuang et al. 2017). Briefly, rubber waste was chopped in square shape. Samples were dried in oven at 105 °C for 24 h to eliminate moisture. Then, 30 gm of sample was soaked into 300 cm^3 NaOH or H_3PO_4 solution. Further, pyrolysis was done at 800 °C with heating rate of 5 °C for 4 h underneath nitrogen flow of 600 cm^3/min. The synthesized porous carbonic material was washed thoroughly by double distilled water until the pH become 7 followed by oven drying at 105 °C for next 24 h. Now, the device was fabricated having two symmetric carbon electrodes, graphite rods, 1.0 M sulfuric acid aided as working electrodes, current collector and electrolyte, respectively. The mass loading of 0.18–0.22 g was done over the representative surface area of 2.25 cm^2. Polyester sheet was used as the separator for the developed carbon electrodes and acts as the in between bridge. The

CV plots were plotted after the performance testing over the potential window of 0.0–1.0 V at the scan rates of 1, 5, 10, 20, 50, and 100 mV/s and showed excellent specific capacitance of 129 F/g and volumetric capacitance of 104 F/cm^3. From this discussion it can be concluded that the volume of pores and the average size of pores along with specific surface area play very crucial role in capacitance storage mechanics of the supercapacitors (Thubsuang et al. 2017; Zhi et al. 2014). The chemical activation of carbon usually enhances the surface area and also reduces the presence of any pollutant as it causes the separation in between layers of carbon. However, very rare reports are available on rubber derived activated carbon as electrodes for batteries, supercapacitors and fuel cells. Waste tyre derived carbon have high surface area, excellent porosity, huge electrical conductivity and also have delocalized π electrons which make it highly approachable candidate for energy storage applications (Sathiskumar and Karthikeyan 2019).

3.6 Waste Tyres Recycling for Wastewater Treatment

Activated carbon and other forms of the nanocarbons were exhibited significant attention for due to their excellent efficiency for the removal of pollutants from waste waters. Because of the high surface area and porosity of activated carbon has shown tremendous interest for the water purification properties (Bhatnagar et al. 2013; Khan et al. 2019). Because of high carbon content present in rubbers, activated carbon can be produced in bulk amount. In this regard, a group of researchers have used waste tires to obtain activated carbon framework and used them for the absorption of the methylene blue dye and reported higher absorption rate of tire obtained activated carbon in comparison to commercially available activated carbon (Dimpe et al. 2017). Further, another group of researcher reported have that waste rubber material can be used for qualitative production of activated carbon by physical vapor deposition (PVD) through steam and carbon dioxide along with chemical activation by H_2SO_4, KOH, H_3PO_4 for several applications especially for industrial wastewater and air treatments (Shah et al. 2006). Pesticides removal such as methoxychlor, methyl parathion and atrazine were also reported by the utilization of the waste rubber tire derived activated carbon. This work is showed that activated carbon from waste rubber tire acted as cost effective sorbent in comparison to the commercially available carbon as well as showed better efficiency for the pesticide removal than the other similar commercially available products (Gupta et al. 2011). This group is also reported the efficient removal of chromium (III) from waste water by utilizing the activated carbon derived from waste rubber tire (Gupta et al. 2013). Thus, it showed an effective approach for the development of cost effective routes for the removal of the chromium (III) type heavy metal ions from waste water, while at the same time it showed a way of the confronting waste rubber disposal methods.

3.7 Cementing Applications

Waste tire-based rubber (WTR) has become critical problem to the global ecology due to abundance in their productivity and excessive utilization in the human society. Although, disposal of WTRs usually include diverse pathways to manage the situation around the globe, mostly by landfilling and burning (Siddique and Naik 2004; Weiguo et al. 2013). However, such practice causes hazardous effects onto the universal health system, ecological growth and socio-economical outcomes (Weiguo et al. 2013). However, WTR and their counterpart materials can be utilized into different construction applications. Also, they can be used as the replacement of natural aggregates in concrete mixture which will not only utilize the waste rubbers as useful products but can also act as the relatively eco-friendly approach to deal with such huge environmental crisis. But different kinds of waste rubber derived materials have diverse properties like as random stiffness, flexibility, particle size and particle shape etc., which affect the properties of materials with which they get incorporated (Eiras et al. 2014; Shu and Huang 2014; RMA, USA 2014). Various researchers have reported excellent properties and good utilization potential of WTR as additional aggregates for the cementing concrete mixture. However, the basic properties that get affected by the incorporation of such WTR and based materials with cementing concrete are the abrasion resistance of cementing concrete mixture along with thermal conductivity and chemical resistance (Benazzouk et al. 2006). WTRs and their counterparts such as rubber derived carbon nanomaterials (CNMs), porous carbon, micro rubber etc., can be used in cementing mixtures as the replacement of fine aggregates (FA). Concrete mixture with WTR and their counterparts as the incorporating agent display asymmetrical structural network with porous morphology (Bassuoni and Nehdi 2007). The electron microscopy (SEM) image was displayed the vacant space inside the structural network of WTR based concrete and concluded the decrement in the composites density while increasing the amount of WTR and based material, as they have lighter structural networks which can trap the cementing mixture. Also, they have reported the developed composite material depicts good sound absorptivity due to waste rubber-based material was shows excellent porous nature ((Bassuoni and Nehdi 2007). Furthermore, rubber-based composite can so diverse mechanical strength from higher to lower, as the composite with 5% WTR was shows nearly 85% compressive and 96% flexural strength in comparison to virgin concrete. WTR based composite was depicts plastic failure at higher distortion resistance that occurs due to overloading of composite material beyond its ultimate tensile strength (Thomas et al. 2015). However, addition of some chemicals as the binder along with rubber or by using rubber based CNMs in place of only WTR can be used to enhance the properties such cementing composite. However, coatings of concrete surface with limestone along with silica fumes can enhance the interaction between concrete mixture and WTR based materials on mixing, this can also improve the total strength via decreasing capillary based absorption of the materials (Thomas et al. 2015). WTR based concrete mixture was exhibits good durability thus can be used into shielding plasters. These distinguishing properties are basically due to better hydrophobic characteristics of WTR based concrete mixture in comparison to the conventional ones, however their performance can be increased by modulating the quantity of WTR based materials (Gonen 2018). A group of researcher was examined the penetration of chloride ion in WTR based concretes and they have noticed 56% enhancement in chloride ions penetration on replacing 12.5% of fine sand by WTR and its counterparts as suspension in concrete composite (Rivas-Vázquez et al. 2015). Similarly, the chemical reactions can be prevented between alkali metal and silica by little bit addition of WTR based materials. In addition, the damage is happen during the drying and shrinkage which can also be prevented by addition of WTR and its counterparts to the concrete mixture (Thomas et al. 2016).

Although, in some physical properties such as shrinkage properties the incorporation of WTRs with lower stiffness can play vital role, which can reduce the cracks number due to shrinkage as well as reduces the internal constrain (Khyaliya et al. 2017). Though, addition of WTRs to cementing concrete reduces their elasticity modulus, shrinkage stress which can also regulator their shrinkage cracks up to certain extent, using WTRs as the replacement in the fine aggregates (FA) by 20% can expand the shrinkage cracking resistance of the material (Thomas et al. 2015). Some mechanical properties of WTR based concretes like as compressive strength can be modulated by addition of rubber or derived materials in the cementing concrete mixture. Roughly, 4–70% of reduction in compression strength has been observed in cementing concrete containing WTR with 5–50% of fine aggregates, the sizes of fine aggregates particle may vary from 0.075 to 6 mm (Fraile-Garcia et al. 2016; Ramdani et al. 2019). However, complete reduction in the compression strength by incorporating WTR based cementing concretes depends upon the mechanical and structural properties, also on the percentage replacement level of WTR (Ganesan et al. 2013). The decrement in the compressive strength of WTR based cementing concrete while enhancing the WTR content is mainly due to lower adhesion rate among WTR and the cementing concrete, because here WTR acts as the space which regulates and lowers the density of material (Pham et al. 2018; Ganesan et al. 2013). A group of researcher was reported microscopic observation and confirmed the presence of voids along with cracks in rubber added concrete which indicate very weak bonding between rubber and cement (Mishra and Panda 2015). Further, studies this was showed that grounded WTRs can also used as fillers for the partial replacement of the natural sand in concrete mixtures. One of the study was showed the effect of the crumbed rubber in concrete based pavements where the crumbed rubbers were mixed with concrete based pavement as rubber sand (Mohamaddi et al. 2014). The study was showed that concrete based pavement with crumbed WTRs at the weight% of 20 and 40% could hold themselves strongly without the shattering of pieces even after the sudden occurrence of the failure cracks (Fig. 11).

Further, some additional effects may include the compressive and tensile stresses developed with the surface modeling of WTR particles closed to the cementing concrete such stress arises due to softness in of WTR particles started close to the joint of WTR particles and cementing concrete.

Fig. 11 Effect of the rubber sand on concrete cracking failure test in concrete based pavements, **a** zero rubber sand, **b** 20% rubber sand, **c** 40% rubber sand. Reprint with the permission of Elsevier 2014 (Mohamaddi et al. 2014)

4 Challenges and Realistic Solutions

Although, several technique has been identified in order to recycling waste rubbers, but still there is huge information and technological gap present, because of which only few percentage of the waste rubbers has undergone for the recycling. Still proper characterization of the rubber waste has not established because of which full proof concept and real time waste rubber recycling is lacking behind from the laboratory scale derived concepts. Especially, situation sounds more problematic when the choice of recycling techniques goes in wrong direction. For example, pyrolysis of the waste rubbers is leads to the formation of the oil, gas and carbon which are later on used for variety of the applications. But without proper knowledge of the chemical properties of the rubber based materials, the production of the value added products may suffer which causes loss of time and money both. Another disadvantage is seen from the development of established large scale pyrolysis plants where still extraction and disposing of the toxic gases has become a challengeable question. Further, still a deep research on the upcycling of waste rubber is on the back row which must be taken seriously in order to bring out some novel technologies for ecology and economical sustainability. Hence a proper solution must be extract in order to take out all possible recycling technologies in ground level. Policy makers, governmental authorities and researchers must have made a single window channel where the real time solution can be carried out for a sustainable future. One of the solutions can be meeting out by establishing proper industrial symbiosis between the industries and users. As discussed in previous sections, various recycling techniques have been developed such as WTR derived nanocarbons for energy harvesting and cementing applications. These two fields are the most emerging field of twenty-first century, hence recycling methods may be driven in these sectors, where a possible industrial symbiosis and cost benefit analysis can be meeting out according to the conservation of “EEE” i.e. Energy, Ecology and Economy.

5 Conclusions and Future Prospective

The present methods of disposal and recycling of the waste rubbers has driven the attention of the various researchers towards the search of the cost effective solutions to get the value added products from different kind of the waste rubber materials. The degradation time of the end products from rubbers has taken longer time, because of which several environmental problems are growing day by day. Especially, the vulcanized form of the rubbers which are currently involved into variety of the automobile products has shown difficulty in recycling due to their cross-linked structure. Hence, various another routes have been explored in recent years for the potential recycling of the rubber based goods. The present chapter is descried variety of the rubbers, their chemical structure and the possible route of recycling of these rubbers in the end life of their products. Pyrolysis of some of the waste rubber materials showed an effective way of tackling the problem rubber waste. Value added fuels, gas and carbon char were the end products of pyrolysis process for the tyres. These end products can be used for the variety of the applications. The obtained fuels can be used in variety of the automobile and similar industries, while gases thus obtained can be used to run the pyrolysis plants, thus giving a sustainable way for running cost of the big plants of the tyre pyrolysis. Carbon char is one of the end product from the tyre pyrolysis which is majorly used as solid carbon fuel for many boiler plants, but due to low cost of these carbon product, now research are focusing on its upcyclization process. Present book chapter is showed the various ways by which this carbon can be converted into nanocarbons. Variety of the nanocarbons such as graphene, carbon naotubes and carbon nanoparticles have been synthesized from waste rubbers by using pyrolysis and CVD techniques. However, only pyrolysis approach seemed to economical viable due to its ability to produce bulk amount of the nanocarbons. The industrial symbiosis with economical cost benefit analysis is showed the future sustainability of the WTR derived nanocarbons. Due to the various extraordinary properties of the derived nanocarbon have been in energy storage applications which were also discussed in the present chapter. Apart from this, another recycling technique was showed that the use of grounded rubber were also used as filler material into various kinds of polymers to synthesize thermoplastic elastomers (TPE) and potential electrical insulators. This was showed another cost effective route for the recycling of the waste rubbers, although cost benefit analysis revealed low value addition than the production of nanocarbons. Additionally, the present chapter is also discussed about the use of WTRs for the cement applications, where the grounded form of WTR was used as filler materials to enhance the properties of concrete based pavements. Overall, the present chapter will gives a realistic idea about the various kinds of the recycling techniques along with their advantages and disadvantages. Further, the futures sustainability of the recycling techniques and need of the upcycling techniques were also discussed in the chapter, which showed that an effective waste tyre management could be done adopting a well established technique which not only reduced the carbon -footprint of the waste rubbers, but also give the way to get "Waste to wealth".

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Recycling of Thermosetting Plastics

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Abstract Covalent crosslinking point within the conventional thermosetting plastics routinely results in outstanding performance in mechanical property and solvent resistance yet leads to poor degradability and limited recyclability. In light of the context of sustainable development and the demand of environment protection, new methods for disposable thermosetting wastes have been brought out, including thermal and mechanical processing, to replace simply landfilling. However, these methods generally suffer large energy consumption, complicated product component, untoward separation, and low economic feasibility. Aiming to reduce energy inputs and improve circularity in recycling process, chemical recycling strategy has been widely studied as an alternative, which employs dynamic covalent bonds to rearrange whole crosslinking network. This chapter summarized some important dynamic covalent bonds in establishing exchangeable crosslinking networks based on detailed analyze of the polymer rearrangement mechanisms. With comprehensive understanding of dynamic polymer networks, we introduce some typical applications of recyclable thermosetting plastics that might reach the market in the near future.

Keywords Thermosets · Recycle · Cross-linked network · Dynamic covalent bond · Vitrimer

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1 Introduction of Thermosetting Plastics

Thermosetting plastics refer to polymer materials with highly cross-linked networks composed of covalently bonded repeating segments. From the structural point of view, at least one of the monomer units possesses three or more functionalities, which can provide enough crosslinking points and ensure the formation of crosslinking networks when the average functionality exceeds two. Once the linear polymer chains are cross-linked by permanent covalent bonds, the rigid structure can rarely be corrupted unless in harsh conditions. Such a crucial structural feature has been regarded as a key element in determining the unique properties of thermosetting polymers, which has presented significant achievements in influencing human production and life.

Thermosetting plastics generally own two attractive physical properties which are completely different from those of thermoplastics. The first one is the pervasive insolubility in all kinds of non-reactive solvents. According to the dissolution of thermoplastic polymers, the solvent penetrates into the framework to swell the linear chains and then jeopardizes the intermolecular interactions among those chains so as to loosen and dissolve the whole polymer. Similar swelling phenomena also take place when the thermosetting polymer is exposed to good solvent. However, in contrast to the linear structure of thermoplastic polymer, the crosslinking points in the thermosetting polymer are mainly based on the permanent covalent bonds which provide a strong pinning force rather than weak interactions of Van der Waals force, dipole–dipole or hydrogen bonding. Thus, the solvent molecules can only swell the cross-linked networks instead of breaking them down even at high temperatures. The second unique property of thermosetting polymer is non-meltable or non-malleable behavior during high-temperature processing before thermal degradation. Nevertheless, in thermoplastic polymers, those non-covalent intra- or intermolecular forces that hold linear backbones together are particularly sensitive to heat, accounting for the relaxation and free movement of polymer chains under thermal treatment. The thermoplastic polymer can reach a fluid state with the increased temperature while turning back into solid state when cooled down. Yet this evolution has rarely been observed if the intermolecular forces are replaced by the covalent interactions. In the case of cross-linked network, the slippage of the polymer chains can be significantly suppressed by the involvement of the permanent linking points. Unless the temperature reaches high enough to break the covalent bonds, thermosetting polymers retain solid-like performance but only become softer when the polymer chains are thermally relaxed. The stiffness change of the material under different temperatures is important for understanding the physical properties of thermosetting plastics. In principle, due to the random orientation during the crosslinking process, a thermosetting polymer network generally possesses amorphous structure which stays at a rigid glassy state corresponding to a high modulus value within a low temperature window. As the temperature increases over a specific range, the glassy state transforms into an elastic state, along with a process of chain relaxation in the polymer network. Such temperature range is defined as glass transition temperature (T_g) and accounts for the distinct change of stiffness and modulus over the course of thermal treatment. T_g is the macro-manifestation of network flexibility in thermosetting polymers. Tuning the rigidity of the chain segments will accordingly affect the T_g of the polymer network as well as the physical characteristics of the thermosetting materials.

Taking the fact that the crosslinking points in the polymer networks are established in a permanent form into account, thermosetting plastics cannot be reprocessed once their final shapes are chemically settled. The permanently fixed property of thermosetting polymers requires the curing reaction and the shaping process to be completed at the same time. The mold for shaping process also serves as a chemical reactor for polymerization. Due to the insoluble and infusible properties of permanent networks, the defective products will be discarded and unlikely to be reprocessed in a sustainable way (Winne 2019).

2 Thermosetting Recycling Strategies

With the extended application and continuous consumption of fossil-based thermosets, thermosetting plastics waste ending-up is becoming one of the most intensively concerned issues of twenty-first century. From the practical and technical considerations, the intrinsic reprocessability without addition of other chemical excipients enables thermoplastics to be reused and recycled more easily, though limited numbers of successful examples are exploited. In general, the unopenable feature of cross-linked polymers renders limited possibility to serve thermosets as recyclable polymers. In a long time, conventional thermosetting materials have been categorized as one of the most difficult types of materials for degrading and recycling. Current management of most thermosetting plastic waste is mainly based on landfilling (or burning/combustion) which is considered as the least preferred approaches. In the face of this challenge, great insights have been provided into innovating feasible methods for repeated utilization of thermosetting materials (Fig. 1) (Post 2020).

2.1 Mechanical Recycling Strategy

Mechanical recycling method for plastics generally involves shredding and grinding followed by screening separable fiber-rich and resin-rich fractions for reutilization. The whole process is relatively energy-intensive and the quality of recycling products routinely to be inferior. At the beginning of the mechanically recycling process, proper cutting is usually preferred to reduce the size of thermosetting plastics below 100 mm. This process facilitates the removal of metal inserts and also assists the transportation of the wastes. After applying high speed milling for fine grinding, the size of thermosetting scrap can be further reduced (0.5–10 mm). Then classified by centrifugal cyclone sieves, these fine particles can be separated into fractions with different quality (Pickering 2006). Despite these processing treatments are relatively

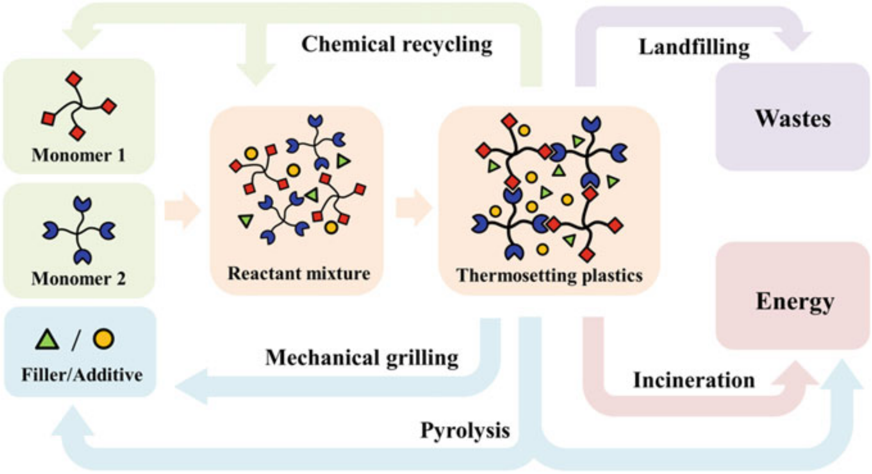

Fig. 1 Summary of thermosetting plastic recycling strategies

simple to fulfill, the high energy consumption and poor mechanical property of recycled product restrict the wide application of mechanical recycling strategy.

2.2 *Thermal Recycling Strategy*

Conventional thermal processing for thermosetting plastics can be divided into three categories, including incineration for energy recovery only, combustion for blended fiber and filler recycling with energy recycling, and anaerobic combustion. Although the first strategy is the most straightforward one to reutilize thermoset wastes, no material can be recycled from the whole process, which is excluded from the recycling strategies. In that case, fluidised-bed combustion is invented to combust the matrix as energy and collect the blended fibers or other non-flammable fillers for material recovery. In short, the thermoset wastes are firstly decomposed into small size before they are added into the fluidised-bed reactor. After heating up to 450–550 °C, thermoset matrix, like epoxy resin, can be removed and the left products are mainly composed of those non-flammable fillers. The commercial availability has been estimated by Pickering in 2010, suggesting that only when treatment capability reaches above 10,000 tonnes/year can the recycling process be economical (Pickering 2000).

In contrast to aerobic combustion, the anaerobic combustion can depolymerize the thermosetting network into small molecules and produce less amount of carbon dioxide. In the absence of oxygen, this method is also defined as pyrolysis recycling process. The pyrolysis temperature can be very different ranging from 300 to 800 °C according to various degradation requirements. Under the anaerobic atmosphere, the carbon-based polymer structure is efficiently protected from violent oxidation and thus results in the generation of small molecule products. In spite of rapid development, there still remain obstacles standing in the way of industrial applications of pyrolysis strategy, including high energy consumption, complicated product component, untoward separation, and low economic feasibility.

2.3 Chemical Recycling Strategy

Although above-mentioned conventional recycling strategies have been investigated for decades, they are still far from the practical applications in thermosetting polymer industry, because they are facing the challenges of enormous amount of energy consumption and limited efficiency of collecting recycled product. Therefore, new approaches are under emergent demand for designing degradable or recyclable architecture with low energy input. Dynamic covalent chemistry, well-known as a reversible bonding-debonding strategy under equilibrium control, has been emerged as an attractive innovation in organic synthesis, polymer assembly, materials development, and biological applications (Zhang 2018). The cleavage of dynamic covalent bond can temporarily separate the robustly cross-linked network into chemically active fragments (Chakma and Konkolewicz 2019). Different from the irreversible destroy in ordinary organic structure, these active fragments can be dramatically reconnected through the controllable formation of dynamic bonds. Since conventional recycling strategy can hardly regenerate the original reactant, introducing dynamic covalent bonds into thermosetting architecture seems to be a feasible way to approach fully recycling of reactive monomers or reactant mixtures from the thermosets wastes.

3 Dynamic Polymer Networks

Within a given polymer network, the involvement of dynamic covalent bonds can dramatically result in the exchange reactions between the chain segments. The reversible exchange will promote the diffusion of polymer chains, offering the thermosetting plastic with plasticity and reprocessability. Many dynamic covalent bonds have been introduced to the polymer networks for recycling of thermosetting plastics. The diversity of reversible bonds provides different mechanistic pathways which can influence the intrinsic physical properties of the polymer networks. Although the exchange mechanisms in some dynamic networks have not been clearly discerned yet, through the summarizing of former literatures, mechanistic pathways in exchangeable polymer networks can be sorted into four categories: addition/elimination pathway, elimination/addition pathway, concerted pathway and small molecule mediated pathway. It is worth noting that these reaction pathways are not exactly the same mechanisms as reversible bonds but the mechanisms of network rearrangement processes (Scheutz 2019).

3.1 Addition/Elimination Pathway

In a chain exchange reaction which undergoes an addition/elimination pathway, the rearrangement process experiences a prior association of two polymer chains to generate a crosslinking point among three or more chain segments, followed by the dissociation of the original bond (Fig. 2). Such an associative stepwise mechanism is the most common explanation in the network rearrangement reactions. During the addition reaction process, the formation of the intermediate state causes the increase of crosslinking density, which temporarily changes the connectivity of the polymer network. As the overall network fluctuates without de-crosslinking, the polymer chains can diffuse similarly to the plastics as well as remain fixed property of insoluble at the same time. According to the latest literatures, there are generally four types of model reactions that obey this mechanism. Each of them is described in detail as follows.

Transesterification reaction

Known as one of the most important dynamic reactions, transesterification reaction can transform one ester into another by exchanging the alkoxy moiety with free hydroxyl group. Considering the mechanistic nature of the carboxyl acid derivatives, this interchange process usually involves the formation as well as breakdown of a tetrahedral intermediate (Fig. 3). In a polyester network, the free hydroxyl groups

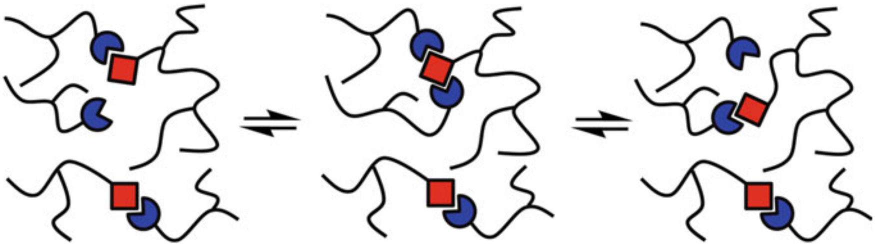

Fig. 2 Addition/elimination network rearrangement mechanism

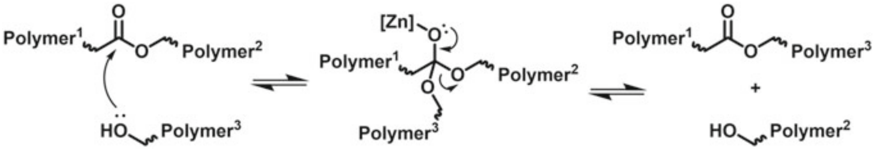

Fig. 3 Reversible transesterification reaction in addition/elimination dynamic polymer network

on the edge of the polymer chains generally act as nucleophilic reagents to attack the positive center of the ester group followed by the change of configuration. This addition reaction can produce tetrahedral intermediates with two alkoxy moieties on the backbones of polymer networks, which temporarily cause the appearance of new crosslinking points. The alkoxy moieties of the initial ester groups then dissociate from the new crosslinking points as leaving groups and become a new polymer chain edge with free hydroxyl units.

However, such an alcoholysis process is extremely slow under common conditions, which accounts for the proper requirement of catalysts such as Lewis acids or Brønsted bases. Typical metal catalysts including zinc (II), lanthanum (III), aluminum (III) are frequently used to initiate rapid transesterification reactions (Montarnal 2011). These high valence metal salts have empty orbitals in their metal center, which allows the coordination of the carbonyl groups on esters. Acting as Lewis acids, the metal catalysts efficiently enhance the electrophilicity of carbonyl groups and elevate the ease for alcoholysis process. Besides Lewis acids, Brønsted bases such as triazobicyclodecene (TBD) are also reliable to induce exchange reactions of alkoxy moieties to generate new ester groups.

Boronic ester exchange

Boronic ester chemistry has been widely applied in designing covalent adaptable networks. The condensation between boronic acid and alkoxy unit is entropically favored by the expulsion of two molecules of water. The electron-deficient boronic ester structure can be stabilized by the lone pair donation of the oxygen atoms. Since the central boron atom still owns unoccupied p-orbital, it is easy for the nucleophilic reactants to attack at the positive center. Similar to the carboxyl exchange reaction pathway, the formation of the tetrahedral intermediate during the addition process can significantly enhance the dissociation ability of the alkoxyl groups. After the alkoxyl leaving process, a new boronic ester structure forms at the crosslinking point. Such boronic ester exchange reactions are generally categorized as three types, including transesterification, dioxaborolane metathesis and boroxine exchange reaction. Although there still remain some complex pathways in the exchange process, most of the boronic ester based networks undergo an associative rearrangement mechanism with few loss of connectivity or crosslinking density (Röttger 2017).

Siloxane-silanol exchange reaction

Siloxane-silanol exchange reaction is formally similar to the transesterification reaction of boronic esters yet not perfectly consistent (Fig. 4). The lack of valence electron enables the boronic ester to be considerably attractive to the nucleophile. In contrast, however, the siloxane structure reaches the eight-electron arrangement in the outer shell of silicon atom. Under this circumstance, the third period element shows its advantage of possessing *d*-orbit which is willing to accept coordinator with lone pair. When the nucleophilic reaction happens between the siloxane and the silanol, the lone pair of the hydroxyl group will be donated into the empty *d*-orbit of the silicon atom, which normally formulates a pentavalence intermediate. As the siloxane moieties possess low reactivity under common conditions, appropriate

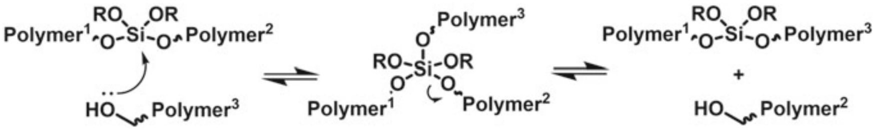

Fig. 4 Reversible siloxane-silanol exchange reaction in addition/elimination dynamic polymer network

thermal energy is required to activate the exchange reaction. After experiencing first increased and then declined approach in the density of crosslinking points, the dynamic network will preserve its initial degree of connectivity through the whole rearrangement process (Nishimura 2017).

β-amino-enone exchange reaction

Urethane groups have been proved to be considerably stable, because the electron-rich nitrogen atoms significantly improve the electron density of ester groups and afford stabilization effect in the ground states before addition reactions. Due to the disfavored attack of nucleophilic reactants at urethane groups, the aminolysis process usually calls for more vigorous reaction condition than alcoholysis process in trans-esterification reaction. To reduce the difficulty of the transamidation reactions of urethane, many strategies have been proposed including exploring the reactivity of vinylogous urethane (Fig. 5) (Denissen 2015). Formally, vinylogous urethane is a kind of α, β-unsaturated ester with amine group at the β site, which can be obtained by the condensation reaction between β-ketoester and alkylamine. The condensation product will provide a Schiff base form at first, followed by a tautomerization into an enaminone resonance structure. The vinylic bond can be regarded as an insert moiety between the electron-donating amine group and the electron-withdrawing ester group. Such an α, β-unsaturated ester structure is favored for the addition of alkylamine to undergo a Michael-type mechanism. During the first step of addition process, the network can maintain its connectivity without the loss of crosslinking density owing to the formation of tetrahedral intermediate. The instability of the ketal-like structure in the intermediate will cause the release of an alkylamine group to provide a new vinylogous urethane structure. Notably, the whole reversible exchange process is catalyst-free and inert to the aqueous environment.

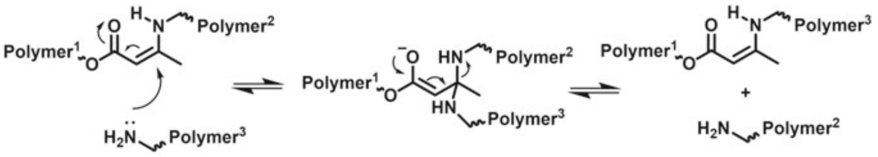

Fig. 5 Reversible β-amino-enone exchange reaction in addition/elimination dynamic polymer network

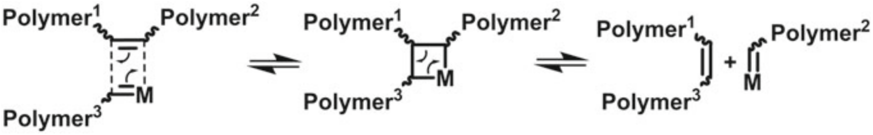

Fig. 6 Reversible olefin metathesis reaction in addition/elimination dynamic polymer network

Olefin metathesis reaction

Olefin metathesis is a transition-metal-catalyzed reaction which can realize the rearrangement of olefin fragments. Significantly developed by Grubbs group, olefin metathesis has shown great popularity in achieving chemical exchange reaction (Vougioukalakis 2010). Not only employed widely in macrocyclic construction and conjugated polymerization, olefin metathesis has also been proved to possess considerable potentials in establishing dynamic networks (Lu 2012). As a matter of fact, rearrangement reactions based on C=C bond exchange are not very common, as the consequence that the breaking of C=C bond desires too much energy to destroy the non-polar binding impact. However, C=C double bond can combine with transition metal catalyst proceeding through [2 + 2] cycloaddition, and thus form a metallacyclic intermediate (Fig. 6). Such a four-membered ring intermediate can undergo a ring-opening process which results in the regeneration of a new C=C double bond. Although the crosslinking density of the network experiences a slightly decrease when the Grubbs catalyst provides a carbene intermediate at the end of the polymer chain, no obvious compromise can be observed in the whole connectivity of the polymer network. Therefore, this transition-metal-mediated exchange reaction can be regarded as an associative reaction carry out the addition/elimination pathway.

3.2 Elimination/Addition Pathway

In a chain exchange reaction performing the elimination/addition pathway, two or more chain segments firstly experience a dissociation pathway to generate de-crosslinked intermediates at the chain ends (Fig. 7). These temporarily active chain ends will match with each other freely and form new bonds to accomplish the rearrangement process. The key point of the elimination/addition pathway is the dissociation behavior of the polymer chains, which is essentially important for the physical performance of the materials. With the network breaks into pieces via elimination reactions, the crosslinking density will experience a temporary decrease and simultaneously induce the change of solubility. Compared to the insolubility of associative networks, dissociative networks theoretically possess great opportunities to be dissolved into good solvents, indicating the possibility of solution-based recycling approach for this type of thermosetting plastics.

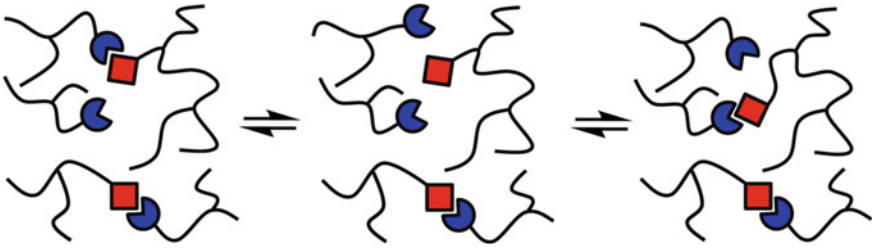

Fig. 7 Elimination/addition network rearrangement mechanism

Diels–Alder Reaction.

Non-reversible bond fission reaction can often generate high energy ionic fragments or radical species which are able to lead secondary reactions as well as cause the compromise of the polymer structure. In order to design a perfect dissociative dynamic network, the reactive chain ends should not only be active enough to accomplish the reversible bonding and debonding process but also preserve appropriate inactivity to avoid side reactions. Pericyclic reactions, especially cycloaddition, are adapted to establishing rapid reversible adducts between two or multiple stable reactants. Among all these pericyclic reactions, Diels–Alder reaction, well known as a typical [4 + 2] cycloaddition, has been broadly studied for many decades. When an electron-rich dienophile and an electron-poor diene are employed, two σ-bonds form with the expense of two weak π-bonds. Both of the dienophiles and the dienes are inert segments under mild condition before they meet each other. Some reversible Diels–Alder reactions require exoteric heat supply to overcome the activation energy barrier, while others can realize the bonding/debonding process under room temperature. One of the most frequently used Diels–Alder moieties in dynamic polymer networks is exemplified in Fig. 8 (Reutenauer 2009). Although these cycloadditions are normally categorized as concerted reactions for experiencing one-step adduction process, the overall rearrangement process experiences two stepwise mechanism to complete the chain exchange. The addition adducts will firstly dissociate into individual fragments via retro-Diels–Alder reaction, and then these cleaved chain

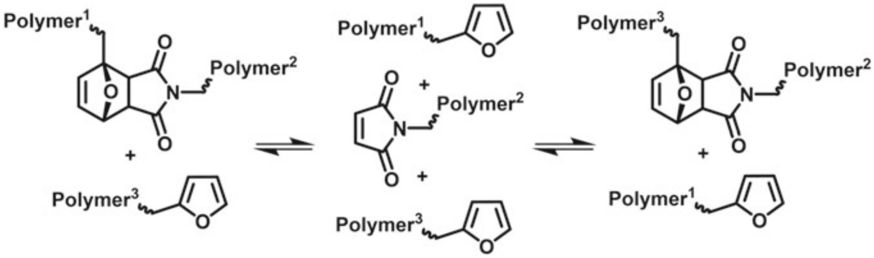

Fig. 8 Reversible Diels–Alder reaction in elimination/addition dynamic polymer network

Fig. 9 Reversible urethane/urea bond exchange reaction in elimination/addition dynamic polymer network

ends are redistributed and reconnected with other neighboring chains to form new reversible bonds.

Urethane/urea bond dissociation.

As demonstrated in the β-amino-enone exchange reaction, the amide structure is well-protected by the electron delocalization of amine group. The lack of positive charge on the carboxyl group prohibits the attack of most nucleophiles. Therefore, the exchange of urethane or urea bonds can hardly execute an associative pathway under common condition. Moreover, it has been reported that the involvement of hindered amine or alcohol moiety in reactant is beneficial for the dissociation of urea/urethane. Deblocking isocyanate step takes place at high temperature, resulting in the formation of highly reactive isocyanate moieties (Fig. 9) (Ying 2014). Despite being sensitive to moisture, such isocyanate group can rapidly connect to another neighboring amine or hydroxyl group and form a new dynamic bond. The free energy of the exchange reaction is considerably associated with the employed hinder group, which results in a very different reaction condition between two different types of urethane or urea. It is noteworthy that some of the rearrangement reactions also follow a mechanism of addition/elimination pathway in the networks of polyurethane of polyurea, yet they require specific catalysts and harsh conditions to achieve the bond exchange.

Disulfide/diselenide exchange reaction

Disulfide chemistry has been widely applied in biological process, especially protein folding, which is attributed to its dynamically exchangeable feature (Imbernon 2015). Other chalcogen exchange reactions such as selenide–selenide and sulfer-selenide exchange are also well studied to establish new type of dynamic polymer (Liu 2020). Interestingly, the dynamic bonds in these systems are dramatically sensitive to multi-stimulations. The rearrangement of polymer networks can experience totally diverse reaction mechanisms under different stimuli-conditions (Fig. 10). Upon the irradiation of UV light, a chalcogenide-chalcogenide bond can be broken into two chalcogen radicals and connect with other neighboring radicals to form a new bond. The temporary loss of the connectivity suggests that this exchange procedure undergoes an elimination/addition pathway, where the chalcogen radicals are

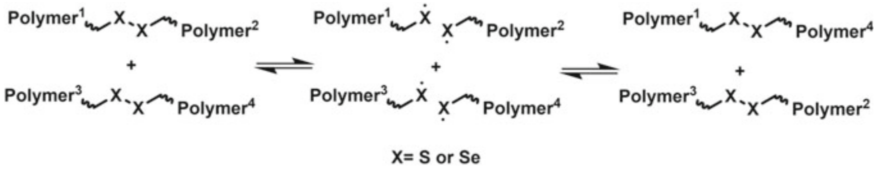

Fig. 10 Reversible disulfide/diselenide exchange reaction in elimination/addition dynamic polymer network

regarded as the dissociative intermediates. In contrast, however, many classical polysulfide rubbers are recognized as the associative networks which rearrange via addition/elimination pathways. The homolytic fission between two chalcogenide atoms is suppressed without addition of UV irradiation. Alternatively, the exchange reactions are generally initiated by the attack of a nucleophilic thiol on the disulfide bond, followed by the regeneration of a new disulfide. Despite widely existing in rubber materials, the rearrangement procedures in different systems are so complicated that their mechanisms are still under uncovering.

3.3 *Concerted Pathway*

Unlike above-mentioned two-step pathways which evolve with the formation of associative or dissociative intermediates, the concerted rearrangement reactions only undergo one-step pathway with involving transition states rather than intermediates (Fig. 11). The cleavage of the initial bond is simultaneously accompanied by the generation of a new dynamic bond without decreasing the number of crosslinking points. Such concerted network will maintain its insolubility during the exchange process between different polymer segments. Even if the concerted mechanism is an ideal way for network rearrangement which maintains constant crosslinking density, there are still limited numbers of S_N 2-type reactions that are proved to undergo concerted pathway.

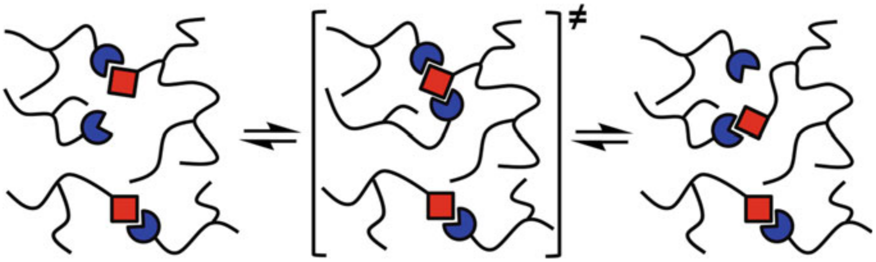

Fig. 11 Concerted network rearrangement mechanism

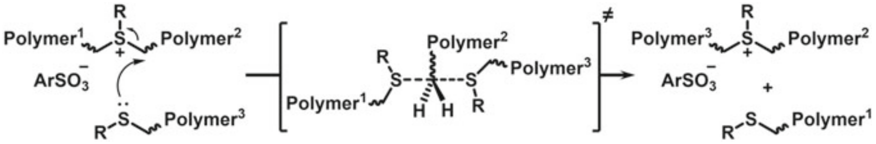

Fig. 12 Reversible sulfonium-sulfide transalkylation reaction in concerted dynamic polymer network

Sulfonium-sulfide transalkylation reaction

S_N 2-type reaction is a substitution process by the direct displacement mechanism via a single rate-determining transition state. During the nucleophilic attack, the reagent will connect to the electrophilic center of reactant from the other side opposite to the leaving group. The attacking and leaving process are occurring at the same time, which leads to a second-order kinetics. Despite famous in organic reactions, S_N 2-type mechanism is not so widely reported in the rearrangement of polymer networks. Sulfonium-sulfide transalkylation is one of the representative exchange reactions that have been proved to experience concerted S_N 2-type pathways (Fig. 12) (Hendriks 2017). Similar to other alkyl cations, sulfonium ion is an efficient leaving group upon the substitution of nucleophile. The involvement of free thioether can initiate the substitution routine and remarkably improve the exchange rate of the polymer network. As the generation of new sulfonium and the dissociation of sulfide take place simultaneously, the network integrity can be maintained without any change of crosslinking density. It is worth noting that the nucleophilic anions such as halogen ions are not preferred as the counter ions against sulfonium cation ions owing to the significant sensitivity of sulfonium against nucleophiles.

3.4 *Small Molecule Mediated Pathway*

Small molecule mediated pathway is a special type of dissociative exchange mechanism (Fig. 13). Instead of forming independent elimination intermediate during

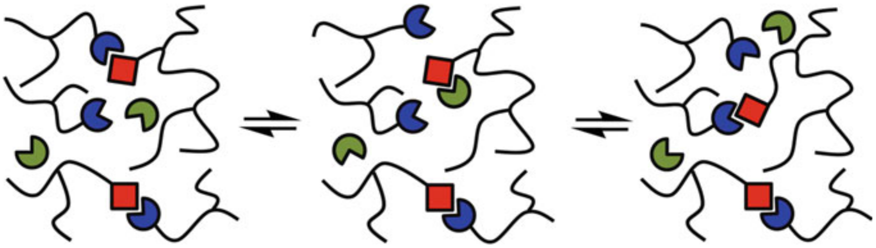

Fig. 13 Small molecule mediated network rearrangement mechanism

the network rearrangement, the involvement of a mediator will cause the fragmentation of dynamic bond and result in the combination between the small molecule and the chain segments. After condensation with other neighboring chain segments, the mediator-contained intermediate can unleash small molecules as well as regenerate a new dynamic bond. The small molecule mediator here is more like a catalyst to initiate the exchange process which exhibits temporary fluctuation of network connectivity. As long as these small molecules remain in the system, the polymer network will always keep active to perform dynamic exchange.

Imine exchange reaction

Imine unit, which is often referred as Schiff base, is the condensation product between amine group and aldehyde or ketone. Well known as one of the most typical dynamic bonds, imine group has been reported to be sensitive to pH, temperature, moisture, and other stimulations. Such versatile bonding property enables Schiff base structure to be widely applied in the field of polymer degradation and responsive assembly. When the polymer chains are connected through imine bonds, the released water molecules during the condensation reaction can serve as the small molecule mediator in the system for imine hydrolysis (Xu 2018). With appropriate stimulation including heat or acid, the imine group can be rapidly corrupted by water molecules thus dissociates into amine moieties and carbonyl segments. The separated chain segments can be reversibly combined with each other through condensation again and form the newly reconfigurable polymer network. Undoubtedly, the crosslinking density will show a temporarily decrease when the hydrolysis happens. This stepwise rearrangement reaction as shown in Fig. 14 clearly experiences a dissociation pathway where small molecules (water) present as mediators. Additionally, the reversibility of the Schiff base structure extraordinarily relies on the types of amine and carbonyl compound that are used. In fact, the systems composed of alkylamine and alkylaldehyde are more sensitive to environmental stimulations. In contrast, however, the systems conjugated with aryl group structure can protect the imine bonds from nucleophilic addition, which requires rigorous reaction conditions to realize the fragmentation of Schiff base (Skene 2004).

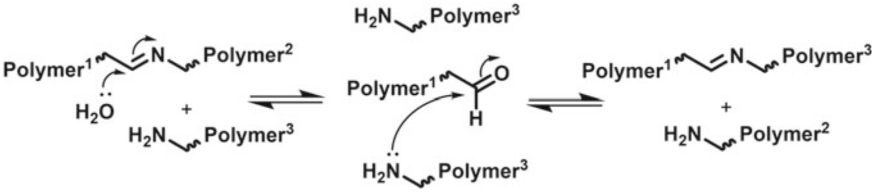

Fig. 14 Reversible imine exchange reaction in small molecule mediated dynamic polymer network

4 Recyclable Thermosetting Plastics

Exchangeable covalent bonds provide great opportunities for the development of dynamic polymer networks. Introducing dynamic structures into cross-linked networks can endow the thermosetting materials with other new properties, including repairability, reconfigurability, recyclability and adaptability. These attractive characters are barely found in conventional thermosets yet can be achieved by dynamic chemistry. As we emphasized above, the process of bond rearrangement within the polymer network mainly be explained by four different mechanisms. Each pathway gets the access to the various physical properties of dynamic networks upon heating or other environmental stimulations. On one hand, all of the four varied dynamic networks can flow when they are heated, accounting for the viscoelasticity characteristic. Possessing elastic and viscous behaviors at the same time, the dynamic network can experience a permanent shape deformation under the applying of stress for a relatively long time. Owing to the chain diffusion property in the dynamic system, the viscoelasticity has become the key point of configuring recyclable and reprocessable thermosetting polymers. On the other hand, the rearrangement pathways substantially affect the solubility of polymer networks. For dissociative pathway and small molecule mediated pathway, the temporary decrease of connectivity in the system tends to decompose the whole network into small polymer fragments. The swelling effect of good solvent will further destroy the physical linking points based on Van der Waals force or hydrogen bond, which can partially cause the dissolution of polymer network. Behaving either fusible when heated or soluble in a good solvent, the reversible dynamic networks are more similar to thermoplastic polymers rather than thermosetting polymers. In contrast, however, for associative pathways and concerted pathways, the crosslinking density of the network appears not to decline but even experiences temporary increase under some circumstances. The preservation of connectivity during the rearrangement process makes it difficult for polymer network to be dissolved in any good solvents. Such dynamic network with fusible yet insoluble property behaves like both thermoplastics and thermosets, which has been defined as *vitrimer* (Denissen 2016).

Vitrimer is a new class of thermosetting plastic material based on dynamic networks, which was invented and named by Leibler and coworkers in 2011 (Montarnal 2011). Compared to conventional cross-linked networks, vitrimers can experience topology fluctuation via dynamic bond exchange reaction resulting in the thermal malleability. The viscoelasticity of the vitrimer is highly correlated to the exchange rate of dynamic bonds according to the Arrhenius law. The increase of heating temperature can dramatically promote the exchange reaction and accelerate the relaxation of the dynamic network. Through chain diffusion and segment exchange, vitrimers can be easily healed, welded, fixed and reshaped, laying the ground for recycling. In addition, the permanent connectivity endows the vitrimer network with insolubility which prevents the materials from being corrupted by inert solvents. Hence, it can be very hard to reprocess vitrimer materials via solution casting.

Generally, two transition temperatures are applied to describe the viscoelastic behavior of vitrimers, including glass transition temperature (T_g) and topology freezing transition temperature (T_v). T_g is well-known as a phase transition temperature between glassy state and rubbery state, while T_v refers to the initiate temperature of dynamic bond exchange reaction. When the vitrimer network possesses a higher T_v than T_g, the material will show a rubbery behavior before the temperature reaches T_v. After heating up above T_v, the elastomer will transform to a viscoelastic liquid which is beneficial for the stress relaxation and shape manipulation of rubbery material. Conversely, when the T_v is lower than T_g, the vitrimer will behave as thermosetting plastic before the temperature reaches the level for bond exchange reaction. Yet T_v here cannot be considered as the initiate temperature of network rearrangement because barely no segmental motions can be observed below T_g. In that case, only after heating up to T_g can the material perform viscoelastic behavior. Based on the diffusion-controlled rearrangement reaction, thermosetting plastics are reasonably expected to be recyclable and reprocessable. Several classes of materials are introduced as below to give a prospect on the recycling chemistry of thermosetting plastics.

4.1 Epoxy Resin

Epoxy resin, containing more than one epoxy or oxirane group per molecule, is a kind of polyether which can be converted into thermosets after contacting with curing reactant (Capricho 2020). The highly cross-linked network structure considerably enhances the robustness of epoxy resin which determines the material performance. In terms of its moderate growth rate and outstanding mechanical properties, epoxy resin has become one of the most prevalent thermosetting materials in polymer industry. By offering unique processability and adhesion behaviors, it has been widely employed in the fields of coatings, engineering glues and conductive adhesives. Moreover, the advantages of light weight, high strength, chemical resistance and thermal stability enable the application in fiber reinforced composites which can produce structural parts in aerospace or aviation manufacture. Due to the ubiquitous utilization and rapid development, epoxy resin has occupied nearly 70% of the commercial thermosets market. However, with the increasing consumption of epoxy resins, the environmental pollution seems to be unavoidable owing to the lack of degradability and recyclability in conventional thermosets. To settle these problems, many efforts have been devoted to introducing dynamic covalent bonds into the epoxy resin, which significantly promotes the reprocessability of the cross-linked network (Altuna 2018).

An epoxy-based vitrimer was pioneered by L. Leibler using transesterification as the exchange reaction in the polymer network (Fig. 15) (Montarnal 2011). This network shows malleable, repairable and recyclable performance under the catalysis of 5–10% $Zn(acac)_2$, even in a classical epoxy resin system cured by the reaction between the diglycidyl ether of bisphenol A (DGEBA) and the mixture of fatty

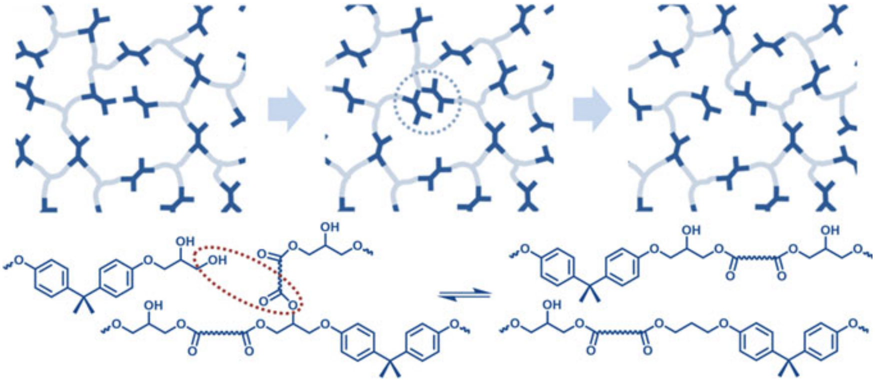

Fig. 15 Schematic illustration of epoxy-based vitrimer and exchange process via transesterification during network rearrangement

dicarboxylic and tricarboxylic acids. Although such epoxy-based vitrimer shows fluidic characteristic when heated up to T_v, it mechanically behaves like conventional epoxy resin with tough modulus of 1.8 GPa and high stress at break of 55 MPa at room temperature.

Considering the formability, the epoxy-based vitrimer is also able to be applied in advanced manufacturing techniques such as 3D printing (Shi 2017). Typically, DGEBA and fatty acids Pripol 1040 were dissolved in anhydrous ethylene glycol to form a mixture which can be extruded through syringe and nozzle. 18 wt% nanoclay was mixed in the system to tailor the rheology properties of the ink. Based on classical extrusion-based printer, an epoxy resin model with preset shape could be printed and then further cured for desired mechanical strength. By adding $Zn(ac)_2$ as transesterification catalyst, the epoxy resin can not only be formulated into complex architectures, but also be recycled as the printing ink for many times.

Nowadays, nearly 90% epoxy resins are produced by bisphenol A, which has been proven to be harmful to human health, especially for immune and productive system. Many countries have prohibited the use of bisphenol A in drink bottles, food packings and medical devices. To develop environmental-friendly thermosets, a significant number of small biomolecules have been investigated in producing bio-based epoxy resin, including plant oils, rosin, tannins, cardanol and so on. Taking palm oil as an instance (Fig. 16), unsaturated fatty chains were epoxidized by using 3-chloroperoxybenzoic acid (m-CPBA) (Mu 2020). Methyl methacrylate groups were modified at the chain end of palm oil to promote the robustness of the production via free radical polymerization. Citric acid served as the crosslinker to generate ester bond with epoxy group on the palm oil chain, producing a mechanically strong epoxy resin network. Owing to the exchange ability of ester bond, this bio-based epoxy resin can experience rearrangement reaction under high temperature up to 170 °C, which enables the reshaping and recycling of thermoset network.

Apart from the transesterification reaction, other bond exchange reactions can also realize the recycling of epoxy resin. For example, bis(4-glycidyloxyphenyl)disulfide

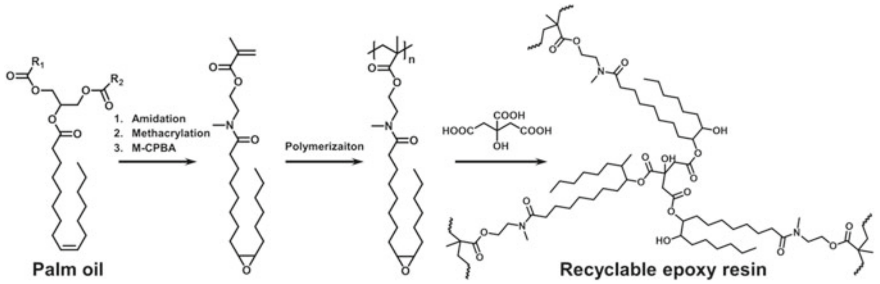

Fig. 16 Synthetic route of mechanically recyclable epoxy resins based-on palm oil

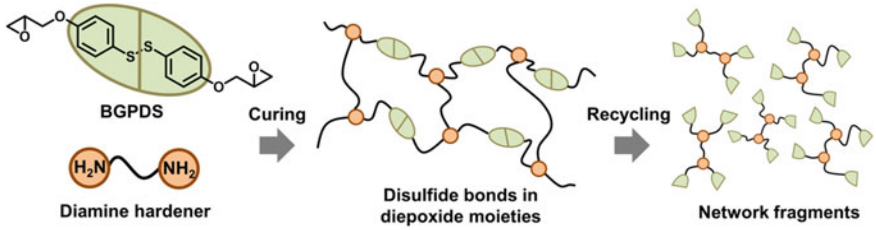

Fig. 17 Schematic illustration of the disulfide-based epoxy resin and the recycling mechanism

(BGPDS), a kind of epoxy compound containing disulfide bond, has been investigated to produce a thermosetting network with diamine hardener (Fig. 17) (Takahashi 2016). The bond dissociation energy of disulfide bond normally reaches 210–270 kJ/mol, which can dramatically maintain the original strength of epoxy resin material at room temperature. Under the irradiation of UV light, such disulfide group can experience a bonding-debonding process to complete rearrangement of the network. Specifically, this dynamic process can be accelerated in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), endowing the cross-linked epoxy resin with highly-efficient recyclability.

4.2 Polyurethane

Polyurethane is a class of polymer synthesized via polyaddition reaction between polyisocyanates and polyols. Depending on the different chemical and morphological components, polyurethane can display either thermoset or thermoplastic performance. The thermosetting polyurethane normally requires at least one monomer to process three or more functional groups for establishing a cross-linked network. Amongst many kinds of polyurethane raw materials, over nearly 66% of them are employed in foam applications (Engels 2013). On one hand, the flexible polyurethane-based foam has been widely used in fabricating cushions, mattresses and other soft furniture, owing to the efficient fabrication procedure, excellent breathability and long-service lifespan. On the other hand, those highly cross-linked polyurethane with closed pores can be formulated into rigid foam which is suitable for the construction applications and electrical insulation. Besides foam materials, thermosetting polyurethane can also be applied in the fields of coatings, paints, elastomers and fiber composites. After developed for 83 years, this versatile thermosetting polymer is now playing an increasingly important role in human life. Because of the dependence on limited fossil fuels, the cost of synthetic petroleum-derived polyurethane materials is skyrocketing, which makes recyclable polyurethane at the cutting edge. As discussed in Sect. 3.2, urethane bonds can undergo dynamic exchange reaction to rearrange the whole cross-linked polymer network under high temperature. Through the transcarbamoylation, such polyurethane based thermosets can possess reprocessability and recyclability, which will partially alleviate the environmental burden.

Organotin compounds, especially dibutyltin dilaurate (DBTDL), are classic catalysts to promote the generation of carbamate bonds in polyurethane. They serve as Lewis acid in the polymerization reaction with only 0.5–2.0 wt% and often present remarkable catalytic efficiency. Although some researchers believe that the difficulty of removing metal catalysts in the material can cause adverse effect such as toxicity, the residual organotin compounds also provide great opportunities for solving the recycling problem of polyurethane thermosets. For example, a typical recyclable polyurethane thermosets can be produced by mixing (polyethylene glycol)diol (PEG), glycerol (GLY) and hexamethylene diisocyanate (HDI) with DBTDL together (Fig. 18) (Zheng 2016). Under the catalysis of DBTDL at 130 °C, such polymer network presented quick and complete iso-strain stress relaxation due to the carbamate exchange reaction. Interestingly, this polyurethane material exhibited non-flowing nature which behaved as a viscoelastic solid with creep and a large instantaneous recovery after the stress was removed. Despite dramatic reshaping performance when heated, this polyurethane material did not present an excellent recyclability because of the slow exchange rate. Different from urethane units which require relatively high temperature to active exchange, the urea units can realize reversible bond breakage and reformation at approximate room temperature (Fang

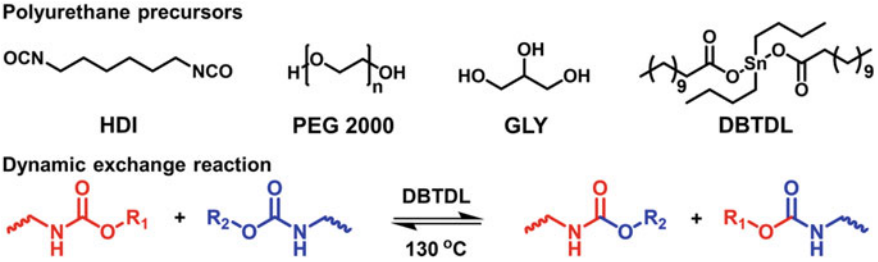

Fig. 18 Representative synthetic precursors and reprocessing mechanism of thermosetting polyurethane

2017). Attributed to the steric hindrance and electronic effect, the hindered urea bond always shows a faster exchange rate than the urethane bond. In that case, the hindered amine applied in the system establishes a reliable dynamic polymer network with reprocessable, healable and reconfigurable properties. Furthermore, these polyurethane-based thermosetting networks can utilize melting transition as the shape memory transition to manipulate the temporary shape of whole material. With the involvement of dynamic covalent bond exchange, such shape memory materials can also experience permanent shape fixing under a higher temperature above the melting point.

Besides organotin compounds, other Lewis acid catalysts have also been investigated to promote the transcarbamoylation reaction. Both bismuth neodecanoate [Bi(neo)$_3$] and iron (III) acetylacetonate [Fe(acac)$_3$] have been applied as new alternatives to compete with DBTDL owing to their lower toxicity (Fortman 2019). These Lewis acid catalysts showed remarkable catalysis efficiency when combined with polyether-polyurethane network. Similar to the systems containing DBTDL, with the presence of 2.5 wt% catalysts, the polymer networks exhibited excellent stress relaxation performance at 140 °C. It has also been confirmed that similar exchange rates and active energies of network rearrangement can be observed with these catalysts according to Arrhenius formula. In contrast to many other Lewis acid compounds with limited influence on transcarbamoylation, Bi(neo)$_3$ and Fe(acac)$_3$ emerge as promising candidates to fulfill the aim of recycling and reproducing polyurethane thermosets.

The catalyst-free reaction has always been a hot topic in the development of organic chemistry for many years. Many catalyst-free systems have been investigated to circumvent the problems which are mainly caused by metal catalysts, such as toxicity, environmental threat and expensive price. Dynamic exchange reaction in polyurethane was no exception. Oximes, usually generated by the condensation between hydroxylamine and aldehydes or ketones, have been widely applied in synthesizing functional materials. After connecting oxime group to isocyanate group, novel oxime-carbamate bonds can form and further construct the poly(oxime-urethane) network rather than conventional polyurethane network (Fig. 19) (Liu 2017). The oxime-carbamate bond has been proved to possess facile reversibility which is beneficial for the transcarbamoylation process. On the basis of rapid exchange reaction, the poly(oxime-urethanes) network showed an extraordinarily fast stress relaxation process above 100 °C. This poly(oxime-urethanes) network was

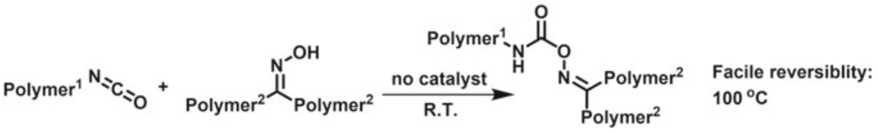

Fig. 19 Catalyst-free addition reaction for constructing oxime-based recyclable polyurethane

then cut into small pieces followed by hot press to reform bulk material. The reformation process can be repeated at least four times which confirms the considerable recycling performance.

4.3 Silicone Resin

Silicone resin is a thermosetting polyorganosiloxane with highly cross-linked structure, which is usually composed of inorganic silicon-oxygen backbone (…–Si–O-Si–O–…) and organic alkyl branches. Because of the unique structure compared to other organic resins, silicone resin shows excellent properties of heat resistance. After heating up to 350 °C for 24 h, the weight loss of common organic resin is 70–99%, while that of silicone resin is generally less than 20%. Another outstanding property of organosilicone materials is its excellent electric insulation over a wide range of temperatures and frequencies. It typically bears breakdown strength at 50 kV/mm, volume resistivity at 10^{13}–10^{15} Ω cm and relative permittivity at 3 at room temperature. In addition, the remarkable weather fastness endows silicone resin materials with considerable stability against ultraviolet exposure and moisture environment, which enables the wide application in electrically insulative coatings, heat-resistant paints, surface treatments of glasses and structurally stable elastomers. As one of the most common organosilicone, polydimethylsiloxane (PDMS) has been widely applied in microfluidic technology due to its advantages of simple preparation and low cost. After cured into a cross-linked silicone network, it is completely insoluble and infusible even under the treatment of high temperature. The high stability as well as excellent physical property results in the popularity of silicone resin, especially PDMS, yet also suppresses the degradability, reprocessability and recyclability. Owing to the high energy of Si–O bond (369 kJ/mol), it seems extremely hard to realize bond exchange in a conventional silicone network. Therefore, some researchers have mainly focused on developing catalysis systems to promote the dynamic formation and fragmentation processes of Si–O bond. Relying on these catalysts, the thermosetting silicone resin can be recyclable for the sustainable application.

Despite easily available by the Müller–Rochow synthesis and subsequent hydrolysis, the silicone materials require high energy input to access starting reactants, such as chloromethane. In that case, low-temperature depolymerization methodologies are suitable for silicone recycling with small energy consumption. However, the degradation temperature of Si–O bond in silicone was investigated to be around 200 °C, which severely limited the environmental-friendly recycling process. Inspired by the reliable degradation reaction of end-of-life polyethers, the presence of simple metal catalyst, such as zinc or iron salt, can cleave the Si–O bond and generate new Si–F bond with the help of benzoyl fluoride (Fig. 20) (Enthaler 2014). With the disconnection of Si–O bonds, the whole polysiloxane backbone can be decomposed into low-molecule-weight fragments, such as R_2SiF_2 or $FR_2SiOSiR_2F$. These degradation products can experience hydrolysis again so as to regenerate polysiloxane material.

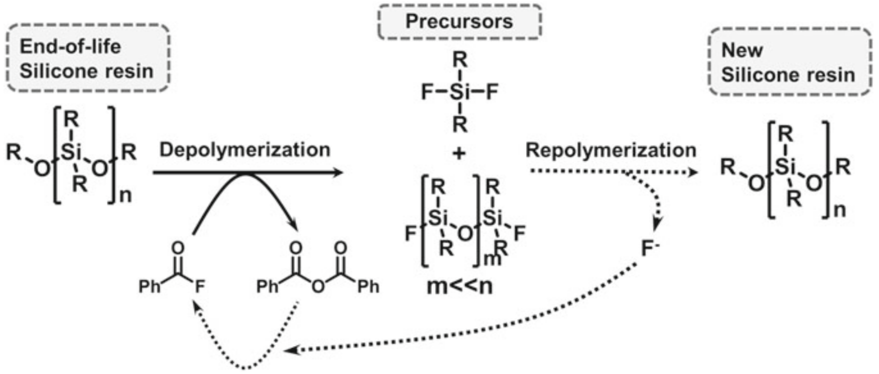

Fig. 20 Recycling approach for the conversion of polysiloxanes

Even if such a strategy provides an efficient recycling method, the unstable structure and expensive price of benzoyl fluoride seriously impede the application prospects. Improved approaches have been brought out by using acid chlorides/KF or benzoic anhydride/KF system instead of benzoyl fluoride in the degradation process, which also shows considerable efficiency.

Predominantly based on the fluorophilicity of silicon atom and the activation of Lewis acid catalysts, polysiloxane materials can be converted into small molecules with repolymerization ability. However, there remains many disadvantages in such a strategy, including embedding side product residue, requiring depolymerization reagents derived from fossil resources and costing enormous price. In this regard, boron trifluoride diethyl etherate (BF_3OEt_2) has been brought as a promising alternative for catalyzing the degradation of polysiloxane (Döhlert 2015). By killing two birds with one stone, BF_3OEt_2 acts not only as a fluorine compound but also as Lewis acid to activate Si–O bond. Such "fossil-resources-independent" reagent promotes the sustainability of the recycling methods as well as shows remarkably low cost compared to other systems. The degradation process using BF_3OEt_2 requires low energy consumption with only heating up to 100 °C. The side product residual, boronic ester, can be easily removed from the system by being converted to BF_3. The obtained decomposed compound, R_2SiF_2 or $FR_2SiOSiR_2F$, can experience hydrolysis reactions to regenerate the polysiloxane backbone.

Although it is difficult for polysiloxane network to experience rearrangement reaction, the dynamic exchange for Si–O bond is not completely impossible. It has been confirmed that the rate of alkoxysilane hydrolysis varies over a wide window based on a neighboring amine-group effect (Fig. 21). The involvement of amine group promotes the exchange ability of Si–O bond, which renders great opportunity for the rearrangement of polysiloxane network (Nishimura 2017). The silyl ether exchange-based vitrimer can be synthesized by designing bis-alkoxysilanes crosslinkers with neighboring amine groups, which has a strong effect on the kinetics of the exchange reaction. Thus, faster stress relaxation can be observed. The reprocessing temperature

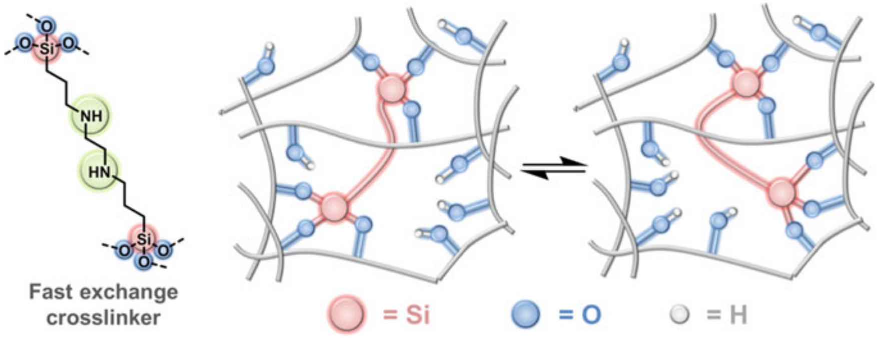

Fig. 21 Fast exchange silyl ether linkage and the schematic illustration of silicone vitrimer

of the material strongly depends on the backbone of bis-alkoxysilanes. For example, the amine group results lower hot-pressed temperature (160 °C) than alkyl group (190 °C). The reprocessed material shows the same tensile property as the original one.

5 Conclusion and Future Perspective

Owing to the properties of the readily scalable access and the straightforward adjustability, thermosetting materials have been raising increasingly scientific and industrial attention in the past decades, and this research topic is believed to receive more concerns in the future. With the increasing demands on thermosetting plastics, the accumulation of the discarded or end-of-life materials is leading a severe environment burden to the whole world. In regard to the recent requirements in sustainable energy utilization and environment protection, the innovation of the degradable and recyclable thermosetting plastics is recognized as one of the promising choices in the success of reducing polymer waste. The conventional waste-management mainly depends on the downcycling of low-quality materials or thermal recycling for energy purpose, which significantly suppresses the number of recycling times. By contrast, thermosetting plastics based on dynamic covalent polymer networks possess the advantages of multiple recycling times. Thermal-sensitive dynamic covalent bonds enable the rearrangement of cross-linked networks when heated, which endows the thermosetting polymers with the similar reprocessability with thermoplastics. This book chapter typically summarizes some attractive achievements in using bond exchange reactions in order to establish reprocessable thermosets. Particularly, vitrimer, as the most promising rearrangement network, is becoming the forefront of the pioneer researches in innovating recyclable thermosetting plastics.

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Recycling of Marine Plastic Debris

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Abstract Although marine debris has been accumulating for many decades, only during the last three the accumulation of millions of waste tons at seas and oceans has generated interest and concern of scientists and governments. While marine debris may present different origins and nature, polymers lead in abundance. Annually, 1.15–2.41 million tons of plastic arrive to the ocean from rivers. Wastes are distributed at different marine compartments according to their density, with a huge impact in both marine fauna and water pollution. It becomes necessary, consequently, besides avoiding further waste dumping, to collect and manage the waste, not only marine one, but also the land waste. Both terrestrial and marine plastic waste can constitute resources or raw materials for different applications such as fuel, energy and of materials production. Research on suitable management and recycling/valorization are required to move towards a circular economy for generating more sustainable societies. In the present chapter, the main studies carried out about the recyclability of the main polymers present in marine waste are presented and analyzed, together with the main limitations and opportunities related with this recycling process.

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Keywords Debris · Plastic waste · Recycling · Ocean

Contents

This chapter lies on the recyclability of marine debris. The actual situation regarding marine plastic waste is presented as state of art for analyzing in the subsequent sections the main experimental techniques used for characterizing the debris together with the recyclability and actual situation about different plastics suchs as PA from fishing nets PET from bottles HDPE and microplastics. Limitations and future perspectives of the recycling process are also presented.

1 Introduction

Marine debris (also called as marine waste or litter) is defined as any persistent solid material, manufactured or processed, that is directly or indirectly, intentionally or unintentionally, disposed off or discarded into the marine environment (Cornell University 2006). Even if this definition includes a wide range of materials, taking into account the relevant literature on the field, it seems apparent that polymeric materials or plastics constitute the most abundant type of marine debris.

In fact, marine plastic debris is a subcategory of waste, consisting in residues that can be found in the seas and oceans, that are composed by synthetic materials derived from fossil fuel–based compounds named polymers, such as polyethylene (PE), poly(ethylene terephthalate) (PET), polystyrene (PS), poliamide (PA), among others. They constitute industrial raw materials as pellets, consumer items such as bags, food packaging, bottles, cigarette butts or rubber tires, industrial components and those related to fisheries such as fishing nets or buoys.

Due to their durability and absence of biodegradability, plastic materials are found in oceans, lakes, and rivers, trending also to accumulate in sediments. Moreover, plastics can be degraded to smaller sizes, but they will never completely disappear, pointing out the need of recovering them from nature, and especially from water. As even once they are recovered, constitute a very durable waste, the need of recycling marine debris becomes evident.

Up to 1990's the information and worries about marine plastic wastes were almost inexistent (June 1990), but during the following decades and especially in the 21st century there is an increasing concern on the research about the origin and management or those plastic wastes. Several factors can be underlined as main causes for the accumulation of plastic waste in marine environments. From one side, the big human costal populations together with the inadequate consumer behavior and waste treatment, mainly due to an ineffective legislation. On the other side, the increasing plastic production and the inability of treatment plants to recover all the waste can be cited, together with the absence of awareness about the effects that may have on wildlife, and consequently in human life (Niaounakis 2017).

Regarding the plastic production, probably the most important factor, it is worth to note that in 2018 the production of plastics totaled around 359 million metric tons worldwide, and it seems that it will continue growing year after year (Garside 2020). In fact, 62 million metric tons were produced in Europe. China, the largest plastic producers in the world, accounts for more than one quarter of the global production. In 2018, the 39.9% of European plastic demand came from packaging industry, while the 19.9% was from building industry. The most demanded plastics were PE (films, tubes, toys, containers) (29.7%) and PP (food packaging, pipes, car accessories) (19.3%) (PlasticsEurope 2019). Figure 1 shows the evolution of plastic production since 1950. If plastic production continues growing as predicted, it can be estimated that around 2,000 t of plastic materials will be produced during 2050 (UNEP 2016), which would result in an increased waste accumulation at the oceans if urgent steps in production, waste management and reuse/recycling are not taken. With this purpose, marine plastic debris must be first localized (that is, the distribution must be investigated, taking into account the different sources), then properly collected from the ocean and finally, recycled or reused in different applications. Regarding the localization and geographic distribution, systematic investigations about it have been only carried out in the last decade (Moore 2008).

Annually, 1.15–2.41 million tons of plastic are entering the ocean from rivers (Lebreton et al. 2017). As more than half of this plastic is less dense than the water, it will not sink once it encounters the sea. This plastic debris are moved by oceanic currents and winds. Moreover, oceanic phenomena like gyres or litter windrows tend to accumulate them in zones called plastic soups or islands. Five main ocean gyres have been identified: The North Atlantic, South Atlantic, North Pacific, South Pacific, and Indian Ocean ones (Ross 1995; NOAA 2007), as can be seen in Fig. 2. In the

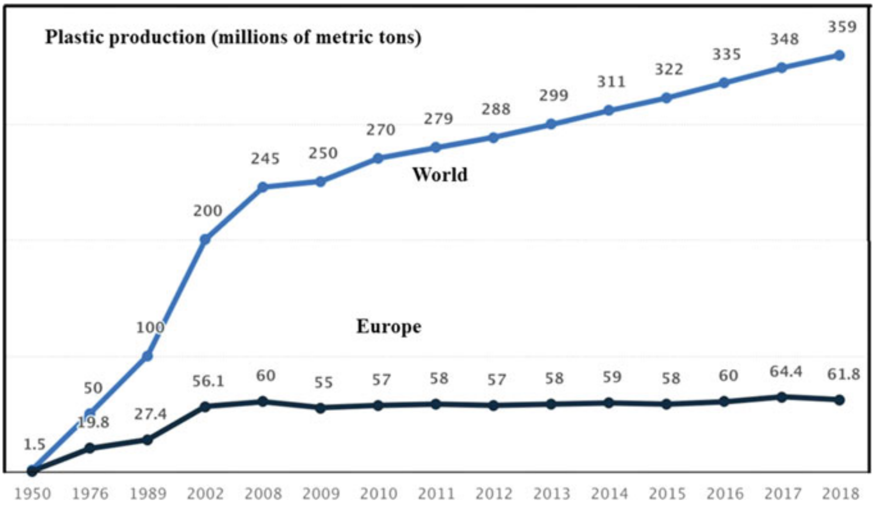


Fig. 1 Evolution of plastic production, in millions of metric tons, since 1950 in Europe and the world

Fig. 2 Geographic distribution of the five main ocean-wide gyres

Pacific Ocean, the so-called "Great Pacific Ocean Garbage Patch" or Eastern Patch is an area of marine debris found floating in the North Pacific gyre (Moore 2003), in which the abundance of marine plastic waste, in an area of 1,000 km in diameter, has been estimated to be around 262 million pieces/km^2 with a weight of around 4,000 t (Moore et al. 2001). Another Garbage Patch has been identified and called Western Patch, near Japan (NOAA 2013). Finally, Eriksen and Coworkers (2013) also found the presence of a third garbage patch in the South Pacific subtropical gyre.

Regarding the two Garbage Patches in the Atlantic Ocean, an average concentration of 20,328 pieces/km^2 with an average weight density of 0.05 g/km^2 was estimated the for northern one (Niaounakis 2017), orders of magnitude smaller than the corresponding amounts estimated for the North Pacific gyre. It was predicted, on the other hand, that South America contributes with the 60–80% of land-based litter to the South Atlantic Garbage Patch, with most of the remainder coming from Africa (Lebreton et al. 2012). Finally, in the Indian Ocean, Eriksen (Eriksen 2011) described as a massive area of at least 2 million mi^2 (about 5 million km^2) in size but with no clear boundaries, changing with season. It must be mentioned that out of the ocean-wide gyres, the Mediterranean Sea must be considered as a region of high load of plastic pollution. The sources are mainly land based (around 80%) and mostly associated with plastic and wastewater management (European Comission 2017).

The origin or source of marine plastic wastes can be land-based or sea-based. Land-based sources constitute up to 80% of marine debris, transported to the sea by drainage systems, rivers or another natural waterways as storm water drains, wind, or human factors as landfills, illegal dumping, water drains or untreated sewerage (Gregory 1996; Liffmann and Boogaerts 1997; Fendall and Sewell 2009). The rest 20% comes from sea-based sources such as recreational boats including tourist cruises or aquaculture facilities, offshore installations, or commercial fishing, from which debris is directly thrown into the ocean. (Gregory and Andrady 2003; Fendall and Sewell 2009).

Once the distribution and sources are analyzed, the identification of different plastic types in the waste must be carried out. Plastic debris can be classified into three main groups, depending on the size: macroplastic debris (≥2.5 cm), meso- (2.5 cm–5 mm) and microplastic (MPs) (≤5 mm) ones (Galgani et al. 2013; Lippiatt et al. 2013). The biological effects depend on their size. Larger sizes are easily swallowed and thrown away; the smaller ones would have a cellular effect on organisms. However, the potential effects of MPs on natural populations and food webs are not well understood yet, and further research on marine organisms is needed to better understand the environmental implications of MPs.

The amount of each type of marine debris is proportional to their global production. The composition of plastic debris are the following: high density polyethylene (HDPE) and PET from bottles, containers and packaging straps; PE and PP from plastic bags; rubber latex items (balloons, condoms, etc.); expanded polystyrene (EPS) from foams for floating structures; fibre reinforced plastics (FRP) from composites used in kayaks, surfing or boats; cellulose acetate (CA) from cigarette butts; nylon or PET fibres from textile industry (clothes, ropes, etc.) or from domestic washing clothes (Browne et al. 2011); rubber from tyres (Rochman et al. 2013; Gomiero et al. 2019).

Once marine plastic waste has been localized and identified, it must be treated for reuse, for recycling or for other uses such as energy recovery. The treatment techniques of marine plastic debris are very similar to those used for land ones but taking into account the marine origin, which implies the presence of salt, marine organisms or sand and the effect of mechanical forces (wind, currents, etc.) and UV radiation.

Recovered debris can not be normally reused in a similar application, because they present heterogeneous composition and is not easy to separate individual plastics. These types are being reused in other applications such as artificial reefs, artificial stones, soil cement, etc. However, some types composed only by one type of polymer (like nylon from fishing nets or EPS from buoys) can be reused to produce products of the similar material, like the use of recovered fishing nets as sport nets (Western Cape Government 2014). However, as only an infinitesimal part of the plastic residue can be reused, while their disposal is not environmentally acceptable, the recycling by mechanical (secondary recycling) or chemical methods (tertiary recycling) constitutes the most important process for marine plastic debris treatment. Both require pretreatment processes, in order to reduce the cost of transport and to improve the processing efficiency.

As the recycling of marine plastic debris is the main objective of the present chapter, the most useful characterization techniques, and both mechanical and chemical recycling processes carried out for the main types of polymers present in marine debris will be reviewed and presented in the following pages, analyzing the main procedures employed with this purpose.

2 Characterization Techniques

During their lifetime, polymers are usually submitted to UV radiation, oxygen, heat, mechanical stress, microbes and moisture causing their partial or complete breakdown (Ragaert et al. 2017; Iñiguez et al. 2018). In the case of marine debris, the degradation in marine environment includes a combination of UV radiation, saltiness of the sea, atmospheric oxygen (Andrady 2003; Iñiguez et al. 2018). As a result, five degradation mechanisms may occur: hydrolytic, thermooxidative degradations, photo-degradation, biodegradation and mechanical one (Niaounakis 2017).

The different external agents directly affect the physical and chemical properties of plastic materials. In order to characterize them, the structural changes must be evaluated by different experimental or analytical methods to determine their recycling feasibility.

Chemical changes can be analyzed by Fourier transform infrared spectroscopy (FTIR). By this technique, the presence of new bonds or the disappearance of representatives ones can be detected from the resulting spectrum. These changes could be attributed to the incorporation of oxygen atoms into the polymer or to modifications of the functional groups by the UV rays, which presents enough energy to break the chemical bonds in polymers as PET (Ghosh et al. 2000; Beyler and Hirschler 2002; Ioakeimidis et al. 2016).

Chemical changes are usually related with differences in characteristic temperatures of materials, such as the glass transition temperature (T_g), the melting temperature of the crystalline fraction (T_m) or degradation temperature T_d (related to the thermal stability). By differential scanning calorimetry (DSC) changes in T_g and T_m due to degradation of the material can be evaluated in a wide temperatures range (–100 to 300 °C) (Stolte and Schneider 2018). In addition, changes in enthalpy values related to changes of polymer backbone length induced by the marine environment or by the thermomechanical processing during recycling can be also detected by DSC (Mondragon et al. 2019). Degradation temperature ranges are usually analyzed by thermogravimetric analysis (TGA) in a wide temperature range (25–800 °C), in which the monitoring of mass changes in the sample with the temperature allows the estimation of thermal stability and the possible lifetime of samples (Ray and Cooney 2013).

Besides DSC, changes in the crystalline fraction of materials can also be characterized by wide angle X-ray diffraction (WAXD), by which the crystallinity or any changes in molecular orientation can be determined from the ratio between the areas of crystalline reflections to the total areas of the scattering curve (Achhammer et al. 1951; Najafi et al. 2015, 2017).

By gel permeation chromatography (GPC) the decomposition of thermoplastic polymers originated by different degradation mechanisms can also be analyzed. The change in molecular weight distribution of polymers, can provide useful information about the mechanism of decomposition, which would directly influence the mechanical behaviour of polymers (Beyler and Hirschler 2002; Ragaert et al. 2017).

Even if cited characterization techniques can help determining the type of degradation suffered by the material in marine environment, the effects on the final viscosity of the material is the main factor for determining the potential industrial themo-mechanical recycling. As an example, if marine debris shows high oxidation level, differences in characteristic temperatures, molecular weight and mechanical properties will be observed. As a result, the viscosity will be lower than that of the raw material, and the recycling by extrusion processing will not be suitable due to the low quality of obtained products, as could be observed by poor mechanical properties. Among others, melt flow index (MFI) or capillary viscometer are outstanding tests, being probably the former the most suitable for industrial applications, due to the low cost and short time required.

3 Recycling Polyamide from Fishing Nets

One of the most abundant type of waste found in the sea is that related to fishing activities. It is estimated that around 640,000 t of abandoned, lost and discarded fishing gears (ALDFG) are annually thrown to the ocean (Richardson et al. 2018), constituting around the 10–11% of marine litter (Surfrider Foundation Europe 2017). These fishing nets are ingested and may entangle and trap some marine organisms such as sea mammals and fishes with mortal consequences (Wang et al. 2016; Richardson et al. 2018; Wyles et al. 2019). These ALDFG are known as ghost nets, being the so-called ghost fishing the possible capture of sea animals by them (Anderson and Alford 2014; Wang et al. 2016). In addition to the effects generated on marine fauna, they also can lead to significant economic waste in the fishing industry due to the decrease in biodiversity, besides being a potential danger for navigation (Richardson et al. 2018).

Nowadays, the problem of ALDFG in coastal and marine areas is receiving attention or concern at national, European and global levels (NetMap Project 2015). As most of these materials are not fastly breaking down or decomposing, they are especially critical at the seabed (Cho 2011; UNEP-MAP 2015). Trying to solve this problem, a better management of the use and maintenance of fishing nets is required, giving a chance to their recycling (NetMap Project 2015).

Different materials are used for the manufacture of fishing nets to satisfy the requirements of each type of fishing. The most used polymers are polyamides, as nylon 6 or 6,6 and other polymers such as polyolefins (PE, PP) or polyesters. All of them usually include additives for UV protection in the formulation.

US Federal Trade Commission defined nylon as a manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide with less than 85% of amide linkages directly joined to two aromatic rings (Deopura and Mukherjee 1997). The polyamides are one of the most versatile thermoplastics due to properties such as stiffness, toughness, lubricity, and resistance to temperature, fatigue, and abrasion (Najafi et al. 2017), constituting important engineering polymers (Mondragon et al. 2019). A high tenacity nylon fiber is usually made from aliphatic polymers with structural methylene units $(CH_2)_n$ tied together by amide (peptide) groups (NH–CO) (Najafi et al. 2017). Polyamides are identified as nylon-n (PA-n) or nylon-mn

(PA-mn), *m* and *n* representing the number of carbon groups at monomeric units:

$$\text{Nylon} - \text{n} : -\left[-(\text{NH} - \text{CO}) - (-\text{CH}_2)_{\text{n}-1} - \right]-$$

$$\text{Nylon} - \text{mn} : -\left[-(\text{NH} - \text{CO}) - (-\text{CH}_2)_{\text{n}-2} - (\text{CO} - \text{NH}) - (\text{CH}_2)_{\text{m}} - \right]-$$

Polyamides are also used in many synthetic textile fibres and filaments for cloth manufacture that can be constituted only by nylon or combined with yarns from other materials. As they are non-renewable and non-biodegradable materials, prior to being discarded, they could be properly recovered via mechanical and/or chemical recycling that generate rewarding products (Shukla et al. 2006; Patil and Madhamshettiwar 2014).

In the case of polyamide marine wastes, several researchers and companies have evaluated their potential recycling. In fact, mechanical recycling seems to be a suitable method for the manufacture of new nylon 6 products (Mondragon et al. 2019). The process includes several stages, as shown in Fig. 3.

Fishing net wastes are washed, cut, milled and dried before extrusion processing, performed at 255–270 °C. Filaments or pellets obtained by extrusion can be further employed for the manufacture of new products.

Characterized filaments showed very similar physicochemical, rheological and mechanical properties than virgin samples. In fact, while the tensile strength of commercial polyamide is around of 67 MPa, processed ones showed values around 63–68 MPa (Mondragon et al. 2019). Obtained melting temperature values (T_m 221 °C) are very similar to those of virgin materials and seem to confirm th

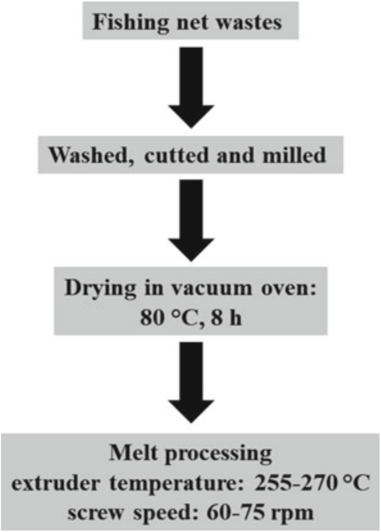


Fig. 3 Different stages of extruded filament processing from recovered fishing nets

at the stay of fishing nets at the marine environment and their subsequent processing did not cause any degradation (Mondragon et al. 2019).

However, depending on the material, a loss of properties in the final products obtained after mechanical recycling has also been found (Shukla et al. 2006). In this context, fishing nets used are submitted to a chemical reaction obtaining raw materials or monomers for the production of new nylon fibers or yarns. As an example, nylon-6 monomer (caprolactam) has been obtained from thermal decomposition of nylon fishing nets (Kanehiro 2004).

Another possible application is the incorporation of recovered nylon, PET and poly (vinyl alcohol) (PVA) fishing nets as short reinforcing fibers reinforcement in cement mortars. The most promising results have been obtained for nylon fibers, for which flexural and tensile strength of mortars increased up to a 41%, obtaining 13 times greater toughness values in comparison with unreinforced material (Spadea et al. 2015). However, it must be pointed out that those values may vary depending on the surface characteristics of the fiber and the compatibility with the matrix (Orasutthikul et al. 2017).

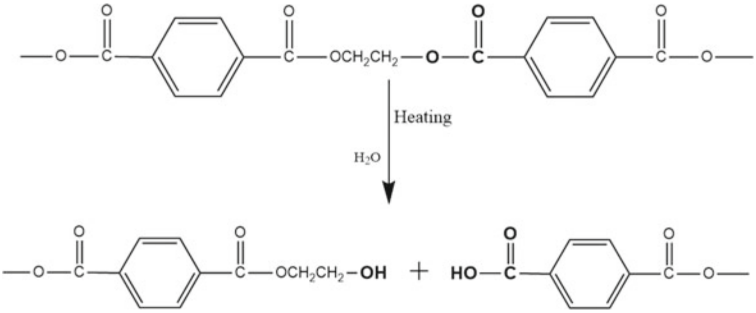
4 Recycling PET from Bottles Recovered in the Sea

PET is a polymer with a high T_m of around 260 °C, showing high chemical and mechanical resistance. Due to its suitable barrier properties, is widely used in the manufacture of beverage bottles and other food and pharmaceutical products. The 7% of global plastic production belongs to PET materials, with approximately 18.8 million tons produced per year (PlasticsEurope 2019). However, more than 40% of consumed PET bottles and containers are not collected (Petcore Europe Conference 2018), many of which end up in the sea (Fig. 4). According to data from recent years, is estimated that around 5–13 million tons of plastic are dumped into the seas each year (Iñiguez et al. 2018), being PET one of the most abundant (Rochman et al. 2013).

Marine PET debris shows different degradation mechanism as a function of the marine compartments in which is found. In fact, mechanisms for PET degradation can be different if the bottle is found at the upper compartments of the sea, in which hydrolytic degradation occurs by UV radiation effect, or at the seafloor, in which it seems to be stable for approximately fifteen years (Ioakeimidis et al. 2016; Iñiguez et al. 2018; Mendiburu-Valor et al. 2019). This hydrolysis is carried out mainly in the PET ester bonds (Scheme 1), generating carboxylic (–COOH) and hydroxyl groups (–OH) (Dubelley et al. 2017).

Most of the PET recovered from the sea is that from water surface or that arrived to the coastal area, which, due to degradation by UV radiation, usually present a drop in viscosity. In addition, when it is mechanically recycled, additional types of degradation, including thermal, oxidizing and hydrolytic ones, tend to occur due to the high temperatures, above 250 ºC, used in the processing (Venkatachalam et al. 2012). Therefore, in order to perform mechanical processing of degraded materials,

Fig. 4 Plastic waste accumulation in the coastal. *Source* Pxfuel



Scheme 1 Hydrolisis reaction for PET

it is essential to include other strategies such as their mixing with raw material, or the use of additives.

The best option for recycling PET samples with low purity such as marine PET, however, seems to be the chemical recycling (Petcore Europe 2020). The degradation in the marine environment induces a breakdown of polymer chains, but it is not a critical aspect for chemical recycling. Even more, it could be considered as a favorable factor, since depolymerization consists on the breaking of polymer chains in order to obtain the monomer. Several researchers have analyzed the chemical recycling or depolymerization of PET by processes like methanolysis (Chandra and Adab 2018; Myren et al. 2020), hydrolysis (Carta et al. 2003), and glycolysis (Barboza et al. 2009), among others. These methods are suitable for marine plastics because they are not sensitive to the degradation presented by marine debris. Among the depolymerization possibilities of PET, the glycolysis can be considered as the most common (Sangalang and Bartolome 2015). PET glycolysis consists on a molecular fracture by transesterification mechanism, in which PET reacts with low molecular weight molecules as glycols (being the ethylene glycol the most common) to produce monomers (alcohols), diols and monohydroxy polyols. Several types of catalysts have been used with this purpose: acetates, strong acids and ionic liquids (Sangalang and Bartolome 2015).

The glycolysis with ethylene glycol is considered to be a versatile chemical recycling method, because besides bis(2-hydroxyethyl)terephthalate (BHET) monomer formation, specialized oligomer products such as polyols are also obtained (George and Kurian 2014). These sub-products can be further employed for the synthesis of different polymers such as unsaturated polyesters, polyurethanes, vinyl esters or epoxy resins (Güçlü et al. 1998; Nikles and Farahat 2005; Abdelaal et al. 2011).

When the purity of recovered PET waste is too low for recycling by chemical methods, the energy recovery appears as the best option (Petcore Europe 2020). In this method, PET is used as a fuel for energy generation by burning, taking advantage of its hydrocarbonated nature. As result, carbon dioxide and water are obtained, with the consequent energy release (Alves et al. 2012).

5 Recyclability of High and Low Density PE Recovered from Marine Debris

It is the most common plastic in use today, mainly used for packaging (plastic bags, plastic films, containers including bottles, etc.). Annually, around 100 million tons of PE are produced, consisting around the 34% of total plastics market (Geyer et al. 2017). It can be low density (LDPE) or high density (HDPE). LDPE is used for trays and containers, packaging for computer hardware or as a part of tetrabriks. HDPE is used in the production of plastic bottles, corrosion-resistant piping, geomembranes, etc.

Due to improper disposition of this material after use, and for being considered inert to degradation, PE can stay in our environment for many years. As it is constituted by carbon and hydrogen, PE should not degrade but the presence of chromophoric groups coming from the synthesis and processing, can make the polyolefin susceptible to degradation such as photooxidation (Nechifor 2016). By absorbing the UV rays, free radicals are produced, which can lead to oxidation and degradation of the material. Normally, the oxidation process is slower in the marine environment when compared with materials exposed to air, due to the lower temperature of the former (Andrady 2017).

In the last years, some authors have analyzed the degradation level and the effect on properties for PE recovered from marine waste (Pellegrini et al. 2019; Garvey et al. 2020). Moreover, the mechanical recyclability and biodegradation by microorganisms has also been studied (Devi et al. 2015; Pellegrini et al. 2019). In this way, Pelegrini et al. (2019) evaluated the degradation of post-consumer PE samples present in the marine environment, as well as their recyclability regarding mechanical recycling. They used PE obtained from the Great Pacific Garbage Patch. They selected four samples, by using a criterion adapted from the method of classification of the material surface levels of biodegradation described by De Paoli (2008): considering the surface area covered by the apparent degradation. Samples were named as a function of their degradation level: G1 with degradation coverage of up to 10%, G2 from 10 to 30%, G3 from 30 to 60%, and G4, from 60 to 100%. The degradation level of samples was determined by Fourier transform infrared spectroscopy (FTIR), showing different levels of carbonyl in different layers below the surface and by scanning electron microscopy (SEM) which showed the presence of some cracks and microorganisms. In a second step, after washing and drying the samples, mechanical (bending tests) and rheological properties (melt flow index, MFI, determination) were evaluated in order to check the recyclability of samples exposed to the marine environment. Properties obtained were compared with those of two different grade PE. They concluded that the ocean-collected materials used in their work, despite being degraded in the environment, can be submitted to recycling, exhibiting mechanical and rheological properties close to those of virgin materials found in the market.

Several attempts on the investigation of marine PE degradation have also been made by other authors, by both trying to understand the effect of marine environment (Garvey et al. 2020) on the degradation of samples at a molecular level, and trying to biodegrade some PE samples with the use of microorganisms (Devi et al. 2015). Garvey et al. (2020) examined the structural changes in the lamellar arrangements of semicrystalline PE packaging waste recovered from the Atlantic, with the aim of understanding the physical mechanisms of embrittlement in PE exposed to the marine environment by comparing with new PE samples. Both macroplastics and microplastics were collected from the accumulation area of the North Atlantic subtropical gyre. While macroplastics were visible from the ship, microplastics were collected using a manta net. Several experimental techniques were used to evaluate the degradation of samples: size exclusion chromatography (SEC) for the determination of the molecular weight distribution of the PE polymer chains, differential scanning calorimetry (DSC) for the analysis of the crystallinity. Small- and wide-angle X-ray scattering for the analysis of the packing of PE chains and longitudinal acoustic mode Raman spectroscopy for the measurement of the length of PE polymer chains. They claimed that even if the structural conclusions of their work were clear for the samples examined, the direct relation of the changes with the long-term effects of physical aging in the marine environment is more difficult.

In the case where the linage of aged samples was clearly established, they observed important changes in the polymerization degree of the polymer: chain scission induced by exposure to high-energy radiation (photochemical degradation), with changes in crystallinity and consequently, the embrittlement of samples. The most

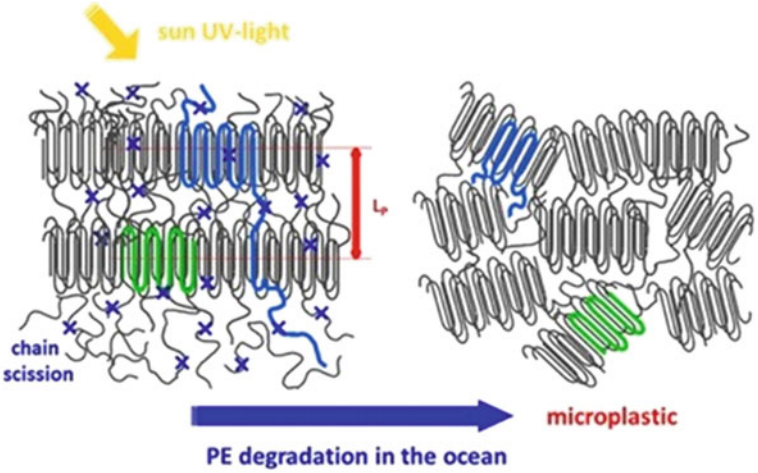


Fig. 5 Summary of the observed evolution of semicrystalline PE submitted to environmental conditions. Reproduced with the permission of (Garvey et al. 2020), copyright 2020 American Chemical Society 2020

important conclusion they obtained, as shown in Fig. 5, is the loss of an ordered lamellar structure in aged microplastics.

As crystalline regions constitute a barrier to diffusion of oxygen or other oxidants into PE, the loss of the lamellar structure would allow an easier chemical degradation. They pointed out that it could enhance a further chemical degradation of the polymer. Regarding the possible biodegradation of PE samples by microorganisms, Devi et al. (2015) studied the degradation of HDPE collected from the coastal area of Gulf of Mannar (India) with *Aspergillus tubingensis* and *Aspergillus flavus*, isolated from the PE waste dumped marine coastal area and screened under in vitro condition. They claimed that biofilm formation observed showed the viability of fungal strains even after one month of incubation. They underlined biodegradation of HDPE by microorganisms and enzymes as the most effective process for its treatment. The most important conclusion from their study was that the colonization, biofilm formation and biodegradation of HDPE film by *A. flavus* was higher than by *A. tubingensis*. Both strains released extracellular enzymes to degrade the polymer, but authors claimed that a detailed characterization of these enzymes is necessary, together with further studies focused in genomics and proteomics, which could accelerate the degradation.

The biodegradation of PE by marine microorganisms has also been analyzed by other authors, even if by the moment, most of trials have been made with virgin PE pellets, as a first step for a posterior application to PE coming from waste, or even to study the effect of microorganisms present in the marine environment on the biodegradation of PE. In this way, Paço and coworkers (Paço et al. 2017) evaluated the response of the fungus *Zalerion maritimum* to different times of exposition to PE pellets, in a minimum growth medium, finding a decrease, in both mass and size, of the pellets. They pointed that naturally occurring fungus may contribute to the biodegradation of microplastics, requiring minimum nutrients. In the same way, Delacuvellerie and coworkers (Delacuvellerie et al. 2019) claimed for the first time the ability of *Alcanivorax borkumensis* microbial degrader to form thick biofilms and degrade specifically the LDPE recovered from plastic waste in the Mediterranean Sea. Those studies seem to open a door to the biodegradation of marine waste as a way to reduce its presence and negative effects.

6 Microplastics

Microplastics (MPs) constitute a very important fraction of marine debris. They include plastic particles lower than 5 mm in size, that can be classified according to their source of origin as (i) 'primary' MPs, those manufactured for direct use in industrial products and applications, and (ii) 'secondary' MPs, resulting from the fragmentation of larger objects (Cole et al. 2011). The distinction between primary and secondary MPs helps identifying potential sources and taking mitigation measures to reduce their entry into the environment. Pictures of recovered primary and secondary MPs are shown in Fig. 6.

Primary MPs include industrial abrasives used to clean surfaces, plastic powders used in moulds, microspheres of cosmetic products and plastic nanoparticles used in a wide variety of industrial processes. In addition, virgin resin granules and powders, used as raw material plastic products manufacture are also included in this category (Fig. 6a). Primary MPs enter in the marine environment by rivers or via sewage systems, as they cannot be effectively removed by wastewater treatment plants (Talvitie et al. 2017; Kazour et al. 2018). Secondary MPs result from the exposure to weathering and fragmentation of larger plastic items (Fig. 6b). This can occur during the use and wear of products such as textiles, paint and tires, or once

(a) **(b)**

Fig. 6 Photographs of **a** primary MPs, constituted by industrial pellets recovered from a beach, and **b** primary and secondary MPs the articles have been dumped into the environment. For example, clothes washing is one of the main sources of plastic microfibres that end up in the sea (Browne et al. 2011; Napper and Thompson 2016). On the other hand, the largest plastic waste elements in the sea become increasingly fragile under the action of UV rays and heat, and end up fragmenting by the physical action of wind and waves (Andrady 2015). Therefore, the macrolitter represents a considerable source of MPs (Andrady 2003, 2011). PP, PE, EPS, PA and polyesters like PET are the most common materials found in MPs, in agreement with the most widely used plastic materials in the world (Hidalgo-Ruz et al. 2012; Mendoza et al. 2020). Usually MPs samples present a high variety of size, shape, colour, chemical composition, density and other characteristics, which together with their small size and dispersion, make it strongly difficult not only to collect, but also to sort for further recycling. Those presenting a density lower than that of seawater, as PE, float on the water surface, but MPs can also be found suspended in the water column. Seabed sediments may be a sewer hole for denser MPs as PET and microfibers like nylon (Woodall et al. 2014; Sánchez-Vidal et al. 2018; Sherrington 2016). Beaches, on the other hand, contain both floating and sedimentary particles (Hidalgo-Ruz et al. 2012). However, MP dynamics in the oceans are not the same as those of macroplastics. While the spatial distribution of macroplastics can be explained by currents and winds, the mechanisms affecting the distribution of MPs are less known, as particle aggregation or biota activity may affect. Thus, MPs tend to create a biofilm at the sea, which increases the specific density of the particle and promotes its sink. In contrast, erosion may result in a decrease of specific density and, as a result, MP transfer beteween the surface, water column, and seabed may be variable (Hidalgo-Ruz et al. 2012). The MPs abundance vary significantly depending on the compartment, the measurement methodology, the geographic area and even on the sampling period. The use of different methodologies difficults the comparison of different studies and consequently, the urgent need to standardize procedures in this scientific area rises up (Mendoza et al. 2020). There are evidences on the MPs ubiquity at the sea, even in the most remote areas and deep sea beds (Barnes et al. 2009; Ryan et al. 2009; Woodall et al. 2014; Cózar et al. 2017; Sánchez-Vidal et al. 2018). They have also been found in the biota (Lusher, 2015), as well as in freshwater springs, rivers, lakes, or polar ice (Eriksen et al. 2014; Cole et al. 2011; Obbard et al. 2014; Sadri and Thompson 2014). Currently, these studies are being completed by evaluating the presence of MPs inland, as landfills or the use of sludge generated in wastewater treatment plants as crop fertilizer may create new sources (IMPASSE Project 2019). All the environmental compartments are interrelated through water cycles and currents, allowing MPs mobility. However, the information on the distribution and impacts of MPs in the oceans is still limited. Worldwide studies highlight a huge spatial and temporal variability in MP distribution, and therefore, monitoring programs are needed to compile data over time at different scales and thus, evaluate the historical trends of MP pollution in the oceans ant the possibility of recovering for recycling purposes.

The wide distribution of MPs in extensive matrices (water, sediments, biota) is the main obstacle for their recovery. Due to the high dispersion and small size, efficient collection would require filtering or sieving large amounts of water or sediments, making it impossible to discriminate them in situ from other small natural particles. In addition, their composition and their relatively high specific surface area make them suitable for adding organic pollutants such as POPs (Persistent Organic Pollutants) or leaching toxic plastic additives (stabilizers, plasticizers, etc.) to seawater, that could lead to health problems or difficulties for cleaning and processing (Andrady 2017).

Thus, the enormous impact of an indiscriminate collection of particles would make the recovery of MPs unfeasible from a technical, economic and environmental point of view, except in extreme accidental cases of large occurrences.

7 Limitations and Opportunities of Marine Waste Recycling

The recycling of marine plastic waste presents a number of difficulties towards terrestrial residues, which reduce the possibilities for the development at an industrial level. The physical and chemical degradation caused by the marine environment, the wide distribution, the fractionation into MPs and the collecting difficulties related with the lack of management for this kind of residues, can be cited among others. As in some cases, the separation of wastes is neither economically nor technically viable, the chemical recycling constitutes a good alternative way of recycling (Ragaert et al. 2017). The challenges in the case of MPs are different. Their small size (less than 5 mm) makes them difficult to collect. In addition, they are usually found as a mixture of small pieces from the fractionation of different macroplastics with pellets from polymer transformation industry, other type of residues and the natural components.

However, various examples of products made from marine waste can be found in the market. As an example, mechanical recycling has been used to obtain the yarn needed to make trousers, coats and backpacks from PA fabrics obtained from fishing nets, T-shirts from PET bottles collected from the sea (by companies as Ecoalf, Ternua®) or new sustainable floor products (Net Works program). Some beverage packaging companies, as Coca-Cola with DEMETO consortium, have opted for the chemical recycling of PET for the manufacture of new bottles. In this case, the new bottles include 25% of the material recycled from marine waste through chemical recycling. In each case, several strategies have been found for collecting materials and to improve the quality of obtained recycled products.

The management of residues is another critical aspect to be considered. The experiences of mentioned market examples are based in the collaboration of anglers and voluntary marine waste collection campaigns. From obtained raw materials, companies usually makes small collections. Legal requirements are necessary in order to improve the cleaning process of marine residues and the required management for their recovery, facilitating the raw material valorization.

The use of marine waste need to be regulated and management in order to increase the recycling possibilities of this type of residue as the New Circular Economy Action Plan, a legislative proposal of the European Commission, proposes. This area is one of the main blocks of the European Green Deal, related with the Europe's new agenda for sustainable growth.

8 Conclusion and Future Perspective

Recycling marine debris shows several difficulties related with the degradation of materials, the distribution of residues, the size of plastics and the collecting process, among others. Thermomechanical and chemical are the most useful processing methods for these type of residues. In fact, PA from fishing nets or PET bottles recovered from the sea are being industrially recycled. As the reduction of marine debris affects in the sea has become urgent, the requirement of further research to generate sustainable recycling processes that include economic, environmental and human health benefits raises up worldwide, as it constitutes a global problem. Recovery and recycling of marine plastic waste must be optimized in order to assure the health of our oceans and that of species living there.

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Recycling of Synthetic Fibre Reinforced Plastics

Runcy Wilson, Gejo George, Tomlal Jose E, and Kuruvilla Joseph

Abstract Fibre reinforced polymer composite materials have been widely used in industries owing to their good strength, light weight nature and their remarkable mechanical properties. The increased use of synthetic fibre based composites have led to a large amount of composite waste being produced annually and that too globally and their management is becoming an important issue. The conservation of resources and environment is having a negative impact due to the current increasing amount and recycling of composite waste at their end of life cycle. This chapter focuses on the classification of various composites materials, recycling methods of fibre reinforced materials and their waste management.

Keywords Composite materials · Fibre reinforced composites · Recycling and reuse

1 Introduction

The mixing of a polymeric matrix (thermoset or thermoplastic) with a fibre reinforcement in the form of basalt, carbon, glass, aramid, asbestos, natural fibre etc. leads to the formation of materials referred to as fibre reinforced plastic composites (FRPs). These FRP materials have received significant interest in the last few decades owing to their extensive use in different areas like aircrafts (Soutis 2005) construction (Riedel and Nickel 1999), sports goods, automobile (Njuguna et al. 2011) space crafts and wind energy applications. Generally a fibre reinforced composite is composed of

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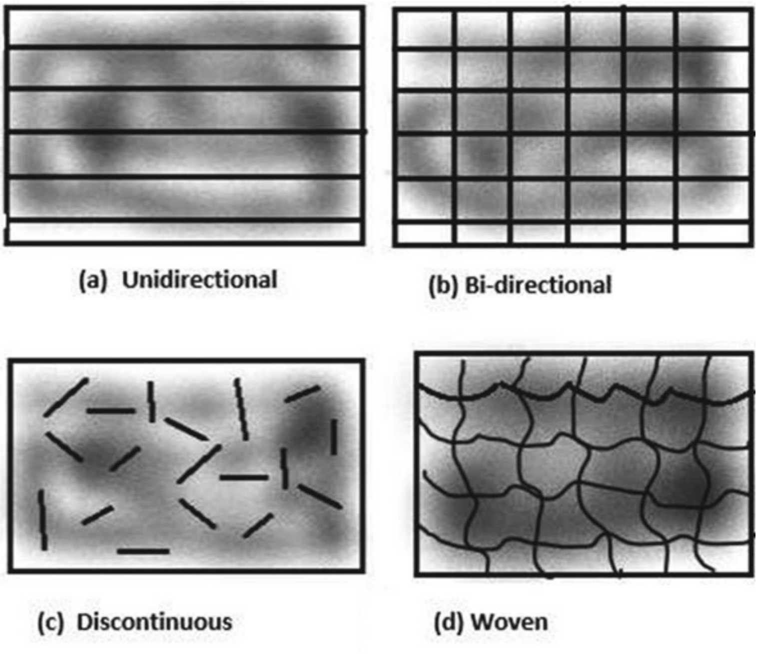
many fibres incorporated into a matrix and the fibre form can vary from unidirectional, bidirectional, discontinuous, and woven types (Scheme 1).

The different varieties of fibre reinforced composites include metal matrix, ceramic matrix, carbon/carbon and polymer matrix fibre reinforced composites. The reinforcement material (fibre or particulate) is held together by the matrix component in the composite and hence has a significant role. Polymer matrix/fibre reinforced composites can be further classified into thermoset, thermoplastic and elastomer matrix based composites. The major advantages of such materials include low weight, excellent mechanical strength and stiffness coupled with resistance to corrosion. Fibre reinforced composites have found a significant amount of applications in various fields which in turn has necessitated the urgent need for better recycling of fibre reinforced composites. Normally once a material completes its intended life cycle it is disposed off in landfills leading to severe environmental concerns. An approximate $12 billion, with an annual growth rate of 6.6% by 2020 is estimated for FRCs in the US market (Karuppannan Gopalraj and Kärki 2020).



Scheme 1 Different types of fibre reinforced composites

1.1 Metal Matrix Composites

A composite material consisting of metallic matrix reinforced or embedded with ceramics or metallic dispersed phase is referred to as metal matrix composite. The characteristics of such materials include high ductility, toughness as a result of the metallic constituent and strength and modulus due to the ceramic constituent. The resulting metal matrix composites leads to materials with greater shear strength and compression which can withstand higher temperatures also. They have found a range of applications in aerospace, automotive and in structural areas (Chou et al. 1985). It can be broadly classified as, Aluminum Matrix Composites (AMC), Magnesium Matrix Composite (MMC), Titanium Matrix Composite (TMC) and Copper Matrix Composites (CMC).

1.1.1 Aluminium Matrix Composites

The class of aluminium centric materials with low weight and high performance are referred to as Aluminium matrix composites (AMCs). Fibres (continuous or discontinuous), particulates or whiskers ranging from few percent to 70 volume fractions can be used as the reinforcement in AMCs. The perfect combination of the reinforcement, matrix and the processing method can lead to materials tailor made for the demands of various industrial applications. The different applications of AMCs include robotics, machinery, automotives, brake parts etc. (Kumar et al. 2017). The fracture toughness and behaviour of COMRAL-85^{TM} (a 6061 aluminium–magnesium–silicon alloy reinforced with 20 vol% Al_2O_3-based polycrystalline ceramic microspheres) was thoroughly studied by Park et al. They monitored the effect of Al_2O_3 in Aluminium for volume fractions varying from 5 to 30%and determined that with increasing volume fraction the fracture toughness of the material decreased. The reason for this decrease was attributed to the decrease in inter-particle spacing between nucleated micro voids (Park et al. 2008). In a similar work Kwon et al. Utilized a combination of spark plasma sintering and hot extrusion methods to increase the tensile strength of aluminium-carbon nanotube composite without compromising the elongation at break. The authors observed that the average thickness of the boundary layer with relatively low CNT incorporation utilizing optical, SEM, and high-resolution transmission electron microscopies. However, the important observation was that the composite did not show any decrease in elongation at break even though a significant increase in tensile strength was attained compared to that of pure AI. It was concluded that in the presence of CNT as filler in the boundary layer the mechanical properties are affected leading to well-aligned CNTs in the extrusion direction which in turn favours the effective stress transfer between the Al matrix and the CNTs due to the generation of aluminum carbide (Kwon et al. 2010).

1.1.2 Magnesium Matrix Composites

The low density, impressive mechanical properties and physical properties have made composite based on magnesium as matrix an apt candidate for different applications of aerospace and defence organisations. Compared to conventional materials used for engineering, the addition of reinforcing elements into a metallic matrix significantly increases the strength, stiffness, damping and wear properties (Dey and Pandey 2015). An ever increasing trend in research on the area of Magnesium based materials has been witnessed in the last few decades. However the major disadvantages include poor corrosion resistance and low mechanical properties. To overcome these drawbacks several approaches have been tried including composite fabrication with bioactive reinforcements, alloy formation and surface modifications (Dutta et al. 2020). Properties like reasonable strength, good biocompatibility have made magnesium, its alloys and composites to be apt candidates for biomedical applications. However, the poor corrosion resistance of magnesium and its alloys can lead to loss of properties before the proper healing of the bones. However, many researchers believe that the further development of such materials will lead to an era where such materials will satisfy a lot of orthopaedic applications. The properties of magnesium based composites like tensile strength, elastic modulus, ductility and resistance to corrosion can be fine-tuned based on end application needs. The most common magnesium based materials used for biomedical applications consists of magnesium alloys like Mg–Ca, Mg–Al, Mg–Zn, and Mg–REE alloy etc. as the matrix and hydroxyapatite (HAP), calcium polyphosphate (CPP), and β-tricalcium phosphate (β-TCP) particles etc. as the reinforcement (Bommala et al. 2019).

1.1.3 Titanium Matrix Composites

A material consisting of titanium matrix and continuous reinforcing fibres as the reinforcement is known as Titanium matrix composites (TMCs). These materials came to the market almost 20 years back when the primary reinforcing fiber being used was boron fiber. However, the discovery of new fibers like silicon SiC fibers has made these materials to be evolved with improved properties. The major attraction of these materials includes excellent strength and stiffness. Compared to conventional titanium alloys these materials have almost two times the ultimate strength coupled with good toughness when the properties are measured parallel to the fibre direction. Hence, they are considered to be one among the most structurally efficient engineering materials known (Lütjering and Williams 2003). In SiC based titanium composite materials the SiC fibers are reinforced within the titanium matrix and they make use of the high strength & stiffness and creep resistance at high temperatures of SiC fibers along with the damage tolerance behaviour of titanium alloys. The processing of these materials is of utmost significance as it can affect the properties of the final product. Along with processing techniques reinforcement-induced anisotropy of the material and thermal residual stresses formed during the consolidation process must be well thought-out and understood for the proper designing of the final material. The elucidation of failure mechanisms in the materials and reduction in time needed for the development of the materials can be achieved using modelling techniques like FE (Leyens et al. 2003). The main applications of TMCs include in the aviation, aerospace, chemical industries owing to the high specific strength, specific rigidity, and excellent mechanical properties at high temperatures of the said material (Saba et al. 2019).

1.1.4 Copper Matrix Composites

For applications where high temperature resistance and micro structural stability is required Copper metal matrix composite is the most promising candidate for such engineering applications. The properties like strength, hardness, resistance to wear & tear, resistance to corrosion, low cost nature, easy availability etc. of the reinforcement influences the choice of reinforcement in a given material. The high sustainability, conductivity and good resistance to different factors have made copper and its composites attain very good popularity in recent years (Jamwal et al. 2020).

The area of engineering sciences has recently witnessed increased use of copper, its alloys and composites in a variety of applications. In production field also these materials are now getting significant attention. The key advantages of these materials include low density, good fatigue strength, high corrosion resistance coupled with specific strength (Tu et al. 2002). Owing to the advantages of composite materials over other conventional metals they have been receiving increased importance and significance in the areas of aerospace, automobile and construction industries (Schubert et al. 2008). When metallic matrix composites MMCs are comprised of metal as matrix and ceramic as the reinforcement then the resulting composite will have the Metallic properties such as toughness and ductility, and ceramic properties, such as elastic modulus and high strength, which bequeath shear strength providing service at high temperatures (Gautam et al. 2018).

1.2 Ceramic Matrix Composites

Ceramics are a solid material that, in general, contains strong ionic bonding and in a few cases covalent bonding can also be observed. Ceramic composites (CMCs) are apt candidates for applications that require high temperature resistance (above 1500 °C) owing to their high melting point, corrosion resistance and good compressive strength (Chawla 2003). The reinforcement in these materials can be fibers (continuous or discontinuous) or particulate in nature. Conventional ceramic methods can be utilized to prepare short fiber (discontinuous) reinforced CMC composites where in an oxide like alumina or non-oxide like silicon carbide ceramic matrix is reinforced with whiskers of silicon carbide (SiC), titanium boride (TiB_2), aluminum nitride (AlN), zirconium oxide (ZrO_2), and other ceramic fibers. However, in the case of long-fiber (continuous) composites the reinforcement is either in the form of long monofilament or long multifilament fibers. By using chemical vapour deposition (CVD) technique on silicon carbide on a substrate of tungsten or carbon can lead to dispersed phase in form of continuous fibers as reinforcement in CMCs and are expected to have the best strengthening (Samal and Lanka 2012). Cooper and Chyung (1987) reported the preparation of Silicon carbide continuous fibre-reinforced glass and glass–ceramic matrix composites and demonstrated that these materials show high strength and fracture toughness which was characterized by means of thin-foil transmission electron microscopy and scanning transmission electron microscopy. The authors reported that these materials showcased excellent mechanical properties which can be directly related to the formation of a cryptocrystalline carbon (graphite) reaction-layer interface between the fibres and the matrix. The authors also attributed these excellent properties to the relatively rapid diffusion of silicon and oxygen from fibre to matrix due to the involved solid-state reaction and hence are in good agreement with that of the experimental observations. The graphitic interface is created by the controlled chemical reaction and the silica amount and activity in the glass/ceramic matrix has a pronounced effect to control the said chemical reaction leading to the formation of the graphitic interface (Cooper and Chyung 1987). King et al. (2013) reported the preparation of silicon carbide/titanium diboride ceramic composites and studied the effect of TiB_2 content on mechanical properties of these composites. A decrease in the hardness for the ceramics was observed from 27.8 GPa for the pure SiC to 24.4 GPa for TiB_2. However, fracture toughness increased from 2.1 MPa $m^{1/2}$ for SiC to $\sim$6 MPa $m^{1/2}$ for SiC with TiB_2 contents of 40 vol.% or higher. The two parameter Weibull analysis was used to determine the flexural properties of the composites containing 15, 20, and 40 vol% TiB_2.The modulus of 12 at 15 vol% TiB_2 increased to 17 for both 20 and 40 vol%. It was later determined using micro structural analysis that the samples with 20 and 40 vol% TiB_2 had microcracking in them. Among the samples it was reported by the authors that the sample with 40 vol% TiB_2 had the best properties (fracture toughness of 6.2 MPa $m^{1/2}$, hardness of 25.3 GPa, Weibull modulus of 17, and a strength of 423 MPa) (King et al. 2013).

1.3 Carbon/Carbon Composites

A composite material made up of carbon matrix (or graphite) reinforced with carbon nanoparticles (carbon dots, quantum dots etc.) or carbon fibers are referred to as carbon/carbon composites. In these materials the attractive properties of carbon is coupled with good strength, versatility and excellent toughness of the composite materials. In carbon/carbon composites the excellent strength and modulus of carbon fibers is exploited to reinforce a carbon matrix in order to withstand extreme environmental conditions. Another attractive aspect of carbon/carbon composites is that they offer high performance, high strength and low cost alternative to metals at one tenth of their density. The common aerospace parts produced using carbon/carbon composites include rocket motor nozzle throats, nose tips, exit cones, thermal protection systems etc.

Xie et al. (2019) reported the preparation of 1D MnO_2 nanowire grown on hierarchical ordered mesoporous carbon/graphene composites by means of an economical, facile and eco-friendly redox method. The authors reported that the formation of ordered mesoporous or amorphous carbons would likely serve as an apt position for nucleation for the growth of MnO_2 nanowires and these assumptions were supported by both experimental as well as theoretical simulations. The good deposition efficiency of MnO_2 coupled with good stability of the decorated hierarchical porous carbon composites and relatively low equivalent series resistance may be attributed to the strong adsorptive interactions between the carbon matrix and MnO_2 nanowires. The authors were able to make electrode materials from these composites and demonstrated that they exhibited excellent electrochemical behaviour of specific capacitance of 756.2 F g^{-1} in KOH electrolytes. Similarly an excellent energy density of 34.56 Wh kg^{-1} at a power density of 450 Wkg^{-1} and excellent cycling stability was attained for an asymmetric supercapacitor (ASCs) assembled by using MnO_2@C and C as the positive and negative electrodes in 1.0 M Na_2SO_4.The above mentioned results clearly indicate that the said materials are apt candidates for the future high-performance super capacitor applications (Xie et al. 2019).

When a carbon matrix is reinforced with carbon fibre they form a unique kind of composite material known as Carbon Fibre Reinforced Carbon (CFRC), or Carbon–carbon composites. These unique materials have exceptional properties like low density, good thermal and electrical conductivity, good mechanical properties even at high temperatures and hence were originally designed for aerospace applications like rocket nozzles, brakes, re-entry nose tips etc. These materials have the capability to withstand even high temperatures like 2000 °C without major deformation. However, it should be clearly noted that the final properties of such carbon/carbon composites depend mainly on the processing methods used for their production. They can however be produced by common methods like internal mixing, extrusion, injection moulding etc. but tailored properties can be achieved by the combination of production methods which are however, the expertise of few limited particular manufacturers (Windhorst and Blount 1997).

2 Methods for the Disposal of Synthetic Fibre Reinforced Composites

The worldwide manufacturing of composite materials is in thousands of tons every year for a number of varying applications. Even though carbon and glass fiber composite materials have a range of useful applications one major issue associated with such materials is their recycling at the end of life phase because these reinforcing synthetic fibers and composite materials can remain in the environment for a long duration of time leading to pollution (Pimenta and Pinho 2011; Pickering 2006).The recycling of synthetic fibre reinforced composite materials is a serious issue which is a potential barrier to the growth and continued use of fibers and other composite materials in the society. Interesting point to note is that such kind of restriction is not seen in the case of competing materials like aluminium or steel (Asmatulu et al. 2014).

Wang et al. (2019) reported the recycling of carbon fiber reinforced thermosetting composites and concluded that from these materials the carbon fibers (CFs) can be reclaimed easily and these reclaimed fibers were able to retain their original initial high performance and value, and it was also claimed that the degraded thermosetting matrices can also be reutilized. In this review the different methods used to recycle synthetic fiber reinforced composites is presented along with the necessities and the need to prepare recyclable CFRPs. The review also aims to differentiate between traditional and readily recyclable CFRPs. The categorization of readily recyclable CFRPs based on degradable thermosets can be done into several categories based on the thermoset matrix being used in the material and different types of cleavable linkages (bonds) in the thermosets like ester, acetal linkages, Schiff base bonds, disulfide bonds, hexahydrotriazine structure, boronic ester bonds and di-*N*-benzylaniline linkages.The different mechanisms of recycling involved and synthetic approaches associated with degradable thermosets, their recovery and method of reuse of CFs are depicted in Fig. 1 (Wang et al. 2019).

The glass fiber and carbon fiber reinforced composites have huge long term demands as well as wide range of applications and in turn this has led to the use and development of a number of different recycling processes for them. In the earlier age most of the disposal of synthetic fiber reinforced materials was done by land filling or incineration, however the recent advent in technology has led to other techniques also, the following section will address these area.

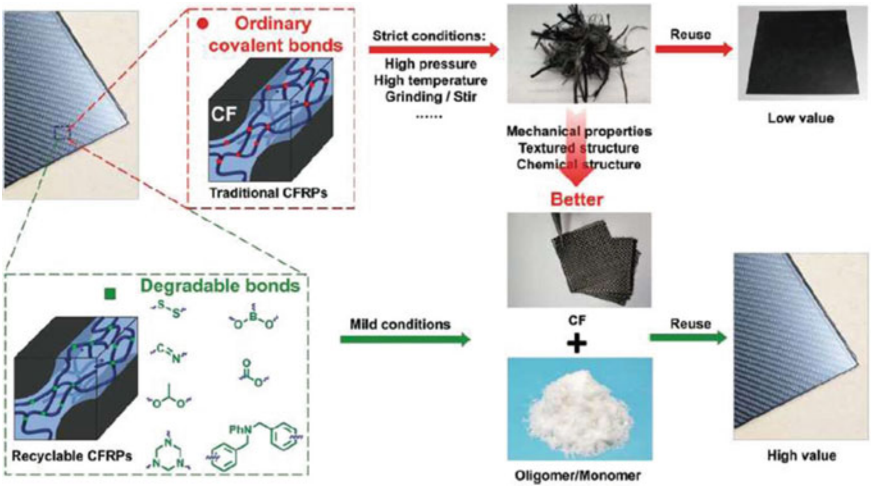


Fig. 1 Recovery and reuse of CFRPs based on traditional thermosets and degradable thermosets (Wang et al. 2019). Reproduced from (Wang et al. 2019) with permission from The Royal Society of Chemistry

2.1 Landfilling

There has been a growing call for the need of a sustainable society due to the increasing environmental pollution which involves greenhouse gases, both water and air pollution which is accompanied with energy crisis and the insufficiency for resources which is expected to increase in the coming years. The increased release of carbon dioxide along with other harmful chemicals (like volatile organic compounds and nitrogen oxides) is a major drawback of extensive use of fossil resources for energy production. The combustion of fossil fuels has contributed to an estimated 90% of the global emission in CO_2 (which reached approximately 34 billion tons of greenhouse gases in 2011) (Arancon et al. 2013). Another important factor associated with the environmental problem is the increasing amount of waste generated and its disposal. This accumulated waste creates a lot of serious problems for the environment and hence has recently received much increased public awareness. On the other hand if the society is able to recycle these huge amounts and variety of waste that are produced globally into some high value applications the boon it can bring to the society and to the economy will be immense (Lin et al. 2013).

In the present scenario the number of different types of plastics being used globally for a number of applications is numerous. The most important applications include packaging, wrapping, shopping and garbage bags, toys, household products, building materials, fluid containers etc. However, the merits of plastic based materials is outnumbered by the harmful effect it can have on the environment and hence society, since eventhough plastics are small they are a significant part of the waste streams (Subramanian 2000). A major waste fraction that has the potential to be recycled is the plastic waste present in huge areas of landfills. However, it should be noted that during the landfilling process the plastic waste may be subjected to contamination by trace metals or even corrosive compounds and they may also be subjected to structural changes during the landfilling process and hence may not be suitable candidates for conventional recycling processes (Canopoli et al. 2018).

Canopoli et al. (2020) reported a detailed study on the physicochemical properties of different types of plastics that are found in landfills and they also studied in detail their chance of recovery and recycling using different characterizations including scanning electron microscopy energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) etc. It was observed that compared to fresh plastic samples the samples that were buried demonstrated visual loss of gloss (polyethylene and polypropylene). The main factor contributing to the surface alteration of these buried samples was found out to be oxygen content by means of SEM-EDS analysis. It was also reported that the carbonyl index (CI) of buried samples (greater than 10 years) was in between 1.5 and 2 times greater than both the fresh samples and samples that were buried for less than 10 years. In conjunction with this it was also found out that the samples that were buried for more than 10 years had a degree of crystallinity that was 2 times higher than that of samples buried for less than 10 years and fresh ones. The authors concluded based on these findings that tertiary recycling processes like pyrolysis can

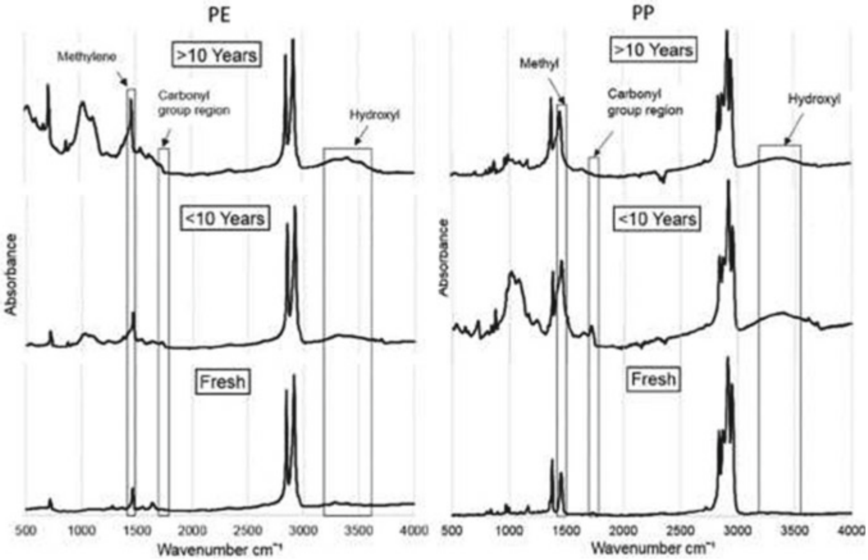


Fig. 2 FTIR spectra of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years) (Luisa Canopoli et al. 2020)

be an apt route/method for the upcycling of plastic materials that are recovered from waste landfills.

In order to determine the oxidation level of polymers the most common method used is to determine the carbonyl index of the polymer. Mathematically carbonyl index CI is the ratio of the band area attributed to the carbonylgroup –C=O to the band area attributed to methylene group -CH_2. In Luisa et al. study the carbonyl peak was integrated between 1779 and 1680 cm^{-1} and the methylene group between 1490 and 1420 cm^{-1} for PE and 2700–2750 cm^{-1} for PP (Fig. 2) (Luisa Canopoli et al. 2020).

(1) **Incineration**

The incineration with energy recovery is considered to be a viable option for the recycling of FRPs owing to their high calorific value. It should also be clearly understood that the primary application of an incinerator is to dispose of the domestic waste and the production of electricity from waste by means of energy recovery is only a secondary business. Another drawback of incinerating FRPs is that the relatively lower amount of incineration of FRPs will lead to considerable amounts of domestic waste (which is of unlimited supply) being send to landfills (Conroy et al. 2006). Based on reports it can be conclusively stated that among the different methods being used for the disposal of thermoset matrix based composites including synthetic fibre reinforced composites, incineration is a less commonly adopted process (Cunliffe and Williams 2003; Broekel and Scharr 2005). The high calorific value of FRPs leads to the incineration process producing significant amounts of heat during the process which can be used for energy recovery (Meira Castro et al. 2014). However, in an economic point of view the cost of incinerating FRPs is considerably higher compared to landfilling process. However, the cost of FRP incineration is higher than landfilling. In general, incineration facilities charge more for incinerating FRP waste because both the high calorific content and the toxic emissions tend to overload the system, meaning they can only process a limited amount of waste (Halliwell 2010). An additional drawback of incinerating glass fibre reinforced composites that is worth mentioning is that around 50–70% of residue left after incineration of GFRP is mineral in the form ash and this further needs to be disposed of in landfills. In Germany a co-processing method referred to as cement-kiln which is similar to that of incineration has recently been introduced (Job 2013). The cement-kiln method involves the size reduced GFRP wasted being introduced into a cement production kiln (hence the method name cement-kiln) in the form of a precursor for the preparation of cement clinker and also in the form of a secondary fuel. During the process the organic part of the GFRPs burn leading to the production of energy in the form of heat and the mineral (from the reinforcing fiber or filler) is converted to calcium oxide a primary constituent of portland cement thereby providing feedstock for the cement clinker (Yazdanbakhsh and Bank 2014).

The biggest advantage of incinerating CFRPs is that it gives the additional option of recovering a part of the embodied energy in the form of heat which can be utilized for other useful purposes. The recent development in incinerators have led to the co-production of both heat and electricity to provide for the local energy heat energy demands in cold parts of the world coupled with exporting the electricity produced to the grid. Previous reports have suggested that carbon fibre reinforced polymer wastes can be mixed or joined with municipal solid waste as a 10% loading and can be further utilized as a proper energy source (Pickering 2012). However, in general it should be clearly noted that the process of energy recovery from waste incineration has less efficiency compared to producing heat and electricity from refined fuels. The generation efficiencies are assumed to be 13 and 25% for heat and electricity respectively, thereby leading to a total conversion efficiency of 38% (Hischier 2014).

3 Various Methods for Recycling of Synthetic Fibre Reinforced Composites

The different types of waste recycling methods used for synthetic fibre reinforced composites are depicted in Fig. 3.

3.1 Mechanical Recycling

The mechanical recycling process of materials consists of first reducing the size of the materials to be recycled using a number of steps like shredding, crushing and

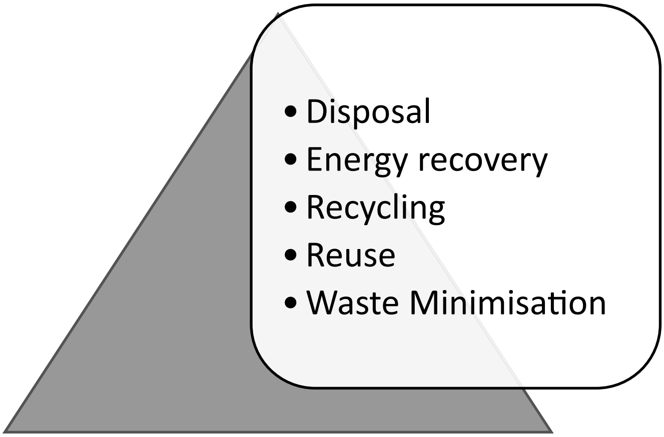


Fig. 3 The waste hierarchy (Zaman et al. 2014)

milling. This reduction of the size of the material helps in the separation of the fibres/fillers and the resin matrix. The first step involves the very slow cutting of the material to small size. Small metal particles are then extracted and then separated from the composite materials during the initial stages of the process using magnetic fields in order to facilitate the transport by reducing the volume of the material to be recycled. The metal extraction is followed by use of high speed mills to further reduce the size of the material. Later, once the downsizing process is completed sorting of the resulting materials takes place based on size by means of hydroclones, sieves, and shaking screens. The resulting rough/coarse product is comprised of higher fiber content compared to the starting material and the same trend is observed in the fine powder like material also (higher filler and polymer composition compared to the starting original material) (Chou et al. 1985).

Li et al. (2016) reported the assessment on the mechanical recycling of carbon fibre composite waste on the environmental and financial viability. The researchers used different life cycle costing and environmental assessment models to study the effect of recycling these materials on the economical and environmental aspects based on different waste processing methods like landfills, incineration coupled with energy recovery and mechanical recycling with special context to UK needs. In UK the current landfill tax laws have led to incineration becoming the most economical waste treatment method, however, the very high green house gas emission associated with the incineration process has led to them exceeding the CO_2 emission savings from the displacement of electricity/heat generation in the UK and hence has led to becoming a net greenhouse gas emissions source. Among the different recycling methods the processes of mechanical recycling and reuse of fibre/filler to replace virgin glass fibers is considered to be the best to provide reduction in green house gas emissions (-378 kg CO_2 eq./t composite waste), however, this can be achieved only when residual recyclates are landfilled rather than incinerated.The major drawback however, for this pathway is that it is not economically feasible due to being highly costly, which exceeds £2500/t composite waste ($3750/t composite waste). The mechanical recycling process is weakened by its financial performance (extremely high cost for the dismantling and recycling processes, the fibre recovery rate is very low and the likely markets available are low). In order to be made feasible this technique need to achieve very high (nearly 100%) fibre recovery rate and the degradation subjected to the fibres during the recycling should be minimal so that they can retain their mechanical properties which will enable them to be used in high end applications again (like replacement for virgin carbon fibres). Hence, it can conclusively be stated that the financial viability and environmental benefit of carbon fibre reinforced polymer recycling hangs in balance and depends on the recent developments in the area of carbon fibre recovery methods and the further processing of these recycled fibers to make composites leading to improved material (Li et al. 2016).

Bernasconi et al. (2007) on the other hand studied the effect of mechanical recycling on the mechanical properties of injection moulded polyamide 6, 6 composite that was filled with 35% weight of glass fibres. The authors conducted tensile property analysis of pure samples and also samples that had different amounts of mechanically recycled material. The method employed by Bernasconi et al. (2007) involved regrinding the specimen and then injection moulding the granules again into samples of the same type and size. Fibre breakage associated with decrease in fibre contribution to the strength of the composite is the main effect of this type of mechanical recycling. The authors were also able to compare the experimental results with theoretical predictions obtained using a micro-mechanical model which took into account the effect of fibre length distribution and different phases in the composites contributing to properties of the final composite. The authors believe that this kind of modelling can be utilized as an effective tool in the eco design methodology where it can be predicted regarding the property change of the materials brought about by the recycling process compared to the pure ones. This will help in the assessment of different recovery methods on the properties of materials made from recycled fibres and also on the environmental effects (Bernasconi et al. 2007).

García et al. (2014) reported the ability of mechanically recycled glass fibre reinforced plastics from different precursors to be considered as short fibres in the production of precast micro concrete components. For materials to be considered as flat micro concrete elements the fibres need have optimized fibre lengths and the recycled product should also have high fibre content, all of these were attained by the authors by means of shredding and screening processes (Fig. 4).

The material obtained was subjected to calcination process and later the structure and arrangement of the glass fiber after calcination was observed (García et al. 2014). The mechanical recycling of GFRP from electric panel boards resulted in a mat of short and intertwined threads of glass fiber which had very high calcium carbonate content as filler. However, when the same process was applied to GFRP from train fairing the recycled materials was found to contain inorganic fillers mixed with glass fiber which also included a surface coating of some kind of gel. The morphology of this glass fiber was found to be in the form of chopped strand mat. The authors have also stated that a sandwich type (three layers) of structure was observed for the

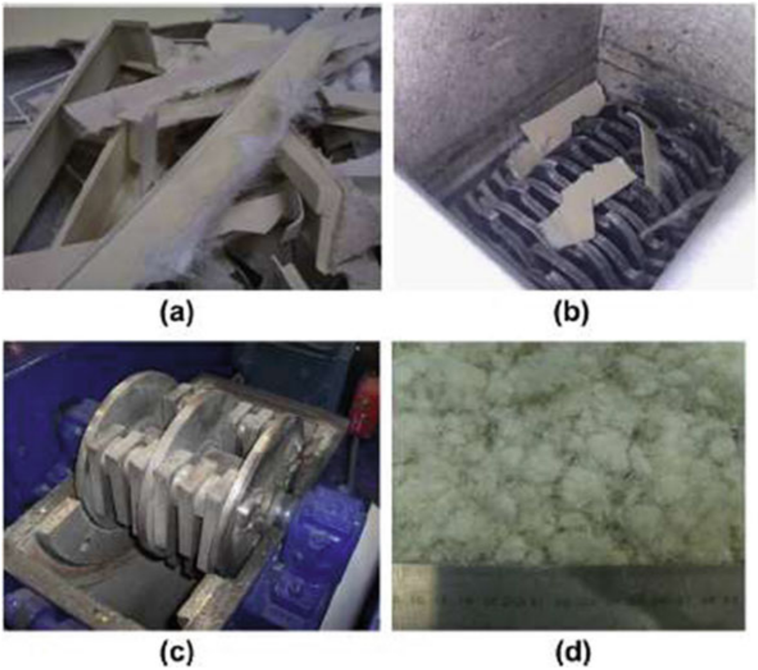


Fig. 4 Shredding and milling processes of the GFRP fiber: **a** Offcuts of GFRP components, **b** two-shaft shredder, **c** hammer mill and **d** Fluff GFRP (García et al. 2014)

glass fiber when it was pultruded from profiles of GFRP. In this sandwich structure, the two outer exterior layers were made of chopped strand mats composed of long randomly oriented fibers whereas the inner layer was found to be made of thick and long fibers which were arranged longitudinally with respect to the profile. Similarly when pieces of GFRP from leisure boat hulls were subjected to mechanical recycling the resulting material consisted of a sandwich structure of five layers of glassfiber and a surface gel coating.The obtained glass fibers were found to have knit fabrics in the core layer of the structure with short threads of 30–40 mm woven mats in the external layer (García et al. 2014).

3.2 *Thermal Recycling*

Among the different recycling methods for the recycling of plastics, thermal recycling is considered to be one of the simplest to retrieve glass and carbon fibers wherein the composites are subjected to high heat so that the matrix material is burned off and the reinforcing fibers are retrieved and reused. However, one of the major drawbacks of this technique is that the properties of the retrieved fibres tend to decrease depending on the applied temperature and the duration of the recycling process (Feih et al. 2015; Thomason et al. 2014). During the process of thermal recycling the synthetic reinforcing fibers like glass etc. are liberated or released by the incineration or burning of polymeric matrices followed by the reuse of these fibers in secondary composite applications. However, the readers should bear in mind that these liberated or released reinforcing fibers via thermal recycling may suffer from different extends of property degradation depending on the specific recycling process employed and the duration for which the process was employed. Researchers have reported that glass fibers that were recycled from fluidized bed systems were found to have significant loss to mechanical properties upon retrieval and hence were found to be not suitable for high strength components (Feih et al. 2011; Thomason et al. 2014). It was also reported that the use of fluidized bed for glass fiber recycling led to the recycled glass fibers demonstrating strengths that were only 50–90% to that of the original fiber strength and it was also reported that this decrease depend very much on the duration of recycling and temperature of recycling (Pickering et al. 2000).

Pender and Yang (2017) reported the effect of thermal recycling (in presence of catalyst) of epoxy matrix reinforced with glass fiber on improving the recycled materials commercial viability. The major bottleneck in retaining the commercial value and viability of recycled materials is the decrement or degradation of strength of the recycled material after the recycling process. This can be controlled a bit by fine tuning the temperature at which the recycling process is performed, the lower the temperature for the recycling the lesser will be its effect on strength degradation. In order to reduce the recycling temperature different metal oxides were studied to assess their ability in reducing the high operating temperatures of recycling process that currently limits the reusability of the recycled or recovered fibers. This kind of metal oxide acting as a catalyst will have dual role, one in which it will be integrated within the thermal recycling system to facilitate the increase in fiber residual strength and the second to reduce the total energy consumption of the whole process. During this work it was observed by the authors that the metal oxides like CuO, CeO_2 and Co_3O_4 were able to significantly reduce the temperature required for recycling process thereby accelerating the whole thermal degradation process of epoxy matrix (Pender and Yang 2017). The utilization of these catalyst during the thermal recycling of GF-epoxy system it was observed that both the time required for the recovery of fibers and the temperature required for recycling was reduced considerably, thereby leading to a wholesome reduction in energy consumption by 40%. It was also observed by the authors that the recovered fibers using the above mentioned metal oxides had significantly higher strength, however it should be clearly noted that full retention of strength has not be achieved so far and would be a significant achievement in the area of thermal recycling processes (Pender and Yang 2017).

Table 1 shows the different qualitative epoxy matrix degradation/decomposition temperatures and time taken for the decomposition for GF-epoxy composite samples that were thermally recycled in a furnace using the above mentioned metal oxides. It can be clearly noted that the use of CuO lead to the largest decrement in required temperature for the thermal decomposition of epoxy matrix to completely degrade or decompose. It was observed that the metal oxide CuO, CeO_2 and CO_3O_4 were

Table 1 Energy consumption required for fibre liberation by thermally degrading epoxy matrix with different temperature and duration (Pender and Yang 2017)

Sample	Temperature (°C)	Time (min)	Furnace energy consumption (kJ)
GF-epoxy only	500	80	64,200
GF-epoxy + CuO	380	330	20,200
	400	180	6030
	430	65	3720
GF-epoxy + CeO2	450	60	4000
GF-epoxy + Co_3O_4	450	65	4090

able to decrease the decomposition temperature by 120, 50 and 50 °C respectively and are in close agreement to the results obtained by thermo gravimetric analysis (TGA). The data shown in Table 1 also proves that when the temperature of recycling process is reduced then considerably lengthy heating periods are required for the recycling even when CuO is used. This kind of phenomenon is normally seen in typical temperature dependence of reaction kinetics. The authors in this work were also able to demonstrate when similar temperature reduction is performed on GF-polymer composites it can hardly affect the period of epoxy degradation even when highly efficient catalyst, such as CuO, is used during the recycling process. This also led to the conclusion that the extensive decomposition (extended period) observed in GF-epoxy system when a furnace is used is probably due to the large quantity effect as compared to the minute quantities being taken in TGA machine. The authors expected that the effects of such long periods of decomposition can be controlled when different recycling methods like fluidized bed is used (because in such systems smaller composite scraps are used and they may provide more effective interaction among them). The effect of heat treatment of GF-epoxy system in presence of CuO in a fluidized bed is shown in Fig. 5. Here the authors report that in both the cases the samples were heated at 380 °C for 330 min. However as evident from Fig. 5 the interesting observation is that when GF-epoxy degradation takes place in presence of CuO, clean glass fibres are obtained as shown in Fig. 5b in contrast with its counterpart in Fig. 5a.

(a) **Pyrolysis**

When composite materials are decomposed by using external heat (temperature) in presence of inert atmosphere, the process is referred to as pyrolysis. The by-products of this process are mainly fiber and fillers (the inorganic constituents of the composite). During this process the normal temperature used for the decomposition of composites is in between 400 and 600 °C. It should be clearly noted that in pyrolysis process also researchers tend to use the lowest possible temperature for decomposition because in any recycling process of composites the primary aim is to recover valuable fibres or filler, and hence the use of very high temperature may affect the strength of recovered fibers or fillers. The products obtained after pyrolysis

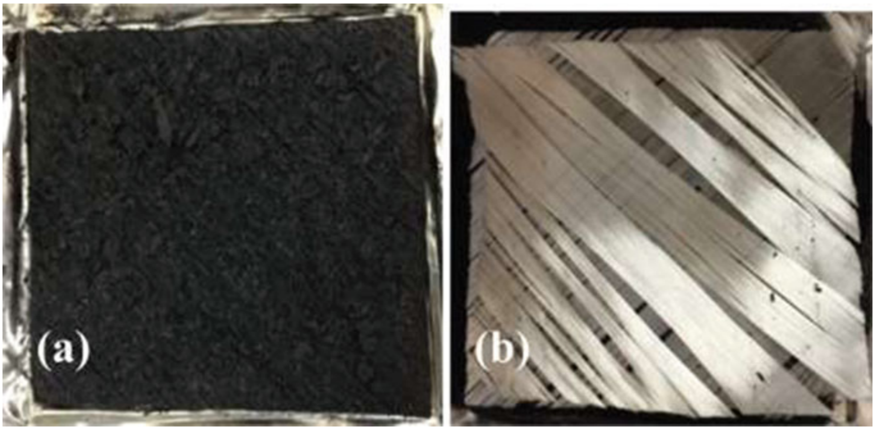


Fig. 5 Image of **a** GF-Epoxy after heat treatment at 380 °C for 330 min without CuO. **b** GF-Epoxy after identical heat treatment with CuO (Pender and Yang 2017)

process can be classified as gases, liquids and solid char residue wherein the first two have ability to provide energy for other processes.

Yun et al. (2014, 2015) reported the pyrolysis of glass fiber reinforced composite for recovery purposes under non-isothermal and isothermal conditions. Composite scarp parts were used as the starting material and their pyrolysis behaviour under non isothermal conditions were studied carefully at different heating rates and temperatures in a batch type pyrolyzer and also in TGA apparatus. Arrhenius equation was used to determine the kinetics of pyrolysis of GFRC and was found to be in between 41.4 and 78 kJ/mol. However, it was determined that the structure of GFRC in biomass and nature are entire different and during pyrolysis cannot retain the structure when very high temperatures are used. The analysis of char obtained after GFRC pyrolysis using FTIR and SEM revealed that the structure appears to be more stable at high temperatures and the ash produced have a tendency to breakdown under further heating process. In isothermal conditions the GFRC pyrolysis was performed at a temperature range of 500–1000 °C. During this study it was reported by the authors that the activation energy tend to decrease at higher temperatures and showed an activation energy of 28.1 kJ/mol. The authors concluded the findings that polymer scission and re-polymerization can take place if the temperature and residence time of pyrolysis process is increased.

Åkesson et al. (2012) on the other hand explored the possibility to utilize microwave pyrolysis for recycling glass fibre-reinforced composites. For this purpose the authors used a scrap blade derived from a wind turbine as the starting material and it was fragmented and later microwave-pyrolysed. Interestingly the authors were able to retrieve 70% of the initial mass of glass fiber by the microwave pyrolysis of the glass fiber reinforced composite. The tensile strength of the glass fibre before and after pyrolysis was measured and found that the recovered fibers tend to lose 25% of their tenacity. The authors also demonstrated the practical use of such recovered glass fibers by preparation of non woven mats based on their recovered fibers. These were then made into laminates together with virgin glass fibers and the mechanical strength analysis revealed that composites with 25% recovered glass fiber composition can be prepared with good mechanical properties. In this step the fragmented pieces of the composites were pyrolyzed at 300–600 C in inert atmosphere. During this step the samples were filled in a reactor (a jar to be precise) which was made from micanite which is transparent to microwave heating and the jar had a total volume of 10 L. The typical process involved the filling up of the micanite jar with around 3 kg of the composite pieces and was then sealed tightly. Three magnetrons (each having 1 kW power) was used to generate the microwaves. During the entire process the temperature inside the reactor jar was closely monitored and it was observed that the decrease in reactor temperature led to disruption of the pyrolysis process which was observed to be normally after around 90 min.

The recovered fibers after pyrolysis by microwave heating was examined using TGA and was found out to have around 3–8 wt.% organic content. The fibers were also found to be covered by some type of residue (mostly carbonaceous in nature) which the authors believed was from the polyester that may have not degraded completely during the pyrolysis process. The authors also observed two types of layers covering the recovered fibre (sample obtained after plasma treatment of wind turbine blade). The authors claimed that the layers appeared to be damaged however, the removal during pyrolysis was not complete. In order to further understand what these coatings on the fibers were, the glass fibers were soaked in chloroform for 48 h and then extracted which was then analysed using GC–MS. The authors were able to identify the following compounds; di-isobutyl phthalate, hexadecane, octadecane, dodecanamide, eicosane, 9-octadecanamide, octadecanamide and several cyclic organosilicon compounds. Along with the above mentioned compounds some compounds containing nitrogen were also identified (Åkesson et al. 2012).

Pickering et al. (2000) recovered glass fibers at different temperatures using a fluidized bed reactor. The authors during this study observed that when temperature of 450 °C was used the recovered fibers lost about 50% of their tensile strength while higher temperatures were more damaging to the tensile strength. Similar to tensile strength it was also observed that at temperatures of 360 °C the tenacity also dropped to around 25% of the initial virgin fiber value. However, in case of tenacity further increment of temperature to 440 °C seemed to make no further effect. The authors also tried to study the effect of 300 and 600 °C pyrolysis on the tensile properties and tenacity of the recovered fibers. The authors concluded that 300 °C is too low of a temperature for pyrolysis and hence no effect was observed on the fibers even after 90 min. On the other hand it was observed that the pyrolysis of fibers at 600 °C led to fibers becoming very brittle indicating that most of the fiber has been destroyed. (Pickering et al. 2000).

Cunliffe et al. (2003) reported the use of bench scale static bed reactor functioning at 350/800 °C for the recycling of few different types of composite wastes. The different types of wastes included composites of polyesters, phenolic and epoxy resins, and polypropylene, reinforced with glass and/or carbon fibre. The authors observed that during the pyrolysis of different wastes the composition of gas produced and the product mass balance were dependent on the type of matrix in the composite, the temperature used for the pyrolysis and when higher temperatures were used then the decomposition of thermally unstable fillers present in the system also played a role. The study revealed that the residues obtained after the pyrolysis of PE1 (a Thermoset polyester/styrene resin matrix reinforced with calcium carbonate and aluminium trihydrate fillers (36 wt.%) and glass fibre (12 wt.%)) at 350 °C retained their strength and size compared to the original ones even thought the recovered once were brown in colour and had shiny surfaces. It was also observed by the authors that when the pyrolysis temperature was increased further the residues were able to retain the original size of the pieces but appeared to be dark (black) and friable with charred and porous finishing. Interestingly enough when the samples were pyrolysed at 350 °C the condensable products obtained was a mixture of pale yellow wax (around 40 vol%) coupled with around 5 vol% water with low viscosity and very low quantity of yellow/brown oil. It was concluded that the moisture content obtained may be from the decomposition of aluminium trihydrate filler, however, water may also come from the oxygen present in the ester bonds. When the pyrolysis process was performed at 400/800 °C around 80 vol% of the total condensable yield was made up of oil and remaining part 15% was water. It was observed by the authors that the waxy part condensed out of the vapour phase initially in the form of crystalline needles at the start of each experimental procedure. However, when the authors repeated the experiment with PH1(Phenolic resin as the matrix with magnesium oxide and calcium carbonate reinforcement (41 wt.%) and glass fibre (31 wt.%)), it was noticed that the char produced fell far away from the edges of the solids during handling leading to the residues being able to retain their size, shape and hardness, this the authors believed will lead to recovery of glass fibre by mechanical methods becoming rather difficult and cumbersome. Compared to the above mentioned results the residues obtained after the pyrolysis of EP (epoxy resin) based systems yielded thin pieces of residue that were equivalent to the layers of glass and carbon fibre that were present in the raw composite as reinforcement. It was also noticed that if final temperatures of 800 °C were used for pyrolysis it lead to residues being hard solid and in some rare cases were adhered to the walls of the crucible in which the process was performed. The process when performed at 500 °C and above lead to the fibres being easily recovered from the residue by breaking the solids between the fingers rather easily. The 400 °C sample was however mostly aqueous in nature whereas the thermal degradation of the PH1 sample yielded yellow brown oil, water and wax. EP sample on the other hand which was made from epoxy resin and reinforced with inorganic filler (30 wt.%) and carbon fiber (45 wt.%), yielded viscous dark brown oil along with very low quantity of water (10 vol%) and less quantity of wax at all the conditions that were studied (Cunliffe et al. 2003).

(b) **Chemical Recycling**

Thermal recycling involves the degradation of polymeric composite materials by means of chemicals to release or recover the reinforcing fiber or filler for reuse. During the course of this process thermosetting polymeric matrices are first broken down to low molecular weight mixture of various hydrocarbons by the utilization of a chemical catalyst in the presence of heat, pressure etc. in suitable reaction vessels which is equipped with liquid heat transfer fluid. A huge advantage for chemical recycling methods is that the recovered fibers, nanomaterials, whiskers or fillers have almost near original properties compared to the virgin ones and hence has great reuse potential. The chemical recycling process is very fast and can be scaled up to handle around thousands of tons of composite waste. Another advantage of chemical recycling process is that both cured and uncured composite wastes can be recycled using this process. The process involves few steps like collection and then size reduction of the waste material followed by the processing of this size reduced scrap in the reaction vessel, then the separation of heat transfer fluid, addition of catalyst, purification of the recovered materials and then in the final steps or stages surface modification of the recovered materials, production of non-woven mats from these recovered materials and then finally packaging of these recovered products for the reuse (Allred and Gosau 2016).

Oliveux et al. (2012) reported a study on the degradation behaviour of an unsaturated polyester resin based on dicyclopentadiene which was crosslinked with styrene acting as a matrix material for a composite reinforced with long glass fibres. The authors used a hydrolysis process for the degradation of the above said material. In the case of simple esters subcritical conditions of water was chosen regarding the involved chemistry. The efficiency of the hydrolysis process was determined by taking the quality of the recovered fibers and the nature of the recovered organic products as benchmark and hence several different experiments were conducted to measure the effect of different process parameters. The authors after their several experiments revealed that the washing of fibres prior to the hydrolysis is an important step of the process realized in batch conditions. The analysis of the final recovered products also revealed that the process was able to successfully recover the monomers of the resin after the process but we should also keep in mind that during the hydrolysis process secondary reactions are also taking place.

The authors were able to observe that in the first set of experiments the formation of an organic gluing substance was clear that was able to make a coating on the fibers which resulted in fibres getting brittle during the drying process. This necessitated the need for a washing step soon after the fibres are extracted from the reactor and the authors tested different solvents for the same with more or less efficiently. In a standard procedure the fibres recovered in the first plant trial were separated into three sets of batches. To the first batch of fibre a second hydrolysis sequence at 250 °C for 10 min was performed. Dichloromethane was used for washing the second batch of fibres whereas in the case of third batch benzyl alcohol was used (Oliveux et al. 2012). It was determined that the eliminated resin yield increased to 74% after the second hydrolysis process. The promising observation was that they were less gluing after the drying process eventhough they were more coloured. It was also concluded that acetone and ethanol were not good enough solvents for the removal of the organic substance. On the contrary dichloromethane and benzyl alcohol were found out to be more effective in nature. Just after two washes dichloromethane was able to completely eliminate the resin from the recovered materials. Benzyl alcohol on the other hand was able to remove only 61% resin then also it was concluded that benzyl alcohol is efficient because the fibres looked cleaner than with dichloromethane. However, the drawback of using benzyl alcohol is that it's very viscous in nature and hence has a tendency to coat the fibres rather than clean it. This coating could be removed by a third washing with distilled water to a bit thereby reaching the final eliminated content of resin to 97% (Oliveux et al. 2012).

Piñero-Hernanz et al. (2008) utilized the supercritical or near critical temperatures conditions of water to recycle carbon fibre reinforced epoxy composites. The authors designed the entire experiment in such a way that at the end of the whole study they would be able to determine the different process parameters that significantly affect the composites recovery potential and the factors included were temperature, time, oxidant used and concentration of the catalyst. The pyrolysis study in this work was conducted in a batch type reactor with a volume of 10 mL and the whole process was done without stirring and the temperature ranged from 523 to 673 K, pressure ranged from 4.0 to 27.0 MPa and the reaction times varied from 1 to 30 min. The researchers were able to produce upto 79.3 wt% resin removal using supercritical water conditions and they claimed that this percentage can be further improved by the use of potassium hydroxide as an alkali catalyst. The authors concluded that the overall rate of the extraction depend on the surface reaction of the degrading resin as well as the solubility of the resin products in the medium of reaction. It was observed that the degraded resin product was highly viscous oil. Raul et al. (Piñero-Hernanz et al. 2008) stated that the overall reaction success depends on both the mass transfer steps and the surface reaction taking place on the resin. It was also concluded that the increment in degree of mixing in the reaction mixture by either thermal convection or by stirring mechanically can induce improvement in the mass transfer coefficient. However, it should also be noted that mechanical stirring can improve the mass transfer and kinetics of the recycling process but would lead to decrement in mechanical properties of the recovered fibres due to inducing damage to the fibres during the stirring (Piñero-Hernanz et al. 2008).

Liu et al. (2004) decomposed epoxy resin reinforced with carbon fibres in glass vessel (diameter 100 and length 30 mm) at a temperature of only 90 °C using nitric acid (8 M) and a ratio of the sample weight to the nitric acid of 60 g: 1L. It was observed that the epoxy resin degraded into low molecular weight compounds and carbon fibres (undamaged) were recovered with tension strength loss of only 1.1% (Liu et al. 2004). In another work Kamimura et al. (2006) recycled glass fibre reinforced plastic composite using supercritical alcohol in the presence of a catalyst (N,N dimethylaminopyridine) and it was observed that the GFRPs were completely decomposed at a temperature of 275 °C, 10 MPa pressure and 5 h retention time. The final recovered products included organic monomeric units, polymeric materials and finally inorganic additives all of which were ready for reuse. The authors were thus able to clearly prove that the catalyst has a significant effect on the degradation kinetics of GFRPs. The authors also concluded that the recycled glass fibres retained enough mechanical strength and surface properties so that they can be reused readily with virgin glass fibres for the fabrication of new glass fibre reinforced composite materials (Kamimura et al. 2006).

(c) **High voltage fragmentation**

It was first introduced in 1960s as a method which was traditionally used for rock mining applications (Bluhm et al. 2000). The principle is that this method can disaggregate large rock pieces into smaller individual components from which high value minerals and other crystallographic forms can be easily separated out and then recovered for further utilization, the best example for this technique is the Gold excavation. In high voltage fragmentation or HVF repeated pulses of electrical discharges within a dielectric medium (normally water) is applied thereby disintegrating solid materials. During the process the pulses are discharges in very small time intervals between two electrodes and wherein the solid rock parts are held together in between these electrodes. It was observed that when the pulse rise time is less than 500 ns and the voltage applied is very high (in between 100 and 200 kV) the water molecules had higher breakdown strength compared to the solid rock materials. The basic principle of HVF method is that the spark channel (created by the electrical discharges) generates a very severe shockwave with high pressure (10^9–10^{10} Pa) coupled with high temperature (10^4 K) that in turn creates internal mechanical stress within the rock that exceeds the tensile strength of the solid material thereby disintegrating the said material (Bluhm et al. 2000).

Mativenga et al. (2016) stated in their work that when high voltage fragmentation was used for the recycling of glass fibre reinforced thermoset composites it was able to produce cleaner fibres with good fibre length distribution and lower content of resin retained than those recycled mechanically. It was determined that the number of electrical pulses applied during the HVF process determines the amount of resin present in the residue. The authors stated that the higher the number of pulse (maximum 2000 pulse) residues with the lowest resin content was obtained. An important thing about HVF is that the specific energy required for HVF utilization is around 2.6 times higher than that of mechanical recycling process. However, it should also be understood that for both these process (HVF or mechanical recycling) when they operate at very high recycling rates the energy used should decrease as a result of better utilization of the basic energy that dominates in these two processes. This study demonstrated that HVF can be used as a very efficient method over conventional recycling methods for the recycling of GFRP composite scraps and wastes. However, the up scaling of current lab scale HVF methods to higher capacity is a must if we need to utilize HVF on a higher rate (Mativenga et al. 2016).

4 Conclusions and Future Perspective

The last decades have witnessed continuous increment in the use of synthetic fibre reinforced composites for a variety of applications including aerospace, automobile, energy production (wind turbine), sports, marine etc. owing to their good strength, light weight nature and more than impressive mechanical properties. This increased use of synthetic fibre based composites have led to a large amount of composite waste being produced annually and that too globally and hence their complete decomposition or recycling to recover the resin or reinforcement for further reuse has become an important research area of the current scenarios. The resources conservation scenario and the environment both are now having a negative impact due to the current increasing amount and recycling of composite waste at their end of life cycle.

The present review focuses on the different types of synthetic fibre based composites and the different types of recycling methods that can be used effectively to recover a part or high amounts of the reinforcing fibres for reuse. The review clearly shows that the need of the hour is to focus on greener, economical and sustainable recycling process which can cope with the ever increasing amounts of composite waste in our society and environment. The current increased research on low cost, sustainable and greener recycling methodologies is due to the stricter legislation that now applies to landfill disposal, carbon dioxide emission standards during the recycling process and the ever increasing cost of production of virgin fibres like carbon and glass. The review focuses on different recycling methods in general like thermal recycling, mechanical recycling, pyrolysis, chemical recycling and high voltage fragmentation method for recycling purposes. The future works on recycling process will focus more on utilizing supercritical fluids for the fibre recovery by optimising the technique leading to better mechanical properties for the recovered fibres, scaling up of the above mentioned processes in an economical way and make these processes in such way that their impact on environment will be low (in the sense of low energy consumption, producing lower amounts of residue that needs to be discarded after recycling etc.).

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Recycled Thermoplastics: Textile Fiber Production, Scientific and Recent Commercial Developments

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Abstract Plastic production always stands out with the difficulty of recycling after use. Tens of millions of tons of utilized polymeric materials are disposed each year. Polymer recycling is a pathway to diminish ecological obstacles caused by polymeric waste accumulation from daily applications of polymer materials such as packaging and textiles. Yet, the recycling trouble is still a main challenge. Recycling of plastics requires knowledge in four areas. These areas are plastics collection, their separation, rework technology and recycled products. Existing markets will ensure that post-consumer polymer waste has an economic value. These markets are generally textile sector. Recycled thermoplastic polymers take their place in the market after being converted into textile fiber. Recycling of waste plastics into new textile products is very important for ecology and world sustainability. Today, many fashion and sports textile companies use different textile fibers recycled from waste plastics in many different products (from sportswear, from casual wear to textile products used in shoes). In this chapter, information regarding the stages of the recycling processes and recycling types applied to plastic waste materials was given. Furthermore, the important recyclable thermoplastics polymers types such as PET (polyethylene terephthalate), PP (polypropylene), PA (polyamide), and PLA Poly(lactic acid), their recycling processes, and their recent commercial developments were also covered from the textile point of view. In the coming period, it is expected that the interest of textile producers and consumers in recycling and new textile products produced by recycling from plastic wastes will increase day by day.

Keywords Plastic · Thermoplastic · Recycling · Recycled thermoplastic · Fiber · Textile · Fiber production · Melt spinning · Polyester · Polyamid · Polylactic acid · Polypropylene · PET · PA · PLA · PP

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1 Introduction

Consumption and environmental problems continue to increase with population growth in the world. Due to the increasing environmental problems and the waste they cause, different industrial and social researches and studies have recently been carried out to reduce the harmful effects of many products and materials and to ensure sustainability (or recycling) (Askiner et al. 2009). In the current situation of our world, the recycling of plastic solid wastes/recovery of these wastes/effective management of these wastes cause different concerns. The reason why sectors are more interested in plastic production is that many products are produced from plastic. Due to their lifetime and ease of use, plastics have become an important part of our lifestyle leading to increasing global plastic production. For this reason, global plastic manufacture has enhanced enormously in the last five decades (Gu and Ozbakkaloglu 2016). The production of plastic products, which started in 1907 in the world, brought convenience to people's lives (Pagev 2018). Plastic is one of the most widely used and regularly waste materials today. Worldwide studies estimate that approximately 10% of environmental waste produced by humans consists of plastic materials. It should be noted that there is no real estimation of total plastic waste generation, but considering that 70% of overall plastic consumption is disposed of as waste, nearly 5.6 million tons of plastic waste is created per annum. This corresponds to approximately 15,342 tons per day (CPCB 2013). Plastics exhibit various different benefits for specific application types and moreover they are easy to shape. It can therefore be tailored to specific needs by adding certain layers or additives. These properties are additionally the basis of some troubles with plastics. Accordingly, environmental pollutants from synthetic plastics have been detected as a major problem (Zheng et al. 2005). When we consider the recycling of plastic material, the first things we will associate with it will be plastic water bottles, nylon bags similar food cans, shampoo and other cosmetic bottles.

Today, excessive consumption of plastic and low recycling rates have become an environmental problem. Consumption needs are met at this rate through plastic products, and if the recycling rates remain at the current level, according to scientists, it is stated that by 2050 there will be more plastic than fish in the seas (Law 2017). The most effective way to conserve natural resources and use them more efficiently is recycling. Recycling is important in order to protect the ecological balance of our world and to leave our resources to future generations (Yüce 2020). Plastic can remain in nature intact for centuries. A plastic bottle does not perish in nature for 3,000 years and a ton of plastic saves 14,000 kWh when recycled (Kumartasli and Avinc 2020; Pivnenko et al. 2016; Shen et al. 2010). In the framework of increasing demands and environmental concerns, research and efforts in the latest years have focused on the recycling and sustainability of all products used. Of course, this is the case in the textile industry. Textile recycling sector is one of the oldest sectors in our planet. However, there are unfortunately people and communities that do not fully understand the importance of the recycling and recycling industry for the sustainability of the world or do not implement such practices effectively. Of course, there are also companies, people and communities that know the importance and effects of recycling and sustainability very well and try to increase these environmental efforts. As a result of increasing efforts to protect the environment and the world in recent years, many companies and organizations around the world produce new textile and ready-to-wear products by recycling waste plastic products and used waste textile products (Wang 2006). Every day, this and similar efforts and applications are increasing worldwide. Of course, these positive steps and efforts made for the protection of the environment and the sustainability of the world give all of us hope for a beautiful and sustainable future.

Unfortunately, the added value created by recycling is unfortunately lower than expected and remains at low levels for now. When the life cycle of these plastic materials and synthetic textiles, which are used in large quantities, is over, only a small part is recycled and therefore their impact on the economic cycle is less than expected. Additionally, unlike metals and ceramics, the recycling of polymers can somewhat change their properties. So in no way does it mean that the quality of the products cannot be made from recycled polymers (Ignatyev et al. 2014b).

Recycling of plastics is one of the main policies to diminish ecological troubles related with plastic waste. Besides, plastics are primarily produced from petrochemical raw materials, whose price has increased in the last decade. The supply of petrochemicals is expected to further decrease in the next decades due to the rapid depletion of oil resources. Therefore, plastic recycling will lower the dependency on fossil fuels. Recycling is an important strategy for managing end-of-life plastic waste. Recycling is very important in terms of preventing the damage of plastic wastes to the environment and contributing to the economy. Recycling methods continue to be used today, but problems still persist in collecting plastic waste due to technological, economic and social reasons. Consumed plastic packaging must be separated from other plastic waste and domestic organic waste in order to be recycled on a larger scale. In order to increase recycling rates and use recycled plastic instead of original plastic, polymer manufacturers and manufacturers of thermoplastic products need to make more effort and do different studies to contribute to this goal (Tasdelen and Oran 2017). Currently, we can only understand the real problems of plastics when we consider recycling, ecological problems and health effects. The simplest examples of this are far east countries. Far Eastern countries, where synthetic fiber production is intensive in terms of textiles, has a high share in the world textile market. Apart from synthetic textile fibers, many plastic product groups are produced using petrochemicals, also obtained from petroleum. Naturally, sectors and countries that use virgin petrochemical products in large quantities as raw materials may unintentionally contribute to ecological damages if waste plastic products and waste synthetic textile products that have completed their useful lives cannot be recycled efficiently. That is why companies and all countries in the world should increasingly give importance to the recycling of plastic materials. Today, many fashion and sports textile companies use different textile fibers recycled from waste plastics in many different products (from top wear to sportswear, from casual wear to textile products used in shoes). For example, Adidas, H&M, Levi Strauss & Co, Nike, M&S, Gucci, Zara, Patagonia, The North Face and many other big brands use recycled textile fibers from plastic wastes in their products.

In this chapter, the information regarding the progress on polymeric wastes, technics for thermoplastic recycling from some conventional polymers, stages of the recycling processes, different separation methods, recycling types applied to plastic waste materials and the concepts of mechanical and chemical recycling was given. Moreover, more information was given about the important recyclable thermoplastics polymers types {such as PET (polyethylene terephthalate), PP (polypropylene), PA (polyamide), and PLA [Poly(lactic acid): an example of biopolymer]}, their recycling processes, and their recent commercial developments from the textile point of view.

2 Technics for Thermoplastic Recycling

Recycling and incineration are among the methods applied to thermoplastic products in waste state. Incineration displays some troubles such as the procurement of toxic gases and residual ash containing lead and cadmium. Recycling offers benefits such as reducing ecological troubles and conserving both material and energy (Grigore 2017; Francis 2016). Mechanical or chemical recycling processes are the best way to use plastic waste (Kumartasli and Avinc 2020; Ignatyev et al. 2014a). It is vital to note that the recycling procedure doesn't lower costs, however maintaining the ecological balance is necessary for a sustainable planet. Although many different methods can be applied for recycling thermoplastic wastes such as PET (polyethylene terephthalate), PE (polyethylene), PP (polypropylene), PA (polyamide) waste polymers, there are basically four main recycling approaches (Voncina 2016). These are respectively, primary recycling (obtaining products with properties equivalent to mechanical reprocessing), secondary recycling (obtaining inferior properties to mechanical reprocessing), tertiary recycling (recycling of chemical components), quaternary recycling (energy recovery gain). Primary recycling, generally closed loop recycling, secondary recycling is described as recycling with the same system but based on waste collection. Tertiary recycling is defined as chemical or raw material recycling obtained by depolymerizing the chemical components of polymers. It is stated that quaternary recycling is the energy recovery route from wastes (Tasdelen and Oran 2017).

- *Primary Recovery*: In primary recovery, waste plastics are mechanically shredded and mixed with the original plastics, and the product can be produced in a final process. The commonly used method has been demonstrated with primary recycling as it is economical and simple. This process shows that the products can be reused in their original form. The disadvantage of this process is that a certain number of recycling can be made (Francis 2016; Hopewell et al. 2009; Singh et al. 2017).

- *Secondary Recovery*: It is a method used for the production of low quality products in the process where different products are obtained from waste thermoplastic products. Here, re-meltable polymers can be used in the process and recycled as different use products. Mechanical recycling does not cause much change in the structure of the polymer. This method is a physical technique in which plastic materials are crushed and melted to make the material to be used in the subsequent process, into granules or pellets suitable for further production. The disadvantage in this technique is related to the weakening of the properties of the resulting products due to the low molecular weight of the recycled waste. Reprocessing with good drying and vacuum degassing is recommended to avoid molecular weight reduction. Also, this technique is relatively inexpensive (Hopewell et al. 2009; Grigore 2017).
- *Tertiary Recovery*: This method is defined as chemical recycling. The aim here is to separate the polymer into its monomers. After the monomer is obtained, the desired materials can be produced. Chemical recycling has not been developed at the desired level. Some companies are working on the process. This technique is a costly method. Currently, procedures with commercial experience are glycolysis and methanolysis (Francis 2016; Achilias et al. 2007; Karayannidis and Achilias 2007).
- *Quaternary Recovery*: In this technique, plastic waste materials are the process of burning with heat. In this process, energy is obtained by burning plastic waste materials. The most efficient way to reduce the volume of waste materials is incineration. This technique is a good solution as it produces a significant amount of energy from polymers, but causes air pollution. Among the techniques above, chemical recycling is the most suitable method for sustainability (Achilias et al. 2007; Al-Salem2009; Andrady 2003; Fisher et al. 2005).

In recycling factories, plastic wastes are passed through a vibrating screen to remove unnecessary substances such as impurities and sludge, and these materials are separated from steel and tin materials with the help of a magnet at the end of the conveyor belt (Sevencan and Vaizoglu 2007). At this stage, it would be appropriate to provide information about the stages of the recycling process in order.

Separation: Each plastic part must be separated according to its construction and type in order to be processed properly in the shredding machine. The different separation methods are summarized in the section below.

- Induction sequencing: The material is sent to a conveyor belt equipped with an inductive sensor. These sensors then separate the various substances with air jets.
- Eddy current separator: “Eddy current” is an electric current that occurs while changing the magnetic field in a conductor and separates non-ferrous materials.
- Drum separator/strainer: Those materials are divided in proportion to particle size. The waste is fed into a large rotating drum drilled with holes of different sizes. Materials smaller than the diameter of the holes fall off and larger particles stay in the drum.

- Synephloate separation: It separates plastic waste according to the density of materials in a water. In the presence of water, some plastics (eg PET, PVC and PS) sink and others float and show buoyancy (eg PE, PP and EPS).
- X-ray technology: X-rays could be utilized to differentiate different kinds of materials based on density.
- Near infrared sensor: Plastics reflect light differently in the near infrared (NIR) wavelength spectrum. The near infrared sensor can differentiate between various materials depending on the way these materials reflect light. It is a method used to separate different polymers.

Sorting: Each plastic material should be spared in accordance with to its structure and kind thus that it could be treated in the shredding machine accordingly.

Washing: After separation, plastic waste must be properly washed to eliminate impurities such as labels-adhesives. Washing procedure improves the quality of the finished product.

Shredding: After the process of washing, the plastic wastes are loaded on various conveyor belts which pass the waste within different shredders. These grinders break the plastic into small lumps and prepare it for recycling in other products.

Identification and Classification of Plastic: After shredding, appropriate tests for the plastic pellets are carried out to determine their quality and grade.

Extruding: Extruding comprise melting the shredded plastic as a result it could be extruded into pellets and afterwards utilized to make various kinds of plastic products (Norcal Compactors 2020).

In the following part, information on recycling types applied to plastic waste materials is given. These are mechanical recycling and chemical recycling, respectively.

3 Recycling Types

3.1 Mechanical Recycling

The material properties obtained here are generally slightly worse than the virgin material. This type of process is also known as physical recycling. In this type of recycling, plastics are milled and then reprocessed and combined to produce a new component that may be the same or different from the original use (Cui and Forssberg 2003). However, the molecular weight, thermal charges change during melting and therefore the fiber tensile strength, tensile and dyeing properties can change. For this reason, manufacturers may choose to regenerate products by polymerization, according to an option for melting and extrusion. Because molecular weight and properties remain the same (Kumartasli and Avinc 2020; Oktem 1998). One of the main matters which mechanical recycling companies face is the degradation and heterogeneity of plastic solid waste. Because chemical reactions which ensure polymer formation (i.e. polyaddition, polycondensation, polymerization reactions) are all reversible in theory, energy or heat supply could result in photo-oxidation and/or mechanical stresses that arise as a result (Al-Salem et al. 2009).

3.2 Chemical Recycling

In this process, waste plastic materials are used as raw materials. With the help of chemicals and catalysts, the decomposition and depolymerization of the materials are provided. In this way, it decomposes into polymer monomers (Garcia and Robertson 2017; Ademiluyi and Akpan 2007). Chemical recycling technique appears economical, however it can reduce the yield of new products made from recycled products by this method (Park et al. 2002). Chemical recycling seeks to convert waste polymers to numerous levels such as oligomers or monomers. In this way, the reproduction of the same type of polymers from monomers or oligomers obtained from waste polymers by chemical recycling and then the production of textile fibers from these produced polymers is done by different applications such as polymerization (Gupta and Kothari 1997). Recently, there has been great interest in chemical recycling as a technique for producing various fuel fractions from plastic solid waste (PSW). Many polymers by their nature are useful for this type of process. Polyethylene terephthalate (PET) and certain polyamides [Nylon 6 (PA 6) and Nylon 6.6 (PA 6.6)] can be effectively de-polymerised. Especially, polyethylene (PE) was aimed as a prospective feedstock for fuel (gasoline) manufacturing technologies (Al-Salem 2009).

The following section gives detailed information about some of the important recyclable thermoplastics polymers types.

4 Recyclable Thermoplastics Polymers Types

In this part of the book chapter, information is given about some types of thermoplastic polymers that can be recycled. The waste thermoplastic materials described here are recycled and these recycled polymers can be used to produce new textile fibers. In short, new textile fibers and thus new textile products can be produced from waste plastics. In this section, information is given about the recycling of polyamides, polyester, polyolefins and biopolymers.

4.1 Polyamides

Worldwide, polyamide 6 and polyamide 6.6 (PA 6 & PA 6.6) are the most utilized polyamides, also important for large scale manufacture of melt-spun fibers (Anton and Baird 2001). The polymer transformed into pellet form becomes fiber with the fiber spinning process (Fig. 1). Both types of fibers display similar properties such

Fig. 1 PA pellets

as very good wear and abrasion resistance, high strength and toughness, brilliant fatigue behaviour and nice flexibility and their slight differences are mainly due to alterations in molecular weight distribution and molecular orientation due to the shrinkage (Mukhopadhyay 2009).

The international plastic recycling market reached U.S. $ 34.80 billion in 2017, and one of the most crucial and precious recycled plastics is PA 6. Amongst recycling techniques, physical recycling of Polyamide 6 (PA 6) by melt re-processing is the most preferred recycling method, because this process type is a comparatively simpler method, requires low investment and is more eco-friendly (Murphy 2001). Nevertheless, during the recycling process, PA 6 is exposed to high temperatures and mechanical forces which cause the polymer chains to deteriorate. The decrease in the molar mass of PA 6 causes the loss of mechanical and thermal characteristics and restricts the application areas of recycled PA 6 (r-PA 6). Some companies around the world can recycle polymaide waste by mechanical or chemical methods. Related information about this was mentioned in the commercial applications section.

4.2 Polyesters

Polyamide is more challenging to recycle than polyester, the market share of recycled polyamide (r-PA) is much lesser than that of recycled polyester (r-PET). R-PA could be manufactured from pre- or post-consumer waste. It can be pre-consumer waste and scraps processed. It is made from materials such as post-consumer polyamide, discarded fishing nets, carpets or other utilized textiles and the its recycling process could be mechanical or chemical.

PET (polyethylene terephthalate) is the major polyester utilized in fiber manufacturing not only due to its end use characteristics and production economy, but also mainly owing to its physical and chemical ease of use (Militky 2009). The spun polyethylene terephthalate forms a stable, supercooled melt because of the relatively high glass transition temperature (Tg ~ 75 °C). Only when fully drawn is a molecular

Fig. 2 Recycled PET pellets

orientation in the direction of the fiber that develops oriented crystallites (Sattler and Schweizer 2011). Its excellent properties are responsible for polyester fibers and filaments that find utilization in all fiber application areas. Pellets are used for PET fiber production (Fig. 2).

Recycled polyester is more sustainable raw material, as the use of recycled polyester saves natural re-sources, conserves energy in the manufacturing process, and results in lower greenhouse gas emissions and the utilization of chemicals (Shen et al. 2010). PET wastes could be recycled by both mechanical and chemical techniques. Mechanical recycling is cheaper and environmentally friendly (Kumartasli and Avinc 2020). It is the right point to state in here that polyester fiber (especially PET fiber) is a textile fiber that is the most produced-consumed textile fiber in the world. Therefore, the recycling of polyester plastics and the use of this recycled polyester polymer to produce new polyester fibers is very important and essential not only for the environment but also for the world textile industry. For this reason, the production of polyester textile fibers from the recycled waste polyester plastics is increasing day by day worldwide. Many companies around the world can recycle polyester waste by mechanical or chemical methods. Related information about this is also mentioned in the commercial applications section.

4.3 Polyolefins

The most important polyolefins utilized for melt spinning are polypropylene, low density polyethylene and high density polyethylene (PP, LDPE and HDPE), which are mainly composed of saturated aliphatic hydrocarbon macromolecules (Mather 2009). Technologies for converting polyolefins to fiber and fabrics comprise monofilament and multifilament spinning, staple fiber, spunbond, meltblown and slit film (Ouederni

Fig. 3 PP granuls

2016). It is the material of preference for disposable hygiene and medical applications such as polyolefin based spunbond and meltblown fabrics, diapers, incontinence pants, hygienic pads, surgical gowns and masks (Malkan 2017). Polyolefin filaments, which are polymeric hydrocarbons, have luster and a waxy handle that can be lowered by non-circular fiber cross-sections such as trilobal or cross-shaped (Mather 2009). Polyolefins (LDPE, HDPE, PP) are the main thermoplastic type utilized in applications such as bags, toys, containers, pipes (LDPE), household items, industrial packaging and film, gas pipes (HDPE), film, fiber, battery boxes, automotive parts, electrical components (PP). In the western European countries alone, about 21.37 million tons of these three polymers are consumed each year (2003 data) and represent 56% of total thermoplastics Unlike condensation polymers [i.e. poly (ethylene terephthalate) (PET)], additional polymers (such as polyethylene) cannot be easily recycled by any method (Karayannidi and Achilias 2007). Instead, recycling techniques such as thermochemical pyrolysis have been proposed as the procedure that produces a range of refined petrochemical products. Polypropylene reprocessing involves melting at a temperature above 200 °C in an extruder and then granulation for utilization in novel manufacturing (Fig. 3). Polypropylene is ultimately influenced by thermal degradation that concedes the structural density of the plastic because of the weakening of the bonds between hydrogen and carbon. This depends on the utilization of polypropylene, but it is generally accepted that four closed recycling loops are probable before the negative impact of thermal degradation is detected (Thomas 2012).

4.4 Biopolymers

The term “biopolymer” is usually bio-based (manufactured from biogenic materials considered as renewable resources), but frequently biodegradable (biodegradable), biocompatible (no adverse effect on humans or animals). The key biopolymers considered for melt-fiber spinning are PLA [Poly(lactic acid)], PCL (Polycaprolactone), PGA (Poly glutamic acid), PBAT (polybutyrate adipate terephthalate), PEF (polyethylene furanoate) and PHA (Polyhydroxyalkanoate). One of the most important (probably the most important) of these biopolymers is PLA. PLA is a type of biopolymer that is on the agenda today with its positive environmental and performance characteristics and its use is expected to increase day by day in the future. Therefore, this part of the book section focused on PLA polymer, waste PLA plastics and the production of new PLA fibers from these wastes. PLA could be manufactured from lactic acid, the raw material of which is naturally occurring starch, usually derived from corn (Mochizuki 2009). PLA can also be produced from rice, wheat, sugar beet or bio waste. Composed of L lactic acid (LLA), fiber-grade PLA is one of the most gifted bio-based, biodegradable and biocompatible polymers commercially available (Mochizuki 2009; Niaounakis 2015; Avinc and Khoddami 2009; Avinc 2011a, b; Avinc et al. 2006, 2009, 2010a, b, c, d, 2011c, 2012a, b; Khoddami et al. 2010, 2011; Hasani et al. 2013). The natural biodegradability of PLA is less than that of other biopolymers and less sensitive to microbial attack (Tokiwa and Calabia 2006). The major disadvantage with melt processing is the low thermal stability in the existance of moisture (hydrolysis) (Södergård and Inkinen 2011).

The appearance of the r-PLA (recycled PLA) and r-PET (recycled PET) fiber samples and the comparison of their mechanical and dyeing properties displayed that r-PLA fibers could be a nice replacement for r-PET fibers. This determination shows that PLA waste plastics can be recycled and reused, and that PLA fibers showing adequate textile performance properties can be produced from these waste PLA plastics.For this reason, and also due to the environmental, renewable, sustainable and biodegradable properties of PLA, biodegradable PLA bottles and plastic packaging are expected to replace PET bottles and plastic packaging in the near future. Moreover, this could provide an cost-effective and beneficial recycling method for PLA's valuable waste compared to the traditional recycling process (Tavanaie 2014). Additionally, PLA waste streams could also be processed utilizing composting, chemical recycling (hydrolysis depolymerization) and anaerobic digestion (Farrington et al. 2005). These PLA waste recycling methods are expensive and difficult. The mechanical recycling of PLA is better than the chemical recycling of PLA from the point of human and eco-system health and the utilization of resources. Otherwise mechanical recycling results in down-grading thus the recycled poly(lactic acid) would be of a lesser quality that if it was chemically recycled (Cosate de Andrade et al. 2016). When PLA is mechanically recycled, it is likely to include a chain extender that aids partially recover the impaired molar mass and other mechanical characteristics, making the recycled poly(lactic acid) more comparable with virgin poly(lactic acid) (Fig. 4) (Cosate de Andrade et al. 2018).

PLA offers some exciting characteristics such as biodegradability, sustainability, renewability, recyclability, environmentally friendly characteristic, nice processability, low manufacturing cost, low environmental impact and optical and mechanical characteristics akin to that of polystyrene or poly (ethylene terephthalate) (PET). These nice characteristics have led to an increased interest in PLA and this made it

Fig. 4 PLA pellets

one of the most critical bioplastics in the market, especially in packaging applications, with a worldwide manufacturing capacity of 0.21 million tons in 2016. PLA reached 0.5 million tons in 2020 (Aeschelmann and Carus 2016). It should be noted at this point that PLA can be recycled mechanically or chemically (Castro-Aguirre et al. 2016). Mechanical recycling involves the recovery, sorting, re-grinding and re-processing of poly(lactic acid) (Chariyachotilert et al. 2012). Even though this method necessitates simpler techniques and can be easily implemented, it lead to deterioration of the physical characteristics of PLA and foreign contaminants that cannot be completely removed, as the molecular weight is decreased because of shear and temperature (Hamad et al. 2013). Otherwise, chemical recycling transforms PLA polymer to monomer LA (Lactic Acid) by hydrolysis and separation of contaminants so that lactic acid could then be utilized as raw material with the same characteristics as virgin poly(lactic acid) for new PLA production (Piemonte et al. 2013). Here we have seen that PLA waste plastics can be successfully recycled and used in the production of new PLA textile fibers. Here, an important point should be emphasized. The biodegradability of PLA polymer, PLA plastic waste, PLA fiber textile products is incredibly important for the sustainability of the environment and the world. It is known that PLA plastic wastes or PLA textile wastes turn into water and carbon dioxide (the basic necessities for new growth) when biodegrades. The recycling of PLA wastes, to new plastic materials or new textile fibers, instead of allowing them to be biodegraded as much as possible will provide added value to the world both economically and in terms of efficient use of resources.

In the next part of the book chapter, commercial steps, commercial developments and final products regarding the recycling of thermoplastics and the creation of different textile fibers obtained from different recycled thermoplastics are mentioned.

5 Recent Commercial Developments

In this section, recent commercial developments regarding the creation of different commercial textile fibers produced from different types of recycled thermoplastics are discussed. First of all, it would be appropriate to take a look at the generally applied recycling steps from plastic waste to the production of new textile fibers. For this purpose, general transformation steps required for the transformation of thermoplastic wastes into textile products are shown in Fig. 5.

As mentioned above, new thermoplastic textile yarns are produced from the polymers produced after the recycling steps from waste plastic materials with the help of fiber melt spinning process; in the desired fiber cross-section, filament number and yarn count (Fig. 5). Later, these recycled thermoplastic yarns are then used to create many different textile products for many different purposes after their respective classical textile product production processes such as conventional fabric surface forming process (knitting, weaving etc.), coloration process (dyeing, printing), finishing processes (softening, water repellency finishing, antimicrobial finishing, flame retardant finishing process etc.), and finally end-use manufacturing processes (such as garment manufacturing etc.).

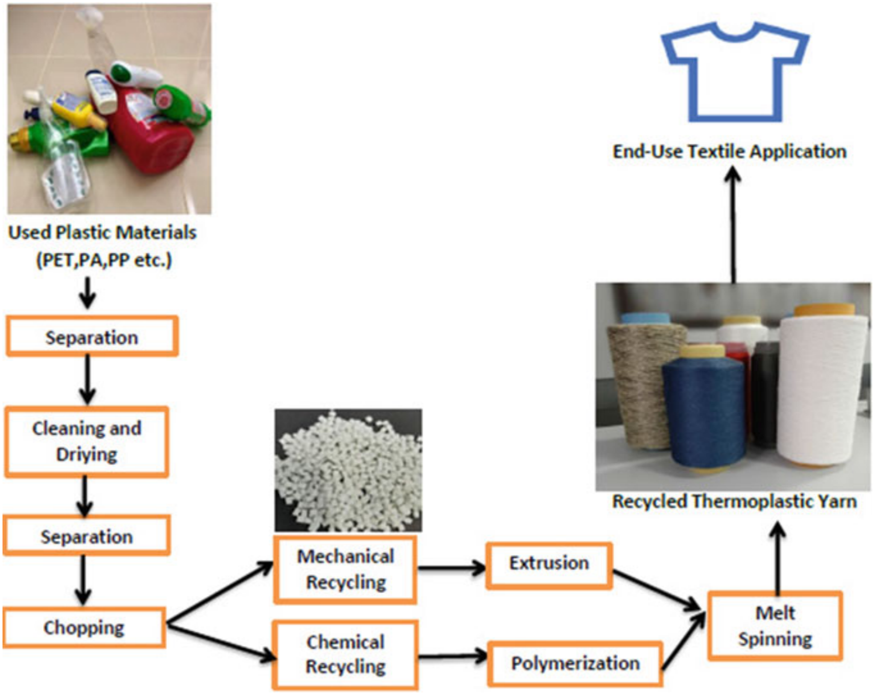

Fig. 5 The stages of transformation of thermoplastic wastes into textile products

According to 2019 data, 52% of the annual total fiber production is polyester. When looking at the recycle polyester market, an increase of approximately 5% is seen between 2009 and 2019 (Textile Exchange Report 2020).

Recycling and use of PET bottles in recycled plastics is an important issue for the textile industry. One reason for this is that unprocessed polyester is manufactured in much greater volumes. Sports equipment manufacturers such as Nike and Adidas are increasing the use of recycled polyester in their new textile products. In recent years, large companies have increasingly started using fibers recycled from PET bottles. The steps taken by some of these fashion giants towards the use of textile fibers recycled from plastic waste in the new textile products they produce are summarized later in this section.

Polyteks production of polyester yarn from Turkey is performing. The company's recycled PET yarn brand is POLY-eco®. Turkey is one of the leading brand of recycled PET yarn (Fig. 6). This type of recycled polyester yarn is used in a variety of textile products. Figure 6 shows the transformation steps of used waste PET bottles into recycled PET yarn (POLY-eco®).

One of the important commercial developments in this field is that Igloo has announced their softside cooler collection woven with REPREVE, a fiber generated from recycled, post-consumer plastic bottles. Several of the most well-known worldwide international textile brands in our planet utilize the REPREVE brand. These companies have recycled more than 14 billion plastic bottles to date. Based on this momentum, Unifi intends to recycle 20 billion bottles by 2020 and 30 billion bottles by 2022 (Södergård and Inkinen 2011).

One of the textile recycling company called as Waste2Wear alleges to have manufactured the planet's first collection of plastics generated from recycled ocean plastic fabrics that is fully traceable utilizing blockchain technique. Waste2Wear introduced a beta version of its blockchain system, embedded in its new Ocean Fabrics collection, at the Première Vision international textile fair in Paris. The company, a frontrunner in creating fabrics from plastic waste, says using blockchain technology will bring more transparency to the supply-chain of recycled textiles.

H&M, one of the important textile companies, included the use of recycled textile fibers in its new products. It was reported that world-wide clothing company H&M utilized 325 million PET bottles in recycled polyester in 2018. H&M textile company

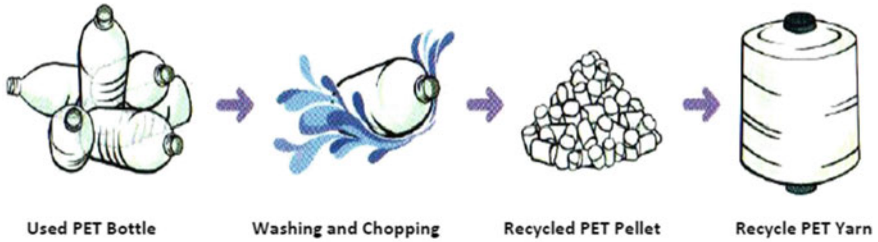

Fig. 6 The plastic bottles to turn into recycled PET yarn (POLY-eco® recycled PET yarn brand, POLYTEKS)

is the 6th largest consumer of recycled polyester (r-PET) in our planet as said by the company's 2018 sustainability report (Inside Waste 2019).

Sports equipment giant Adidas has been introducing Parley sports shoes made from recycled plastics since 2015 (ISPO 2019).

One of the main ways brands add sustainability to their products is via the utilization of recycled materials, especially recycled polyester (r-PET). Main international brands have taken this approach, containing Zara, H&M, Marks and Spencer, Levi's, G star and many other companies (Kumartasli and Avinc 2020; InsideFasion 2020). Today, many fashion and sports textile companies use different textile fibers recycled from waste plastics in many different products (from top wear to sportswear, casual wear to textile products used in shoes).

It was earlier reported that Henkel tapped Austrian manufacturer Greiner Packaging to develop the novel design sleeve and container. It was stated that the outer cardboard sleeve was made from 92% recycled content. Even Though the inside of the plastic container was still made from white virgin material, its exterior layer now contains recycled polypropylene from the post-consumer sources (Halbrook 2020).

It is the reason why Trützschler and EREMA started the production of recycled yarn in cooperation. Both companies combined their efforts to develop a one-step system for pretreatment of polyester flakes and spinning to BCF (Bulked Continuous Filament) for carpet applications.The new system precisely connects EREMA's VACUREMA technique with Trützschler Switzerland's symTTex BCF machines. The EREMA part comprises a vacuum reactor, a directly connected single screw extruder and a high performance filter. The washed r-PET flakes are dried in the reactor and decontaminated, melted in the extruder and then passed through a variable fineness large area filter. The high-quality melt is then fed into the Trützschler spinning system. Well-known and well-established high-quality spinning packages, double-shell draw rollers, HPc texturing system and fully driven winders form filaments and wind them into bobbins. An industrialized line based on this latest model is already running effectively in Poland (Textile Magazine 2020).

In Canada, a partnership for the PET waste chemical recycling facility was established in 2018 in partnership with Loop Industries/Indorama venture (Textile Exchange 2020).

Many companies in the USA recycle PET wastes mechanically and chemically. Ambercycle company recycles PET from waste clothes. The recycling process is completed using biological and chemical methods (Ambercycle 202; ChangeMakers 2020). BIONIC® fibers, yarns and fabrics are produced from plastic collected from the sea and seaside. Bionic yarns form durable fabric yarns from recycled plastic (Textile Exchange 2020; BionicYarn 2020).

Eastman Chemical Company announced that Avra, a family of high performance fibers, will be produced from 100% post-consumer recycled PET plastic from spring 2020. The process will take place with the new chemical recycling process through Carbon Renewal Technology. Eastman will collect the polyester carpets, separate the polyesters and recycle them chemically (Eastman Chemical 2020).

Lycra EcoMade fiber is the company's first branded spandex made from pre-consumer recycled materials and more than 65% of the T400® EcoMade fiber total fiber content comes from a combination of recycled plastics (PET bottles) and renewable plant-based resources (corn). PET recycling is done chemically (Textile Magazine 2020; Textile World 2019).

Focusing on developing bio-industrial solutions, the French company Carbios started construction of its industrial facility for the enzymatic recycling of polyethylene terephthalate (PET) plastic. The recycling used is different from mechanical recycling. PET wastes separated into their monomers biologically and chemically can then be recycled to the desired product (Textile Exchange 2020).

Seaqual is an initiative in Spain to clear the oceans of marine litter. Seaqual yarn is a 100% recycled material with full traceability and Madrid-based Seaqual combines creativity and eco-responsibility by turning the litter trapped in fishermen's nets into a revolutionary new fiber (Seaqual 2020; Apparel Staff 2017).

ECOPET™, launched by the Japanese company Teijin, are polyester products (fibers, textiles, clothing and products) made from recycled resources: it uses various types of polyester waste through a mechanical or chemical recycling process. Provides efficient use of limited natural resources (Teijin Fibers 2020). The ECOUSE™ brand, launched by Toray from Japan, is yarn, cotton, textile and fiber products made from PET bottles and materials from the production process. Toray actively promotes fiber recycling with its basic "Total Recycling" concept, using less energy under ECODREAM™, the general brand name for environment and recycling (Toray 2020).

Japan-based firm Jeplan envisions a world where all used or unwanted personal items are collected, materials are recycled, and new products are launched and sold. Starting with cotton and polyester, the company is redesigning waste disposal to reduce oil use and reduce carbon emissions. The firm has set up nationwide collection points to collect discarded garments, collaborating with major retail and apparel brands. Jeplan then recycles the materials and sells them back to these brands and consumers, supporting a circular economy. One of his projects turned used clothes into bio-ethanol, which was later used to sustainably power a car. Jeplan is working towards its goal of recycling 10% of used and unwanted clothing around the World (Jeplan 2020).

Nan Ya Plastics is a SAYA branded, commercially available, chemically recycled, GRS certified PET made from pre and post consumer textile products. Nan Ya Plastics, the parent company of SAYA, is one of the world's largest producers of recycled PET and targets more than 75 billion bottles each year (Textile Exchange 2020; Saya 2020).

The Swiss company Gr3n has once invented a new process for chemically recycling PET bottles and food containers. They developed an innovative technique based on a novel application of microwave technology to a well known chemical reaction, which enables an economically effective chemical recycling method of PET (Polyethylene Terephthalate) and allows the industrial application of this recycling technique. This new process could potentially change the way PET is recycled worldwide and could provide a massive financial gain for the recycling industry.

Launched by former Slovak professional cyclist and twins Martin and Peter Velits, Isadore produces an Alternative Preferential clothing line that includes jerseys, bib shorts, jackets and base layers, all made from recyclable materials. The jerseys were produced utilizing plastic bottles (30 pieces each) and the bib shorts are made from chamois leather, while the rest of the shorts are generated from recycled Italian Lycra. All garments that reduce weather resistance are produced locally where the Veltis brothers are based in Slovakia (Calvert 2020).

Along textile waste, nonwoven manufacturers supply recycled polyester bottles to produce PET nonwoven. The need for these bottles is gradually increasing due to foreign demand as well as recycling companies in the USA. Like the National Container Resources Agreement, NAPCOR0 rPET reduced energy consumption by 84% and greenhouse emissions by 71%. The conversion of 1.5 billion pound PET bottles into textile fiber has saved 46 trillion BTUs of energy, enough to power 486,000 homes.As a result, 85 16-oz polyester bottles will produce fiber filling source for 1 sleeping bag, 72 tissue box 5 pieces two liter bottle and 5 16-oz bottles can form a collection distribution layer (Mclntyre 2013).

Some Japanese companies also give an importance to the use of materials recycled from plastic waste. One of these companies is Teijin firm. Teijin hybrid fiber contains chemically recycled PET. Solotex is the brand name for the Japanese firm's highly flexible yarn made from recycled and plant-derived materials (Taylor 2020).

H&M, for example, said it will switch to fully recycled and sustainable materials by 2030. Likewise, Uniqlo casual wear operator Fast Retail has introduced the use of biofiber in its products. Additionally, in 2020, the company announced its accession to the UN's Fashion Industry Charter for Climate Action, which is designed to reduce greenhouse gas emissions from the clothing industry by about 30% by 2030 (Walimbe 2020). Adidas, H&M, Levi Strauss & Co, Nike, Patagonia, The North Face and several other big brands view sustainability hand in hand with invention and innovation. In the last few years, those firms have been seeking the paths to diminish their ecological effect, launching special programs and encouraging sustainable inventions and innovations (Tonevitskoya 2019).

Recycled Nylon (r-PA) possess the similar advantages as recycled polyester (r-PET). Much of the recycled nylon generated from old fishing nets. This is a good solution for removing garbage from the ocean. Polyamide is still more costly to recycle than new virgin nylon, however possesses several ecological benefits. Many different studies are currently carried out to improve the quality and to diminish the costs of the recycling procedure. Econyl® is a nice example of certified, environmentally friendly, recycled polyamide textile.

Recycled polyamide is generally produced from post-industrial waste (for example; polyamide yarn manufacturing waste or carpet cuts) as well as post-consumer waste (used carpets, discarded fishing nets). This chemical recycling allows for reducing waste, reducing dependence on oil resources, and minimizing the pollution of consumer and post-industrial polyamide waste (Recycled Nylon 2020).

The NUREL company recycles pre-consumer waste by recycling it into a higher quality sustainable yarn from nylon. Reco branded nylon performance is similar to standard nylon 6 threads and is sustainable (RecoNylon 2020).

Nilit company (from Israel) recycles polyamide wastes through the re-melting process. The process diminishes energy consumption in comparison with fiber spun from virgin polymers (Haemek 2009).

Q-NOVA®, a brand of Fulgar company, is a traceable and environmentally sustainable nylon 6.6 fiber obtained from regenerated raw materials.In particular, Q-Nova yarn is supported by many companies especially in the footwear and woven material industry for the apparel, intimate apparel and sportswear industry, has been adopted (Q-Nova 2020; Nylstar 2020).

Meryl® yarn can now be produced using INVISTA recycled nylon 6.6 polymer with Global Recycled Standard (GRS) certification. Although the yarn contains 50% or more recycled content, it will retain the world-renowned quality of Meryl®. INVISTA buys post-industrial nylon 6.6 material from its factory in Kingston, Canada, where fibers for airbags and carpets are produced. Through its proprietary process, INVISTA converts post-industrial fiber waste into pellet form and supplies it to Nylstar for spinning, enabling some of the world's best fashion houses to bring sustainable clothing to the market. "Through our Advanced Recycled Materials Research Center, it is the first company to commercialize and manufacture these recycled materials for use in fine denier yarns for the athleisure market" said Nylstar CEO and president Alfonso Cirera (Nylstar 2020). Athleisure is a type of hyrid clothing of athletic wear and leisure wear and a new fashion trend that started with the combination of stylish clothes (clothing worn at work, school and other casual and social occasions) and sports pieces (clothing worn during athletic activities) (Athleisure 2020).

Prior to fall 2020–21, Gucci developed Gucci Off The Grid, the first collection of Gucci Circular Lines, an initiative designed to boost House's vision of circular manufacture. Designed for those who care about their ecological effect, Gucci Off The Grid utilizes recycled, organic, bio-based and sustainably sourced materials, comprising ECONYL® (Econly 2020).

Britain's swimwear brand Fatface has launched a new swimsuit using Hyosung's Mipan regen fiber made from recycled polyamide, reducing energy consumption.He stated that Control Union is an environmentally friendly product with Global Recycling Standard (GRS) certification.

Procotex is one of the market leader companies in recycled 100% PP fibers. Usually, any PP waste from the extrusion industry or carpet industry is recycled. Procotex guarantees 100% purity. This way, any possible contamination with other fibers is guaranteed to be eliminated (Procotex 2020). In this way, many PP plastic wastes are evaluated and new PP fibers are produced.

The French company Veja, known around the world for producing sustainable shoes, takes fair trade shoes and accessories to the next level by launching a material called B-mesh ("Bottle Mesh"). Each pair of sneakers comprises three bottles. The fabric created from them is both breathable and waterproof—perfect for shoes. In addition, by way of example, our shoes can be made from environmentally friendly renewable products such as organic cotton and natural rubber produced by farmers who maintain their livelihoods through farming (Textile Focus 2020). Sheico Group produces recycled spandex from spandex waste. It has Global Recycled Standard certification (Spanflex 2020).

As can be seen, many textile companies around the world produce recycled textile fibers and include recycled textile fibers in their many different products. All these developments indicate that the importance and interest given to recycling will increase day by day.

6 Conclusions

Disposing of plastic instead of recycling unfortunately means that these plastics will go to landfills and oceans. The biggest problem here is that storage areas are overcrowded and occupation of areas that can be used for different needs. In addition, these discarded plastics pose a great danger to animals living in the oceans. The recycling of plastic must be considered for our future. As a result, thermoplastics must be recycled to use landfills for different purposes and to protect the environment. Therefore, recycling is very important. Today, the use of recycled thermoplastic yarns is expected to expand its market share. When yarn manufacturing in the world is examined, it is visible that the highest production amount belongs to synthetic fibers. Nowadays, thermoplastic fibers are important for the textile industry owing to their important properties. Recycled thermoplastics are a more ecological and sustainable raw material, as conversion to recycled thermoplastic yarn saves natural resources, saves energy in the manufacturing process and results in low greenhouse gas emissions. It is very important for the sustainability of our planet to produce new textile fibers and textile products or different types of products from thermoplastic waste and to realize the recycling processes. For this reason, large textile companies are increasingly using recycled thermoplastic products. Therefore, recycling is an irremissible cure for a more sustainable and greener world and to carry our planet to the future in the best possible way for future generations. It is expected that the interest of textile manufacturers and consumers in new textile products produced by recycling from recycling and thermoplastic waste is expected to increase in the upcoming period. The combined effect created by the increase in the production and utilization of new textile products produced by recycling from thermoplastic wastes, as well as the increase in the production of sustainable textile products, will make greater contributions to the goal of a more sustainable world.

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Rheological Behavior of Recycled Plastics, Blends and Composites

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Abstract Rheological properties are useful in evaluating materials performance during processing operations. Rheology is a sensitive tool in identifying and/or detecting any microstructural changes that is directly related to mechanical properties of the final products. In order for polymer wastes to be reprocessed in standard plastics equipment and produce high yields of molded and film products, the rheological properties must first be understood. Recent development in the green polymer composite has attracted a significant interest to sustain the ecological friendliness of the Recycled poly(ethylene terephthalate):rPET (rPET) and recycled poly(propylene) (rPP) blend. The common problem during polymer recycling is the degradation of the polymer that leads to the reduction of its molecular weight (M_w). Reprocessing at high temperatures with thermal exposure, shear as well as the presence of moisture and physical contaminants (poly(ethylene) (PE), poly(vinyl chloride) (PVC, adhesives) lead to a remarkable $M_{w"}$ loss. This chapter presents an overview of rheological properties of plastic waste blends and composites. It mainly focuses on rPET and rPP and natural fibers composites of recycled polymer.

Keywords Rheological behavior · Recycled poly(ethylene terephthalate) · Recycled poly(propylene) · Natural fibers · Kenaf

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1 Introduction

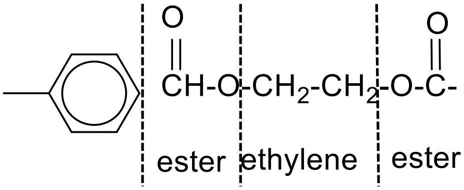
Rheology is the science of deformation and flow of matter when external forces are applied. It is a study to understand why a material behaves in a certain way when a force is applied. An important aspect of polymer rheology is the study of the viscoelastic behavior of the molten polymer and its relation with molecular structure. Unlike simple fluids, most polymeric materials are rheologically viscoelastic. Polymeric materials possess rheological properties similar to viscous liquids (they dissipate energy) and similar to elastic solids (they store energy) components which depend on the time scale of the deformation. Concentric and parallel plate rheometers are commonly used to study the viscoelastic properties of polymers at low shear rates. On the other hand capillary rheometer is pressure flow type rheometer which primarily is used for measuring viscosity at high shear rates (Dealy and Wissbrun 1999). These are used extensively in industry for quality control purposes because experimental data from the measurements can be collected rapidly to reveal structural information (Dealy and Wissbrun 1999).

Polymer waste streams from packaging are often mixed streams as often can consist of different polymers or include other impurities. Most of single application polymers are typically polypropylene (PP) and poly(ethylene terephthalate) (PET) (Wyser et al. 2000; Zander et al. 2019). In the effort of limiting the production of waste and reducing natural resource use, recycling of polymer waste is one of the economical ways. However, the major challenges for reprocessing of plastic wastes is to optimize the processing conditions to ensure of minimal costs and compatible with common processing equipment. Formulating and fabrication of polymer blends and composites require proper knowledge of flow mechanism and reliable evaluation of flow performance of these reprocessed polymers blend and composite melts. The flow mechanism and flow performance can be obtained by rheological characterization. In chapter presents an overview of rheological behavior of recycled polymers, blends and composites which mainly focuses on PET and PP. The understanding of structure, degradation mechanism and interfacial adhesion between the matrix and additives is important for processing which relates to the properties of the final products.

PET is the most favorable material in beverage packaging industries. Large demand of the PET packaged water containers eventually leads enormous volume of PET waste at the landfill which PET were already known have no ability to self-degrade in normal condition which has prompted an increasing environmental awareness and health consciousness in public. Attempts have been made to maximize and diversify the use of PET waste into useful and valuable end products such activated carbon, fibers for separation process (Rahimi and Garcia 2017).

PET is a hydrophilic and non-degradable polymer that belongs to the family of polyesters with high toughness. Due to its beneficial outcomes, PET has been widely used in many fields particularly for packaging or beverage container. In general, PET mainly consists of carbon, hydrogen and oxygen, which the molecules can be clustered into the terephthalate group, ethylene group and ester group as shown in Fig. 1. The good elasticity and strength are the physical attribute of short ethylene

Fig. 1 The molecular structure of PET



group that affects PET structure-related properties. Meanwhile, ester group, which made of a carbon–oxygen double bond, is selected to describe bonding mechanism between the terephthalate group and ethylene group. The difference in electronegativity charges of the respective carbonyl carbon atom and the carbonyl oxygen atom in the ester groups have attracted nearby ester groups chains to line up with each other in crystal form. Yet, the presence of weak ester linkage makes PET unstable and vulnerable to such attack mechanisms i.e. degrading agents and moisture which will substantially lead to hydrolytic degradation. Such degradation in particular affects the impact resistance to crack propagation, whereby PET possesses high notch sensitive and brittleness behavior. These setbacks of PET cause the limitation for their use in demanding application.

Commonly, PET is produced by polymerization or also known as esterification process (Fig. 2) or commercially produced via trans-esterification reaction as shown in Fig. 3. Additionally, the PET production also involves a poly-condensation reaction of the *bis*-(hydroxyethyl) terephthalate (BHET) at the temperature of 270 °C immediately after trans-esterification as the outcome of PET and ethylene glycol (EG) is show in Fig. 4. FTIR analysis of PET showed significantly at absorption band of

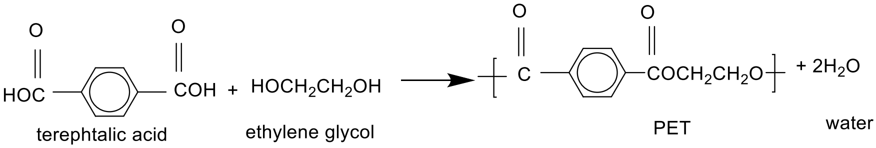


Fig. 2 PET esterification reaction

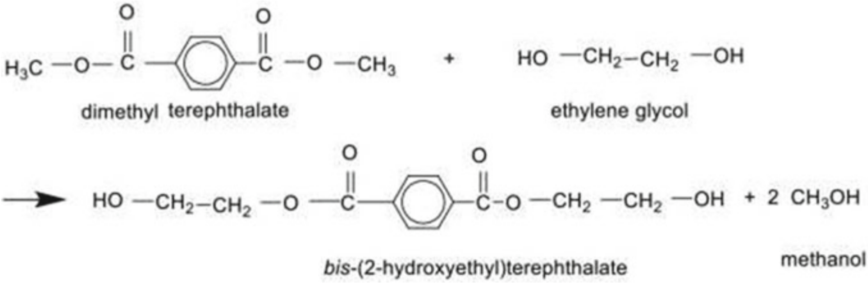


Fig. 3 PET trans-esterification reaction

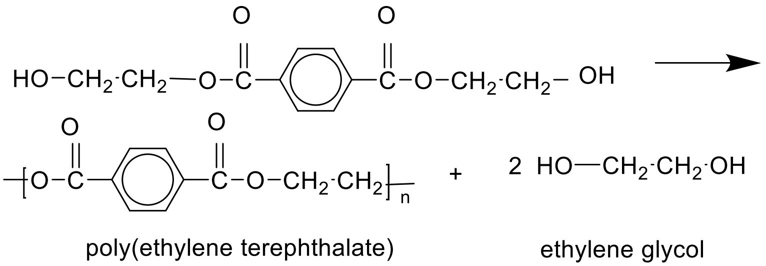


Fig. 4 PET poly-condensation process

1715 cm^{-1} and a small peak at 1578 cm^{-1} which are assigned to the stretching of carbonyl (C=O) and skeleton stretch vibrations of the aromatic ring, respectively (Van Kets et al. 2019). Furthermore, another PET related peak presented in carbon–oxygen (C=O) region can be found between 1320 and 1160 cm^{-1}, which peak at 1238 cm^{-1} close to an aromatic moiety. Similar peaks have been observed in other studies (Zhu et al. 2015a, b).

High production of PET, however, has always been interrelated with the challenge of their further utilization after use, as the traditional methods such as combustion or burying underground are responsible for giving a serious ecological threat upon slow self-decomposition rate (Thumsorn et al. 2013). In accordance with the environmental and cost-effective consideration, the development of new material dealt through mechanical reprocessing is foreseen as the most favorable method to manage the increasing volumes of PET waste (Datta and Kopczyńska 2016). This approach of simple steps to recuperate plastic involving contaminants removal, grinding into flakes and pellets, washing, drying and melting (Lopez et al. 2014; Awaja and Pavel 2005). As the market for recycled PET (rPET) exhibit extensive demand throughout the world by the year, Jankauskaite et al. (2008) emphasized the importance of selecting appropriate process of plastic recycling in regard to obtain successful PET bottle recycling. Consider the case of PET recycling, the source of poor stability in recycled material usually comes from the presence of the contamination such as water content, coloring pigments or acetaldehyde (extracted from printed ink labels) bring a challenge in determining final properties of recycled material which are refined from low molecular weight (M_w) and low crystallinity (Salminen 2013). Meanwhile, Pawlak et al. (2000) emphasized worthless material for advanced application relevant to higher PVC content in rPET. Awaja and Pavel (2005) proposed a requirement for rPET to be reprocessed as listed in Table 1.

In other study, Duarte et al. (2016) found that degradation in rPET is attributable to hydrophilic nature of PET. For reducing the effect of degradation, drying step is regarded as an essential step in PET recycling to minimize the moisture content and leads to higher rPET melt strength. Ranges of literature on comparative studies involving virgin PET, rPET and modified PET properties have been undertaken to assess the macromolecular changes (de Souza and Caldeira 2015; Ardekani et al. 2014; Rosnan and Arsad 2013; Dehghani et al. 2013; Inoya et al. 2012a, b).

Table 1 Minimum requirements for the rPET (Awaja and Pavel 2005)

Properties	Value
Viscosity coefficient [η]	>0.7 dl g^{-1}
Melting temperature, T_m	>240 °C
Water content	<0.02 wt%
Flake size	0.4 mm < D < 8 mm
Dye content	<10 ppm
Yellowing index	<20
Metal content	<3 ppm
PVC content	<50 ppm
Polyolefin content	<10 ppm

Despite of the amount of contaminant, another destructing factor in rPET properties is the processing cycles. The increasing number of processing prompted subsequent deterioration in M_w of rPET due to chain scission. In practice, hydrolysis and thermal degradation reactions evident in low M_w rPET involves shorter PET chain with high hydroxyl or carboxyl end groups content as can be seen in Fig. 5.

The performance of PET and multiple extruded rPET has been studied in detail by Van Kets et al. (2019). The Young's modulus and tensile strength for PET was reported to be 2505 MPa and 53.9 MPa, respectively. In other study, PET exhibit high flexural properties and more resistant to crack propagation (2.32 kJ m^{-2}) (Kuzmanović et al. 2016). The reason of the high flexural and toughness properties in PET, probably lies in the presence of the great size and amount of PET spherulites. However, after being recycled, the tensile strength for rPET sample reduced almost half value to 26–37 MPa while break at a level of 2–5%, corresponding to the decreasing in M_w induced by chain scission. The processing cycle influenced PET structure, hence reasonably responsible for the reduction in mechanical properties, flow behavior including the melt flow index (MFI) measurement (Baccouch et al. 2017; Lopez et al. 2014; Nait-Ali 2016). The brittleness of rPET also reported by others (Pawlak et al. 2000; Zander et al. 2019).

The structure of semi-crystalline PET involves long undercooling time process to form a perfect PET crystalline structure. Therefore, PET is known for having very slow crystallization rate in thermal analysis. Additionally, the crystallization process profoundly influences the mechanical and flow properties. It was noted that PET is crystallized at 150–200 °C (T_c) during cooling while in heating cycle, a large single endothermic peak appeared at 256 °C was corresponding to PET melting temperature (T_m) (Baldenegro-perez et al. 2014). Similar values of T_c and T_m for PET have been reported (Oromiehie and Mamizadeh 2004; Cui et al. 2013; Zhu et al. 2015a, b; Kuzmanović et al. 2016). A comparative study on thermal measurement corresponding to multiple recycling increased the crystallisation temperature (T_c) but reduced the T_m for rPET. Degradation of rPET can be detected from the increase in T_c, and reduce of T_m (Pawlak et al. 2000). As the number of processing cycle increases, increasing amount of imperfect crystal were detected. Meanwhile, TGA

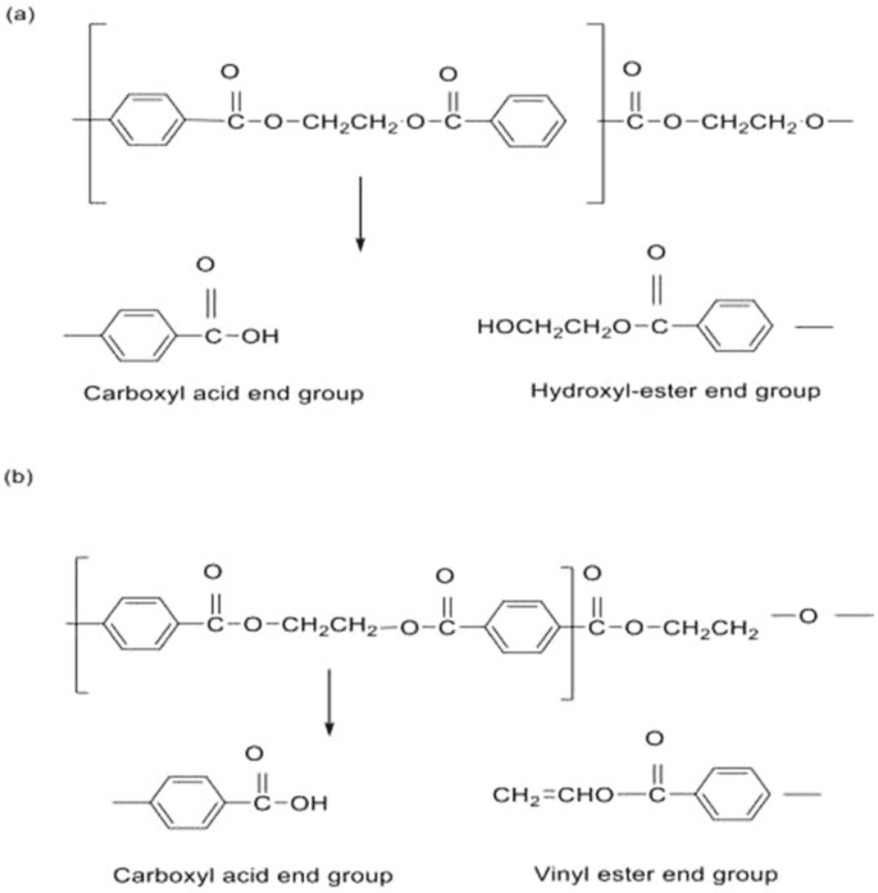


Fig. 5 Degradation reactions of PET: **a** Hydrolysis reaction of PET and **b** thermal degradation reaction (Awaja and Pavel 2005)

analysis for rPET traces a single step of mass loss with 87–89.8% occurs within 396–491 °C under nitrogen atmosphere (Pawlak et al. 2000). In this state, the degradation products present in rPET contributes to the depression of M_W.

Figure 6 shows the PP structure which consists of carbon atom which attached to a methyl group (CH_3). PP is a downstream petrochemical product, derived catalytically from the propylene. The process of monomer connection is called as addition polymerization whereby a catalyst with the presence of heat and high-energy radiation is added to the olefin monomer propylene to initiate the amalgamation of monomers and produced a very long polymerized propylene molecules or chains. The existence of methyl groups in PP molecular chain structure has given rise to PP hardness. PP as amorphous and hydrophilic polymer is a good candidate for processing because its superior characteristics caused a broad prospective in blending

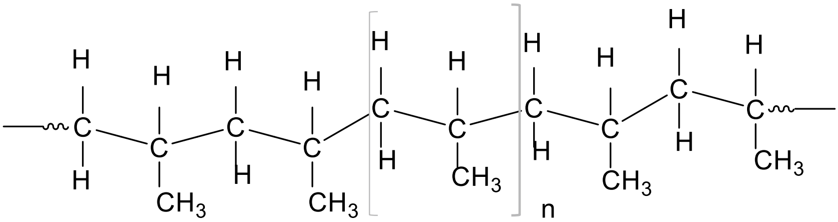
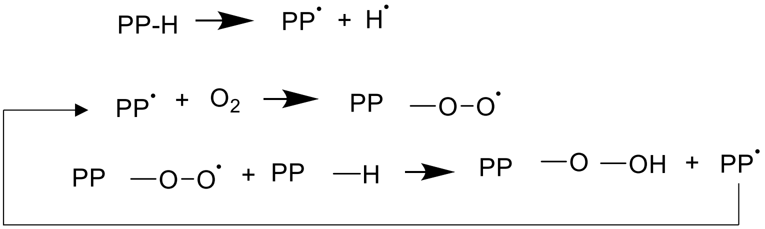


Fig. 6 Chemical structure of PP

or reinforcing (Maddah 2016). This major advantage related to the process ability in injection molding and extrusion since it has high temperature resistance. Moreover, as is well known, this polyolefin polymer has high versatility in structural designs and ideal for long-life applications due to great properties of PP; low density (0.90 g cm^{-3}), excellent chemical resistance also cost-effective. These capabilities of PP is reasonably favorable after polyethylene (PE), which applicable in large scale production, for instance; automotive components, laboratory equipment, plastic parts, food packaging and containers (Pawlak et al. 2000).

The main problem with PP recycling is degradation of polymer during extrusion which leads to degradation of the properties of the final product. Heat and mechanical stress strongly modify the structure and the morphology and thus the characteristics of PP. Although the degradation behavior is common to all polymeric materials, the effects of thermomechanical degradation on PP are dramatic because of the tertiary carbon present in the chain of this polymer. The degradation of PP occurs through the following series of reactions describing its oxidative degradation which represent in Fig. 7. The degradation kinetics depends on many factors, in particular the type and level of the external stresses and morphological characteristics of the polymer (molecular weight, crystallinity, etc.). Finally, oxygenated groups, formed during oxidative degradation, act as catalysts of the reactions, accelerating the degradation rate. The main effects of the degradation phenomena on the PP structure are the decrease of the M_w, change of the molecular weight distribution (MWD) and formation of oxygenated functional groups. Hence, the properties of the recycled polymer (rheological, mechanical, etc.) are strongly altered as a result of changes in structure and morphology (La Mantia 1999).



$$PP\text{-}H \rightarrow PP^{\bullet} + H^{\bullet}$$

$$PP^{\bullet} + O_2 \rightarrow PP{-}O{-}O^{\bullet}$$

$$PP{-}O{-}O^{\bullet} + PP{-}H \rightarrow PP{-}O{-}OH + PP^{\bullet}$$

Fig. 7 Recycling PP mechanism (La Mantia 1999)

PET can undergo different chemolysis reactions (hydrolysis, alcoholysis, acidolysis and glycolysis) to produce mainly the monomers from which they have been produced or other oligomers. Unlike PET, polyolefins PP and polyethylene (PE) cannot be degraded with simple chemicals to their monomers due to the random scission of the C–C bonds. Two main chemical recycling routes are the thermal and catalytic degradation of these polyolefins. PP related peaks noticed in the carbonyl region (1750–1600 cm^{-1}). The peaks of PP include (1) carbonyls from ester stretching at 1732 cm^{-1}, (2) double bonds at 1650 cm^{-1}, and (3) carboxylates or conjugated C–C bonds at 1592 cm^{-1}. In addition, two distinct peaks with a shoulder observed for PP; (1) 1453 cm^{-1} (shoulder 1435) and (2) 1375 cm^{-1} (shoulder 1362 cm^{-1}). The first region can be associated with main chain scission for PP (CH_2) while second region is related to methyl scission from the main chain (CH_3). Due to the architecture of PP (long linear polymer chains), only small amounts of main chain scission (1453 cm^{-1}) are possible since PP would preferably scission in the middle. This behavior gave stability to the PP, as also indicated in other study by Van Kets et al. (2019).

Bourmaud and coworkers; have examined PP under 7 cycles of extrusion for the effect of recycling operations on the mechanical properties of PP (Bourmaud et al. 2011). it was emphasized the environmental interest in using rPP compared to PP, due to reduction in global warming (70%) with low energy consumption from 74 to 9 MJ kg^{-1}. It was found that the Young's modulus of rPP (9.1%) is lower than of PP (13.5%) while the elongation at break of the rPP is very low compared to PP (6.4% against 148%). Similar trend found for the elongation at break, the recycling induced decrement in elongation at break of rPP (Aurrekoetxea et al. 2001). However elastic modulus was found to increase due to higher degree of crystallinity of rPP as a result of decrease in M_w. Few review papers summarized other works on the effects of recycling on thermal and mechanical properties of recycled polymers (Zdiri et al. 2019; Najafi 2013; Oromiehie and Mamizadeh 2004; Pawlak et al. 2000).

2 Rheological Behavior of Recycled Polymers

Rheological measurements are able to measure the amount of degradation occurring during the reprocessing by correlate with the average molecular weight M_w, and the molecular weight distribution (MWD). Incarnato et al. (1999) analyzed the effect of recycling operations on the rheological properties of a commercial PP, supplied by Montell, extruded up to seven times. It was observed that the viscosity decreased after reprocessing cycle due to reduction of M_w, and a narrowing of MWD of PP. The rheological behavior of the binary blends of virgin and rPP is intermediate between those of the pure components in all cases examined. It was verified that empirical equation (Eq. 1) of binary blend of certain weight fraction (ω_i) of monodisperse and polydisperse materials can satisfactorily prediction of the zero shear viscosity (η_o) values of the virgin and recycled blends. It is valid for both versus the weight fraction of the recycled polymer also versus the number of reprocessing.

$$\eta_{0,\mathrm{mix}}{}^{1/3.4} = \omega_1 \cdot \eta_{01}{}^{1/3.4} + \omega_2 \cdot \eta_{02}{}^{1/3.4} \tag{1}$$

MWD values can be calculated from cross-over coordinates (cross-over frequency w_c, at which storage modulus, G' =loss modulus, G'' and the cross-over modulus, $Gc, = G' = G''$). The cross-over coordinates are related to molecular weight M_w, and to MWD as reported for PP (Utracki 1991) as:

$$\omega_{C\propto}(1/\eta_0)^a \tag{2}$$

$$G_{C\propto}(M_n/M_w)^b \tag{3}$$

$$lnM_w/M_n = 0.689 + 0.86 \cdot lnP.I. \tag{4}$$

where a and b are constant parameters, P.I. is the polydispersity index = $10^5\ G_C{}^{-1}$, where G_C, is expressed in units of Pa.

PET is hygroscopic thermoplastic; therefore drying process is very important since it affects the rheological properties, processing and the product characteristics. Comprehensive rheological behavior of PET has been reported by Hatzikiriakos et al. (1997). The linear viscoelastic, shear and extensional rheological characterization of linear and branched PET by means of parallel plate and capillary rheometers were performed. It was found that PET degraded in the presence of moisture at high temperature. A materials-time correction was applied to the data which accounts the structural changes happened during the experimentation. The rheological data obtained were fitted by multi-mode Phan-Tien-Tanner constitute relation. The flow activation energy of three different PET also reported by assuming the validity of the Arrhenius relation.

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right] \tag{5}$$

where; Ea is the flow activation energy, R is the universal gas constant, and T_{ref} is the reference temperature.

Rheological measurements and intrinsic viscosity were performed by Cruz et al. (2017) to determine how the presence of contaminants, reprocessing and solid state polymerization (SSP) affects the degradation of post-consumer PET. The post-industrial PET resin was contaminated with a series of surrogates according to a US-FDA protocol to simulate the worst-case scenario of misuse of PET packaging. The rheological data demonstrated that contaminated samples present degradation, even without any additional process. The degradation increased as the contaminated samples are melt extrude. For the SSP process it was found that the surrogates do not interfere in the degradation process. The molar mass changes of the PET samples, which underwent different conditions, were investigated. Based on the intrinsic viscosity and melt rheological results it was concluded that reprocessing and contamination reduced the molar mass of the PET and the SSP process induced the molar mass increase. Comparing the results of melt rheology and intrinsic viscosity by applying the Mark-Houwink-Sakurada equation allowed confirming the separate influence of contamination and reprocessing processes. The empirical method showed correlation of molar mass index from solution and melt samples. Based on the existing relationship which allowed the use of complex viscosity in higher frequencies, above the Newtonian plateau region and it is as efficient as the zero-shear rate viscosity. In addition the method is able to quantify the degradation in the polymer system.

Flow curves of PET and rPET were presented at different temperatures by Bata et al. (2017). The measurements were performed by an ARES G2 rotational rheometer and a Goettfert Rheograph 25 capillary rheometer at temperature of 270, 280 and 290 °C. The shear rate was changed from 0.05 to 20 s^{-1} and 100–10 000 s^{-1}. The viscosity of rPET was lower than the value of virgin PET at measured temperature. The molecules of the recycled material were supposed to shorten during the recycling and grinding processes. As the temperature increases, the shear viscosity decreased however there was no linear correlation between these two variables.

Few efforts have been reported to control the degradation of PET and rPET during processing. The study by Tavares et al. (2016) aims to evaluate the influence of a multifunctional epoxidic oligomer (Joncryl Polyad PR 002), commercialized as a chain extender for condensation polymers such as PET. The increase of PET molar mass and, consequently, on restoring its rheological properties. Virgin PET and recycled (post-consumer) rPET polymers were processed in a laboratory internal mixer, with and without the incorporation of the additive at different levels. The samples were characterized by torque and parallel-plate rheometry. According to the results, both PET and rPET melts behave as Newtonian fluids at the test conditions used. It was possible to assess the molar mass changes from torque and temperature measurements obtained from the internal mixer. The measurements based on real time torque are fast and accurate indicators of the effectiveness of chain extension in PET. The incorporation of Joncryl Polyad PR 002, a chain extender additive into PET and rPET significantly increased the molar mass of both PET and rPET. However, the chain extender additive was found to be more efficient for increasing the molar mass of the rPET compared with virgin PET. Under the same conditions, molar mass increase for the PETPC was slightly over 10% higher than virgin PET. Increasing the additive concentration from 1.5 to 3% resulted in a 20% increase of the molar mass.

The mechanical and molecular properties of long-chain branched PET (LCB-PET) were analyzed by linear and non-linear viscoelastic rheology in the melt state and by size-exclusion chromatography (SEC) measurements with triple detection by Kruse and Wagner 2017. The two tetra-functional chain extenders (pyromellitic dianhydride (PMDA) and tetraglycidyl diamino diphenyl methane (TGDDM)) increased the viscosity significantly, strain hardening effects, and increasing LCB with increasing chain extender concentration. Molecular stress function model predictions showed a good agreement with the elongation data measured. The branching was confirmed by a decreasing Mark-Houwink exponent. Depending on the type and concentration of chain extender, the PET structure varies either star-like, comb-like, random tree-like or hyper branched structures which agreed with MSF model predictions. The dynamic linear viscoelastic analysis revealed a broader spectrum of relaxation times due to large molecules generated. The zero shear viscosity increased by two decades and the shear thinning onset is shifted to lower shear rates. The activation energy of flow shows strong indication of LCB formation for both chain extenders, presented in a van Gurp-Palmen plot. Gel-like structure was confirmed by the linear viscoelastic measurements indicating random attacks at the backbone of PET. The Mark-Houwink relation between intrinsic viscosity and molar mass as well as a similar power law for the relation between radius of gyration and molar mass were determined for linear PET. Low concentrations of both chain extenders revealed a more star-like structure PET. With increasing concentration, the structure changed to more comb-like for PMDA and random tree-like or hyper branched for TGDDM. The rheological findings showed that the non-linear parameter β correlates with the coil contraction factor and that the 3.4 zero-shear viscosity versus molar mass power law is not valid for LCB PET. This indicates a limited sensitivity of rheology in providing information on weight-average molar mass and radius of gyration, but sensitivity enough to the type and concentration of LCB structure of the molecule.

3 Rheological Behavior of Polymer Waste Blends

The preparation of polymer blends of recycled polymers is an attractive way to reuse mixed waste streams at a lower cost. In addition, polymer blending is a facile way to tailor mechanical properties of polymers or improve certain properties while maintaining the processing conditions.

Main problem to overcome to use polymers waste is its viscosity which compromises the processing and the final product properties. As it is known, PET undergoes thermo-mechanical and hydrolytic degradation during its mechanical recycling decreasing its viscosity and causing a loss of mechanical properties. Few attempts have been reported on this matter and will be discussed in this sections.

In Kostov et al. (2013) studied on rheological behavior of different sources of recycled (Coco Cola Co. bottle, old beverage bottle and bottles of various drinks offered on Bulgarian market) and virgin PET and the blends. Different blend ratio of virgin PET, rPET (100–80 mass%) for textile fibers were prepared. The rheological characteristics were studied at various temperatures (543, 548 and 553 K) and shear stresses in the range of 6.2×10^3 to 14×10^3 Pa. The flow curves of PET melts studied was found to obey the power law at the three temperatures with melt index lower than 1. A weak tendency of increase of the flow index was observed with the increase of temperature. The effects of two different stabilizers (Irganox 1076 and butylated hydroxytoluene (BHT)) on the thermooxidative degradation were also studied. The stabilizing ability of Irganox 1076 was found to be the better than BHT since it increased viscosity from 50 to 100 Pa.s without any significant changes in

PET appearance. It is found that rPET had partly destructed (after 3–4 years) due to the effects of atmospheric conditions under prolonged storage have resulted in polymer ageing which reflected on its viscosity. Good stabilizing effect of Irganox 1076 can be clearly seen at higher temperatures and higher shear stresses.

Another study by Elamri et al. (2017) studied behavior rPET from different source of waste and blend with virgin PET. The viscosities of all blends ratio lie between those of pure PET materials. It is found that PET from blue post-consumer bottle more likely to degrade than the heterogeneous deposits of various colored bottles (white, green etc.). The experimental curves show a negative deviation from the logarithmic additivity rule (model polymer/polymer blends viscosity). Cole–Cole plot (G' versus G'') showed almost the same slope for all the PET blends and independence of composition which is a good criterion proving the miscibility of recycled and virgin PET polymers. This indicated that rPET and virgin PET are miscible down to the macromolecular level and the absence of phase separation.

Asensio et al. (2020) performed a rheological modification of rPET to achieve the necessary fluidity while maintaining the mechanical properties of thermoplastic composites. Most composites are made by thermosetting matrices and being replaced by thermoplastics to improve the recyclability of these systems (Van De Velde and Kiekens 2011). The capability of thermoplastics materials to flow with heat makes it recyclables and post-formable (Novo et al. 2016). The main problem of thermoplastic materials for composites is their high viscosity which compromises the impregnation with the fibers or fabrics. It has been proved that thermoplastics with low viscosity improved the impregnation and the consolidation process (Kazemi 2013). Rheological modification was carried out by physical and chemical methods. Physical method was performed through blending of rPET with virgin PET of low melt viscosity (low M_w 15,000–18,000 g mol^{-1}). Chemical method was performed on rPET with addition of additive (5-amino isophthalic acid ($C_8H_7NO_4$)), by reactive extrusion. Both methods are able to decrease the viscosity without compromising mechanical properties. The chemical method during the reactive extrusion provided higher elastic modulus values and lower complex viscosity as compared to physical method. During the reactive extrusion, the additive found to catalyze the hydrolysis reaction acted as scission breakage and a functional graft. Thus low viscosity (25–100 Pa s) and flowability within the composite processability zone is achieved. On the other hand physical method reduced the viscosity by degradation during extrusion process (thermal and hydrolytic) and the effect of the blend. The additive enable melt processing of rPET with low viscosity at lower pressures and/or temperatures for performance composite application.

Zander and his workers investigated blends of recycled PP/PET and PP/PS, compounded with or without a block copolymer poly(styrene-co-(ethylene-butylene)-styrene) (SEBS) compatibilizer for fused filament fabrication (FFF) additive manufacturing processes (Zander et al. 2019). It is notable that the rPP/rPET blends had higher viscosity than rPP or rPET due to volume filling effect. However, the addition of block copolymer poly(styrene-co-(ethylene-butylene)-styrene) grafted with maleic anhydride (SEBSgMAH) led to substantial increase in the viscosity relative to the unfunctionalized SEB blend, implying strong interaction and increased molecular weight. It is possible that the hydrogen bonding of maleic anhydride reacted with the PET chain ends, resulting discontinuity in the fluid flow. Instead, the phenomenon observed for the SEBSgMAH compatibilization on PP/PS blends was not expected. It should be noted that SEBSgMAH had less capability to interact strongly with rPS phase than SEBS due to the polarity mismatch, thus only slight improvement in interaction happened. Consequently, the domain sizes increased due to coalescence which served to reduce viscosity. The viscosities of the recycled PET, PP and blends were lower than that of polymers typically used in FFF processes such as ABS (zero-shear viscosity 18,000–75,000 Pa s).

The stabilizing effect of rPP/rPET (75/25) blends with and without 5 wt% SEBSgMAH was reported by Van Kets et al. (2019). A sudden viscosity drop was reported at the third cycle of extrusion as a result of destabilization and poor interfacial adhesion between rPP and rPET. Moreover, the rPP/rPET set did not reach the Newtonian plateau within the 0.2–100 s^{-1} range. The destabilization of the rPP/rPET blend was observed from the SEM images indicating a decrease in M_w. Diameter of PET particles (>2 mm) increased and the total number of PET particles decreased at the third extrusion step. In the presence of SEBSgMAH, small PET particles were well dispersed in the PP matrix as a result of good interfacial adhesion. The complex viscosity increased in the presence of SEBSgMAH and reduced only slightly over five extrusion cycles. The overall stabilization of the compatibilized rPP/rPET was discussed using rotational rheology, FTIR measurements, DSC-results and SEM-images. Less severe degradation was observed in compatibilized rPP/rPET blends even after five extrusions.

Few works have been devoted to study the compatibilization of PET and PP blends. Heino and Vainio 1996 studied the effects of unfunctionalized SEBS, SEBSgMAH or glycidyl methacrylate grafted (to the midblock) SEBS (SEBSgGMA) on 80/20 PET/PP and 20/80 PET/PP blends. The glass transition temperature of the PET shifted towards that of neat PP and increase in the melt viscosity of the compatibilized blends indicated enhanced interactions between the discrete PET and PP phases induced by the functionalized compatibilizer, in particular SEBS-g-GMA. On the other hand, in PP rich blends, more pronounced shear thinning behavior can be observed indicating that the PET in the blend could not provide sufficient amount of reactions to affect the blend viscosity and thus the viscosities of the blends were controlled by the PP matrix.

In another study, Akbari et al. (2007) investigated the effects of various amount of PPgMAH between of 5–15 wt% in 70/30 wt% PET/PP blends. PPgMAH was prepared by solid state grafting of MAH on PP and the blends were prepared using an internal mixer at 265 °C at 40 rpm with addition of 0.1 wt% antioxidant. Increasing weight percent of PPgMAH in the blends decreased the dispersed particle size and increased the uniformity of dispersed domains. Similar observation also reported by Shi et al. (2007) that PPgMAH compatibilizer caused a distinct decrease in dispersed particle sizes in PET/PP blends. Pang et al. (2000) grafted three different MAH derivatives, namely N, N-dihydroxyethyl monomaleic amide, octodecyl monomaleate, and 2-(N, N-dihydroxyethylamino) ethyl monomaleate onto polypropylene and performed these to compatibilize PET/PP blends. The compatibilizing effects of the three PP grafts were very different. 2-(N, N-dihydroxyethylamino) ethyl monomaleate compatibilizer produced the finest dispersed phase morphology.

Moreover, Papadopoulou and Kalfoglou (2000) reported the comparison of compatibilizer (PPgMAH, LDPEgMAH, SEBSgMAH and thermoplastic polyolefin alloy) effectiveness for PET/PP blends on mechanical, thermal and morphology characterization. The interfacial tension was calculated using the harmonic-mean equation.

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{6}$$

where γ_{ij} is related to free energy $G_{\min}$. It is proven as useful equation in predicting the most stable morphologies. However data on γ_{ij} of compatibilized blends are scarce. It is reported SEBSgMAH improved the compatibility of PET and PP better due to (i) chemical structure of SEBSgMAH leading to microphase domains causes it to concentrate at the interface enhancing its emulsifying effectiveness and (ii) the presence of PS blocks prevents its migration and loss into the polyolefin phase, in contrast to the polyolefin compatibilizer.

With regards of the M_w effect, Inoya et al. (2012a, b) has investigated the effect of PP M_w on thermal, mechanical and morphological behavior for 95/5 and 90/10 rPET/PP blend. Regardless of PP content, low M_w PP provide high degree of miscibility, encouraged good adhesion in the blend hence resulting narrow disparities in polydispersity. Interaction between the compatibilizer and PP particles was more intense with the presence of a large number but shorter PP molecular chains. Low M_w PP resulted in a decrease in particle coalescence and finer dispersion of PP particles in the blends. The homogeneity of the blends significantly affected the mechanical performance. Regardless of PP and compatibilizer loadings the stiffness, yield strength, deformability, and toughness were improved with incorporation of low M_w PP. The blend contained high loading of high M_w PP displayed significant deterioration in properties attributed to the instability of PP phase distribution which correspond to the existence of big disparity in polymer matrix.

4 Rheological Behavior of Polymer Waste Composites

In general, the incorporation of fibers into polymer systems increases the viscosity and further increases with increasing of fiber content. At low fiber concentration, the viscosity is expected to increase rapidly with increasing concentration of the fibers because of the collisions between particles as they become packed more closely to each other. However, at a critical concentration random packing ceases to be possible and further increase in fiber concentration leads to a more orderly anisotropic structure of the fibers in suspension, and slide readily past one another. The viscoelastic behavior of the composites not only affected by the volume fraction, but also by the particle shape and particle–particle or particle–matrix interactions (Gahleitner et al. 1994). The relaxation time spectrum of composites was used to discuss the rheological behavior of PP/talc composites. It was found to be an appropriate tool for investigating the effects of interaction between particles-particles or particle–matrix interaction. Particle–particle interactions in the fluid can also be explained by yield stress behavior in steady-state.

The presence of fillers or nanofillers can alter the rheological behavior of the blend, transforming an emulsion like behavior in a suspension or solid like behavior (Sangroniz et al. 2019). The rheological properties determined by oscillatory flow measurements, have been widely investigated in the linear viscoelastic regime, focusing on the interfacial tension. In the nonlinear regime focusing on the relationship between droplet size and a nonlinear parameters. The properties in the linear viscoelastic regime have been also studied and related with the morphology. The surface tension between the three components and thermodynamically preferred location can be determined using Young equation.

$$\omega_a = \frac{\gamma_{\mathrm{TiO_2}} - \mathrm{LDPE} - \gamma_{\mathrm{TiO_2}} - \mathrm{PET}}{\gamma_{\mathrm{LDPE-PET}}} \tag{7}$$

The viscosity of rPET/LDPE/TiO_2 can be described by the Cross model equation.

$$\eta(\gamma) = \frac{\eta_0}{1 + (\tau_0 \gamma)^a} \tag{8}$$

where η_0 is the Newtonian viscosity, τ_0 is a relaxation time linked to disentanglement kinetics and α is the shear thinning index. The presence of TiO_2 nanoparticles increase the viscosity as the shear rate is decreased and also showing viscoplastic behavior, characterized by a concave upward. Viscoplasticity implies the existence of a yield stress below which flow is not possible. Rheological data of rPET/LDPE/TiO_2 were fitted to a modified Cross model to consider a yield stress value σ_y (Eq. 9)

$$\eta(\gamma) = \frac{\sigma_y}{\gamma} + \frac{\eta_0}{1 + (\tau_0 \gamma)^a} \tag{9}$$

One of the challenges when dealing with natural composites is the adhesion between fibers and matrices, mainly due to the hydrophilic and hydrophobic characteristics showed by the fibers and the polymers. Various surface treatment methods as well as coupling agents and compatibilizers such as maleic anhydride grafted polymers, silane, alkali treatment and etc. have been used to increase the compatibility between natural fibers and thermoplastic matrices, on top of enhancing the composites performance (Pereira et al. 2017; Borchani et al. 2019; Suradi 2015).

Ternary graft copolymer of polyethylene (PEg) was found to be effective in improving the interfacial interactions of recycled polyethylene (rPE) and wood fibers (WF). Further treated WF by braising of WF enlarges the gaps of cells and promotes the infiltration of rPE into the gaps. Improvement in interfacial interaction between WF and PE restricted the movement of PE chains thus increase the viscosity of rPE. At the same frequency, the shear stress is much higher. G′ and G″ of the composites are much higher after the incorporation of graft copolymers and the treatment of WF. At the lower frequency, G′ and G″ of the composites are distinct from each other. At the higher frequency, this distinction reduces. Similar observation have been reported by others. The presence of two compatibilizers in rPET composites increased viscosity due to chemical reactions of the epoxy group of GMA with end groups of the PET chains and reactions of maleic anhydride of PE*g*MAH with linter fibers in the composite (Pereira et al. 2017).

Borchani et al. 2019 discussed the effects of alkali treatment of alfa fiber on the viscoelastic behavior of polyester-starch bioplastic of the Mater-Bi® based on hydrodynamic and percolation. The influence of fiber loading, alkali treatment of fibers, and temperature on the viscoelasticity of biocomposites was examined. Dynamic moduli increase with increasing fibers content. In addition, biocomposites exhibit a plateau of the storage moduli at low frequencies, indicating a percolated fibers network. This low frequency elastic behavior is enhanced by the treatment of the fibers. The incorporation of natural fibers to a polymer causes a perturbation in the flow of the matrix and induces hydrodynamic effects. As the concentration of fillers increases, this effect becomes more important and influences similarly the elasticity and the viscosity, on the whole frequency range. Due to filler to filler interactions the effect of fiber content is much higher at low frequencies than at high frequencies.

Bourmaud et al. (2011) reported that addition of hemp fibers into rPP increased the viscosity as a result of the PP molecular movement restriction due to the presence of the fibers. The Newtonian viscosity decreased with the number of injection molding cycles for rPP and rPP/hemp fiber composite. The incorporation of hemp fibers further induces the decrement of the Newtonian viscosity.

Stanciu et al. 2020 studied the effects of three types of natural fibers wood particle reinforced composites with six different sizes of grains (WPC); hemp mat reinforced composites (HMP) and flax reinforced composite with mixed wood particles (FWPC) on tensile and dynamic mechanical analysis of polyester composites. The results demonstrated that both tensile and rheological behavior depends on the size of fibers, type of fibers (random or fabric) and matrix type. The elastic-viscous responses of the samples depend on the interface of the fibers and matrix. Cole–Cole plot revealed wood particles with a polyester matrix lead to relative homogeneity of composite in comparison with FWPC and HMP samples.

Properties of recycled polypropylene/recycled polyamide 6 (rPP/rPA6) composite reported by other (Suradi 2015). The Melt Flow Index (MFI) of rPP, rPA6, rPP/rPA6/MAPP blend was 23.7 g 10 min^{-1}, 42.9 g 10 min^{-1} and 12.0 g 10 min^{-1}, respectively. The lowest MFI values indicated that the viscosity of compatibilized rPP/rPA6 blend was higher than that of the uncompatibilized blends. The reaction between MAH with the amine end group of rPA6 increased the interfacial bonding between rPP and rPA6, resulting discontinuity in flow dispersion. Further reduction in MFI values i.e. higher viscosity found with addition of 10, 20 and 30 phr KBF, which was 7.8 g 10 min^{-1}, 7.4 g 10 min^{-1} and 7.3 g 10 min^{-1} respectively. However, different trends have been seen for actual shear viscosity of KF reinforced composite in capillary rheometer. It was found that the viscosity inside the capillary decreased with higher KBF composition. Here, carbon layer formed at the surface of burned KBF acted as the lubricant rather than as reinforcement to the composites and helped to improve the flow ability of the composites.

Comprehensive study on rheological and processability of plastic waste composites is still lacking in literature. Zdiri et al. 2018 reviewed the effects of different nanofillers such as clay, calcium carbonate ($CaCO_3$), Silica (SiO_2), Zinc Oxide (ZnO), carbon black (CB), carbon nanotubes (CNT), antioxidizers and others on thermal, mechanical and rheological properties of recycled PP matrix. The effects of nanofillers content and reprocessing on MFI and dynamic rheological behavior were briefly discussed. Addition of nanofillers with sufficient interfacial adhesion improved the mechanical, thermal and rheological properties of rPP nanocomposites.

Rheological measurement also is a powerful technique that provides reliable information on the degree of dispersion the nanofiller although it cannot be conclusive (Honorato et al. 2020; Devendra et al. 2006; Hatzikiriakos et al. 2005). Comprehensive study of linear and nonlinear behavior of polyolefins nanocomposites have been reported by Hatzikiriakos and co-workers. Compatibilizing effects of PEgMAH in PE/clay nanocomposites was discussed based on linear and non-linear rheological measurements. Network structure in nanocomposites was studied using the empirical BSW relaxation time spectrum and it was concluded that the presence of clays gives rise to solid like behavior and Cox-Merz rule cannot be used to predict the shear viscosity of the nanocomposites through complex viscosity measurements. The effects of nanofillers on eliminating the melt fracture of polyolefin was reported due to reduction of the tensile stress growth coefficient of polyolefin nanocomposites as compared to unfilled polyolefin confirmed by melt extensional behavior.

5 Conclusion and Future Perspective

Rheological properties are useful in evaluating the plastic waste performance during reprocessing operations. Rheology is a sensitive tool in identifying and/or detecting any microstructural changes as in crystallinity, long chain branching, molecular weight distribution, and relaxation of polymer chains. Attempts have been made to control the M_w reduction due to thermal and shear degradation during reprocessing of plastics wastes. Processing and rheological behavior of polymers wastes blends and nanocomposites has been reported in various reports, however comprehensive study on natural fibers is still limited. It is critical to monitor for viscous to elastic transition of polymers blends composites to be able to predict the processing operation. It is known that during extrusion of molten polymers when the wall shear stress exhibits a certain value flow instabilities occur and thus manifest as surface distortions. Therefore, by understanding how to process and the rheological of polymer waste shows the potentiality of using polymer waste to sustain the ecological friendliness. Natural fibers composites of recycled polymer are currently developed and explored which might result high impact in diverse sectors.

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Thermal Analysis of Recycled Plastics

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and Marcos Tadeu D'Azeredo Orlando**

Abstract Thermal analysis is a powerful combination of techniques used to characterize materials. In this chapter, three case studies were proposed to demonstrate possible applications of thermal analysis in the context of recycled plastics. By analyzing the pyrolysis of waste of recycled polyethylene, and through methodological procedures, the materials' thermal behavior was delineated. The phase change and pyrolysis reaction enthalpy were estimated, and chemical kinetics was performed via isoconversional methods. As an auxiliary technique, X-ray powder diffraction was carried out to evaluate a biodegradable masterbatch and was established a comparison with the recycled materials in terms of their chemical structures.

Keywords Thermal analysis · Polyethylene waste · Kinetics · XRD

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1 Introduction

The negative impacts of using plastic materials on modern societies have accompanied the drastic production growth of these materials on a global scale, especially in developing countries that have been undergoing a retarded industrialization process (Jomo et al. 2019). It is somehow comprehensive since the plastic production in Europe and North America has experienced a rapid decrease in the last years (Wang et al. 2020). According to the European report about plastics global scenario (Europe, 2019), China owns 30% of the world's plastic production. Latin America is gaining ground globally, but its percentage is still small compared to the countries' size, about 4.0% in volume produced worldwide. The large number of plastic artifacts produced and consumed has contributed to the increasing production of Municipal Solid Waste (MSW) collected. A relatively high percentage of these solid waste (15–49%) has been attributed to plastics. This variation is directly related to the characteristics, habits, and customs of the local population's consumption and disposal (Ryberg et al. 2019).

According to (Dahlbo et al. 2018), the primary collected plastics residues are High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Polyethylene Terephthalate (PET), Polypropylene (PP), Polystyrene (PS), and Polyvinyl Chloride (PVC). The quantities attributed to each one of plastic types vary according to the country and the local industry. In the world, PE is the major plastic component present in the MSW stream. For example, about 43% followed by 19% of PET, 7% of rigid HDPE, and 10% of PP, (Soto et al. 2018). In the USA, about 33% of PP, 15% of LDPE, and 11% of HDPE, (US EPA—United States Environmental Protection Agency 2019). The more abundant in European countries are PP around 19% and after LDPE and HDPE, close to 17% and 12%, respectively (Europe 2019).

In terms of socio-economic issues, a common problem, particularly in developing countries, is a not regulated profession, where citizens in subhuman conditions are acting for their account as a collector to feed the recycling industry, (Gall et al. 2020). These citizens indirectly reduce plastics waste in urban areas but are not accounted for in the statistical data. Another common problem in such countries is the inequality in the infrastructure of different regions, mostly in countries with large land areas interferes with the amount of recovered plastic waste for recycling (Joshi et al. 2019). Figure 1 summarized the conventional plastics stream (commonly practiced in emerging countries). Plastics are derived mainly from modifying crude oil (Refining Process). In a highly purified chemical form (for example, monomer such as ethylene), it is piped from the refinery to a separate polymerization plant to be pelletized under the right temperature, pressure, and catalysis. After that, these pellets follow the industry to be used as raw material where noble plastic products are manufactured to attended food and pharmaceutical companies. Inside the own industry is generated post-industrial plastic waste that can be reused in the process. The final consumer mostly generates the main part of plastic residues. Depending on the infrastructure of each country, the waste plastics can follow different paths.

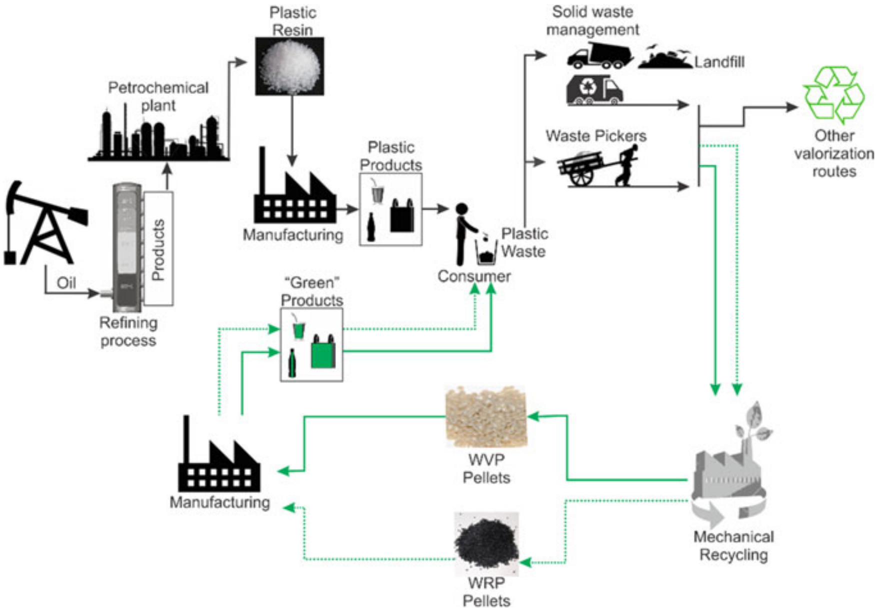


Fig. 1 Scheme of plastics waste stream, adapted from (Duque et al. 2020a, b)

They can be collected by the municipal solid waste service to the landfills or mechanical recycling industries. However, in developing countries, the role of waste pickers has an essential contribution to the mechanical recycling industry. Finally, the recycled material returns to manufacturing as raw material, producing less noble plastic products such as garbage bags and various packaging.

Given the complexities, before mentioned, concerning the recycling stream, (Duque et al. 2020a, b) proposed a classification, for thermal analysis purposes, of at least two categories of waste: the waste of virgin plastics (WVP) and waste of recycled plastics (WRP). As it will be present latter, it implicates different interpretations from the thermal analysis. These are among the reasons for the difficulty of controlling the process of converting plastic waste into useful products (Al-Salem et al. 2009; Bai et al. 2013; Fan et al. 2014; Obeid et al. 2014). In this fashion, if one hand, some characteristics such as density and additives are well known to affect the conversion rate and yields of products recovered (Sarker et al. 2012a, b; Villanueva et al. 2014), on another, physical stress history experienced by the waste in mechanical recycling play an essential role in the conversion processes (Duque et al. 2020a, b). This process typically involves mechanical (separation, grinding, washing, agglutination) and thermal stress (drying, extrusion, and quenching) (Al-Salem et al. 2009; Ragaert et al. 2017). Therefore, the thermal analysis carried out in plastics wastes (WVP or WRP) must be under these premises.

Since the definition of Thermal Analysis is in the context of standardizing/normalizing the procedures and nomenclatures, the definition appointed by the International Confederation of Thermal Analysis and Calorimetry (ICTAC) has been followed in this chapter. That is, “the study of the relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner” (Lever et al. 2014). The primary workhorses in characterizing plastics include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), differential thermal analysis (DTA), dynamic mechanical analysis (DMA), and others. This chapter will explore two techniques from the interpretation of the data processing for kinetics purposes: TGA and DSC. Further details about other techniques applied to polymeric materials can be consulted in (Wunderlich 2005; Menczel and Prime 2008).

Specifically, about reaction kinetics, the ICTAC Kinetics Committee recommended as well as a guide for obtaining kinetic data adequate to the actual kinetics of thermal and thermo-oxidative degradation of polymers and organics; reactions of solids with gases; polymerization and crosslinking; crystallization of polymers and inorganics (Vyazovkin et al. 2011). From where the minimum requirements will be followed in the further sections. Isoconversional methods are commonly used to evaluate the decomposition kinetics of polyethylene. The best-known methods recommended by ICTAC to estimate the activation energy, E, the pre-exponential factor, A, and the reaction model, f(α) and widely used are Friedman (FR) (Friedman 2007), Ozawa Flynn and Wall (OFW) (Ozawa 1965; Flynn and Wall 1966a, b), Kissinger-Akahira and Sunose (KAS) (Kissinger 1957; Akahira and Sunose 1971), and Starink (ST) (Starink 2003). Until nowadays, these methods are frequently employed for all types of solid materials, including plastics (Grammelis et al. 2009; Aboulkas et al. 2010; Das and Tiwari 2017; Duque et al. 2020a, b).

In this chapter, a case study will be presented under the argument that the physical stress undergone by two categories of LDPE waste, in their cycle life, influences the kinetics and pyrolysis pathway. The quantitative aspects, such as the determination of the enthalpy of conversion (phase changes or chemical reactions), are demonstrated from the thermal analysis data interpretation. The methodological pathway will be described in detail to guide the readers to perform such a thermochemical characterization. Although some techniques are not defined as thermal analytical methods, they can be used as support tools for TGA and DSC data/curve interpretations. For that, in this chapter, the X-ray diffraction technique is suggested to concede lucidity to thermal analysis techniques interpretations (Duque et al. 2020a, b).

2 Experimental Techniques

Various properties of the polymers can be measured using thermoanalytical methods. Both absolute values and the rate of change of the sample properties can be determined and further compared with reference material properties. Although these measurements are based on fundamental principles, the interpretation of the results may not be direct, and the application of more than one technique may be necessary.

Some classical thermal analysis techniques used to characterize recycled plastics are presented below.

2.1 Thermal Analysis

2.1.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is one of the principal thermal analysis techniques in the polymers field. This technique provides the sample mass loss data when it is exposed to a controlled heating condition. The analysis can be carried out either in an oxidizing or inert atmosphere, and the heating takes place dynamically, defining a heating rate, or isothermally. The results are usually presented as curves of the sample mass as a function of temperature or time. The derivative of the thermogravimetric data, DTG, is generally plotted to help interpret the results associating with the peaks and slope changes with sample thermal events.

The ICTAC draws attention to the importance of adopting acceptable practices during collecting experimental data to ensure the quality of the results (Vyazovkin et al. 2014). Among the various factors that can affect the thermogravimetric curves (Brown 2001), two will be reaffirmed here: dependence on the sample characteristics and the heating condition.

The amount of sample used must be large enough to provide adequate signal during the heating process, it depends on the heating rate used, and small enough to avoid temperature gradients inside the sample (Coats and Redfern 1964a, b), it usually ranges from 1 to 20 mg (Vyazovkin et al. 2014). Concerning the particle size, it is directly associated with the diffusion of gases inside the sample, and variations in size and shape should be avoided. The smaller the sample size, the higher the extent of the decomposition and lower the temperature of the reaction zone (Brown 2001). For comparative studies, the weight among the samples and the samples particle size must be as close as possible.

Regarding the heating condition, the first point to be considered is the temperature range in which the analysis will be performed. It can be determined with a preliminary test, understanding the sample's behavior, or obtained from the literature. Once defined, a temperature range, an isothermal program, to evaluate the mass evolution over time, or a linear heating program must be chosen. In the latter, unless it is the objective, fast heating rates are not recommended to avoid overlapping essential events. For recycled plastics, heating rates between 1 and 20 °C/min are widespread in the literature. If kinetic parameters evaluation is desired, at least three temperatures or heating rates are usually adopted (Vyazovkin et al. 2011).

An important notice is, in the case of phenomena that do not involve mass loss, e.g., phase changes, TGA cannot identify it and, therefore, it is recommended to complement the measures with DTA and DSC.

Note, as well, that standard proximate analysis is available for compositional analysis by thermogravimetry ASTM E1131-20 (ASTM 2020b). Even if this standard does not preview the moisture content's determination, it can be estimated, but depending on a minimum fraction amount of moisture, following the mass loss curve in the water boiling temperature range.

2.1.2 Differential Thermal Analysis (DTA)

DTA equipment commonly works coupled with a thermogravimetric analyzer, TGA-DTA configuration. Therefore, besides the mass loss recording, the investigated sample and inert reference material are subjected simultaneously to the same heating condition and, any temperature difference between then is recorded. For polymers, DTA is widely used to identify exothermic or endothermic events and, then, assess the characteristic temperatures of phase changes and thermal decomposition. After careful examination of the desired temperature range, the areas under DTA curves are used to calculate the enthalpy values.

2.1.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a classical technique used to evaluate heat capacity, specific heat, and their variation with temperature (Collazo et al. no date; Kousksou et al. no date; Morîntale et al. no date). Although DTA data can be used for that as well, DSC generally provides higher accuracy. The operation principle is very similar to that of DTA, with the difference that DSC provides a quantitative measure of the heat flow. Both endothermic and exothermic events in the sample are registered as deviations from a baseline. DSC is one of the most used thermal analysis techniques and has several applications due to its notable versatility. In the plastics materials field, it is widely used for the measurement of specific heat, and characteristic temperatures and reaction heats of melting, crystallization, and thermal decomposition (Harvey et al. 2018, no date; LIU et al. no date; Brown 2001; Fujino and Honda 2009). Recommendations for collecting DSC data can be found in (Vyazovkin et al. 2014) and ASTM E2160-04 (ASTM E2160-04 2018).

2.2 Complementary Techniques

2.2.1 Ultimate Analysis

The ultimate analysis is a conventional technique used to determine the mass composition of carbon, hydrogen, nitrogen, and sulfur in materials. This technique's essence is based on the complete material combustion and subsequent analysis of the flue gases. Although there are no specific standards for recycled plastics, the literature is full of standard test methods for instrumental determination of these elements that can be taken into account (ASTM D3176-15 (ASTM 2013), D5373-16 (ASTM 2020c)).

Since plastics are non-hygroscopic materials, by definition, the moisture content is not part of the ultimate analysis, and moisture-free samples must be used. Only the moisture content released from the combustion of the sample can be considered. Related to the oxygen content, commonly can be calculated by subtracting the mass percentages of C, H, N, S, and ash from 100.

It is indispensable to complement that if the objective is to determine the different ways in which the basic elements may be present within the sample, such as organic and inorganic carbon matrix, X-ray or FTIR analysis should be performed.

2.2.2 Proximate Analysis

The proximate analysis can determine the moisture, volatile matter, and ash contents and calculated the fixed carbon amount by difference. Standard practices for moisture and ash content determination of plastic materials are available in the literature and can be used for recycled plastics, ASTM D6980-17 (ASTM 2017) and D5630-13 (ASTM no date a), respectively. For volatile matter, adaptations need to be done, and ASTM D3175-20 (ASTM 2020a) can be considered.

In short, once established the experimental protocol, the results can be obtained easily by heating the samples in a muffle furnace under controlled conditions of temperature, time, atmosphere, and sample weight.

2.2.3 Heating Value

The heating value can be obtained experimentally by combusting the material in an adiabatic bomb calorimeter or analytically through correlations based on ultimate and proximate analyses. Several correlations are available in the literature reporting results with high accuracy, see (Sheng and Azevedo 2005). However, while applying these correlations, it is crucial to be aware of the authors' considerations, since extrapolations may result in inaccurate estimations. For experimental estimation, ASTM D4809-18 can be considered (ASTM no date b).

2.2.4 X-ray Diffraction Analysis

XRD is an important technique that can help interpret thermal analysis results and complement plastic materials' characterization. The technique provides information on constructive interference due to the interaction of incident X-rays and crystalline material. For plastics, generally, the main interests in the use of XRD are related to crystallinity and functional groups' determination. These outcomes are obtained comparing the integrated intensities of crystalline and non-crystalline regions (Ruland and Smarsly 2002) and comparing the diffraction patterns with standard crystallography databases. In practical terms, the diffraction patterns can be analyzed using Fityk software, version 0.9.8.57 (Wojdyr 2010) to calculate by curve integration the crystallinity degree; phase identification is performed through the Hanawalt method (and 1983, no date; Faber and Fawcett 2002) using the Crystallography Open Database (COD) (Gražulis et al. 2012) and PDF-2 database (Data, Newtown and 2018, no date; Square and 2010, no date; Gates-Rector and Blanton 2019). The quantification of the phases is performed with Rietveld refinement using the FullProf program (Rodríguez-Carvajalsss 1993).

3 Application for Recycled Polyethylene and Masterbatch

3.1 Materials

The plastic materials used to apply and discuss the examples presented in this section were samples of recycled Low-Density Polyethylene from municipal solid waste provided by LukPlast Ind. (ES-Brazil). A complement essay was carried out using a masterbatch (MB) commonly used in plastics blends to confer desirable plastics properties (Duque et al. 2020a, b). Figure 2 shows their geometric, colors, and size aspects. We notice that the samples were used as they were received, without further treatment. The recycled samples WVP and WRP are a mix of irregular geometries, particle size about 2 mm on average. As expressed in Fig. 2, WPE, with a type of pigmentation resulting from a first and unique mechanical recycling process, WPE, which underwent two to undetermined numbers of mechanical recycling cycles, carries all types of pigmentation, and the masterbatch polymer in pellet geometry type.

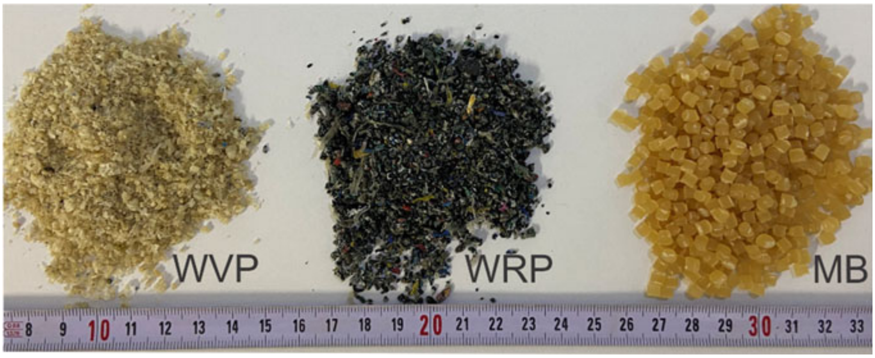


Fig. 2 Plastic samples. From left to the right: WVP, WRP, MB

3.2 Study Cases

For the case studies presented in this section, a series of thermal analysis based on TGA, DSC, proximate and ultimate analysis, beyond a complementary technique, XRD, were carried out to support the experimental interpretations. The configurations of each experiment are presented in Table 1.

Three cases were formulated. The first one investigates the pyrolysis of waste of recycled polyethylene (WRP) from the thermochemical properties determination to the chemical kinetics. The pyrolysis was carried out in TGA under an inert atmosphere at four heating rates, while the properties were estimated using DSC data. The second case deals with a non-standard proximate analysis and its limitations by analyzing TGA under an oxidative and inert atmosphere at 20 °C/min for the WVP sample. Finally, in the third case, we assess the thermal degradation behavior and the chemical structure of a biodegradable masterbatch, comparing TGA curves and XRD diffractograms among all samples.

3.2.1 Case 1: Waste of Recycled Polyethylene

Thermal Analysis

Once we have TGA data, it is necessary to perform some data processing to obtain the onset and offset temperatures Ton and Toff, where starts and ends the thermal conversion, respectively. For that, the TGA curve is plotted with its first derivative, DTG, and second-time derivative, D2TG, curves, as demonstrated in Fig. 3 scheme. The onset temperature was determined by extrapolating the DTG curve slope in correspondence with the first peak in second-time derivatives curves and the zero levels of the DTG axis. The same procedure was used to determine the offset temperature, in this case, picking up the last peak in second-time derivatives curves (Barrall 1973; Dollimore et al. 1992; Das and Tiwari 2017). The peak temperature, related to the maximum rate of sample degradation, can be obtained from the DTG curve and corresponded to its peak. The total mass loss is obtained from the difference between the initial mass and the mass after pyrolysis, closing the data processing in the presented methodology.

Figure 4 presents the TGA and DTG curves under an inert atmosphere for the WRP sample at four different heating rates. The heating rates were chosen to cover the influence of a wide range of temperatures on WRP degradation. When subjected to pyrolysis, the samples lose almost all the mass in a single step at all heating rates. The heating rate increase resulted, as expected, in the lateral shift of the curves along the abscissa without changing its shape. The initial mass used in TGA were on average, about 13.2 mg. The onset and offset temperatures were practically the same regardless of the heating rate, about 367 and 496 °C respectively. From the same analysis, the temperature where the maximum degradation rate occurs can be obtained and the total mass losses after pyrolysis, in this case, 97.7 wt.% on average.

Table 1 Experimental setup

Experiment	Maker	Operating conditions	Reference
TGA	STA 449F3, NETZSCH	Sample mass: 10–15 mg Crucible: Al_2O_3 Carrier gas: N_2, Air, 60 ml/min Temperature range: 20–670 °C Heating rates β: 5, 10, 15, and 20 °C/min	ISO 11,358-1:14 DIN 51,006
DSC	SDT Q600, TA	Sample mass: 20 mg Crucible: Al_2O_3 Carrier gas: N_2, Air, 50 ml/min Temperature range: 20–570 °C Heating rate β: 20 °C/min	ASTM E-2160-04 (2018)
Ultimate analysis	EA 1110, CE	Default settings	ASTM D3176-15/D5373-16
Proximate analysis	–	Moisture and ash: Weight loss Volatile matter: by difference	ASTM D6980-17/D5630-13/D3175-20/E1131-20
XRD	ULTIMA IV, RIGAKU	CuK alpha radiation: average length λ = 0.15419 nm Theta/2-theta Bragg–Brentano geometry 2-theta data range: 5.00° to 125.00° Step size: 0.02° CuK alpha doublet: wavelengths of 0.154056 (65%)/ 0.154439 (35%) nm Radiation detector: LiF monochromator	Duque et al. (2020a, b)

The enthalpies of reactions can be calculated from the DSC data by integrating the areas of the curves (heat flux versus time interval) using scientific graphing and data analysis software (Wojdyr 2010). For that, an isothermal baseline is constructed based on the second derivative of the DSC signal; ergo, the onset and end temperatures of melting and pyrolysis were determined (Barrall 1973). Following this methodology and analyzing the DSC curves under pyrolysis conditions, Fig. 5, two endothermic peaks are observed for WRP pyrolysis. The first one is assigned to the melting point and confirmed by checking TGA under nitrogen, where no mass loss is identified in the temperature range of the first endothermic peak. The second peak is attributed to PE degradation reactions associated with the complete mass loss on TGA.

The DSC curves' integration resulted in the estimated value of enthalpy of melting around 65 and 205 J/g for the enthalpy of pyrolysis.

Regarding the DSC carried out under air reveals one endothermic peak—related to the one found under an inert atmosphere, and various exothermic peaks indicating that competing reactions are taking place. These reactions with some overlapping degrees can be attributed to the samples' key compounds, as will be indicated later in this chapter. By performing the DSC curve integration in the temperature range of reactions, the combustion enthalpy is about 3665 J/g.

Kinetics

The rate of non-isothermal solid decomposition, $d\alpha/dt$, registered by TGA, can be expressed in terms of the rate constant, $k(T)$, and the reaction model, $f(\alpha)$, Eq. (1). The rate constant represents the dependence of the process rate on temperature and is parametrized through the Arrhenius equation, Eq. (2). The reaction model represents the dependence on the fraction reacted, α, Eq. (3), which is determined experimentally as a fraction of the total mass loss during the process.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

$$k(T) = Aexp\left(-\frac{E}{\Re T}\right) \tag{2}$$

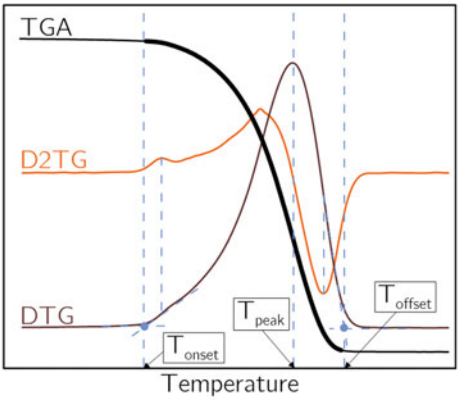


Fig. 3 The onset, offset, and peak temperatures from TGA and their derivatives curves

Fig. 4 TGA and DTG for WRP at four heating rates according to ICTAC recommendations

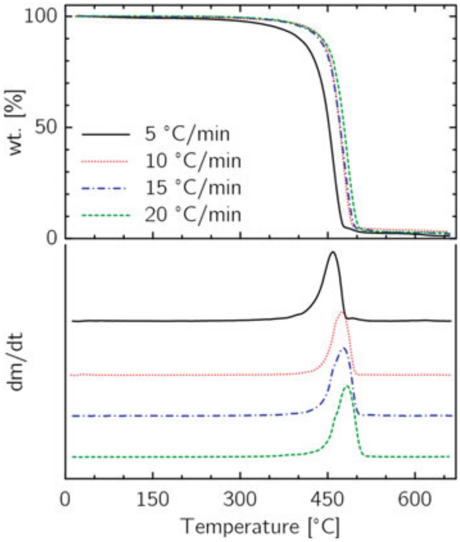
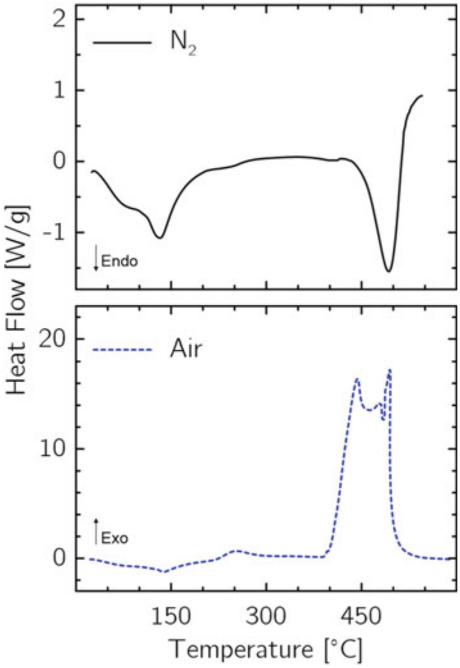


Fig. 5 DSC under N_2 and synthetic air at 20 °C/min



$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \tag{3}$$

A and E are kinetic parameters, the pre-exponential factor, and the apparent activation energy, respectively, $\Re$ is the universal gas constant, T T is the absolute temperature, and m_i, m_0, and m_f represent the instantaneous, initial, and final masses of the sample, respectively.

Combining Eqs. (1) and (2) leads to Eq. (4), that is limited to describe the rate of decomposition of a single-step process (Brown 2001; Vyazovkin et al. 2011). For constant heating rate non-isothermal conditions ($\beta = dT/dt$), Eq. (4) can be written in the form of Eq. (5).

$$\frac{d\alpha}{dt} = \mathrm{A}\exp\left(-\frac{E}{\Re T}\right) f(\alpha) \tag{4}$$

$$\beta\frac{d\alpha}{dT} = \mathrm{A}\exp\left(-\frac{E}{\Re T}\right) f(\alpha) \tag{5}$$

Isoconversional methods are an effective tool that can be used to solve Eqs. (4) or (5) and determine the kinetic parameters as a function of the fraction reacted, based on the assumption that the rate of decomposition, at a constant value of α, is only a function of the temperature (Brown 2001). Taking into account the methodology adopted, the isoconversional methods can be separated into two main categories: differential and integral.

A widely used differential isoconversional method, based on the logarithm of Eqs. (4) or (5), is the Friedman method (Friedman 2007), Eq. (6). By plotting $\ln(\beta d\alpha/dT)$ against $1/T$, the kinetic parameters can be calculated from the slope at each given α. It is essential to point out that, although the differential methods do not use an approximation, they are susceptible to experimental noises.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E}{\Re T} \tag{6}$$

On the other hand, the variables in Eq. (5) can be separated and on integration gives Eq. (7)

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} \exp\left(-\frac{E}{\Re T}\right) dT \tag{7}$$

where $g(\alpha)$ is the integral form of the reaction model. The integral in Eq. (7) does not have an analytical solution, and several approximations can be found in the literature (Brown 2001; Vyazovkin et al. 2011). Generally, the approximated solutions are represented by the general equation:

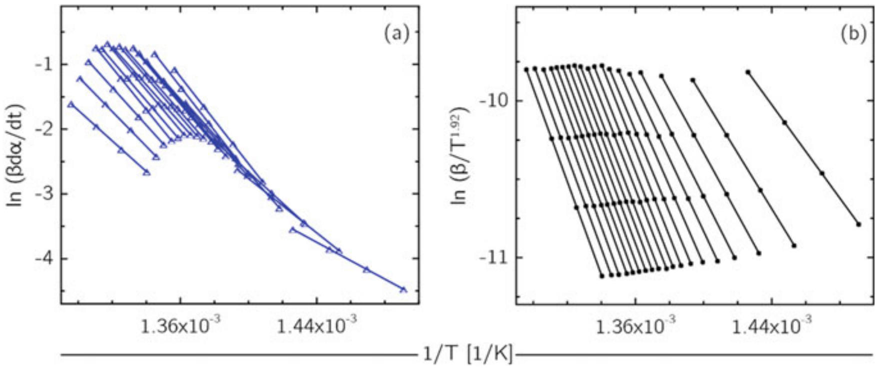


Fig. 6 Isoconversional plot of **a** Friedman and **b** Starink methods

$$\ln\left(\frac{\beta}{T^{B}}\right) = \text{const} - C\left(\frac{E}{\Re T}\right) \tag{8}$$

where B and C are the parameters determined by the type of approximation for temperature integral. Worth noting that the approximation used is directly related to the accuracy of the integral method.

To demonstrate an application of an integral method, the Starink, Eq. (9) (Starink 2003) is considered as follow:

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = \text{const} - 1.0008\left(\frac{E}{\Re T}\right) \tag{9}$$

The left-hand side plotted against $1/T$ for the TGA data, is used to calculate the activation energy from the slope of the straight lines fitted at each value of α. Figure 6 shows the corresponding lines obtained at different fraction reacted and different heating rates. It can be seen that two groups of straight lines are formed depending on the degree of fraction reacted and method: one with smaller slope and lower fraction reacted degree ($\alpha < 0.25$) and the other steeper lines and $0.25 < \alpha < 0.95$. A different tendency is observed when Friedman's isoconversional method is used.

For comparison, the values of the activation energy are determined in a wide range of α from 0.05 to 0.95 with a step of 0.05 and the dependence is reported in a plot E versus α, Fig. 7a. This dependence is a warning about multi-step kinetics existence in a given process (Friedman 2007). As can be seen from the curves presented in Fig. 7, from $\alpha = 0.05$ to 0.95, the activation energy varies significantly, the averaged $E = 185.5 \pm 61.6$ kJ/mol. In percentage terms, the difference between the maximum and minimum values of E is about 66.4%.

To assess the pre-exponential factor's values, the dependence of the decomposition process on the fraction reacted can be expressed using a wide variety of reaction models, each of which has a characteristic reaction profile (Brown 2001). The Criado

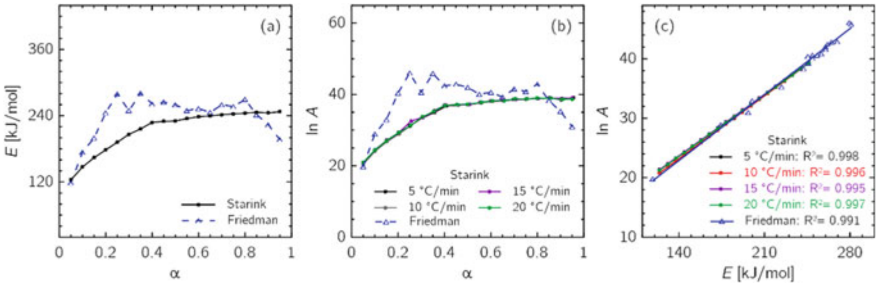


Fig. 7 **a** Distribution of activation energy, **b** distribution of pre-exponential factor, and **c** Estimated ln A versus E

Table 2 Algebraic expressions of theoretical solid-state reaction models

Model	Code	$f(\alpha)$	$g(\alpha)$
First-order	$F1$	$1-\alpha$	$-ln(1-\alpha)$
Second-order	$F2$	$(1-\alpha)^2$	$[1/(1-\alpha)]-1$
Third-order	$F3$	$(1-\alpha)^3$	$[1/(1-\alpha)^2]-1$
Avrami–Erofeev	A_n^*	$n(1-\alpha)[-ln(1-\alpha)]^{1-1/n}$	$[-ln(1-\alpha)]^{1/n}$
Contracting geometry	R_n^{**}	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$
Two-dimensional diffusion	$D2$	$[-ln(1-\alpha)]^{-1}$	$(1-\alpha)ln(1-\alpha)+\alpha$
Three-dimensional diffusion	$D3$	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Ginstling–Brounshtein	$D4$	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$

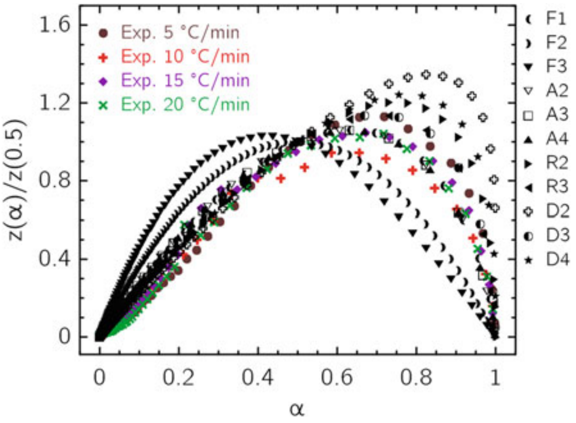
$^*n = 2, 3, 4.$ $^{**}n = 2, 3$

method (Criado 1978) is very recommended to determine the kinetic model able to describe the pyrolysis of each material investigated. The method is based on an approximate solution of the integral in Eq. (7) and leads to the construction of the so-called generalized master plot. The relationship between the experimental data recorded under non-isothermal conditions, the generalized reaction rate, and the differential and integral forms of the theoretical solid-state reaction models, Table 2 (Elder 1996), can be described by Eq. (10).

$$\left(\frac{T}{T_{0.5}}\right)^2 \frac{(d\alpha/dt)}{(d\alpha/dt)_{0.5}} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} \tag{10}$$

The equation above is normalized taking $\alpha = 0.5$ as a reference, being $T_{0.5}$ and $(d\alpha/dt)_{0.5}$, at the left-hand side, and $f(0.5)$ and $g(0.5)$, at the right-hand side, the temperature, the reaction rate, and the functions corresponding to 50% conversion. The generalized master plots are shown in Fig. 8. The most suitable kinetic model is determined by the best match between the plot of the generalized reaction rate vs.

Fig. 8 Masterplots of different reaction models



the fraction reacted and the theoretical models' plots. The Root Mean Square Error (RMSE), Eq. (11), is used to measure how much error there is between the curves, assisting identify the best correspondence.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}\left[\left({}^{d\alpha}/_{dt}\right)_{\text{exp}} - \left({}^{d\alpha}/_{dt}\right)_{\text{model}}\right]^2}{n}} \tag{11}$$

The master plots results suggest that Avrami could govern the thermal degradation of WRP–Erofeev models (A2, A3, and A4), as well as by a first-order model (F1), and by the contracting geometry (R3) and three-dimensional diffusion (D3) models. These model equivalences were already expected since, according to (Obeid et al. 2014), it is not possible to distinguish between the models R3 and D3, and it is also impossible to discern the differences between a first-order and Avrami–Erofeev models. It is noteworthy that, although some experimental curves at different heating rates result in a series of master plots, a single dependence on α can be observed, which is practically independent of β, see Fig. 8.

By recalling the Fig. 7b, the dependence of the pre-exponential factor on the conversion is shown. The dependence of ln A on α increases, following the same trend of $E(\alpha)$. For the values obtained from the Friedman (FR) and Starink (ST) methods, the pre-exponential factor's logarithmic form was plotted against E, Fig. 7c. A linear relationship is observed between them. The correlation coefficient, close to 1, indicates that for all heating rates, A's values are in accordance with the distributed activation energy along the conversion process. Table 3 summarizes the range of activation energies and pre-exponential factor for both methods.

These kinetic parameters obtained from the isoconversional methods are used to reconstruct the conversion profiles compared to the experimental data, Fig. 9. In these situations, a metric should be calculated to check each method's accuracy, e.g. R^2. Table 4 shows the data associated with the curves of Fig. 9a. Note that optimization

Table 3 Activation energy and pre-exponential factor for the pyrolysis of WRP

Heating rate	Starink (ST)		Friedman (FR)	
β [°C/min]	E [kJ/mol]	A [1/min]	E [kJ/mol]	A [1/min]
5	123.9–247.1	9.61×10^8–9.57×10^{16}	118.4–280.9	3.90×10^8–9.87×10^{19}
10		7.36×10^8–8.65×10^{16}		
15		1.14×10^8–9.23×10^{16}		
20		1.25×10^8–8.24×10^{16}		

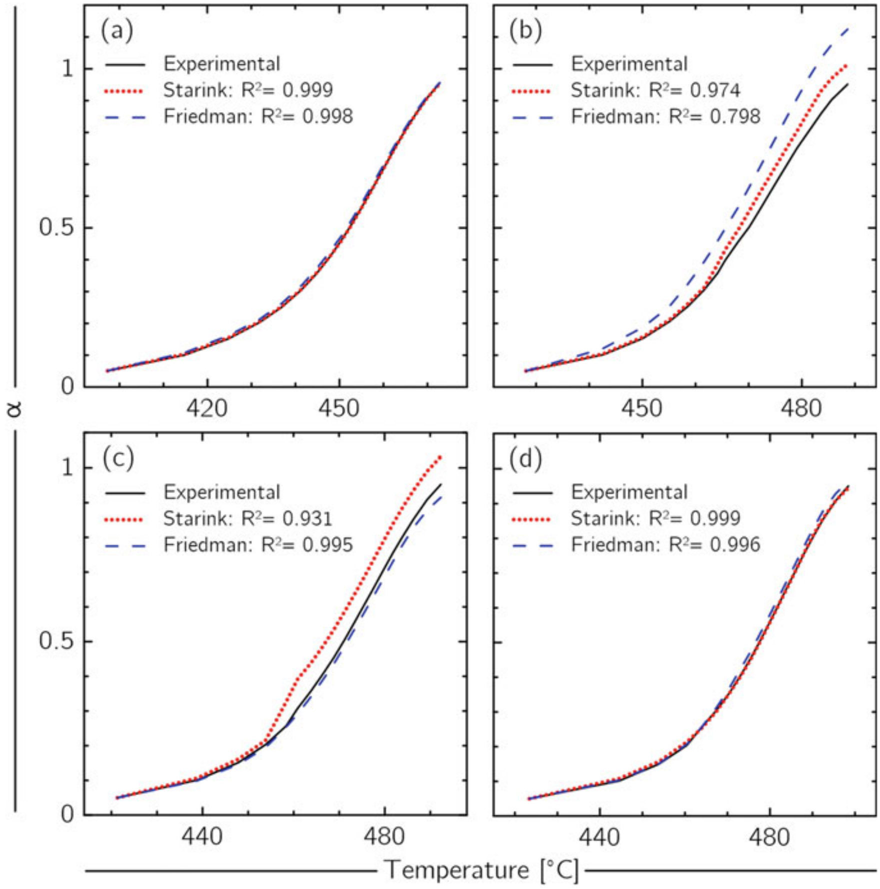


Fig. 9 Fitness of TGA fraction reacted from estimated kinetic parameters at **a** 5 °C/min, **b** 10 °C/min, **c** 15 °C/min, and **d** 20 °C/min

Table 4 Data associated with the fitness of TGA. The percentage deviations between the numerical and experimental values of α are represented by ≠%

Temp. (°C)	α_{Exp}	E [kJ/mol] (ST)	A [min^{-1}] (ST)	E [kJ/mol] (FR)	A [min^{-1}] (FR)	f(α)*	α_{Num} (ST)	α_{Num} (FR)	≠% (ST)	≠% (FR)
397.3	0.05	123.9	9.61×10^{8}	118.4	3.90×10^{8}	0.05	0.05	0.05	0.0	0.0
414.8	0.10	147.1	2.98×10^{10}	174.1	3.62×10^{12}	0.10	0.10	0.11	3.0	7.5
424.8	0.15	164.1	4.32×10^{11}	199.7	2.05×10^{14}	0.14	0.16	0.16	2.3	6.6
431.8	0.20	178.1	3.46×10^{12}	245.5	3.47×10^{17}	0.18	0.21	0.21	1.2	4.7
436.8	0.25	192.0	3.41×10^{13}	279.3	9.87×10^{19}	0.22	0.25	0.26	0.8	4.7
441.3	0.30	206.4	3.26×10^{14}	249.1	4.30×10^{17}	0.25	0.31	0.32	0.7	4.5
444.8	0.36	215.9	1.48×10^{15}	280.9	8.44×10^{19}	0.28	0.36	0.37	0.7	4.3
447.8	0.41	228.0	9.48×10^{15}	261.6	2.62×10^{18}	0.31	0.41	0.42	0.2	3.9
450.3	0.46	229.6	1.15×10^{16}	264.9	4.03×10^{18}	0.33	0.46	0.47	0.3	3.0
452.3	0.50	230.5	1.29×10^{16}	260.2	1.75×10^{18}	0.35	0.50	0.51	0.4	2.6
454.8	0.56	234.8	2.34×10^{16}	249.4	2.55×10^{17}	0.36	0.56	0.57	0.3	2.3
456.8	0.61	238.2	3.71×10^{16}	253.2	4.33×10^{17}	0.37	0.61	0.62	0.1	2.1
458.8	0.66	239.5	4.23×10^{16}	245.7	1.16×10^{17}	0.37	0.66	0.67	0.1	1.9
460.8	0.71	241.9	5.88×10^{16}	260.1	1.11×10^{18}	0.36	0.71	0.72	0.0	1.6
462.8	0.76	243.3	6.47×10^{16}	256.6	5.54×10^{17}	0.34	0.76	0.77	0.0	1.2
464.8	0.80	244.6	7.25×10^{16}	269.4	4.11×10^{18}	0.32	0.80	0.81	0.1	1.0
467.3	0.86	246.3	8.94×10^{16}	241.9	4.33×10^{16}	0.28	0.86	0.86	0.1	0.9
469.8	0.91	245.1	7.06×10^{16}	223.8	2.08×10^{15}	0.22	0.91	0.91	0.1	0.6
472.8	0.96	247.1	9.57×10^{16}	196.7	2.77×10^{13}	0.14	0.95	0.96	0.2	0.1

* Avrami–Erofeev, second order model, n = 2

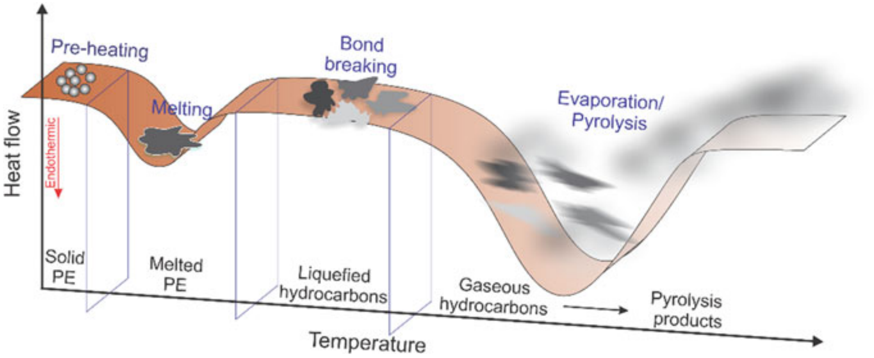


Fig. 10 Conceptual descriptive of recycled polyethylene degradation mechanism

techniques can improve the accuracy in estimation of the kinetics parameters such as in (Bazelatto Zanoni et al. 2012; Pan et al. 2021).

By considering the information brought by the thermal analysis using TG/DSC, plus the multi-step characteristic learned from kinetics, it is possible to graphically abstract the thermal degradation mechanism of polyethylenes, Fig. 10. From where we state that a pre-heating stage takes place and only increases in the sample temperature occur. After that, the melting stage happens in an endothermic process, leading the bond-breaking of the compounds linking the sample in an endothermic process. This stage results in a multi-compound liquid mixture (see Figs. 10 and 13 in Sect. 3.2.3 about X-ray analysis). From this stage onwards, the liquid phase can simultaneously pyrolyze and evaporates, and the pyrolysis in the gas phase can also occur, making the pyrolysis products (Duque et al. 2020a, b). This latter may include oil, wax, and gas, and their yields have been investigated in various works (Qureshi et al. 2020; Ryu et al. 2020; Singh et al. 2020).

3.2.2 Case 2: From TGA to Proximate Analysis

This section focuses on determining the proximate composition of the recycled polyethylene delineating the procedure using TGA data under N_2 and synthetic air atmospheres.

Figure 11 displays TGA/DTG curves for WVP under both N_2 and synthetic air atmospheres. From where we can infer the amount of moisture, ash, and volatile matter. In the temperature range of 50–150 °C, the mass loss associated with water evaporation can be recovered by accessing TGA data. Note that plastics used to be non-hygroscopic polymers means that ~0.2 wt.% of water content determined in the examples given in this section, carry lots of uncertainty. On the other hand, by analyzing TGA under air from higher than 600 ºC, ash content is quickly established, about 0.2 wt.%. If we could consider that, by following the same reasoning under the N_2 atmosphere, the final amount of mass resulted, around 0.2 wt.%, accounted for ash

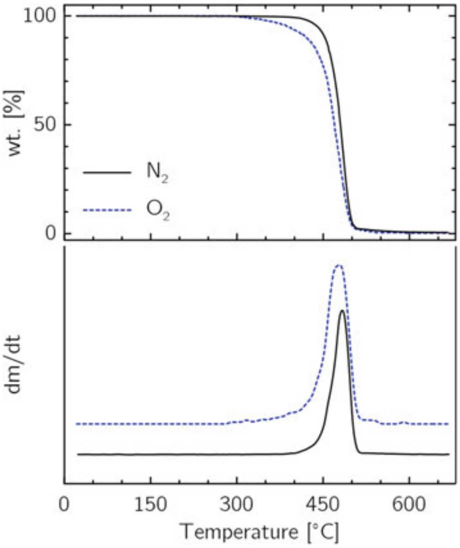


Fig. 11 Thermogravimetric analysis of WVP under inert and oxidative atmosphere and its derivatives. Heating rate of 20 °C/min

plus any unconverted matter. At least for virgin (Duque et al. 2020a, b) and recycled polyethylene samples, Figs. 4 and 11, under N_2 beyond 520 °C, no significative mass loss is observed (flat line on DTG), meaning that polyethylene is almost completed composed of volatile matter, ~99.6 wt.%. These values are equivalents to the ones obtained by standard proximate analysis, see Table 5. In this table, the ultimate and proximate analysis for WVP, WRP, and MB are summarized for comparison purposes.

It is noteworthy that the ASTM 1131-20 (ASTM 2020b) is more appropriate to establish the proximate composition by TGA because the mass loss is monitored (mass loss plateau—a region of a thermogravimetric curve with a relatively constant mass) over a specific temperature ranges and in a specific atmosphere providing the substance compositional analysis.

Table 5 Ultimate and proximate analyses, values in wt.%

Component	WVP	WRP	MB
C	85.4 ± 0.1	84.3 ± 0.1	57.2 ± 0.1
H	14.3 ± 0.3	13.7 ± 0.3	9.8 ± 0.3
N	0	0	0
S	0	0	0
Other elements*	0.3 ± 0.3	2.0 ± 0.3	33.0 ± 0.3
Moisture	0.2	0.2	1.6
Ash	0.4	1.0	0.1
Volatile matter*	99.4	98.8	98.3

*Obtained by difference/Proximate analysis (mean ± 0.1)

3.2.3 Case 3: Assessing a Biodegradable Polymer

The recycled materials in their life cycle finish having many pigments (from organic or inorganic masterbatches) to regain the material properties necessary to reinsert plastics as products in the market. However, in thermal degradation terms, the substance from these masterbatches can carry unwanted components providing a means for catalysis in an obscure way (see the increase in ash amount for WRP in Table 5). For these reasons, an isolated TGA must be regarded with caution, and other techniques must be applied to base the whole analysis. The case where is suitable coupling TGA/DSC assisted by another technique such as XRD analysis to determine the proximate compositions and provide degradation conjectures of recycled materials degradation.

Regarding the masterbatch thermal degradation carried out under an inert atmosphere at 10 °C/min, it is clear that degradation occurs in a more complex way, Fig. 12. As the masterbatch being analyzed is a starch-based mixture (Fig. 2), it is expected that the TGA behaves like biomasses. That is, the mass is lost in multiple steps, although the sample is entirely consumed. This thermal behavior is quite different compared to WVP or WRP; this latter contains more contaminants in the sample composition.

Figure 13 shows the X-ray diffractograms for all samples. The compounds quantification was performed based on the volumetric proposition of the structures found in a sample volume of 1 mm × 10 mm × 0.005 mm, in which the uncertainty volume value proposed for each phase found is limited to 2% taken into account the experimental conditions summarized in Table 1.

The average crystallinity was 54, 51, and 46% for WRP, WVP, and MB. Without considering the amorphous phase, the analysis indicated the chemical compounds of the crystalline phase of recycled samples and the masterbatch. For WRP the matched compounds were 78 vol.% of n-tetracontane ($C_{40}H_{82}$), 16 vol.% of n-nonacosane ($C_{29}H_{60}$), and about 6 vol.% of n-Tricosane ($C_{23}H_{48}$). 2 vol.% of n-Heptadecane ($C_{17}H_{36}$) matched better than n-Tricosane in WVP, which increased the fraction of $C_{40}H_{82}$ to 82 vol.% and slightly decreased the fraction of $C_{29}H_{60}$ to 16 vol.%. The matched compounds for MB were around 6 vol.% of Paraffin wax (C-H), 38 vol.%

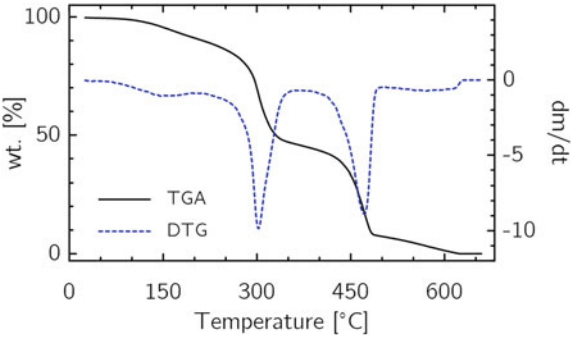
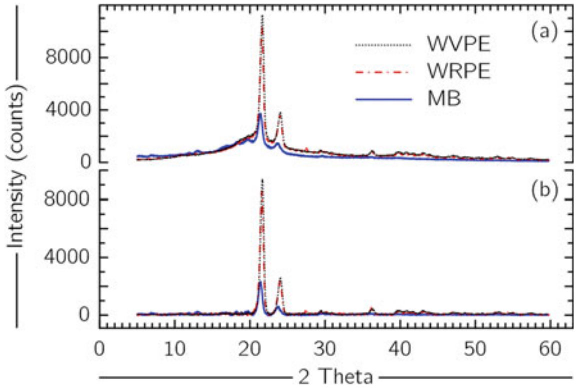


Fig. 12 Thermogravimetric analysis of MB under inert atmosphere and its derivative. Heating rate of 10 °C/min

Fig. 13 X-ray powder diffraction patterns. **a** with amorphous phase, **b** without amorphous phase. The diffraction patterns were taken using CuK radiation (0.15419 nm)



of Heptadecylcyclohexane ($C_{23}H_{46}$), 5 vol.% of n-Nonacosane ($C_{29}H_{60}$), and about 51 vol.% of Pentatriacontane ($C_{35}H_{72}$).

4 Conclusion and Future Perspective

Thermal analyses are a powerful combo of techniques that can be used to characterize recycled plastics. Among these techniques, thermogravimetry and differential scanning calorimetry are the most used due to the simplicity of operations and the direct access of the investigated matter's thermochemical behaviors. In this chapter, three case studies were proposed to demonstrate some possible applications of thermal analysis. By analyzing the pyrolysis of waste of recycled polyethylene, and through methodological procedures, the materials' thermal behavior were delineated, enthalpy of phase change and reactions were estimated, and chemical kinetics were performed via isoconversional methods to determine the Arrhenius parameters. As an auxiliary technique, X-ray powder diffraction was carried out to evaluate a biodegradable masterbatch and then was established, in terms of chemical structures, a comparison with the recycled materials.

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Mechanical Properties of Recycled Plastics

Noor Afizah Rosli and Ishak Ahmad

Abstract Recycled plastics mainly obtained from two primary methods i.e., mechanical and chemical processes. Between these two methods, the mechanical method that goes through physical processes is commonly used instead of the chemical method. Physical processes usually involve heat, mechanical stress, and oxidation, resulting in plastic degradation. The degradation of plastic will affect the molecular structure of the plastic and thus result in the change of plastic properties, especially in mechanical properties. It is interesting to look over every mechanical property change that takes place on recycled plastic. The change involves negative changes, but there are also positive changes in which the mechanical properties improve with recycling. The difference in the mechanical properties of virgin plastic and recycled plastic depends on the recycling cycle frequency. Most of the first recycling cycle plastics do not show significant feature changes compared to virgin plastics. Meanwhile, plastics that undergo several reprocessing show substantial changes in the mechanical properties. Therefore, the more recycling process cycles, the more noticeable difference in mechanical properties displayed by recycled plastics compared to virgin plastics. This chapter explores the various mechanical properties of recycled plastic in detail.

Keywords Compressive · Flexural · Impact · Stiffness · Tensile · Toughness

1 Introduction

The dependence on plastics since the 1990s has expanded the plastics industry regardless of synthetic plastics or bioplastics. Compared to its first use in 1950, which recorded an annual production of 1.5 million metric tonnes, it continued to increase

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to 359 million metric tonnes in 2018. The production is expected to grow from year to year based on the exponential increase shown from 1950 to 2018. The exponential growth is due to the rise in the use of petroleum-based plastics and is now coupled with plastics from renewable sources such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS). Polyethylene (PE) of various densities is the most significant contributor to the production of petroleum-based plastics. It is used in multiple fields, especially in packaging, due to its low price, ease of the process, and excellent mechanical properties. Meanwhile, the plastic market from renewable sources is dominated by PLA due to its good mechanical properties, comparable to non-renewable plastics. The foremost dependence on plastic materials in life is generally influenced by the light-weight, durable, versatile plastic properties and can be used in various applications. From toothbrushes and protective clothing to significant aviation components and building applications, plastic has become essential in daily life.

The impact of high plastic production each year over the past 70 years has resulted in nearly 8.3 billion metric tonnes of disposable plastic that ends up as trash. Most petroleum-based plastics cannot degrade naturally and take hundreds to thousands of years to decompose. Also, renewable plastic such as PLA added to plastic waste increments because it usually takes more than two years to start degrading (Rosli et al. 2018; Karamanlioglu et al. 2017). Therefore, the increasing use of PLA in 3D printing and packaging to replace petroleum-based plastics is also a significant contributor to this waste problem (Anderson 2017). Recently, plastic waste production experienced a sharp increase in 2020 due to single-use plastics due to Covid-19 (Klemeš et al. 2020).

The increase in uncontrolled plastic waste problem reflects what is happening in the world today. Besides, concern over this problem has also increased and led to several approaches that have been introduced. Such processes are (i) combustion, (ii) burial, and (iii) recycling. Burning is an effective method compared to landfill, but it causes air pollution. Of these three approaches, recycling is the most effective option to overcome the problem without causing other adverse effects on the environment. Recycling is seen as the right choice in recovering the value of the discarded thermoplastics. Through recycling, these discarded thermoplastics can be converted to other more valuable products than their virgin plastic.

There are several different recycling techniques such as mechanical recycling, chemical recycling, and energy recovery (Ahmad et al. 2008; Jubinville et al. 2020). Mechanical recycling involves the collection of plastic waste, which is then reprocessed. The chemical recycling technique consists of converting polymers into monomer units by changing the chemical structure of the polymer. Finally, the controlled combustion of plastic to liquid fuel is known as the energy recovery process (Jubinville et al. 2020). Among all these, mechanical recycling is widely practiced around the world. This technique is the primary or in-house technique used in recycling, where the plastic will be ground first before being physically reprocessed (Goodship 2007). Mechanical recycling is also known as thermo-mechanical recycling because it involves the use of heat. Typically, plastic waste will be collected and reprocessed into products with similar or comparable to virgin plastic properties. Plastic waste can be recycled as much as possible through this technique.

Thermo-mechanical recycling involves several sequences of processes: collection, separation, isolation, washing, grinding, compounding, pelletizing, and molding. The plastic waste collected will be separated based on colour, size, chemical composition, and density. After that, it will be compounded using an extruder and then will be pelletized. The pellet recyclates will then go through the molding process using injection molding or compression molding to form the desired product. Mechanical recycling has several advantages, and most importantly, it can recycle most of the thermoplastic known to humankind. Furthermore, this process does not alter the chemical structure of recycled materials because it involves the operation of isolation and reducing the size of plastic waste. Using this recycling process, the plastics waste can retain its structure and molecular weight due to low heat consumption compared with chemical, enzymatic and thermal techniques (Niaounakis 2013). Mechanical recycling can reduce the use of non-renewable resources as it is required in the synthesis of monomer units for thermoplastic. Finally, it is crucial due to its less energy consumption than the production of new plastic products (Niaounakis 2013).

Despite all these advantages, the mechanical recycling technique has a significant limitation. There is a high potential for contamination, and the separation process is costly and requires advanced equipment (Oblak et al. 2015). Additionally, the numbers of plastic recycling cycle will affect the processability and quality of the recycled plastic. The mechanical properties of recycled plastic will mainly be affected because the mechanical recycling process involves heat and some physical processes. Degradation from heat, mechanical stress, and oxidation during reprocessing are among the leading causes of mechanical properties differences between virgin plastics and recycled plastics. Mechanical properties such as tensile, impact, and flexural are among the properties that are often evaluated to study the relationship between degradation undergone by recycled plastics with variations of mechanical properties. Typically, degradation will cause the deterioration of the polymer molecular structure, which leads to a decrease in the mechanical properties of the recycled product (Hamad et al. 2011). The degradation of polymer that occurs during the recycling process can give a misleading idea about the mechanical properties of the recycled plastics. The effects of degradation on the mechanical properties are unidirectional; the toughness may decrease, but the stiffness increases, or vice versa (Vilaplana and Karlsson 2008). For example, the toughness of acrylonitrile–butadiene–styrene (ABS) plastics decreases while the stiffness properties increase with recycling (Rahimi et al. 2014). Therefore, this chapter will delve deeper into each of the mechanical properties of recycled plastic so that it can be adapted in various applications within a specific quality range of mechanical properties.

2 Recycled PE

PE produced from ethylene gas is the most widely used thermoplastic today. It consists of various types of homopolymer and copolymer in which low-density PE (LDPE) and high-density PE (HDPE) are among the most widely used. The ability to produce various PE variations allows manufacturers to customize them in specific applications such as packaging, automotive, plumbing, and electrical. Globally, packaging applications based on PE plastic have contributed to 500 to 1 trillion plastic bags waste (Wagner 2016; Baffour-Awuah et al. 2020). Reprocessing of PE waste often gives the impression that recycled PE will exhibit lower mechanical strength than virgin PE. This is because the reprocessing of plastic will usually be followed by degradation, which causes the scission of molecular chains. Compared to other thermoplastics, recycling of polyolefin such as PE is also accompanied by crystallization (Yin et al. 2015). Thermal degradation during the recycling process is unavoidable. Still, the recycling process that accompanies the crystallization process can be fully utilized as some of the good mechanical properties of virgin plastics can be maintained or improved. Table 1 shows the effects of recycling on the mechanical properties of LDPE and HDPE.

Recycled LDPE showed low tensile strength and elongation at break compared to virgin LDPE. Meanwhile, the stiffness properties of recycled LDPE increase after the recycling process. Mechanically recycled plastics will commonly undergo chain degradation due to high temperature and shear effects. Then chain scission due to thermal degradation contributes to a decrease in the mechanical properties of the recycled LDPE. However, it is believed that LDPE can undergo more than 100 rounds of the recycling process. Jin et al. (2012) stated that during the reprocessing of PE, two competing mechanisms occur, namely chain scission and cross-linking. As for LDPE, the chain scission occurs in the first recycling process, while the subsequent

Table 1 Mechanical property of recycled LDPE

Types of PE	Mechanical property	Before recycling	After recycling	References
LDPE	Tensile strength (MPa)	16	12	Pedroso and Rosa (2005)
	Young’s modulus (GPa)	191	221.25	
	Elongation at break (%)	393.4	285.8	
HDPE	Tensile strength (MPa)	33.7	34.2	Pattanakul et al. (1991)
	Modulus (MPa)	596	640	
	Elongation %	69.7	36.9	
	Impact strength (ft.lb/in)	2.522	2.201	

recycling process results in cross-linking between chains. Therefore, the reduction of the first-time recycled LDPE mechanical properties is due to the chain scission, which dominates the cross-linking mechanism. The mechanical properties of recycled LDPE with up to 40 times reprocessing can be maintained due to the simultaneous occurrence of two competing structural rearrangements (Yin et al. 2015).

The tensile properties of recycled HDPE also show the same trend as the recycled LDPE, as shown in Table 1. The exact degradation mechanism also occurs in recycled HDPE. The chain scission and cross-linking mechanisms compete in determining the mechanical properties of recycled HDPE. The cross-linking mechanism dominates the chain scission mechanism at the beginning of the reprocessing of HDPE (up to 10 rounds of recycling). This is evidenced through the instant modulus and hardness properties of recycled HDPE, as shown in Figs. 1 and 2, respectively.

Thermal degradation during the mechanical recycling of plastics will usually result in the low molecular weight of recycled plastic due to chain scission. Unlike other thermoplastic, recycled HDPE exhibits a molecular weight equivalent to virgin HDPE due to the cross-linking mechanism during reprocessing. The molecular weight of recycled HDPE (up to 10 cycles) is equivalent to virgin HDPE (Oblak et al. 2015). This produces recycled HDPE with instant modulus and hardness properties equivalent to virgin HDPE plastic.

In addition to the molecular weight, the degree of crystallization also affects the mechanical properties of recycled HDPE. No changes in the crystallinity of recycled HDPE after undergo 10th recycling cycles. Recycled HDPE experienced a decrease in modulus in the 20th round of recycling due to a low degree of crystallization (Oblak et al. 2015). The low degree of crystallization facilitates the chains' movement, thus

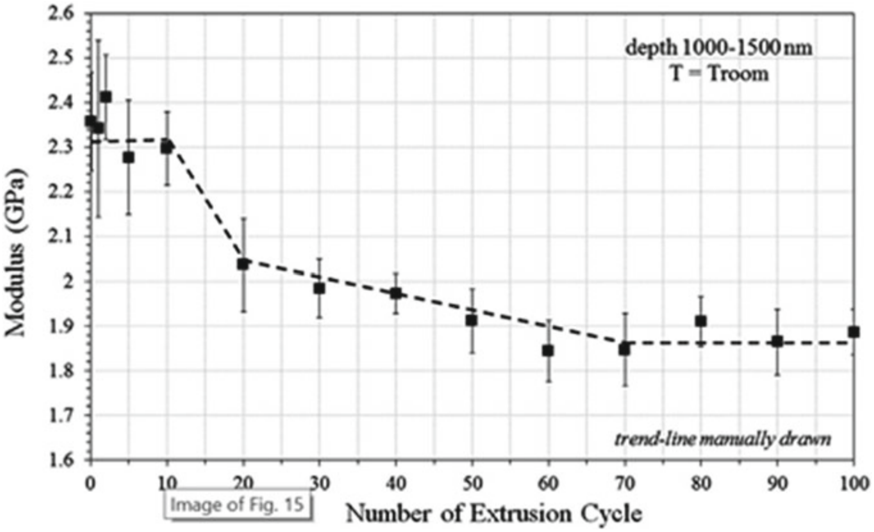

Fig. 1 Instant modulus of recycled HDPE (Oblak et al. 2015)

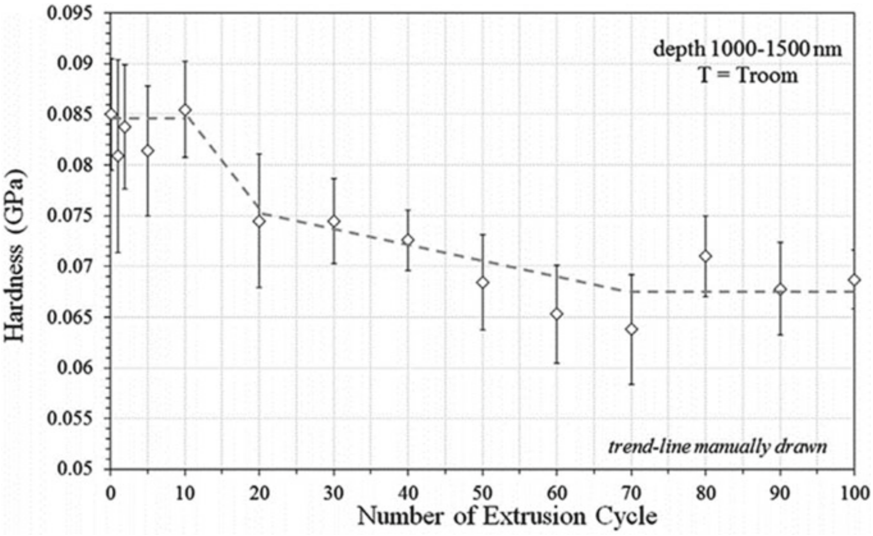

Fig. 2 Hardness properties of recycled HDPE (Oblak et al. 2015)

reducing the stiffness nature of the recycled HDPE. Overall, the mechanical properties of recycled HDPE are highly dependent on thermal degradation, competition between chain scission and cross-linking, molecular weight, and degree of crystallization. Combining these several factors results in a variety of recycled HDPE mechanical properties in each recycling cycle.

3 Recycled Polypropylene

Polypropylene (PP) is the second most widely used thermoplastic after PE. It is widely used in daily necessities such as buckets, bottles, trays, etc. Its advantages, such as color-free material, low-cost, good mechanical properties, and flexibility for molding, cause its production demand to increase by almost 19% compared to other thermoplastics (Maddah 2016). PP plastic can be mechanically recycled to reduce its production, thus meeting its demand in various fields. The mechanical properties of mechanically recycled PP plastic are shown in Table 2.

It is interesting to note that the tensile strength and modulus of recycled PP plastics are higher than that of virgin plastics. Like other thermoplastic, mechanical recycling also causes thermal degradation in PP plastics, where the molecular weight is reduced with the recycling process. However, the thermal degradation that occurs in PP plastics also contributes to the positive effect of increasing the crystallinity index of recycled PP plastics (Greco and Coppola 1986; Aurrekoetxea et al. 2001b). This increase in the crystallinity index answers the difference in tensile properties

Table 2 Mechanical property of recycled PP

Mechanical property	Before recycling	After recycling	References
Tensile strength (MPa)	34.7 ± 0.22	36.3 ± 0.17	Aurrekoetxea et al. (2001a)
	–	~34.7 1 × Re ~35.2 3 × Re ~36.1 5 × Re	Aurrekoetxea et al. (2001b)
Tensile modulus (MPa)	1704 ± 39	1993 ± 49	Aurrekoetxea et al. (2001a)
	–	~1708 1 × Re ~1804 3 × Re ~1948 5 × Re	Aurrekoetxea et al. (2001b)
Elongation at break (%)	66.37 ± 5.38	51.55 ± 2.2	Aurrekoetxea et al. (2001a)

shown by recycled PP plastics compared to virgin PP plastics. The stiffness feature of PP plastic is driven by high crystallinity index, which hindered the rotation of the polymer molecular chain. The orderly structure of the crystalline region than the amorphous region limits the movement between the crystalline chains, thereby, causes the recycled plastic to exhibit high rigidity properties. The increased stiffness properties contribute to the increase in tensile strength and modulus of recycled PP plastic. Previously, Aurrekoetxea et al. (2001b) reported that the crystallinity index of PP plastic increases with the number of recycling cycles. Therefore, recycled PP plastics with five times reprocessing exhibited higher tensile strength and modulus values compared to PP plastics undergoing one recycling process.

The ability for recycled PP plastic chain molecules to rotate also reflects the flexibility properties of the recycled plastic. The flexibility of the recycled PP plastic decreases due to reduced chain movement. Thus, recycled PP plastic exhibits a low elongation at break and impact strength values than virgin PP plastic. In addition to the high crystallization index, the low molecular weight also affects the elongation of recycled PP plastics. The decrease in molecular weight leads to an increase in the ends chain in the recycled PP plastic. The shorter and high numbers of ends chain result in a reduction of the chain fully integrated into the crystal area, a reduction in the entwining of molecules, and a reduction in C–C binding for stretching. These three factors contribute to the decrease in the toughness of recycled PP plastics.

4 Recycled Poly(Ethylene Terephthalate)

Poly(ethylene terephthalate) (PET) is one of the most commonly used thermoplastics that accounts for almost 18% of total polymer production worldwide (Sulyman et al. 2016). Its good mechanical properties and high clarity make it widely used in packaging applications, especially as bottles for various water types (Welle 2011). The production of multiple kinds of water causes the production of PET bottles to be out of control, thus increasing the waste from PET bottles. Mechanical recycling

Table 3 Mechanical property of recycled PET (Frounchi 1999)

Mechanical property	Before recycling	After recycling	Reference
Tensile strength (MPa)	61.37	60.54 1 × Re 59.28 2 × Re 56.42 3 × Re	Frounchi (1999)
Impact strength (J/m)	24.27	21.97 1 × Re 21.81 2 × Re 21.11 3 × Re	

is the most promising technique to deal with vast amounts of PET bottle waste. The mechanical properties of mechanical recycled PET are shown in Table 3.

Mechanical recycling of PET plastic causes a reduction in molecular weight and chain length (Frounchi 1999). Unlike other thermoplastics, the decrease in the tensile properties of PET plastic is continuous with the number of recycling cycles. The degradation of PET chains due to the recycling process is more pronounced compared to other thermoplastics. The chain degradation is measured by the number of end-groups of carboxyl and ethylene in the PET plastic. The more the end-group number, the more chain breakage is recorded. The presence of this end-group increased with the increase in the number of recycling cycles. This indicates that the PET molecular chain undergoes thermal degradation at each recycling process, resulting in a decrease of tensile strength and modulus. The reduction in the molecular chain length of the recycled PET plastic also causes a reduction in molecular weight. Therefore, the decrease in the tensile properties of recycled PET is expected due to the loss of molecular weight (Yuan et al. 2019).

Recycled PET plastic also exhibits low impact strength than virgin PET plastic (Torres et al. 2000). Like tensile strength, the decrease in impact strength with the number of recycling rounds is due to the loss of the molecular weight of PET plastic. At low molecular weight, polymers lose the ability to be effectively entangled due to short polymer chains (Frounchi 1999; Liu et al. 2019). This, in turn, reduced the ductility of the recycled PET plastic, which leads to a decrease in impact strength.

5 Recycled ABS

ABS is commonly used in the electrical, electronics sectors and manufacturing computers and televisions housing. Housing for computers and televisions is one of the contributors to the rapid growth of landfills due to their large sizes. Therefore, ABS plastics are usually mechanically recycled by extrusion or injection molding (Rahimi et al. 2014; Bai et al. 2007; Kim and Kang 1995). The mechanical properties of recycled ABS plastic are shown in Table 4.

The tensile properties of recycled ABS plastic using injection molding are influenced by the processing temperature and recycling process cycle (Bai et al. 2007). The melting temperature (T_m) of ABS is around 200 °C (Li and Shimizu 2009).

Table 4 Tensile properties of recycled ABS

Mechanical property	Before recycling	After recycling	References
Tensile strength (MPa)	~33.3	~35.3	Bai et al. (2007)
	–	~40.9 1 × Re ~41.1 3 × Re ~42.2 5 × Re	Rahimi et al. (2014)
Tensile modulus (MPa)	~1350	~1370	Bai et al. (2007)
	–	~948 1 × Re ~952 3 × Re ~972 5 × Re	Rahimi et al. (2014)
Flexural strength (MPa)	–	~66.4 1 × Re ~66.4 2 × Re ~71.9 3 × Re	Rahimi et al. (2014)
Impact strength (kJ/m^2)	~9.6	~5.4	Bai et al. (2007)
Impact strength (J/m)	–	~9.7 1 × Re ~7.7 3 × Re ~7.2 5 × Re	Rahimi et al. (2014)

The tensile strength and modulus properties of ABS plastic recycled at temperatures above T_m (270 °C) are higher than that of ABS virgin plastic. The tensile strength and modulus properties of recycled ABS plastic do not significantly change at processing temperatures around T_m (190 and 230 °C) (Bai et al. 2007).

The loss of small molecules such as lubricants in ABS plastics at high temperatures leads to increased stiffness and strength properties (Carraher and Seymour 2012). Besides, high processing temperatures lead to the breaking of cross-linking chains in the rubber phase, thus contributing to the increased tensile properties in recycled ABS plastics (Bai et al. 2007). The loss of the small molecule and the degradation of cross-link within the rubber phase in ABS plastic increase with recycling processes. Therefore, ABS plastic with five and four-cycles of recycling process exhibits higher tensile strength than virgin ABS plastic (Rahimi et al. 2014; Bai et al. 2007). Meanwhile, the recycled ABS plastic exhibit less noticeable improvement in tensile modulus compared with virgin ABS plastic. It is interesting to note that the five cycles of recycled ABS resins exhibit no tensile properties changes than recycled ABS plastics (Kim and Kang 1995). From the two various observations, it can be concluded that the loss of small molecules such as lubricants plays a vital role in determining the tensile properties of recycled ABS plastic compared rubber phase degradation factor.

Like tensile strength, the flexural strength of recycled ABS plastics also increases with the recycling cycle numbers (Rahimi et al. 2014; Kim and Kang 1995). As the number of recycling cycles increases, so does the cross-link degradation within the BR phase. Thus, ABS recycled plastics exhibit higher flexural strength properties compared to ABS virgin plastics.

The impact strength of recycled ABS plastic depends on the reprocessing temperature, rotor rotation speed, and the number of recycling cycles. Recycling of ABS, above its T_m (200 °C), caused a reduction of entanglement stabilized by butadiene rubber (BR) particles (Kalfoglou and Chaffey 1979), degradation of BR phase (Bai et al. 2007), and scission of grafted chain between styrene-acrylonitrile (SAN) and BR (Adeniyi 1984). All of the above phenomena cause recycled ABS plastics to exhibit low impact strength values compared to virgin ABS plastics (Bai et al. 2007; Kim and Kang 1995). Therefore, the higher the ABS plastic recycling temperature, the lower the impact strength recorded. The degradation of the BR phase causes the deterioration of toughness properties of recycled ABS plastic, thus lowering the impact strength. The increase of the SAN phase due to the degradation of BR caused a rise in the stiffness properties of the recycled ABS plastic.

In addition to the reprocessing temperature, the impact properties of the recycled ABS plastic was also affected by rotational speed during reprocessing. Recycled ABS plastic shows slightly lower impact properties than virgin ABS (Bai et al. 2007). At high rotational speeds, oxygen becomes more diffusible into the polymer system, which leads to oxidative degradation in the BR phase. However, oxidative degradation does not significantly alter the molecular weight distribution. Hence, the impact properties of recycled ABS plastic do not considerably affect by high rotational speed (Kim and Kang 1995).

Compared to tensile and flexural properties, the impact properties of recycled ABS plastic are more sensitive to the number of cycles of recycling. The more recycling processes, the lower the impact strength values of the recycled ABS plastics compared to virgin ABS plastics (Bai et al. 2007; Kim and Kang 1995). The impact strength of recycled ABS plastic depends on the BR content in ABS plastic. The higher the BR content in ABS plastic, the lower the impact strength recorded by ABS plastic after recycling (Kim and Kang 1995). During recycling, the occurrence of degradation of the BR phase caused a reduction in the impact strength of recycled ABS plastics. Furthermore, recycled ABS plastic suffered low impact strength due to a decrease in BR components after recycling (Kim and Kang 1995).

The change in the stiffness of a polymer can be observed through the glass transition temperature (T_g) alteration of the polymer. Recycling of ABS plastics at high temperatures (270 °C) above its T_m (200 °C) causes an increase in the hardness and stiffness properties of the plastics due to the occurrence of cross-linking reactions in the BR phase (Bai et al. 2007). Thus, the T_g of BR around −110 and −60 °C (Eguiazabal and Nazabal 1990) increase with increasing recycling temperatures. The T_g of BR does increase with increasing processing temperature and the number of recycling cycles. The tan peak representing the BR phase decreases and widens in line with the recycling process (Bai et al. 2007). The thermo-oxidative degradation at each reprocessing cycle in the BR phase causes a change in this tan.

6 Other Recycled Synthetic Thermoplastics

Polycarbonate (PC) is the most commonly used amorphous polymer, especially in engineering applications. Its widespread use in various engineering applications is due to its light-weight properties, impact resistance, high transparency, and heat resistance. It is used in various engineering applications such as electronic components, public construction, automotive, protection components, aeronautics, and aerospace (Zhang and Xu 2019). This, in turn, increases the waste disposal of PC-based plastics. PC is a thermoplastic that can be processed using extrusion and injection molding methods. Therefore, PC can be recycled through mechanical methods. The mechanical properties of mechanically recycled PC are shown in Table 5 and Fig. 3.

Mechanical recycling of thermoplastic will be followed by degradation of the polymer chains. The same goes for recycled PC, where thermal degradation occurs, resulting in a decrease in mechanical properties. The mechanical properties of a recycled PC depend on the selection of the recycling method. The reduction in tensile strength and impact is not significant in PCs recycled through the injection molding process, as shown in Fig. 3. The mechanical properties undergo a drastic

Table 5 Mechanical property of recycled PC

Mechanical property	Before recycling	After recycling	Reference
Tensile strength (Nm/m^2)	–	61.7 ± 0.5 1 × Re 59.6 ± 0.4 3 × Re 62.6 ± 0.4 5 × Re 52.9 ± 8.9 7 × Re 43.7 ± 3.6 9 × Re	Pérez et al. (2010)
Modulus of elascity (Nm/m^2)	–	2614 ± 75 1 × Re 2538 ± 48 3 × Re 2706 ± 68 5 × Re 2671 ± 82 7 × Re 2481 ± 50 9 × Re	
Impact strength (kJ/m^2)	–	13.5 ± 0.8 1 × Re 10.0 ± 1.6 2 × Re 4.5 ± 1.2 3 × Re 2.1 ± 1.4 4 × Re	

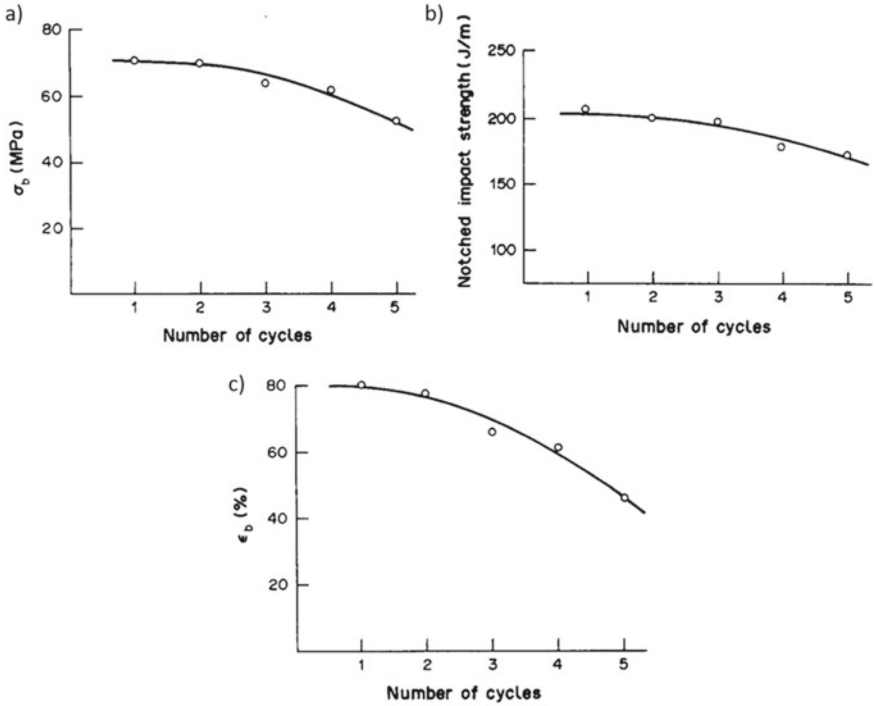

Fig. 3 **a** Tensile stress at break, **b** impact strength, and **c** elongation at break of recycled PC (Eguiazabal and Nazabal 1989)

decline when PC is processed through extrusion and injection molding, as shown in Table 5. Like other thermoplastics, the molecular chain of PC is accompanied by the attractive intermolecular forces sensitive to high temperatures (Ward and Sweeney 2012). Therefore, the mechanical properties of recycled PCs are highly dependent on the method and temperature of processing. Combining the two recycling methods, thus weakens the forces between the molecules and produces a recycled PC with low mechanical properties.

Poly(vinyl chloride) is one of the significant contributors to thermoplastic production. PVC is one of the plastics industry leaders due to its ability to be combined with various additives, low cost, good physical and chemical properties, good weathering properties, and it can be processed using various techniques. PVC is used in a wide range of applications, including heavy and light industries and home appliances such as in manufacturing for pipes, cable insulation, roofing sheets, foil packaging, and medical products (Braun 2002). The use of PVC in various industries thus increasing PVC-based waste. Like other thermoplastics, PVC can also be reused through recycling methods. Mechanical PVC recycling produces recycled PVC with mechanical properties, as shown in Table 6.

Table 6 Mechanical property of recycled PVC

Mechanical property	Before recycling	After recycling	Reference
Tensile stress at break (MPa)	~38	~34	Wenguang and Mantia (1996)
Tensile Modulus (GPa)	1.86	1.59	
Elongation at break (%)	~54	~94	
Impact strength (kJ/m^2)	78.5	163	

Most of the mechanical properties of plastics decrease with recycling, likewise the mechanical properties of recycled PVC. The tensile strength and modulus of recycled PVC are lower than that of virgin PVC. The thermal degradation that occurs during mechanical recycling affects both properties. The degradation that occurs causes chain scission, which in turn lowers the molecular weight of PVC. This, in turn, contributes to the decrease in the value of tensile and modulus of recycled PVC. On the other hand, the increase in elongation and impact strength of recycled PVC compared to virgin PVC is due to plasticizers. Usually, the plasticizer is added as an additive to increase the flexibility of PVC. The plasticizer effect becomes more pronounced when PVC is recycled. As a result, recycled PVC exhibits better flexibility than virgin PVC.

7 Recycled Bioplastic

PLA is obtained from renewable sources and is believed to have less environmental impact compared to petroleum-based thermoplastics. Therefore, it is not surprising why it is widely used in various applications such as packaging, medical devices, and, most recently, filaments in the 3D printing application. Production in these various applications increases plastic waste-based PLA. PLA waste can be managed through various methods such as incineration, composting, recycling, and disposal in landfills (Lanzotti et al. 2019). Of all these methods, recycling is the best option as PLA takes a long time to decompose. Like synthetic thermoplastics, PLA recycling also involves thermal degradation, which provides mechanical properties, as shown in Table 7.

PLA is a polyester that is highly sensitive to thermal treatment (Rosli et al. 2018). The low activation energy (21–23 kJ/mol) is required for PLA to undergo thermal degradation (Shojaeiarani et al. 2019). The scission of the polymer chain usually follows mechanical recycling due to thermal degradation. Thus, the recycling of PLA, followed by chain scission, produces recycled PLA with low molecular weight. Furthermore, the molecular weight reduces with an increased recycling number (Shojaeiarani et al. 2019). The molecular weight of the PLA greatly influences its

Table 7 Mechanical properties of recycled PLA

Mechanical property	Before recycling	After recycling	References
Tensile yield strength (MPa)	40.43 ± 1.8	35.85 ± 3.3	Anderson (2017)
Tensile modulus of elasticity (MPa)	4258 ± 260	4032 ± 498	
Hardness (Shore D)	84.8 ± 0.8	82.8 ± 2.4	
Flexural strength (MPa)	–	77.7 ± 7.4 1 × Re 75.0 ± 3.4 5 × Re	Shojaeiarani et al. (2019)
Flexural modulus (MPa)	–	2.5 ± 0.7 1 × Re 2.2 ± 0.1 5 × Re	
Impact strength (kJ/m^2)	–	7.7 ± 0.2 1 × Re 7.0 ± 0.1 5 × Re	
Short-beam strength (MPa)	119.1 ± 6.6	106.8 ± 9.0 1 × Re 108.5 ± 9.9 2 × Re 75.0 ± 16.2 3 × Re	Lanzotti et al. (2019)

mechanical properties (Liu et al. 2019). Almost all of the mechanical properties of recycled PLA decrease with recycling caused by the low molecular weight of recycled PLA. The values of the mechanical properties of recycled PLA are lower than that of virgin PLA plastics, as in Table 7. In addition to the degradation that causes a reduction in molecular weight, factors such as flow behavior and rheological properties also play a role in determining the mechanical properties of recycled PLA (Lanzotti et al. 2019).

Molecular weight significantly affects the mechanical properties of recycled PLA, predominantly tensile properties. The tensile properties of recycled PLA show a decrease of 5- 13%. Apart from the low molecular weight, the decrease in the tensile properties of recycled PLA is also influenced by interference during the extrusion process (Anderson 2017). Repeating the recycling process several times decreases the molecular weight of PLA in every cycle. Therefore, the tensile properties of the recycled PLA decrease with an increase in recycling cycles, as in Fig. 4.

In addition to chain breakage, thermal degradation that occurs during the recycling process also contributes to the failure of intermolecular bonding between polymer chains. These factors contribute to the decline in the flexural and impact properties of the recycled PLA. The impact properties of recycled PLA continue to decrease with the number of recycling numbers, as shown in Fig. 5.

In addition to thermal degradation, PLA also undergoes hydrolysis and transesterification between molecules during reprocessing (Nicolae et al. 2008). The process of hydrolysis and transesterification between PLA molecules causes the chain's scission, which also contributes to the low molecular weight of recycled PLA. Therefore, most of the mechanical properties of recycled PLA have decreased due to the low molecular weight due to thermal degradation, hydrolysis, and transesterification between molecules.

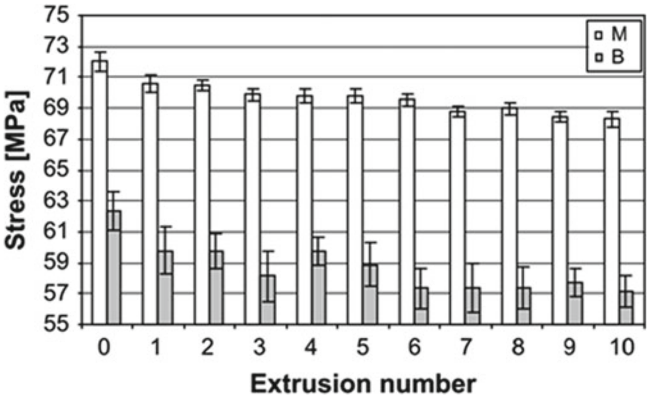

Fig. 4 Tensile strength (M) and tensile stress at break (B) of recycled PLA as a function of extrusion number (Żenkiewicz et al. 2009)

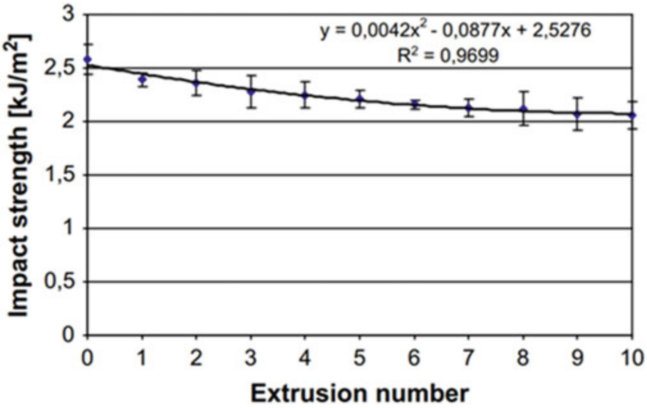

Fig. 5 Impact strength of recycled PLA as a function of extrusion number (Żenkiewicz et al. 2009)

The dynamic-mechanical performance of recycled PLA is shown in Fig. 6. The storage modulus for recycled PLA is lower than the virgin PLA. Recycled PLA also exhibits a decrease in $T_{g,}$ which indicates that the nature of the PLA's stiffness decreases with the recycling process. The low modulus and stiffness properties indicate that the recycled PLA chain's movement increases with the recycling process. Increased chain movement also reflects that recycled PLA is more flexible than a virgin PLA.

Polyhydroxyalkanoates (PHAs) is another widely used bioplastic after PLA. There are various PHA derivatives such as homopolymer poly-β-hydroxybutyrate (PHB) and copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Similar to PLA, the widespread use of PHA is to overcome the waste problem of petroleum-based thermoplastics. However, the use of PHA also contributes to waste

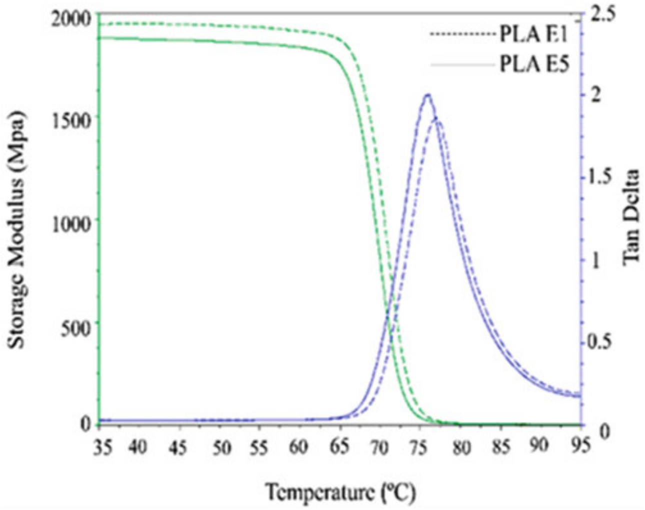

Fig. 6 DMA curve for virgin (E1) and recycled (E5) PLA (Shojaeiarani et al. 2019)

generation problems (Vu et al. 2020). Therefore, the positive impact of PHA on the environment can be enhanced by the recycling process. The mechanical properties of recycled PHBV are shown in Table 8.

The mechanical properties of recycled PHBV bioplastic are dependent on the content of hydroxybutyrate and hydroxyvalerate in PHBV. Although the same reprocessing method is used, the recycled PHBV will not exhibit the same mechanical properties when the copolymer content is different. Recycled PHBV with low valerate content (3%) showed a significant decrease in mechanical properties, as shown in Table 7. On the other hand, recycled PHBV with high valerate content (14%) did not

Table 8 Mechanical property of recycled PHBV

Mechanical property	Before recycling	After recycling	Reference
Flexural strength (MPa)	–	47.4 ± 3.6 1 × Re 46.5 ± 4.9 5 × Re	Shojaeiarani et al. (2019)
Flexural modulus (MPa)	–	3.2 ± 0.3 1 × Re 2.7 ± 0.2 5 × Re	
Impact strength (kJ/m^2)	–	3.7 ± 0.1 1 × Re 2.6 ± 0.1 5 × Re	

show any significant change in mechanical properties (Zaverl et al. 2012). This significant difference is also found in the dynamic-mechanical performance of recycled PHBV (Fig. 7).

Differences in valerate content also affect the molecular weight of the recycled bioplastic PHBV (Shojaeiarani et al. 2019; Zaverl et al. 2012). All recycled thermoplastics undergo molecular weight reduction due to thermal degradation. Molecular weight plays a crucial role in determining the mechanical properties of plastics. Recycling of PHVB also decreased molecular weight, where significant molecular weight reduction was recorded in the recycled PHVB with 3% valerate. A significant decrease in the molecular weight of recycled PHBV with low valerate content results in a significant reduction of mechanical properties of recycled PHBV.

The crystallization phenomenon is another factor influencing the mechanical properties of recycled PHBV. PHBV is a brittle polymer like PLA with low elongation at break (less than 10%). The brittle nature of PHBV is due to the secondary crystallization that occurs in bacterial-based polyester. The secondary crystallization that occurs prevents the chains' movement in the amorphous phase resulting in brittle polymers (El-Taweel et al. 2004). The % crystallinity of PHBV decreased at each recycling cycle. However, mechanical properties such as modulus do not undergo any significant changes. When the % crystallinity of recycled PHBV is above 40%, it will retain its brittle fracture properties.

Most of the mechanical properties of recycled PHBV can be maintained even after five cycles of recycling. This shows that bioplastic PHBV is suitable for recycling like PLA. Unlike other thermoplastic, PHBV is less sensitive to thermal degradation and shear force. Thus, recycled PHBV exhibits almost the same mechanical properties as virgin PHBV due to its molecular weight, which is almost in the same range.

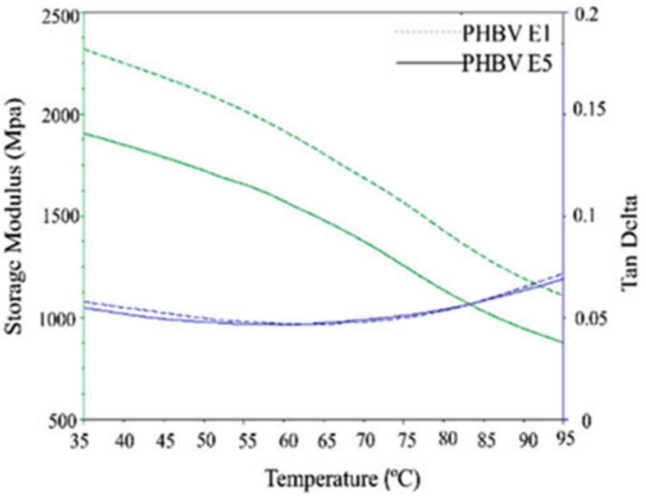

Fig. 7 DMA curve for recycled PHBV (Shojaeiarani et al. 2019)

8 Conclusions and Future Perspective

This chapter has discussed and elaborated on the mechanical properties of various types of recycled thermoplastics. Mechanical recycling is more practical than other recycling methods, as various thermoplastic can be recycled through this method. Mechanical recycling has a different impact on the mechanical properties of recycled plastics. Overall, most of the plastic recycled through this method will undergo thermal degradation and shear force. In general, thermal degradation that occurs will cause a reduction in the molecular weight of thermoplastic, which in turn lowers the mechanical properties of the plastic. However, there are situations where thermal degradation contributes to the increase in molecular weight. This is due to the cross-linking of the chain dominates the scission of the chain during processing. This contributes to the improvement of some of the mechanical properties of recycled plastic. Additionally, the mechanical properties of recycled plastic depend on the processing method used. The plastic reprocessing process using the injection molding method produces plastics with lower mechanical properties than the extrusion process. This is because the shear degradation for the injection molding process is higher than the extrusion. In addition to molecular weight, the mechanical properties of recycled plastics depend on the degree of crystallization. There are some cases where the degree of crystallization increases with the recycling process. As a result of the elaboration from this chapter, it is found that some thermoplastics still retain their mechanical properties after a few recycling cycles. Most recycled thermoplastics do not show significant changes in mechanical properties compared to virgin plastics. This, in turn, shows that recycled plastic is worthy of reuse.

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Recycling of Plastics into Advance Carbon Nanomaterials and Their Application in Energy Storage System

Manoj Karakoti, Sandeep Pandey, Gaurav Tatrari, Satish Chandra Sati, and Nanda Gopal Sahoo

Abstract Plastics are the polymers of their respective constituting monomer units and they are emerging as essential materials in day to day life. Due to the extensive use of plastics, they generate a large trajectory of plastics waste around us which are creating huge environmental pollution. On the other hand, energy is also an important aspect of human society without energy life is unimaginable. The modern lifestyle of human and heavily dependably over the electrical appliances need more alternative and green energy resources. For this, energy storage devices especially supercapacitor emerges as the green and alternative energy source which have the capability to fulfill the world energy demand and will also reduce the dependency over fossil fuels. In addition, carbon nanomaterials such as graphene, carbon nanotubes and other nanostructures evolved as the miracle materials due to their attractive properties and many folds application in different areas. Thus, here, in this chapter, we will discuss the three dimensional approaches for removal of plastics footprints from our environments. In this regard, a three dimensional approach have been discussed which includes waste plastics conversion techniques with their advantages and disadvantages, conversion of waste plastics into carbon nanomaterials and their potential applications in supercapacitor.

Keywords Waste plastics · Carbon nanomaterials · Recycling · Supercapacitor

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1 Introduction

Plastics are high molecular mass containing synthetic or semi-synthetic organic polymers with often having some other substance. Most of the plastics are made from the petrochemicals, but some of them are made from other materials such as cellulosics from cotton linters or polylactic acid from corn. The plastics are flexible and malleable materials that can be mold into the different solid object as according to desire (American Chemistry Council 2005–2021). Due to this property of the plastics they can use for the different applications which makes human life more convenient and comfortable. Such things globally affected the demand and production of plastics. It have been used in nearly every sector such as packaging, construction, textile, consumer products, households, transportation, electrical and electronics as well as in the industrial machinery. The versatility of the plastics in different sectors attracted today's world because of its outstanding strength to weight ratio, resilience, low cost, low maintenance and corrosion resistance which make its an economically eye-catching choice for further applications. As a result, the production of plastics increases year by year and which was more than 20-fold between 1950 and 2018 with 359 million metric tonnes per year, and is predicted to double by 2035, and quadruple by 2050 (Garside 2019). In addition, plastics production needs the natural gas and oil as well other substance such as 185 L of water is requried to make a kilogram of plastic. Its production consumed nearly 6% of global oil production which is expected to increase 20% by 2050. Therefore, this is the major contributor towards the emission green house gases and emitting more than 390 million tonnes of CO_2 which expected to increase 15% by 2050 because of using fossil fuel as primary feedstocks for plastics production (Zygmunt 2007; Hopewell et al. 2009; McKinsey and Company 2016). In addition, use of plastics by human in liner pattern of 'take, make, use, and dispose' which is primary reason for depletion of natural resources, waste generation, environment pollution, climate change and undesirable effect on living organism. In addition, poor plastics waste management and treatment techniques showed that only 9% of plastics were recycled, and 12% incinerated, leaving nearly 80% to gather in landfills or in our surrounding (Jambeck et al. 2015; Geyer et al. 2017; Organization for Economic Co-operation and Development 2018). Due to extensive use and non-biodegradable nature of plastics generated large trajectory of plastics waste around us. The large trajectories of waste plastics are problematic for our environment, human, ecosystem and natural resources because of its toxic chemical and non-biodegradable. So, presently there is no safe approach to dispose the plastics waste, thus, it causes serious damage to our environment during its production process, usage and disposal process (Koushal et al. 2014).

In addition to the waste plastics, energy is also important aspect for the development of human society. Exponentially rising the world population and continuously change in life style of human are the two key causes for the increase in use of energy and electricity consumption in last few decades. Particularly, in industry, constriction sectors, transportation and extensive use of electrical appliances. The total world energy demand estimated to be more than double by 2050 and triple by the end of the century. Due to this, present energy structure is not capable to fulfill the world energy demand (Nault 2005). Presently, most of the energy demand fulfills by fossil fuels but their limited sources and pollution causes by their use force us to think about the alternate energy sources (Libich et al. 2018). Due to this, energy storage systems such as capacitor, battery and supercapacitor (SC) are the best options for green and alternative energy resources. These energy storage devices have their own characteristics and particular applications. Among these, SC evolved as a fascinating energy storage device which is lies between the capacitor and battery. SC is capable to deliver higher power density in compared to the battery and lower energy density which is usually 3–30 times lower in the same volume (Miller and Simon 2008). The power output of SC is lower than the capacitor but mange to reach 10 kW/kg. Also, the specific energy of the SC is much higher than that of capacitor (Pandolfo and Hollenkamp 2006). In addition, SC has the many attractive characteristics properties than battery and capacitor in term of specific capacitance, cost, safety and life cycle. The SC has the higher specific capacitance than the battery and capacitor. Apart from this, SC has the short charging/discharging time and long life cycle due to its charge storage mechanism which involves the physical storage of charge at electrode and electrolyte surface rather than irreversible chemical reaction. In addition, according to the charge storage mechanism of SCs are divided into three categories. First category belongs to the Electrical double layer capacitors (EDLCs), here, the capacitance originate due to the purely electrostatic charge accumulation at the interface of electrode and electrolyte. The capacitance generally depends on the surface area of electrode; more the surface area gives more charge accumulation and capacitance. Second category belongs to pseudocapacitor, here, capacitance originates by fast and reversible faradic charge transfer reaction occurred at electrode (Zhang et al. 2010; Du et al. 2010). Third category belongs to the hybrid supercapacitor, here, capacitance originate by EDLC as well as pseudocapacitor. In addition, selection of electrode material for the above mention types of SCs as it decides the electrical properties of the devices (Li et al. 2011). Presently, lot of challenges need to overcome related to SC such as lower energy density, high production cost, lower voltage per cell and high rate of self discharge. Thus, many scientists try to overcome these issues by developing low cost new electrode materials for SC. Therefore, numbers of materials such as carbon, carbon nanomaterials, metal oxide, conductive polymers and their composite have been used as the electrode materials for SC. Among these materials, carbon nanomaterials such as graphene, CNTs and other nanostructure gain tremendous attention due to their extraordinary properties such as high surface area, uniform pore distribution, high theoretical capacitance, higher electrical conductivity, heat conductivity, and mechanical properties. They are made of pure carbon, consequently, displaying higher stability, good conductivity, low toxicity, environmental friendliness (Yan et al. 2016). Presently, the cost of carbon nanomaterials is very high in the international market; thus, need to develop the low cost synthesis methods as well as finding the low cost precursors materials for the synthesis of carbon nanomaterials (Karakoti et al. 2021). In addition, peoples are looking towards the advance recycling options of plastics waste into more value added products. Therefore, having the high carbon content in the plastics waste it is evolving as the precursor materials for carbon-based value-added products. These products are wide in range such as lighter hydrocarbon (Lovett et al. 1997; Buekens and Huang 1998; Yang and Lin 2009; Jan et al. 2013), activated carbon/carbon black (Esfandiari et al. 2012), graphene (Geim and Novoselov 2007), carbon fibers (Liu and Kumar 2012; Norberg et al. 2013), carbon nanotubes and fullerenes (Howard et al. 1991; Howard and Chowdhury 1994; Richter et al. 1997). Nowadays, among these materials such as graphene, CNTs, fullerenes are considered as the advance materials because of their exceptional properties and their use in different applications. Therefore, conversion or recycling of plastics waste into the carbon nanomaterials can be great approach for removal of plastics footprint from our environment. This type of conversion will be beneficial for environment as well as for generation economy via transformation plastics waste into carbon nanomaterials. In this regard, numbers of approach have been done for the synthesis of carbon nanomaterials and their applications in supercapacitor.

As above mentioned, the plastics can be recycled into the various value added products and their utility in supercapacitor that's why here, in this chapter, we are going to discuss the synthesis methods of carbon nanomaterials from recycling of waste plastics. Further, here also we are going to discuss the potential use of carbon nanomaterials synthesized from plastics in supercapacitor application.

2 Methods for Recycling of Plastics Waste

The number of methods have been discovered and employed for recycling of plastics waste (Fig. 1) into different value added products. In this section we will discussed about the waste plastics and their recycling techniques. The plastics are polymeric form of carbon and its hydrogen counterparts that can be further recycled and converted into various structural forms of carbon viz. CNMs, through different methods i.e. CVD, acid treatment reactions, through heating treatments and etc. The recycling of plastics waste was started in early 1980 (Kim and Pal 2010). Right after that, many European nations have set certain targets for waste plastics recycling (Epro Association of Plastics 2018). In this regard, International Standard ISO 15,270:2008 has outlined various methodologies to recycle the waste plastic through much appropriate scientific way which includes biological recycling, organic recycling, chemical recycling and mechanical recycling etc. (International Organization for Standardization 2008). The recycling of waste plastic is significant method for the recovering of carbonic material with or without significant change in its chemical structure (Schönmayr 2017). The section given below discusses various recycling techniques of waste plastics into various products.

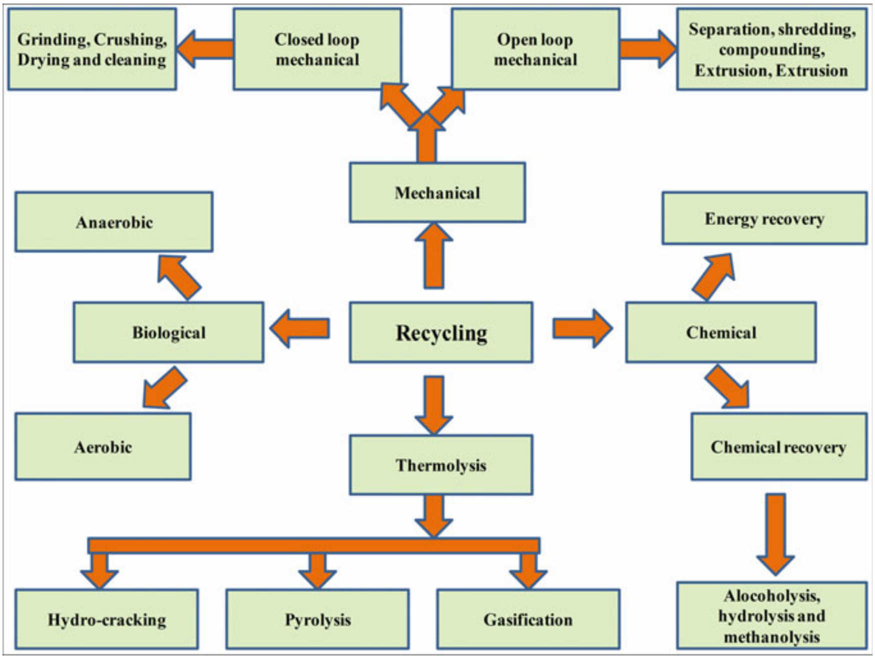

Fig. 1 Various recycling approaches for waste plastics

2.1 Mechanical Recycling

The mechanical recycling is the process of re-using waste plastic as precursor material, further applying into different mechanical applications. This type of waste plastics recycling was very popular in 1970s and it thus was commercialized so well. The more complexity in mechanical recycling process, higher will be the chances of contamination of recycled waste plastics (Al-Salem et al. 2009). The mechanical recycling can be further subdivided into two major processes closed loop mechanical recycling and open loop mechanical recycling process. The closed-loop recycling is the process of mechanical recycling, where waste plastic acts as the raw materials to form some new plastics. In general, waste plastics were directly introduced into extrusion cycle with virgin plastics to reproduce new materialistic form of plastics (Maris et al. 2018). In this process, obtained materials usually possess same qualities as original plastic and this does not reduce the properties of raw plastic on addition of virgin plastic into it while manufacturing. Though, in some cases the closed-loop waste recycling need grinding, crushing, drying and cleaning (Ignatyev et al. 2014).

On the other side the open loop mechanical recycling approach have some lesser advantages as in this case the raw materials are mostly different in manufacturing new products. This approach follows up some new techniques which includes separation, manual sorting then grinding, shredding followed by compounding, granulation and extrusion. These steps may alter their order and may replicate throughout the process (Ragaert et al. 2017). The sorting process separates different plastic polymers from the mixture of waste plastic on the basis of their chemical structure or type. Some basic characterization tools for example Fourier-transform infrared spectroscopy (FT-IR), and electrostatic detection are some techniques for the basic separation of sort polymers on the basis of their structure type. Optical color detector camera is the wide popular technology for the separation of the polymers on the basis of their structural outlining and color (Ignatyev et al. 2014). While some cases are reported where the separation and sorting process is followed by washing and drying process where the washing usually used for the removal of unwanted pollutants from waste plastics. While in some other cases the procedure of chemical washing has been followed which uses caustic soda as the cleanser agent (Al-Salem et al. 2009). The melting of waste plastic with another material is called compounding process, during compounding new materials are generally formed, for example waste plastic, fillers and additives polymers or other materials can be added to raw material in order to improve new manufactured plastics properties or to obtain such polymer with desire properties (Maris et al. 2018). Finally, the extrusion process used to manufacture new polymeric materials, where the desired shape of any materials is extruded with the help of a die. The granules fed onto extrusion machine for manufacture of new polymers from waste plastic. The extrusion consists of two types of extrusion screw, single and double screw. In brief the process involves hopper that are used to feed up the granules, while the screw used to mix the granules with simultaneous heating (Kutz 2011).

2.2 Chemical and Thermal Recycling

In chemical recycling process of waste plastic, the chemical degradation approach being followed, where the larger polymeric molecules are degraded into smaller ones i.e. monomers, gases, and fuels with the help of organic catalysts. This method can be used for the production of fuels, smaller polymers or chemicals (Ignatyev et al. 2014). The chemical recycling process usually follows de-polymerization and thermolytic approach for the decomposition of waste plastic polymers into its smaller counterparts. De-polymerization is the process of catalytic breakdown of plastic into its monomeric forms in another word this is just reversal of polymerization process.

The chemical process likewise alocoholysis, hydrolysis and methanolysis are included in chemical recycling of the polymers (Maris et al. 2018). The methanolysis and glycolysis majorly uses catalysts such as methanol and liquid glycols for de-polymerization process. Whereas alocoholysis and hydrolysis approaches are methods to de-polymerize plastic by treatment of water and alcohol respectively (Goto 2009).

Thermolysis approach of recycling is another approach where the plastics are treated at higher temperature which results thermal breaking of polymeric molecules. Thermolysis approach includes pyrolysis, hydro-cracking and gasification (Maris et al. 2018). Briefly, in thermolysis, waste plastics are heated in low to high temperature furnace in the absence or presence of any catalyst for the thermal degradation of polymers. On the other hand, the pyrolysis process where the waste plastics are processed in the absence of oxygen at high temperature and pressure. In pyrolysis and thermal breaking the polymeric form of plastics melts down and produces solid, fuels and gases as the products. The amount of their production accounts according to the kind of plastic used during the thermolysis process (Ragaert et al. 2017). Hydro cracking or hydrogenation is another kind of thermolysis approach, where high quantity of hydrogen introduced alongside with high temperature and pressure for the thermal degradation of waste plastic polymeric units.

Gasification is another thermolysis approach, where the gases especially oxidative agents likewise oxygen or its steams are introduced into high temperature furnace for the thermal steaming and cracking of waste plastics into its smaller counterparts that generally include smaller hydrocarbons. In Fig. 2, given below showed pyrolytic approach followed for the degradation of plastic polymers, that converts waste plastic into carbon char, bio gases and petroleum oil (Ragaert et al. 2017).

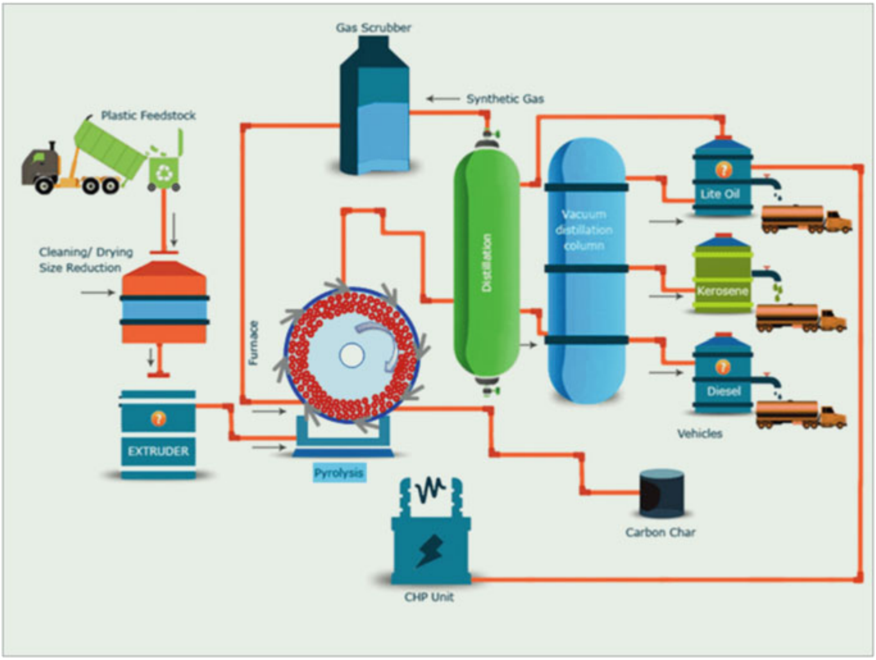

Fig. 2 Pyrolysis process. Reprint with the permission of Elsevier 2017 (Ragaert et al. 2017)

2.3 Biological or Organic Recycling

The organic waste recycling is process which is also known as biological method of waste recycling and used for special types of plastic. This processing method needs removal of pollutants from waste materials before its biological recycling. There are two approaches for biological treatment of waste plastic aerobic and anaerobic organic recycling process. Aerobic recycling includes waste plastic's feeding through microbes in the presence of oxygen while the anaerobic recycling approach microbes feed upon waste plastics in the complete absence of oxygen. According to some specific standard, only ISO 17,088, ASTM D 6400, ASTM D 6868 or EN 13,432 approved waste plastics are able to degrade through biological recycling processing and the final product obtained from biological recycling is usually compost (International Organization for Standardization 2008).

2.4 Energy Recovery

This is the approach where waste plastic is used for the production of heat, electricity, or any other form of energy. This is the most used process nowadays around the globe. Recently, in Europe 39.5% of plastic was recycled to obtain energy through energy recovery process (Maris et al. 2018). The good calorific value of waste plastic avail appreciable thumb reason behind plastic being excellent material for energy recovery in comparison to coal and fuel. The burning of raw fuel generates around 42.6 MJ/kg, while energy recovery from waste plastic liberates energy of 443.5 MJ/kg (Ragaert et al. 2017). As mentioned earlier, the treatment process for waste plastics such as recycling, energy recovery, and land filling are used. However, the land filling of waste plastic is not suggested due to non-biodegradable nature of plastic. Even, some countries such as Finland, Belgium, Switzerland and Norway have restricted the land filling of waste plastic. The energy recovery through the incineration of waste plastic is effortless to method as compared to the other complicated recycling methods (Okan et al. 2019). Due to complex recycling process, the higher amounts of waste plastic is landfilled and incinerated for energy recovery. Thus, from above discussion it is very reasonable to not use landfills as the solutions of waste plastic pollution problem; in fact we need to encounter this issue with aforementioned discussed scientific recycling techniques.

2.5 Recycling into CNMs

All other the above mentioned techniques are not clinical for recycling of waste plastics. Because, generally waste plastics is takes hundreds of years to decompose into its smaller counterparts in normal environmental conditions. Also, some techniques are not environment and cost effective. Thus, nowadays, recycling of waste plastics into carbon nanomaterials is the emerging techniques for recycling of waste plastics. This process not only gives permanent solution for plastics waste as well as gives the high valued products. The recycling of waste plastic into carbon nanomaterials such as CNTs, graphene and other nanostructures especially prepared through high temperature pyrolysis, chemical or acid degradation, and CVD process. However, the recycling process include different type of pyrolysis reactors viz. moving bed rector, fixed bed rector, tube reactor, muffle furnace, autoclave, crucible fixed reactors. Further this approach may be classified into two categories one-pot process and stepwise conversion process. The one pot conversion strategy is in situ technique of CNMs synthesis, while step wise processing involves multiple phases processing of feedstock (Zhuo and Levendis 2014).

2.5.1 Synthesis of Graphene from Waste Plastics

Graphene is the monolayer sheets of sp^2 hybridized carbon atom which are arranged in the hexagonal honeycomb sheet like structure. This graphene can be modified into the various forms such as zero, one and three dimensional carbon nanomaterials due to this it is also called mother of all kind of carbon nanomaterials (Geim and Novoselov 2007; Abergel et al. 2010; Zhu et al. 2010; Avouris and Dimitrakopoulos 2012; Katsnelson 2007). Recently, graphene gain lot of attention due to its various charming properties such as great optical, high mechanical, Electronic and thermal properties with high surface area and uniform pore distribution. Because of these, it becomes a promising material in energy storage and conversion devices, coating, catalyst, water purification polymer nanocomposite and biomedical field (Zhu et al. 2010; Avouris and Dimitrakopoulos 2012). Due to the popularity and utility of graphene, number of have been developed for the synthesis such as mechanical exfoliation, chemical derived, epitaxial growth on SiC, chemical vapor deposition, arc discharge via different precursor materials (Novoselov et al. 2004; Neto et al. 2009; Balandin 2011;Whitener and Sheehan 2014; Edwards and Coleman 2013; Sundaram 2014; Eigler et al. 2013; Frank and Kalbac 2014; Li et al. 2009a, b; Huang et al. 2014; First et al. 2010; Subrahmanyam et al. 2009). Now, recently peoples are looking for transformation of waste plastics into graphene due to its high carbon contain. In this regard, recently, CVD process acquired as a method to synthesis high quality graphene from waste plastic at 1050 °C under continuous H_2/Ar flow. Where, 10 mg of plastic source was placed onto Cu foil. Further quartz boat processed at 1050 °C for 15 min and 500 cm^3 STP/min with Ar and at 100 cm^3 STP/min with H_2 flow. The system was placed at 9.3 Torr pressure and then cooled quickly to room temperature. Further, 4% of PMMA anisole solution coated onto the foil at 3000 rpm for 40 s. The Cu foil further melted by acidic solution of $CuSO_4$, HCl, H_2SO_4 and H_2O. Finally, the washing was done by DI water through multiple steps (Ruan et al. 2011).

In this order, our group reported bulk synthesis of graphene nanosheets from waste plastic through two step pyrolysis process. Firstly, the chopped plastics were treated in primary pyrolysis reactor at 400 °C in catalytic presence of nanoclay, the process was further followed by high temperature pyrolysis at 750 °C under nitrogen flow (Pandey et al. 2019). Sharma et al. reported for the synthesis of high quality single crystal graphene from waste plastics over the polycrystalline Cu foil via CVD (Sharma et al. 2014). In this process, they processed the waste plastics via two stage temperature process for synthesis of graphene at 500 ºC over the ceramic boat and at 1020 °C over the Cu foil in the presence of H_2 and Ar. Gong et al. prepared the graphene flakes from polypropylene waste by using organically modified montmorillonite (OMMT) clay. In this process, the chopped polypropylene waste and OMMT mixed in a crucible and heated at the 700 °C for 15 min. Further, obtained charred residue allowed cooling at the room temperature and wash with HF, HNO_3 and water for eliminate MMT, amorphous carbon, and additives. The obtained graphene flakes from waste plastics are more than one layer, was confirmed through the I_G/I_{2D} of Raman spectra which is more than 1 (Gong et al. 2014).

El Essawy et al. prepared the graphene from recycling of waste polyethyleneterephthalate (PET) bottles. First, the PET bottles are crushed and cut into 1–3 mm size. Further, transferred the 2 g crushed and cut PET into 50 ml stainless steel autoclave reactor and placed inside the electric furnace at 800 °C with heating rate of 8 °C/min. After this, they obtained black products as graphene which was crushed and washed (El Essawy et al. 2017a, b). Cui et al. prepared graphene foil by using solid waste such as mineral water bottle, cleaning agent bottle, valve bag, preservative film, lunch box and various plastic bags via solid-state CVD process in the presence of H_2 and Ar. In this particular process, first, solid waste was washed with acetone, alcohol and water via ultrasonic process. Further, pre-annealed polycrystalline Ni foil used as the catalyst for waste plastics and put inside the quartz tube. After that, the reaction proceeds at 1050 °C for 120 min. Finally, they got the free standing graphene foil after cleaning of Ni foil with ferric chloride/hydrochloride etching and deionized water (Cui et al. 2017).

Algozeeb et al. reported the synthesis of flash graphene from waste plastics via flash Joule heating (FJH) method. This method is very easy and there is no need of catalyst for the conversion of waste plastics into the graphene products. In this method, they have used $\sim$23 kJ/g and can be used for the mass production of graphene (Algozeeb et al. 2020). This group also prepared the flash graphene from pyrolized plastics waste via FJH method for nanocomposite application (Wyss et al. 2021).

2.5.2 Synthesis of CNTs from Waste Plastics

The CNTs is the allotropic form of carbon and having two basic form as single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) (Yanagi 2014). The SWCNTs looks as rolled graphene sheets in cylindrical shape which is open through the both side. The SWCNTs consists hexagonal shape ring with sp^2 hybridized carbon atoms with in plane and out of plane bonding (Jei 2004). The CNTs attains lot of attention in materials science due to its charming properties such as high mechanical, thermal, electrical and optical properties along with high surface area. Also, CNTs incorporating in coatings and films for enhancing the corrosion resistance and provided better mechanical performance (Baughman et al. 2002; Hu and Lu 2014; Corral et al. 2004; Bandaru 2007; Toshishige 2004; Saito and Dresselhaus 2014; De et al. 2013). CNT is made from the different methods such as arc discharge, Laser ablation, CVD and miscellaneous methods via various precursors' materials (Prasek et al. 2011; Iijima 1993; Titirici et al. 2015). Due to the low yield and high processing cost of CNTs, peoples are looking for the alternative methods and precursor for the synthesis of CNTs. Thus, recently, waste plastics evolved as the precursor material for the synthesis of CNTs due to its high carbon contain. In this regard, various approaches have been done for the synthesis of CNTs. In this order, the high temperature exfoliation process with degradation catalyst and absence of solvent has been reported which converts low and high density plastics into carbon multiwall tubes (MWCNTs) (Pol and Thiyagarajan 2010). Where the quantity of catalysts, density of waste plastic, reaction temperature and pressure have played crucial role for synthesis of MWCNTs. Similarly, one step chemical vapor deposition (CVD) process at 600, 700 and 800 °C under argon and hydrogen environment for 1 h., with nickel as the catalyst have been reported as an effective approach for the synthesis of MWCNTs from polypropylene (PP). The obtained CNTs were reported to possess 85% visible light transmittance at 550 nm in comparison to 90% transmittance of traditional ITO films, thus can act as excellent materials for optoelectronic devices (Mishra et al. 2012). The temperature of 800 °C was reported as specific temperature for obtaining the purest form of CNTs.

Jiang et al. were proposed a mechanism for the conversion of polypropylene into CNTs (Jiang et al. 2007). In this process, nickel based catalyst was used as the degradation agent for waste plastics, where carbenium ions acted as active intermediates instead of free radicals which plays crucial role in thermal degradation of waste plastics. Similarly, transition metal catalysts along with acids or organically-modified montmorillonite (OMMT) avails intermediate protonic sites, that provide breaking down of the carbonic molecular chains into CNTs (Jiang et al. 2007; Gong et al. 2012; Marczewski et al. 2013; Zhuo and Levendis 2014). While chlorinated radicals reported to enhance aromatic nature on the degradation of waste plastic (Yu et al. 2009) that certainly results more carbon nanofibers (CNFs) than CNTs (Gong et al. 2014, 2015). Some reaction parameters such as temperature, pressure and catalytic composition are reported as the main parameters for the formation of CNTs. The yield of CNTs can vary from 5 to 50% depending upon catalysts, feeding stock and optimization of temperature and pressure conditions (Bazargan and McKay 2012). The CNTs synthesis from waste plastic through one pot and stepwise conversion process generally consist of catalytic residual along with amorphous carbon (Song and Ji 2011). The optimization of reaction parameters needed to be utilized in order to find much appropriate and less defective CNTs formation.

Further the stepwise thermal pyrolysis approach can also be followed to get qualitative CNMs from waste plastic. The primary step usually consists of thermal degradation of waste plastic into its smaller units, further secondary step results hydrocarbons, raw fuels along with CNMs (Mishra et al. 2012).

In similar pattern, three step pyrolysis recycling approach deployed by Yang et al., they have used the ferrocene metal sandwich as the catalyst in the primary reactor, after that the secondary reactor converts waste plastic into smaller units through thermal degradation and finally the third stage reactor enables the formation of CNTs (Yang et al. 2010). They have finalized the reaction temperatures accordance to each phase, such as the temperature of 120–140 °C was recognized as the sublimation temperature for ferrocene, while 450 °C for degradation of waste plastic into smaller units and 800–850 °C as the temperature for CNTs formation. The obtained CNTs were having the typical length of 100 mm, though it was unclear that iron ions only act as the catalyst for the process of CNTs growth or acted along with thermal degradation for the decomposition of waste plastics as degradation catalysts.

Another two step pyrolysis approach for the recycling of waste plastic was followed by Liu et al., they have used HZSM-5 zeolite for the decomposition of polypropylene (PP) over screw kiln reactor, and further the obtained products were treated with nickel catalysts in a moving reactor. Hydrogen and CNTs were produced as the result of the pyrolysis and 700 °C was reported as the optimum temperature for the formation of maximum amount of CNTs (Liu et al 2011).

Wu et al. were reported two-stage pyrolysis approach for the recycling of waste plastic in presence of inert atmosphere of N_2 at 500 °C, further the secondary reactor was processed to high temperature for the production of CNTs i.e. 800 °C. They have used Ni/Ca–Al or Ni/Zn–Al as the catalyst into secondary reactor which enable CNT synthesis (Wu et al 2012). Yao et al. have reported catalytic degradation and pyrolysis approach for the synthesis of CNTs. They have used two methodologies for the synthesis of catalyst one is sol–gel solvolytic approach and another one is impregnation methodology. The catalyst synthesized through sol–gel solvolytic approach has more vital activity for the degradation of polypropylene into CNTs. Initially they have evaluated the potential activity of catalysts i.e. Fe/Ni in the degradation of polypropylene into CNTs. They have used thermochemical high temperature pyrolysis approach following optimization of each catalyst. The method also produced hydrogen as the fuel along with high scale CNTs production (Yao and Wang 2020).

They have also synthesized a series Fe/Ni based catalysts further tested their degradation potential after their appropriate characterization. In general, the descending nature of activity for the synthesis of products i.e. hydrogen and CNTs, has been reported for the Fe–Ni, Fe and Ni stacking. The catalyst synthesized from the sol–gel solvolytic method was more efficient also exhibited the excellent performance for the production of hydrogen and CMNTs. The Fe–Ni sol–gel processed catalyst produced 360 mg/g of high quality carbon nanomaterials along with 25.14 mmol/g of hydrogen. The high quality of CNTs was ascribed to uniform meso-porous structure which includes high surface area of 212.30 m^2/g and high degree active metal's dispersion i.e. 42.02%. The boosted reduction was invented due to the synergic activity between Fe and Ni in the catalysts. Finally, after the characterization bamboo shaped multi-walled CNTs obtained. The CNTs having good aspect ratio was synthesized via pyrolysis of waste polythene using Ni based catalyst i.e. nickel dichloride as the degradation agent by Yang et al. They have reported CNTs with 30–50 nm diameter and length of few micrometers (Yang et al. 2010). Here the processing temperature of 773–1073 k was used for the pyrolysis of polyethylene under the Ar atmosphere. The CNTs obtained using 0.75% Ni and at the pyrolysis temperature of 973 K was reported as the excellent candidate for the absorption of organic dye i.e. methylene blue (MB). Briefly, waste polyethylene was chopped and powdered before mixing with catalyst. The nickel dichloride which was used as Ni based catalyst in different weight ratios i.e. 0.25, 0.50, 0.75, and 1.00 wt%. First, nickel dichloride was solvated into 10 mL of ethanol with continuous stirring condition at room temperature. Thus obtained catalytic solution of ethanol and nickel dichloride was spread over the 10 g chopped powder of polyethylene. Now they have desiccated the obtained polythene precursor in oven at the temperature of 323 K for 24 h. At last 2 g of polyethylene nickel chloride composite was placed under high temperature tube furnace. The temperature in between 773 and 1073 K was allowed to process in alumina crucible with continuous heating rate of 5 K/min with inert atmosphere of argon for 2 h. Different temperature based evaluations revealed the optimized temperature for the synthesis of CNTs. From the temperature of 973 K, CNTs with 40 nm diameter, 60 mm length and with the aspect ratio of 1500 started to form. The production of CNTs gradually decreased once the temperature rose to 1073 K, thus the study concluded higher temperature of 1073 K as the unfavorable temperature for the synthesis of CNTs (Zheng et al. 2018).

Wang et al. were reported the synthesis CNTs inside the stainless steel tube with having two different heating furnaces by using the plastics waste as a precursor (Wang et al. 2020). This method is based on catalytic conversion of polypropylene (PP) into CNTs by suing Fe/ cordierite, Ni/cordierite and Ni–Mg/cordierite. Here, they have used 1 g of PP was put inside the primary furnace and 0.5 g of catalyst put inside the second furnace. First, heat the catalytic furnace at 750 °C at a heating rate of 40 °C/min and fixed until the end of the process and then heat the primary furnace at 500 °C at the rate of 10 °C/min in the presence of N_2. In the primary furnace pyrolysis of PP was occurred and CNTs growth happened over the catalytic surface.

Aboul-Enein et al. were prepared the MWCNTs from the waste polyethylene to increase the rheological properties of lubricating grease (Aboul-Enein et al. 2021). In this process they have used the two stage heating system, first, pyrolysis of polyethylene with HZSM-5 zeolite in a vertical pyrolysis chamber at the temperature ranging between the 350 °C and 600 °C. Second stage heating of non-condensable gases at 700 °C in a horizontal tube furnace over Co/MgO catalyst which covert these gases into the MWCNTs. Further, resultant MWCNTs was washed with the conc. HCl for removal of unwanted impurities.

2.5.3 Synthesis of Other Carbon Nanostructures from Waste Plastics

Carbon nanomaterials are very important materials in the materials science and have been applied in many fields. In past few years, carbon nanostructure or nanomaterials have been studied and developed due to their extraordinary properties such as electrical, mechanical and high surface area etc. Due to this they have been applied in many fields such as sensing transducers, conducting materials, electronics, and also offering new openings for the advanced biochemical sensors. In this regard, many efforts have been attempted for the synthesis of different kinds of carbon nanostructures by various scientists via different precursor materials. But, in last few years, the plastics create lots of problems thus peoples are looking forwards to conversion of plastics into the carbon nanostructures. In this order, El Essawy et al. were reported the synthesis of carbon nanostructure from PET waste by using ferrocene as a catalyst inside the stainless-steel (SS316) autoclave at 800 °C over 100 min and constant this temperature for 20 h (El Essawy et al. 2017a, b). They have taken 2 g of PET waste with different ratio of ferrocene at above temperature. Finally, they got the dark carbon product after cooled the furnace at room temperature and then this product was collected, crushed and washed to get the resultant carbon nanostructure.

Aboul-Enein et al. were prepared carbon nanostructure from polyethylene waste via catalytic pyrolysis by using MgO supported bimetallic catalysts (Aboul-Enein and Awadallah 2018). During this process, they have used the MgO supported Fe-Mo catalysts with weight ratio of Fe:Mo was 50:0, 45:5, 40:10, 30:20, 20:30 and 10:40. Initially, they have done the pyrolysis at 400 °C of plastics waste (15 g) in the presence of ZSM-5 (0.75 g) catalyst in a vertical pyrolysis chamber which was connected to the condenser. This process allows to maximum conversion of plastics waste into the light hydrocarbon which leads increase the production of carbon products. On the other hand, the collected hydrocarbon pass through the horizontal tube furnace which having the MgO supported Fe–Mo catalysts in the presence of H_2 and N_2. Then, this horizontal tube furnace allow to heat at 750 °C for the conversion of carbon nanomaterials. Further, reaction allowed cooling at the room temperature and different products have prepared via this products such as carbon nanofibers along with graphene nanosheets and CNTs.

The polymer carbon dots are also prepared from the plastics waste. In this order, Aji et al. were reported the synthesis of polymer carbon dots from plastics waste upcycling via simple heating of PP at different temperature of 200 °C, 250 °C, and 300 °C (Aji et al. 2018). At different temperature obtained the different average size of carbon dots of ~15 nm, ~11 nm and ~8 nm for 200 °C, 250 °C and 300 °C, respectively. The synthesized polymer carbon dots are showing the absorption spectra around 400–435 nm. These carbon dots have the potential to be used as performing materials in photocatalyst, bioimaging as well as sensors in optoelectronic materials.

Chaudhary et al. were developed the fluorescent carbon dots via upclcying of waste plastics (Chaudhary et al. 2021). In this particular work they have used different kind of plastics waste such as bottles, used cups and polyethylene bags and transform them into the fluorescent carbon dots by simple heating process. The developed carbon dots are showed the absorption peaks at around 260 nm with 5–30 nm of size. These showed the good emission properties with peak positioned around 422 nm as well showed the good quantum yield of ~62, 65 and 64% for C-dots generated from plastic polybags, cups and bottles, respectively.

Hu et al. were reported the easy synthesis of carbon dots form PET waste. In this work they have used the air oxidation method followed by immersion in conc. H_2SO_4 for the synthesis of carbon dots (Hu et al. 2021). First, they cut the PET bottles into the small pieces and taken 3 g of it and heated at 300 °C in the presence of air in open ceramic crucible for 2 h. After that, they got the brown color product which was immersed in 10 mL conc. H_2SO_4, and heat this product for 6 h at 120 °C. Through this procedure, they got the black color solution of carbon dots which was diluted with deionized water and filtrated to remove the residue.

Tripathi et al. were developed the solid carbon spheres (SCSs), hollow carbon spheres (HCSs), and nitrogen-doped hollow carbon spheres (nitrogen-doped HCSs) form polypropylene (PP) waste via CVD method (Tripathi et al. 2019). In this method, SCSs was synthesized from the PP by using two stage heating furnace at different temperature. First, 2 g of PP waste was placed in primary CVD reactor and simultaneously increase the temperature of secondary CVD reactor at 900 °C with heating rate of 10 °C/min in Ar condition. After that, increase the temperature of primary reactor at 500 °C where PP was placed. This condition maintain for 1 h and then reaction allowed cooled at room temperature. Further, they collected the SCSs from CVD reactor. They also prepared the HCSs by using 1.0 g of silica with PP as above mentioned method and they got the carbon/silica materials. Further, they removed the silica template from the carbon with 10 mL of 10% HF solution for 24 h followed by washing with distilled water until pH reached at neutral and got the HCSs. After that, they prepared the nitrogen-doped HCSs via same procedure by using the melamine as the source of nitrogen and got the nitrogen-doped HCSs.

3 Application of Waste Plastics Derived CNMs in Supercapacitor

Carbon nanomaterials of different dimension (OD, 1D, 2D and 3D) are very useful and having very attractive properties, which have been already discussed in above sections. They have been prepared via different precursors materials and used as electrode material in supercapacitor extensively along with other fields. Also, carbon nanomaterials have been prepared extensively by recycling of plastics via using one of the above mention techniques but less explored in supercapacitor. Still, waste plastics derived carbon nanomaterials especially graphene and carbon nanosheets are frequently used as electrode materials in supercapacitor rather than other carbon nanomaterials. In this regard, our group reported the synthesis of graphene nanosheets from waste plastics via two stage pyrolysis techniques by using montmorillonite nanoclay. Further, the synthesized graphene nanosheets were used as the electrode material over the different current collector for supercapacitor and exhibited the highest specific capacitance of 38.78 F/g in PVA-H_3PO_4 polymer gel electrolyte (Karakoti et al. 2021). Elessawy et al. have prepared the 3D sponge nitrogen doped graphene (NG) from polyethyleneterephthalate (PET) bottles by using urea at two different reaction temperatures one at 600 °C and other at 800 °C with a rate of 10 °C/min in single step. The synthesized NG was used as the electrode material for supercapacitor which displayed the excellent electrochemical performance in terms of specific capacitance of 405 F/g at 1 A/g of current density. Further, they investigated the energy and power density of NG based supercapacitor of 68.1 Wh/kg and 558.5 W/kg in 6 M KOH electrolyte. Also, it showed the good cyclic stability of 87.7% after 5000 charging/discharging cycles (Elessawy et al. 2019). Ma et al. were reported the recycling of polyester into the porous carbon nanosheets by using MgO through carbonization. Further, they activated with KOH at different temperature to convert the mesoporous into micropourous carbon nanosheets with a specific surface area of 2650 m^2g^{-1} and a pore volume of 2.43 cm^3 g^{-1}.The synthesized carbon nanosheets used as the active electrode materials for supercapacitor and showed high specific capacitance of 323 Fg^{-1} at the current density of 0.5 Ag^{-1} in a 6 M aqueous KOH electrolyte with 92.6% cycle stability after 10,000 cycles. Also, the carbon nanosheets exhibited the energy density of 44.1 $Whkg^{-1}$ with a power density of 757.1 W kg^{-1} in an organic electrolyte (Ma et al. 2019). Liu et al. have reported the synthesis of 2D carbon nanosheets (CNS) waste plastics particularly polypropylene (PP) by using ferrocene and sulfur as the catalyst which are promote the formation of resultant product (Liu et al. 2021). From this method, they got 62.8% of carbon and reported 4–4.5 nm thick CNS which has the specific surface area of 3200 m^2/g with pore volume of 3.71 cm^3/g. After this, the symmetric supercapacitor was fabricated with the synthesized materials which showed the specific capacitance of 349 F/g at 0.5 A/g with good energy density of 23 Wh/kg. Wen et al. have reported the synthesis of porous carbon nanosheets (PCNs) via catalytic carbonization of solid waste plastics by using organically-modified montmorillonite (OMMT). Further, the synthesized PCNs was used for supercapacitor application after the activation with KOH. The PCNs was showed the specific surface area of 2198 m^2 g^{-1} and a large pore volume of 3.026cm^3g^{-1} which exhibits the utility PCNs towards the supercapacitor. The derived PCNs displayed the specific capacitance of 207 and 120 Fg^{-1}at a current density of 0.2 Ag^{-1} in aqueous and organic electrolytes, respectively (Wen et al. 2019). They also prepared the porous carbon nanosheet (PCNS) which was synthesized from poly (ethylene terephthalate) with specific surface area of 2236 m^2/g. The synthesized PCNS exhibited the specific capacitance of 169 and 135 F/g in 6 M KOH and 1 M Na_2SO_4 electrolyte (Wen et al. 2020). Wang et al. were prepared the nitrogen doped porous carbon nanosheets (N-PCNs) from plastics waste by using $Mg(OH)_2$@CoZn-ZIFs sheets composite as a templates. The synthesized N-PCNs displayed the higher specific capacitance of 149F/g at 0.5A/g of current density with superior cyclic stability of 97.6% after 5000 cycles (Wang et al 2018). Mu et al. have prepared the 3D porous carbon nanosheets (PCS) via selective carbonization of PET into an autoclave to react at 700 °C for 1 h by using (MgO/$Co(acac)_3$) as combined catalyst. Further, they hybridize it with MnO_2 nanoflakes to prepared PCS-MnO_2 composites. Thus synthesized composite was displayed the specific capacitance of 210.5 F/g with 90.1% cyclic stability after 5000 charging discharging cycles (Mu et al. 2020). Alhokbany et al. have reported the bimetallic $NiCo_2O_4$@nitrogen-doped carbon (NC) nanocomposite via development of nickel/ cobalt metal organic frameworks (Ni/Co–MOF) for supercapacitor application (Alhokbany et al. 2020). In this work, first they prepared 1,4-benzendicarboxylic acid (BDC) from depolymerization of PET bottles further which as used as organic framework for bimetallic system. Then, they prepared the bimetallic $NiCo_2O_4$@nitrogen-doped carbon (NC) nanocomposite with BDC. This composite was showed very good surface area of 813 m^2/g with pore size of 15 nm. Further, electrochemical performance was evaluated and displayed the specific capacitance of 890 and 913 F/g at 5 mV/s and 1 A/g, respectively, in 6 M KOH electrolyte. Cheng et al. were prepared the nanoporous carbon from PVC and $Mg(OH)_2$ in 1:2 after carbonization process at 700 °C with heating rate of 5 °C/min. The developed nanoporous carbon exhibited the good surface area of 958.6 m^2/g with high pore volume of 3.56 cm^3/g. After that, they prepared the composite with MnO_x with different weight ratio. Further, the synthesized materials were used as the active materials for supercapacitor and exhibited the specific capacitance of 751.5 F/g at 1.0 A/g for 1:1 composite of nanoporous carbon and MnO_x which was higher than of the pure nanoporuous carbon of 47.8 F/g (Cheng et al. 2015).

4 Obstacles and Feasible Solutions

The major obstacle for the upcycling of waste plastics into CNMs is the selection of precursor used, as the nature of carbon feedstock i.e. waste plastic which is inconsistent with the quantity of carbon due to impurities and contaminations.

Although, upcycling of the waste plastics into high quality value added CNMs showed significant circular economical cost benefit analysis, but the variety of the plastics present within the ground level system showed huge challenge to upcycle all kind of plastics into CNMs. Different amount of carbon percentage along with various kinds of fillers and dyes demonstrated random quality of the CNMs (Liu et al. 2009). Another comprehensive obstacle is the methodology followed during the conversion of waste plastic into CNMs i.e. pyrolysis approach, which included both stepwise and on step synthesis process that still need scientific optimization and investigations regarding the driving force and mechanism of exfoliation of waste into CNMs during the pyrolysis approach. Similarly, the production of gases and fuels have been ignored in most of the cases which need to be correlated in scientific way with proper mechanism of processing as they act as the intermediate in most of the cases (Kuwana et al. 2006; Ago et al. 2006; Plata et al. 2009). Therefore, just to correlate initial precursor with amount of product obtained is not an appropriate scientific methodology to synthesize of different CNMs. However to obtain simplicity in the production of CNMs, some modifications, and improvements are needed for the better optimization of waste plastic pyrolysis techniques. Along with this, the amount of various gases ejected during the manufacture of CNMs and that has been consumed during the reaction pathway needs to be examined along with the catalytic substrates. While for better understanding the detailed reaction pathway and conversion strategy of the CNMs needs to be marked for much larger scale manufacture and commercialization of CNMs.

Thus purification and identification of right source for the advanced waste segregation and identifications tools needs to be incorporated using electrostatic intelligence, laser-induced plasma spectroscopy, laser-induced breakdown spectroscopy, density media, artificial neural networks, etc. the catalytic decomposition of waste plastic in pyrolysis process can be optimized by incorporating fundamentals of gasification reaction's chemistry, chemical thermodynamics, reaction kinematic studies, free radical reaction mechanism and evaluating their respective processing for the degradation of waste plastic into CNMs at higher temperature ranges corporations(Anzano et al. 2000; Grégoire et al. 2011; Moroni et al. 2018; Faravelli et al. 1999; Tatrari et al. 2021a, b; De et al. 2013). The pyrolysis approach for the conversion of waste plastic into CNMs is one of the best economical and sustainable solution for the promising ecological benefits along with its commercialization (Tatrari et al. 2021a, b).

5 Conclusion and Future Perspective

Plastics waste has become a serious concern for the human civilization as well as for the aquatic and other living organism. Therefore, remediation of waste plastics into value added products is the urgent need of today situation, when plastics waste creates negative impact and gradually covering of land and aquatic system. In this regard, this chapter gives the wide information and possible solution for the treatment of waste plastics into value added products. The carbon nanomaterials such graphene, CNTs and other nanostructures derived from waste plastics have the higher economical importance in compared to the general recycling of waste plastics. In addition, this chapter also gave the idea and best possible methods about the remediation of plastics waste into carbon nanomaterials. Also, this chapter covered the useful application of waste plastics derived carbon nanomaterials into supercapacitors, thereby illustrating the impact of upcycling of the waste plastics into energy applications. Thus, this chapter contains the complete information related to solution for waste plastics via conversion it into CNMs and their application into supercapacitor. Also, this will help to remove the waste plastics footprint from our surrounding in future as well as help for generation of green energy.

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Plastic Wastes to Fuels and Chemicals

Kirtika Kohli, Ravindra Prajapati, Samir K. Maity, Sultan M. Al-Salem, and Brajendra K. Sharma

Abstract Plastic production and use are currently widespread. However, plastic wastes are non-biodegradable and leave a high carbon footprint, posing challenges to ecosystems and the environment. Therefore, innovative recycling technologies should be geared towards waste-to-energy conversion solutions. Chemical recycling technologies that convert plastic wastes into feedstocks for liquid hydrocarbon fuels and chemical production are highly desirable. This chapter provides a detailed discussion of the possible plastic reuses such as for (a) hydrogen production, (b) production of gasoline and diesel fuel, (c) production of chemicals or chemical building materials, and (d) co-processing with other feedstocks. Because of the high carbon and energy content of plastics, environmentally friendly and cost-effective production of carbon nanomaterials can also be achieved by using plastic waste conversion technologies. The technical challenges and future potential of plastic waste recycling are also discussed.

Keywords Plastic waste · Gasification · Hydrogen fuel · Gasoline and diesel · Chemicals from plastic waste · Carbon nanomaterials

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1 Introduction

The non-degradability of plastic, coupled with its high carbon footprint, constitutes a major global concern. The increase in air and marine pollution levels due to plastic waste is putting pressure on researchers and policy makers to valorize this ever-increasing component of the solid waste stream into valuable products. A plastic circular economy offers an opportunity to decrease the negative impact of plastic wastes and maximize the advantages of plastics and their products, thus providing economic, environmental, and social benefits. Possible solutions for the plastics circular economy include producing plastics from alternative non-fossil fuel resources, converting plastic waste to useful products, redesigning plastic manufacturing processes and products, developing a collaboration of consumers and businesses to increase recycling and the value of plastic products, developing robust information platforms to foster the circular economy, and adopting fiscal and regulatory measures to support it. The best way to develop a plastic circular economy could be to produce high-quality recycled materials by using chemical recycling technologies. In addition, chemical processes can treat mixed and contaminated plastic wastes and can break down polymers into monomers to generate valuable products. These products can be used to produce liquid hydrocarbon (HC) fuels and chemicals. As plastics are mainly produced from refined crude oils, the properties of liquid hydrocarbon fuels generated from plastic waste might be close to that of existing fossil fuels. With the increase in energy demand, it is of interest to use plastic solid waste as a raw material for fuel production and energy that could compete with conventional fossil fuel-based products while decreasing the dependency on them in a greener fashion.

Lately, research has focused on renewable fuel production from plastic wastes and recycled plastics. Moreover, cleaner fuels are the ultimate goal in such processes where high molar ratios of hydrogen (H) to carbon (C) are evident (Karagöz 2019). These encompass fuels with gaseous aliphatic HCs and hydrogen gas (H_2), which can achieve complete oxidation due to high rates of mixing between oxygen (O_2) and the fuel (Xue et al. 2018). It must be noted here that hydrogen is the ultimate green and renewable fuel that plastic waste-to-fuel conversion processes can produce (Dinesha et al. 2019; Yilmaz et al. 2020). Hydrogen as a renewable fuel can be easily used in both hydrogen-fueled turbines and fuel cells as a transportation fuel or for the generation of electricity in internal combustion engines. It is also used as a main utility source for almost every process in heavy industry, namely in petroleum refineries where such a concept of waste to fuel can serve as an integration platform to reduce environmental burdens.

Gasoline and diesel fuels have been produced when treating various feedstock materials originating from plastic waste streams. These fuels are typically produced when the technology of pyrolysis is applied, treating the feedstock in an inert atmosphere (e.g. nitrogen gas, N_2) in either thermal or catalytic set-ups (Al-Salem et al. 2017). Pyrolysis is also a proven technology in heavy industries related to oil and gas. A review of pyrolytic setups is presented in (Al-Salem et al. 2009). This technology has also received attention in the past decade because of its ease of operation and relatively low maintenance costs. Pyrolysis has been heavily linked with the production of diesel fuel, and other oils (i.e., pyro-oil) also have been associated with low nitrogen and carbon emissions in engines (Kalargaris et al. 2017). Various diesel fuels could be recovered and subsequently blended to produce compatible fuels for engines when treating plastic solid waste (PSW), namely polypropylene (PP) using a ZSM-5 catalyst (Mangesh et al. 2020). Furthermore, ultra-low sulfur diesel (ULSD) has been targeted lately by using catalytic pyrolysis in the range of 370–440 °C (Sarker et al. 2011; Sharma et al. 2014). The making of high-value chemicals from the liquid feedstock, generated from plastic wastes, is considered a breakthrough for hard-to-recycle plastics. In the present scenario (pandemic situation), demand for fossil fuels has become historically low and may continue for a while. Therefore, researchers have also focused on the production of other value-added products such as chemicals or chemical building blocks from plastic wastes.

Plastic wastes, particularly single-use plastics, have become a major challenge for the environment, and therefore its possible re-use for (a) hydrogen production, (b) production of gasoline and diesel, (c) production of chemicals or chemical building materials, and (d) co-processing with other feedstocks has been discussed in detail.

2 Potential Fuels from Plastic Wastes

2.1 Plastic to Hydrogen Fuel

Plastics possess a high hydrogen content and a higher heating value (HHV) compared to biomass or other solid waste components, which ensures a higher hydrogen production (Ahmed and Gupta 2009). The calorific value of plastic is 40000 kJ Kg^{-1}, whereas it is 18000–21,000 kJ Kg^{-1} of biomass on a dry basis. Moreover, the ash content in plastic is almost nil. Hydrogen as a fuel would play a promising role in the future energy supply chain as a renewable and sustainable energy source. Therefore, hydrogen production from plastic waste is an area of active research (Elordi et al. 2011; Amutio et al. 2012; Alvarez et al. 2014; Cho et al. 2015; Saebea et al. 2020; Lazzarotto et al. 2020). Hydrogen is mainly produced from plastics by the gasification process. The major steps (depicted in Fig. 1) in a typical gasification process are drying, pyrolysis, combustion, and gasification. Drying is generally performed at 150 °C to remove moisture content, and it is a very rapid process. Although plastic contains a low moisture content compared to other solid wastes, this step is needed for plastics too. Pyrolysis breaks the dried feedstock into lighter volatile HC gases (CO, H_2, CH_4), char (carbon), and tar (unconverted feedstock with high molecular weight HC) in the absence of air. In particular, plastics contain many volatiles, so lighter gases (CO, H_2, CH_4) and char are mainly produced, irrespective of the polymer feedstock used. To reduce the tar formation, either a temperature higher than 900 °C or catalysts are used. In the presence of catalysts, gasification can be done even

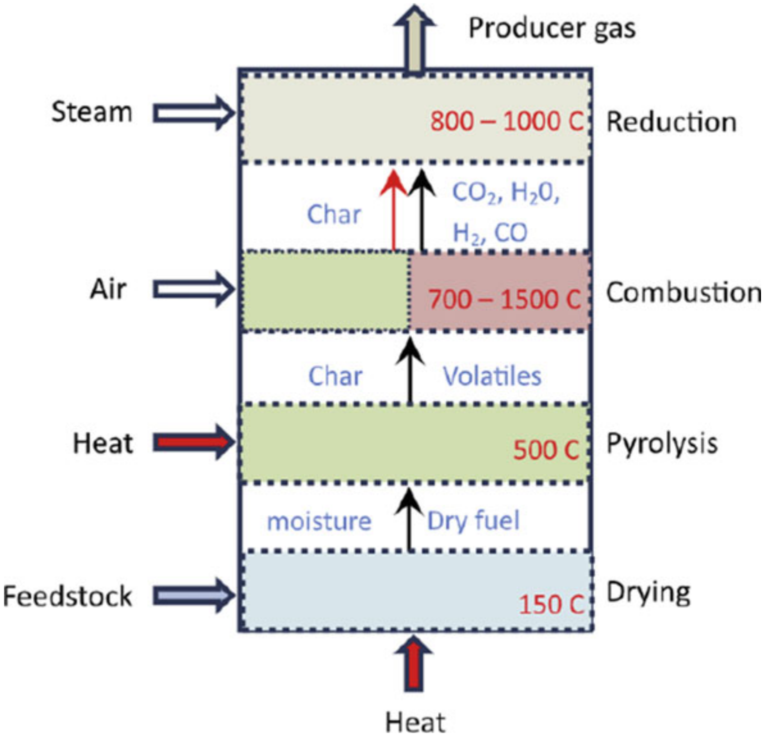

Fig. 1 Steps involved in a typical gasification process (Kannan et al. 2013)

at a lower reaction temperature. Overall, the pyrolysis step alters the physical and chemical properties of the feedstock so that it can be best suited for the combustion process. In combustion, volatiles and char produced from pyrolysis react with very little air to produce CO_2, water, and a trace of CO. In the final step, the hot, gaseous product with char is subjected to a gasification process, CO_2, and steam (or other gasifying agents) to generate producer gas or syn gas as the major product.

In general, gasifying agents, such as air, steam, oxygen, or carbon dioxide, and reforming catalysts are used to produce hydrogen (used as a fuel) in the plastic waste gasification process. Table 1 lists the advantages and limitations of the different gasifying agents used.

2.1.1 Reactor Systems Used

The reactor systems or gasifiers used for the gasification are of types such as fixed or moving bed, fluidized bed, and spouted bed. The schematics of the reactor systems are shown in Fig. 2.

Table 1 Advantages and limitations of different gasifying agents used in the plastic waste gasification process

Gasifying agent	Advantages	Limitations	Syngas
Air	Low cost and simple process	Diluted syngas, low heating-value gas, possibility of NOx formation	Significant amount of nitrogen in product gas
Steam	Improved gas quality and heating value. Improvement in reforming and water gas shift reactions	External heating and steam generation plant is required; thus, it is a high energy-intensive process. High tar formation compared to air and oxygen	Syngas with increased H_2 and CO concentrations
Oxygen	High calorific value and clean gas product compared to air, enhances combustion reactions in gasification and reduces cost of preheating reactor	Production of pure oxygen is capital and energy-intensive process	Increased formation of combustible gases with reduced nitrogen in syngas
Carbon dioxide (CO_2)	Direct conversion of greenhouse gas, i.e., CO_2 reduces the cost of carbon capture and storage, increases H_2/CO ratio for various applications	Require external heating and catalysts for reducing tar formation	CO-enriched syngas

In the fixed-bed type, the gasifying agent is passed through the fixed-bed, which is categorized as upflow, downflow, and crossflow, depending on the direction of the gasifying agent (Belgiorno et al. 2003; Al-Salem 2018). In the upflow type, feedstock moves against the flow of the gasifying agent and then goes through drying, pyrolysis, combustion, and gasification zones. The major advantages of this system are a simple process, low exit temperature, high char burnout, good heat exchange, and efficient use of the available thermal energy. In downflow, a feedstock, gasifying agent, and product gas move in a downward direction, and product gas is drawn from the bottom. The main advantage of this system is the low tar formation. In crossflow, the feedstock is passed from the top and through gas injection, combustion, reduction, and syngas production zones all on the same horizontal level.

In fluidized bed reactors (FBR), feedstock is gasified in a bed of small particles (mainly sand) in the presence of gasifying agents. In this system, the bed behaves as a fluid in the presence of a fluidizing gas. This system is preferable because of its better gas–solid reaction, better char conversion, higher throughput, longer residence time, and high-calorific-value gas production. Based on the fluidization velocity, FBRs are of two types: bubbling and circulating beds. FBRs are found to

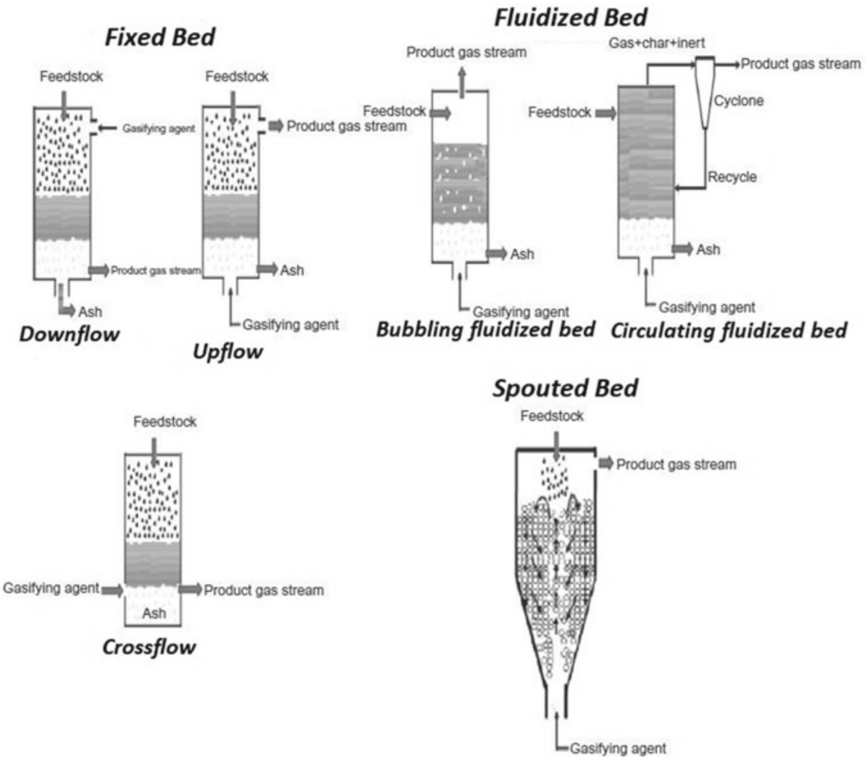

Fig. 2 Schematics of conventional gasification reactor systems (Belgiorno et al. 2003; Al-Salem 2018)

be suitable for plastic waste gasification because these systems are isothermal and can operate under various operating parameters. The use of FBRs is always more favorable compared to the fixed bed reactor to easily control coking of the catalyst, particularly at very high temperatures, where coking is a main concern. However, there are certain difficulties that are reported while using FBRs for the plastic waste gasification, including agglomeration and defluidization problems (Amutio et al. 2012; Elordi et al. 2011). These can be overcome by using a conical spouted bed reactor (CSBR).

The CSBR system is also a fluidization technique. The difference between spouted and fluidized beds is in the dynamic behavior of solid particles. In this system, a gasifying agent is passed through a small, centrally located single orifice at the bottom. Thus, central spouts are formed as particles move upwards. The major advantage of this reactor system is its ability to agitate feedstocks that are coarse, sticky, uniform in size, and heat sensitive. In this reactor system, high heat transfer rates (Makibar et al. 2011) with vigorous solid flow ensure almost immediate melting, sand particle coating with fused plastic, pyrolysis, and subsequent gasification of the plastic waste to minimize the undesired tar and solid residue formation. Also, the CSBR reactor design is easy, it has a low pressure drop, and its throughput by reactor volume unit is much higher compared to fluidized beds because of the lower amount of sand required for fluidization. Another advantage is the low segregation involved in the operation with catalysts in situ for tar cracking or reforming. These reactor systems can be useful for large-scale processes. This technology has been scaled up, and a biomass pyrolysis pilot plant (25 kgh^{-1}) is currently operative (Makibar et al. 2011, 2012). The main difficulty of the plastic waste gasification is energy integration in a highly endothermic process. This can be overcome by (a) operating with a dual-spouted bed reactor, i.e., gasifier and combustor (Erkiaga et al. 2013) and (b) co-feeding a mixture of steam and oxygen to balance the energy required in the process, although this might reduce the hydrogen content in the generated syngas.

2.1.2 Reaction Conditions Used

Gasification is mainly performed in the temperature range 850–1300 °C (Saebea et al. 2020). Process conditions such as feedstock properties, type of catalyst, catalyst-to-feedstock ratio, steam-to-feedstock ratio, gasifying agent, reactor system type, and gasification temperature significantly affect hydrogen production (Wu and Williams 2008). The most important parameter is an equivalence ratio (ER) to improve the gas yield and quality when gasification is performed in the presence of air. ER is defined as the actual air–fuel ratio to the stoichiometric air–fuel ratio for combustion. To show the ER effect on gasification of mixed plastic, a few examples are: (i) ER increases from 0.2 to 0.45 during air gasification of PP, and HHV decreases from 11.3 to 5.17 MJ Nm^{-3} (Xiao et al. 2007) and (ii) ER increases from 0.2 to 0.3 during air gasification of polyethylene (PE), resulting in a decrease of the tar yield from 14.6 to 7 kg h^{-1} (Arena et al. 2009). Overall, ER should not be too high to generate producer gas with more hydrogen.

Another significant parameter is the gasification temperature used. An increase in the gasification temperature enhances the gas–solid reactions, thereby improving the efficiency of the processes by increasing the gas yield and reducing heavier HCs, tar, and char yields (Erkiaga et al. 2013). At a high temperature, Boudouard and reforming reactions enhance hydrogen and CO evolutions from plastic waste gasification (He et al. 2009). The selectivity and yields of hydrogen are dependent on the catalysts and the operating temperatures used. Despite the many advantages of using higher temperatures, these have their own limitations. At a high temperature, gasification reduces the HHV of the producer gas.

Feedstock property analysis, i.e., ultimate and proximate analysis, is required to design a gasifier for plastic wastes because these properties signify the quality of a given fuel. The elemental analysis of plastic wastes has a significant effect on the quality and composition of the producer gas produced from plastic waste gasification. For instance, polyethylene terephthalate (PET) is rich in oxygen content; therefore, gasification of its mixture with PE significantly affected HHV and gas yields in terms of a higher CO evolution, flue gas temperature increases, and a greater hydrogen yield (Kannan et al. 2013). The presence of chlorine (>20 wt%) in polyvinyl chloride

(PVC) material is very challenging for PVC gasification. Because PVC produces hydrogen chloride (HCl) during the gasification process, more gas cleaning processes are required prior to the immediate use of producer gas. Cleaning is crucial because of the corrosive and harmful nature of HCl, which will contribute to acid rain and halogenated HCs (Bhaskar et al. 2002). PP can be a good source of hydrogen, even without a catalyst; therefore, PP can be used in co-gasification to increase the gas yield and hydrogen content in the producer gas (Alvarez et al. 2014). Saebea et al. (2020) has used both PE and PP as a feedstock in their gasification simulation exercise in contact with steam as a gasifying agent. The steam-to-feed (S/F) ratio of 1:5 was optimal for producer gas production under an operating temperature of 900 °C.

Catalysts are considered an important parameter used to maximize hydrogen production. Nickel-based catalysts are found to be effective for gasification technologies because of their lower price and high catalytic activities (Wu et al. 2012; Wang et al. 2012; Acomb et al. 2013; Cho et al. 2015). Ni catalysts have high catalytic activity to break the C–C bond and hydrogen formation from H atoms with a high rate in the water–gas shift reaction. Steam gasification using calcium carbonate in an FBR reactor has also proven effective at a high temperature of 900 °C (Lazzarotto et al. 2020). Gasification of PE and PP using air as a gasifying agent yields a product gas with a lower heating value (approx. 6 MJ Nm^{-3}). The producer gas composition mainly depends on the amount of fluidization air and bed material. Tar formation can be reduced by using in-bed catalysts. Cho et al. (2015) used a plastic waste mixture having 45 wt% LDPE, 45 wt% PP, and 10 wt% PVC-rich fractions. The authors used a two-stage gasifier system that consisted of an FBR and a tar cracking zone. In addition, the effect of a Ni-loaded activated carbon and Ca-based additive (in particular, oyster shells) on chlorine content and tar removal was investigated. The results showed that in the presence of Ca-based additives, the HCl content in the producer gas was below 1 ppm. The use of Ni-based (~5 wt%) activated carbon led to an increase in hydrogen production. However, the carbon deposition on the nickel catalyst surface is a major challenge in hydrogen production, as it can deactivate the catalyst. Three types of carbon deposition such as whisker type carbon (filamentous carbon), pyrolytic, and encapsulating carbon are seen on the surface of the catalyst. Wu et al. (2012) confirmed the presence of carbon nanotubes on the surface of the catalyst using transmission electron microscopic (TEM) analysis of the filaments deposited on the catalyst surface. Therefore, simultaneous production of carbon nanotubes and hydrogen from plastic feedstocks increases the efficiency and economic value of the process.

A few research studies that demonstrated the use of real plastic waste feedstocks for the production of hydrogen are presented in Table 2. Wu and Williams (2010) studied the production of hydrogen from post-consumer plastic waste (from municipal solid waste, MSW) using a two-step pyrolysis-gasification approach. The authors demonstrated the effect of reaction parameters such as a catalyst (Ni–Mg–Al) to gasification temperature, plastic ratio, and water injection rate for hydrogen production. The findings included the following. (a) With 0.26 g of catalyst, hydrogen production was enhanced to 0.26 g H_2g^{-1} plastic waste compared to 0.015 g H_2g^{-1} plastic waste without a catalyst at a temperature of 800 °C and a water injection rate of

Table 2 List of a few recent studies related to the production of hydrogen from plastic wastes

Feeds	Catalyst	T, °C	Steam injection rate, gh^{-1}	Gas yield, wt%	H_2 yield	Tar yield, wt%	References
MSW	Ni–Mg–Al	800	4.74	205.7	0.258 $gH_2\ g^{-1}$ feedstock	19.4	Wu and Williams (2010)
MSW	NiO supported on modified dolomite	800	–	1.62 Nm^3kg^{-1}	80.68 gH_2kg^{-1}	0.23 g/Nm^3	Wang et al. (2012)
WEEE	Ni/Al_2O_3 (10% Ni)	800	4.74	28.3	52vol%*	–	Acomb et al. (2013)
HIPS		800	4.74	40.5	63vol%*	–	
ABS		800	4.74	16.2	63vol%*	–	
LDPE	–	800	4.74	85.7	9.2^a	12.5	Acomb et al. (2014)
PP	–	800	4.74	80.3	6.9^a	14	
PS	–	800	4.74	56.1	7.4^a	12.3	

T = gasification temperature; H_2 = hydrogen; MSW = municipal solid waste; WEEE = waste electrical and electronic equipment; HIPS = high impact polystyrene; ABS = acrylonitrile–butadiene–styrene; LDPE = low-density polyethylene; PP = polypropylene; PS = polystyrene; * = H_2 by gas composition; and a = H_2 g/100 g feedstock

4.74 gh^{-1}. (b) Coke deposition on the catalyst was decreased with the increasing catalyst-to-plastic ratio; however, no significant change was observed for hydrogen production. (c) With an increased temperature from 600 to 900 °C, total gas and hydrogen production yields increased. The amount of coke deposited on the catalyst was first increased and then decreased. (d) With an increase in the water injection rate from 1.90 to 14.20 gh^{-1}, total gas yields were increased from 183 to 295 wt%. In the total gas yield, CO concentration decreased, the hydrogen concentration showed no significant change, and total hydrogen production increased. The hydrogen yield increased in the order of low-density polyethylene > polystyrene > PP (Acomb et al. 2014) when the steam injection rate was increased. Plastic waste from waste electrical and electronic equipment (WEEE) was processed using the pyrolysis-gasification method to produce hydrogen with an added Ni/Al_2O_3 catalyst. The results were also compared with high-impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS), the main constituents of WEEE plastics (Acomb et al. 2013). With the increase of Ni in the catalyst, an increase in hydrogen production was observed. This indicated that the metal concentration plays a promising role in catalytic activity. The increasing order for the H_2 yield was HIPS > ABS > WEEE.

Recently, gasification in supercritical water and using plasma processes was also reported (Cao et al. 2020; Su et al. 2020). Hydrogen was produced at high yields and purity by performing gasification with supercritical water when plastic solid waste (PSW) and black liquor soda lignin were treated (Cao et al. 2020). The addition of lignin showed a great increase in the overall efficiency, and the highest hydrogen yield of 64 $molkg^{-1}$ at 700 °C was observed. A similar principle employing supercritical water gasification treating PSW and food waste was studied by Su et al. (2020) to produce 3.11 molkg^{-1} of hydrogen when using 0 to 3.5 wt% range of plastic content in the feedstock.

Furthermore, plasma gasification is receiving renewed attention for hydrogen production which depends on the ultimate analysis and seasonality of solid wastes encompassing plastic solid wastes (Mazzoni and Janajreh 2020). Plasma gasification is a process in which plasma torches create an electric arc via the passage of an electric current through a gas. Plasma is created through plasma torches by heating up gas (mainly air), to an extremely high temperature (approx. 3900 °C). In this process, high temperatures of 1500 and 5000 °C are used with a very short residence time, and the gasifiers used have a high tolerance to low-quality feedstocks. Organic material is converted into syngas, while inorganic matter ends up as slag. Compared to the conventional gasification process, plasma gasification results in a high purity of producer gas with a low amount of tars. The drawbacks associated with plasma gasifiers are very high electricity requirements, higher operating costs, and higher investments.

2.2 *Plastic to Gasoline and Diesel Fuels*

The calorific value of common fuel oils is 20900 Btulb^{-1}. Plastics such as PE, PP, polystyrene (PS), PET, and PVC have caloric values of 20,000, 19,300, 17,900, 9290, and 8170 Btulb^{-1} (Shah et al. 2010), which make these potential feedstocks for fuel production technologies. Table 3 presents properties of plastic waste fuel and regular gasoline. Hydrocracking, thermochemical conversion/pyrolysis, and catalytic conversion are the most widely used methods for fuel (mainly gasoline and diesel) production from plastic wastes. Hydrocracking involves treating plastic waste with a catalyst in the presence of hydrogen at a moderate temperature (150–400 °C) and pressure (3–10 MPa). With this method, a high-quality gasoline is obtained

Table 3 Properties of regular gasoline and plastic waste fuel

Properties	Regular gasoline	Plastic waste fuel
Color, visual	Orange	Pale Yellow
Specific gravity at 28 °C	0.7423	0.7254
Specific gravity at 15 °C	0.7528	0.7365
Gross calorific value	11,210	11,262
Net calorific value	10,460	10,498
API gravity	56.46	60.65
Sulfur content, by mass	0.1	<0.002
Flashpoint (Abel), °C	23	22
Pour point, °C	≤20	≤20
Cloud point, °C	≤20	≤20

by using a wide variety of feedstocks. Typically, feedstocks used were PE, PET, PS, PVC, plastic waste from MSW, co-processing of plastic waste with coal, co-processing of plastic waste with different refinery oils like vacuum gas oil (VGO), scarp tyres, and co-processing of scrap tyres with coal. Catalysts such as transition metals (Pt, Mo, Ni, Fe) supported on alumina, amorphous silica-alumina, zeolites, and sulfated zirconia have been studied for plastic hydrocracking. Both cracking and hydrogenation functions were performed with these catalysts. Solvents like 1-methyl naphthalene, tetralin, and decalin have been used sometimes for proper mixing of the reactants.

Table 4 summarized some of the research studies on gasoline and diesel fuel production. Thermal cracking or pyrolysis includes a breakdown of the polymer chains into useful low molecular weight compounds by heating in the absence of oxygen. Typically, thermal cracking is performed at temperatures of 350–900 °C, resulting in the formation of non-condensable high-calorific gas, a volatile fraction, and carbonized char or solid residues. The volatile fractions can be separated into hydrocarbon oils that mainly consist of paraffins, isoparaffins, olefins, naphthalenes, and aromatics. Hydrocarbons between the boiling range of 35–190 °C can be used as motor gasoline, between 190 and 290 °C as diesel #1, between 290 and 340 °C as diesel #2, between 340 and 538 °C as VGO, and >538 °C as the residue (Sharma et al. 2014). Product compositions and yields depend primarily on the nature of the plastic wastes and the process conditions such as reaction temperature and residence time. Among these, residence time is affected by the reactor design. The major drawback associated with thermal cracking is that it requires high temperatures, and a broad range of products can be obtained.

In catalytic cracking, effective and selective catalysts are used to perform the cracking reactions. Catalysts that are mainly reported for the plastic pyrolysis are fluid cracking catalysts (FCC) (Miskolczi et al. 2009; Elordi et al. 2009), reforming catalysts (Buekens and Huang 1998), and activated carbon (Scott et al. 1990; Aguado et al. 2008). Less severe reaction conditions such as lower reaction temperature and reaction time are used in catalytic cracking. Besides this, catalytic cracking produces a much narrower product distribution of carbon atom number with lighter HCs, and reactions occur at a considerably lower temperature compared to thermal cracking. To make this process even more attractive, cheap catalysts (by using low cost metals) are required. In addition, this can be optimized by reusing the catalysts and using effective catalysts in low quantities. The catalytic pyrolysis of high-density polyethylene (HDPE) using ultrastable-Y-zeolite produces HCs in the gasoline range (C_4-C_{12}). The major products were iso-paraffins having a high octane number and used as a high-quality fuel (Manos et al. 2000). A 10 wt% NiO/ZrO_2 catalyst showed promising conversion for the catalytic pyrolysis of PS beads. With this catalyst, more than 80 wt% of the liquid product oil was obtained. The tested acidic catalyst was found to be more selective towards C_{16} carbon number HCs (diesel fraction) (Amjad et al. 2020).

Most researchers used batch or semi-batch reactors for the thermal and catalytic pyrolysis of virgin and post-consumer plastic wastes because it is easy to control the process operation and parameters. In general, the reaction parameters used were

Table 4 Details of the research studies that discussed the production of fuels (gasoline and diesel) from plastic wastes

Feeds	Catalyst	Reaction conditions	Product oil yields, wt%	Oil composition	References
HDPE grocery bags	–	T = 420–440 °C	74	19.4% < 190 °C fraction; 41.4% 190–290 °C fraction; 23.4% 290–340 °C fraction; 15.8% 340–538 °C fraction	Sharma et al. (2014)
Waste PE and PP	–	T = 500 °C; t = 4.7 min	70–80	40% motor gasoline; 25% diesel#1; 10% gas oil; 25% VGO	Kunwar et al. (2017)
PS beads	10% NiO/ZrO_2	T = 350 °C; Catalyst: Plastic = 1:40	80	~60% diesel range HCs	Amjad et al. (2020)
Microwave-assisted pyrolysis					
HDPE	Tire or carbon as MW absorber	T = 490–600 °C; Tire/Carbon:HDPE = ~1.3–2.1	43.9–83.9	38.73–88.37% aliphatics; 6.61–17.31% aromatics	Undri et al. (2014)
LDPE	MgO	T = 350–550 °C; MgO:LDPE = 1.15–1.3	24.2–38.5	79.5–96% gasoline fraction; 15–50% MAHs	Fan et al. (2017)
LDPE	NiO and HY	T = 450–600 °C; NiO:HY:LDPE ratio = (1–5):15:150	48.08–51.23	>2% C_5–C_{12} gasoline fraction; 34.56–46.61% aromatics; 26–30% isomerized aliphatic	Ding et al. (2019)

HDPE = high-density polyethylene; LDPE = low-density polyethylene; PS = polystyrene; T = temperature; MW = microwave; MgO = magnesium oxide; NiO = nickel oxide; and HY = zeolite

reaction temperature 300–900 °C, reaction time 30–90 min, mass ratio of reactants to catalyst 30:1 to 2:1 (Escola et al. 2011; Renzini et al. 2011). Catalytic pyrolysis reportedly can be performed even at a low temperature (200–275 °C). Thermal cracking of LDPE bags at 275 °C produces 41 wt% gases, 49 wt% oil, and 10 wt% solid residues (Marcilla et al. 2009). On the contrary, catalytic pyrolysis using zeolite at 255 °C produces 36 wt% gases, 51 wt% oil, and 13 wt% waxes, clearly indicating the preferred selectivity of the zeolite catalyst toward liquid yield. Since the temperature of the reaction is lower in a catalytic reaction, its gas yield becomes lower. The use of FBR reactors were also reported for the plastic waste upgrading. These have several advantages such as excellent mixing properties and improved heat transfer from reactor to feedstock compared to batch reactors (Yuan et al. 2014). In these reactor systems, a narrower and more uniform product spectrum can be produced by optimizing the residence time of the plastic wastes in the reactor (Jung et al. 2010). The most advantageous is that the catalyst is continuously regenerated in the regeneration section. Even the thermal balance is quite optimal. Therefore, in this system, the whole reactor system needs not shut down periodically to unload and reload the spent catalyst. In this way, the effective use of man-hours is maximized. This process might be feasible in terms of the economy because of the reduction of costs in catalyst replacement and regenerations. However, attention should be paid to avoid bed fluidization, as this can easily happen when melted plastic sticks on the fluidized bed. To avoid this problem, use of the CSBR was proposed. In the CSBR reactor system, vigorous contact between different phases and collision between particles decrease the chance of particle agglomeration in the bed material. In addition, other advantages associated with CSBR are a lower pressure drop and extremely short residence time (20 ms^{-1}), which helps to avoid secondary reactions resulting in coke formation (Elordi et al. 2009). Waxes with high selectivity are generally obtained from plastic waste upgrading by using CSBR. Waxes produced from LDPE, HDPE, and PP showed that these are rich in heavy crude oil. However, when increasing the pyrolysis temperature, the percentage of gasoline and light cycle oil fractions can be increased in these waxes. Paraffin-rich waxes can be produced at a lower temperature; however, the olefin content can be increased with temperature. The wax is a suitable feedstock that can be used in FCC units to produce gasoline, naphtha, and other commercial HC fractions. The waxes produced can be treated in another reactor to produce gases and liquids. In some countries such as India, Africa, and South East Asia, the produced wax is extensively used to produce candles and related materials, providing employment in non-organized sectors. Beside these, two-stage pyrolysis reactor systems including pyrolysis followed by catalytic hydroreforming were also explored. In these systems, the plastic waste was first melted and thermally cracked in the reactor at the bottom, and the vapors produced were then flown upwards and reacted with the catalyst in the fixed bed reactor. In this system, there is no direct contact with melted plastic, so problems such as catalyst recovery and catalyst deactivation can be avoided. At 475 °C, a complete conversion of LDPE was observed with 16% of lighter products, 41% gasoline fraction, and 40% diesel fraction.

The use of microwave-assisted pyrolysis (MAP) has also been reported recently having several advantages compared to traditional pyrolysis, such as a faster heating rate and higher cost effectiveness. In this pyrolysis process, microwave power is applied to the polymer materials. Using a high temperature up to 1000 °C in a short period of time is feasible when using a microwave absorber (metal or carbon materials). The shape of the absorber plays an important role in MAP because it affects the amount of heat generated in the microwave. Different microwave absorbers like tire or carbon were used for the MAP of HDPE and PP plastics. Liquid products obtained after MAP of HDPE contain a mixture of linear alkane and a very low amount of aromatics, and the liquid from MAP of PP contained a mixture of methyl branched alkanes and alkenes with very few aromatics and dienes (Undri et al. 2014). The addition of MgO during ex-situ catalytic MAP improved the hydrogenation of alkenes to alkanes and enhanced the catalytic conversion of a diesel fraction to a gasoline fraction. Increasing the catalyst loading along with the pyrolysis temperature favored the conversion of alkenes to mono-aromatics (Fan et al. 2017). Ding et al. (2019) performed the catalytic MAP of LDPE using NiO and HY as in-situ and ex-situ catalysts to produce gasoline-range HCs. The results indicated that HY zeolite improved the production of gasoline-range HCs with a higher oil yield and higher octane number of oil compared to the non-catalytic process. The optimized reaction conditions used were a pyrolysis temperature at 500 °C, HY-to-LDPE ratio of 1:10. The addition of NiO in an appropriate amount enhanced the yield of high-octane number compounds with a high oil yield. These literature studies showed that the catalytic MAP of the commingled polymer waste can be done without using manual sorting.

Ultra-low sulfur diesel (ULSD) is a type of diesel fuel that contains 15 parts per million (ppm) or less than 15 ppm of sulfur content. This ULSD fuel is also known as "clean diesel." Currently, ULSD is produced from crude oils. However, in the past five to six years researchers have demonstrated the conversion of plastic wastes to ULSD. In addition, a few technologies have been reported. Recycling Technologies (U.K.) developed a technology that converts residual plastic waste into a low-sulfur hydrocarbon compound known as Plaxx (Link1). Plaxx can be used as a petrochemical resource or as a clean and sustainable fuel substitute for fossil-based heavy fuel oil. In 2017, Plastic2Oil® (P2O) technology that can produce high-quality ULSD from a plastic waste feedstock (Link 2) was demonstrated. RES Polyflow technology was designed to process mixed plastic wastes including single-use, difficult-to-recycle items such as expanded PS foam, film, children's toys, and flexible packaging, (Link 3). This plant is America's first commercial-scale plastic-to-fuel plant, located in Ashley, Indiana. This facility was expected to process 100,000 tons of plastic waste annually into 18 million gallons of ULSD and naphtha blend stocks and 6 million gallons of commercial-grade wax.

Because of the very low or negligible sulfur content in plastics, it is expected that the pyrolyzed fuels from plastic waste pyrolysis would have a lower sulfur content compared to conventional fuels. To produce ULSD fuels, those obtained from pyrolysis of plastic waste materials need to be further processed using either double distillation (Sarker et al. 2011) or desulfurization technologies (Al-Lal et al. 2015). In the case of desulfurization processes, refineries or industries require a secure supply of hydrogen, which will be expensive. Sarker et al. (2011) developed a process in which depolymerized plastic waste was refined using a mini-scale double condensation process and a fractional distillation process. The plastic materials used for the demonstration process had 85% C, 13% H, 0.8% N, and 1.2% S. In this process, first the plastic waste was converted into a liquid slurry through a thermal liquefaction process at 370–420 °C, then the slurry was cooled, and then the slurry was distilled using a cracking process, condensing the liquid slurry with distillate to recover the liquid hydrocarbon fuels. Produced fuel (first distillation) was passed through another distillation process (second distillation) to recover low-sulfur fuel.

A comparative examination using differential scanning calorimetry (DSC) analysis showed that fuel obtained after the second distillation contained HCs in the range of C_9 and C_{27}, which can be used as a diesel fuel. In addition, the fuel produced after the second distillation had only 3 ppm of sulfur. In another study, the authors recovered the four fractions: motor gasoline (<190 °C); diesel#1 (190–290 °C); diesel#2 (290–340 °C); and VGO (>340 °C+) from the plastic crude oil (PCO), which was obtained by pyrolysis of waste plastic grocery bags (Sharma et al. 2014; Kunwar et al. 2017). The fractions were recovered by the distillation process. Blends of diesel#1 and diesel# 2 were prepared in different volume percentages (10–50 vol%) in ULSD, and the properties were analyzed as per ASTM specifications (Table 5). Pyrolyzed polyethylene hydrocarbons, diesel#2, met all ASTM D975 and EN 590 specifications after the addition of suitable antioxidants, except density (as per EN590).

Table 5 Fuel properties of pyrolyzed polyethylene hydrocarbons (PPEH) and ultra-low sulfur diesel (ULSD) and comparison to petrodiesel fuel standards (Sharma et al. 2014)

Properties	ASTM D975	EN 590	PPEH-L	PPEH-H	ULSD
Low temperature, °C					
CP	–	–	−30.1 (0.1)	4.7 (0.2)	−17.5 (0.3)
PP	–	–	−37.3 (0.6)	4 (0)	−20.3 (0.6)
CFPP	–	–	−31 (0)	3.7 (0.6)	−16.0 (0)
Oxidative stability					
IP at 110 °C, h	–	≥20	3.9 (0.3)/14.4 (0.8)[d]	12.9 (1.5)/>24[d]	>24
OT, °C	–	–	175.2 (0.3)/186.9 (0.4)	190.1 (0.7)/202.1 (0.5)[d]	196.2 (0.5)
KV at 40 °C, mm^2s^{-1}	1.9–4.1	2.0–4.5	1.20 (0.01)	2.96 (0)	2.28 (0.01)
DCN	≥40	≥51	54.6 (1.1)	73.4 (1.4)	47.4 (0.9)
Flash point, °C	≥52	≥55	<30	81.5 (0.7)	65 (0.7)
Wear scar at 60 °C, μm	≤520	≤460	293 (3)	198 (10)	581 (5)
Sulfur, ppm	≤15	≤10	3	2	8
Density at 15 °C, kgm^{-3}	–	820–845	776 (1)	802 (0)	840 (1)
ST at 40 °C, Mnm^{-1}	–		106 (2)	64 (3)	25.1 (0.2)
Moisture, ppm	–	≤200	45.86 (0.22)	46.16 (0.09)	49 (3)
HHV, $MJkg^{-1}$	–				45.15 (0.19)

– Not specified
[d] With 1000 ppm BHT added

3 Chemicals from Plastic Wastes

The upgradation of plastic wastes can generate a range of HCs such as paraffins, olefins, and aromatics. The HCs yields are based on the type of plastic and reaction parameters used. For instance, chemical recycling of polyolefins that contains 2/3 of the plastic wastes produces mainly light olefins and benzene, toluene, and xylene (BTX). The pyrolytic product from PS waste can be refined to produce styrene. Table 6 provides the lists of major chemicals that can be produced from various plastic wastes and are discussed in the following section.

PE and PP can be decomposed into a range of paraffins and olefins. In the case of PE pyrolysis, an increase in paraffin yields was observed from 31 to 45%; olefins decreased from 45 to 32% when raising the pyrolysis temperature from 350 to 600 °C (Demirbas 2005). In comparison, the yield of aromatics increased from 3 to 6% and the yield of naphthalenes decreased from 22 to 17% (Demirbas 2005). In PP pyrolysis, however, the paraffin yield decreased (33–27%) with an increasing temperature from 350 to 520 °C, and aromatics increased (0.8–11%) on increasing temperatures from 350 to 600 °C. A two-step process involving pyrolysis and downstream catalytic cracking was applied for the light olefin production from HDPE. Pyrolysis was performed in a CSBR at a reaction temperature of 500 °C. The volatile stream obtained from the HDPE pyrolysis in a CSBR mainly contained waxes ($>C_{21}$), and this volatile stream was passed through a fixed-bed (downflow) catalytic reactor in the presence of HZSM-5 zeolite. It was found that 67% of the waxes were converted

Table 6 List of various chemical products that can be obtained from different plastics

Polymer	Chemical products
PE, PP	Paraffins and Olefins
PS	Styrene, Benzene, Toluene, Ethylene, and Xylene
PET	Bis(hydroxyethyl)-terephthalate, Terephthalic acid (TPA), Ethylene glycol, Dimethyl terephthalate, Diamides of TPA, Acetophenone, Acetaldehyde, Benzoic acid, and Benzene
PU	Bi or polyfunctional amines and alcohols, Phosphorous containing oligourethanes
PA	Cyclic ɛ-caprolactum, Hydroxyalkanoates, Diols, and Hexamethylene diamine
Plastic waste	Waxes (HCs > 21), Microcrystalline waxes, and Lube and grease basestocks
Carbon-containing materials from plastics	
PE, PP, PS, PET, PAN, PFR, PVA, PVC	Amorphous carbon (activated carbon, carbon spheres, and carbon nanofibers) Graphitic carbon (carbon nanotubes and graphene)

PE = polyethylene; PP = polypropylene; PS = polystyrene; PET = polyethyleneterephthalate; PU = polyurethane; PA = polyamide; PFR = phenol–formaldehyde resin; PAN = polyacrylic nitrile; PVA = polyvinyl amide; and PVC = polyvinyl chloride into light olefins. This is because of the shape selectivity, low hydrogen transfer capacity, and moderate acid strength of the HZSM-5 zeolite (Artetxe et al. 2013). Besides the acidity of the HZSM-5 zeolite, the short residence time in the reactor was found to increase the selectivity of the light olefins and decrease the coke formation. The high-value aromatic chemical raw materials such as benzene, toluene, and other aromatic HCs can also be obtained by refining the pyrolytic product. For instance, the pyrolysis of PE and PP produces a liquid product that mainly contain BTX compounds (Jung et al. 2010). The BTX yield can be increased by an increase in reaction temperature and using suitable catalysts. In general, aromatic compounds are formed due to secondary reactions and shape selectivity of the catalysts.

A styrene monomer with a high selectivity can be obtained via PS pyrolysis by thermal and catalytic routes. A 63% yield of styrene at 477 °C was observed (Demirbas 2005). In another study, the product oil containing 83% (w/w) styrene was generated by PS pyrolysis at 520 °C using an FBR reactor (Ward et al. 2006). Catalytic pyrolysis using ZSM-5 zeolite produces oil, which mainly contain single-ring aromatics like ethylbenzene and toluene (de la Puente and Sedran 1998). Zhang et al. (1995) reported that the various basic catalysts helped to increase monomer yields compared to thermal and/or acid-catalyzed pyrolysis. The production of monomers such as benzene, toluene, ethylene, and xylenes (BTEX) was reported by using the two-stage pyrolysis process, which includes an auger and an FBR (Park et al. 2020). A high value, i.e., 26%, of BTEX was obtained.

For treating PET wastes, glycolysis (Yue et al. 2013), hydrolysis (Sinha et al. 2010), methanolysis (Kao et al. 1998), and aminolysis (Zahn and Pfeifer 1963) methods are mainly used. In the glycolysis process, PET is treated with glycols such as ethylene glycol (EG), propylene glycol, diethylene glycol, and triethylene glycol (TEA) with transesterification catalysts to yield bis(hydroxyethyl)-terephthalate (BHET) (Yue et al. 2013). In contrast, by the hydrolysis method, terephthalic acid (TPA) and EG are mainly produced at a high pressure (1.4–2 MPa), high temperature (200–250 °C), and longer reaction times (Sinha et al. 2010). Hydrolysis can be acidic (sulfuric or nitric acid), alkaline (sodium hydroxide), or neutral (metal catalysts). The cost associated with the process is very high, and therefore this process is not commercially used. The next treatment method is methanolysis, i.e., treatment with an alcohol, in which dimethyl terephthalate (DMT) and EG are mainly produced (Kao et al. 1998). The produced DMT is purified by crystallization and distillation processes. Finally, the aminolysis method involves the reaction of PET with amines such as allylamine, morphine, hydrazine, and polyamines to produce diamides of terephthalic acid (TPA) (Zahn and Pfeifer 1963).

Other chemicals such as vinyl benzoate, benzoic acid (BA), and acetaldehyde can be produced from PET pyrolysis. PET pyrolysis using ZSM-5 zeolite and $NiCl_2$ catalysts decreased the waxy product yields and produced more liquid products (Jia et al. 2020). Pyrolysis of waste PET takes place by cleavage of an ester linkage, leading to the formation of vinyl ester and carboxyl compounds, mainly BA. The produced vinyl ester can be decomposed into compounds like acetophenone, acetaldehyde, and lighter HCs (C_1–C_3) (Cit et al. 2009). BA, which is a high-value chemical around $4000 Mton (Loong 2011), is mainly used in the food and beverage industries. BA is also used as a feedstock for manufacturing phenols, benzoates, and other antifungal preservatives. Thus, the recovery and production of BA from waste PET can produce a potentially useful chemical. Dimitrov et al. (2013) demonstrated that in the presence of a different medium or contaminants, different pyrolyzed products can be obtained. For instance, when pyrolysis of PET is performed with acidic contaminants, CO_2/acetaldehyde, BA, and vinyloxycarbonyl benzoic acids are formed. In the presence of a base, tetramethylammonium hydroxide (TMAH), dimethyl terephthalate, short-chain alcohol, and trimethylamine (TMA) can be produced. TMA and short-chain alcohol are formed from the dissociation of TMAH. In another study, TPA was produced from the pyrolysis of PET, which later can be converted to benzene in the presence of CaO under controlled conditions.

Chemical compounds such as polyols and amine intermediates can be produced from PU (flexible foams) hydrolysis. The reaction of PU foams in the presence of water, glycols, and basic catalysts is widely used (Sheratte 1978; Grancharov et al. 2007). Multifunctional alcohols and amines can also be obtained by treating PU with diamines or amino alcohols. For this process, PU is dissolved in suitable solvents such as cyclic ether, a chlorinated HC solvent, or N-methyl pyrrolidone; the reaction temperature for this reaction ranges from 200 to 210 °C with catalysts (Sheratte 1978). Phosphorous containing oligourethanes can also be produced from PUs and can be used to make new PUs with an enhanced flame retardant, UV resistance, and adhesive properties. These urethanes can be produced by treating PUs with esters of phosphoric and phosphonic acids (Grancharov et al. 2007). This technology has been less explored.

Cyclic ε-caprolactam (CPL) as a monomer that can be recovered from PA depolymerization. The depolymerization of PAs can be carried out by alcohols/glycols, ammonia, water, or in the presence of catalytic agents (Herzog et al. 2013; Chen et al. 2010). The major challenge associated with PA depolymerization is the harsh reaction conditions, which lead to the formation of undesired side products that create problems in purification. For instance, a 78% CPL yield was obtained from PA6 by hydrolysis in the presence of phosphotungstic acid at a reaction temperature of 300 °C and reaction time of 85 min. Products like 6-amino-caproic acid and water-soluble oligomers were produced as side products (Chen et al. 2010). The combination of diols and diesters can be produced from PA-based wastes in supercritical methanol at 330 °C (Kamimura et al. 2014; Matsumoto et al. 2017). Aminolysis can convert PA 66 and PA 6 plastics to hexamethylenediamine (HMDA). This occurs by the conversion of carboxylic groups through the amides to nitrile, and then these can be hydrogenated to provide a final amine group (Duch and Allgeier 2007).

Besides producing chemical raw material and chemicals, the use of plastic wastes for other useful applications have also been reported, for example, as an additive in asphaltic mixtures (Taherkhani and Arshadi 2019; Merkel et al. 2020), microcrystalline wax, paraffin wax (Jixing et al. 2003), and lube and grease base stocks (Miller 2005).

Plastic wastes can also be used to generate carbon materials such as amorphous and graphitic carbon. The amorphous carbons mainly include activated carbon, carbon spheres, and carbon fibers, while carbon nanotube (CNT) and graphene are graphitic carbon materials (Bazargan and Mckay 2012; Zhou and Levendis 2014). Typically, pyrolysis followed by carbonization is mainly used to produce carbon materials. These processes produce various HC gases and a residual product that has a high amount of carbon (carbon materials). These processes are classified as anoxic pyrolysis, catalysis, and pressure carbonization, as described by Chen et al. (2020).

In the anoxic pyrolysis process, plastics are treated at a high temperature in an inert environment under atmospheric pressure. The carbon atoms present in plastics are converted into carbon materials during the heat treatment process by an aromatization mechanism. Gases such as NH_3, CO, CO_2, HCl, CH_4, and H_2 are also formed. Phenol–formaldehyde resins (PFR) are mainly used to produce amorphous carbon in an inert environment using a high-temperature pyrolysis process (Wong et al. 2015). The carbonization of PET alone or mixed with coal/pitch produces high-quality activated carbon (Castelo-Quiben et al. 2019). To make carbon materials from LDPE, a thermo-oxidative process in the presence of air at 270–330 °C temperature is generally used (Choi et al. 2019). Chemical stabilization processes such as the sulfonation process (treatment with sulfuric acid or chlorosulfonic acid) are also applied for polyolefins and PS before making carbon materials by carbonization (Behr et al. 2016).

Catalytic carbonization of the plastics is performed in the presence of catalysts such as transition metal materials and solid acids to obtain carbon nanomaterials such as CNTs, graphene, and carbon spheres. Catalysts containing iron (Fe) and/or nickel (Ni) such as iron hydroxide, Ni metal, ferrocene, and stainless steel are generally used to convert plastics to carbon materials.

Pressure carbonization is mainly carried out under high-pressure conditions and follows two routes: (1) direct carbonization, which is performed under the pressurized atmosphere of the decomposition gases, and (2) hydrothermal carbonization (HTC), which is performed in the presence of water vapor (>100 °C and 0.1 MPa). The pressure carbonization method could prepare carbon materials (with micro- or nanostructures) with high yields compared to other carbonization techniques (Adolfsson et al. 2018). Jie et al. (2020) investigated the depolymerization of plastic waste (mixture of commonly used PP, PE, PP, and PS) using the microwave-assisted catalytic process into hydrogen and multi-walled CNTs. The results showed that with the FeAlOx catalyst, a high production with >92 wt% multi-walled CNTs was obtained.

4 Co-processing of Plastic Waste with Other Feedstocks

A synergistic effect was observed while co-processing of plastic waste with different feedstocks such as biomass (Brachi et al. 2014), oil shales (Mu et al. 2020; Aboulkas et al. 2012), vacuum gas oil (VGO) (Ucar et al. 2002), and petroleum residues (Kohli et al. 2019). Co-pyrolysis leads to improved quality of the products formed. It is hypothesized that one of the materials used in co-pyrolysis, either biomass/coal/VGO/petroleum or residue/oil shale, degrades at a low temperature, thus free radicals are produced that initiate the degradation of another compound. However, catalysts are sometimes required to induce the synergistic effect. This effect between two feedstocks was influenced by the type of feedstock, reaction temperature, heating rate, and reaction time used for co-processing.

Various proven technologies are also available in the market that can co-gasify plastic solid waste with other feedstock materials at a high reaction temperature using sand as a circulating/fluidizing media (Morrin et al. 2012; Brachi et al. 2014; Kim et al. 2019; Alam et al. 2020; Mu et al. 2020). Co-gasification of biomass and plastic waste improved the quality and quantity of the producer or syngas. The advantages of the co-gasification process are (i) it helps to overcome difficulties of seasonal biomass availability; (ii) by adding more plastics in feed, the formation of char and tar can be reduced; (iii) operational problems can be reduced by co-gasification; (iv) co-gasification can be performed even if impurities such as wood, paper, or cardboard are present in plastic wastes; and (v) Brachi et al. (2014) showed that co-gasification of wood and PET produces a syngas that does not require conditioning in a water–gas shift reactor for downstream methanol production, hence simplifying the whole process.

Liquid fuel or bio-oil produced by pyrolysis of biomass cannot be directly used as a transportation fuel because of poor properties such as high viscosities, high water and oxygen content, and high corrosiveness (Rahman et al. 2018; Kim et al. 2019). Biomass also has a low H/C ratio that results in a low aromatic yield and high char formation (Li et al. 2014). For these processes, hydrogen-rich plastic wastes can be used as a feedstock to enhance the H/C ratio into the products obtained from biomass. Thus, by co-pyrolysis of plastic waste and biomass feeds together, a better quality of bio-oil can be produced. Because the oxygen content will be reduced, the selectivity of aromatic compounds increases (Uzoejinwa et al. 2018). The synergistic effects of the co-pyrolysis of linear LDPE and bamboo sawdust were studied by Alam et al. (2020), and a drop of 36% in activation energy was seen with a 1:3 blend of biomass and LDPE. A higher liquid yield was obtained by co-pyrolysis of sugarcane bagasse and HDPE in a fixed-bed reactor (Hassan et al. 2020). The highest yield was obtained with 60:40 HDPE and sugarcane bagasse ratio at a 600 °C reaction temperature.

Shale oil contains a higher concentration of nitrogen, sulfur, aromatics, and a slightly lower amount of heavy oil compared to crude oil. Therefore, it requires more hydrogen, a catalyst, and heat for the upgradation. Thus, many researchers have investigated the pyrolysis of shale oil with waste materials such as biomass, coal, and plastics. Co-pyrolysis of PE and shale oil enhanced the volatiles formation. In the co-pyrolyzed oil obtained after pyrolysis of PE and shale oil, more aliphatic compounds were found (Aboulkas et al. 2012). Mu et al. (2020) used the thermogravimetric-mass spectroscopy (TG-MS) technique to investigate the co-pyrolysis of Huadian shale oil and plastics (LDPE and PP) by monitoring the H radicals, H_2, and hydrocarbon volatiles. The results showed that PP having more side groups in the polymer chains decomposed easily and released H radicals and H_2 compared to LDPE. This results in more interaction between PP and oil shale during co-pyrolysis. Overall, the addition of plastics results in an increase in the light fraction product oil, total product yield, and decreased aromatic and olefin content in the product oil.

The use of plastic waste as a hydrogen donor for upgrading heavy oils/residues was reported (Kohli et al. 2019). It was found that during the upgrading of heavy feeds with plastic waste, hydrogen migrates from the plastics to heavy feeds via radical abstraction and radical combination reactions. Thus, an increase in hydrogen content in the reaction mixture was observed. Moreover, control of the coking process during catalytic hydrocracking of petroleum residue is the most challenging task of the refinery. The presence of active hydrogen coming from plastic dissociation can control the coke formation. Catalytic pyrolysis using HZSM-5, DHC-8, and Co-Ac catalysts for the hydropyrolysis of plastics (LDPE, PE, PVC, and PP) with VGO was also reported (Ucar et al. 2002). The synergisms and kinetics of the plastic and vacuum residue blends in a N_2 and H_2 atmosphere using thermogravimetric analysis were studied (Mominou et al. 2009). Peter et al. (1993) described a liquid phase hydrogenation of plastics. For this process, slurries were prepared by mixing the petroleum vacuum residues with shredded waste PE, PP, and PVC.

5 Conclusions and Future Perspectives

Plastic wastes, a growing global concern, has negative impacts on human and environmental health. These wastes are destroying habitats, entangling marine animals, and enhancing the transportation of invasive species across habitats. Therefore, innovative recycling technologies should be geared towards waste-to-energy conversion solutions. The depletion and disappearance of fossil fuels due to a growing population and increasing energy demand is a global concern, steering research to find uses for existing material wastes and finding alternative resources for fossil fuels. Plastic properties such as high heating values (>40 $MJkg^{-1}$), high carbon and hydrogen content, and low ash content make them a suitable, valuable resource to substitute fossil fuels. This can be done either by directly refining pyrolytic plastic oils or blending them with conventional fuels. However, there are numerous challenges that restrict the plastic waste conversion to fuels. These challenges are economic infeasibility, complexity of plastic materials, and harmful materials such as brominated flame retardants and phthalates present as additives in plastics. To enhance the conversion of mixed plastic wastes, a holistic approach with an optimal solution is required. In this direction, several steps need to be taken: (i) increase the efficiency of plastic waste collection and (ii) improve sorting to produce suitable feeds for desired products.

Plastic pyrolysis has proven to be an interesting technology as it can handle additives and/or harmful substances and minimize their transfer into new materials. In this process, when the polymers break down, the desired products vaporize, and the value-added compounds can be separated. However, special separation technologies are still required. In addition, pyrolysis reduces the plastic product C-footprint by minimizing CO and CO_2 emissions compared to combustion and gasification processes. The challenges associated with plastic pyrolysis include a high investment, high process cost, low product yields, and the use of expensive catalysts. The literature reports that by adding catalysts, a synergism was observed between catalyst and pyrolysis techniques, and the catalyst selectivity plays a promising role for product oils, hydrogen, and chemical production. Therefore, there is a need to find highly selective and active catalysts to obtain the desired products. Although there is plenty of research work showing the production of liquid/oil/wax/chemicals from plastics, there is lack of studies that test the fractions obtained in engines to investigate their performance. Advanced techniques such as plasma-assisted pyrolysis/gasification, microwave-assisted pyrolysis/gasification, and UV-assisted pyrolysis/gasification need to be explored further to assess the potential industrial implementation of these technologies. A life-cycle approach is necessary to evaluate the environmental impacts and benefits.

A wide range of valuable chemicals such as paraffins, olefins, naphthalenes, benzene, toluene, xylene, carboxyl compounds, microcrystalline waxes, and lube and grease base stocks can be generated from plastic wastes. The state-of-the-art processes based on operating conditions play a promising role in the production of these chemicals. Limitations of large-scale application are the harsh reaction conditions, aggressive reagents, low reaction rates, low chemical yields, and high purification steps involved. The most challenging part is the recovery of the chemicals because of the difficulty in separating catalysts from the products. Innovative solutions including nanoparticles, ionic liquids, or deep-eutectic solvents as catalysts should be considered. These catalysts promote depolymerization reactions and a better yield of monomers.

Co-pyrolysis/co-gasification with another feedstock is a cheap alternative to fuel and chemical production. Further investigations exploring different temperatures, alternate feedstock-to-plastic ratios, residence times, and reactor systems would be beneficial. Nevertheless, further research is needed to evaluate the performance of the products obtained before these processes can be considered for future use.

Finally, different future research paths should be explored to develop better connections between the plastic circular economy and the distribution of value-added products to achieve the full potential.

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Food Packaging Plastics: Identification and Recycling

Eliezer Velásquez, Matías Guerrero Correa, Luan Garrido, Abel Guarda, María José Galotto, and Carol López de Dicastillo

Abstract This chapter describes the principal conventional polymers and bioplastics used in food packaging in terms of their resources or raw materials, properties, uses and applications. Food packaging plastics represent an important part of total plastic waste that ends up in landfills or accumulates in the environment when they are not properly managed. For counteracting this contamination problem, plastic recycling is the best alternative. Nonetheless, one of the challenges to guarantee recycling efficiency is the adequate polymer separation of plastic waste streams because of contaminants or the presence of polymers different than the target recycled plastic, which can cause processability problems or variation of its original properties. This chapter presents the principal polymer identification techniques applied to post-consumer plastic streams in order to improve the sorting and separation of plastics before recycling. Likewise, plastic waste recycling methods associated with single and multilayer polymer systems and their stages are described. Finally, a comparative analysis of the properties variation of polymers used in food packaging with mechanical recycling is presented based on recent research studies, showing the principal

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degradation reactions taking place for each polymer. Polyethylene, polypropylene, poly(ethylene terephtalate), polystyrene and polylactic acid were reviewed. Some thermal, mechanical and processability parameters of these polymers were plotted as a function of the reprocessing cycles.

1 Introduction

The food industry has continuously adapted to the lifestyle of consumers, eating habits and increasing population growth in order to provide a good service and allow a varied and nutritious diet around the world. In this mission, packaging and its evolution have played a crucial role, going from being a simple food container to a complex system that allows containing, handling, protecting, extending shelf life, delivering information and facilitating distribution, among others.

Three types of packaging are typically used depending on their function: (i) primary packaging: protects the food in direct contact during storage and distribution, which can be edible coatings (Hammam 2019); (ii) secondary packaging: protects food products without direct contact with the food, such as plastic/cardboard boxes and flexible bags; and (iii) tertiary packaging: protects a group of food packages against mechanical damage and environmental conditions during transportation, commonly used as an outer layer to assemble packages, such as pallets and stretch films.

Food packaging can be made of tin, cardboard, glass or polymers. This chapter is focused on plastics used for food packaging applications. Over the last decades, plastics have shown interest and success due to their properties, including low cost, flexibility, resistance, lightness, stability, impermeability, ease of sterilization and processing versatility, since many polymers can be molded, extruded, melt and blow into different shapes, films, membranes or foams (Ferreira et al. 2016).

The principal plastics commonly used in food packaging are conventional polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). The use and disposal of these plastics produce great amounts of post-consumer waste that generate severe environmental problems due to their biodegradation resistance. Packaging represents 63% approx. of worldwide plastic waste (Ferreira et al. 2016). Plastic consumption is projected to increase and the estimation of accumulated plastics in the oceans will probably exceed the weight of fish in 2050, considering that 10 tons of floating plastics per minute end up in the ocean, comprising PE, PP and expanded PS (Siracusa and Blanco 2020).

As alternatives to manage plastic waste and reduce its negative impact on the environment towards sustainable development, use fewer materials in the design stage, formulate new materials as substitutes to non-renewable ones, and valorize plastic residues by efficient recycling, are needed. Regarding recycling, this process provides new business opportunities and promotes innovative companies, favoring the society and contributing to a circular economy (Di Maio and Rem 2015).

Recycling is divided into four basic processes that consist of: (i) primary or pre-consumer, mechanical recycling carried out internally in the industries mostly with plastic scrap and in which there is no risk of contamination with other materials; (ii) secondary or post-consumer, mechanical recycling consisting of several stages such as collection, shredding, removal of contaminants or other materials and extrusion; (iii) tertiary or chemical, chemical reactions such as chemolysis and thermolysis to transform plastics in monomers or oligomers which are subsequently used to produce the same or similar material, and (iv) quaternary or energy recovery by incineration, involving the release of toxic gas emissions. The secondary or post-consumer mechanical recycling provides better benefits since it allows the collection and recovery of plastic waste with a lower carbon footprint to generate new products. However, mechanical recycling can affect the physical–mechanical properties in a mode and magnitude that depends on polymer and reprocessing cycles.

The recycling of food packaging made of a single polymer is relatively simple in terms of processing. In contrast, recycling multipolymer containers or multilayers is more complex, as they require the separation of the polymeric layers, or the use of compatibilizers can be needed. The techniques used to separate polymers from multilayers are solvent extraction and chemical delamination. Once the different materials have been isolated, these can be recycled separately, increasing process time and associated costs.

This chapter describes the principal polymers used in food packaging in terms of their properties and applications, as well as the polymer identification techniques used to reach efficient separation and classification of the post-consumer plastics from plastic waste streams before their recycling. Likewise, the methods for recycling plastics used in food packaging and their application to single polymer or multilayer packaging are defined. Finally, the effect of recycling on some processability, mechanical and thermal parameters of these polymers is reviewed.

2 Plastics Used in Food Packaging

Conventional polymers from fossil sources are the most used plastics for food packaging applications. Nonetheless, polymers from renewable sources with varied characteristics have been incorporated into the market due to technological advancement and the need to reduce the negative impact on the environment.

In Fig. 1, polymers are classified as: (i) from fossil or non-renewable origin and (ii) from renewable origin, called biopolymers. The latter are certified according to EN 16,640: 2015, ISO 16,620-4: 2016 and ASTM 6866-18 standards, which measure the content of biobased carbon ^{14}C in a material, or through EN 16,785-1 standard (2015) which measures biobased content using radiocarbon analysis and elemental analysis (Niaounakis 2019). At the same time, these two polymers groups include (i) non-biodegradable polymers which remain for a long time in the environment and (ii) biodegradable polymers which, according to ASTM D-5488-94d standard,

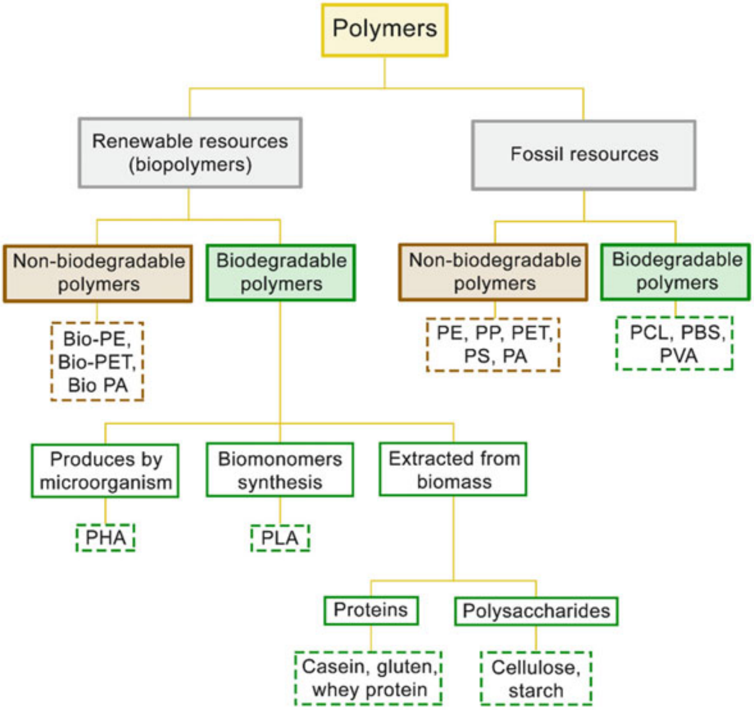

Fig. 1 Classification of polymers used in food packaging

are defined as polymers capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds and biomass.

Specifically, the most common type of biodegradable polymers are those whose biodegradation occurs under compostability. These polymers are certified according to international standards for composting under specific conditions (ISO 17,088: 2012, EN 13,432: 2000, EN 14,995: 2006, ASTM D6400-12, AS 4736, ASTM D5338-15, ISO 14,855-2: 2018) (Niaounakis 2019).

2.1 *Conventional Polymers*

Non-biodegradable fossil-based polymers are highly demanded due to their low cost, lightness, easy processability and wide range of physical, mechanical and barrier properties (Saha et al. 2016). The main characteristics of the conventional polymers widely used in food packaging are presented below.

Poly(ethylene terephthalate) (PET) is the third polymer more used in the packaging industry, monopolizing the market for beverage bottles. 65% of the world PET production is addressed to synthetic fiber manufacturing and the rest to the packaging industry. In this last area, bottles (76%), containers (11%) and films (13%) are produced (Plastics Insight 2020; Siracusa and Blanco 2020). PET is a lightweight semi-crystalline thermoplastic, which can be semi-rigid to rigid, mechanically resistant to impact, stretchable during processing, transparent or opaque. Besides, PET has good thermal resistance and stability, excellent chemical resistance to dilute acids and alkalis, oils, fats, hydrocarbons and alcohols, as well as good gas barrier properties against humidity and CO_2 (Plastics Insight 2020; Nisticò 2020).

Polyethylene (PE) is the most globally used polymer and one of the most applied in food containers and packaging production. It is classified according to its density into high density polyethylene (HDPE) (density > 0.940 g/cm^3), medium density polyethylene (MDPE) (density: 0.940–0.925 g/cm^3), low density polyethylene (LDPE) (density: 0.925–0.910 g/cm^3) and ultra low density polyethylene (ULDPE) (density < 0.910 g/cm^3), known as homopolymer (Ospina Arias 2015). HDPE and LDPE are the most used in food packaging.

HDPE is a highly crystalline polyethylene constituted of straight chains and very few branches. It is opaque, hard, water vapor barrier, and has excellent mechanical properties (high modulus, medium tensile properties, low impact and tear resistance) (Zhang et al. 2004; Lu and Lu 2018). HDPE has higher tensile strength and better temperature resistance than LDPE and linear low density polyethylene (LLDPE), but its toughness and processability are lower than PVC and LLDPE. In the packaging sector, milk and juice containers, vinegar and butter bottles, chocolate syrup containers, shopping bags, among others, are made of HDPE (ChemicalSafetyFacts.org 2020; Wu and Wang 2020).

LDPE has a structure with 1–3 long chain branches and 10–30 short chain branches per 1000 carbon atoms. Tensile strength and modulus of LDPE are low but it has medium impact and tear resistance (Zhang et al. 2004). It has good sealing properties, moisture barrier, transparency, and the thermal stability required to be industrially processed (Zia et al. 2019). This polymer is used primarily in plastic films that require heat sealing but in rigid applications either. For example, lids of coffee cans, bags for bread, holding rings for packs of soft drinks, bags for fruits and vegetables, among others (ChemicalSafetyFacts.org 2020).

Polyvinyl chloride (PVC) is a transparent polymer with high chemical resistance, good mechanical performance, flexibility and low barrier properties (Zhu et al. 2008; Azlin-Hasim et al. 2016). It is used in foil or film-type packaging, e.g., packaging for blisters, refreshing mints or chewing gum (ChemicalSafetyFacts.org 2020). Flexible PVC films, known as “sticky” films, are widely used both at home and in supermarkets to wrap various foods such as cheese, red meat, poultry, bakery products, fruits and vegetables. These sticky films contain a significant amount of plasticizers, light and heat stabilizers, lubricants, among others (Goulas et al. 2007).

Polypropylene (PP) is a thermoplastic with easy processability, balanced mechanical properties, high chemical stability but low oxygen barrier (Khalaj et al. 2016). It can be translucent to opaque, with a high melting point that makes it suitable for containers to be used in microwave ovens and dishwashers. Plastic transformers use this polymer to produce containers of yogurt, maple syrup, cream cheese, sour cream, cookies, chips, snacks, chocolate, confectionery, ice cream, frozen food, tea and coffee (Polat et al. 2018; ChemicalSafetyFacts.org 2020).

Polystyrene (PS) is a low-cost thermoplastic with good resistance during processing, low moisture absorption, ease of processing and molding (Pilevar et al. 2019). It is produced mainly in the form of: (i) crystal or general-purpose polystyrene (GPPS), a colorless solid, rigid, brittle and with limited flexibility, used in the manufacture of egg boxes and rigid foams known as polystyrene extruded (XPS) for food packaging trays and cups for hot infusions and cold smoothies (Retorna Poliestireno EPS 2020; Pilevar et al. 2019); (ii) expanded polystyrene (EPS) made up of 95% PS and 5% gas, which is a lightweight material with high protection and thermal insulation capacity, widely used in disposable food containers (Lin et al. 2017; Pilevar et al. 2019); and (iii) high impact polystyrene (HIPS), more resistant to impact and environmental stress cracking than original polystyrene (Grassi et al. 2011; Pilevar et al. 2019).

Others: other resins or polymer blends distinct to those mentioned above can be used to produce food plastic containers. Some examples are: (i) *polycarbonate* (PC): strong transparent plastic and heat resistant used for bottles and cups, synthesized from bisphenol A monomer, which is a potential endocrine disruptor; therefore, its use is subjected to migration limits (Park et al. 2018); (ii) *polyamide* (PA): polymer with high resistance to impact, temperature and pressure, widely used in cooking utensils, spatulas, ladles, spoons, oven bags and intermediate layers of laminated films (Abe et al. 2020); and (iii) *styrene-acrylonitrile* (SAN) copolymers: transparent polymers with high heat resistance, excellent gloss, chemical resistance, good toughness, rigidity, dimensional stability and relatively high tensile and flexural strength, being applied in the production of bottles, bottle caps, containers, boxes, films and jars, due to its transparency (Wu 2000).

2.2 Newest Materials: Bioplastics

Bioplastics include polymers produced from renewable sources named bio-based polymers, biodegradable polymers from renewable or fossil sources, or polymers with both characteristics, bio-based and biodegradable (Siracusa and Blanco 2020). Bioplastics production represents around 1% of the 359 million tons of plastic produced annually in the world (European Bioplastics 2020). Meanwhile, packaging sector occupied more than 53% of the 1.14 million tonnes of produced bioplastics in 2019 (European Bioplastics 2020).

The natural and renewable raw materials mainly used in the production of biopolymers or their intermediaries are starch, cellulose, sugar, vegetable oil and wood (Queiroz and Collares-Queiroz 2009a). Biodegradable biopolymers tend to have poor mechanical properties and low barrier (Malathi et al. 2014). In contrast, bio-based polymers such as bio-PE, bio-PET, bio-PP have similar structures and properties to the equivalent petrochemical polymers but are no biodegradable. The biobased and/or biodegradable polymers used currently in food packaging are described below.

2.2.1 Non-Biodegradable Biopolymers

They are synthesized from renewable resources such as starch, cellulose, sugar, vegetable oil and wood, and present the same benefits and recyclability as polymers processed from fossil derivates (Queiroz and Collares-Queiroz 2009b; Reddy et al. 2013; Yadav et al. 2018; Siracusa and Blanco 2020). Although the amount of carbon required to manufacture a certain amount of polymer is independent of the raw material, it is considered that these bio-based polymers have a lower carbon footprint than conventional polymers because they are produced from renewable raw materials. However, they do not counteract possible ecological problems due to their accumulation in the environment, nor are they necessarily associated with lower carbon emissions due to energy requirements for manufacturing, processing and treatment at the end of their service life (Walker and Rothman 2020).

Bio-PE is produced from ethylene obtained by dehydration of bioethanol from glucose (sugar cane, corn, wheat, among other). The ethylene polymerization is the same as when petroleum-derived ethylene is polymerized, and bio-HDPE, bio-LLDPE and bio-LDPE can be obtained through these processes (Morschbacker 2009). The first companies to produce bio-PE for food packaging applications and other purposes were Braskem-Dow (Brazil) and Mitsui JV (Brasil). Bio-PE is the most used in milk packaging and its price is 30% approximately higher than fossil-based PE (Siracusa and Blanco 2020).

Bio-PP is produced from propylene obtained from butylene, which is synthesized by dehydration of isobutanol from glucose fermentation. This polymer has been produced by Braskem, although its commercialization is not massive yet (Hatti-Kaul et al. 2020; Siracusa and Blanco 2020).

Bio-PET is obtained from renewable sources at least a fraction of the constituent monomers (Salvador et al. 2019). It is produced from a bio-based diol and a diacid or diester. The latter can be bio-based such as succinic or adipic acid, or fossil-based such as purified terephthalic acid or dimethyl terephthalate. However, currently, bio-PET is produced from ethylene glycol (30%) obtained from biomass, and purified terephthalic acid (TPA) from fossil sources due to the limitations of industrial obtaining of TPA from renewable source (Volanti et al. 2019). Like conventional PET, its use dominates the beverage bottle market. Toyota Tsusho Corporation and Futura Polyesters have carried out bio-PET commercialization (Reddy et al. 2013).

Bio-PA is synthesized from diamines and dicarboxylic acids, where all or one of the monomers can be obtained from biomass (11-aminoundecanoic acid, 1,8-octanedicarboxylic acid, 1,10-decanediamine, adipic acid, caprolactam and 1,4-butanediamine). Bio-PA11 is a polyamide exceptionally produced from the polycondensation of 11-amino-undecanoic acid obtained from castor oil, commercially available with the trade name Rilsan (Radzik et al. 2020). The leading producers are Arkema, DSM, BASF, and DuPont (Reddy et al. 2013).

2.2.2 Biodegradable Fossil-Based Polymers

These polymers comply with the biodegradability condition although they are produced from fossil derivates. Some of these polymers are described below.

Polybutylene succinate (PBS) is an aliphatic polyester with low melting temperature, (approx.114 °C) and good mechanical properties in terms of tensile strength and rigidity, comparable to PE and PP. It is used in bottles and trays, but its applications are limited due to its low barrier (Vytejčková et al. 2017; Xu et al. 2019).

Polycaprolactone (PCL) is a biodegradable semi-crystalline hydrophobic polyester with a melting point between 59 and 64 °C, with good resistance to water, oil, solvents and chlorine. It is expensive and has low mechanical performance for high load applications so that its use in food packaging is limited (Mohamed and Yusoh 2016; Khalid et al. 2018).

Polyvinyl Alcohol (PVA): is soluble in water and obtained from poly(vinyl acetate) hydrolysis. It has high resistance and can be blended with natural polymeric materials. It is used for coatings, adhesives, and additive in paper and cardboard (Wagner 2014; Gaikwad et al. 2016).

2.2.3 Biodegradable Biopolymers

These polymers are biodegradable and synthesized from renewable resources. At the end of their service life, they can biodegrade; some are biodegradable under composting conditions. According to their origin, they are classified as:

(a) Polymers directly obtained from biomass
These polymers are hydrophilic with certain crystallinity and good gas barrier properties. Their processability is complex and presents low yield, especially in the packaging of wet food products (Malathi et al. 2014; Yadav et al. 2018).
Polysaccharides: starch is one of the more used polysaccharides in producing films and coatings due to its low cost and availability. This type of polymers acts as carriers of food additives, such as antioxidants and antimicrobials. Furthermore, they provide an esthetic or practically imperceptible appearance, and do not generate waste due to their edible nature (Pelissari et al. 2019).
Proteins: include whey protein, gelatin, wheat gluten, zein, soy protein, among others used as edible coatings (Pelissari et al. 2019). They conserve moisture, are a barrier to gases and aromas, inhibit microorganisms growing, serve as carriers of additives and improve food appearance by adding color or shine (Hammam 2019).

(b) Synthetic polymers obtained from renewable bio-based monomers
PLA is the polymer, classified in this category, more used in food packaging, which is a polyester polymerized from lactic acid monomers obtained by fermentation of carbohydrates from various raw materials. PLA is hydrophobic, easy to process and has a high molecular weight (Swaroop and Shukla 2018; Mangaraj et al. 2019). In addition, it exhibits some characteristics

similar to conventional polymers, such as the thermal stability and processability of PS, as well as the printability, tensile strength, fat resistance and barrier properties of PE. Nonetheless, PLA is brittle and tended to degrade with increasing temperature. It can be found as films, packaging and coatings for paper and cardboard (Mangaraj et al. 2019).

(c) Polymers obtained from microorganisms or genetically modified bacteria

These polymers are mainly polyhydroxy-alkanoates (PHA), a family of intracellular biopolymers synthesized by a wide range of microorganisms under nutritional stress conditions. They are structurally composed of simple macromolecules as monomers of 3-hydroxy-type fatty acids. In this category, polyhydroxyvalerate (PHV), polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-hydroxy valerate) (PHBV) are found. These polymers are characterized by good tensile strength, printability, taste and odor barrier properties, heat sealability, resistance to fats and oils, thermal stability, and ease of staining. Its applications include films, bottles and coatings (Leja and Lewandowicz 2010; Mangaraj et al. 2019).

Finally, it is highlighted that packaging requirements for some food products in terms of barrier properties, mechanical properties, sealability or other characteristics cannot be reached with a single material. Two or more polymers can be blended or multilayer structures can be designed to find combined properties. The latter include films constituted only for polymeric layers or involving different materials among plastic, metal and paper.

3 Identification and Sorting of Plastics Packaging Waste

Sorting and identification of plastic packaging materials are two essential and challenging steps during recycling. Their efficiency and reliability can result in recovered materials of high purity and therefore, they can reach their maximum market value for later uses. Furthermore, these processes need to be cheap and automatic in order to generate a cost-effective recycling infrastructure. Thus, there is a high interest in improving the separation and identification processes towards the most remarkable balance between optimal efficiency over cost ratio (Dodbiba and Fujita 2004; Gala et al. 2020).

The classification of the technologies used to separate and/or identify plastic residues is ambiguous since both purposes have the common goal of sorting and classifying polymers, so that several techniques present both functions. Below are the main techniques for separating and identifying divisions primarily based on their application prospects. The separation techniques are applied mainly in large installations of waste management companies, and the identification tests are commonly capable of being processed in more specific centers of materials analysis. In this section, the main materials separation and identification mechanisms used in today's market will be explained.

3.1 Sorting Techniques

Designing and performing efficient separation and sorting technologies to recover valuable materials from waste to be further reprocessed to form new products is of great importance in order to maintain the quality and the corresponding properties of each specific polymer.

The sorting techniques can be divided into two groups depending on the procedure used, WET and DRY separation techniques (Serranti and Bonifazi 2019; Grigorescu et al. 2019).

3.1.1 Wet Separation Techniques

Sink-float separation: This technique is probably one of the oldest methods proposed for the separation of plastics. This strategy was first proposed in the 70's by Japanese researchers. This technique is based on the separation of materials by density and different liquid systems with specific densities to reach the desired separation. It is a very efficient technique to separate plastics from other materials such as cardboard and glass. Among polymers, it allows the separation of polymers with significant density differences such as PVC (approx. 1.4 g/cm^3) and PP (approx. 0.9 g/cm^3), but this process is difficult between polymers with similar densities such as PP, LDPE and HDPE (Dodbiba and Fujita 2004; Serranti and Bonifazi 2019; Grigorescu et al. 2019).

Jigging: Jigging is an improved technique for separating materials by density. It is a process based on the application of water streams to a perforated container where the materials are deposited. Streams of water are moved up and down by pistons whose frequency and amplitude can be controlled, and the separation of the materials by stratification is reached based on the specific densities and the continuous flow movement (Hori et al. 2009; Pita and Castilho 2016; Serranti and Bonifazi 2019).

Hydrocycloning: Hydrocycloning is a technique based on the combination of the separation of materials by gravity and centrifugal/centripetal forces. The liquid and the materials are introduced into the equipment at a certain pressure that generates a rotational movement that allows the separation of the materials based on their densities. It is an economical and efficient alternative to separate materials with different densities and to remove contaminants. The combination of several units in series allows the separation of materials with similar densities (Pascoe 2006; Yuan et al. 2014; Serranti and Bonifazi 2019).

Magnetic density separation: This process separates materials using the magnetic density reached by mixing a liquid (water) and incorporating magnetic particles. By applying a special magnetic field, artificial gravity is obtained that allows the different position (height) of the materials and their separation. This technology is very interesting because it allows the separation of polymers with similar densities such as PP and PE (Bakker et al. 2009; Rem et al. 2013; Hu et al. 2013; Luciani et al. 2015).

3.1.2 Dry Separation Techniques

Below are several techniques that can facilitate the separation of plastic waste. Still, it is essential to mention that primary manual sorting by trained operators is always included as a complementary process.

Ballistic separators: This machinery is typically used in the early stages of waste separation because it allows the selection of any recyclable or residual material, and its transport through a conveyor belt for further processing (Serranti and Bonifazi 2019; Gala et al. 2020). Efficient separation of flat or 2D materials with bottles or 3D containers is driven by their movement through an inclined belt with oscillating rotating blades. This process also enables the removal of fine particles and impurities.

Air Suction: This technology is based on the application of a constant air flow capable of separating the materials by weight. Heavier materials fall onto a discharge conveyor and light materials are caught in the air streamt and transported through a conduit copper diverter plate or rotating drum (Gala et al. 2020). This equipment presents a similar efficiency as the ballistics separation process.

Tribo-electric separation by electrostactic charge: The migration of electrical charges across the surface is used to discriminate between plastic and no-plastics due to the differences on the intrinsic electrical conductivity of materials (Hearn and Ballard 2005). Furthermore, the property of triboelectrification allows to distinguish between different polymers due to the positive or negative charges that are generated when they are rubbed together and subsequently separated. These generated charges are retained on the surface of plastics and can be measured, and each polymeric material presents different electrostatic charge relaxation rates. This technique can show two drawbacks: (i) the presence of surface contaminants, labels or coatings may interfere the tribo-electric probe for the identification process, and (ii) a low efficiency for wide-scale applications (Grigorescu et al. 2019).

Fourier transform infrared spectroscopy: Infrared spectroscopy has proven to be a very useful technique for identifying materials because it allows the identification of different types of functional groups of organic molecules by studying the vibration of their bonds. This spectroscopy type allows identifying chemical bonds in IR spectrum regions, from the near-infrared (NIR) to the middle-infrared (MIR) and the far-infrared region. The mid-infrared region is the area of the spectrum with the most significant wealth of information, commonly called “fingerprint”, and, therefore, highly desirable for the analysis and identification of compounds. This technique allows the differentiation between polymeric films and other flat materials such as paper. The IR beam can be incorporated into the material conveyor belt, and the type of material can be identified and separated from air streams (Florestan et al. 1994; Ahmad 2004; Serranti and Bonifazi 2019; Grigorescu et al. 2019). Although it is the most popular technique, it lacks versatility and is not able to identify grades and/or types of polymers, and can present problems of identification of black or dark-colored materials.

3.2 Identification Techniques

UV fluorescence spectrometry: When FTIR technique presents problems, as within black or dark-colored material, a solution can be the incorporation of tracers to the primary materials in order to be latter identified and sorted by UV fluorescence spectrometry. The incorporation of fluorescence tracers as markers for polymer identification should consider the sufficient reliability in these compounds, their environmental impact and the mechanical appropriateness of resulting polymeric blends. Therefore, further research on efficient tracer dyes for higher fluorescence quantum yields for specific applications is of high interest and need (Ahmad 2004).

X-ray fluorescence technique: This technique is based primarily on the energization of materials with X-ray fluorescence radiation and its subsequent classification based on the wavelengths emitted and the energy released that varies depending on the compound. The use of this type of radiation requires high-security measures. It is a potent technique because it allows identifying black/dark colored polymers and contaminants. It is mainly used to separate plastics from other materials because it does not distinguish between polymers with high efficiency (Serranti and Bonifazi 2019).

Fourier Transform Raman spectroscopy scattering: Unlike FTIR, which involves infrared absorption, Raman is a scattering technique. It measures the intensity and frequency of photons scattered in the material when it is irradiated with high-intensity monochromatic light (laser, typically 785 nm). It is fast and effective in the range of 250–2900 cm^{-1}, when measuring the displacement of the wavelength of the scattered light with respect to the incident (Raman displacement). Like FTIR, the Raman technique investigates fundamental modes of vibration, resulting in excellent molecular selectivity; however, Raman is a much more attractive technique in terms of sampling convenience, as it can be easily used without the need to come into contact with the material, through various container materials such as glass and plastics (Florestan et al. 1994; Ahmad 2004). However, it is currently a technique with little industrial viability, and as occurs with FTIR identification, it can present problems with black or dark materials because they absorb the laser pump resulting in final broad signals.

Coding: This classification is carried out from comprises the identification of the polymers by the Society of the Plastic Industry that established the numbers 1 to 7 to identify the polymers PET, HDPE, PVC, LDPE, PP, PS and others, respectively.

Burning tests: At burning conditions, each polymer forms a flame of a specific color and intensity, a characteristic odor and smoke, and an amount of ash that allows its identification. It is not a highly efficient technique because the presence of additives can affect the identification process or even some polymers have almost invisible flames. For instance, LDPE polymer exhibits a yellow-orange flame and a burning rubber smell at burning conditions (Grigorescu et al. 2019).

Thermal analysis (DSC & TGA): Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) are two standard techniques to measure thermal properties of polymers (Wei et al. 2016).

Thermogravimetric analysis (TGA) allows the measurement of thermal stability of materials by analyzing the loss of their weight over a heating process. On the other hand, DSC allows obtaining various thermal parameters, such as the glass transition temperature and the melting temperature and enthalpy. All these parameters are specific to each polymer, so either of the two techniques allows the identification of a polymer and the presence of an additive. Mainly, thermal analysis can give an idea of the degradation degree of the recycled polymers. The only drawback of these techniques is the economic value of these types of equipment (Grigorescu et al. 2019).

4 Recycling of Food Packaging Plastics

Plastic film applications can be divided into two broad categories: packaging and non-packaging. The first one includes consumer or "primary packaging" (mainly LDPE, HDPE, PP and PET) and non-consumer or "secondary/tertiary packaging" (mainly LDPE). The non-packaging category includes plastics used in agriculture, construction, trash bags, among others (mainly LDPE) (Horodytska et al. 2018). This section will be focused on recycling of plastics from packaging category which represents 46.6% of all plastic manufactured in 2015, becoming the primary source of global plastic waste (Ritchie 2016; Geyer et al. 2017).

The plastic's contamination is one of the major challenges to face in the recycling of primary packaging because these materials are used in direct contact with food, and some residues and volatile compounds can remain in postconsumer plastic waste (Liu et al. 2018). This fact makes it necessary to establish different processes depending on the source of plastic waste, adding several steps to wash and remove these contaminants when it is required (Cabanes et al. 2020). FDA proposes some considerations included in the "Guidance for Industry: Use of Recycled Plastics in Food Packaging (Chemistry Considerations)" which describes recommendations related to chemical contaminants that could remain in the recycled material and migrate to the food (Food and Drug Administration 2006). In order to evaluate the cleaning efficiency of the recycling processes, US and European sanitary authorities recommend to emulate contamination applying contaminants as surrogates, e.g. lindane or diazinone, tetracosane or metal–organic compounds like zinc stearate, copper octoate or the toxic crabgrass killer disodium monomethyl arsonate (Franz and Welle 2002).

Packaging plastics can be classified according to their final structure as monolayers or multilayers. Monolayer package consists of a single thermoplastic polymer sheet with a thickness between 20 and 200 µm. On the other hand, a multilayer film is made of two or more layers that can be polymeric and non-polymeric, like paper or aluminum foils (Butler and Morris 2016; Horodytska et al. 2018).

There are four basic recycling processes, and depending on the type of recycling procedure and its purpose, contamination level, raw material and products, among other factors, can be classified in primary, secondary, tertiary and quaternary recycling. Primary and secondary recycling refer to mechanical recycling; meanwhile, tertiary and quaternary corresponds to chemical recycling and incineration, respectively. The recycling process for single polymers or multilayers systems differs because of the different physical and chemical characteristics of the packaging, e.g. multilayer systems' polymers need to be separated before they can be singly recycled, as it will be explained in the next sections.

4.1 Single Polymer

In this section, the recycling processes focused on monolayer films or packaging made of a single polymer were defined.

Primary recycling

Consist in a re-extrusion of a single and clean polymer scrap, usually from the same manufacture line. Thus, it is not suitable for recycling postconsumer packages and is only adequate for closed-loop waste, also called pre-consumer or post-industrial waste (Hahladakis and Iacovidou 2019).

Secondary recycling

Also known as mechanical recycling, this process is the most widely used technique to recycle postconsumer plastic waste. It consists of several steps in order to transform the recovered material to grinded particles by mechanical methods, followed by separation of contaminants through washing and flakes floating (Briassoulis et al. 2020). The screw extrusion is the most used processing technique to handle recycling plastic waste, having versatile configurations like single screw or twin-screw to create new materials (Kittikunakorn et al. 2020). During extrusion, the polymer is heated until a temperature above its melting point. The extruded material with desired shapes is obtained due to the driving of the malleable plastic by a screw. The shapes usually are cylindrical or laminated. Important factors that are controlled in this process are mixing, cooling time and rolling speed that define a good homogenization and thickness of the product (Goli et al. 2020).

Tertiary recycling

This process is also known as chemical recycling, and it is capable of transforming plastic material into molecules through chemical reactions whose products are monomers or partially depolymerized oligomers. There are several well-known technologies to depolymerize polymer chains, categorized into two types: Chemolysis, including glycolysis, methanolysis, alcoholysis and hydrolysis; and thermolysis, including pyrolysis, gasification and hydrogenation (Kumar 2020). For example, PET can be depolymerized by acid, alkaline or neutral hydrolysis, glycolysis, or alcoholysis, obtaining different products in each case (Langer et al. 2020). PS can be depolymerized using supercritical solvents. Toluene is the most efficient solvent to recover styrene from PS at 360 °C and 6 MPa for 20 min (Grigore 2017). Tertiary recycling methods as pyrolysis and gasification are under research to establish optimal conditions to be commercially suitable (Artetxe et al. 2015; Kumar 2020).

The monomers and oligomers obtained from this process can be used in a new reaction to produce the original polymer or a related polymeric product, or can be used as raw material for combustion in quaternary recycling (Grigore 2017).

Quaternary recycling

This recycling method consists in energy recovery by incineration, where the plastic waste is used as combustion feed due to its high calorific values (Carlos Escobar Palacio et al. 2019). After several recycling processes, plastics lose their properties up to there is no possible using them to obtain new materials, so that incineration can be an alternative. There are several reasons to avoid this method due to the contribution to the greenhouse effect and emissions of toxic volatile as heavy metals and polycyclic aromatic hydrocarbons. Emissions can be minimized by technologies such as activated carbon systems, flue gas cooling, acid neutralization, ammonia addition to the combustion chamber and/or filtration (Yassin et al. 2005; Singh et al. 2017).

4.2 Multilayer Systems

Mechanical recycling is the most attractive technique due to the simplicity of the procedure and lower investment cost. This process can only be applied to multilayer systems' polymers after a component separation process. However, milled multilayer films have been used as a composite filler to reinforce another postconsumer plastic matrix (Tartakowski 2010; Favaro et al. 2017). If multilayer films are composed of incompatible polymers that limit extrusion recycling, adding compatibilizers or other additives favors blending and improves processing and properties, producing, in some cases, non-food grade materials (Moreno and Saron 2018; Geueke et al. 2018). The principal characteristics of multilayer processing using compatibilizers or additives, and separation methods of multilayer's polymers, are described below.

4.2.1 Blending Processing

Multilayer films can be processed without layer separation at certain proportions and properties of each component. This alternative has been used to obtain materials for several applications different from packaging. For example, postconsumer HDPE has been reinforced by extrusion with up to 50 wt% of PET/aluminum/PE multilayer, reaching an impact resistance and elastic modulus higher than pure postconsumer HDPE, obtaining a material to be used in the automotive and civil construction sectors, among others (Favaro et al. 2017).

Nonetheless, the performance of the new material is usually poor with respect to mechanical behavior and barrier properties, especially when multilayer's polymers are immiscible such as PVA/PET, PP/PS or PP/PET, hampering its use in new packaging applications (Akshaya et al. 2020). As an alternative to overcome this issue, additives as compatibilizers are needed to improve blend stability (Li et al. 2019).

Compatibilizers are often macromolecules with an interfacial activity that increase the miscibility between polymers by regulating the interfacial tension. Some of them are copolymers of ethylene-ethylacrylate (EEA) and ethylene-methacrylate (EMA) for PP/PA blends, ethylene-butylacrylate (EBA) for PLA/PP blends, among others (Kang et al. 2015; Biron and Biron 2017).

4.2.2 Separation of Components of Multilayer Systems

Two methods can be used to isolate components of multilayers in order to recover polymers to be separately recycled. The first technique is solvent extraction which consists of dissolving and recovering components differentially, and the second method consists of mechanical or chemical delamination of films.

Solvent extraction or selective dissolution/precipitation method

This technique is based on the differences in solubility conditions of the polymers forming a multi-component system. The material is exposed to an adequate solvent at certain temperature, e.g. xylene for extracting PS and PE (Pappa et al. 2001; Achilias et al. 2009a), toluene for PS (Achilias et al. 2009a), dichloromethane for PS, PC and PVC (Achilias et al. 2009a; Weeden et al. 2015), N-methyl-2-pyrrolidone for PET (Achilias et al. 2009b), among others. At a fixed solvent, the polymer whose solubility occurs at a lower temperature will be firstly dissolved, and the remaining solid residue is separated by filtration. Subsequently, higher temperatures or different solvents can dissolve the rest of the components (Zhao et al. 2018). This method can be applied in both bilayer and multilayer films due to the solvent diffuse even into inner layers, delaminating the film and exposing the whole structure to the solvent. Then, the polymer recovery is carried out by its dispersion generally in an aqueous tenside solution, forming a multiphase solution, an aqueous phase and an organic phase containing the precipitated polymer (Kaiser et al. 2018; Niaounakis 2020). If more than one polymer is dissolved at a single temperature, solvents can be changed based on flash evaporation technique to improve solubility of specific components of the multilayer systems. Several factors of the process have to be controlled, such as size and molar mass of polymers, dissolution temperature, dissolution time, and concentration (Gutiérrez et al. 2013). Some patents have described the dissolution/reprecipitation method as an optimal process to recycle postconsumer packaging waste (Lindner 1998; Gorski et al. 2001; Mauldin and Cook 2005).

Chemical delamination

This method causes the layer separation to allow the recycling of polymers in separate streams. Delamination can be achieved either by decomposing an inner layer, which is not recovered in many cases, or by interacting with the layer-joining adhesive. Solvent extraction can be used to reach delamination, but frequently dissolved polymers are not recovered or can no longer be used for creating new materials (Horodytska et al. 2018).

Some multilayer packaging contains water-soluble polymers in their inner components, e.g. polyvinyl alcohol (PVA). This polymer can be easily dissolved by water at 90 °C and can be separated from insoluble layers such as PET, PE, aluminum, among others at certain conditions (Bergerioux 1991). Paper-based multilayered packaging also containing plastic and metallic layers can be delaminated by treatment with a mixture of inorganic bases (sodium sulfite, potassium sulfite, sodium sulfate and sodium hydroxide), leaving the paper material at the bottom of the container as pulp, the plastic portion as floating material on the surface and the aluminum is dissolved (Mukhopadhyay 2004, 2010).

Regarding multilayer structures with adhesives, acetone can be used to interact with a two-component solvent-based polyurethane adhesive to separate the components of a multiyear constituted by PET, 12 μm of aluminum and a blend of LLDPE and LDPE (70/30) (Fávaro et al. 2013). Besides, an enzymatic treatment has been reported to separate layers when whey protein has been used as an adhesion and barrier layer against oxygen and moisture in PET/PE multilayer systems (Cinelli et al. 2016).

Several patents have described the use of solvents and/or chemical agents to separate components of multilayer packaging films. Methyl formate, methyl acetate, toluene, chloroform, acetone–water, nitric acid, acetic acid-formaldehyde, among others, can be used depending on the adhesive type (Mukhopadhyay 2004, 2010).

5 Impact of Recycling on the Properties of Polymers Used in Food Packaging

During recycling of plastics, a degradation process of the polymer chains occurs that affects the processability and properties of these materials, and therefore, deteriorates their performance for further packaging applications. The thermal cycles and shear stress applied during the mechanical recycling promote different reactions comprising mainly chain scissions and thermo-oxidative processes (Yin et al. 2015). The degradation of the polymer takes place in the synthesis, processing, storage, handling, use of the final product and mechanical recycling by exposure to oxygen, heating, light, humidity, shear forces and other factors that cause aging during plastic service life (Cruz and Zanin 2003). This section is focused on explaining the changes in the physical–mechanical polymer properties due to mechanical recycling. For this purpose, it is necessary to describe the degradation reactions that occur during reprocessing. The principal oxidative and thermal–mechanical degradation reactions for polymers used in food packaging are shown in Figs. 2, 3, 4 and 5 (Ghaffar et al. 1977; Adeniyi 1984; Cruz and Zanin 2003; Culbert and Christel 2004; Awaja and Pavel

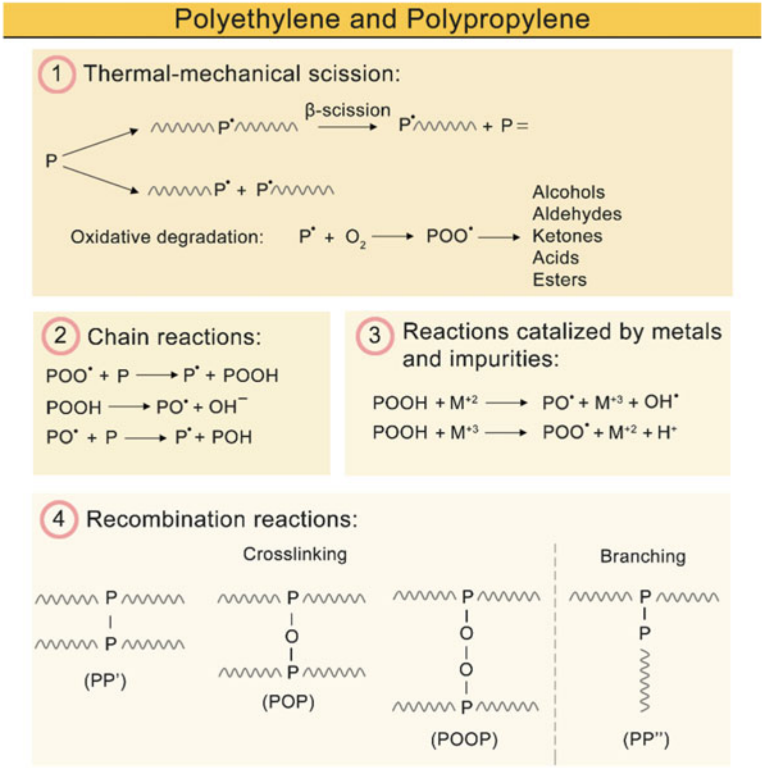

Fig. 2 Main degradation reactions of polyethylene and polypropylene due to thermal–mechanical reprocessing cycles

2005; Vilaplana et al. 2006; Strömberg and Karlsson 2009; Badía et al. 2011; Remili et al. 2011; Yin et al. 2015; Cruz et al. 2017; Shojaeiarani et al. 2019; Esmizadeh et al. 2020).

Figure 2 exhibits the reactions for oxidative thermal–mechanical degradation of polyethylene and polypropylene, which can also occur in other polymers. Meanwhile, Figs. 3, 4 and 5 present the reactions that particularly highlight for PS, HIPS, PET and PLA degradation processes, according to their structures. Generally, simultaneous reactions can occur, including chain scission producing polymer radicals which could be oxidized and form peroxy radicals, which turn in hydroperoxides by chain transfer reactions. Then, chain reactions are propagated by a free radical mechanism. Finally, polymer radicals, mainly oxyl and peroxyl ones, can combine by branching and crosslinking (Yin et al. 2015). Besides, degradation could be enhanced by hydroperoxide decomposition producing free radicals due to the metal traces from catalysts and impurities, whose presence is highly probable in recycled materials (Cruz and Zanin 2003).

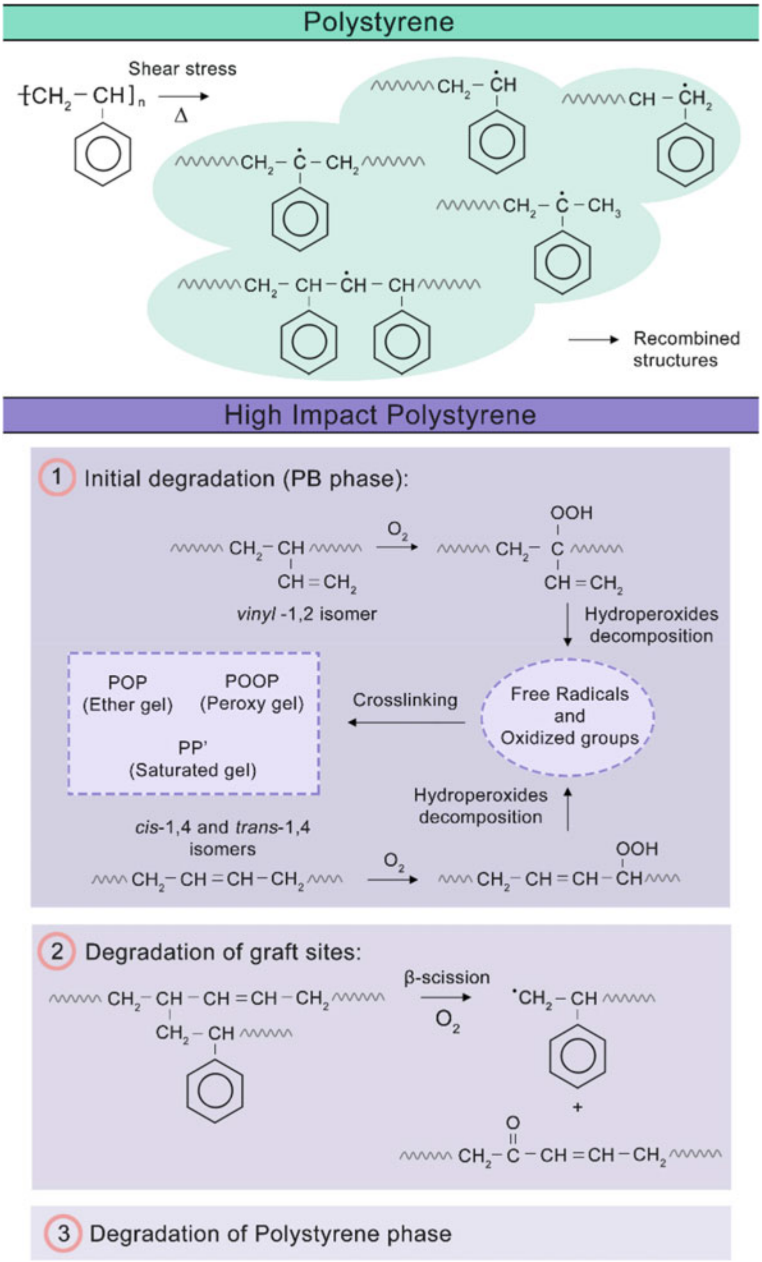

Fig. 3 Main degradation reactions of polystyrene and high impact polystyrene due to thermal–mechanical reprocessing cycles

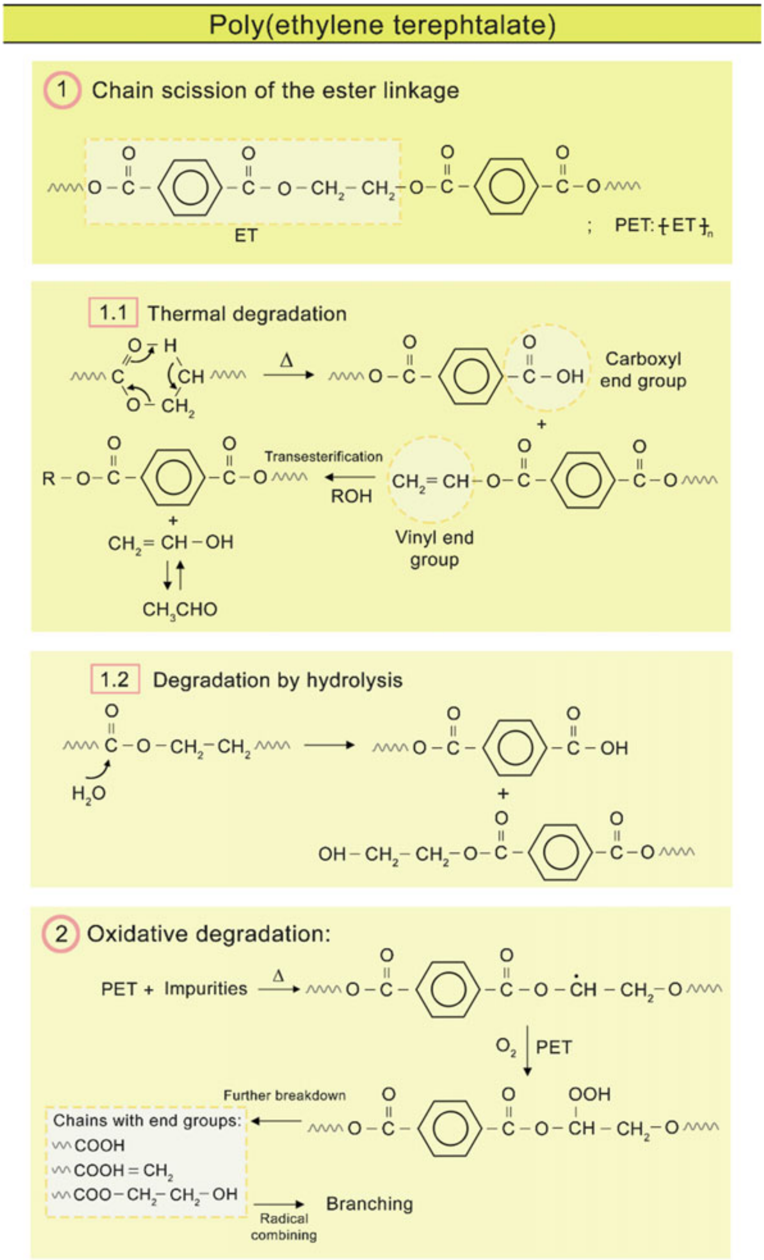

Fig. 4 Main degradation reactions of poly(ethylene terephthalate) due to thermal–mechanical reprocessing cycles

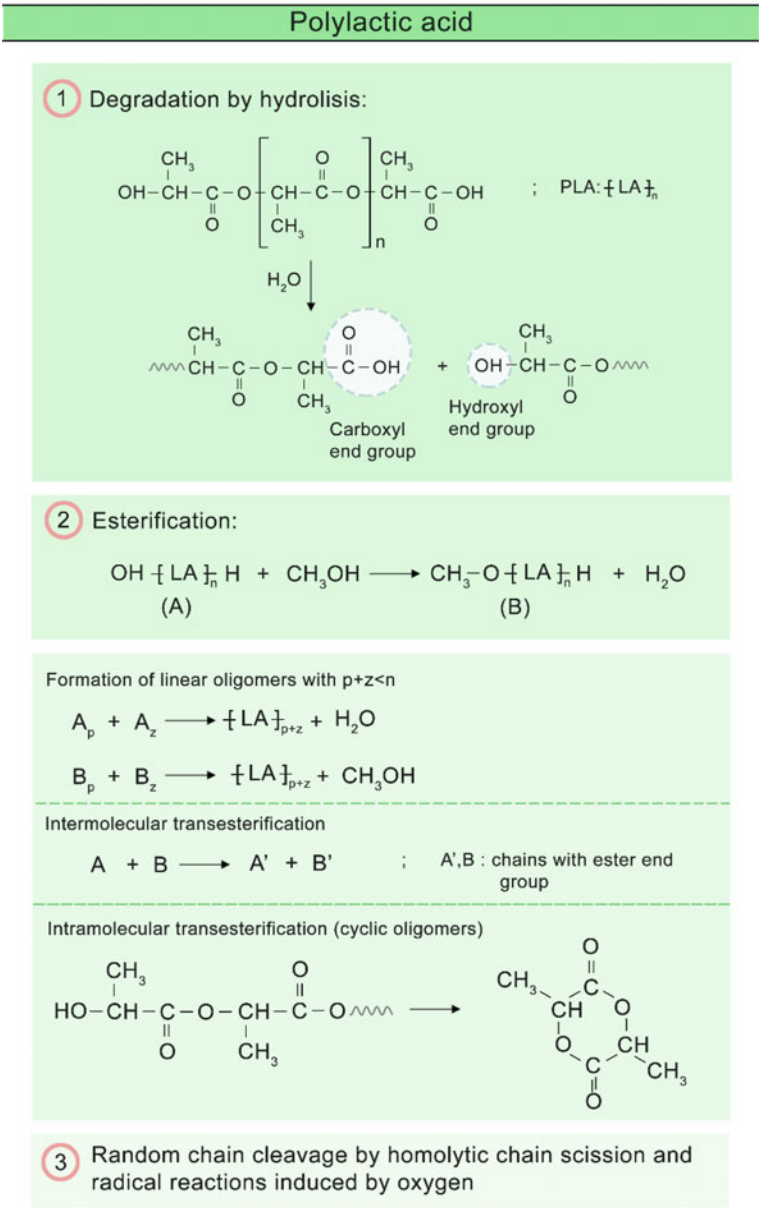

Fig. 5 Main degradation reactions of polylactic acid due to thermal–mechanical reprocessing cycles

The degradation behavior is highly dependent on the type of polymer, the number of reprocessing cycles and the processing conditions, prevailing one of the reactions among chain scission, branching or crosslinking (Yin et al. 2015). In the case of post-consumer HDPE, research has shown that crosslinking reactions have predominated during the first cycle-reprocessing, evidenced by a decrease of the melt flow index (MFI) (Cruz and Zanin 2003).

However, a study on extensively reprocessing of HDPE by extrusion reported a significant impact of the chain branching before 30 cycles, showing an increase of the molar mass and MFI reduction (Oblak et al. 2015). Between 30 and 60 cycles, MFI slightly increased due to a significant chain scission coinciding with branching, but after 60 cycles, chain scission was accompanied of a crosslinking process which increased viscosity and affected the processability. On the other hand, chain scission has been reported as a predominating degradation reaction in the first re-extrusion cycle of LDPE and crosslinking had a more significant impact between 2 and 100 reprocessing cycles (Jin et al. 2012). These results were verified by MFI, rheological and GPC analysis. Meanwhile, PP is mainly affected by chain scission in a greater magnitude than polyethylene (Strömberg and Karlsson 2009; Esmizadeh et al. 2020).

Chain scission by thermal–mechanical degradation has been reported as the predominant event during PS reprocessing, causing a continued reduction of the polymeric chain length and the complex viscosity along with cycles (Remili et al. 2011). Nonetheless, the degradation process in high impact polystyrene is more complex due to the presence of a dispersed rubber phase into the polystyrene matrix and some mechanisms have been proposed (Fig. 3). The unsaturated fractions in the polybutadiene phase promote thermo-oxidative reactions to form hydroperoxides, turning to chains containing oxidized groups and free radicals. The radical species can crosslink and form gels. Furthermore, breaking of the graft chains PS-*g*-PB that maintain the compatibilization between the glass and rubber phases is produced by oxidation of the tertiary carbons in the grafting sites. Finally, the degradation of PS matrix proceeds (Fig. 3) (Vilaplana et al. 2006).

On the other hand, recyclable polyesters such as PET and PLA can undergo hydrolytic degradation during mechanical recycling by chain scission at the ester linkage, producing chains with hydroxyl and carboxyl end-groups (Figs. 4 and 5) (Awaja and Pavel 2005; Badía et al. 2011). The presence of impurities in PET can produce polymer radicals by hydrogen extraction, which can undergo thermo-oxidative degradation, chain breakdown, and branching (Culbert and Christel 2004; Venkatachalam and Nayak et al. 2012). Additionally, oligomers and small molecules are formed by transesterification during PLA and PET reprocessing (Figs. 4 and 5) (Badía et al. 2011; Venkatachalam and Nayak et al. 2012).

The degradation reactions modify the molar mass distribution of the polymer, and therefore, viscosity and melt flow index, affecting its processability, crystallization behavior and physical–mechanical properties. Several works have studied the properties of plastics obtained from post-consumer food packaging (Lisperguer et al. 2011; Bhilat et al. 2019; Eriksen et al. 2019; Velásquez et al. 2020). Post-consumer polymers can be mixed with the same virgin or other polymers for tuning properties (Curtzwiler et al. 2019; Latko-Durałek et al. 2019; Velásquez et al. 2019) or be incorporated into multilayer systems for different applications (Radusin et al. 2020). Nonetheless, multilayer packages recycling is more complicated considering the incompatibility of their components, the presence of non-polymeric materials, and problems with the separation of layers to be singly recycled (Moreno and Saron 2018).

Most of the works have studied the reprocessing effect on the properties of polymers used for food packaging by simulating the mechanical recycling stages at pilot scale. Figures 6 and 7 show comparative graphics of thermal parameters, crystallinity, mechanical properties, MFI and molar masses of different polymers with respect to the number of extrusion cycles, according to the results reviewed in related works. The re-extrusion processes exhibited an insignificant effect on melting and crystallization temperatures of polymers such as LDPE, PP, PET and PLA at least during the first five cycles (Fig. 6a, b) (Spinacé and De Paoli 2001; Tri Phuong et al. 2008; Peres et al. 2016; Shojaeiarani et al. 2019). Nonetheless, crystallinity significantly changed with reprocessing in the case of polyesters (Fig. 6c). Specifically, the crystallinity degree of PET increased after two extrusion stages because hydrolytic chain scission reduced molar mass and improved chain packing (Spinacé and De Paoli 2001). On the contrary, the reduction of the crystallinity degree observed after 5-cycles-reprocessed PLA with different crystalline structures was attributed to the radical reactions resulting from PLA thermal degradation (Shojaeiarani et al. 2019). The most probable reaction was random chain scission of PLA due to high temperatures and high shear forces.

Regarding mechanical properties (Fig. 7), LDPE has revealed a high level of reprocessability because its elastic modulus and elongation at break have been registered unchangeable by at least 10 extrusion cycles (Peres et al. 2016). A significant increase of Young’s modulus and tensile strength have been reported for HDPE, attributed to the predominance of crosslinking at the studied injection molding conditions producing a stiffer and stronger material, but a lower ductility or elongation at break than virgin material (Mendes et al. 2011). The ductility reduction is more drastic for PP, associated with a large drop of the molar mass, turning material to a brittle condition at three re-extrusion cycles (Touati et al. 2011).

The substantial Young’s modulus reduction of more rigid polymers, such as PS, along reprocessing cycles has been also attributed to a lower molar mass resulting from thermal degradation (Fig. 7a) (Remili et al. 2011). Nonetheless, HIPS, which is less stiff because it contained an elastomer dispersed phase, has its principal recycling limitation in the reduction of elongation at break with reprocessing, according to Vilaplana et al. (2006) (Fig. 7c). They reported a 30% approx. drop of elongation at break of HIPS after nine extrusion cycles due to structural changes resulting in a more brittle material. Likewise, PET molar mass changes and an increase of its crystallinity with the simulated recycling stages reduced its tensile strength (Spinacé and De Paoli 2001). However, the elongation at break tended to increase until two cycles and then decreased dramatically. It is important to highlight that variations of PET elongation behavior have been reported due to differences in molar masses, crystallinities, and the occurrence of stress oscillation during the tensile test (Velásquez et al. 2019).

Mechanical recycling also deteriorated impact resistance of several plastics as it has been reported for HIPS (Ribeiro et al. 2012; Bhilat et al. 2019), PP (Tri Phuong

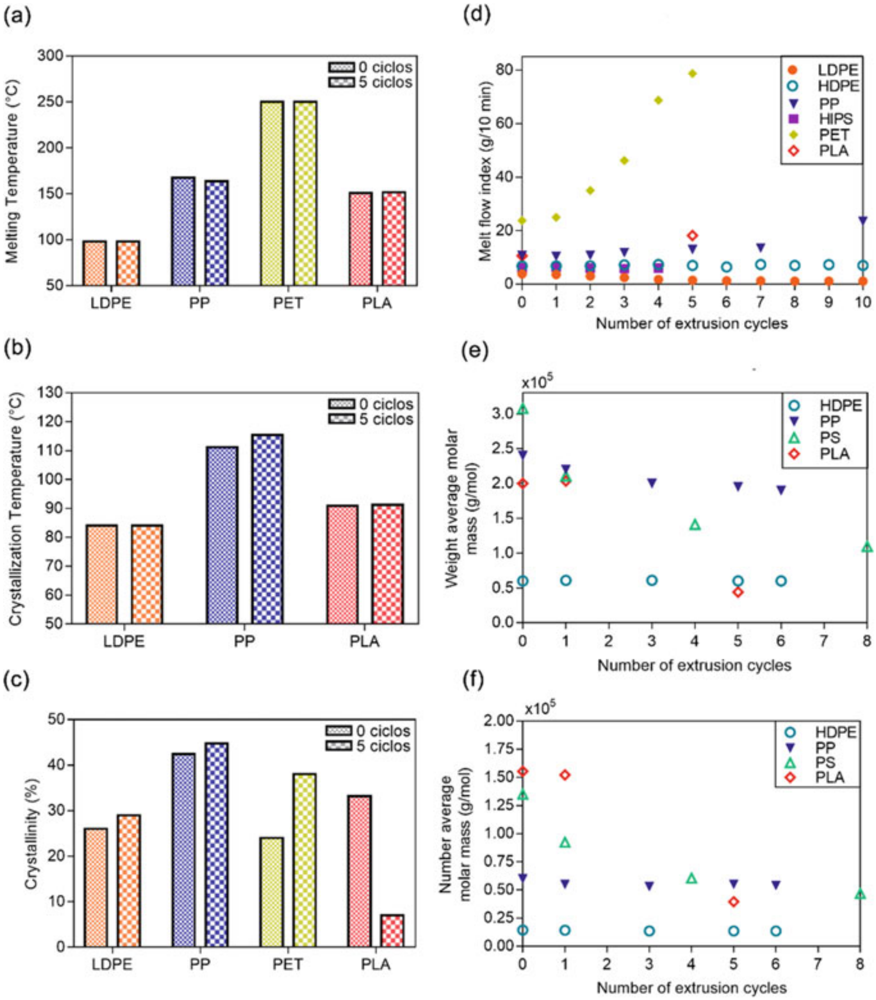

Fig. 6 Effect of the number of extrusion cycles on: **a**–**c** thermal parameters and crystallinity; and **d**–**f** melt flow index and molar mass of some polymers used in food packaging. These comparative graphs were plotted from the data reported for LDPE (Mendes et al. 2011; Peres et al. 2016), HDPE (Strömberg and Karlsson 2009; Mendes et al. 2011), PP (Tri Phuong et al. 2008; Strömberg and Karlsson 2009), PS (Remili et al. 2011), HIPS (Nunes et al. 2016), PET (Spinacé and De Paoli 2001) and PLA (Shojaeiarani et al. 2019)

et al. 2008), PET (Lim et al. 2013) and PLA (Shojaeiarani et al. 2019) (Fig. 7d). Likewise, polymer processability is modified depending on the degradation degree and molar mass variation, determining viscosity and flow properties. Thus, MFI is generally diminished in polymers mostly undergoing crosslinking during reprocessing, e.g. HDPE and HIPS (Fig. 6d).

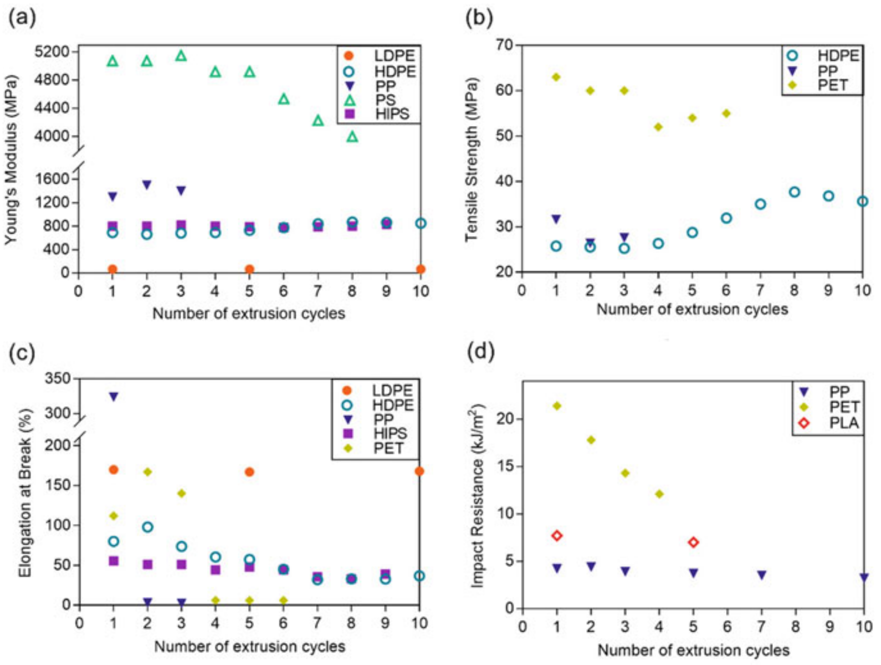

Fig. 7 Effect of the number of extrusion cycles on mechanical properties of some polymers used in food packaging. These comparative graphs were plotted from data reported for LDPE (Peres et al. 2016), HDPE (Mendes et al. 2011), PP (Tri Phuong et al. 2008; Touati et al. 2011), PS (Remili et al. 2011), HIPS (Vilaplana et al. 2006), PET (Spinacé and De Paoli 2001; Lim et al. 2013) and PLA (Shojaeiarani et al. 2019)

On the other hand, color and opacity are important characteristics in polymers for food packaging applications. For example, transparency is required when showing food to consumers is attractive. The recycling process can affect the optical properties of the polymer due to degradation. Velásquez et al. (2019) reported a higher color difference of films made of virgin/bottle recycled PET blends when the recycled plastic portion was increased. Likewise, Spinacé and De Paoli (2001) found an increase of the PET yellow index and opacity along with five processing cycles due to the thermal degradation and higher crystallinity and crystal size. Similarly, Remili et al. (2011) concluded that thermal degradation of 8-cycles reprocessed PS caused a color difference equal to eleven times the color change of 1-cycle-processed PS.

6 Conclusions and Future Perspectives

Plastics are widely used in food packaging due to their unique properties to contain and protect food products. In the last decades, research efforts have been conducted to design new polymers, biodegradable or synthesized from renewable resources, in order to reduce the generation of plastic waste and negative impact on the environment mainly by long-term accumulation of conventional polymers. Nonetheless, expansion of biopolymers' use in packaging has been limited because of their low mechanical performance, prices and current low availability of raw materials. On the other hand, mechanical recycling has been consolidated as a primary alternative due to the simplicity of reincorporating post-consumer plastic as secondary raw material to the production processes. Nowadays, the challenge is reaching a new plastic article's performance, as good as virgin plastics due to the variation of polymer properties after their service life and recycling, mainly in terms of mechanical and melt flow parameters. Thus, counteracting environmental problems caused by food plastic waste and contributing to sustainable development, require combining different strategies according to their application feasibility. These possibilities can be: changing some polymers to non-renewable ones, designing mono-materials, reducing the number of materials in multilayer systems (especially incompatible ones), recycling plastics and improving the separation process of polymers in plastic waste streams, avoiding blend of polymers with difficulty of being separated, compatibilized or recycled, tuning the properties of recycled plastics, among others. Finally, it is highlighted that new trends in food packaging are also focusing on incorporating micro- and nanoparticles into biopolymers or recycled polymers matrices in order to improve their physical–mechanical performance.

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Applications and Future of Recycling and Recycled Plastics

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Abstract The plastic recycling sector in its transition to the Circular Economy model is facing numerous challenges such as multilayer films recovering, flexible plastics, low-quality recyclates, consumers safety, and bioplastics, among others. The demand for high quality recycled products is expected to increase due to social pressure and new legislation, especially in the EU. Nevertheless, conventional recycling processes are not able to meet the quality requirements of more demanding applications intended to become in direct contact with the consumer. Therefore, new recycling technologies must be implemented to ensure the recovery of more challenging materials (for instance, multilayer films) and to maintain the quality of recycled products at a high level. Some innovative technologies that are being developed are delamination of multilayer films in a water-based solution, removal of undesired odours by steam stripping, and removal of less volatile contaminants using a water-soluble heavy solvent. High quality recycled pellets will be used in high added value applications usually in direct contact with the consumer such as cosmetics packaging, personal care products packaging, toys, kitchenware, car interior parts, etc. In this way, the highest environmental benefits will be produced, and the plastics sector will be more circular.

Keywords Plastic · Recycling · Technology · Application · Circular economy

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1 Introduction

Plastics have reached almost every aspect of our lives mainly because they are cheap, easy to produce and present numerous mechanical and thermal properties. Indeed, our modern lifestyle would not be possible without plastics. Their production has been constantly increasing since the middle of the last century when the first synthetic plastics were produced. The global production reached 368 million tonnes in 2019, which represents an increase of around 40% over a decade (Plastics Europe 2020). Despite all their benefits, plastics have become a serious environmental problem due to the massive production and inefficient or inexistent waste management strategies. Many plastic products are currently designed for a single-use or have a short service life. These products are immediately discarded after use contributing enormously to waste generation. For all this, plastics consumption should be reduced where it is possible. For instance, by avoiding over-packaging, using refillable containers, stop using plastic straws and cutlery, etc. Nevertheless, plastics cannot be fully substituted or eliminated because they provide multiple benefits to our society. Therefore, it is necessary to reduce the environmental footprint of the plastics sector.

The life cycle of plastics consists of several stages from raw materials production until plastic products end-of-life. Plastic polymers are produced by polymerization and polycondensation with the use of catalysts, solvents, fluid carriers and other secondary chemicals. The monomers come from different sources such as crude oil, coal, starch, etc. Depending on the origin of the starting materials, the plastics are divided into fossil-based and bio-based. The processing of plastic resins implies the addition of certain additives during extrusion or moulding stages. After their use, plastics are discarded. Waste management comprises several stages like collection, sorting, transportation, treatment, and disposal. The main waste treatment options are mechanical recycling, chemical recycling, and energy recovery. Geyer et al. estimated that around 6300 million metric tonnes of cumulative waste have been generated between 1950 and 2015, only 20% of which has been incinerated or recycled and the rest is accumulating in landfills or the environment (Geyer et al. 2017).

Depending on the source of waste generation, plastics waste can be classified as post-industrial, post-commercial, and post-consumer. The post-industrial waste consists of the production scrap generated during plastic converting processes like extrusion, trimming, and die-cutting. It is usually clean and homogeneous. The post-commercial waste is gathered in the retail industry area and contains mainly secondary and tertiary packaging (clear bags and stretch wrap films). It is usually homogeneous, clean, and of known composition. Finally, post-consumer waste is the domestic waste collected by municipal collection schemes. It is a mixture of different polymer types, dirty, highly contaminated and has suffered degradation during the service life (RSE USA 2017). The volume of post-consumer waste is considerably higher than the other two (29.1 million tonnes in 2018 in the EU28+No/CH). Moreover, this type of waste is much more challenging for the recycling process. The recycling rate is still low. Plastics Europe reported that 32.5% of collected plastic waste was recycled in 2018 (Plastics Europe 2020). But this data includes the plastics exported outside the EU and the collected waste includes commercial and industrial packaging, which recycling rates are usually higher. Therefore, the percentage of recycled post-consumer plastics waste is much lower and mainly polyethylene terephthalate (PET) and high-density polyethylene (HDPE) bottles and containers were recycled. Other plastics products like plastic films and plastics that are not bottles were mostly sent to landfills or incineration. In the U.S. and Canada, the recycling rates are even lower. In 2015, around 34 million tonnes (U.S. short tonnes) of plastic waste (including residential, commercial, and institutional sources) were generated. Only 9.1% of this waste was recycled, 15.5% was incinerated and 75.4% was landfilled (EPA 2018).

Despite the low recycling rates, plastics waste has a high potential to become a resource again owing precisely to its low biodegradability. The total number of possible material cycles depends on the degradation of the material through all stages of its life cycle. Therefore, product design and waste management strategies must be intended to maintain the quality of plastic products. In the EU, recycling is considered the best waste treatment option ahead of incineration and landfilling. Mechanical recycling is most frequently applied due to its technical and economic feasibility. It consists of different mechanical processes and the polymer structure of the product remains unchanged. During conventional mechanical recycling, plastics waste is usually ground or shredded, washed with water, dried, and pelletized in an extruder. When the plastic waste is contaminated, decontamination operations before the re-granulation are necessary. The cleaner and more homogeneous the waste stream, the simpler the recycling process. Chemical recycling is another waste treatment option, but it is still underdeveloped, and the energy costs are usually too high. It is based on breaking down processes of the polymer structure to obtain the original monomers or other valuable chemicals (Achilias et al. 2007). Nevertheless, the costs of separation operations are often too high, and the recycled products are used as fuel.

The plastics recycling sector is currently facing numerous challenges since the Circular Economy is gaining importance, especially in the EU. The fundamentals of the Circular Economy model lie in trying to mimic the natural ecosystems in order to reuse the products and materials in a large number of life cycles. For this to be possible, products, components and material should be kept at their highest utility and value (Webster 2017). Furthermore, recyclability must be ensured from the product´s design stage. The plastic sector’s interest in recycled materials is growing since plastic producers are more committed to green marketing, mainly due to social pressure. Therefore, recycled plastics demand is on the increase, although it is still low. The EU launched a pledging campaign to ensure that 10 million tonnes of recycled plastics are used for new products manufacturing by 2025, which means to triple the demand (European Commission 2018). In total, 70 companies and business associations have shown their interest in participating. Among them, important brand owners of food and non-food applications can be found (e.g., Danone, LIDL, P&G, Unilever). Despite the efforts made, it has been estimated that the real demand for recycled plastics that can be reached is only 6.4 million tonnes (European Commission 2019). The main barriers are the low quality of recycled plastics and the lack of traceability, which brings uncertainty about the chemical composition.

In this Chapter, the main challenges that the recycling sector must face have been reviewed. Conventional recycling methods cannot ensure the circularity of plastic materials. Therefore, new innovative technologies are being developed aiming to produce high-quality recyclates. Until now, recycled plastics have been used mainly in low added applications like trash bags, lumber, pipes, etc. But in the new Circular Economy model, recycled plastics must be suitable for high added applications such as packaging or toys. The greatest advances in mechanical recycling and future applications of recycled plastics are discussed here. Although waste management strategies are variable depending on the part of the world, the geographical scope of this Chapter includes only Western countries where recycling technologies are more developed.

2 Plastics Market Sectors and Applications

Understanding virgin plastics properties and being aware of which are their target markets is crucial to determine the best applications for recycled materials. The diversity of plastic applications is even greater than the variety of polymer types. In Europe, the three main end-markets for plastic products are packaging (39.6% of total plastic demand), building and construction (20.4%), and automotive (9.6%). Other sectors with a smaller market share but very significant regarding waste generation are electrical and electronic products (6.2%), and agriculture (3.4%) (Plastics Europe 2020). The packaging sector can be split into consumer and non-consumer packaging, depending on whether the product is intended to become in direct contact with the consumer or not. The former is in turn divided into food and non-food packaging. And the latter refers to commercial and industrial packaging (also known as secondary and tertiary packaging) from retail industry areas (for instance, clear bags and stretch wrap films). Food packaging is the biggest end market for the majority of polymers, but it is also one the most restrictive. In this section, the properties and applications of the main thermoplastics are presented because this type of plastics constitutes the biggest fraction of the plastic waste stream. Table 1 is a schematic summary of target markets and specific applications of different polymers.

Polyolefins such as polyethylene (PE) and polypropylene (PP) are the most demanded plastic materials. There are several types of polyethylene but all of them can be grouped into two categories: branched and linear. The polymer chain structure strongly influences the final properties of the plastic material. Branched PE presents lower density due to irregularities in the structure leading to lower crystallinity, thus is called low density polyethylene (LDPE). The main properties of this material are clarity, flexibility, heat sealability and good water vapour barrier but a poor gas barrier. It is widely used as plastic bags, agricultural films and shrink and stretch wrap films, among others (Selke and Culter 2016). It is also frequently used in food packaging multilayer structures as sealable material. Medium density PE (MDPE) also presents a branched structure. It is to some extent stronger, less flexible, and less permeable than LDPE. Among its main applications are gas pipes and fittings, sacks,

Table 1 Applications of main thermoplastics

LDPE/LLDPE	HDPE	PP	PET	PVC	PS
Food packaging					
Squeeze bottles (e.g. ketchup, mustard) Baked goods and meat Sealable material in multilayer films Caps and closures of containers Cling films	Milk and juice bottles Cereal box liners Butter containers	Yoghurt and margarine pots Sweet and snack wrappers Single-serving tubs Dishwasher-safe and microwave-proof food containers Reusable food storage containers	Water bottle, sports and carbonated soft drinks, fruit juices Oven bags and boil-in-bag products Single-slide cheese wrap Support material in multilayer films Ovenable frozen food and prepared meals Cooking and salad oils, sauces and dressings bottles, peanut butter jars	Stretch wrapping for fresh meat trays Inserts from chocolate boxes and biscuit trays Fruit juices and edible oils Cling films	Disposable drinking cups Dairy and fishery Egg cartons Meat and poultry trays Fast-food containers
Non-food packaging					
Collapsible tubes Carrier/shopping bags Dispensing, wash, and pharmaceutical bottles	Personal and home care products Carrier/shopping bags	Medical packaging and appliances	Cleaners bottles Cosmetic jars Pharmaceuticals	Pharmaceuticals	Cosmetic and medicine containers Cushioned packaging, foam peanuts CD and DVD cases

(continued)

Table 1 (continued)

LDPE/LLDPE	HDPE	PP	PET	PVC	PS
Commercial and industrial packaging					
Shrink and stretch films Heavy-duty industrial bags	Industrial wrapping and film Crates and boxes				
Building and construction					
Building irrigation systems	Pipes and tubes	Indoor-outdoor carpet Air and moisture barrier membranes Building wraps and durable siding Industrial adhesives and tapes Plastic parts included in piping	Building envelope Modular housing PET foams: sandwich composites, highly insulating roofs or facades, balconies, bridges	Flooring, roofing, and siding Pipes, cable insulation Window frames, swimming-pools, and reservoirs Fencing and decking Linings for tunnels	Insulation Floorings, ceilings, and roofing system Road construction Lighting and plumbing fixtures Bath and shower units

(continued)

Table 1 (continued)

LDPE/LLDPE	HDPE	PP	PET	PVC	PS
Automotive					
Seat and trunk liners Wing mirror seals Dashboard padding Carpet backing Energy-absorbing/noise-reduction foams Tapes and self-adhesive foam strips and gaskets	Wiring and cables Seats Fuel tanks	Bumpers Seats, upholstery, and gloveboxes Cable insulation, carpet fibres Plastic helmets Instrument panels, interior trims, and airbag doors Grilles and housings, side mouldings, wheel flares, panels and spoilers, and fender liners	Automotive flooring Wiper arm Gear and connector housing Engine cover	Instrument panels and car cables Upholstery and door parts Floor mats and auto tops Underbody coating Hoses, flexible profiles Foamed films/artificial leather	Knobs, instrument panels, and sound dampening foam. Child protective seats Equipment housings and displays Crash helmets
Electrical and electronic					
Cable and wire insulation	Cable and wire insulation	Computers, cell phones, and televisions Kettles and microwaves	Handles and housings for appliances Plug connectors, relays, keyboards, switches, and distribution boxes	Cable and wire insulation, cable trunking Injection moulding parts	Housing and other parts for televisions, computers, and all types of IT equipment Refrigerator trays/linings, TV cabinets

(continued)

Table 1 (continued)

LDPE/LLDPE	HDPE	PP	PET	PVC	PS
Agriculture					
Bale wrap and shrink wrap films Greenhouse, low-tunnel, mulching, silage, and disinfection films Irrigation pipes and tapes Fertilizer bags/sacks Hydroponic sacks	Bale wrap and shrink wrap films Irrigation pipes and tubes Nets and bale wraps Fertilizer bags Agrochemical packaging	Bale wrap and shrink wrap films Silage films Strings, bags, twines Specific nets (nonwoven layers) Fertilizer bags/sacks	Agrochemical packaging Mesh fabrics	Bale wrap and shrink wrap films Irrigation pipes and tapes	Seed and hydroponic trays, flowerpots, horticulture items Packaging of fruit and vegetables Agricultural storage floor vent
Others					
Toys Trash bags	Toys Housewares Kitchen tools Garbage containers	Toys Mouthguards Protective padding Goggles Garden furniture	Toys Fabrics, synthetic fibres, cloth Bedsheets and bedspreads Curtains and draperies Tape	Toys Thin surgical gloves, blood bags, and transfusion tubes Labels and presentation trays Garden hoses, footwear, inflatable pools, tents Tarpaulins and rainwear	Toys Laboratory ware: tissue culture trays, test tubes, Petri dishes, diagnostic components, and housing for test kits. Housewares and dining utensils Windsurfing boards

crew closures, and shrink and packaging films when blended with LDPE (Vasile and Pascu 2005). Regarding linear PE, the chain structure is nearly linear, and the polymer presents higher crystallinity and density. Thus, linear PE is known as high density PE (or HDPE), which is less transparent, presents good mechanical and moisture barrier properties but is highly permeable to oxygen and organic compounds. HDPE is widely used as a rigid container in the beverage sector (milk and juices) and personal and home care products (detergents, bleach, shampoo, etc.). HDPE films are also commonly used in packaging applications (for instance, cereals and snacks) and as carrier bags (Selke and Culter 2016). The linear low density PE (LLDPE) presents a linear structure with very short branches resulting in lower density than HDPE (similar to LDPE). It is commonly used in industrial packaging films, stretch films, and heavy-duty shipping sacks owing to its improved mechanical properties such as tensile strength, tear properties, elongation, and puncture resistance (Vasile and Pascu 2005; PlasticsEurope 2021).

Polypropylene covers around 19% of the plastic demand in Europe (Plastics Europe 2020). It has good resistance to chemicals, mechanical fatigue, and stress cracking. PP presents a lower density and higher melting point than PE and it can be processed in both flexible and rigid forms. Flexible PP is commonly used in packaging applications especially for dry food owing to its high moisture barrier properties. Rigid PP is used for the manufacturing of food packaging (e.g. yoghurt, margarine pots), microwave containers, sterilizable materials, pipes, and automotive parts among others.

Other common thermoplastics are polyvinylchloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). PVC is a tough and rigid polymer with a small degree of crystallinity, and a higher melting temperature and density than PE and PP. The main applications of rigid PVC are window frames, pipes, garden hoses, floor and wall covering, etc. (Plastics Europe 2020). This material can be transparent and opaque, and it has good barrier properties. Flexible PVC is commonly used as cling film and food packaging (Leadbitter 2003). Nevertheless, its use as food contact material has been challenged due to the migration of residual vinyl chloride monomer, which is a carcinogen (Selke and Culter 2016). PET is a semi-crystalline polymer and the degree of crystallinity defines the final application of the material. Oriented PET is transparent, tough, and possesses good oxygen and carbon dioxide barrier properties, thus it is largely used in soft drink bottles and other containers manufacturing. Regarding PET films, biaxially oriented PET is an excellent odour and gas barrier, and it is widely used in multilayer food packaging (Selke and Culter 2016). The main advantage of PET over other plastics in food packaging applications is its high inertness, in other words, low migration of substances from the package to the food (Welle 2014). Finally, PS is an amorphous polymer with low strength and heat resistance. This is why it is commonly used in less demanding applications such as dairy and fishery packaging, building insulation, foam plates, and cutlery (Plastics Europe 2020).

3 Recycled Plastics End Uses

Deciding whether recycled plastics can be used in a specific application is strongly influenced by the quality of the material and the requirements of the target market. Recycled products can be used in the same application as the original material, which is known as closed-loop recycling. Or they can be used in a different application. If the quality of the plastic material is maintained or even improved, the recyclates are suitable for high added value application different from the original. This process is known as upcycling. On the contrary, if the quality of recycled plastics decreases, these materials can be used only in low added value applications, which is denominated downcycling. Figure 1 shows pictures of high quality upcycled pellets (a) and lower quality downcycled pellets (b) Low-quality recycled products can be introduced for some applications in sectors like agriculture, building and construction, and automotive. In the case of PE, the market share of these sectors covers around 24% of the total demand (Eriksen et al. 2019). This means that around 76% of the market cannot be circular if only low-quality recyclates are available. On the contrary, it is considered that upcycled plastics can be used in all applications including food packaging because their quality is similar to virgin plastics. Therefore, upcycled plastics reach 100% of the market.

Currently, downcycling processes are predominantly used, especially, in the case of polyolefins. Recycled products are intended for low added value applications due to the lower quality of the material (inferior physical properties, dark colours, disturbing odour, etc.). PE and PP products are usually recycled into trash bags, irrigation pipes, outdoor applications, and auto parts, among others. PET is one of the few materials that can be recycled in closed-loop (PET bottles recycled into new bottles). Also, recycled PET (rPET) is used in the manufacturing of other high added value products such as fibres and fabrics for the fashion industry (Clark 2018). Low-grade rPET can be used in the building and construction sector, for instance, to replace traditional bricks (Sharma 2017). This material shows high recycling rates especially

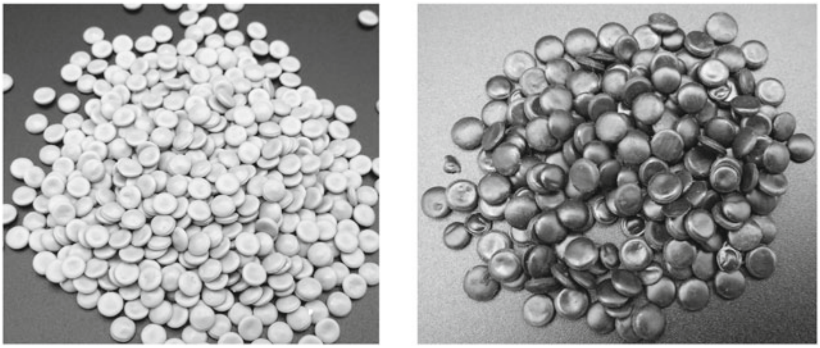

Fig. 1 Recycles plastic obtained through different processes. **a** Higher quality pellets. **b** Lower quality dark pellets

in countries like Norway, Japan and Sweden where it exceeds 80% (Tiseo 2020). This can be attributed to its inertness, clearness, well-established recycling technologies, and adopted deposit return schemes for efficient waste collection. Recycled PS is mainly used in the building and construction sector, for instance, in insulation, lamp posts, light switches, among others. It can be also found in hot cup lids and disposable cutlery (EcoProducts 2021). Recycled PVC is also mainly used in building and construction in applications such as cables, carpet backing, decking and fencing, among others (Belsey Priebe 2011).

Secondary products usually contain a mixture of virgin and recycled plastics. Virgin plastics are added mainly for two reasons. The first one is to achieve the desired quality level of the final product according to the requirements of the target market. The second one is the lack of recycled plastics, especially with high quality, to cover market demand. The substitution ratio, calculated as the amount of recycled plastic that can substitute virgin resins over the total amount of plastic necessary for the manufacturing of a product, depends on the intended application of the recycled product. Thereby, the substitution ratio is high in low demanding applications such as pipelines, flowerpots or trash bags. On the contrary, the recycled content decreases (lower substitution ratio) in less forgiving applications like packaging or toys. For instance, trash bags can contain 80–100% of recycled plastic, nevertheless, diapers producers only accept around 20% of recycled content. Of course, the substitution ratio in high added value applications can increase if high-quality recyclates are used. However, potential risks of using recycled plastics in products that are in direct contact with the consumer (both food and non-food contact) have not been thoroughly studied. This hampers the implementation of the Circular Economy model in the plastic sector. Furthermore, the environmental benefits of plastics recycling strongly depend on the substitution ratio and the market share of the intended applications.

4 Challenges in Plastics Recycling

The plastics sector has two main problems regarding the recovery of plastic products. The first one is that there are products that cannot be recycled using conventional technologies. And the second one is that the quality of the recycled products which are currently recovered is usually low. All the relevant stakeholders such as brand owners, converting companies, inks and adhesives producers, and recyclers must strive together to ensure the circularity of plastics by redesigning some plastic products and investing in new recycling technologies.

Several plastic products cannot be recycled through conventional recycling technologies at large scale. Multilayer plastic films are one of these products representing a big challenge for the recycling industry. Multilayer films are composed of several layers of different material that can be polymeric or not (e.g. paper, aluminium, fabric). These plastics cannot be extruded without previously separating the layers due to the combination of frequently incompatible materials, for instance, PET, PE, and aluminium. Despite their low recyclability, multilayer films are widely used in the food packaging sector because they provide weight reduction and help preserve foodstuff thereby reducing the amount of food waste, among other benefits. Kaiser et al. estimated that around 1.86 Mt of polymer-based multilayer packages were produced in 2016 in Europe, without considering packaging with paper (Kaiser et al. 2018). It can be extrapolated that the global production amounts to 10 Mt. Drink carton laminates usually are treated separately due to their specific composition (polyethylene, aluminium, and paper) and high production rates. In Germany, 178 kt were used in 2016 (Kaiser et al. 2018) and in Spain, around 150 kt are used every year. The world leader Tetra Pak put 300 billion multilayer beverage cartons in the market in 2017 (Tetra Pak 2020), of which between 30–40% corresponds to plastic and aluminium difficult to recycle. Although there are some initiatives to substitute or ban multilayer materials, it is proving difficult to find a sustainable solution with the same benefits (Kaiser et al. 2018). Therefore, efficient recycling technologies along with better design is key to avoid the accumulation of multilayer plastics in the environment.

The treatment of flexible plastics or films also represents a challenge for the recycling sector. Traditionally, recycling has been applied to rigid plastics. Nevertheless, the demand for flexible plastics has increased, especially in the packaging and agricultural sectors, owing to several advantages such as lightness, versatility, and costs reduction. The problem is that recycling rates of flexible plastics are considerably lower compared with rigid plastics because flexible films behave differently during recycling operations and the efficiency decreases. Plastics films retain more dirtiness and contamination from the use phase than rigid products, which affects the quality of recycled products. Also, they retain much more water due to their higher surface area and tortuosity (Horodytska et al. 2018a). An excess of water during the extrusion of the plastic mass increases the chance for defects to occur, causes deterioration, and pushes up energy costs. Therefore, good drying is paramount to ensure high efficiency and proper quality of recycled materials. Moreover, drying is one of the most expensive operations (de Lima et al. 2016) and one of the stages that contribute most to global warming and fossil depletion potentials (Chen et al. 2019). But in practice, the drying technologies have not been optimized for the treatment of flexible plastics and frequently the dewatering efficiency does not reach the required level. Furthermore, the information existent in the literature about the behaviour of plastics films during drying is very scarce. Only one study developed at the University of Alicante (Spain) that addresses the centrifugal dewatering of plastic films has been found (Horodytska et al. 2018a) As a consequence, the economic benefits from plastic films recycling decrease, and these materials are mostly sent to landfills or incineration.

Regarding the quality of recycled products, conventional recycling processes most frequently produce low-quality pellets suitable to be used only in low added value applications with very few exceptions such as PET bottles that are used to produce new beverage bottles. The secondary products produced with low quality plastics will be surely sent to landfill or incineration at the end of their service life. Therefore, the downcycling processes are more akin to the Linear Economy model. On the contrary, in the Circular Economy model plastics must be recycled in a closed-loop (i.e. for the same application as the original material) or in an open-loop where the recycled pellets are used in high added value applications but different from the original material. Currently, the quality of recycled plastics is a big impediment for the implementation of the Circular Economy because around 70% of the market cannot accept the use of low-quality pellets for the manufacturing of new products. The quality can decrease due to several factors such as loss of mechanical and thermal properties, colour, undesired odours, and contamination, among others. For instance, flexible non-food packaging is usually printed on the surface. The presence of inks during extrusion produces defects in recycled plastic pellets and gives them usually a dark colour. As a consequence, these plastics can be only used in low added value applications such as trash bags, pipelines, flowerpots, etc. (Horodytska et al. 2018b). Another indicative example is the detergent and personal care products bottles. These bottles are most frequently made of rigid HDPE and have a high potential to be recycled due to their homogeneity and rigidity. Nevertheless, the recycled pellets present a strong odour after conventional recycling due to a high amount of fragrances and aromas (Strangl et al. 2018; Horodytska et al. 2020). As a result, these plastics are not suitable to produce bottles again and they are usually used in outdoor applications with lower added value.

Food packaging represents the biggest market share of LDPE films (54%), followed by non-food packaging (18%) (Eriksen et al. 2019). So, the plastic industry cannot be fully circular without incorporating recycled products in the packaging sector, which is currently not possible due to their low quality and lack of traceability. The food packaging sector is very restrictive. The European Food Safety Authority (EFSA) is the organization in charge of assessing and communicating risks related to the food chain in the EU. There are several legislations applicable to all materials intended to become in contact with food (FCM) such as REACH, Regulation (EC) No 1935/2004 on Food Contact Materials, and Regulation (EC) No 2023/2006 on Good Manufacturing Practices. Also, Commission Regulation (EU) No 10/2011 is applied in the case of plastic products. This Regulation establishes a list (called positive or Union list) of substances that can be intentionally added in the manufacturing of food contact plastics, as well as a migration limit for the substances that can be transferred from the plastic material into the food. Using recycled plastics in FCM presents further challenges and difficulties. These materials are regulated by the Commission Regulation (EC) No 282/2008 according to which only recycled plastics produced by EFSA authorised recycling processes can become in contact with food (De Tandt et al. 2021). The vast majority of approved technologies are intended for PET recycling. In contrast, there are only a few PP and PE recycling technologies approved for food contact end-uses. For instance, recycling of PP and HDPE crates for fruits and vegetables, and recycling of HDPE milk and juice bottles, as well as trays for fruit and vegetables or animal products (EFSA CEF Panel 2010, 2012, 2013a, b).

Finally, the recycling sector will have to deal soon with a new challenge: the biopolymers in the waste stream. These types of polymers reached a market segment above 2 million tons in 2019 and the perspective is to overcome 3 million tons in the next decade (European Bioplastics 2019). Even though the production of biopolymers is less than 1% of the overall plastic production (368 million tons in 2019 (Plastics Europe 2020)), the increasing consumption of biopolymers poses an additional challenge for solid waste management, mainly because these materials complicate sorting processes, thus hindering conventional recycling regimes (Alaerts et al. 2018) (most thermoplastics are incompatible). The biopolymers must be also circular to be fully sustainable, which means that they must be recyclable. Thereby it is interesting to study these type of materials from the point of view of the circular economy and taking into account the new policies implemented by the public administrations like the European Commission (2015/720/EU and 2019/904/EU), where the restriction in the use of plastic, for example in the packaging industry, makes necessary to find stable and viable solutions for the recovery of post-process materials. It is paramount to study the end-of-life scenarios of biopolymers and their implementation to ensure the sustainable development of these products.

5 Future of Mechanical Recycling

In the last years, mechanical recycling has been progressing aiming to improve packaging recyclability as well as quality in terms of colour, odour, and mechanical properties, while preserving the polymer structure. Currently, conventional mechanical recycling is technically feasible for single materials, but it does not work for multilayer materials or composites (Horodytska et al. 2018b). For this reason, emerging technologies are establishing a new age of mechanical recycling by introducing chemicals and additional units that improve polymers quality.

5.1 New Technologies to Improve Multilayer Packaging Recycling

Several publications and industry solutions depict the possibility of recycling multilayer materials by three principal methods: polymers compatibilization, dissolution of one or various layers, and interfacial delamination.

Compatibilization consists of adding specific chemicals to the mixture of polymers to enhance the unity among the different components. Some studied compatibilizers are maleic anhydride-grafted polypropylene, oxazoline groups, ethylene/acrylic acid copolymer or block copolymer styrene-ethylene/butylene-styrene-grafted-succinic acid (Jeziórska 2003; Wyser et al. 2017). Several researchers analysed the compatibilization effects between PET and PE with the addition of ethylene-glycidyl methacrylate (EGMA) and styrene-ethylene-butylene-styrene grafted with maleic anhydride. The results showed that it is possible to process these two incompatible polymers together (Pawlak et al. 2002; Uehara et al. 2015). This type of additives are already used in the industry and important chemical producers offer several compatibilizers (The Dow Chemical Company 2017; DuPont 2017). Nevertheless, their price is usually high so that compatibilization cannot be used at a large scale because the operational costs rise too high.

The dissolution methods can be described as a recycling process between chemical and mechanical recycling, as the material structure changes due to its dissolution, but the plastic is not depolymerized, maintaining the molecular structure. The following research publications describe some dissolution methods used to delaminate multilayer packaging. Cervantes-Reyes et al. treated LDPE-aluminium composites originating from rigid liquid cardboard packaging (Tetra Pak) after cardboard recovery by hydropulping. Several polar and non-polar solvents, such as xylene, toluene, and hexane among others, were used to dissolve the LDPE layer. Finally, the LDPE was isolated from the solvent by solvent evaporation. As a result, a maximum recovery yield of 56% was obtained using xylene at reflux conditions (Cervantes-Reyes et al. 2015). In a similar study, Georgiopoulou et al. achieved a recovery yield above 99% by using xylene to dissolve the LDPE layer and isopropanol as a precipitating agent (Georgiopoulou et al. 2021). Another study, in this case by Samorì et al., showed the effectiveness of switchable hydrophilicity solvents (SHS) in the recovery of LDPE from LDPE-aluminium composites, achieving a recovery of more than 99% for the aluminium layer and above 80% for LDPE (Samorì et al. 2017). The use of SHS presents environmental advantages, as after LDPE dissolution the polymer precipitates by switching the polarity of the solvent with CO_2. This effect avoids the addition of new solvent into the process or solvent evaporation to recover the polymer, lowering the environmental impact of the process.

A few patented technologies also show diverse possibilities to recover polymers from multilayer structures by dissolution. García patented a process to recover PET/EVOH/LDPE multilayer structures by dissolving the PE layer with xylene at a temperature around 95 °C. PE is usually the minor material in this kind of packaging and it is not recovered in the process (García Fernández 2011). On the contrary, Patel et al. proposed a method to recover PET from PET/PE structures using a solution containing sulfuric acid (Patel et al. 2016). This reactant hydrolyses the PET producing terephthalic acid and ethylene glycol. In the patent, the recovery of these chemicals is not considered. However, it could be highly valuable to recover all the compounds as it would lead to a zero-waste recycling process (Achilias and Karayannidis 2004; de Carvalho et al. 2006). Linder et al. designed a method for recovering LDPE from plastic film waste by conveying a selective dissolution of the various polymers and recovering uniquely LDPE (Linder et al. 2004).

In the industry, two companies are working towards the recovery of multilayers that use dissolution of at least one of the layers, these are Sulayr and APK AG. Sulayr is a Spanish company dedicated to the recovery of PET/LDPE trays by dissolving the LDPE layer and preserving the PET in a flake shape. APK AG recovers PA and LDPE from both post-industrial and post-consumer packaging by selective dissolution of the materials with the Newcycling process.

Last but not least, interfacial delamination is a promising method to recycle multilayer packaging. This technology disassembles the layers of the multilayer films by dissolving the tie layer while maintaining the structure of the polymer. Mukhopadhyay published a process for the recovery of constituents in packaging multilayer structures. The separation of the different layers or components occurs by soaking them in an inorganic acid solution (e.g., nitric acid) for 4–7 h. Afterwards, the adhesive binding the layers is completely dissolved, and, consequently, the layers are disassembled (Mukhopadhyay 2004). Likewise, Johansson and Ackermann published a "Method of recovering individual component parts from packaging material waste" that consists of washing with organic acids, such as formic acid, acetic acid, propanoic acid, butyric acid, citric acid, sorbic acid, and lactic acid, to disassembly the different layers comprising metal and plastic multilayer packaging (Johansson and Ackermann 1995). Similarly, the patent published by Lovis et al. describes a process for the delamination of multilayer packaging comprising metal and polymer layers by dissolving the inner adhesive binding the multiple layers with a dissolution of carboxylic acids and swelling agents (Lovis et al. 2015). This last-mentioned patent belongs to the company Saperatec GmbH that has developed said process at a pilot scale.

Additionally, a recent Technological Offer publication from the University of Alicante describes a new process able to delaminate multilayer packaging with diverse structures, such as PE/PET, PP/ink/PP or PP/aluminium/PE, by dissolving the adhesives, tie layers and inks. The principal innovation in this technology is creating access points on the packaging to accelerate the inlet of the delaminating and deinking solution to the interphase (Fullana 2020). This technology is currently patent pending and developed at a Technology Readiness Level 5. The spin-off company FYCH Technologies S.L. will commercialize this technology at an industrial scale (Fych Technologies 2021).

5.2 Deinking Technologies

During mechanical recycling, the inks present on the surface of the printed plastics must be removed before the extrusion stage to avoid quality loss of recycled pellets. Existing deinking methods are based on removing the inks in a washing tank using a deinking solution that can be solvent-based or water-based. Gecol et al. studied the effects of different surfactants and concluded that cationic surfactants are the most effective at alkaline pH for the removal of both water-based and solvent-based inks (Gecol et al. 2001, 2002, 2003, 2004). Several researchers used alkyltrimethylammonium bromides (such as dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide or DTAB, TTAB, and CTAB, respectively) as a deinking agent and optimized parameters like temperature, concentration, alkyl chain length, and pH (Chotipong et al. 2003, 2007; Songsiri et al. 2002). Chotipong et al. suggested that adsorption of surfactant on the ink pigments and solubilisation of the binder into surfactant micelle are two mechanisms that enable the deinking of the plastic surface (Chotipong et al. 2006). Another possibility, studied in a European-funded project CLIPP+ , is to use carbon dioxide in supercritical conditions (AIMPLAS 2013).

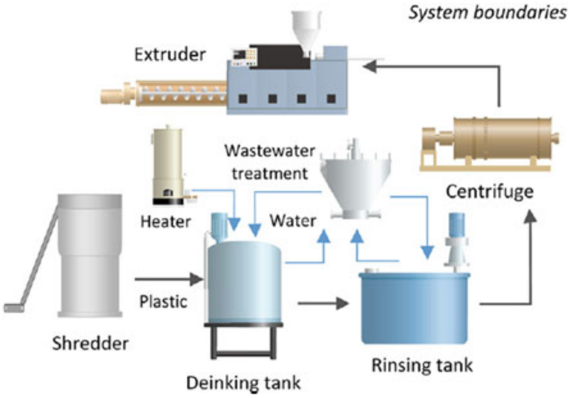

Fig. 2 Schematic representation of the deinking process developed in the University of Alicante

Researchers from the University of Alicante developed an innovative deinking technology using surfactants in water-based solution (Fullana and Lozano 2015). The process consists of grinding the plastic materials, washing with the deinking solution, rinsing, drying and extrusion. The process includes a wastewater treatment so that the water is cleaned and recirculated with the deinking reactants to the washing tank (Fig. 2). The only residue generated during the process is a small amount of non-hazardous wastewater sludge that contains inks pigment and colourants. Currently, this process is commercialized by the company Cadel Deinking located in Spain. Another common practice is removing the inks from unwound film rolls without grinding the material, which is described for instance in the Duchenaud Uniflexo patent (Piolat 2004) and Gamma Meccanica patent (Gamma Meccanica 2016). These processes consist of immersing the material in the deinking solution and rubbing the inks with rotating brushes. The deinking solution is a mixture of non-ionic surfactants and organic solvents. Finally, there are processes where only solvents are used. This is the case of Rhaaplex Company in Brazil (Metalúrgica Rhaaplex 2011). The problem with using solvents is the inferior mechanical and optical properties, undesired odours, high investment, and operational costs.

5.3 Decontamination Technologies

Apart from inks, other contaminants are present in recycled plastics as a consequence of their previous use phase. For instance, carboxylic acids and sulfur compounds related to food spoilage were identified in polymers used for food packaging such as LDPE (Cabanes and Strangl et al. 2020). Likewise, ingredients from detergents such as β-ionone and α-isomethyl ionone were identified in post-consumer HDPE, commonly used as fragrances for home care and body care products (Strangl et al. 2018). Although these substances are mainly related to odour-causative compounds, there is a large number of compounds not related to smell that are also present in post-consumer packaging materials identified as non-intentionally added substances (Horodytska et al. 2020). Some of these NIAS derive from detergents and food migration into the package. In addition, polymers and additives degradation related substances are also present in recycled plastics. In this study, volatile and semi-volatile organic compounds from HDPE and LDPE post-consumer recycled pellets were analysed, obtaining that benzyl acetate and 2-phenoxyethanol are the predominant substances in post-consumer HDPE which belong to cosmetics ingredients, and methyl 3,5-dicyclohexyl-4-hydroxybenzoate, caused by the degradation of an antioxidant additive, was the most abundant substance among those identified in LDPE.

Polymers must be decontaminated to warrant packaging safety at any level and attain a circular economy model in the plastics sector. However, as regulations are quite restrictive to use post-consumer recycled polymers for food applications, the existing decontamination processes are mostly focused on odour reduction as this is one of the main impediments to use recycled polymers for non-food contact applications, such as home and body care packaging, furniture or car upholstery (SUSCHEM 2020).

In the industry, the existing solutions to remove odour-related contaminants are focused on post-treatment after extrusion. In 2016, the company Erema launched the Refresher unit to mitigate the issue of smells in recycled plastics. This unit consists of a first in first out vertical reactor with a cylindrical geometry in which the pellets leaving the extruder are fed to the top of this column thus falling to the bottom by gravity. Hot air is fed from the bottom to the top of the column to extract the odour-causative substances from the plastic. The energy consumption of this unit is 0.13 kWh/kg of recycled pellets, about half of the energy consumed in the extrusion line (Cabanes and Valdés et al. 2020).

Due to the increasing demand for odourless recycled plastics, research publications on decontaminating technologies increased in the past few years. In a recent study, Roosen et al. studied the influence of various washing mediums on the removal of 19 odour components from plastic film waste (Roosen et al. 2021). Water, caustic soda, hexadecyltrimethylammonium bromide (CTAB) surfactant, and ethyl acetate were tested at different temperatures obtaining the highest efficiency—above 90% reduction—with ethyl acetate at 65 °C. Washing with caustic soda dissolution resulted in lower efficiencies than using only water due to the higher polarity on the media that decreased the miscibility of the organic substances producing odours. The addition of surfactant improved the efficiency of organics removal in comparison with washing with water because first decreases the contact angle between the washing media and the surface of the plastic facilitating the removal of the organics from the surface of the plastic, and second, because stabilizes the organics in the dissolution avoiding deposition on the plastic surface. Nonetheless, these effects do not equal the ethyl acetate extraction efficiency, as the increased solubility of the organics in this solvent improves the removal of said substances compared to the surfactant washing media.

Another study by Cabanes and Fullana shows the influence on the reduction of volatile organic compounds by two different removal methods (Cabanes and Fullana

2021). One technique uses polyethylene glycol as an extracting agent, and the other consists of a steam stripping process to extract VOCs from plastics. Polyethylene glycol is used based on its higher solubility with VOCs than water; it is water-soluble and non-volatile. These properties improve the extraction capacity compared to the conventional water wash, facilitate the residual solvent removal from plastics by rinsing with water, and the low volatility of the solvent ensures the process safety as explosive vapours are not emitted to the environment and also avoids solvent evaporation. The steam stripping process favours the devolatilization of organic substances by lowering the organic compounds boiling point due to the partial pressure effect (Hassan and Timberlake 1992). These two methods are compared to the technologies already developed at an industrial scale: the extrusion-degassing unit and the hot air extraction (Refresher). Accordingly, steam stripping shows a higher reduction of unwanted VOCs originating from the previous use phase than the rest of the methods. Polyethylene glycol extraction, however, offers a higher reduction on polar VOCs than hot air stripping but lower in the case of non-polar molecules. The steam stripping technology for odour removal is being developed by the spin-off company FYCH Technologies S.L (Fych Technologies 2021).

Extractive extrusion has also demonstrated its effectiveness in minimizing odour intensity from recycled plastics. Fraunhofer Cluster Circular Plastics Economy (CCPE) showed a reduction of odour intensity from above 5 to less than 2 (in a 0–10 scale) according to the ISO 16000-28 standard, by using CO_2 as a stripping agent through the extrusion process (Fraunhofer ICT n.d.). Similarly, Ben Said et al. (2016) studied PP pellets decontamination using CO_2 as an extracting agent. In this research, food-grade virgin PP was contaminated in the laboratory with four organic compounds, namely stearin, dilaurin, trilaurin, and tripalmitin, covering a range of polarities and molecular weights to represent possible external migrating substances to the packaging. Complete extraction of all contaminants was achieved at 200 bar and 90 °C after 7.5 h of extraction (Ben Said et al. 2016).

5.4 Biopolymers Recycling

To consider a polymer as a biopolymer their monomers must be obtained from a renewable feedstock (crops, tubers…) that consumes carbon dioxide (CO_2) when it grows. So that the overall production of bioplastics has a smaller carbon footprint compared with the fossil-based polymers (Zhu et al. 2016). But only this does not guarantee that the biopolymer is environmentally friendly over its complete life cycle (Soroudi and Jakubowicz 2013) because biopolymers can be both biodegradable or non-biodegradable. For example, a bio-PET is a non-biodegradable biopolymer because although the ethylene glycol and terephthalic acid components are obtained from renewable feedstock, the later chemical polymerization process is the same as the conventional polymerization of PET (Shen et al. 2010; Tabone et al. 2010) making both polymers chemically identical. From the point of view of recycling, this can be considered as an advantage because bio-PET and petro-PET can be blended and recycled together. Some companies such as PepsiCo and Coca-Cola have shown interest in the implementation of bio-PET and recycled PET as an alternative to virgin petro-based PET used in their bottles (Barret 2018). In this sense, the same consideration can be made between the rest of biopolymers like bio-HDPE, bio-LDPE or bio-PP and their fossil-based counterparts. This group of non-biodegradable biopolymers makes up approximately 40% of the global biopolymers market size. Nevertheless, their market volume growth has slowed down compared with biodegradable polymers (European Bioplastics 2019; Dilkes-Hoffman et al. 2019).

Biodegradable polymers can be divided based on the origin of the renewable feedstock of their monomers into (a) polysaccharides and derivatives (starch, chitosan, cellulose…); (b) proteins (gluten, keratin…); and (c) bacterial polymers like polyhydroxy acids. Among all, polylactic acid (PLA) and starch blends are the most biodegradable polymers used by the industry, followed by poly (butylene adipate co-terephthalate) (PBAT) and polyhydroxyalkanoates (PHA) (European Bioplastics 2019; Plavec et al. 2020). PLA has been traditionally used in the field of biomedical applications due to its biocompatibility (Ruderman et al. 1973; Gourlay et al. 1978; Casalini et al. 2019). But during the last decade, PLA has been also used in the packaging industry due to its similar characteristic to other petro-based polymers like PET (Castro-Aguirre et al. 2016; Auras et al. 2004). Starch is the second most abundant polysaccharide and it is used since the 80 s in the food sector (Egharevba 2019; Santana and Meireles 2014) and the adhesive (Janković-Častvan et al. 2015) industries, among others. Starch also has been used as filler within other petro-based and bio-based polymers. The starch grain structure can be disrupted to form thermoplastic starch (TPS) using a plasticizer (Domene-López et al. 2019a, b). TPS and its blends are continuously increasing their potential applications in the field of the packaging industry (Domene-López et al. 2018, 2020) and currently, they are the second most used biodegradable biopolymer in the industry. Another common biodegradable biopolymer is PBAT having similar properties to LDPE, with good thermal stability, simple processability and suitability for flexible packaging production (Spiegel 2018; Jian et al. 2020). PBAT can be blended with other biopolymers like PLA to increase its ductility and reduce the fragility of the final blend (Lule et al. 2020; Musioł et al. 2018). Also, PBAT can be used blended with some PHA to increase the flexibility of the final polymeric system (Pawar et al. 2015). PHA can be produced by a combination of more than 300 different types of microorganism that can accumulate polyhydroxy acid and be processed to produce PHA (Lenczak and de Aragão Gláucia Maria Falcão 2011). Traditionally, they have been used in the field of biomedicine due to their high cost. But their similar properties to PE or PP make them suitable for other applications, like the packaging industry (Bugnicourt et al. 2014).

The biodegradability of biopolymers in biological environments, i.e. composting systems, is one of their main advantages. But from the point of view of the circular economy, reuse and recycling processes implemented before the final composting of the material could increment its environmental benefits. In this sense, mechanical and chemical recycling is considered as a better end of life option for biodegradable biopolymer before the “biological recycling”, considered as a composting process. Mechanical recycling, as happened with other petro-based polymers, Biopolymers, as with petro-based plastics, can undergo thermomechanical degradation during the reprocessing processes. So their recyclability is limited by the number of reprocessing cycles (Hatti-Kaul et al. 2020). Oliveira et al. observed this when reprocessing different PP/PBAT-TPS blends up to 7 cycles in a single screw extruder (Oliveira et al. 2017). They found that the blends turn to a more rigid system with a consequential decrease of the impact strength. Other biopolymers like PLA can be reprocessed up to 10 cycles with a small loss in mechanical and thermal properties (Soroudi and Jakubowicz 2013), but it will depend on the type of PLA in terms of its molecular grade (Lamberti et al. 2020). For example, Agüero et al. found an increase of the MFI of PLA from 10 g/10 min to 20 g/10 min after only 6 reprocessing cycles and the yellowing of the samples, both clear evidence of the degradation of the material (Agüero et al. 2019). Rivas et al. studied the processability of PHB, the most used type of PHA, concluding that PHB is very sensitive to multiple extrusion cycles. They observed a decrease in mechanical properties of 50% of the tensile strength at break and an increase in the crystallinity only for 3 cycles. The introduction of stabilizer or chain extenders in the matrices could increment the number of processability cycles (Rivas et al. 2017). In any case, mechanical recycling has the associated problem of sorting the materials. Åkesson et al. studied the effect of the incorporation of TPS and PLA blends in the recycling process of PE, PP and PET. They found that for the case of PE it does not affect the tensile strength and modulus but reduces dramatically the elongation and break from 1300 to 150%. For the case of PP, they observed a 50% reduction in Charpy impact strength. Finally, they concluded that the introduction of only 1% of contamination of TPS and PLA in the PET provokes a degradation effect making these substances incompatible (Åkesson et al. 2020). Lamberti et al. proposed in their recent work a schematic route of the different plastic waste treatment options associated with plastic quality. They first consider the mechanical recycling of the biopolymer until the properties decrease making it impossible continuing with its use. After that, they propose a chemical recycling of the materials to recover the monomers and resynthesize the start polymer. Finally, if these two processes cannot be implemented, they propose energy recovery (Lamberti et al. 2020).

It can be concluded that for the best profitability of the biodegradable biopolymers they must be reused and mechanically and chemically recycled before composting or energy recovery system, closing the loop of the circular economy. But more research is needed to adjust these strategies to the real situation, solving problems like the sorting of the materials.

6 Future Applications

The transition to the Circular Economy model is almost unstoppable, especially in the EU where legislative and awareness-raising measures are being taken to reduce waste littering and stimulate the use of recycled materials. Upcycling processes must

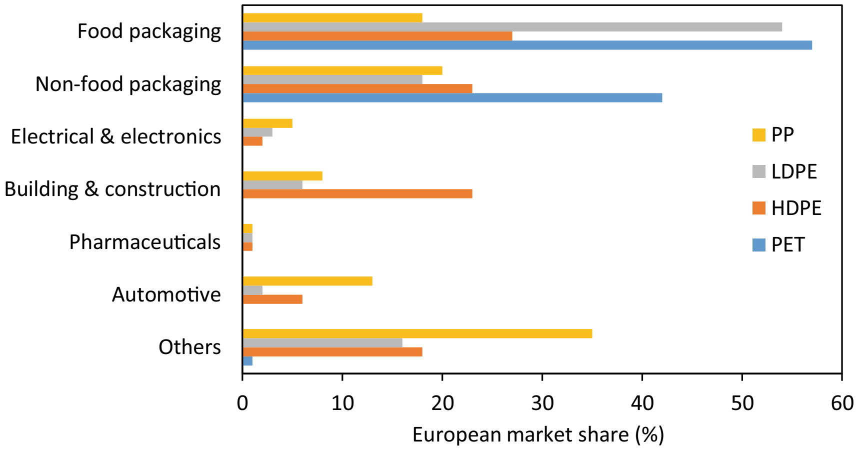

Fig. 3 European market shares of different plastic applications

prevail in this new model to maintain the quality of plastics and ensure the highest number of material's life cycles. Therefore, recycled plastics must be suitable for high added value applications with a large market share. Figure 3 shows the European market share of several applications where the major thermoplastics (PET, PE, and PP) are used (Eriksen et al. 2019).

As seen in Fig. 3, the packaging sector should be the main target market for recycled plastics since it represents the biggest plastic demand. Therefore, it can be foreseen that introducing recycled content in the packaging industry will provide great environmental benefits and increase the circularity of plastics. rPET is already reused in the production of beverage bottles. But, the use of recycled polyolefins for food packaging is still very limited mainly due to the lack of efficient decontamination technologies. The non-food packaging sector is less restrictive than food packaging. Nevertheless, there is still a big concern regarding chemical contaminants present in recycled plastics, especially, from post-consumer waste. Some companies from the fashion or hygienic sector have established their own restrictions on substances allowed in raw materials and finished products, excluding, for instance, bisphenol A, chlorophenols, alkylphenols or polycyclic aromatic hydrocarbons (PAHs) (Burberry 2018; Procter and Gamble 2020). Furthermore, the lack of legislation in the non-food packaging sector regarding recycled materials represents a barrier to the incorporation of recycled plastics in new products. The band owners need some common guidelines regarding the use of recycled materials in order to ensure consumers safety. Nonetheless, some progress is being made by using recycled content for instance in clear garment bags and pallet wraps.

The HDPE shows a similar market share in food packaging, non-food packaging, and building and construction sectors. This suggests that high-quality recyclates should be used in packaging applications and lower grade plastics obtained through downcycling processes or after several reprocessing cycles should be used in building and construction. On the contrary, the biggest LDPE demand corresponds to the food packaging sector (54%). Therefore, considerable efforts should be made to develop food grade LDPE. Otherwise, a huge amount of this material will continue to be sent to landfills or incineration. Non-food grade high-quality rPP has the potential to be used in the automotive sector, for instance, in the manufacturing of interior components of a car (e.g. seats, upholstery, gloveboxes, instrument panels). Plastics with lower quality, for example, in terms of colour or odours are usually used in external parts like bumpers, insulation foams, fender liners, etc. The rPP could be also used in large quantities in other applications like leisure, sports, and banknotes. Finally, although it has not been explicitly depicted in Fig. 3, the toys sector represents a big opportunity for high quality and safe recycled plastics.

7 Conclusions

The plastics recycling sector is entering a new era where optimization and upgrading of conventional technologies are required. The Circular Economy model is gaining importance and recyclers must be prepared to fulfil the growing demand and more demanding quality requirements. There are several challenges for the recycling sector, among which are multilayer plastics, flexible films, low-quality recyclates, consumer safety, and biopolymers. Fortunately, new recycling technologies are being developed and researchers and stakeholders are putting efforts to increase the circularity of plastics and minimize their environmental footprint.

Delamination technologies seem to be preferable for the recovery of multilayer films because solvents are not used, and the different layers are recovered without destroying the material. The inks can be removed in a water-based solution using surfactants and efficient deinking technologies are already on the market. Removing the inks before extrusion increases considerably the quality of recycled pellets, which can be used in high added value applications. Several technologies have been developed to remove undesired odours from recycled plastics by stripping volatile organic substances either with steam or hot air. Nevertheless, less volatile substances remain inside the plastics. So additional decontamination technologies are necessary. Besides, the percentage of biopolymers in the plastic waste stream is expected to grow. This means that sorting and recycling of these materials either separately or along with conventional plastics must be studied and new technologies must be implemented.

Plastics are used in countless applications owing to their versatility and numerous mechanical and thermal properties. Until now, recycled plastics have been used in low added value applications with few exceptions like PET bottles. But according to the Circular Economy principles, recycled plastic must be used in high-quality applications to ensure the highest number of material's life cycles. This also permits to expand the market and increase the demand for recycled plastics. It is considered that the major benefits will be obtained by introducing recycled content in packaging applications and, especially, in food packaging. For this to be possible, the quality of the recyclates must improve considerably. The automotive sector is another sector where high quality recycled pellets can be introduced, for instance, in interior car parts.

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