POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

ENHANCING THE VISUAL AND MECHANICAL PROPERTIES OF MULTILAYER FILMS CONTAINING PCR

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Ce mémoire intitulé :

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présenté par **Mahdi SALEHI MORGANI**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

a été dûment accepté par le jury d'examen constitué de :

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Amir SAFFAR, membre

DEDICATION

Dedicated to

My beloved parents,

Who have always encouraged me to soar toward my dreams,

Thank you for your endless love, sacrifices and supports.

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First of all, I would like to express my sincere gratitude to Prof. Abdellah Ajji as my supervisor for all the supports he provided. His expertise has been always a great help for me. His solid support, motivation, as well as patience provided a calm atmosphere for me to have my ultimate concentration on my research. I appreciate his patience, encouragements, and guidance.

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RÉSUMÉ

Avec 40% de la demande mondiale de plastique, l'emballage plastique est actuellement le principal secteur de l'industrie plastique (PlasticsEurope, 2019b). Le fait que la majorité des matériaux plastiques ne soient pas biodégradables met en évidence l'importance cruciale des méthodes de traitement des déchets d'emballages plastiques dans la réduction de leur impact négatif sur l'environnement. Malgré des améliorations significatives dans les technologies de recyclage du plastique, le recyclage des déchets d'emballages plastiques reste un défi. La consommation intensive d'énergie, les coûts élevés et la complexité des étapes de tri, le nettoyage et les prétraitements, les problèmes de recyclage, ainsi que la qualité inférieure des matériaux recyclés par rapport aux plastiques bruts sont parmi les nombreux obstacles associés au recyclage des déchets d'emballages plastiques. Il est possible d'améliorer le taux de recyclage actuel et d'augmenter la qualité des matériaux recyclés dans les emballages plastiques en concevant des emballages recyclables, en améliorant la collecte et le tri, en faisant progresser les technologies de recyclage et, surtout, en incorporant les produits recyclés dans de nouvelles structures d'emballage.

Toutes les technologies et activités de recyclage sont inutiles si la demande de plastiques recyclés n'est pas suffisante. Actuellement, les autorités et les grandes entreprises d'emballage plastique tentent d'augmenter l'application des contenus recyclés dans les nouvelles structures d'emballage. Par exemple, la fondation Ellen MacArthur collabore avec des entreprises d'emballage géantes du monde entier pour augmenter de 400 % le contenu recyclé des nouveaux emballages d'ici 2025 (ELLENMCARTHOR_Foundation, 2019). Toutefois, cette transition vers une économie circulaire pour le marché de l'emballage nécessite des travaux de recherche et de développement pour surmonter les principaux obstacles. L'un des principaux défis qui perturbent la qualité mécanique et visuelle des plastiques recyclés par rapport aux matériaux vierges, est la présence de défauts et d'imperfections dans les structures contenant des matériaux recyclés. Dans cette étude, des films de polyéthylène flexibles multicouches avec différents contenus de polyéthylène haute densité (HDPE) recyclé post-consommation (PCR) ont été préparés par soufflage de film. Les sources de ces défauts dans les échantillons de films à base de HDPE PCR ont été étudiées en combinant des techniques de microscopie optique, de spectroscopie à rayons X à dispersion d'énergie (EDX), de microscopie à platine chauffante, d'extraction par solvant et de calorimétrie différentielle à balayage (DSC). Il a été déterminé que les défauts dans les échantillons de film PEHD PCR peuvent être principalement classés comme des défauts de fibres provenant d'étiquettes et de papiers et de gels ponctuels. Les résultats de la microscopie en phase chaude montrent que les gels ponctuels peuvent être sous-catégorisés en tant que gels non-fondants, non-déformables et défauts déformables. En outre, il a été constaté que les défauts déformables, qui peuvent être des gels de HDPE à réseau d'enchevêtrement, présentent une déformation élevée à des températures plus élevées, spécifiquement supérieures à 200 °C. Les résultats obtenus indiquent que l'augmentation de la température de mélange ou le traitement avec des éléments de mélange dispersifs dans une extrudeuse bi-vis, mélange et disperse des gels fortement enchevêtrés. Il a également été constaté que l'ajout d'antioxydants réduisait le contenu en gels en empêchant la réticulation et la stabilisation des espèces actives.

ABSTRACT

With 40% share of the global plastic demand, plastic packaging is currently the major sector in plastic industry (PlasticsEurope, 2019b). The fact that majority of plastic materials are not biodegradable points out the critical importance of plastic packaging waste treatment and its role in reducing their negative environmental footprint. Despite significant improvements in plastic recycling technologies, recycling of plastic packaging waste remains challenging. Intensive energy consumption, high costs and complexity in sorting, cleaning and pre-treatments steps, re-processing issues, as well as inferior quality of the recycled materials compared to raw plastics are amongst the many impediments associated with recycling of plastic packaging wastes. Enhancing the current recycling rate and up taking the quality of the recycled martials in plastic packaging is achievable through designing for recyclability, improved collection and sorting, advancements in recycling technologies, and more importantly, incorporation of the recyclates into new packaging structures.

All the recycling technologies and activates are meaningless without having a sufficient demand for recycled plastics. Currently, authorities and major plastic packaging companies are trying to increase the application of the recycled contents in new packaging structures. For instance, Ellen MacArthur foundation is collaborating with giant packaging companies around the world to increase the recycled content in new packages by 400% by 2025 (ELLENMCARTHOR_Foundation, 2019). However, this transition to circular economy in packaging market requires research and development to address major obstacles. One of the major challenges disrupting the mechanical and visual quality of recycled plastics compared to virgin materials, is the presence of defects and imperfections in the structures containing recycled materials. In this study, multilayer flexible polyethylene films with different post-consumer recycled high-density polyethylene (HDPE PCR) contents were prepared by film blowing. The sources of these defects in the film samples based on PCR HDPE were investigated by combining optical microscopy, energy dispersive X-ray (EDX), hot stage microscopy, solvent extraction, and dynamic scanning calorimetry (DSC) techniques. It was found that the defects in PCR HDPE film samples can be mainly categorized as fiber defects originating from labels and papers and point gels. Hot stage microscopy results show that point gels can be subcategorized as non-melting, non-deformable gels and deformable defects. In addition, it was found that melting defects, that can be entanglement network HDPE gels, show high deformation at higher temperatures specifically above 200 C. The obtained results indicate that increasing mixing temperature or processing with dispersive mixing elements in a twin-screw extruder mix and disperse highly entangled gels. It was also found that the addition of antioxidants reduced the gel contents through preventing of crosslinking and stabilization of active species.

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LIST OF SYMBOLS AND ABBREVIATIONS

BUR	Blow-up ratio
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-Ray
FDA	Food and Drug Administration
GHG	Green-house gas
HDPE	High-density polyethylene
LCA	Life cycle analysis
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MD	Machine direction
MFI	Melt flow index
MRF	Material recovery facility
MRFF	Materials recovery for the future
Mw	Molecular weight
MWD	Molecular weight disribution
PCR	Post-consumer recycled
PE	Polyethylene
PET	Polyethylene terephthalate
PIR	Post-industrial recycled
PP	Polypropylene
PS	Poly styrene
TD	Transverse direction

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CHAPTER 1 INTRODUCTION

1.1 Context of the study

The depletion of natural resources, very high carbon footprint and non-biodegradability of common plastic materials have raised significant concerns about their vast applications in our daily life. With 40% share of the global plastic market demand (PlasticsEurope, 2019b), plastic packaging is currently the major sector in plastic industry. This indicates the critical importance of plastic packaging waste treatment in reducing their negative environmental impact. There exist different end-of-life scenarios for plastic packaging wastes including disposal, energy recovery, and recycling. However, amongst different approaches in plastic packaging waste treatments, recycling of plastic packaging is the most promising approach that complies with the circular economy concept and sustainable materials management (European-Commission, 2008). Higher cost and complexity in sorting, cleaning and wastes pre-treatments steps, as well as re-processing issues are among many challenges associated with recycling of plastic packaging wastes, particularly flexible films and multilayer packaging. The potential and challenges in recycling plastic packaging have attracted significant attention in scientific community and packaging industry.

To increase the circularity in this sector, the focus of plastic packaging recycling is divided into various activities including; recyclable packaging design, quality collection and sorting, and enhanced recycling technologies. Even though the mentioned tasks promise higher recycling rate and quality, they would be meaningless unless there exists a sufficient demand for the recycled plastics in packaging applications. This can be fulfilled by incorporation of the recycled plastics in the new packages (PRE, 2019a). For instance, a group of packaging companies and food production sectors committed to increase the recycled content in their packaging structures by 5 times the current percentage by 2025 (UN-Environment-Programme, 2018). The constrains to be addressed for inclusion of the recycled content in multiple service life are the health issues associated with the recycled materials in food packaging, poor visual and mechanical properties of the recycled plastics compared to the virgin materials, and the technical and economic viability of the process.

1.2 Plan of the dissertation

Current thesis is provided in six chapters. Chapter 2 presents a comprehensive literature review on the mechanical recycling of plastic packaging. In this chapter, a short description of plastic packaging market and its different sectors will be presented. End-of-life scenarios of plastic packaging waste including landfilling, recycling (chemical, mechanical and chemo-mechanical processes), composting and energy recovery as well as advantages and disadvantages of each scenario will be described. Circular economy concept and sustainability will be explained, and it will be shown that recycling of plastic packaging is the strategy that complies best with these concepts. Then, pre-treatment steps of plastic packaging waste before the recycling processes will be reviewed. Details of the main plastic packaging mechanical recycling processes will be reviewed. Chapter 3 is devoted to identification of the research objectives and problems. In chapter 4 the main aspect of research is provided through a journal paper. Detailed experimental and analytical procedures along with the materials and facilities implemented in this study is presented in this paper. Besides, the major research results are described in the mentioned chapter. Then, general discussion is presented in chapter 5 and finally concluding remarks and the recommendations are provided in Chapter 6. In the appendix A, further results obtained from PCR HDPE project is provided. Appendix B is dedicated to the review paper on the recycling of the plastic packaging. In this appendix, different recycling technologies, trends and perspectives of the recycling of plastic packaging along with the regulations is reviewed and discussed in detail.

CHAPTER 2 LITERATURE REVIEW

2.1 Plastic packaging recycling overview

Polymeric materials are large macromolecule composed of repeated monomer units. They can be produced via polymerization reactions which can be categorized into two main groups of step-growth polymerization and chain polymerization (Brydson, 1999). Plastics are a sub-category of polymers that can have natural or synthetic origin (Piringer & Baner, 2008). They can be categorized based on their thermal behavior into thermoplastics and thermosets materials (Crawford & Martin, 2020; Piringer & Baner, 2008). Thermoplastic materials exhibit tough and viscoelastic properties and melt upon heating. On the other hand, thermosetting plastics have a 3D network of cross-linked molecules which prevents melting and flowing upon heating and results in a highly elastic behavior. Nowadays, plastic materials can be found everywhere, from ordinary plastic shopping bags to highly sophisticated electronic or medical devices. Plastic materials demand per sector and per polymer type is provided in the Figure 2.1. Plastic products can be produced through different processing methods such as thermoforming, injection molding, blow molding, or extrusion. In 2018, global plastics production almost reached 360 million tons with a positive trade balance of more than 15 billion euros (PlasticsEurope, 2019b). Although the advantages of plastic materials are unquestionable, they have a very high carbon footprint and are petroleum-based materials (Crawford & Martin, 2020). The service life of plastics can be as short as less than 1 year or as long as 50 years or more depending on their applications. However, the increasing amount of plastic materials used in our daily life caused a growing challenge for the industries for disposing plastic waste with the least environmental impact.

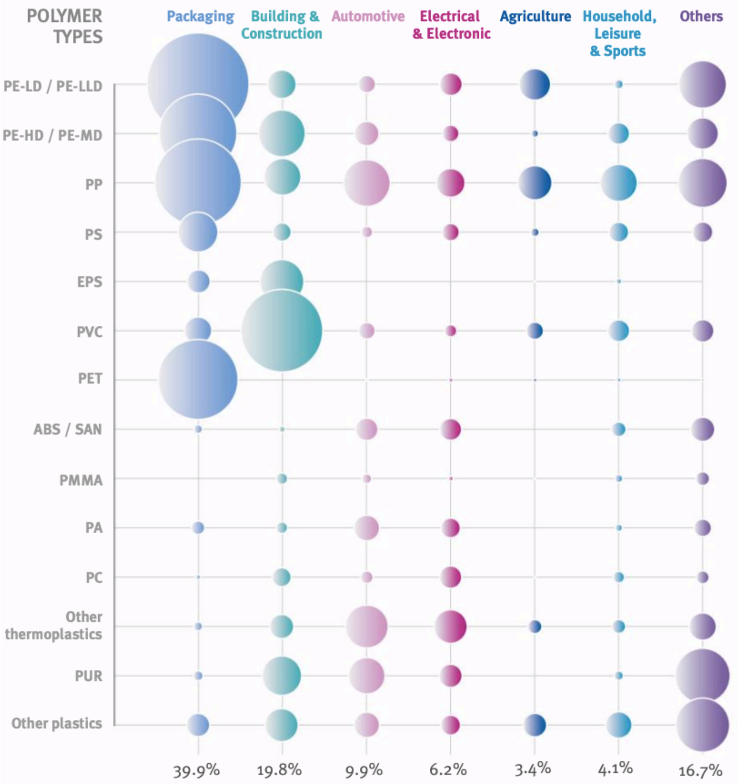


Figure 2.1 Plastics demand per sector and per polymer type in 2018 (PlasticsEurope, 2019b)

2.1.1 Plastic materials in packaging

Plastic materials have been used in many different applications such as in packaging, building and construction, automotive, agriculture, households, leisure and sports and other fields (PlasticsEurope, 2019b). With about 40% share in plastic demand, packaging is the main sector of plastic materials (PlasticsEurope, 2019b). Plastic packaging is used in food, drug, chemicals, cosmetics, etc. The main purpose of packages is preserving the products with minimal impact on the product and the environment. Amongst different products, the food packaging is very important due to chemical instability of food. Packaging enhances the shelf life of the products and can be effective in reducing food waste (Gaukroger, 2018). Designing packages is done based on different factors such as performance, cost, and environmental considerations (Niaounakis, 2019). Different advantages of the polymers and variation of them outweigh the impediments of incorporation of them in the packaging sector. Packaging industry is unimaginable without plastic materials. The major polymers used in packaging applications this application is low-density polyethylene, linear low-density polyethylene, high density polyethylene, polypropylene, polyethylene terephthalate, and polystyrene. A variety of properties could be achieved by using different polymers such as flexibility and sealability (LLDPE), good film physical strength (LDPE), mechanical strength (PET) or toughness (HDPE, PP), transparent and gloss surfaces (LDPE,LLDPE), barrier properties for increased shelf life of products (EVOH, PA, PVDC). According to the product and requirements, plastic packaging may come in rigid (e.g. plastic containers, trays) or flexible (e.g. films, pouches) forms (Morgan, 2010). Compared to rigid packaging, flexible packaging requires less plastic material and less energy for production (Niaounakis, 2019). However, the complexity of structures, problematic sorting and collection and high residual contamination make flexible packaging more difficult to recycle. This can be clearly seen by considering that the recycling rate of rigid packaging is 40% while only 1% of flexible packaging are recycled (Covenant, 2013).

2.1.2 End-of-life scenarios for plastic packaging

The significant market of plastic packaging was discussed before, however; most plastics are produced from non-renewable natural resources and have high carbon footprints and GHG emissions (Cross, 2019). In addition, non-biodegradability of common plastic materials makes plastic packaging waste an essential challenge for the environment after their service life (Crawford & Martin, 2020). In addition, Currently, four main scenarios exist for managing plastic packaging wastes: landfilling(disposal), energy recovery, composting and recycling. Figure 2.2 shows these scenarios within the waste management hierarchy according to their compatibility to the environment and sustainable use of resources (European-Parliament-Directive, 2008).

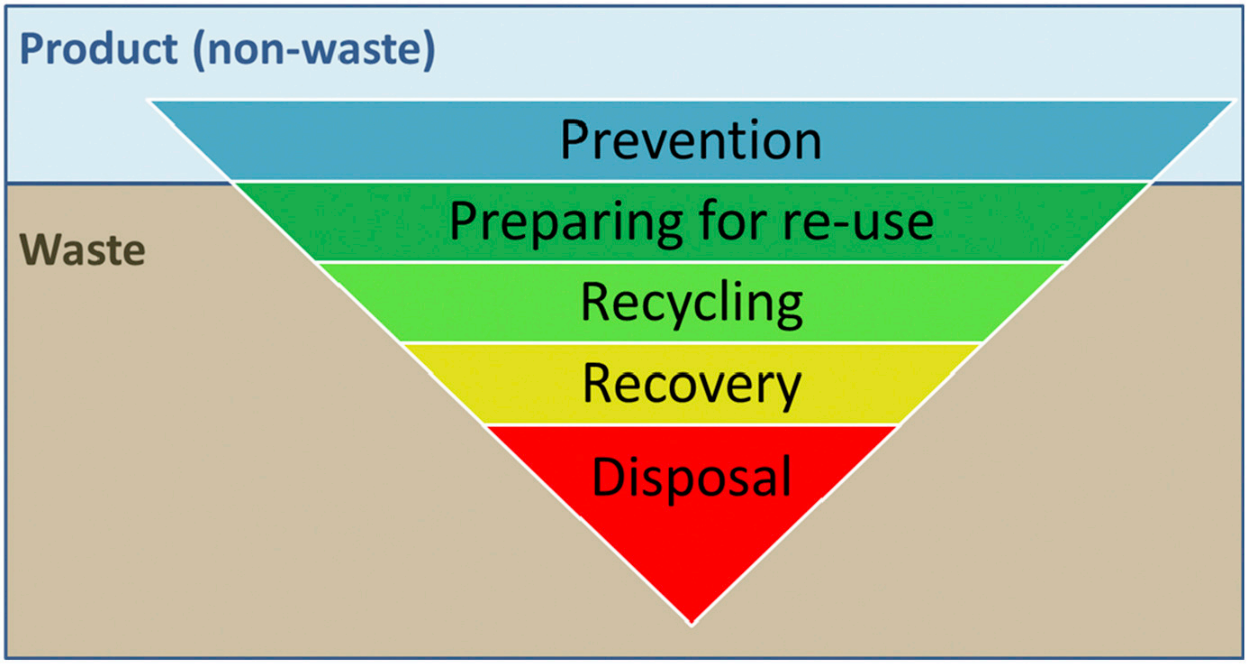


Figure 2.2 waste management hierarchy (European-Parliament-Directive, 2008)

- Landfilling (disposal): It is the worst method with respect to environmental stewardship which should be limited to the materials that cannot be treated by other methods. landfilling may be applied to all types of plastics and it requires relatively low energy for disposal. However, due to very low degradation rate of plastics, they will remain in landfilling sites for hundreds of years which will cause environmental disaster. Materials that are sent to landfill sites are discarded without further benefits leading to high pressure on the natural resources for production of new materials. In 2016, more than 85% of the plastic wastes in Canada were sent to landfilling sites, however, based on the zero plastic waste objective this number needs to be reduced to less than 10% by 2030 (Deloitte, 2019). The same scenario exists in Europe where 25% of plastics are sent to landfilling sites (PlasticsEurope, 2019a).
- Composting: this scenario is limited to biodegradable and compostable polymers. It can be a green approach but many of composting facilities do not accept compostable packaging since there are no standardized operating condition and degradation time for them (Deloitte, 2019) and also the biodegradation condition cannot be achieved in normal environments like soil and sea (Niaounakis, 2019). Another challenge for biodegradable packaging is that

they must degrade quickly in the environment but should keep their performance during shelf life of packaged products (Garcia & Robertson, 2017).

- Energy recovery: This is one of the main recovery options that is widely used. Energy recovery through incineration of plastic wastes is beneficial because of its high calorific value. Even though the incineration of the plastic wastes produces acceptable amount of energy, the energy recovered from this process does not compensate the energy consumption for the plastic productions and also the recovered energy through recycling is approximately double the energy recovered from incineration of plastic wastes (Rahimi & García, 2017). Based on the waste management hierarchy, Figure 2.2, incineration should be the last recovery option and must be limited to non-recyclable resins such as thermosets, multilayer structures or mixed plastics (except chlorine components). In addition, the production of hazardous products such as dioxins, furans, and other organic volatiles during incineration process (Deloitte, 2019) leads to authorities' and social oppositions (Barlow & Morgan, 2013).
- Chemical recycling (also known as feedstock recycling): In this process, polymer molecules are broken down and converted to shorter molecules. The molecular conversion occurs through thermal degradation or (partial) depolymerization and the final products of this process are monomers, oligomers, fuels or other valuable chemical components which can be entered to the production process of plastic raw materials. The quality of the final products produced in this scenario is comparable to the virgin materials. However, some limitations such as energy intensive and low efficiency of this process prohibit application of this approach in industrial scale and chemical recycling is as a complementary method to mechanical recycling. This process is referred as chemo-mechanical process and will be discussed in section 2.4 of this paper (Deloitte, 2019).
- Mechanical recycling (also known as closed loop or primary recycling): Through mechanical recycling, molecular structure of plastics is preserved and using melt processing the materials enters the conversion step. The mechanical and visual quality of the mechanically recycled plastics is the biggest challenge in this method, however, the inexpensive and relatively easy-to-follow steps during this method, make it the best

recycling option specially for the packaging industry (Deloitte, 2019; PlasticsEurope, 2019a).

There is a wide gap between the energy intensity of the virgin materials and the recycled materials which translates into reduced carbon footprint for the plastic recyclates. Incorporation of PCR materials into new plastic packaging, therefore, reduces carbon intensity, carbon emissions and increases the amount of plastic materials returned to the processing cycle (P. Europe, 2017).

Development of new applications for recycled materials is critical to meet the ambitious targets of recycling such as Zero Waste target in EU. Considering the fact that food packaging is the largest sector in plastic packaging, incorporation of the recycled materials in food packaging is a promising approach but requires significant precautions due to the strict regulations for materials used in food contact articles (P. Europe, 2017). Figure 2.3 illustrates the evolution of plastic packaging waste treatment between 2006 to 2018 in Europe in different scenarios of landfilling, energy recovery and recycling. It can be seen that plastic recycling industry moved toward reducing landfilled wastes (reduced 52%) and increasing recycling rates (increased 92%). In some cases, the industry may not be able to recycle the materials (like complex packaging structures or highly contaminated items) in which they must select the best option using some measures such as Life Cycle Assessment (LCA). LCA is a technique to ensure a more enlightened decision through a better understanding of the environmental and social impact of the products, process, and activity via their effects on air, water, land and energy consumption (EDA, 2018).

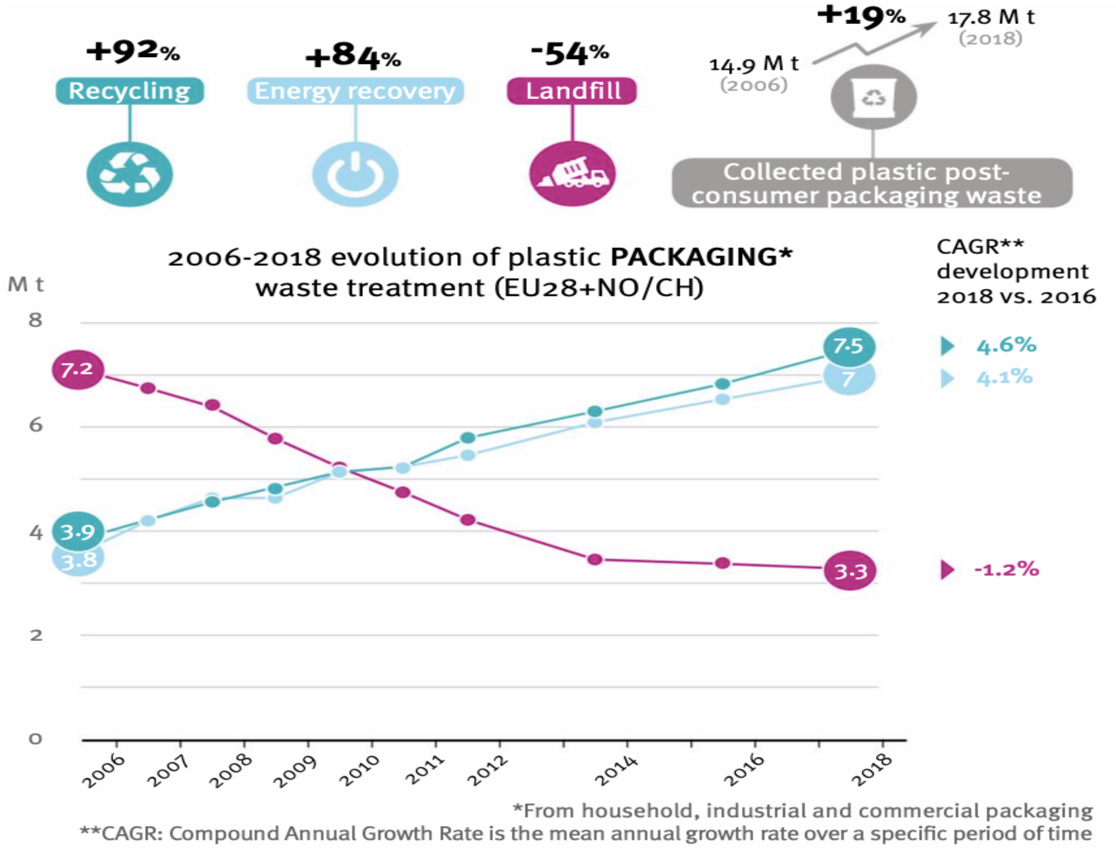


Figure 2.3 Evolution of plastic packaging waste management in Europe (PlasticsEurope, 2019b)

2.1.3 Circular economy concept and sustainability models in plastic packaging

Circular economy is the opposite of the linear economy, which is based on take, make, and dispose steps. Circular economy is extracting maximum value of the resources during the service life of products, and regenerate and recover the products and materials at the end of their service life. Linear economy, however, applies pressure on the natural resources and environment for extracting raw and virgin materials leading to progressive waste production and increased environmental impacts. Consequently, the traditional methods based on linear economy need be replaced by methods based on circulation of the materials back in the processing/consumption chain (PlasticsEurope, 2019a).

The significance of circularity in packaging industry is evident where the amount of packaging waste is growing continuously and in 2017 packaging waste in Europe raised to a value of 173 kg per inhabitant (Commission, 2020). The European Union (EU), as well as policy makers and companies, aim to reduce or eliminate the amount of plastic packaging waste sent to landfills. For example, Kraft Heinz announced that it aims to make all of its packaging recyclable, reusable or compostable by 2025 (Rebecca Briedis, 2019). The American Chemistry Council's (ACC) Plastics Division announced targets of fully recyclable or recoverable plastic packaging by 2030 and 100% of plastic packaging to be reused, recycled or recovered by 2040 (ACC, 2018). In 2016, the Plastic Industry Trade Association announced the Zero Net Waste (ZNW) program in EU, which recognizes plastic companies who participate to reduce net waste in manufacturing and reducing raw materials and energy consumption (P. I. T. Association, 2016). In 2015, the EU published an action plan for transitioning to a circular economy (Europian Commission, 2015). The main development in circular economy for plastic packaging happened in 2018, when EU revealed its strategy on plastics as part of its transition towards a more circular economy. The "European Strategy for Plastics in a Circular Economy" (Plastics Strategy) (Commission, 2018) calls for all plastic packaging on the EU market to be either reusable or recyclable in a cost-effective manner by 2030. Certain steps need to be taken to fulfill these targeted goals including, but not limited to, more integrated supply chain, replacement or elimination of substances that hamper recycling processes, the development of innovative materials and alternative feedstocks for plastic production, reduction of the consumption of single-use plastics and reducing the complexity of packaging materials, including the number of materials and polymers used (Commission, 2020; Misko, 2019). The EC identifies four action steps for achieving a circular economy for plastics:

- Improve the quantity and quality of plastics recycling.
- Curb plastic waste and littering.
- Drive innovation and investment towards circular solutions.
- Harness global action.

For the flexible packaging which are of challenging wastes the Circular Economy for Flexible Packaging (CEFLEX) predicted that by 2025 there will be an established collection, sorting, and recycling infrastructure for flexible packaging in Europe to deliver the best economic, environmental, and technical benefits of the Circular Economy (CEFLEX, 2018). The flowchart of a circular model for plastic packaging waste recycling and management is provided in Figure 2.4.

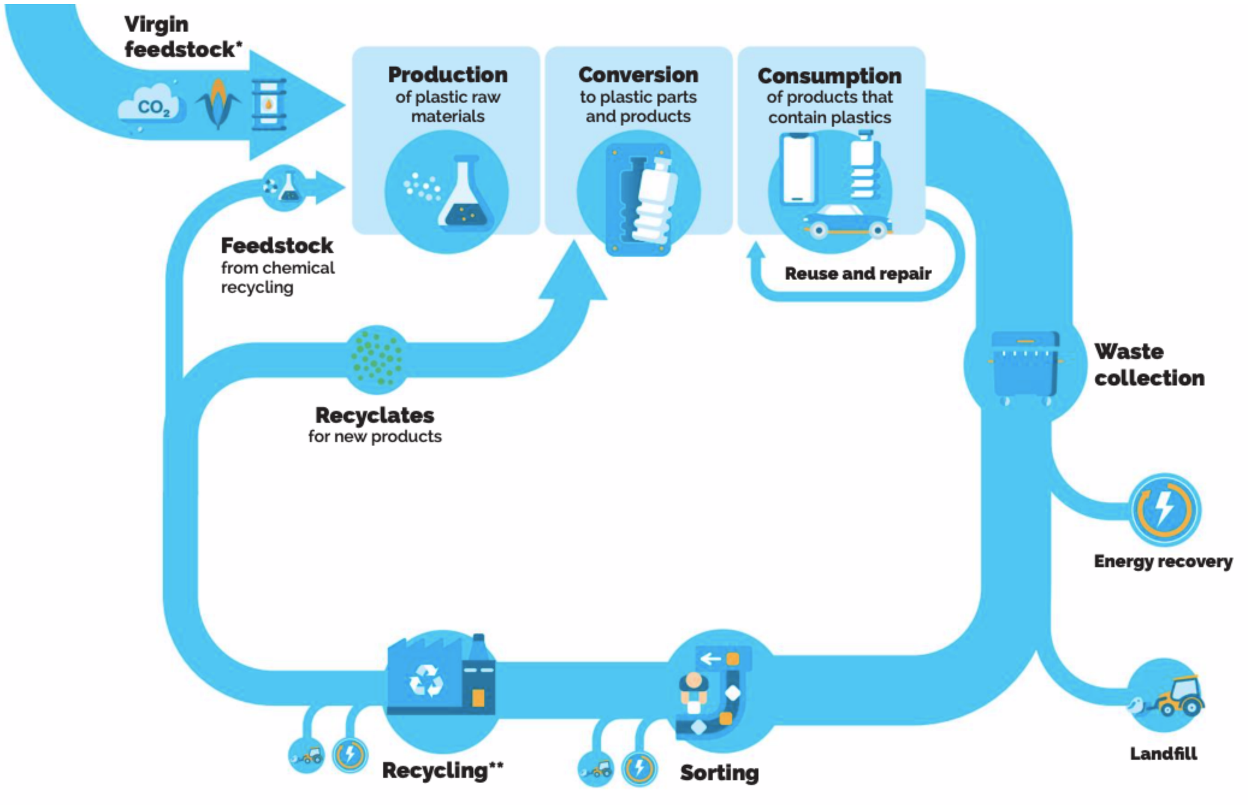


Figure 2.4 circular model for plastic packaging waste recycling and waste treatment (reprinted with the permission from *(PlasticsEurope, 2019a)*)

Furthermore, Sustainable Materials Management (SMM), defined by Organization for Economic Cooperation and Development (OECD), is a systemic model for using and reusing materials efficiently (with the least negative environmental impact) within their life cycles. According to this approach, the consumption of natural resources and environmental protection are revised through examining how materials are used with the objectives of (EDA, 2018):

- Productive material using with an emphasis on using less.

- Reduction of toxic chemicals and environmental impacts throughout the material life cycle.
- Assurance of sufficient resources to address the present and future demand.

The U.S. EPA has announced its SMM strategic priority for 2017 to 2022 in the areas of sustainable food management and packaging with the goals as (EDA, 2015):

- Decrease the disposal rate, which includes source reduction, reuse, recycling and prevention;
- Reduce the environmental impacts of materials across their life cycle;
- Increase socio-economic benefits; and
- Increase the capacity of state and local governments, communities and key stakeholders to adopt and implement SMM policies, practices and incentives.

2.2 Recycling pretreatment technologies

2.2.1 Collection and Separation

The first step in recycling is collecting the plastic packaging wastes for recycling purposes. Low efficiency of the collection step leads to the loss of materials and energy which will not comply with circular model. So, the collector must ensure all recyclable items are collected and sent to Material Recovery Facilities (MRFs). There are mainly two main types of plastic packaging wastes: post-consumer recycled (PCR) and post-industrial recycled (PIR) materials. PCR materials are those recovered after being used by the consumer and are the main source of the plastic packaging wastes which usually contain more contaminations and impurities. On the other hand, PIR materials are the ones reclaimed from manufacturing (scraps, trims, edges, etc.) sites and since they have not been in the consumption market, they have a low level of contamination and impurities. Two routes for collection of the plastic packaging wastes for recycling purposes are curbside collection by local authorities and store drop-off points at groceries. Compare to rigid packaging, flexible packaging and polymer films are usually considered as contaminants and rejected by MRFs since they are lighter, more contaminated by residual organics and also more complex (multilayers, metalized components.) to recycle (Horodytska, Valdés, & Fullana, 2018). Incentive retail return system or separate collecting of the multilayers and films are two common methods to prevent the loss of materials in the flexible packaging waste stream (F. P. Association, 2014). However, the curbside collection offers a bigger capacity of collection for recycling than the retail return programs ((ACC). 2016). The quality of sorting and more importantly the recycling performance is highly controlled by the collection schemes and establishments since it directly impacts the level of contamination found in the waste stream entering the sorting centers and later the recycling facilities. In the system where packaging wastes are mixed with other wastes, the recycling performance as well as the cost of the process is very high since the organic wastes, food residues or other materials, contaminate the recyclable items. In contrast, using separated schemes not only reduce the costs, but it also elaborates the application of the recycled materials even for the food packaging (PRE, 2019b).

Collected plastic wastes are then separated through different stages in MRFs. The main idea in this step is to receive commingled plastics and separate them based on the type of polymers to send them to the recycling sites. There are different sorting methods for separation of target components. Aside from the manual separation, the main components are:

- Screen and trommel are employed to group the items based on their size and dimensions. Screens are usually equipped with shaker for better performance.
- Magnetic separator consists of a magnetic conveyor to remove the ferrous materials from the waste stream.
- Eddy current separator is used to separate the non-ferrous metals like aluminum. In this stage the sensor uses a powerful magnetic field and detects the non-ferrous items to be extracted from the stream.
- Ballistic separator is used to separate flexible flat items (e.g. films, pouches) from bulky rigid items (e.g. bottles, containers). It consists of an inclined set of oscillatory paddles. Each paddle is 60 to 120 degrees out of phase from the adjacent paddle. The agitation results in bulkier rigid items to roll down and collected while lighter flexible items move upward and collected from the top. The paddles usually have a meshed surface which results in finer waste such as glass pieces to drop and collected using a converter under the ballistic separator. Star screens are also an alternative for separation of the flexible films and bulkier 3D items.

- Air separator is an alternative (or complementary) to the ballistic separator to separate the lightweight materials using air (the 2D items are conveyed in the air stream and the heavier items remains in the wastes) (RRS, 2017).
- Optical near IR (NIR) separator is usually the last stage for sorting in the waste separation process. This technology is based on detection of the reflected waves of materials and by comparing the wavelengths with its library, the separator would be able to understand the type of the polymers from the absorbed wavelengths by material.

Figure 2.5 provides a typical flowchart of the sorting process for plastic packaging waste stream. In this step of recycling, the commingled materials are separated into the distinguished groups for further steps including PE and PP films, PET bottles and trays, HDPE, PP, and PS containers. The nonrecyclable items will be removed from the streams to be sent for energy recovery or disposal and unknown fractions will be sent back to the soring steps to be identified. The flexible packaging and films usually are discarded and mainly sent to landfilling sites. However, there are enhancements to limit loss of such items like Material Recovery for Future (MRFF) project. MRFF is established to employ different technologies to sort loose and flexible films using state-of-the-art equipment like advanced optical sorters (RRS, 2015). The sorted items then would be compacted to have a lower volume for the ease of transportation and will be sent in the bales to the recycling sites.

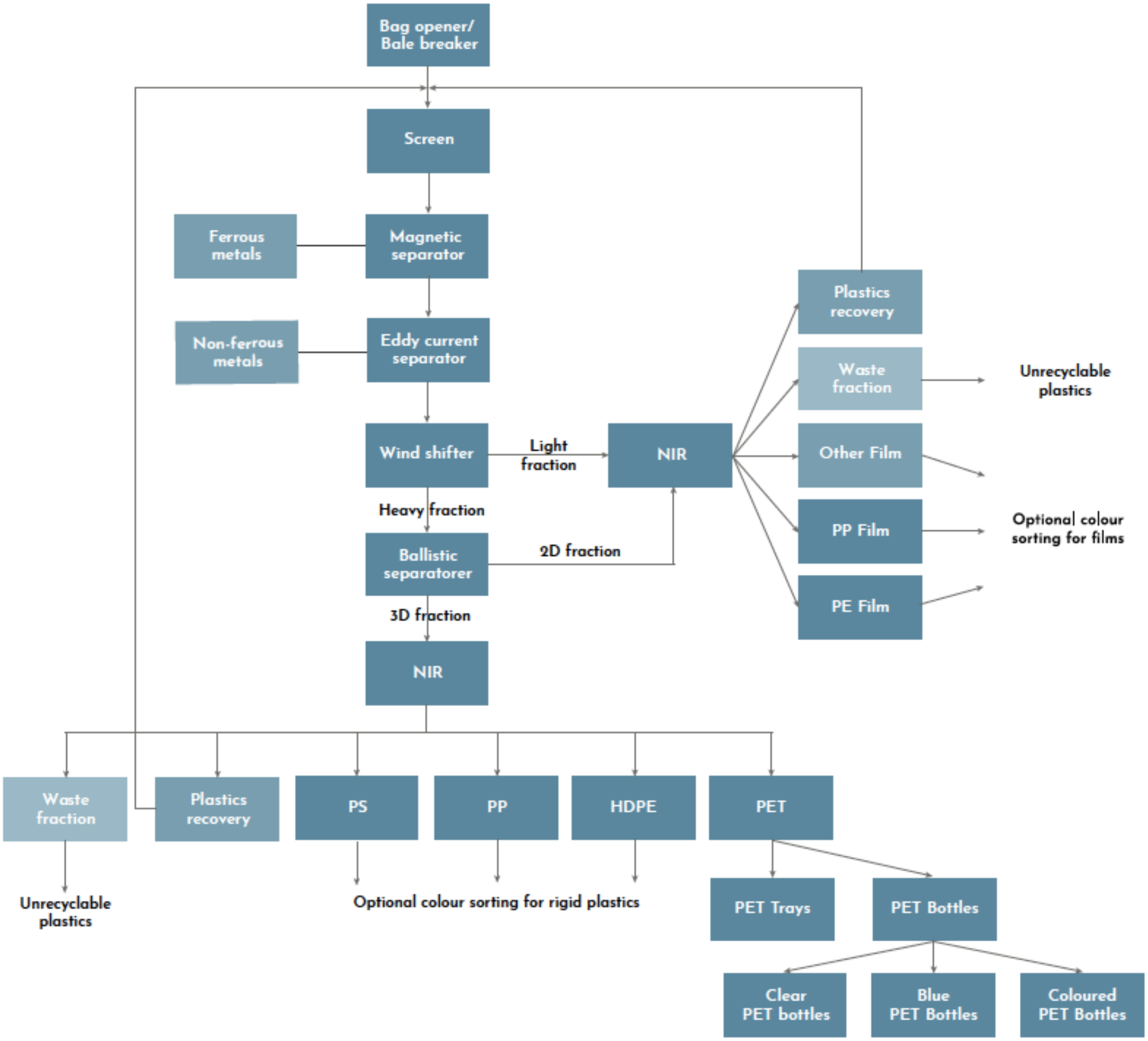


Figure 2.5 packaging sorting flowchart (PRE, 2019b)

2.2.2 Size reduction

The first step in a recycling plant is reducing the size of sorted and separated materials. Size reduction is beneficial for enhancing the surface to volume ratio to improve the cleaning as well as chemical or mechanical processes. Size reduction is done by shredders or/and by grinders (granulator). Shredders work at low speed and high torque which allows bales of sorted materials to be fed entirely into the shredders to reduce the size of the wastes into pieces of hand size (about 1 to 5 in)(Niaounakis, 2019). Flexible packaging and films are the items more problematic to the shredders since they stick (or melted by the heat for rotating shafts) and roll around the blades and shafts. In addition, the stretching nature of most flexible packaging make them difficult to cut by shredder. This caused rejection of flexible packaging waste by recyclers. There are some advancements in shredding technologies to increase the recycling rate of the flexible structures such as water-cooling shaft and rotor, specialized rotor and blade design, etc (Technology, 2015).

For further reduce the size, the output of the shredders is fed into grinders which, unlike shredders, work at high speed and low torque. A sizing screen is installed to control the dimensions and uniformity of the flakes (commonly controlled between 6 to 12 mm).

2.2.3 Cleaning and decontamination

Cleaning plastic packaging wastes is the most critical stage in recycling pre-treatment. |The major source of plastic packaging waste is food packaging which is more contaminated by organic residues and volatiles. Furthermore, inks, labels and adhesives are other components to be eliminated in plastic packaging wastes.

Water cleaning is the common washing step in the waste recycling. Using water cleaning the shredded plastics, food residues, organic contaminants, dust and dirt, pulps and papers will be eliminated. To have a more efficient washing, friction washer and hot water can be employed. Treatment of the generated wastewater in this step is also a costly step that should be managed in cleaning facilities (Ontario, 2013). The water cleaning method usually begins with friction washer/dryer and then the particles are fed into a hot water tank for agitation and removing labels and glue. Finally, a press conveyer mechanically squeezes the plastics and hot air dryer ensures the moisture content below 2-3 wt.%. For cleaner mono-material plastic wastes, dry cleaning can be used where the plastic particles are subjected to high speed stress from rotating paddles in a confided space. There is no need for water or solvents in such cleaning and depending on the waste stream, the efficiency of this method can be up to 90% (WRAP, 2019).

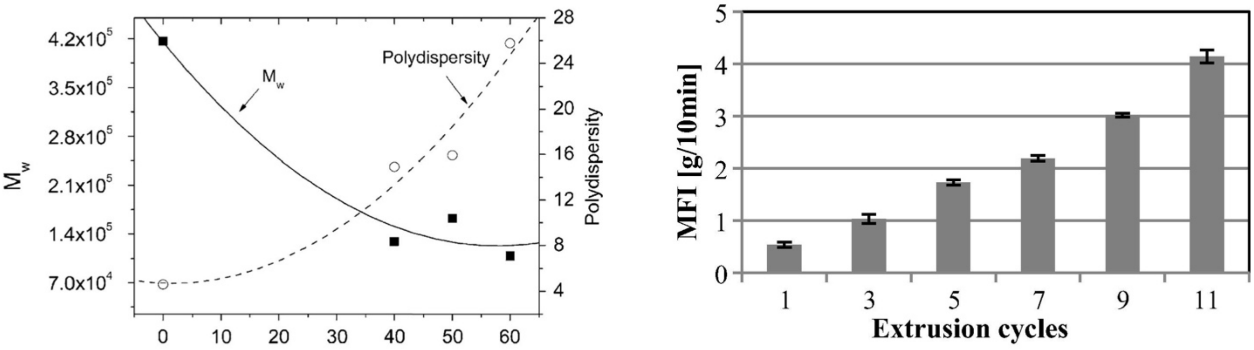
Cleaning can also be via solutions including solvents or aqueous surfactants to remove inks and impurities. Selection of the chemical solvents is conducted based on the composition of the waste stream and also the required quality of the final products. To enhance the performance of the cleaning agents, their boiling temperature should be lower than the melting temperature of the polymers to avoid sticking the flakes to each other and also preventing embedding of the printing ink particles into the polymers. Cleaning solvents are mostly acetic acid esters (low melting temperature) and alcohols. As solvent residue remains on the surface and diffuses into the wastes after this stage, further steps are needed remove them, otherwise the quality of the recycled product will be disrupted (Niaounakis, 2019).

2.3 Mechanical recycling

One of the recycling approaches is the re-extrusion of the shredded plastic packaging wastes and use the recycled materials in a new multi or mono layer structures. During mechanical recycling of the resins, the polymer chains are preserved and by melting the clean flakes and extrusion, a new life will be given to the polymers. Since the polymers can keep their properties for a long time, the potential for multiple service life is noticeable (Jin, Gonzalez-Gutierrez, Oblak, Zupančič, & Emri, 2012). This method is gaining interest in the industry of packaging even in the food packaging applications. The reason behind this interest is that this method is very feasible in compared to previous methods. In addition to its simplicity and low capital costs, very limited environmental impact and high capacity for huge amount of polymer packaging wastes are other advantages of this method (Al-Sabagh, Yehia, Eshaq, Rabie, & ElMetwally, 2016). However, the challenges of this method are the disruption of the appearance and mechanical strength of the final recycled products compared to virgin materials.

2.3.1 Single component waste

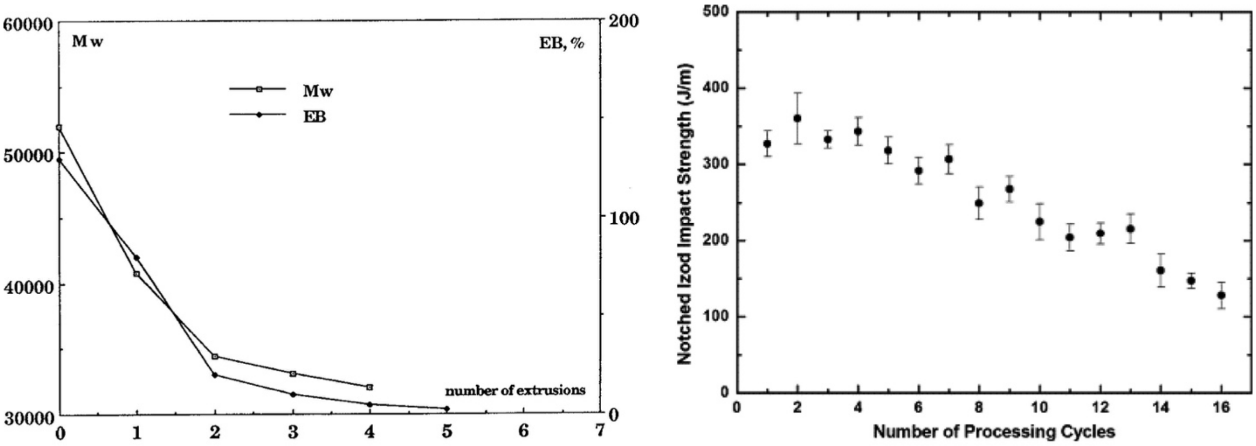
Multiple extrusion and exposure to heat increase the chance of thermal or mechanical degradation of the materials and chain scission due to moisture or acidic contaminations in wastes which lead to reduction of the melt viscosity and reduction of molecular weight of the samples (Achilias & Karayannidis, 2004). Figures 2.6 and 2.7 provides the changes in molecular weight, MFI, and mechanical strength due to the reprocessing of the materials. This also may lead to yellowish color due to oxidation reactions or crosslinking (Al-Sabagh et al., 2016). Presence of different components (like contaminations, adhesives, and inks) may enhance the chance of crosslinking or nucleation in the samples. Although the costumers accept a part of the mentioned weaknesses to help the environment, there are ways to enhance the recycled plastic properties and limit these effects. One idea is to use these recycled polymers in a multilayer structure with a low thickness (around 25% of the whole film thickness) to compensate the weaknesses with other virgin layers. Further ways are to limit these effects by adding some chemical additives (antioxidants, compatibilizers, chain extenders (Scheirs, 1998), etc.) or by optimizing the processing conditions. Polyolefins are major resins in packaging industry ranged from LDPE and HDPE to PP. Mechanical recyclability of this polymers has been studied in different Investigations. Jin et al. Observed that the melt flow index of the LDPE changes during multiple reprocessing (Jin et al., 2012), which can be due to the crosslinking reaction during recycling process by reactive carbon radicals (Kabdi & Belhaneche-Bensemra, 2008; Waldman & De Paoli, 1998). However, the results showed these changes are slight and Even after 5 extrusion cycles the material shows processing stability (Kartalis, Papaspyrides, & Pfaendner, 2000). PP recycling, also, was studied in multiple publications. Reprocessing of this resin results in higher crystallization rate and higher crystallinity (Aurrekoetxea, Sarrionandia, Urrutibeascoa, & Maspoch, 2001), lower melt viscosity and higher MFI due to thermal degradation of the polymer (Bahlouli et al., 2012; Gao, Kaneko, Amasaki, & Nakada, 2003; Liang & Peng, 2009; Tri Phuong, Gilbert, & Chuong, 2008; Yang, Liang, & Tang, 2009), and the rigidity of the PP resins was observed to be stable after reprocessing due to good stabilization (Bourmaud & Baley, 2009). Polypropylene is more vulnerable to oxidation in mechanical recycling since the C-H group at tertiary carbon center would react with oxygen more easily. Consequently, the disruption of the mechanical properties of the PP is more noticeable after re-extrusion compared to polyethylene (Rahimi & García, 2017). Another component that is widely used in the packaging industry is PET polymer. Badia et al. investigated the reprocessing PET resin and the effect of that on the mechanical properties as well as the melt flow index and oxidation temperature (Badia, Vilaplana, Karlsson, & Ribes-Greus, 2009). PET polymers are very sensitive to moisture that the presence of that can change the crystallinity and nucleation rate of the recycled wastes and consequently the mechanical strength of the final sample (Avila & Duarte, 2003), however, the mechanical properties of the mechanical recycled PET resins drop slightly and it made mechanical recycling a good approach for PET wastes (Frounchi, 1999). However, mechanical recycling of polystyrene leads to decreasing melt viscosity and mechanical properties due to the decrease of the molecular weight after multiple processing (Remili, Kaci, Benhamida, Bruzaud, & Grohens, 2011).



a

b

Figure 2.6 Molecular weight and polydispersity evolution of a PP sample (Qian, Igarashi, & Nitta, 2011), (b) MFI evolution of a multiple reprocessed PP sample (Delva, Ragaert, Degrieck, & Cardon, 2014)



a

b

Figure 2.7 (a) Molecular weight and elongation at break as function of number of extrusions for a PET sample (La Mantia, 1996) (b) Impact strength for a number of processing cycles of a PA6 sample (Su, Lin, & Lin, 2007)

2.3.2 Multi component waste

In packaging industry specially in food packaging, multilayer and composites structures are designed to enhance the packaging quality. It should be taken into account that mechanical recycling of these multicomponent polymer wastes is challenging due to the immiscibility of the polymers in each layer. Since the separation of the layers is very hard and costly and also the majority of polymers are immiscible and blends of them can deteriorate the properties. The minor polymer components form small phases in the matrix and this phenomenon either can be seen by naked eye (D= 100-400 microns) as the defects or can be problematic through week mechanical properties due to very week interface of the phases (Dow, 2014).

In a thermodynamically point of view, to have a miscible polymer system, the Gibbs free energy of mixing ΔG_{mixing} should be negative or zero (N. Liu & Baker, 1992; Manias & Utracki, 2014) and based on the Gibbs-Helmholtz equation:

$$\Delta G_{mixing} = \Delta H_{mixing} - T \cdot \Delta S_{mixing}$$

And due to the fact that polymers have high molecular weight, the effect of the changing in entropy is negligible. So, to have a miscible polymer system, the enthalpy of mixing should be negative or the mixing should be exothermic (Feldman, 2005). More to the point, to have a complete miscible polymer system, the second derivative of G in respect to volume fraction, should be positive.

$$\partial^2 G / \partial^2 \phi > 0$$

The basic theory of calculation of Gibbs free energy was introduced by Flory and Huggins (Flory, 1942) as:

$$\Delta G_{mixing} = \kappa T N \{ \chi_{12} \phi_1 \phi_2 + \phi_1 \ln(\phi_1) + \phi_2 \ln(\phi_2) \}$$

Where κ is the Boltzmann constant, N is the mole fraction, T is the absolute temperature, ϕ_i is the volume fraction of component i and χ_{12} is the Flory-Huggins interaction parameter, which has to be negative to have a miscible mixing. The exact calculations of this parameter are complicated and is dependent to temperature, pressure, concentration, and type of polymer (Manias & Utracki, 2014). The compatibility of a polymer blend is a function of the polymers' chemical affinity and special interactions such as hydrogen bond, ionic bond, ion-dipole, dipole-dipole, etc. (Koning, Van Duin, Pagnoulle, & Jerome, 1998).

The morphology of the blends plays the major role in the characteristics of the final polymer packaging. In the blending of immiscible polymers, the minor component forms a separated phase or domain within the major matrix (for example in a typical multilayer structure of barrier film PE/tie/PA/tie/PE, the minor phase would be the polyamide in the polyethylene matrix). The morphology (domain size and shape) is influenced by chemical interactions (compatibility), rheology and flow deformation (shear or elongational flow) (Dupont, 2014).

Using interfacial agents (compatibilizers), the polymer mixture's chemical affinity can be enhanced. Compatibilizers can improve poor properties of recycled plastics caused by lack of compatibility between immiscible polymers. By having a stronger interface, the mechanical properties of the recycled layer would be enhanced. Interfacial agents also can be effective in the case of the size reduction of the dispersed phase which can prevent the agglomeration of the phase and gel formation (Ajji & Utracki, 1996; Utracki, 2002; Xanthos, 1988). The effect of compatibilizer on the morphologies of the PP/PET blend is provided in the Figure 2.8.

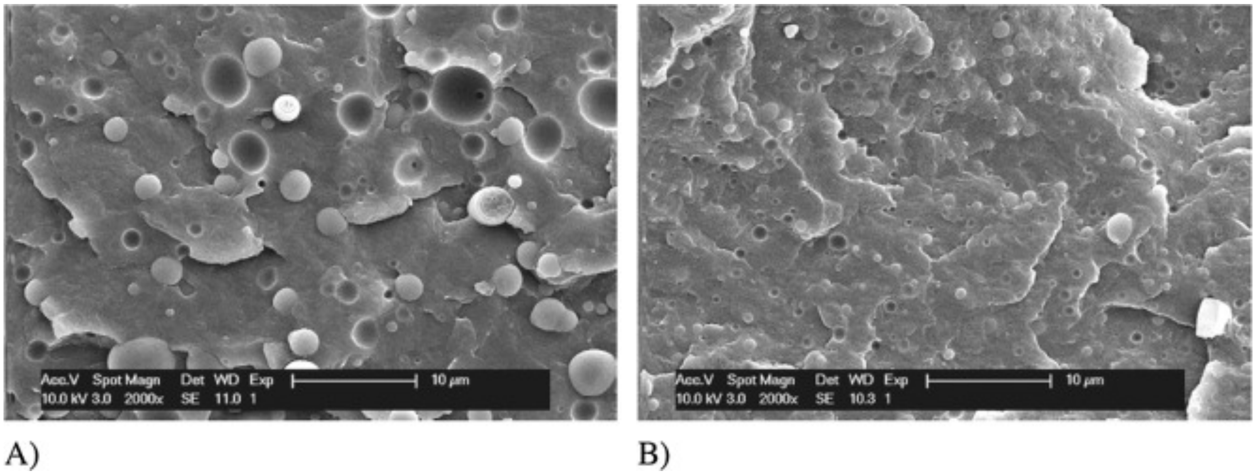


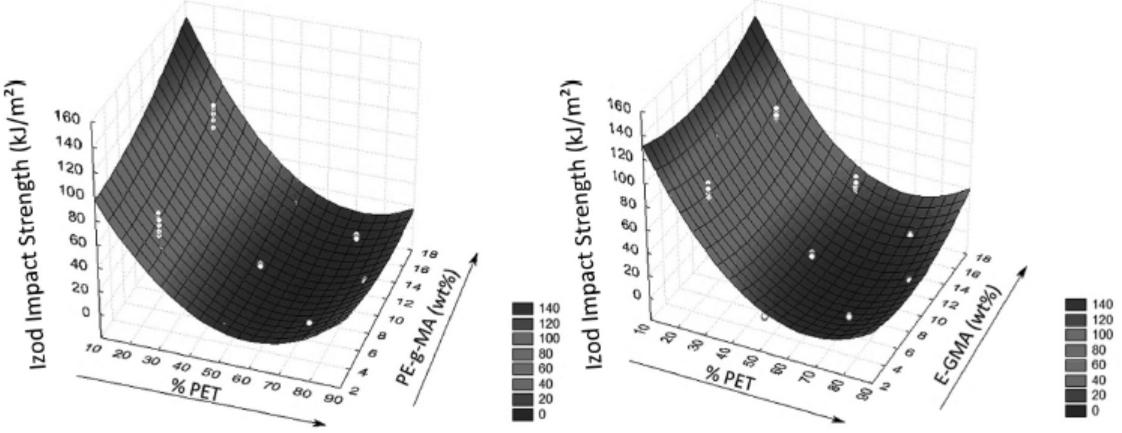
Figure 2.8 morphology of PP/PET blend (85%/15%) a) without compatibilizers, b) with 2.5 wt.% compatibilizers (Van Bruggen, Koster, Picken, & Ragaert, 2016)

Compatibilizers come in different types including copolymers, grafted polymers, nanoparticles, Ionomer, etc. (Maris et al., 2018). Main interfacial agents used for recycling of plastic packaging are polypropylene-grafted maleic anhydride (PP-g-MAH), polyethylene-grafted maleic anhydride (PE-g-MAH), ethylene and glycidyl methacrylate copolymer (E-GMA), and ionomers.

Choudhury et al. (Choudhury, Mukherjee, & Adhikari, 2006a) studied the recycling of waste oil pouches with the structure of PE/tie/PA/tie/PE. This structure gives perfect barrier properties (by polyamide as barrier layer) and very good mechanical (elongation at break) and sealing properties. Their film structure composed of 85% of polyethylene (LLDPE and LDPE) and 15% of Nylon-6. They have used the effect of two compatibilizers as Surlyn ionomer and polyethylene-grafted maleic anhydride (PE-g-MAH). It was obtained that in the FTIR pattern the Surlyn was more successful in terms compatibilization with a more intense amide banding. In the compatibilization reaction of the ionomer and polyamide, the bonds between the end group of the polyamide and ionomer are very strong (Hydrogen bonding and ion-dipole interaction). In the compatibilization reaction, it was observed that this reaction also produces water during the processing. So, to increase the compatibilization rate, moisture should be removed in the system. For this purpose, they have installed a ventilating equipment on the extruder to remove the moisture (Choudhury et al., 2006a). The morphology of the recycled stream was also studied and in the compatibilized systems the PA particle size were lowered resulting in more uniform and stable morphology and better mechanical properties (Choudhury et al., 2006a).

In 2015, Uehara et al. (Uehara, França, & Canevarolo Junior, 2015) have conducted a study on the recyclability of the multilayer films containing PET and HDPE based on the blending method. They have selected two compatibilizers as PE-g-MAH with 1 wt.% reactive agents and copolymer of ethylene and glycidyl methacrylate (E-GMA) copolymer with 8 wt.% reactive agents. During compatibilization mechanism of PET with E-GMA, epoxy group of the E-GMA can undergo reactions with both carboxyl and hydroxyl end groups of the PET. The high reactivity of the E-GMA makes it possible to have parallel reactions and crosslinking which could reduce the mechanical properties.

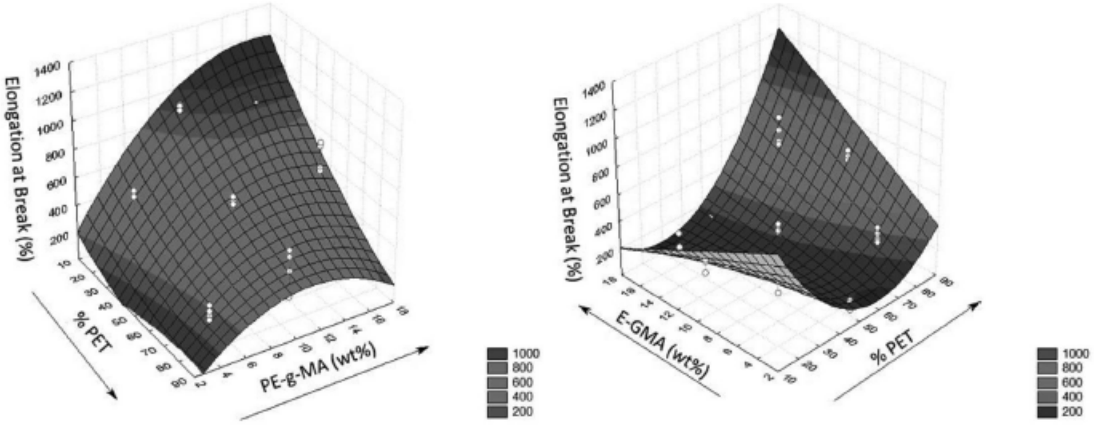
As a crucial parameter in the packaging, they have also measured the mechanical properties of the recycled polymer stream. The Izod impact strength using two compatibilizer is depicted in Figure 2.9. It is clear that the impact strength of both compatibilizers are approximately identical. It is also worth mentioning that E-GMA is highly reactive in compared to PE-g-MAH. So, we can conclude that PE-g-MAH showed a better performance in compatibilization of the samples.



(a) (b)

Figure 2.9 impact strength of the PE/PET compatibilized blend by a) PE-g-MAH, b) E-GMA (Uehara et al., 2015)

As another indication of effectiveness of the compatibilization, they studied the elongation at break. As it can be seen in the Figure 2.10 the elongation at break for the samples containing higher percentages of the PET could be better enhanced using E-GMA. This is due to the fact that at higher concentrations of the PET, reactions with E-GMA leads to chain extensions which can increase the elongation strength. At lower PET concentrations, however, the PE-g-MAH performed better due to high polyethylene content in the compatibilizer in compared to the E-GMA (Uehara et al., 2015).



(a) (b)

Figure 2.10 Elongation at break of the PE/PET compatibilized blend by a) PE-g-MAH, b) E-GMA (Uehara et al., 2015)

In this study, they also investigated the post-industrial recycled oil pouches. The film structure contained 70% HDPE, 10% PET, 10% Nylon and 10% ink and adhesive. Compatibilization process has been examined by E-GMA and PE-g-MAH in this study. Based on this study, the reaction rate of the MAH and polyamide terminal groups was obtained higher than GMA (Becker, Porcel, Hage, & Pessan, 2008). Mechanical properties of the compatibilized and non-compatibilized recycled films are illustrated in the Figure 2.11 and 2.12. There is a sudden rise from 5% to 10% of the case compatibilized with PE-g-MAH which is due to the fact that the reaction rate of the MAH with PA is higher compared to the PET (Macosko, Jeon, & Hoye, 2005). So, the interfacial modifiers first saturate the PA/PE interface and then attack the PET/PE interface. This saturation concentration occurs around 3 to 5 % of PE-g-MAH. In this case the effectiveness of the PE-g-GMA was better than the E-GMA. It can be due to the possible crosslinking of the PET molecules with OH when using E-GMA modifiers (Uehara et al., 2015).

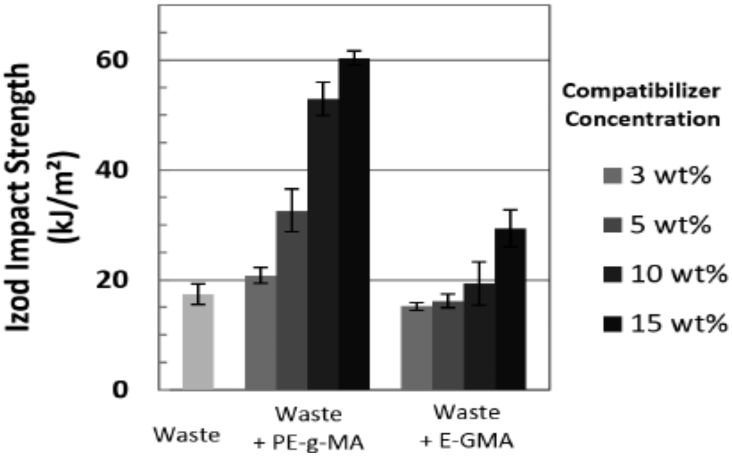


Figure 2.11 Impact strength of the recycled sample (Uehara et al., 2015)

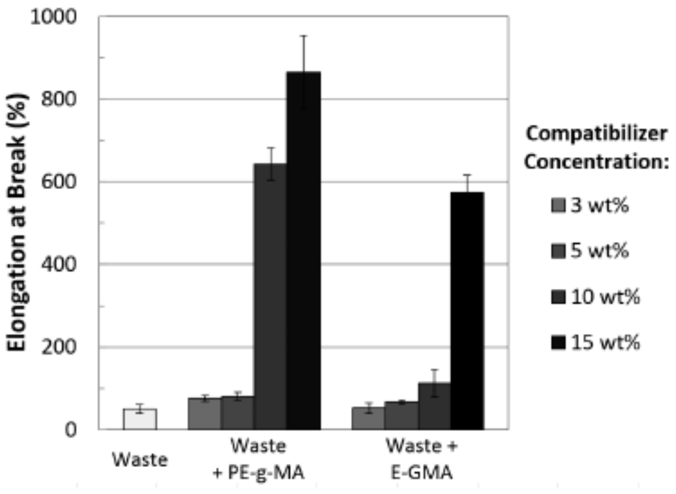


Figure 2.12 Elongation at break of the recycled samples (Uehara et al., 2015)

Unfortunately, the morphology images were not mentioned in this study as a major parameter. Furthermore, the film contained ink and adhesive which may lead to crosslinking or formation of gels in the recycled samples, however, the author did not mention any information regarding that.

As it was discussed before, one of the main polymers in barrier films is EVOH. So, the recycling of the structures containing this polymer is gaining interests over and over. This is no surprise that giant packaging companies are working on the recycling of the barrier films with a huge market behind. Dow (Parkinson, Oner-Deliormanli, Chirinos, & Walther, 2019) is one of that companies which has selected the compatibilization method for recycling due to the advantages that this method. They patented self-recyclable barrier packaging in flexible, semi-flexible, and rigid applications. The polar polymer barrier components that they have studied were Nylon6, Nylon6-6, Nylon6/66, and EVOH. The idea is to blend compatibilizer, Retain 3000, into the outer PE skin layer in the multilayer structure. The post-industrial film trims with this structure will be shredded into flakes (and optionally pelletized) and can be either employed in a new mono-multilayer film structure or simultaneously added to the same structure in blown or cast film. The ratio of the compatibilizer in the film to the EVOH was 1:1 (Parkinson et al., 2019). The recycled films with this structure showed improved mechanical properties in compared to the samples without compatibilizer in the structure. Furthermore, the visual appearance of the samples was better with lower number and size of visual imperfections (Parkinson et al., 2019).

Furthermore, compatibilization recycling of the post-consumer recycled oil pouches was investigated by Choudhury et al. (Choudhury, Mukherjee, & Adhikari, 2006b) the films containing LDPE/LDPE/PET were reactively compatibilized using PE-g-MA (Fusabond) and Surlyne ionomer. Before recycling, the recycled multilayer oil pouches (RMOP) were washed using detergent, NaOH, and hot water to remove oil and contaminations and dried before reprocessing in single screw extruder. Melt viscosity, thermal stability, and mechanical properties of the PCR were improved using 5 wt.% compatibilizers. The MFI of the compatibilized samples were reduced due to improved interfacial adhesion between the phases and also higher molecular weight of the compatibilized blends.

2.3.3 Effect of additives in recycling of plastic packaging

To elaborate the recycling process and the recyclability of the plastic packaging items, some additives should be added and also some additives must be avoided or limited as much as possible. Inclusion of additives must be analyzed to demonstrate that they do not impair the first service life of the polymers as well as their further applications in future.

Firstly, to have the polymers with durability and stable quality, incorporation of the degradable additives (bio, oxo, photo) must be avoided since they are detrimental to the recycled products' quality and shorten their effective service life. These additives should be separated from the plastic packaging wastes or have no adverse impact on the recycled product. So, inclusion of degradable additives should be minimized to limit the possible contamination and reduce the separation costs (A. o. P. Recyclers, 2018). In addition, optical brighteners can be detrimental to recycling which are used specially in PET bottles for better appearance. Presence of this additive creates an unwanted fluorescence in the recycled products and they just can be identified after recycling in the final products when it is too late for removing them and this impairs the value of the recycled PET (A. o. P. Recyclers, 2018).

On the other hand, there are some additives that can enhance the recyclability of the polymers and help the materials to keep their properties over the lifetime and reprocessing. These additives, however, are required to be tested to meet the appropriate recyclability standards like APR recyclability standards (A. o. P. Recyclers, 2018). De-nesting, anti-static, anti-blocking, anti-fogging, anti-slip, UV barrier, stabilizer and heat receptor agents and lubricants are of the additives that can enhance the performance of the recycling and up take their quality (Hahladakis, Velis, Weber, Iacovidou, & Purnell, 2018). For example, MFI of the HDPE increases after reprocessing due to heat degradation and chain scission of the materials. This phenomenon compromises the mechanical properties since the molecular weight of the rHDPE decreases by re-extrusion and this limits the application of the recycled polymers. By use of heat stabilizers it was observed that the recycled HDPE material can maintain its original MFI in multiple processing (Abad et al., 2004). Chain scission can also be addressed using chain extenders.

CHAPTER 3 PROBLEM IDENTIFICATION AND OBJECTIVES

3.1 Problem identification

The main experimental challenge in this research is the weak mechanical properties and poor visual appearance of the films containing PCR. The main reason for the challenges mentioned, is the defects that are present in the film samples. Number, size, and type of these defects affect film extrusion, lamination process, and end use (ExxonMobil, 2018):

- Large gels can break films or reduce the drawdown ability, especially at high line speeds in commercial scale.
- Defects can reduce the barrier properties of flexible barrier packaging structures particularly in laminated or metalized films.
- Gels disrupt the appearance of the films especially in transparent packages through diminishing their aesthetic appeal.
- Presence of such defects compromise the mechanical strength of the packages which can cause tearing of the films or scratches on the surface.
- Excessive gel content can cause printing imperfection and sealing properties or damage expensive printing plates.

3.2 Objectives

The general objective of this dissertation is incorporating of Post-Consumer Recycled (PCR) High Density Polyethylene (HDPE), which was the only available food grade PCR PE in the market, in flexible multilayer structure for food packaging applications along with proposing solutions for improving the appearance and strength of the mentioned flexible packages.

This study also seeks specific objectives including:

1. Achieving a comprehensive understanding of the plastic packaging recycling technologies, as well as the regulations and trends in this sector.

2. Blown-filming and characterizing flexible polyethylene-based films with PCR contents.
3. Diagnosing the sources of the poor visual and mechanical properties of the films derived from PCR HDPE.
4. Analysing the effectiveness of different solutions to mitigate the poor quality of the films containing PCR HDPE.

CHAPTER 4 ARTICLE 1: SUSTAINABLE MULTILAYER PLASTIC FILMS BASED ON POST-CONSUMER RECYCLED MATERIALS: A STEP TOWARDS CIRCULARITY IN FOOD PACKAGING

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The article has been submitted to Waste Management

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Abstract:

Sustainability of plastic packaging has a significant importance in reducing their negative environmental impacts particularly after their service life. Mechanical recycling is a major approach that complies with circular economy. However, the presence of defects in recycled materials results in final products with relatively poor visual and/or mechanical properties. In this work, the origin of the visual defects in post-consumer recycled HDPE (PCR HDPE), as well as the effects of processing method, processing condition and the addition of antioxidants on the visual defects were studied in multilayer flexible polyethylene films. Different types of the defects in the film samples were investigated by combining optical microscopy, energy dispersive X-ray (EDX), hot stage microscopy, solvent extraction, and dynamic scanning calorimetry (DSC) techniques. It was found that the defects in PCR film samples can be mainly categorized as fiber defects and point gels. Hot stage microscopy results show that point gels can be subcategorized as non-melting, non-deformable gels and melting, deformable defects. In addition, it was found that deformation of these defects increases at higher temperatures specifically above 200 °C. Further characterization showed that the observed deformable defects are highly entangled high molecular weight HDPE. The effect of processing temperature, processing with a twin-screw extruder and the addition of antioxidant on the visual defects in film samples were also discussed in detail.

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4.1 Introduction

Plastic packaging helps reducing significantly food wastes through increasing food shelf life while meeting all food safety standards. Using plastic alternatives such as glass and metal in food packaging increases energy consumption as well as greenhouse gases (GHG)s emission (Council, 2020). Even though plastic materials can offer many advantages, their very low degradation rate makes them a significant environmental issue after their service life. Current main approaches to reduce landfilling of plastics are energy recovery, composting, chemical and mechanical recycling (Niaounakis, 2019). Among them, recycling is the most environment friendly scenario for majority of plastics (European-Parliament-Directive, 2008). Recycling of plastic packaging wastes allows keeping plastic materials in the production-application-recycling loop and reduces significantly landfilling. However, without a demand for recycled materials in the market, recycling of plastic materials will not have an economic value (PRE, 2019a). Despite the growing use of recycled materials and the ambitious objectives such as the Zero Net Waste (ZNW) program in Europe and US (ACC, 2018; P. I. T. Association, 2016), the poor quality and properties of recycled materials compared to the virgin polymers have limited their applications(P. R. Europe, 2018).

The low cost, high flexibility, low sealing temperature, toughness and chemical resistance of polyethylene (PE) resins have made them the major plastic material in packaging applications(PlasticsEurope, 2019b; Rahimi & García, 2017). Among different types of PE, high density polyethylene (HDPE) is used in both rigid and flexible packaging and provides mechanical strength and toughness required during transportation and handling of packages. Previous studies showed that incorporation of recycled HDPE instead of virgin HDPE resin in packaging can reduce the energy consumption up to 88% and limits GHG emissions up to 71%(T. A. o. P. Recyclers, 2020). Among different recycled HDPE suppliers in the market, Envision plastics is the only company that provides food contact approved PCR HDPE. They use their patented technology (Plastics, 2019) to reduce the volatile content of PCR HDPE to below 320 μg/kg (FDA, 2006). However, film samples produced by PCR HDPE still suffer from poor visual properties and contain high visual defects. These film imperfections can also compromise final mechanical properties (ExxonMobil, 2018). Table 4.1. summarizes literature findings on common sources of defects with their physical features in polyethylene films.

Table 4.1 Different defects in polyethylene films and their characteristic physical features (ExxonMobil, 2018)

Type of defects	Sources	Visual features
Point gels	• Crosslinked resin • Non-melted High molecular weight resin • Foreign resin • Inorganic agglomerates • Dirt, dust • Oxidized resin	• Glassy • Glassy • Various colors • Opaque, sandy • Black or brown • Yellow, orange, brown, black
Arrow-shaped defect	• Melt Flow Index (MFI) variation or interlayer flow disturbances in coextruded films	• Arrow-shaped flow lines
Flurries of defects	• Occasional release of higher molecular weight resin from the polymerization process	• Shower of clear, translucent gels that appear randomly on the film
Irregular-shaped defects	• Foreign resin • Degraded resin • Dirt, dust or die build-up • Oxidized resin	• Various colors • Yellow, orange, brown, black • Black, brown • Yellow, orange, brown, black

Fiber defects	• Nylon, PP fibers • Wood • Paper, cellulose • Cotton	• Fibers that can be melted • Brown irregular chip, non-melting • Colored, fibrous, non-melting • Colored string, non-melting
Fisheyes	• Moisture or excessive humidity	• Lens-shaped specks with "fisheyes" at both ends

The variety of the defects and their nature results in complexity of resolving defects issue in PCR HDPE. Determining the source of the defects in PCR HDPE is the most important step in improving visual and mechanical quality of PCR-based films. In this work, attempts will be made to identify the origin of defects in PCR HDPE films and find approaches to reduce the defects in multilayer flexible films containing PCR HDPE.

Furthermore, degradation of the recycled HDPE resin can also be challenging that can change the properties of the materials. Previous results in the literature show that thermal degradation of HDPE generally occurs through chain scission(Hinsken, Moss, Pauquet, & Zweifel, 1991; Moss & Zweifel, 1989). Macromolecules exposed to heat and stress, undergo a chain scission degradation which produces macro-radicals. Previous results indicate that increasing Mw increases chain scission by increasing the mechanical stress impose to chain backbone and the lack of chain mobility due to the high entanglement density(Pinheiro, Chinelatto, & Canevarolo, 2004). Concentration of oxygen and active species play an important role on how chain scission can affect Mw and chain morphology of polymer molecules. In the absence of oxygen and active components, the formed macro-radicals with chain scission react with other macromolecule and this process yields to the formation of highly branched and high Mw HDPE molecules and in the extreme cases even cross-linked HDPE (Pinheiro et al., 2004). On the other hand, in the presence of oxygen or other highly active components, macro-radicals formed after chain scission can react with them which results in formation of stabilized smaller macromolecules (Pinheiro et al., 2004). Therefore, the effect of thermal degradation can vary depending on the concentration of oxygen and active components in the system. This can explain why some studies reported reduction of MFI during multiple extrusion cycles of HDPE (Oblak, Gonzalez-Gutierrez, Zupančič, Aulova, & Emri, 2015) while other studies observed an increase in MFI after multiple processing steps (Abad et al., 2004; Luzuriaga, Kovářová, & Fortelný, 2006). This indicates the complexity of the effect of processing on Mw of HDPE and the importance of the knowledge of the present component in the system. It should be noted that controlling or even the complete knowledge of present components in recycled materials is very challenging which increases the complexity of analysing degradation in these materials.

4.2 Experimental

4.2.1 Materials

Food contact grade PCR HDPE (Ecoprime) was supplied by Envision Plastics. Table 4.2 shows some of properties of PCR HDPE. The PCR HDPE is coming from controlled sources of wastes of rigid food packaging structures (milk jugs and water bottles).

Table 4.2 Ecoprime PCR HDPE properties (Plastics, 2018)

Property	**Method**	**Range***	**Unit**
MFI	ASTM D1238	0.55 to 0.85	g/10min at 190 ^{o}C
Density	ASTM D792	0.958 to 0.965	g/cm^3
Volatiles Content	Gas Chromatograph	<320	ppb
Flexural Modulus	ASTM D790	768	MPa
Elongation at break	ASTM D638	197	%

Defects larger than 0.25 mm^2	TAPPI Chart	11 Max.	#defects/10g PCR

*refer to PCR HDPE datasheet

A bio-based LDPE (SBF0323/12HC) with an MFI of 0.32 g/10min was purchased from Braskem. Octene-based LLDPE (SCLAIR® FP120) was provided by Nova Chemicals with an MFI of 1 g/10 min. Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate) (Irganox 1010) is phenolic antioxidants supplied by Sigma-Aldrich and Baeropol DRS 6812 SP stabilizers were provided by Baerlocher.

4.2.2 Film extrusion

Blown film extrusion was done using a lab-scale multilayer extrusion line equipped with single screw extruders with screw diameter of 20 mm, and L/D=30. All extruders were equipped with a Maddock mixer and 60 mesh size screen packs. An annular die with the outer diameter and die opening of 50 mm and 1.5 mm, respectively, was used in the film blowing process. The speed of the nip and windup rollers were set to achieve a target total thickness of 75 μm and a blow-up ratio (BUR) between 2.5 to 3. The film samples had a symmetrical three-layer structure with PCR HDPE sandwiched between two skin layers of LLDPE/LDPE (80/20 wt.%) blend. Using this blend composition helps optimized processability of the material (stabilization of the blown film extrusion) and ensures good mechanical properties (tear strength, elongational at break) and visual properties (transparency), as well as saleability of the flexible films. The thickness of PCR layer was kept at 40% of the total film thickness in all samples except when 100% PCR films. The screw speed for all extruders was set at 100 rpm. Film samples were prepared using two temperature profiles: high temperature profile (230-250-250-230 ºC), and low temperature profile (170-185-185-175 ºC). The blown film die temperature in all experiments was set at 200ºC.

In order to examine the effect of melt-processing with a twin-screw extruder, a single layer cast film of 100% PCR HDPE was prepared using a twin-screw extruder (Leistriz) with 18 mm co-rotating screws and L/D = 30 operated at a temperature profile of 170 to 200 ºC and screw speed of 50 rpm. The twin-screw extruder was connected to a cast film die at 200ºC. The produced film was cooled by passing through an air knife and collected with a calendar. The line speed was set to obtain 75 µm thick film samples.

In order to examine the effect of combining twin- and single screw extrusion, PCR HDPE strand was extruded first using the twin-screw extruder and cut with a pelletizer. Then the obtained processed PCR granules from the twin-screw extruder were processed using the multilayer extrusion line at the same processing condition as for the multilayer films prepared using the virgin PCR HDPE. Finally, a multilayer film with the total thickness of 75 µm was obtained.

4.2.3 Melt flow index measurement

In order to examine the effect of processing on PCR HDPE, the melt flow index (MFI) of the virgin PCR HDPE and the one processed by the twin-screw extruder were measured according to ASTM D 1238 at 190 °C and 2.16 kg load force.

4.2.4 Energy dispersive X-ray (EDX) analysis

EDX analysis was employed to investigate the origin of the observed defects from their elemental analyses. Film samples with defects were cut and the EDX analyses were done on the cross-section of the defects in a scanning electron microscope (Hitachi TM3030) equipped with an EDX detector. The experiments were done at 15 kV acceleration voltage and 7.4 mm working distance.

4.2.5 Solvent extraction

In order to determine the gel content of PCR HDPE, solvent extraction was done using boiling Xylene in a Soxhlet extraction setup according to the standard method ASTM D2765 for determining the gel content in polyethylene samples. First, 300 mg PCR granules were put in a metal cage made of 120 mech-size screens. The cage was weighted and placed in boiling xylenes for 12 h. Irganox 1010 was also added to the cage as an antioxidant to prevent degradation of HDPE during the extraction process. The cage was then dried in a vacuum oven and weighted using a balance (Sartorius, Geottingen, Germany) with an accuracy of 0.1 mg. The difference between the initial and final weight of the cage with samples is considered as the amount of non-soluble gels.

4.2.6 Optical microscopy and hot stage

An optical microscope (Optiphot-2, Nikon) equipped with a controlled temperature hot stage (FP82HT, Mettler) was used to analyze the nature of the defects in this study. Defects were cut from the PCR film using a razor blade and put between two glass slides on the hot stage. Heating was started at 25 ºC and temperature was increased with a heating rate of 20 ºC/min to the final temperature of 300 ºC. The sample then was cooled down to room temperature at 20 ºC/min. The heating process was recorded using a camera mounted on the optical microscope.

4.2.7 Differential scanning calorimetry (DSC)

DSC analysis was conducted using Q2000 DSC (TA Instruments LLC, USA). DSC tests were done on 3 mg of gels that were cut using a razor blade from film samples. Heating was started at 25 ºC and temperature was increased with a heating rate of 10 ºC/min to the final temperature of 300 ºC. Sample then was cooled down to room temperature at 10 ºC/min.

4.2.8 Defects size estimation

To determine the size of defects in film samples, the same method as the one used by PCR HDPE supplier was used. A standard size estimation chart (TAPPI T 564) was used which can detect be applicable for the defects larger than 0.02 mm^2, however, for small sizes the identification is so hard and requires magnifiers or microscopes. In this study, defects were categorized in three size groups of large size (> 1.0 mm^2), medium size (between 0.25 mm^2 and 1 mm^2), and small size (between 0.08 mm^2 and 0.25 mm^2). The reported values are an average of three measurements based on 25 g of film samples. Considering the 40% PCR content of film samples, this is equal to 10 g of PCR HDPE.

4.3 Results and discussion

4.3.1 Identifying source of defects in PCR HDPE

Figure 4.1 shows optical microscopy images of some defects in 100% PCR HDPE film sample prepared by multilayer extruder line. Considering the physical features listed in Table 4.1, defects in the produced PCR films have physical characteristics similar to point gels, and fiber defects.

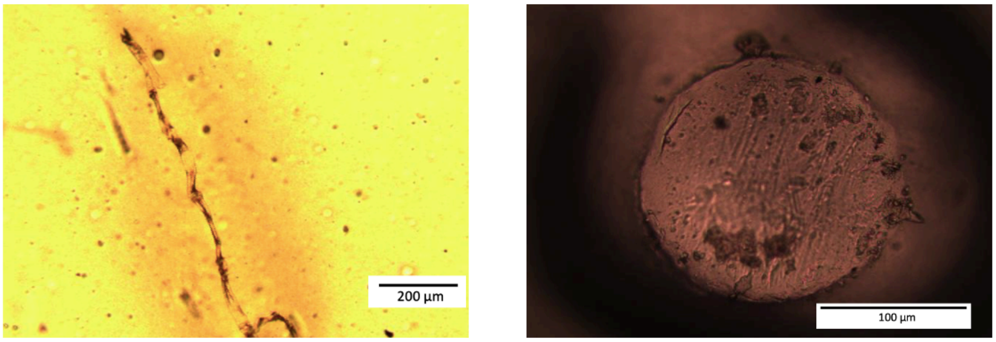

Figure 4.1. Optical microscopy images of typical defects in 100% PCR film, left) a fiber defect, and right) a point gel.

EDX analysis provides elemental identification and can be employed to identify inorganic contamination (metal oxide, etc.) in the film imperfections. EDX analysis results for different defects indicated very low level (less than the resolution of the detector) of elements such as silica, chlorin or metals that can be found in inorganic contaminations. The results confirm that inorganic contaminations should not be a major source of the observed defects in PCR HDPE.

Hot stage microscopy images of the fiber defects are provided in Figure 4.2. The results show that heating of a fiber defect up to 300 °C did not change its morphology which confirms that the fiber defects should be cellulose-based fibers that are likely from paper and labels in PCR materials.

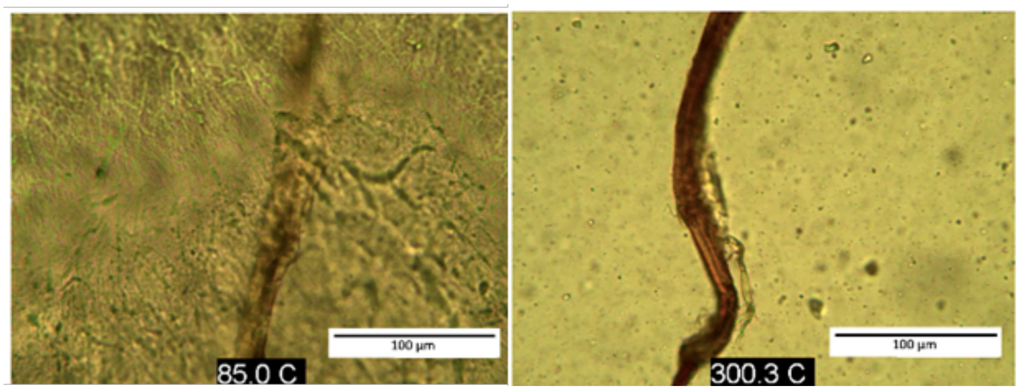

Figure 4.2 Hot-stage microscopy images of fiber defect. The temperature for each image is shown in the black box under the image.

The hot stage results of the point gels, however, show two main behaviors for differently point gels. Some gels, as shown in Figure 4.3., do not melt when hot-stage temperature increased even up to 300 ^{o}C. Considering that the EDX results did not show a considerable source of inorganic contaminations, the non-melting gels can be cross-linked HDPE or adhesives (ExxonMobil, 2018; RAUWENDAAL, 2004; Spalding, Garcia-Meitin, Kodjie, Campbell, & Womer, 2018), which do not have a melting point.

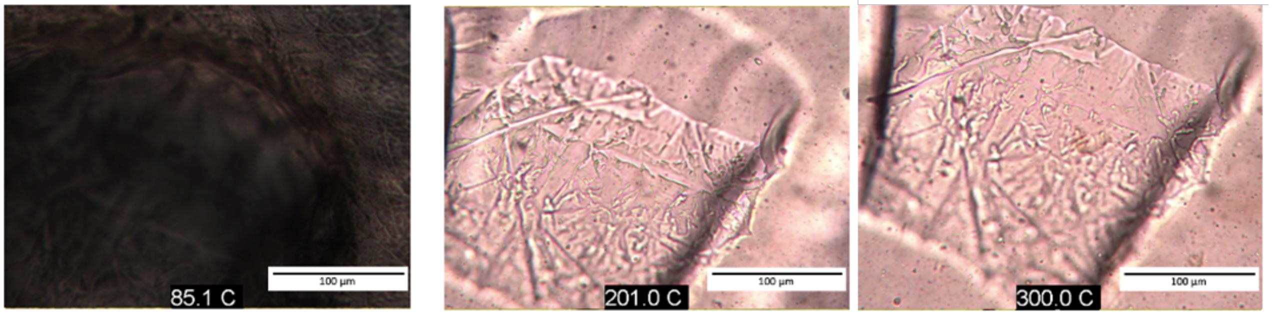

Figure 4.3 Hot-stage microscopy images of point gels that do not melt or deform by heating. The temperature for each image is shown in the black box under the image.

In order to examine the effect of multiple processing on MFI of PCR HDPE, PCR HDPE was processed multiple times using a twin-screw extruder at temperature profile of 170-200^{o}C. Figure

4.4 shows the effect of the reprocessing on MFI of the PCR granules. The obtained results show a slight increase in the MFI of PCR HDPE from 0.6 g/10 min for the initial granules to 0.7 g/10 min after three processing cycles. The observed increase in the MFI indicates that the chain scission followed by stabilization of macromolecules by active species should be the dominant degradation mechanism of PCR HDPE during melt processing.

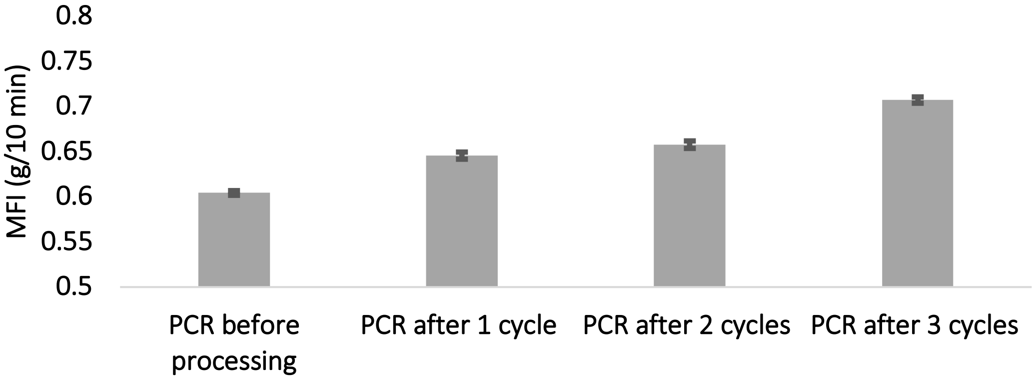

Figure 4.4 Effect of multiple melt processing with a twin-screw extruder on MFI of PCR HDPE

However, it should be noted that formation of highly branched HDPE also occurs but at a lower rate. Highly branched HDPE can form in high resident time regions such as sharp channel corners (Campbell & Spalding, 2013). In sharp corners, Moffatt eddies (Moffatt, 1964) are formed where the resin circulates in eddies rather than being transported forward along the screw length axis. This increases significantly the residence time of the materials in these regions and increases the chance of thermal degradation. (Spalding et al., 2018). It has been shown that highly entangled HDPE are soluble in boiling xylene while cross-linked HDPE cannot be dissolved.

In order to estimate the cross-linked gel content in PCR HDPE, the gel content of PCR granules was determined using the procedure explained in experimental section. The optical microscopy images of the cage after extraction is shown in Figure 4.5. Despite the presence of some fiber residue from fiber defects, no cross-linked gel was left in the cage which show that no cross-linked gel larger than the mesh size of the cage (125 μm) exists in PCR HDPE granules results. The weight measurements of the cage after extraction was also found to be the same as the empty cage which confirms that no considerable amount of cross-linked gel or non-HDPE gels exist in PCR granules.

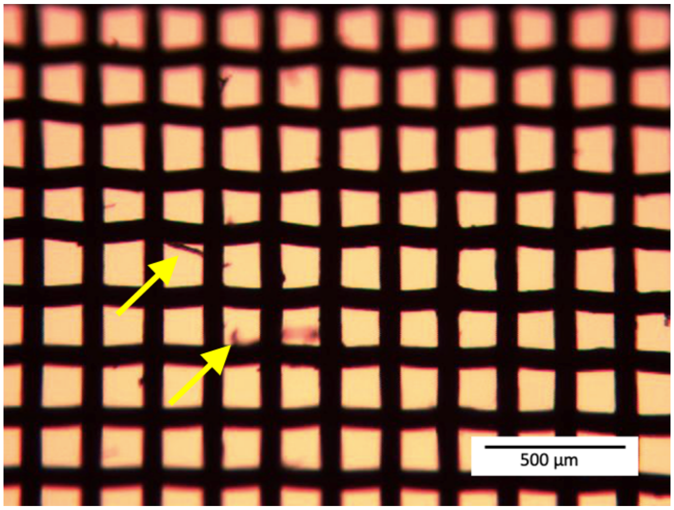

Figure 4.5 Microscopic image of the cage after extraction process. Fiber residues after extraction are shown with yellow arrows.

In addition to defects that do not melt even at high temperatures, hot stage microscopy results show some defects that melt and deform by increasing the temperature specifically over 200 ºC. A typical result of hot stage microscopy for this type of defect is shown in Figure 4.6. It should be noted that despite melting and deformation of these defects at high temperatures, they are not disappeared even at high temperatures and solidify and form a separate region upon cooling. Figure 4.7 shows the diameter of the defect in Figure 4.6 versus the temperature in the hot stage. The diameter of the defect changes slightly by increasing temperature but it begins to increase significantly over 200 ºC and reaches a plateau after 250 ºC. It should be noted that the observed deformation of the defect in Figure 4.6 is due to the weight of the heater plate in the hot stage applied on the glass slides that hold the defect between them. Therefore, the observed deformation is a result of spreading of the defect between the holding glass slides rather than expansion of the defect volume.

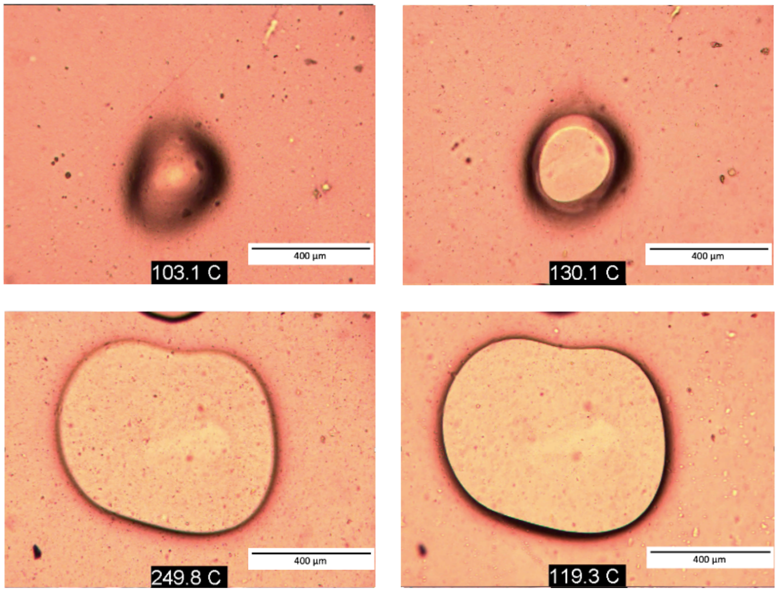

Figure 4.6 Hot-stage microscope images of a typical point gel that melt and deform by increasing temperature. The last image shows the defects after cooling from high temperatures. The temperature for each image is shown in the black box under each image.

As these defects are optically similar to PCR HDPE matrix and they melt at temperatures below 200 °C, it is very likely that they are highly entangled high Mw HDPE regions which exhibit similar optical properties as HDPE but have higher melting temperature than HDPE(RAUWENDAAL, 2004).

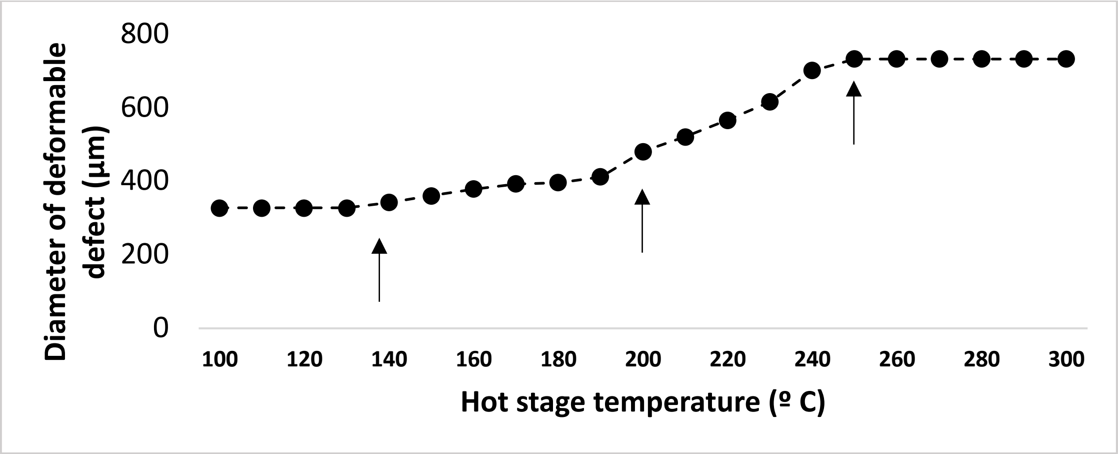

Figure 4.7 Variation of the diameter of the deformable defect samples in the Figure 4.6 by increasing the temperature. The dashed line is only drawn for better visualization of the trend. The arrows from left to right point to the low deformation region at lower temperatures, the increased deformation rate at 200 °C and the final plateau region observed at high temperatures.

Furthermore, DSC test was also used to examine the melting point of the gels in PCR HDPE films. The obtained DSC curve, not presented here, showed only one melting peak at the melting peak temperature of PCR HDPE. However, due to the very small size of the core of point gels, complete separation of their core from PCR HDPE matrix is impossible. Considering the very small size in DSC tests, it is likely that the contribution of the core of the gels in the final signal is ignorable and therefore no other melting peak than PCR HDPE matrix could be seen in DSC results.

4.3.2 Effect of melt processing on defects in PCR HDPE

Effect of melt processing on the number of defects was examined by comparing the reported number of defects in PCR HDPE datasheet with the number of defects in the multilayer film samples prepared with the low temperature extrusion profile (170-185-185-175 ºC). It should be noted that all reported numbers are based on 10 g of PCR HDPE for the sake of comparison with the reported number of defects in the PCR HDPE granules. The total number of defects increased from 11 defects larger than 0.25 mm^2 in PCR granules before processing to 1720 ± 101 specks (larger than 0.25 mm^2) in the multilayer film sample prepared at low temperature extrusion profile. However, when multilayer film samples were prepared using the high temperature extrusion profile (230 250 250 230 ºC), the number of defects decreased to less than the half of the defects in the samples prepared at low temperature. The results are provided in Figure 4.8.

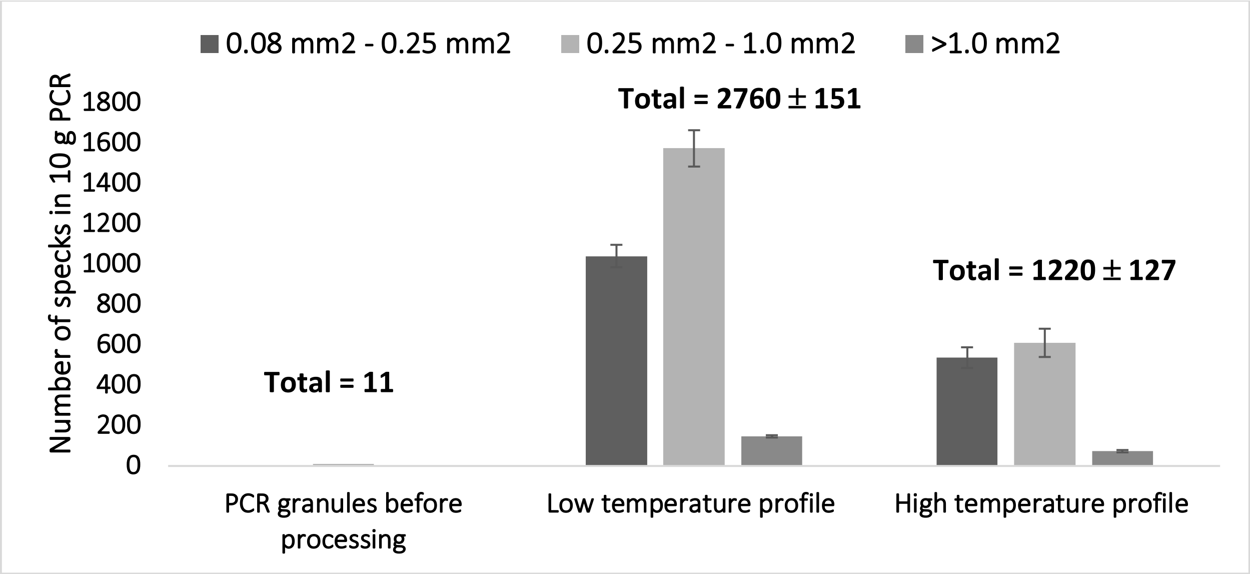

Figure 4.8 The effect of melt processing at low and high temperatures on the number of defects in PCR HDPE. The numbers on top of the column show the total number of defects in each sample.

These results indicate that processing at either low or high temperature increased the total number of defects in PCR films compared to the PCR granules before processing. However, as increasing processing temperature reduced the number of defects, the observed defects cannot only be attributed to the formation of highly branched or crosslinked HDPE due to thermal degradation, since crosslinking accelerates by increasing processing temperature(Piffer, 2007; RAUWENDAAL, 2004; Spalding et al., 2018). As it was shown previously, processing reduced Mw of PCR HDPE matrix, Figure 4.4. At the same time, highly entangled high Mw HDPE can form during processing due to thermal degradation and branching(Kavanagh & Ross-Murphy, 1998; Pal & Banerjee, 2018). These two phenomena occur simultaneously during the melt processing and increase the Mw gap between the highly entangled regions and the PCR HDPE matrix which increases the chance of formation of discrete highly entangled HDPE regions in PCR HDPE matrix(Kavanagh & Ross-Murphy, 1998; Pal & Banerjee, 2018). Although chain scission (as the first step in degradation mechanisms of HDPE) is accelerated at higher temperatures, but the higher deformability of the highly entangled regions at high temperatures (specially above 200 ^{o}C) results in deformation and breakup of these regions when PCR HDPE is processed at high temperature extrusion profile. This conclusion is in agreement with the hot stage microscopy results which showed that highly entangled HDPE defects show much higher deformation at temperatures above 200 ^{o}C.

In addition, the effect of melt-processing with a twin-screw extruder on the number of defects in PCR HDPE was also studied and the obtained results are shown in Figure 4.9.

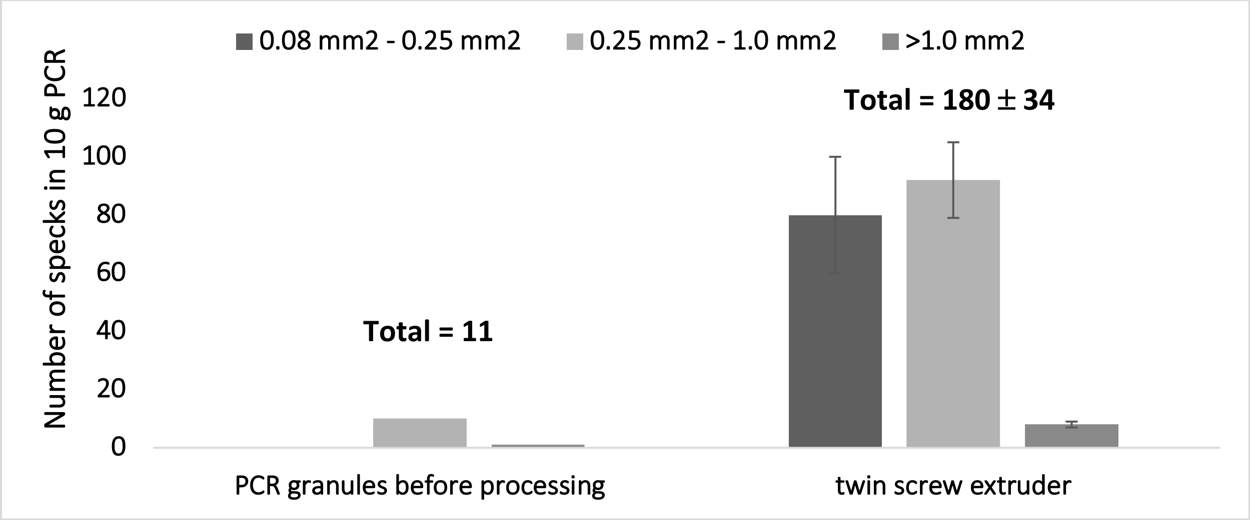

Figure 4.9 The effect of melt processing on the number of defects in PCR HDPE with a twin-screw extruder. The numbers on top of the column show the total number of defects in each sample.

As can be seen, melt processing of PCR HDPE with the twin-screw extruder also increased the counted number of defects but at much less extent compared to the single screw-extrusion. These results are in line with the previous conclusion that the source of the defects should be mainly the highly entangled HDPE because the much higher dispersive mixing capability of twin-screw extruders(Chin & Han, 1980; Han, 1980; Zhidan, Juncai, Chao, & Xiuju, 2011) allows break up and dispersion of the highly entangled HDPE domains. Considering the much higher viscosity and elasticity of highly entangled HDPE, the elongational flow and dispersive mixing elements in twin-screw extruder can breakup these regions much effectively compared to single screw extruders(Piffer, 2007; RAUWENDAAL, 2004; Spalding et al., 2018). Therefore, the obtained results point to the important role of dispersive mixing as a tool in reducing the negative effect of processing on defects in PCR HDPE.

The effect of processing PCR HDPE with the combination of twin-screw extruder and single-screw extruder on the number of defects in multilayer PCR HDPE films was also examined and the results are shown in Figure 4.10.

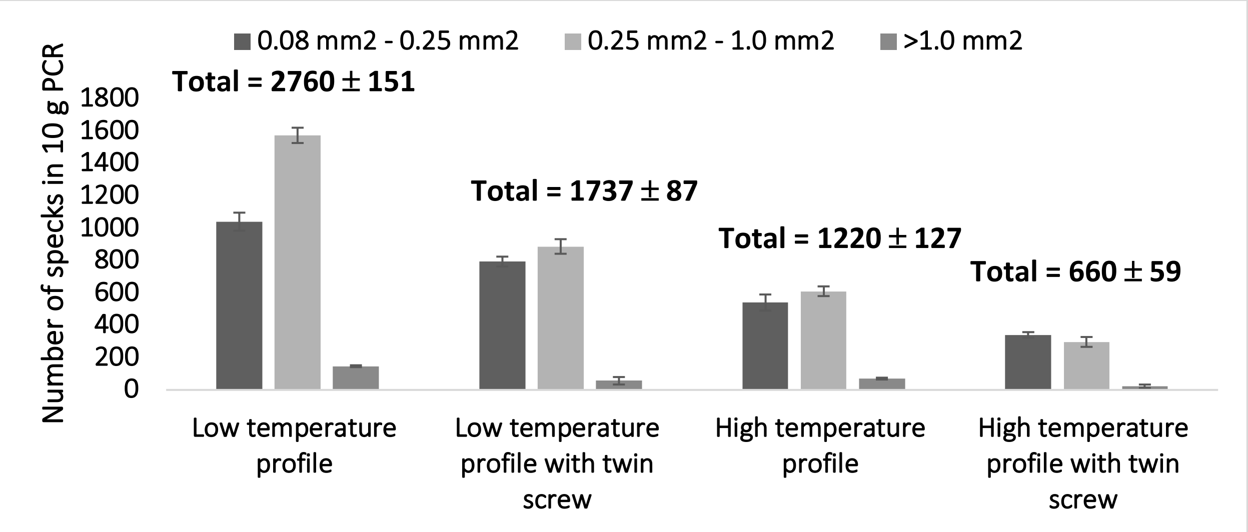

Figure 4.10 The effect of processing PCR HDPE with twin-screw and then single screw at low and high temperatures on the number of defects in PCR HDPE multilayer films. The numbers on top of the columns show the total number of counted defects in each sample.

By comparing the number of defects in these samples with the samples prepared only with single-screw extruder, it can be seen that the initial processing of PCR HDPE with twin-screw extruder reduced the number of defects in the final multilayer film sample. This result indicates that the effect of twin-screw extruder should not be only limited to dispersion of the formed highly entangled HDPE defects during processing. As shown before, Figure 4.4, processing reduces the Mw of PCR HDPE. It has been shown that higher Mw chains are more susceptible to chain scission due to their higher density of entanglement (Pinheiro et al., 2004). Therefore, reducing Mw of PCR HDPE in the twin-screw is likely to reduce the chain scission in single-screw extrusion as well. In addition, reducing Mw of HDPE after the twin-screw extrusion, reduces its viscosity and the resident time (Busse & Longworth, 1962) in the single-screw extrusion step which itself reduces the formation of highly entangled Mw HDPE.

4.3.3 Effect of the addition of antioxidants

The addition of antioxidants is a common approach to reduce degradation of polymer materials during melt processing (Bhunia, Sablani, Tang, & Rasco, 2013). Highly reactive radical species generated by heat, and mechanical stress during melt processing initiate the polymer degradation and lead to either cross-linked/highly branched defects or to the formation of smaller polymer chains. Antioxidants reduce polymer degradation by stabilizing the formed radical species (Hahladakis et al., 2018). Phenolic and phosphite-based (also known as secondary stabilizer) are among the major antioxidants used in polymer processing to prevent degradation of resin and discoloration (Merrington, 2017). In order to examine the effect of the addition of antioxidants on defects in PCR HDPE, four multilayer film samples were prepared at low and high temperature profiles with 1 wt.% Baeropol 6812 antioxidants and without antioxidants. The counted number of defects in these samples are provided in Figure 4.11. The results show that the addition of antioxidant at both low and high temperature reduced the number of defects. however, the effect if more pronounced in the sample prepared at low temperature profile.

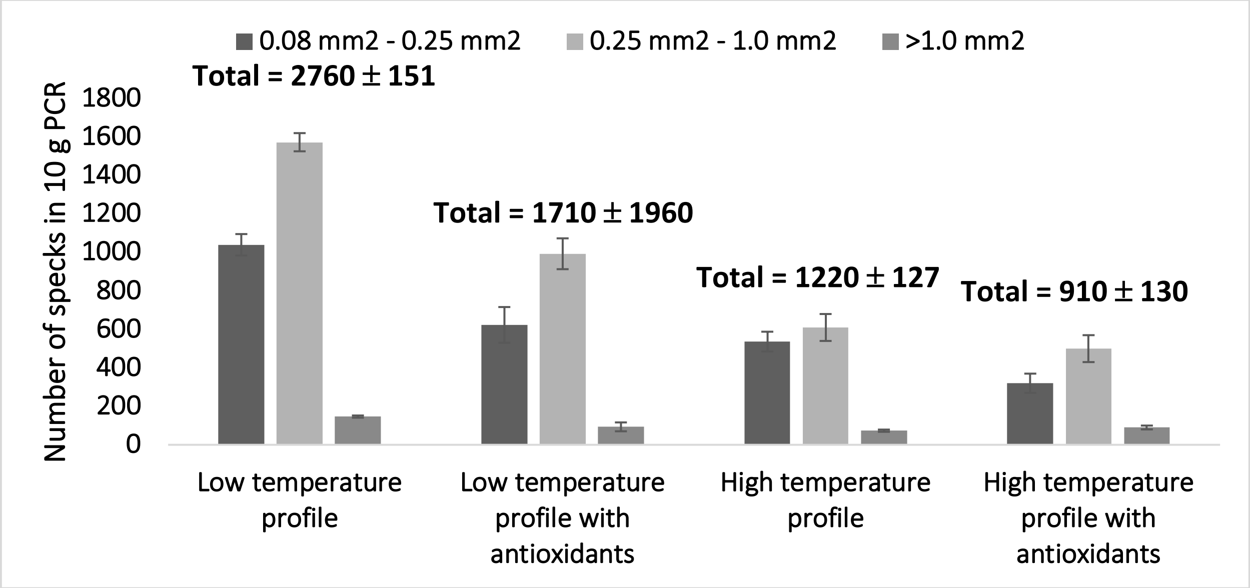

Figure 4.11 The effect of antioxidants on the number of defects in PCR HDPE multilayer films. The numbers on top of the columns show the total number of counted defects in each sample.

4.4 Conclusion

Incorporating of post-consumer recycled (PCR) materials is a key to circular model in plastic packaging. However, replacing virgin materials with PCR sacrifices visual properties of the film samples due to the presence of defects. Different characterization techniques including hot-stage microscopy, energy dispersive X-ray (EDX), solvent extraction and dynamic mechanical analysis (DSC) were used to determine the source of the defects in PCR HDPE. It was found that the formation of highly entangled high Mw HDPE is the major source of formation of defects in melt processing of PCR HDPE. Hot stage microscopy results show that these defects have higher melting temperature than HDPE and exhibit high deformation at temperatures above 200 °C. The effect of processing temperature was studied, and it was found that increasing processing temperature reduced considerably the number of defects. This result can be explained by considering easier deformation and breakup of the defects at high temperatures. The effect of processing with twin-screw extruder was also investigated and it was shown that the dispersive mixing capability of twin-screw extruders are an important tool in reducing the number of defects in PCR HDPE. The effect of combination of twin-screw extruder and single screw-extruder on defects in PCR HDPE was also studied. The results showed that the initial processing with a twin-screw extruder reduced Mw and viscosity of PCR HDPE which led to reducing formation of highly branched HDPE in the single screw extrusion. The effect of the addition of antioxidant was also examined and it was found that the addition of antioxidants is more effective in reducing the number of defects at low processing temperatures.

4.5 Acknowledgement

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CHAPTER 5 GENERAL DISCUSSION

Plastic packaging brings numerous advantages to the food and beverages industry according to the features of polymers which outperforms other metal or glass alternatives. However, the issues related to plastics' end-of-life warns key players, ranged from the authorities to packaging companies, to step in and collaborate to overcome the problem. Recycling is one of the promising solutions which guarantees circularity of the natural resources and is capable to cover almost all polymers. This scenario is not only an absolute necessity to reduce natural resource depletion, but it is also a powerful mean for fighting marine and land pollution. This process is, however, complex considering the challenges associated with recycling of plastic packaging.

Lack of systematic monitoring of the flow of plastics, variations in the quality of materials delivered to recyclers and end-users, very high quantity of plastic wastes being exported to other countries, high disposal rate and lack of regulations to limit landfilling, very complex plastic structures for packaging, and more importantly negative social image and health concerns associated with the incorporating recyclates particularly for food packaging are among the major obstacles in plastic packaging recycling (P. R. Europe, 2018).

On the other hand, positive environmental impacts triggered by circular economy model, enhanced awareness among consumers, governments, and businesses, re-engineering packaging items for recycling and increased use of PCR by brands, improved collection and sorting schemes, developing and implementing of standards and certificates in this field guide the market on the right direction to grow (P. R. Europe, 2018).

This study tries to address different aspects of plastic packaging recycling and inclusion of PCR content in films for food packaging applications. During the research on this subject a series of technical issues appeared which added to the complexity of the system. The first issue was inconsistency in the materials. Due to the fact that the target resin was coming from different HDPE bottles wastes, there seem variations in the system. While the PCR supplier has a controlled source of input materials, the lack of consistency is inescapable when using recycled polymer content coming from different resin grades, contaminations, additives, etc. Besides, since all the results were obtained using lab scale tools, the results were extrapolated to commercial levels. Equipment limits like small size extruders and different screw and die design might cause variations in the system when scaling the project to commercial levels. Furthermore, the best approach to diagnose the nature of the visual defects is FTIR mapping but since the machine was not available during this study relied on other experiments including hot stage, EDX, extraction, and data obtained in different extrusion conditions. FT-IR microscopy can be beneficial in terms of ensuring the source of these defects through identification of the present chemical bond in the defects. We also tried to produce multilayer blown film using twin-screw extruder directly, to compare the samples with the single screw extruder. However, since the right connection and joint was not available for the twin-screw extruder in multilayer blown film line, we assembled the multilayer line using long pipes that increased the residence time up to 30 min. Consequently, the results were not reliable to achieve conclusions due to increased chance of crosslinking.

CHAPTER 6 CONCLUSIONS AND RECOMENDATIONS

Incorporation of the plastics in the packaging applications benefits in both environmental and economic sides, since such materials in packaging demand lower level of energy (renewable and non-renewable energy sources), consume less water during production, emit fewer amounts of green-house gas (GHG), and produce lighter weight solid wastes compared to other alternatives (Perspectives, 2019). However, this sector must be developed in a more sustainable model in which less pressure is applied to the environment for taking the resources and also disposing the wastes of plastic packaging. Recycling is the solution that requires more advancements in different stages to limit the landfilling of incineration of plastic packaging wastes. Even though the market of recycling of the plastic packaging is rising, more advancements are required in different stages of this process including recyclability engineering, sorting and collection, recycling technologies, as well as the promising demand for recycled contents by incorporation of such materials in new applications as a substitute to virgin materials.

Incorporating of post-consumer recycled (PCR) materials is a key to circular model in plastic packaging. However, replacing virgin materials with PCR sacrifices visual properties of the film samples due to the presence of defects. Different characterization techniques including hot-stage microscopy, energy dispersive X-ray (EDX), solvent extraction and dynamic mechanical analysis (DSC) were used to determine the source of the defects in PCR HDPE. It was found that the formation of highly entangled high Mw HDPE is the major source of formation of defects in melt processing of PCR HDPE. Hot stage microscopy results show that these defects have higher melting temperature than HDPE and exhibit high deformation at temperatures above 200 ^{o}C. The effect of processing temperature was studied, and it was found that increasing processing temperature reduced considerably the number of defects. This result can be explained by considering easier deformation and breakup of the defects at high temperatures. The effect of processing with twin-screw extruder was also investigated and it was shown that the dispersive mixing capability of twin-screw extruders are an important tool in reducing the number of defects in PCR HDPE. The effect of combination of twin-screw extruder and single screw-extruder on defects in PCR HDPE was also studied. The results showed that the initial processing with a twin-screw extruder reduced Mw and viscosity of PCR HDPE which led to reducing formation of highly branched HDPE in the single screw extrusion. The effect of the addition of antioxidant was also examined and it was found that the addition of antioxidants is more effective in reducing the number of defects at low processing temperatures.

To further improve the visual properties of the PCR films, using ‘depth filtration’ medium can capture the fiber gels and contaminations. However, using such a filtration is costly (needs to be replaced repeatedly) and reduce the line production capacity. Incorporation of the dispersive elements on the single screw extruder can be helpful to disperse the highly entangled gels in the system. It is of great value to identify and test the Mw of the high Mw highly entangled defects in the system. Furthermore, as a potential approach to eliminate the high Mw gels we can analyse the effectiveness of using high Mw polyethylene in the PCR to bridge the Mw gaps between defects and matrix. Analysing Rheology of the PCR HDPE can also help to optimize the processing condition to reduce the number of defects in our samples. Elimination of the cross-linked gels is achievable through streamlined die and screw design, excluding oxygen from extruder, redesigning screws with minimum stagnant regions (sharp corners of channel), and stabilization of the melt using processing-aid additives. Using simulation, actual temperature in the extruder and the stagnant regions in the extruder can be identified and redesign the imperfections in the extruder.

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APPENDIX A FURTHER RESULTS FROM PCR HDPE PROJECT

In this section, further results from the PCR HDPE project would be presented. It should be noted that the materials and methodologies are provided in the chapter 4 and the added experiments are provided in the experimental section. First, the effect of screen packs on the number of defects will be presented. Then, the combined effect of melt processing at high temperature, twin-screw extruder, and antioxidants on the number of defects in multilayer PCR HDPE films will be provided. Furthermore, effect of incorporation of the PCR HDPE in the multilayer film structure on the mechanical properties of the flexible film samples will be presented. As a key feature of the films, the transparency of the films containing PCR HDPE is evaluated. Afterwards, the influence of the extruder scale will be investigated.

1. Experimental

1.1. Materials

Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate) (Irganox 1010), and octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate (Irganox 1076) are two phenolic antioxidants supplied by Sigma-Aldrich. In addition, Baeropol T-Blend 1102 TX, and Baeropol DRS 6812 SP stabilizers were provided by Baerlocher.

1.2. Extrusion

The effect of screen pack is also investigated using three different opening size which are 60, 120, and 200 US mesh sizes on the multilayer line.

For tracking the effect of the scale of the extruder, single layer polyethylene films comprising of 100% PCR were also prepared using a Killion single screw (screw diameter is 44 mm with a L/D value of 80) connected to an annular film blowing die. A screw speed of 45 rpm was used to prepare these samples. The nip and winding roll speeds were controlled to achieve 75 μm thick films. The higher output of this single screw extruder allows analyzing the effect of scale up on the visual defects in PCR HDPE films.

1.3. Tear resistance

Tear resistance measurements were performed using a tear tester (Pro Tear from Thwing-albert, US) according to ASTM D1922 standard test method.

1.4. Mechanical properties

Mechanical properties of film samples were measured using a tensile machine (Instron 3365) according to ASTM D882 standard test method for tensile properties of plastic films.

1.5. Haze measurements

Transparency of the film samples was evaluated by %haze using LAMBDA 1050 Spectrophotometers (PerkinElmer Inc.) according to ASTM D1003 standard test method for haze and luminous transmittance of transparent plastics.

2. Results

2.1. Effect of screen packs

One of the major solutions to extract the contaminants from the melt during extrusion is to put screen pack at the end of the extruders. To see the effect of the screen packs on the number of defects in the film samples containing PCR HDPE a trial was conducted at high temperature profile 230 250 250 230 ºC. The results of the numbers of defects in the samples point out small improvements only by using very small opening size screens. The results are provided in Figure A.1.

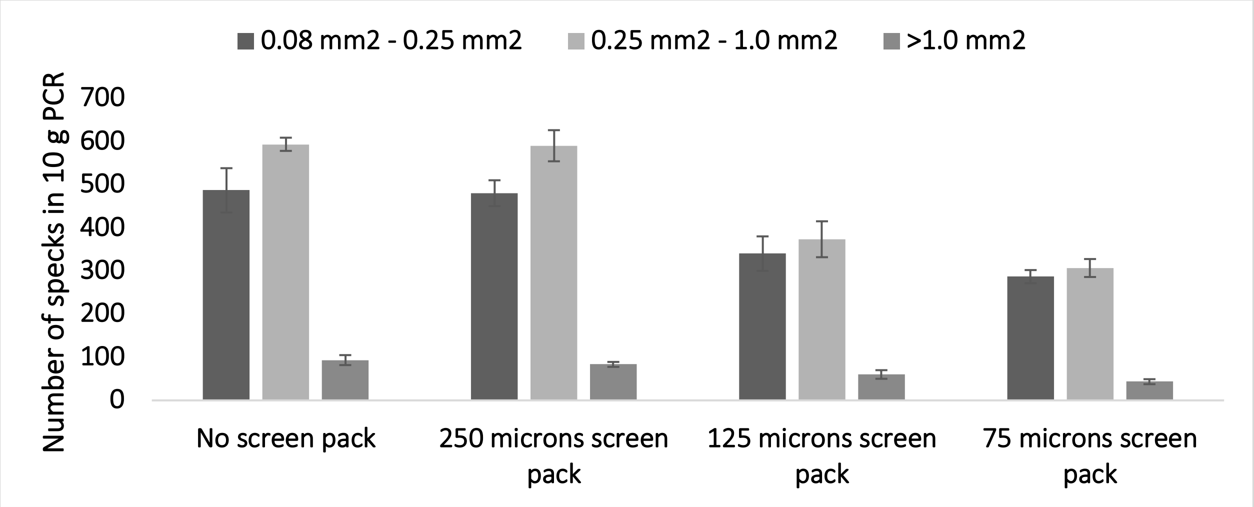


Figure A.1 The effect of screen packs on the number of defects in PCR HDPE film samples

Furthermore, using very fine screens on the extruders rises the pressure in the extruder and also increases the torque on the motor. On the other hand, screens must be changed regularly and for doing so, all the line is shut down to be able to change them. And this could not be economically feasible to shut the line repeatedly.

2.2.Synergic effect of processing temperature, dispersion, and antioxidants

Furthermore, to see synergic effect of processing temperature profile, dispersive tool, and addition of antioxidants in reduction of number of defects, multilayer samples were extruded at low and high temperature profiles without the effect of twin-screw extruder, high temperature profile with the effect of twin-screw extruder, and high temperature profile with effect of twin-screw extruder and effect of addition of four different antioxidants. The results are provided in Figure A.2. which show a synergic effect on the number of gels when incorporating high temperature profile, twin screw extruder, and antioxidants.

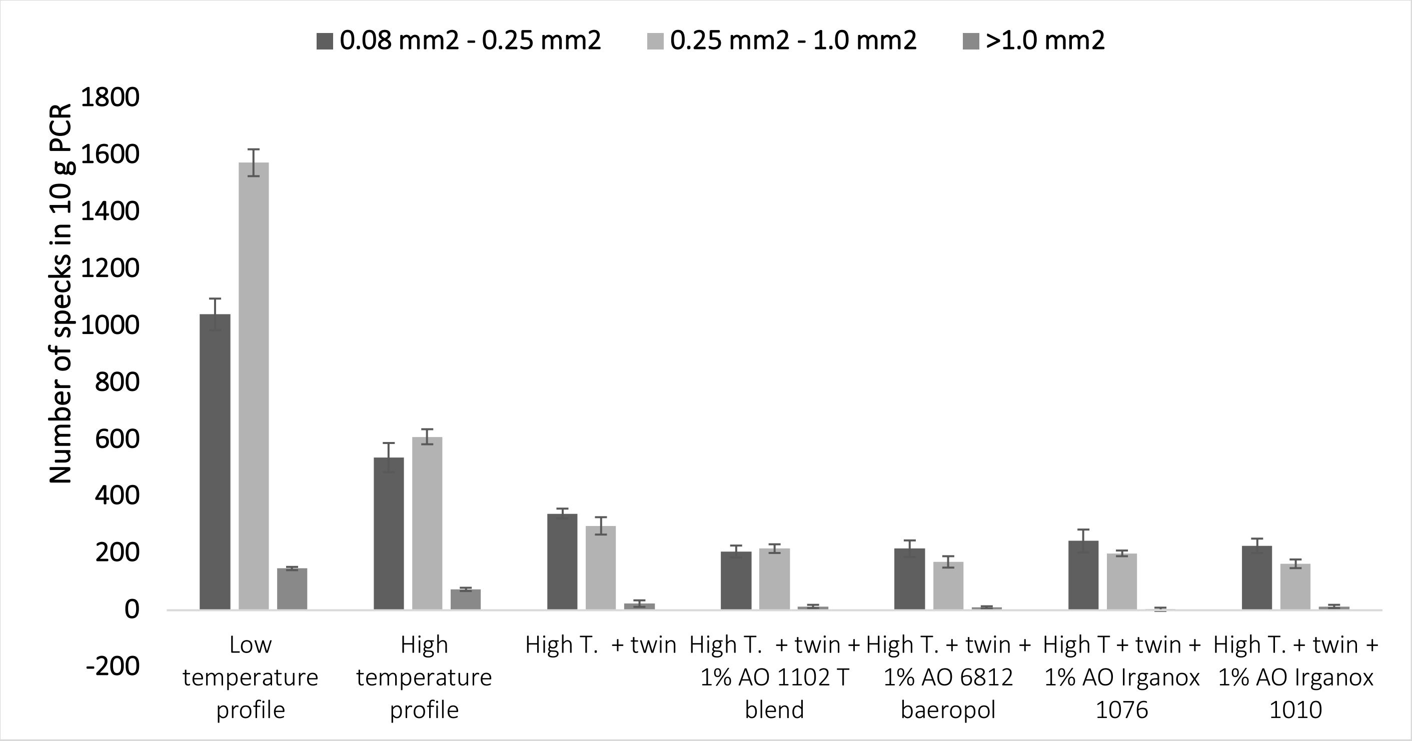


Figure A.2 The synergic effect of high temperature profile, twin screw extruder, and antioxidants on the number of defects in PCR HDPE

2.3. Effect PCR content on Mechanical properties of multilayer films

After discussing about the source of defects and the approaches to reduce their effect on visual appearance of multilayer film samples, it is necessary to examine the effect of PCR HDPE content on mechanical properties of film samples. Tear resistance of multilayer films with different thicknesses of the PCR layer is shown in Figure A.3.

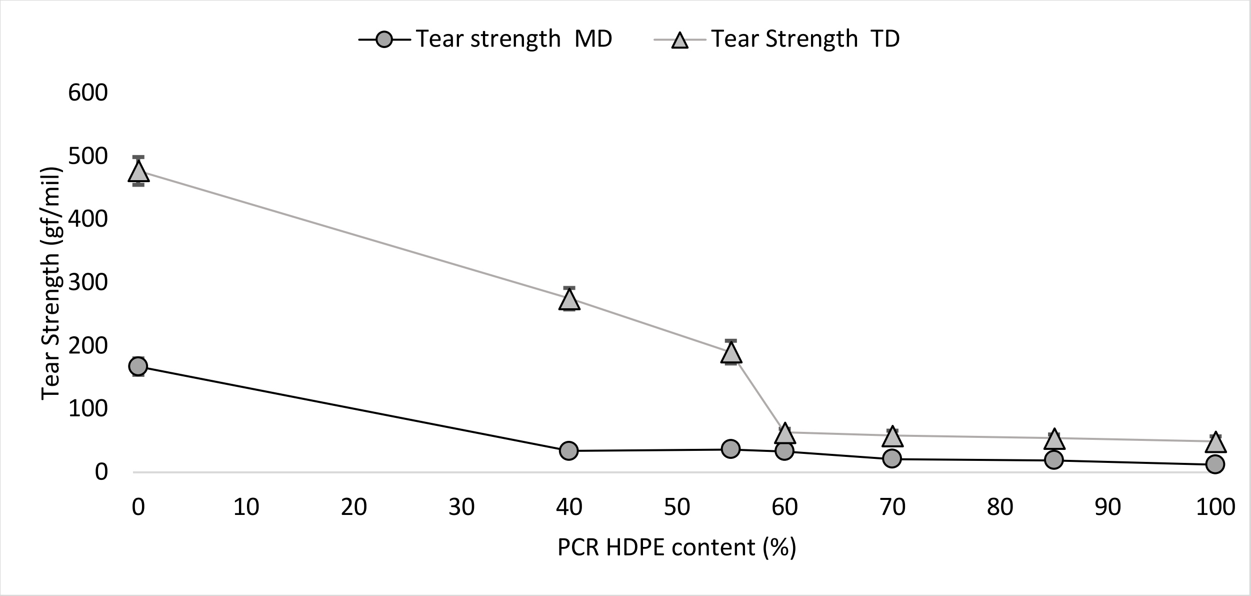


Figure A.3 Tear strength of the PCR films versus the volume % of PCR HDPE in the film samples

The obtained results show a decrease in tear resistance in both machine direction (MD) and transverse direction (TD) of prepared film samples. This can be attributed to the much lower tear resistance of PCR HDPE compare to both LDPE and LLDPE. Interestingly it can be seen that the the tear resistance of samples with PCR content above 60% is very close to the neat PCR which indicates that above 60%, PCR is the controlling component in the structure. It is known that the molecular and lamellar orientation in machine direction (MD) of blown films can result in higher tear resistance in their TD compare to their tear resistance in MD (X. Zhang, Elkoun, Ajji, & Huneault, 2004).

Tensile properties of multilayer films were also examined at different PCR contents and the results are shown in Figure A.4. Increasing the PCR HDPE content in the multilayer structure up to 40% reduced the elongation at break by only 7%, but further increasing the PCR content up to 60%, reduced dramatically the elongation at break by more than 60%.

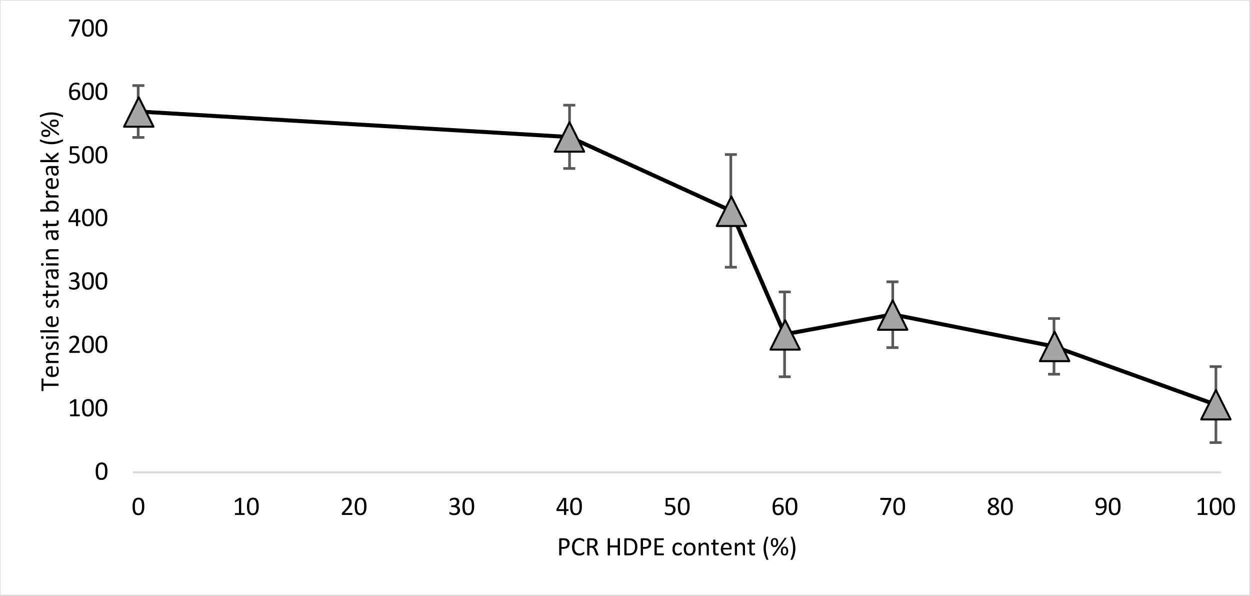


Figure A.4 Tensile strain at break versus the volume % of PCR HDPE in the film samples

The disruption of the mechanical properties by using the PCR HDPE can be seen in both tear resistance and tensile strain. A part of this trend can be due to the negative effect of thermo-mechanical or thermo-oxidative degradation of HDPE and reduction of MW of polymer molecules after multiple reprocessing (Abad et al., 2004). Furthermore, presence of the small gels in the matrix of the PCR compromises the mechanical strength. A microscopic image of these gels is provided in the Figure A.5. Due to the weak interfacial adhesion between the gels and the matrix, by applying force to the structure, the fractures easily propagate through these weak interfaces.

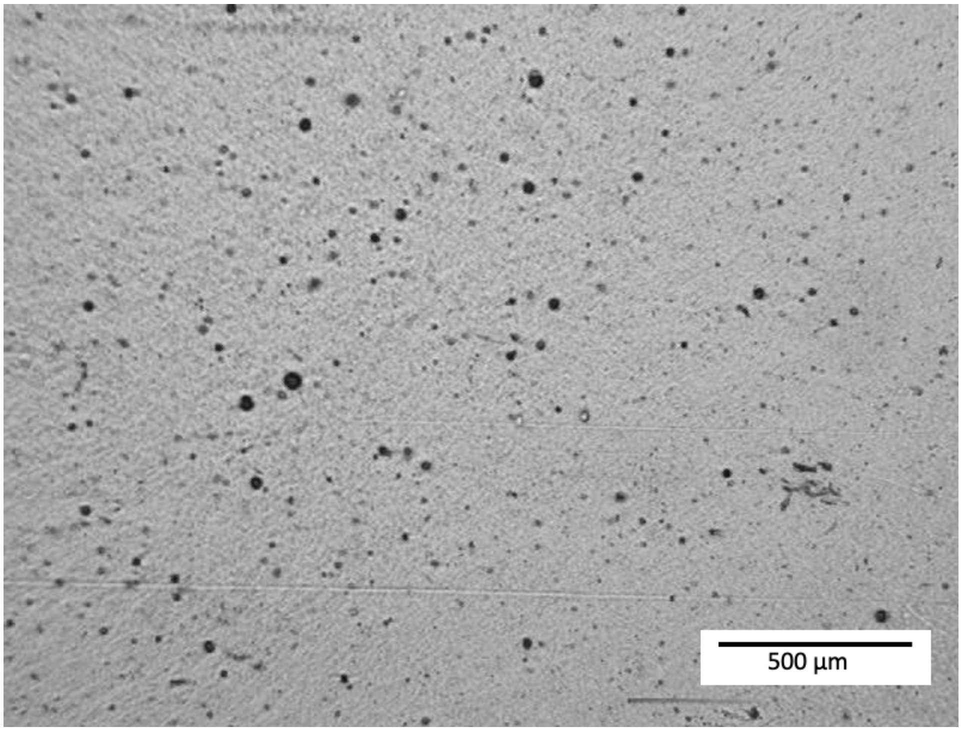


Figure A.5 Optical microscopy image of the small gels in the PCR HDPE films

2.4. Effect of PCR percentage on transparency properties

The transparency of the samples was measured based on the haziness of the PCR films processed at low temperature profile, and the results are provided in Table A.1. According to the results, application of virgin LLDPE/LDPE gives a noticeable transparency to the structure. Increasing the percentage of the PCR layer in the films, reduces the transparency and this can be related to the milky color of the HDPE PCR, yellowing of the HDPE after reprocessing (Berg et al., 2016), as well as the presence of the small gels that prevent the transmitting of the light through the films. Furthermore, there observed a huge difference between the monolayer PCR HDPE films versus the samples with skin layer of LLDPE/LDPE blend due to the fact that the HDPE PCR scatters light waves at the surface while LLDPE/LDPE gives the structure a transparent surface and transmits light through the films. Consequently, this is another reason for using multilayer structure for the PCR films.

Table A.1 Transparency measurements of the PCR films

Film sample	Haze %
0 % PCR	17.1 ± 3.1
40% PCR	19.6 ± 2.1
55% PCR	19.7 ± 1.4
62% PCR	24.1 ± 1.3
72% PCR	25.0 ± 0.8
83% PCR	25.6 ± 1.5
100% PCR	66 ± 1

2.5. Effect of extruder scale on the number of defects

To investigate the effect of extruder scale on the number of defects two monolayer 100% PCR film samples were produced at low temperature profile in lab scale extruder and large-scale extruder (Killion single screw extruder). Comparing the results of the detected number of defects which is provided in Figure A.6. Point out an increase in the number of defects when using a larger-scale extruder. This increase can be attributed to the formation of the crosslinked gels in the large-scale extruders where deeper channels (more stagnant regions) are used to maintain higher production rates.

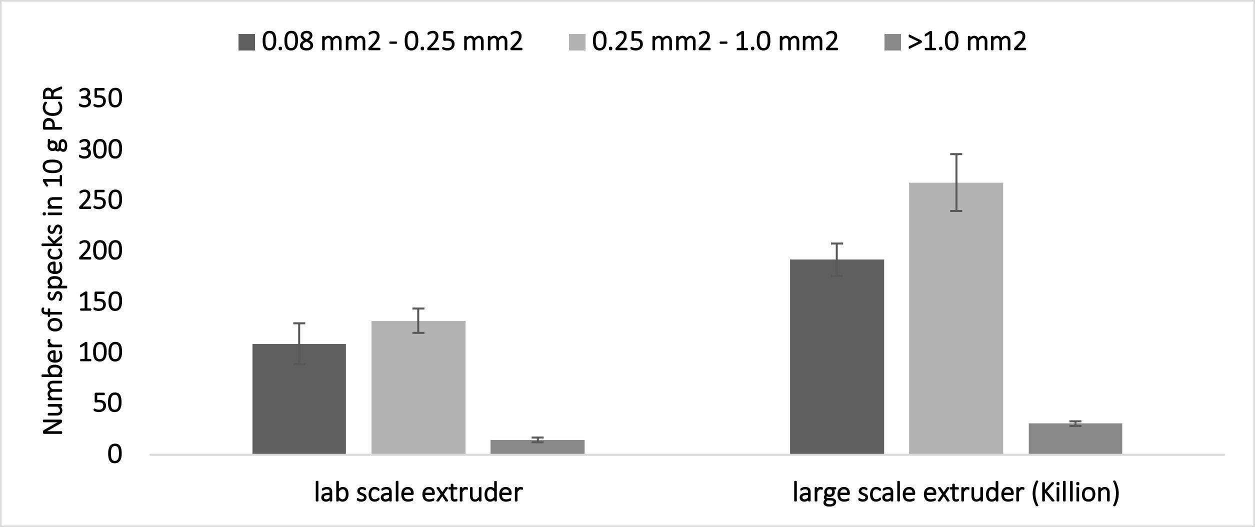


Figure A.6 Number of specks in 100% PCR monolayer films; effect of extruder size

APPENDIX B RECYCLING OF PLASTIC PACKAGING: A ROUTE TOWARDS SUSTAINABLE PACKAGING

With 40% share of the global plastic demand, plastic packaging is currently the major sector in plastic industry. The fact that majority of plastic materials are not biodegradable points out the critical importance of plastic packaging waste treatment and its role in reducing their negative environmental footprint. Despite significant improvements in plastic recycling technologies, recycling of plastic packaging waste, particularly flexible films and multilayer packaging, remains challenging. Intensive energy consumption, high costs and complexity in sorting, cleaning and pre-treatments steps, as well as re-processing issues are amongst the many impediments associated with recycling of plastic packaging wastes. This paper provides a comprehensive review of previous studies conducted to address these challenges and their possible solutions in different recycling steps of plastic packaging waste. First, different end-of-life scenarios of plastic packaging waste including landfilling, recycling, composting and energy recovery will be delineated. Then, it will be discussed why recycling is the most promising approach that complies best with the circular economy and sustainable materials management models in plastic packaging. Pretreatment steps including collection and separation, cleaning, decontamination and size reduction of plastic packaging wastes will be described with the challenges and possible solutions in each step. Furthermore, details of main recycling approaches for plastic packaging waste including chemical, mechanical and chemo-mechanical processes will be reviewed. Regulations and benchmarks for incorporation of recycled plastic packaging waste in new packaging applications, particularly for food packaging applications as the main and most sensitive sector, will be summarized. Finally, future trends and perspective of plastic packaging recycling market will be presented. It will be outlined how the market is taking up the recycling rate and quality through design for recyclability, improved collection and sorting, advancements in recycling technologies, and incorporation of the recyclates into new packaging structures.

Table of contents:

1. Introduction

Polymeric materials are large macromolecule composed of repeated monomer units. They can be produced via polymerization reactions which can be categorized into two main groups of step-growth polymerization and chain polymerization (Brydson, 1999). Plastics are a sub-category of polymers that can have natural or synthetic origin (Piringer & Baner, 2008). They can be categorized based on their thermal behavior into thermoplastics and thermosets materials (Crawford & Martin, 2020; Piringer & Baner, 2008). Thermoplastic materials exhibit tough and viscoelastic properties and melt upon heating. On the other hand, thermosetting plastics have a 3D network of cross-linked molecules which prevents melting and flowing upon heating and results in a highly elastic behavior. Nowadays, plastic materials can be found everywhere, from ordinary plastic shopping bags to highly sophisticated electronic or medical devices. Plastic materials demand per sector and per polymer type is provided in the Figure B.1. Plastic products can be produced through different processing methods such as thermoforming, injection molding, blow molding, or extrusion. In 2018, global plastics production almost reached 360 million tons with a positive trade balance of more than 15 billion euros (PlasticsEurope, 2019b). Although the advantages of plastic materials are unquestionable, they have a very high carbon footprint and are petroleum-based materials (Crawford & Martin, 2020). The service life of plastics can be as short as less than 1 year or as long as 50 years or more depending on their applications. However, the increasing amount of plastic materials used in our daily life caused a growing challenge for the industries for disposing plastic waste with the least environmental impact.

Figure B.1 Plastics demand per sector and per polymer type in 2018 (reprinted with the permission from (PlasticsEurope, 2019b))

1.1. Plastic materials in packaging

Plastic materials have been used in many different applications such as in packaging, building and construction, automotive, agriculture, households, leisure and sports and other fields (PlasticsEurope, 2019b). With about 40% share in plastic demand, packaging is the main sector of plastic materials (PlasticsEurope, 2019b). Plastic packaging is used in food, drug, chemicals, cosmetics, etc. The main purpose of packages is preserving the products with minimal impact on the product and the environment. Amongst different products, the food packaging is very important due to chemical instability of food. Packaging enhances the shelf life of the products and can be effective in reducing food waste (Gaukroger, 2018). Designing packages is done based on different factors such as performance, cost, and environmental considerations (Niaounakis, 2019). Different advantages of the polymers and variation of them outweigh the impediments of incorporation of them in the packaging sector. Packaging industry is unimaginable without plastic materials. The major polymers used in packaging applications this application is low-density polyethylene, linear low-density polyethylene, high density polyethylene, polypropylene, polyethylene terephthalate, and polystyrene. A variety of properties could be achieved by using different polymers such as flexibility and sealability (LLDPE), good film physical strength (LDPE), mechanical strength (PET) or toughness (HDPE, PP), transparent and gloss surfaces (LDPE,LLDPE), barrier properties for increased shelf life of products (EVOH, PA, PVDC). According to the product and requirements, plastic packaging may come in rigid (e.g. plastic containers, trays) or flexible (e.g. films, pouches) forms (Morgan, 2010). Compared to rigid packaging, flexible packaging requires less plastic material and less energy for production (Niaounakis, 2019). However, the complexity of structures, problematic sorting and collection and high residual contamination make flexible packaging more difficult to recycle. This can be clearly seen by considering that the recycling rate of rigid packaging is 40% while only 1% of flexible packaging are recycled (Covenant, 2013).

1.2. End-of-life scenarios for plastic packaging

The significant market of plastic packaging was discussed before, however; most plastics are produced from non-renewable natural resources and have high carbon footprints and GHG emissions (Cross, 2019). In addition, non-biodegradability of common plastic materials makes plastic packaging waste an essential challenge for the environment after their service life (Crawford & Martin, 2020). In addition, Currently, four main scenarios exist for managing plastic packaging wastes: landfilling(disposal), energy recovery, composting and recycling. Figure B.2 shows these scenarios within the waste management hierarchy according to their compatibility to the environment and sustainable use of resources (European-Parliament-Directive, 2008).

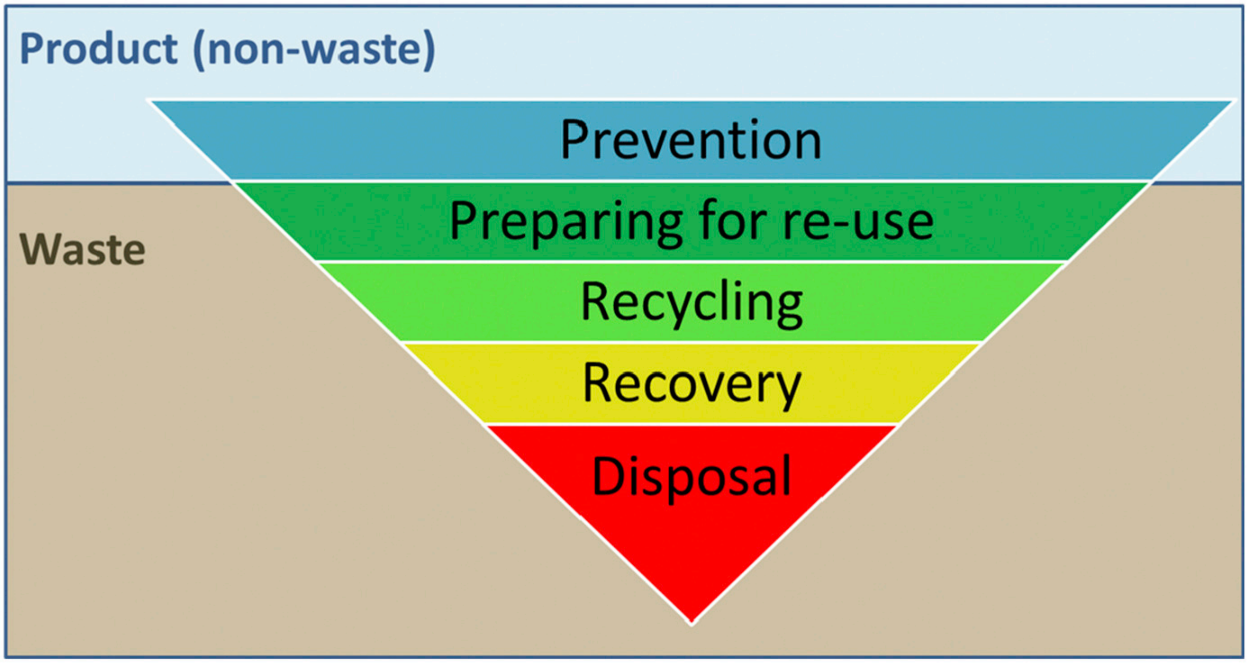


Figure B.2 waste management hierarchy (reprinted with the permission from (European-Parliament-Directive, 2008))

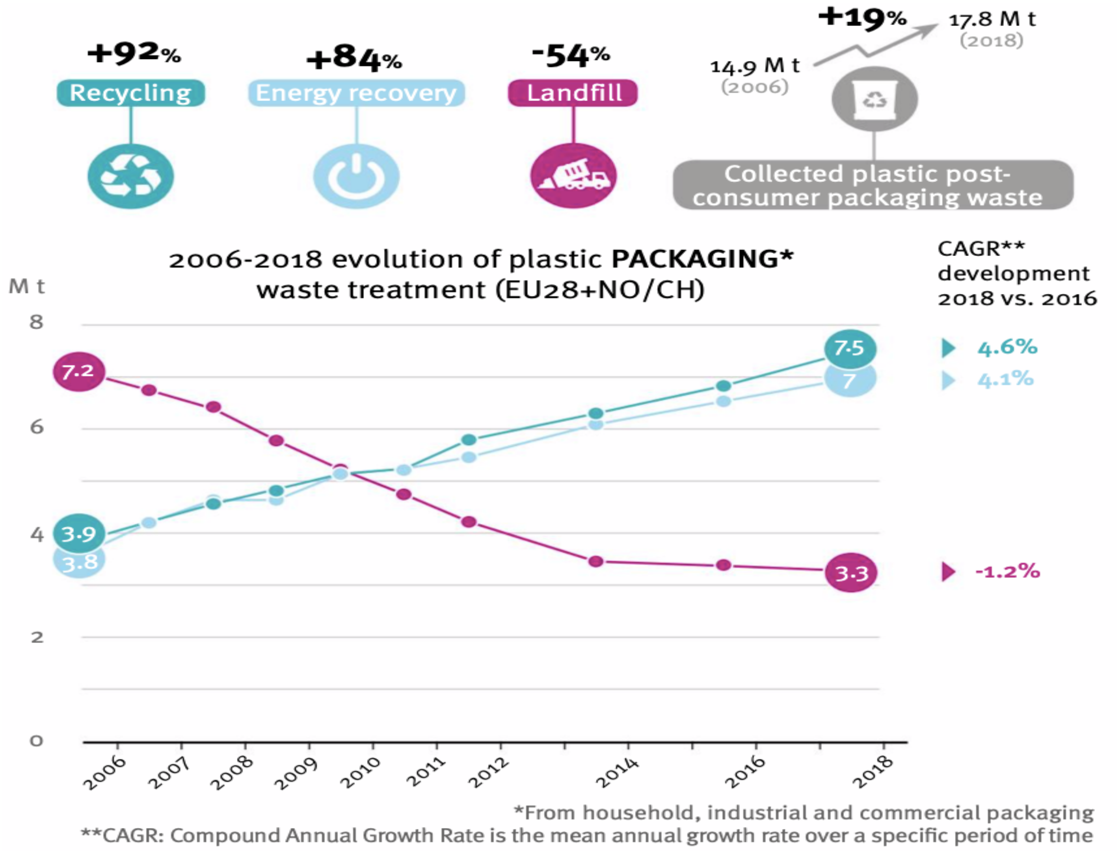
- Landfilling (disposal): It is the worst method with respect to environmental stewardship which should be limited to the materials that cannot be treated by other methods. landfilling may be applied to all types of plastics and it requires relatively low energy for disposal. However, due to very low degradation rate of plastics, they will remain in landfilling sites for hundreds of years which will cause environmental disaster. Materials that are sent to landfill sites are discarded without further benefits leading to high pressure on the natural resources for production of new materials. In 2016, more than 85% of the plastic wastes in Canada were sent to landfilling sites, however, based on the zero plastic waste objective this number needs to be reduced to less than 10% by 2030 (Deloitte, 2019). The same scenario exists in Europe where 25% of plastics are sent to landfilling sites (PlasticsEurope, 2019a).
- Composting: this scenario is limited to biodegradable and compostable polymers. It can be a green approach but many of composting facilities do not accept compostable packaging since there are no standardized operating condition and degradation time for them (Deloitte, 2019) and also the biodegradation condition cannot be achieved in normal environments like soil and sea (Niaounakis, 2019). Another challenge for biodegradable packaging is that

they must degrade quickly in the environment but should keep their performance during shelf life of packaged products (Garcia & Robertson, 2017).

- Energy recovery: This is one of the main recovery options that is widely used. Energy recovery through incineration of plastic wastes is beneficial because of its high calorific value. Even though the incineration of the plastic wastes produces acceptable amount of energy, the energy recovered from this process does not compensate the energy consumption for the plastic productions and also the recovered energy through recycling is approximately double the energy recovered from incineration of plastic wastes (Rahimi & García, 2017). Based on the waste management hierarchy, Fig. 2, incineration should be the last recovery option and must be limited to non-recyclable resins such as thermosets, multilayer structures or mixed plastics (except chlorine components). In addition, the production of hazardous products such as dioxins, furans, and other organic volatiles during incineration process (Deloitte, 2019) leads to authorities' and social oppositions (Barlow & Morgan, 2013).
- Chemical recycling (also known as feedstock recycling): In this process, polymer molecules are broken down and converted to shorter molecules. The molecular conversion occurs through thermal degradation or (partial) depolymerization and the final products of this process are monomers, oligomers, fuels or other valuable chemical components which can be entered to the production process of plastic raw materials. The quality of the final products produced in this scenario is comparable to the virgin materials. However, some limitations such as energy intensive and low efficiency of this process prohibit application of this approach in industrial scale and chemical recycling is as a complementary method to mechanical recycling. This process is referred as chemo-mechanical process and will be discussed in section 2.4 of this paper (Deloitte, 2019).
- Mechanical recycling (also known as closed loop or primary recycling): Through mechanical recycling, molecular structure of plastics is preserved and using melt processing the materials enters the conversion step. The mechanical and visual quality of the mechanically recycled plastics is the biggest challenge in this method, however, the inexpensive and relatively easy-to-follow steps during this method, make it the best recycling option specially for the packaging industry (Deloitte, 2019; PlasticsEurope, 2019a).

There is a wide gap between the energy intensity of the virgin materials and the recycled materials which translates into reduced carbon footprint for the plastic recyclates. Incorporation of PCR materials into new plastic packaging, therefore, reduces carbon intensity, carbon emissions and increases the amount of plastic materials returned to the processing cycle (P. Europe, 2017).

Development of new applications for recycled materials is critical to meet the ambitious targets of recycling such as Zero Waste target in EU. Considering the fact that food packaging is the largest sector in plastic packaging, incorporation of the recycled materials in food packaging is a promising approach but requires significant precautions due to the strict regulations for materials used in food contact articles (P. Europe, 2017). Figure B.3 illustrates the evolution of plastic packaging waste treatment between 2006 to 2018 in Europe in different scenarios of landfilling, energy recovery and recycling. It can be seen that plastic recycling industry moved toward reducing landfilled wastes (reduced 52%) and increasing recycling rates (increased 92%). In some cases, the industry may not be able to recycle the materials (like complex packaging structures or highly contaminated items) in which they must select the best option using some measures such as Life Cycle Assessment (LCA). LCA is a technique to ensure a more enlightened decision through a better understanding of the environmental and social impact of the products, process, and activity via their effects on air, water, land and energy consumption (EDA, 2018).



*From household, industrial and commercial packaging

**CAGR: Compound Annual Growth Rate is the mean annual growth rate over a specific period of time

Figure B.3 Evolution of plastic packaging waste management in Europe (reprinted with the permission from (PlasticsEurope, 2019b))

1.3. Circular economy concept and sustainability models in plastic packaging:

Circular economy is the opposite of the linear economy, which is based on take, make, and dispose steps. Circular economy is extracting maximum value of the resources during the service life of products, and regenerate and recover the products and materials at the end of their service life. Linear economy, however, applies pressure on the natural resources and environment for extracting raw and virgin materials leading to progressive waste production and increased environmental impacts. Consequently, the traditional methods based on linear economy need be replaced by methods based on circulation of the materials back in the processing/consumption chain (PlasticsEurope, 2019a).

The significance of circularity in packaging industry is evident where the amount of packaging waste is growing continuously and in 2017 packaging waste in Europe raised to a value of 173 kg per inhabitant (Commission, 2020). The European Union (EU), as well as policy makers and companies, aim to reduce or eliminate the amount of plastic packaging waste sent to landfills. For example, Kraft Heinz announced that it aims to make all of its packaging recyclable, reusable or compostable by 2025 (Rebecca Briedis, 2019). The American Chemistry Council's (ACC) Plastics Division announced targets of fully recyclable or recoverable plastic packaging by 2030 and 100% of plastic packaging to be reused, recycled or recovered by 2040 (ACC, 2018). In 2016, the Plastic Industry Trade Association announced the Zero Net Waste (ZNW) program in EU, which recognizes plastic companies who participate to reduce net waste in manufacturing and reducing raw materials and energy consumption (P. I. T. Association, 2016). In 2015, the EU published an action plan for transitioning to a circular economy (Europian Commission, 2015). The main development in circular economy for plastic packaging happened in 2018, when EU revealed its strategy on plastics as part of its transition towards a more circular economy. The "European Strategy for Plastics in a Circular Economy" (Plastics Strategy) (Commission, 2018) calls for all plastic packaging on the EU market to be either reusable or recyclable in a cost-effective manner by 2030. Certain steps need to be taken to fulfill these targeted goals including, but not limited to, more integrated supply chain, replacement or elimination of substances that hamper recycling processes, the development of innovative materials and alternative feedstocks for plastic production, reduction of the consumption of single-use plastics and reducing the complexity of packaging materials, including the number of materials and polymers used (Commission, 2020; Misko, 2019). The EC identifies four action steps for achieving a circular economy for plastics:

- Improve the quantity and quality of plastics recycling.
- Curb plastic waste and littering.
- Drive innovation and investment towards circular solutions.
- Harness global action.

For the flexible packaging which are of challenging wastes the Circular Economy for Flexible Packaging (CEFLEX) predicted that by 2025 there will be an established collection, sorting, and recycling infrastructure for flexible packaging in Europe to deliver the best economic, environmental, and technical benefits of the Circular Economy (CEFLEX, 2018). The flowchart of a circular model for plastic packaging waste recycling and management is provided in Figure B.4.

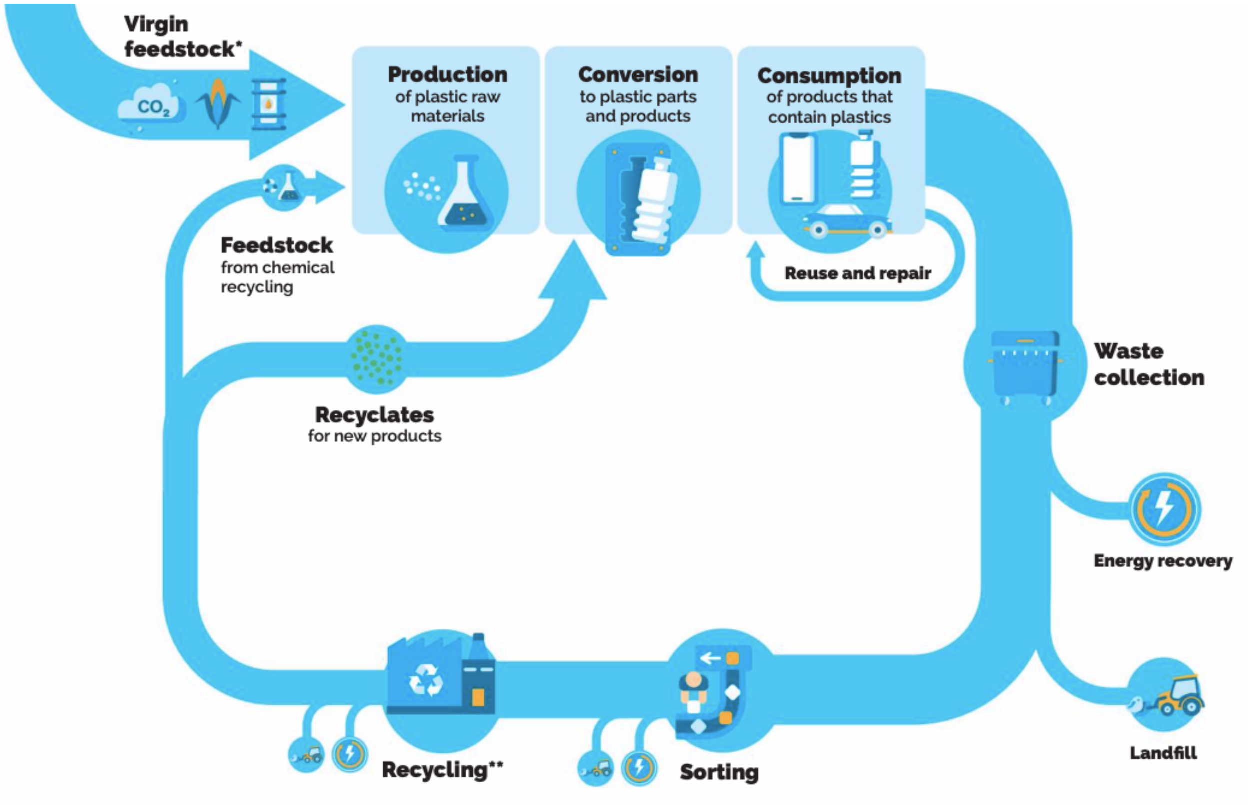


Figure B.4 Circular model for plastic packaging waste recycling and waste treatment (reprinted with the permission from (PlasticsEurope, 2019a))

Furthermore, Sustainable Materials Management (SMM), defined by Organization for Economic Cooperation and Development (OECD), is a systemic model for using and reusing materials efficiently (with the least negative environmental impact) within their life cycles. According to this approach, the consumption of natural resources and environmental protection are revised through examining how materials are used with the objectives of (EDA, 2018):

- Productive material using with an emphasis on using less.
- Reduction of toxic chemicals and environmental impacts throughout the material life cycle.
- Assurance of sufficient resources to address the present and future demand.

The U.S. EPA has announced its SMM strategic priority for 2017 to 2022 in the areas of sustainable food management and packaging with the goals as (EDA, 2015):

- Decrease the disposal rate, which includes source reduction, reuse, recycling and prevention;
- Reduce the environmental impacts of materials across their life cycle;
- Increase socio-economic benefits; and
- Increase the capacity of state and local governments, communities and key stakeholders to adopt and implement SMM policies, practices and incentives.

2. Recycling technologies

2.1. Plastic packaging waste collection and sorting

2.1.1. Collection and Separation

The first step in recycling is collecting the plastic packaging wastes for recycling purposes. Low efficiency of the collection step leads to the loss of materials and energy which will not comply with circular model. So, the collector must ensure all recyclable items are collected and sent to Material Recovery Facilities (MRFs). There are mainly two main types of plastic packaging wastes: post-consumer recycled (PCR) and post-industrial recycled (PIR) materials. PCR materials are those recovered after being used by the consumer and are the main source of the plastic packaging wastes which usually contain more contaminations and impurities. On the other hand, PIR materials are the ones reclaimed from manufacturing (scraps, trims, edges, etc.) sites and since they have not been in the consumption market, they have a low level of contamination and impurities. Two routes for collection of the plastic packaging wastes for recycling purposes are curbside collection by local authorities and store drop-off points at groceries. Compare to rigid packaging, flexible packaging and polymer films are usually considered as contaminants and rejected by MRFs since they are lighter, more contaminated by residual organics and also more complex (multilayers, metalized components.) to recycle (Horodytska et al., 2018). Incentive retail return system or separate collecting of the multilayers and films are two common methods to prevent the loss of materials in the flexible packaging waste stream (F. P. Association, 2014). However, the curbside collection offers a bigger capacity of collection for recycling than the retail return programs ((ACC). 2016). The quality of sorting and more importantly the recycling performance is highly controlled by the collection schemes and establishments since it directly impacts the level of contamination found in the waste stream entering the sorting centers and later the recycling facilities. In the system where packaging wastes are mixed with other wastes, the recycling performance as well as the cost of the process is very high since the organic wastes, food residues or other materials, contaminate the recyclable items. In contrast, using separated schemes not only reduce the costs, but it also elaborates the application of the recycled materials even for the food packaging (PRE, 2019b).

Collected plastic wastes are then separated through different stages in MRFs. The main idea in this step is to receive commingled plastics and separate them based on the type of polymers to send them to the recycling sites. There are different sorting methods for separation of target components. Aside from the manual separation, the main components are:

- Screen and trommel are employed to group the items based on their size and dimensions. Screens are usually equipped with shaker for better performance.
- Magnetic separator consists of a magnetic conveyor to remove the ferrous materials from the waste stream.
- Eddy current separator is used to separate the non-ferrous metals like aluminum. In this stage the sensor uses a powerful magnetic field and detects the non-ferrous items to be extracted from the stream.
- Ballistic separator is used to separate flexible flat items (e.g. films, pouches) from bulky rigid items (e.g. bottles, containers). It consists of an inclined set of oscillatory paddles. Each paddle is 60 to 120 degrees out of phase from the adjacent paddle. The agitation results in bulkier rigid items to roll down and collected while lighter flexible items move upward and collected from the top. The paddles usually have a meshed surface which results in finer waste such as glass pieces to drop and collected using a converter under the ballistic

separator. Star screens are also an alternative for separation of the flexible films and bulkier 3D items.

- Air separator is an alternative (or complementary) to the ballistic separator to separate the lightweight materials using air (the 2D items are conveyed in the air stream and the heavier items remains in the wastes) (RRS, 2017).
- Optical near IR (NIR) separator is usually the last stage for sorting in the waste separation process. This technology is based on detection of the reflected waves of materials and by comparing the wavelengths with its library, the separator would be able to understand the type of the polymers from the absorbed wavelengths by material.

The flexible packaging and films usually are discarded and mainly sent to landfilling sites. However, there are enhancements to limit loss of such items like Material Recovery For Future (MRFF) project. MRFF is established to employ different technologies to sort loose and flexible films using state-of-the-art equipment like advanced optical sorters (RRS, 2015). The sorted items then would be compacted to have a lower volume for the ease of transportation and will be sent in the bales to the recycling sites.

2.1.2. Size reduction

The first step in a recycling plant is reducing the size of sorted and separated materials. Size reduction is beneficial for enhancing the surface to volume ratio to improve the cleaning as well as chemical or mechanical processes. Size reduction is done by shredders or/and by grinders (granulator). Shredders work at low speed and high torque which allows bales of sorted materials to be fed entirely into the shredders to reduce the size of the wastes into pieces of hand size (about 1 to 5 in)(Niaounakis, 2019). Flexible packaging and films are the items more problematic to the shredders since they stick (or melted by the heat for rotating shafts) and roll around the blades and shafts. In addition, the stretching nature of most flexible packaging make them difficult to cut by shredder. This caused rejection of flexible packaging waste by recyclers. There are some advancements in shredding technologies to increase the recycling rate of the flexible structures such as water-cooling shaft and rotor, specialized rotor and blade design, etc (Technology, 2015).

For further reduce the size, the output of the shredders is fed into grinders which, unlike shredders, work at high speed and low torque. A sizing screen is installed to control the dimensions and uniformity of the flakes (commonly controlled between 6 to 12 mm).

2.1.3. Cleaning and decontamination

Cleaning plastic packaging wastes is the most critical stage in recycling pre-treatment. |The major source of plastic packaging waste is food packaging which is more contaminated by organic residues and volatiles. Furthermore, inks, labels and adhesives are other components to be eliminated in plastic packaging wastes.

Water cleaning is the common washing step in the waste recycling. Using water cleaning the shredded plastics, food residues, organic contaminants, dust and dirt, pulps and papers will be eliminated. To have a more efficient washing, friction washer and hot water can be employed. Treatment of the generated wastewater in this step is also a costly step that should be managed in cleaning facilities (Ontario, 2013). The water cleaning method usually begins with friction washer/dryer and then the particles are fed into a hot water tank for agitation and removing labels and glue. Finally, a press conveyer mechanically squeezes the plastics and hot air dryer ensures the moisture content below 2-3 wt.%. For cleaner mono-material plastic wastes, dry cleaning can be used where the plastic particles are subjected to high speed stress from rotating paddles in a confided space. There is no need for water or solvents in such cleaning and depending on the waste stream, the efficiency of this method can be up to 90% (WRAP, 2019).

Cleaning can also be via solutions including solvents or aqueous surfactants to remove inks and impurities. Selection of the chemical solvents is conducted based on the composition of the waste stream and also the required quality of the final products. To enhance the performance of the cleaning agents, their boiling temperature should be lower than the melting temperature of the polymers to avoid sticking the flakes to each other and also preventing embedding of the printing ink particles into the polymers. Cleaning solvents are mostly acetic acid esters (low melting temperature) and alcohols. As solvent residue remains on the surface and diffuses into the wastes after this stage, further steps are needed remove them, otherwise the quality of the recycled product will be disrupted (Niaounakis, 2019).

2.2. Chemical recycling

Chemical recycling is defined as depolymerization and decomposition of polymers into their monomers or in the case of partial depolymerization to their oligomers or other shorter molecules and subsequent production of polymers or other useable chemical substances (e.g. fuels) (Achilias & Karayannidis, 2004; Deloitte, 2019). This method of recycling usually consists of dissolution or/and polymerization (Deloitte, 2019). Decomposition of plastic wastes into raw monomers reduces the need for natural resources like fossil-based resources for production of polymers (Achilias & Karayannidis, 2004). Creating feedstock to produce new materials via chemical recycling complies with the circular economy. Final products of chemical recycling process must follow the regulations of virgin polymers for new food packaging applications to prevent hazardous components in the materials which may impose health or environmental risks (UN-Environment-Programme, 2018).

2.2.1. Solvolysis

During this process, a solvent is added to plastic wastes to break down the target polymer waste into monomers and/or oligomers which are used as feedstock for making new polymers, so the quality of the final product is comparable to the virgin resin. The solvents can be regenerated and filtered for new process. Solvolysis process is mostly applicable to Polyethylene terneplate and polyamide. The manufacturing cost of this method, however, is higher than the virgin materials. Chemical recycling of polymers is conducted through glycolysis, hydrolysis, alcoholysis or other methods such as aminolysis and ammonolysis (Achilias & Karayannidis, 2004; Paszun & Spychaj, 1997; Scheirs, 1998). Glycolysis can be conducted by introducing ethylene glycol (or diethylene or propylene glycol) to PET wastes at high temperatures. The resulting oligomers or other substrates such as bis-hydroxyethyl terephthalate (BHET) can be used in the synthesis of new PET materials(Bartolome, Imran, Cho, Al-Masry, & Kim, 2012; Shukla & Harad, 2005). Figure B.5 shows the reactions involved in the solvolysis of PET with ethylene glycol.

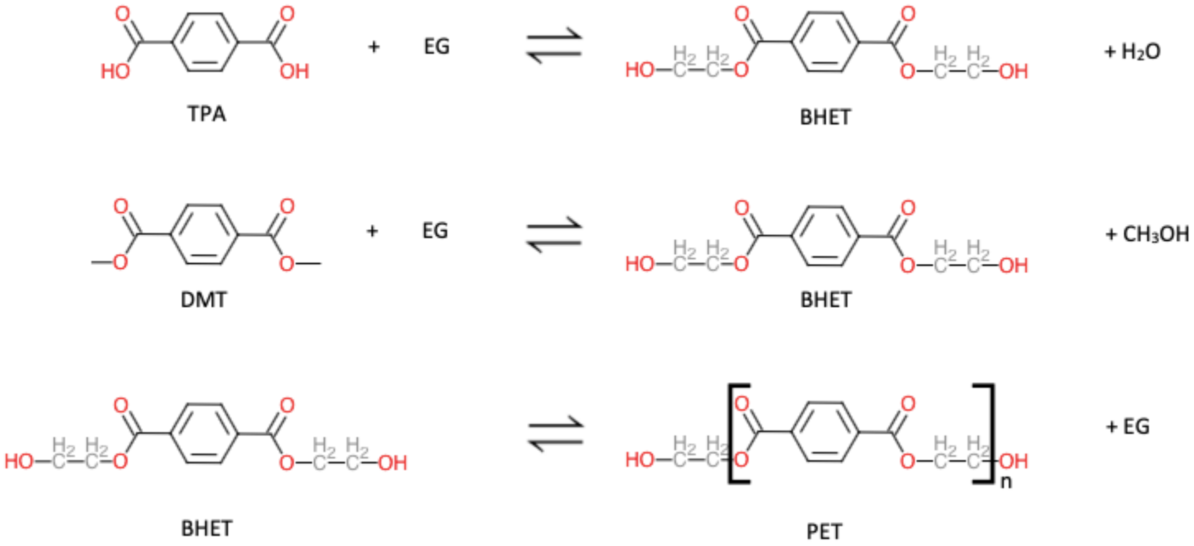


Figure B.5 Reaction scheme for PET synthesis, formation of BHET through reaction of EG with TPA or DMT and then polymerization to PET (Bartolome et al., 2012).

To accelerate the depolymerization process and increase its efficacy, metal salts (like zinc catalysts), or organocatalysts (like Triazabicyclodecene TBD) are introduced to the process (Fukushima et al., 2011; Fukushima et al., 2013). Glycolysis needs a high temperature (about 200 °c) for a couple of hours. High temperature, catalysts contamination, and recovering of catalysts make this approach more costly (Achilias & Karayannidis, 2004; Bisio & Xanthos, 1995). Similar studies have also been conducted to recycle PET-based wastes using glycolysis to produce useful chemicals like alkyl resins (Kawamura, Ito, Nishida, Yoshihara, & Numa, 2002; Suh, Park, & Yoon, 2000). In addition, new technologies like supercritical glycolysis (to eliminate the need for catalysts) (Imran, Kim, Han, & Cho, 2010) or microwave-assisted glycolysis (to increase the heating rate and reduce the time of the process) (Chaudhary, Surekha, Kumar, Rajagopal, & Roy, 2013; Cho, Hong, & Choi, 2013; Pingale & Shukla, 2008) have been introduced.

Degradation of PET at high temperature and pressure using methanol is another Solvolysis method which is called alcoholysis (methanolysis) (Scheirs, 1998). During this process dimethyl terephthalate (DMT), which is an intermediate material for PET production, is produced and purified by distillation, which removes all physical contaminants and can be reused as a raw material for the production of PET (Achilias & Karayannidis, 2004). Alcoholysis requires high pressure and temperature (180 – 280 °c and 2 – 4 MPa) (Scheirs, 1998) which is a drawback of this method. The process is also sensitive to moisture that can poison the catalysts and form different azeotropes (Achilias & Karayannidis, 2004). It is worth mentioning that industries prefer terephthalic acid (TPA) than DMT for production of PET and hydrolyze of the DMT to produce TPA which adds a new step to the recycling process and increases the cost (Achilias & Karayannidis, 2004).

PET recycling using hydrolysis can be done using acid, alkaline or neutral hydrolysis. Acid hydrolysis can be performed using nitric acid, sulfuric acid or phosphoric acid (Achilias & Karayannidis, 2004). A high pressure and temperature is usually needed for acid hydrolysis but lower pressure can also be used at high concentration of acids (Pusztaszeri, 1982). The high temperature and pressure or the need for highly concentrated acid makes acid hydrolysis costly. In order to recover the acid after hydrolysis, Yoshioka et al. proposed dialysis of the acid as an acid recovery method, but it imposes longer process time and higher temperature (Yoshioka, Motoki, & Okuwaki, 2001; Yoshioka, Okayama, & Okuwaki, 1998). The product of the acid hydrolysis can be either TPA or ethylene glycol (EG) and using oxidation of EG the process can produce oxalic acid as a valuable material used in ink industry (Al-Sabagh et al., 2016; Krehula, Hrnjak-Murgić, Jelenčić, & Andričić, 2009; Matsumoto et al., 2014).

Alkaline hydrolysis is usually performed in aqueous alkaline solution of NaOH or KOH to produce TPA (Al-Sabagh et al., 2016; Karayannidis, Chatziavgoustis, & Achilias, 2002; Kosmidis, Achilias, & Karayannidis, 2001). Non-aqueous alkaline hydrolysis has also been investigated in 1997(Oku, Hu, & Yamada, 1997). This method tolerates highly contaminated post-consumer PET like X-ray film or metalized PET (Scheirs, 1998). However, like other methods it requires high temperature and pressure.

Neutral hydrolysis is another chemical recycling method of PET which uses water or steam instead of alkaline or acidic solvent (Mandoki, 1986; Scheirs, 1998). One of the emerging technologies in this field is the incorporation of enzymes for depolymerization of plastic wastes. In 2020, a group of researchers developed an engineered enzyme to enhance the depolymerization conversion of PET bottles up to 90% in 10 h which can be a game changing step in chemical recycling of PET. The enzyme concentration in this study was 3 mg/ g of PET and the monomers resulted from this process were again repolymerized to be used in PET bottles (Tournier et al., 2020). The up-scaling feasibility of this process was also reported and showed a promising step to closing the PET bottles' loop. In the case of aminolysis (Shukla & Harad, 2006) and ammonolysis (Shafer, 1990) the recycling process would be conducted using amine or ammonia aqueous solutions, respectively and catalysts (metal salts) are added to enhance the efficiency of these processes (Fukushima et al., 2013).

Similar study was conducted to see the potential of solvolysis for polyolefins. The target polymer wastes were LDPE, HDPE and PP coming from different waste sources including packaging films, plastic bags, food bag, bottles, etc. Xylene and Toluene were used as the solvents and n-hexane was selected as non-solvent for the precipitation stage. The main parameters affecting this process were found to be the concentration of polymers in the solvent and the temperature. It was observed that increasing the concentration of polymers decreased the amount of recycled polymer and increasing temperature increased the amount of recycled polymer. Using Xylene and n-hexane, more than 98.2% of polymers could be recycled at polymer concentration of 5% wt./v and temperature of 140 °c. The final solid products were examined, and the FT-IR patterns were found to be the same as the virgin resins. The mechanical properties were also comparable to the virgin materials (even better since some lower molecular weight fractions remained in the solvent/non-solvent phase) (Achilias, Roupakias, Megalokonomos, Lappas, & Antonakou, 2007).

Chemical solvolysis for multilayer structures is usually conducted through selective dissolution and precipitation (SDP) process. In this approach, a target polymer in the multilayer structure is dissolved using a selective solvent and then recovered through either precipitation (by the addition a proper antisolvent) or rapid solvent evaporation (Battle, Moore, Nauman, & Lynch, 1992; Pappa et al., 2001). In this method the target polymer can be either at the outer layer or from the inner layers. The routine procedure of this method is to select the best solvent that can selectively dissolve the target polymer in the shredded multilayer films. Shredding increases the surface area and facilitate the dissolution process. Different solvents for a wide range of polymers have been tested by Nauman et al. in 1994 in a US patent (Nauman & Lynch, 1994). For example, for a multilayer film of PP/PP-g-MA/EVOH/ PP-g-MA/PP, they observed that xylene could dissolve PP at 110 °C after 80 min. and the tie layer was dissolved at 125 °C after 120 min. They also found that the EVOH layer, was dissolved by N-Methyl pyrrolidone (NMP) as the solvent at 83 °C after 120 min.

they also studied multilayer structure of nylon-6/tie/EVOH/EVA/ionomer in which for the tie layer they used THF as the solvent, and for EVA and ionomer they used Toluene. NMP was again used for the EVOH layer and for the Nylon-6 layer, a mixture of NMP and LiCl was selected at optimized temperature and exposure time (Nauman & Lynch, 1994).

In 2003, Maurer et al. (Maurer et al., 2003) also introduced a method based on the selective dissolution and precipitation from materials containing mixed polymers (ABS, PVC, PET, etc.). Separation and recovery of target polymers have been done by different solvents such as THF, acetone, alcohols, etc. (Maurer et al., 2003).

In a similar study in 2006 by Mauldin et al. (Mauldin & Cook, 2006) recovery of the polyamide from post-consumer or post-industrial wastes which were mainly polyolefins (polypropylene) was studied using ester solvent at high temperature. The resulted solution will be a two immiscible liquid phase which contains dissolved polyamide and liquid polyolefin phase. These two phases, then, can be separated in further steps and precipitated (Mauldin & Cook, 2006).

In addition, Pappa et al. investigated the recyclability of the PP/LDPE using SDP method with xylene and n-propanol as solvent and antisolvent. They also studied the up-scale potential of mixed polymer recycling based on this approach and proposed a semi-batch process for recycling of mixed polymer wastes which is provided in Figure B.6 (Pappa et al., 2001).

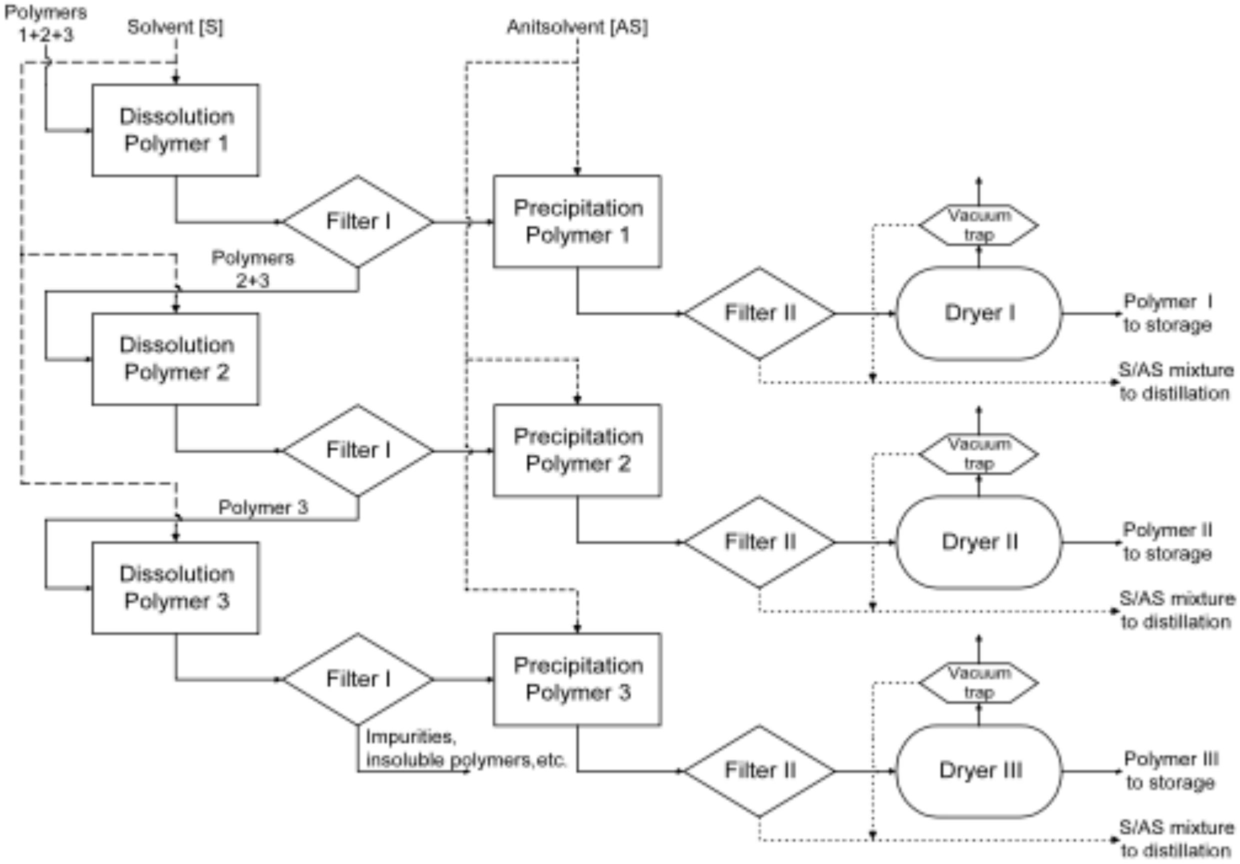


Figure B.6 Flow diagram of a high capacity unit for SDP chemical recycling (reprinted with the permission from (Pappa et al., 2001))

Similar studies have been conducted for different polymer wastes such as PP pipes (Poulakis & Papaspyrides, 1997), rigid PVC bottles (Kampouris, Diakoulaki, & Papaspyrides, 1986), PS wastes (Kampouris, Papaspyrides, & Lekakou, 1987, 1988), LDPE films (Papaspyrides, Poulakis, & Varelides, 1994), and HDPE bottles (Poulakis & Papaspyrides, 1995).

However, this method cannot meet the current recycling market due to the fact that the process of dissolution and precipitation needs expensive solvents and specified temperature. Furthermore, in this method, dissolution of the interlayer is problematic due to very limited exposure to the solvent. Consequently, this approach cannot be a good candidate for recycling of the multilayer films.

2.2.2. Pyrolysis

Pyrolysis by definition is the process in which heating is applied to the target material in absence of oxygen to break down the complex molecules into simpler or shorter molecules. Pyrolysis can be categorized into the chemical recycling only if the recovered materials in this process are used for production of the plastics, otherwise it is a recovery option and should be avoided as much as possible (should be limited to non-recyclable plastic packaging waste streams). This process is conducted at high temperature or/and high pressure. Molecular chains of polymers are attracted to each other via Van der Waals forces and by increasing the temperature in the structure the chains' vibrations will increase and the molecules tend to evaporate and break the intermolecular attractions. However, due to the fact that the Van der Waals force in polymers is higher than the enthalpy of the C-C bonds, the vibration leads to the broken chains and results in shorter and simpler molecules (Sobko, 2008). The main products of this process are liquid products, gaseous products and chars; however, the main substance is the liquid conversion (Sharuddin, Abnisa, Daud, & Aroua, 2016). Pyrolysis requires high temperature/pressure which can be costly for the industry and to enhance the quality and production of the final results, the process needs other modifications like addition of catalysts and catalyst regeneration (Ragaert, Delva, & Van Geem, 2017). In the products, also, there are toxic components and hazardous materials such as carbon monoxide CO, hydrogen cyanide HCN, hydrogen chloride, benzene, and other unsaturated hydrocarbons which can cause corrosion to the facilities. So, to remove these components the process needs posttreatments which can increase the cost and energy (Paabo & Levin, 1987; Yu, Sun, Ma, Qiao, & Yao, 2016). Key parameters in this process that are supposed to be considered and optimized to have higher value products include the temperature, the pressure, heating rate, residence time, reactor type and shape, catalyst, type and rate of fluidizing gas (in the case of fluidized bed reactor) (Sharuddin et al., 2016).

The extracted oil has many applications like boilers, furnaces, turbines, diesel engines even without pretreatments or enhancements (Bridgwater, 2012). The gaseous products have also good thermal values which can compensate the energy requirement for the pyrolysis plant (Abnisa & Daud, 2014) or they can be used in turbines for electricity generation or direct firing in boilers (Fernández Díez, Arenillas de la Puente, & Menéndez Díaz, 2011). In addition, produced char can be used as absorbent in water treatments for heavy metal removal (Sharuddin et al., 2016), solid fuels in boilers, and feedstock in production of activated carbon (Fernández Díez et al., 2011).

PET is one the major plastic components in both rigid and flexible packaging. The pyrolysis of the PET was investigated in different studies. Cepeliogullar et al. studied the potential of pyrolysis of PET wastes in a fixed bed reactor at 500 °c with a heating rate of 10 °c/min. They concluded that the major product of this process in the gaseous products (Çepelioğullar & Pütün, 2013). The liquid oil, however, contained benzoic acid at a high concentration which is not favorable for the quality of the liquid oil. Benzoic acid is a corrosive substance which can damage the pipes and metal facilities. This fact may limit the application of the extracted substances.

High density polyethylene is one of the major polymers in both rigid and flexible packaging due to its high mechanical strength (HDPE has low branching and very high crystallinity) (Sharuddin et al., 2016). Pyrolysis recycling of the HDPE has been studied in different studies because of the high liquid oil fraction which can be obtained out of this process. Ahmad et al. studied this process in a fixed bed reaction with nitrogen gas at temperature between 300 to 400 °c and they could extract up to 80.08 wt.% liquid oil (Ahmad et al., 2015). Similar results were obtained in other publications using semi-batch (S. Kumar & Singh, 2011) and batch reactor (Marcilla, Beltrán, & Navarro, 2009) at higher temperatures. The Hydrocarbon liquid product of this process has very good thermal value comparable to the calorimetric value of the gasoline and diesel (Boundy & Davis, 2010; S. Kumar & Singh, 2011).

Low density polyethylene is one of the major polyolefins that are widely used in polymer packaging due to high branching molecular structure and good processability for molding and blown film (Sharuddin et al., 2016). LDPE pyrolysis has been investigated in different studies using fixed bed reactor (Bagri & Williams, 2002), batch reactor (Aguado, Serrano, San Miguel, Castro, & Madrid, 2007; Marcilla et al., 2009; Uddin, Koizumi, Murata, & Sakata, 1997), and pressurized batch reactor (Onwudili, Insura, & Williams, 2009). Based on the selected process parameters like temperature, heating rate, pressure, and type of reactor they have obtained different hydrocarbon liquid between 74.7 to 95% and make LDPE resin waste a good candidate for the pyrolysis recycling.

Poly propylene has a linear molecular chain structure with a high melting point around 160 °c which make it a suitable resin for a variety of applications such as rigid packaging. Ahmad et al. investigated the potetial of pyrolysis in a micro steel reactor at temperature between 250 to 400 °c And the liquid oil conversion in this process was around 70 wt.% (Ahmad et al., 2015). Sakata et al. Also conducted the similar test and the liquid oil extraction was reported up to 80 wt.% (Sakata, Uddin, & Muto, 1999). Similar results (82% liquid oil conversion) have been published for the pyrolysis process at 500 °c (FakhrHoseini & Dastanian, 2013). However Extreme pyrolysis temperature would reduce the oil conversion and enhance the gaseous products (Demirbas, 2004).

Unlike solvolysis, pyrolysis does not require intense sorting and pretreatment. Several studies have investigated the potential of mixed component pyrolysis which can be applied for the multilayer structures as well. Kaminsky et al. studied recycling of waste mixture (75 wt.% PP and PE, 25wt.% PS and less than 1 wt.% PVC) using fluidized bed reactor at 730 °c, which resulted in 48.4 wt.% liquid conversion which contained chlorine contents comming from PVC resins (Kaminsky, Schlesselmann, & Simon, 1996). The similar results were repeated for the same waste mixture with 46.6 wt.% liquid conversion and 35 wt.% gaseous yields (Demirbas, 2004). Donaj et al. investigated the potential of thermal pyrolysis of mixed polyolefin wastes (46 wt.% wt. of low-density polyethylene (LDPE), 30 wt.% of high-density polyethylene (HDPE) and 24 wt.% of polypropylene (PP)) and applicability of the Ziegler–Natta (Z–N): TiCl4/MgCl2 for cracking the mixture of polyolefins in fluidized quartz-bed reactor. The conversion of gaseous products, liquid oil and solid residues were obtained 36.9 / 48.4 / 15.7 wt.% and 42.4 / 44.7 / 13.9 wt.% at 650 and 730 °c without catalysts and in catalytic process 6.5 / 89.0 / 4.5 wt.% and 54.3 / 41.9 / 3.8 wt.% at 500 and 650 °c, respectively. They also concluded that using catalytic pyrolysis at 650 °c, the monomer generation increased by 55% (Donaj, Kaminsky, Buzeto, & Yang, 2012).

2.2.3. Other methods

The pyrolysis can be modified to enhance the quality of the liquid hydrocarbons or facilitate the reaction method. of the modifications is hydrocracking in which by increasing the hydrogen concentration during thermal decomposition, the quality of the product would be enhanced through enhancing the H/C ratio and reducing aromatic contents(Ding, Liang, & Anderson, 1997).

Gasification is another well-known recycling method which is similar to pyrolysis except that in this process a limited amount of oxygen is introduced to the reaction and the final product would be mostly gaseous which is known as syngas (Puig-Arnavat, Bruno, & Coronas, 2010). The partial oxidation can be happened via pure oxygen, oxidation agents or only air (Trippe, Fröhling, Schultmann, Stahl, & Henrich, 2011)and the main products are CO, CO_2, H_2, CH_4, or other light hydrocarbons(Heidenreich & Foscolo, 2015; A. Kumar, Jones, & Hanna, 2009; Ruiz, Juárez, Morales, Muñoz, & Mendívil, 2013). The process does not need pretreatments, however the presence of impurities (NO_x, H_2S, NH_3) or hazardous components (dioxin) in the products needs complex posttreatments(Dudyński, van Dyk, Kwiatkowski, & Sosnowska, 2015; Munasinghe & Khanal, 2010; Spath & Dayton, 2003; Wilhelm, Simbeck, Karp, & Dickenson, 2001).

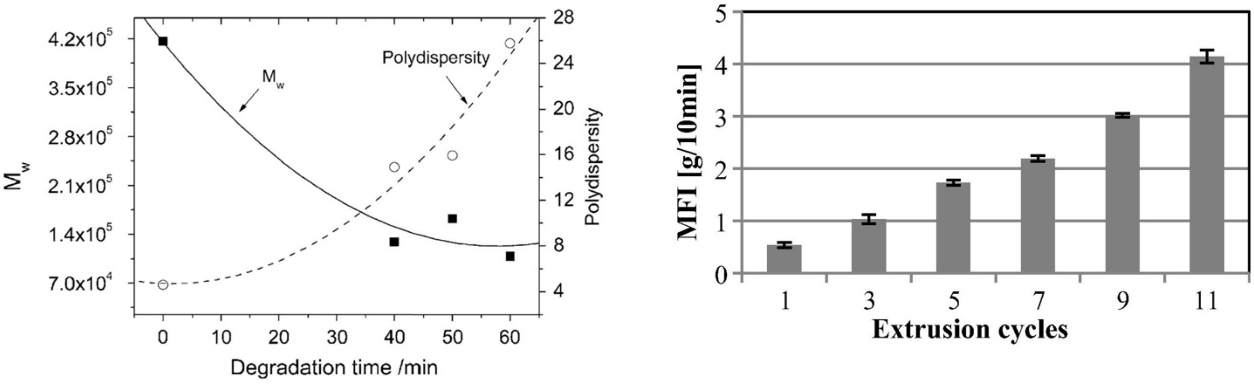
2.3. Mechanical recycling

The other recycling approach is the re-extrusion of the shredded plastic packaging wastes and use the recycled materials in a new multi or mono layer structure again and again. During mechanical recycling of the resins, the polymer chains are served and by melting the clean flakes and extrusion, a new life will be given to the polymers and since the polymers can keep their properties for a long time, the potential for multiple service life is noticeable (Jin et al., 2012). This method is gaining interest in the industry of packaging even in the food packaging applications. The reason behind this interest is that this method is very feasible in compared to previous methods. While this method does not require very expensive and complex pretreatments or solvents, delamination or dissolution methods need harder processing conditions as it was mentioned before. In addition to its simplicity and low capital costs, very limited environmental impact and high capacity for huge amount of polymer packaging wastes are other advantages of this method (Al-Sabagh et al., 2016). However, the challenges of this method are the disruption of the appearance and mechanical strength of the final recycled products compared to virgin materials.

Materials that are commonly recycled using this approach are categorized into post-consumer and pre-consumer wastes. Post-consumer material is generated by households or by commercial, industrial and institutional facilities in their role as end users of the product. Based on ISO 14021, pre-consumer materials should be separately classified since their contamination level is very lower than the post-consumer items (UN-Environment-Programme, 2018). Plastic packaging has the biggest share in the collected plastic wastes in the Europe (61%), however, the application of the post-consumer recycled (PCR) materials in plastic packaging is 24% among other sectors (Facts, 2019). In 2018, 17.8 million tons of post-consumer plastic packaging wastes were collected to be treated (PlasticsEurope, 2019b). Ellen MacArthur as an major initiative in plastic packaging circularity, points out their aims for using PCR in plastic packaging will lead to 5 million tons recycled content by 2025 which is equivalent to save 25 million barrels of oil and reduce 8 million tons of emissions annually (i.e. 1.7 million cars permanently off the road)(UN-Environment-Programme, 2018).

2.3.1. Single component waste

Multiple extrusion and exposure to heat increase the chance of thermal or mechanical degradation of the materials and chain scission due to moisture or acidic contaminations in wastes lead to reduction of the melt viscosity which is due to the reduction of molecular weight of the samples (Achilias & Karayannidis, 2004). Figure B.7 provides the changes in molecular weight, MFI, and mechanical strength due to the reprocessing of the materials. This also may lead to yellowish color due to oxidation reactions or crosslinking (Al-Sabagh et al., 2016). Presence of different components (like contaminations, adhesives, and inks) may enhance the chance of crosslinking or nucleation in the samples. Although the costumers accept a part of the mentioned weaknesses to help the environment, there are ways to enhance the recycled plastic properties and limit these effects. One idea is to use these recycled polymers in a multilayer structure with a low thickness (around 25% of the whole film thickness) to compensate the weaknesses with other virgin layers. Further ways are to limit these effects by adding some chemical additives (antioxidants, compatibilizers, chain extenders (Scheirs, 1998), etc.) or by optimizing the processing conditions. Polyolefins are major resins in packaging industry ranged from LDPE and HDPE to PP. Mechanical recyclability of this polymers has been studied in different Investigations. Jin et al. Observed that the melt flow index of the LDPE changes during multiple reprocessing (Jin et al., 2012), which can be due to the crosslinking reaction during recycling process by reactive carbon radicals (Kabdi & Belhaneche-Bensemra, 2008; Waldman & De Paoli, 1998). However the results showed these changes are slight and Even after 5 extrusion cycles the material shows processing stability (Kartalis et al., 2000). PP recycling, also, was studied in multiple publications. Reprocessing of this resin results in higher crystallization rate and higher crystallinity (Aurrekoetxea et al., 2001), lower melt viscosity and higher MFI due to thermal degradation of the polymer (Bahlouli et al., 2012; Gao et al., 2003; Liang & Peng, 2009; Tri Phuong et al., 2008; Yang et al., 2009), and the rigidity of the PP resins was observed to be stable after reprocessing due to good stabilization (Bourmaud & Baley, 2009). Polyethylene is more vulnerable to oxidation in mechanical recycling since the C-H group at tertiary carbon center would react with oxygen more easily. Consequently, the disruption of the mechanical properties of the PP is more noticeable after re-extrusion compared to polyethylene (Rahimi & García, 2017). Another component that is widely used in the packaging industry is PET polymer. Badia et al. investigated the reprocessing PET resin and the effect of that on the mechanical properties as well as the melt flow index and oxidation temperature (Badia et al., 2009). PET polymers are very sensitive to moisture that the presence of that can change the crystallinity and nucleation rate of the recycled wastes and consequently the mechanical strength of the final sample (Avila & Duarte, 2003), however, the mechanical properties of the mechanical recycled PET resins drop slightly and it made mechanical recycling a good approach for PET wastes (Frounchi, 1999). Mechanical recycling of polystyrene leads to decreasing melt viscosity and mechanical properties due to the decrease of the molecular weight after multiple processing (Remili et al., 2011).



a b

Figure B.7 Molecular weight and polydispersity evolution of a PP sample (reprinted with the permission from (Qian et al., 2011)), (b) MFI evolution of a multiple reprocessed PP sample (reprinted with the permission from (Delva et al., 2014))

2.3.2. Multi component waste

In packaging industry specially in food packaging, multilayer structures are designed to enhance the packaging quality. It should be taken into account that mechanical recycling of these multicomponent polymer wastes is challenging due to the immiscibility of the polymers in each layer. Since the separation of the layers is very hard and costly and also the majority of polymers are immiscible and blends of them can deteriorate the properties. The minor polymer components form small phases in the matrix and this phenomenon either can be seen by naked eye (D= 100-400 microns) as the defects or can be problematic through week mechanical properties due to very week interface of the phases.

In a thermodynamically point of view, to have a miscible polymer system, the Gibbs free energy of mixing $\Delta G_{\mathrm{mixing}}$ should be negative or zero (N. Liu & Baker, 1992; Manias & Utracki, 2014) and based on the Gibbs-Helmholtz equation:

$$\Delta G_{\mathrm{mixing}} = \Delta H_{\mathrm{mixing}} - T \cdot \Delta S_{\mathrm{mixing}}$$

And due to the fact that polymers have high molecular weight, the effect of the changing in entropy is negligible. So, to have a miscible polymer system, the enthalpy of mixing should be negative or the mixing should be exothermic (Feldman, 2005). More to the point, to have a complete miscible polymer system, the second derivative of G in respect to volume fraction, should be positive.

$$\partial^2 G / \partial^2 \phi > 0$$

The basic theory of calculation of Gibbs free energy was introduced by Flory and Huggins (Flory, 1942) as:

$$\Delta G_{\mathrm{mixing}} = \kappa T N\{ \chi_{12} \phi_1 \phi_2 + \phi_1 \ln(\phi_1) + \phi_2 \ln(\phi_2)\}$$

Where κ is the Boltzmann constant, N is the mole fraction, T is the absolute temperature, ϕ_i is the volume fraction of component i and χ_{12} is the Flory-Huggins interaction parameter, which has to be negative to have a miscible mixing. The exact calculations of this parameter is complicated and is dependent to temperature, pressure, concentration, and type of polymer (Manias & Utracki, 2014). The compatibility of a polymer blend is a function of the polymers' chemical affinity and special interactions such as hydrogen bond, ionic bond, ion-dipole, dipole-dipole, etc. (Koning et al., 1998).

The morphology of the blends plays the major role in the characteristics of the final polymer packaging. In the blending of immiscible polymers, the minor component forms a separate phase or domain within the major matrix (for example in a typical multilayer structure of barrier film PE/tie/PA/tie/PE, the minor phase would be the polyamide in the polyethylene matrix). The morphology (domain size and shape) is influenced by chemical interactions (compatibility), rheology and flow deformation (shear or elongational flow) (Dupont, 2014).

Using interfacial agents (compatibilizers), the polymer mixture’s chemical affinity can be enhanced. Compatibilizers can improve poor properties of recycled plastics caused by lack of compatibility between immiscible polymers. By having a stronger interface, the mechanical properties of the recycled layer would be enhanced. Interfacial agents also can be effective in the case of the size reduction of the dispersed phase which can prevent the agglomeration of the phase and gel formation (Ajji & Utracki, 1996; Utracki, 2002; Xanthos, 1988).

Compatibilizers come in different types including copolymers, grafted polymers, nanoparticles, Ionomer, etc. (Maris et al., 2018). Table B.1 provides most popular polymer systems in plastic packaging which have been compatibilized with different compatibilizers.

Table B.1 Compatibilizers for popular plastic packaging polymer systems

Polymer systems	**Compatibilizers**	**References**
PET / LDPE	E-GMA, E-BA-GMA, EVA	(Akkapeddi, Van Buskirk, Mason, Chung, & Swamikannu, 1995; Kaci, Benhamida, Cimmino, Silvestre, &

		Carfagna, 2005; Tawab, Ibrahim, & Magida, 2013)
PET / HDPE	E-GMA, SEBS-g-MA, HDPE-g-MA, SEBS	(Akkapeddi et al., 1995; Chen, Ab Ghani, Salleh, Ahmad, & Gan, 2014; Lei, Wu, Clemons, & Guo, 2009; Pawlak, Morawiec, Pazzagli, Pracella, & Galeski, 2002; Pluta, Bartczak, Pawlak, Galeski, & Pracella, 2001; Salleh, Ahmad, Ghani, & Chen, 2013; Taghavi, Shahrajabian, & Hosseini, 2018)
PET / LLDPE	SEBS-g-MA, SEBS	(Y. Liu, Xu, Liu, & Pu, 2017; H. Zhang, Guo, Yu, Li, & Wu, 2007; Y. Zhang, Guo, Zhang, & Wu, 2009)

PET / PP	E-GMA, E-MA-GMA, PP-g-GMA, PP-g-MA	(Baccouch, Mbarek, & Jaziri, 2017; Barhoumi, Jaziri, Massardier, & Cassagnau, 2008; Tao & Mai, 2007; Zhidan et al., 2011)
PET / PA	POE-g-GMA	(Lin et al., 2014)
PA / PE	PE-g-MA, PE-g-GMA	(Araujo, Vallim, Spinacé, & De Paoli, 2008; Dasdemir, Maze, Anantharamaiah, & Pourdeyhimi, 2015)
PA / PP	PP-g-MA, SEBS-g-MA	(Hong, Hwang, Choi, & Choi, 2006; Kim, Hwang, Cho, & Hong, 2007)
PP / PE	PE-g-MA, PP-g-MA, EPDM, EVA	(Al-Mulla & Shaban, 2014; A. Atiqah, Salmah, Firuz, & Lan, 2014; A. M.

		Atiqah, Salmah, Firuz, & Lan, 2015; Fang et al., 2013; Kazemi, Ramezani Kakroodi, & Rodrigue, 2015)
PP / PS	SEBS, EVA, SBS	(Halimatudahliana & Nasir, 2002; Hlavata et al., 2001; Santana & Manrich, 2003)
PE / PS	EP-g-MA	(Chouiref & Belhaneche-Bensemra, 2012)
PE / PET / PP / PA	E-GMA, SEBS-g-MA	(Correnti et al., 2005)
PE / PET / PP / PS	E-GMA	(Imamura et al., 2014)
PP / PET / HDPE / PVC	EP-g-MA, SEBS-g-MA	(Xanthos et al., 1994)

Choudhury et al. studied the waste oil pouches with the structure of PE/tie/PA/tie/PE. This structure gives perfect barrier properties (by polyamide as barrier layer) and very good mechanical (elongation at break) and sealing properties. Their film structure composed of 85% of polyethylene

(LLDPE and LDPE) and 15% of Nylon-6. The results showed that the melt flow index of the non-compatibilized reprocessed samples decreased due to the reactions which increases the molecular weight of the chains. They have used the effect of two compatibilizers as Surlyn ionomer and PE-g-MAH. It was obtained that in the FTIR pattern the Surlyn was more successful in terms compatibilization with a more intense amide banding. The reaction between Surlyn and polyamide showed that in this reaction the bonds between the end group of the polyamide and ionomer are very strong (Hydrogen bonding and ion-dipole interaction). In the compatibilization reaction between polyamide and PE-g-MAH, it was observed that this reaction also produces water during the processing. So, to increase the compatibilization rate, moisture should be removed in the system. For this purpose, they have installed a ventilating equipment on the extruder to remove the moisture (Choudhury et al., 2006a).

In this study the performance of the ionomer as interfacial agent was better than the PE-g-MAH which should be due to better compatibility of the PE segment of the ionomer with LLDPE/LDPE, Strong polar affinity of the carboxyl group of the ionomer and terminal group of the Nylone-6, and also the production of the moisture in the case of PE-g-MAH. The morphology of the recycled stream was also studied and in the compatibilized systems the PA particle size were lowered resulting in more uniform and stable morphology and better mechanical properties (Choudhury et al., 2006a).

In 2015, Uehara et al. has conducted a study on the recyclability of the multilayer films containing PET and HDPE based on the blending method. They have selected two compatibilizers as PE-g-MAH with 1 wt.% reactive agents and E-GMA copolymer with 8 wt.% reactive agents. Epoxy group of the E-GMA can undergo reactions with both carboxyl and hydroxyl end groups of the PET. The high reactivity of the E-GMA makes it possible to have parallel reactions and crosslinking which could reduce the mechanical properties. Possible crosslinking as mentioned before, caused an increase in the viscosity of the polymer chains (Uehara et al., 2015).

As a crucial parameter in the packaging, they have also measured the mechanical properties of the recycled polymer stream. The Izod impact strength using two compatibilizer showed that the impact strength of both compatibilizers are approximately identical. It is also worth mentioning that E-GMA is highly reactive in compared to PE-g-MAH. So, we can conclude that PE-g-MAH showed a better performance in compatibilization of the samples.

As another indication of effectiveness of the compatibilization, they studied the elongation at break. The elongation at break for the samples containing higher percentages of the PET could be better enhanced using E-GMA. This is due to the fact that at higher concentrations of the PET, reactions with E-GMA leads to chain extensions and PET macromolecules and entanglement happens which can increase the elongation strength. At lower PET concentrations, however, the PE-g-MAH performed better due to high polyethylene content in the compatibilizer in compared to the E-GMA (Uehara et al., 2015).

In this study, they also investigated the post-industrial recycled oil pouches. The film structure contained 70% HDPE, 10% PET, 10% Nylon and 10% ink and adhesive. Compatibilization process has been examined by E-GMA and PE-g-MAH in this study. Based on this study, the reaction rate of the MAH and polyamide terminal groups was obtained higher than GMA (Becker et al., 2008). The Mechanical properties of the compatibilized and non-compatibilized recycled films revealed a sudden rise from 5% to 10% of the case compatibilized with PE-g-MAH which is due to the fact that the reaction rate of the MAH with PA is higher compared to the PET (Macosko et al., 2005). So, the modifiers first saturate the PA/PE interface and then attack the PET/PE interface. This saturation concentration occurs around 3 to 5 % of PE-g-MAH.

In this case the effectiveness of the PE-g-GMA was better than the E-GMA. It can be due to the possible crosslinking of the PET molecules with OH when using E-GMA modifiers (Uehara et al., 2015).

Unfortunately, the morphology images were not mentioned in this study as a major parameter. Furthermore, the film contained ink and adhesive which may lead to crosslinking or formation of gels in the recycled samples, however, the author did not mention any information regarding that.

As it was discussed in the introduction, one of the main polymers in barrier films is EVOH. So, the recycling of the structures containing this polymer is gaining interests over and over. This is no surprise that giant packaging companies are working on the recycling of the barrier films with a huge market behind. Dow is one of that companies which has selected the compatibilization method for recycling due to the advantages that this method has over other method mentioned before. They patented self-recyclable barrier packaging in flexible, semi-flexible, and rigid applications. The polar polymer barrier components that they have studied were Nylon6, Nylon6-6, Nylon6/66, and EVOH. The idea is to blend recycle compatibilizer, Retain 3000, into the outer

PE layer. The post-industrial film trims with this structure will be shredded into flakes (and optionally pelletized) and can be either employed in a new mono-multilayer film structure or simultaneously added to the same structure in blown or cast film. The ratio of the compatibilizer in the film to the EVOH was 1:1 (Parkinson et al., 2019).

The recycled films with this structure showed improved mechanical properties in compared to the samples without compatibilizer in the structure. Furthermore, the visual appearance of the samples was better with lower number and size of gels (Parkinson et al., 2019).

In 2000, Wyser et al. investigated the recycling of a multilayer packaging material consisting of PP–PET–SiOx by using a maleic acid-grafted polypropylene compatibilizer. This study was also conducted based on the blending of multilayer components together. The morphology of the system without and with different percentages of compatibilizers are provided in Figure B.8. It is clear that without any modifier in the system, the separated PET phase is coarse with a weak adhesion. However, by adding more than 10% PET in the system, the interface are saturated and the size of the particles are considerably finer (Wyser, Leterrier, & Månson, 2000).

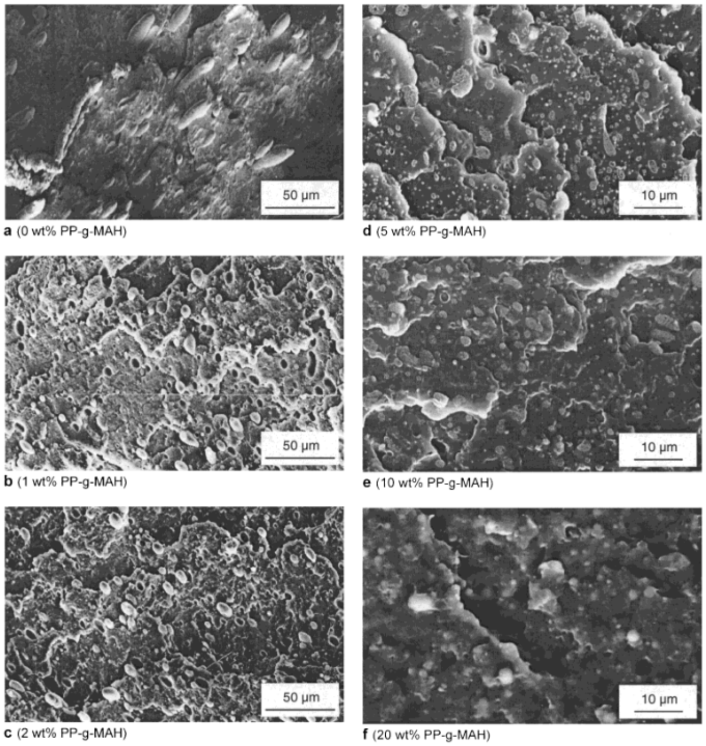


Figure B.8 Morphology of the recycled PP/PET blend (reprinted with the permission from (Wyser et al., 2000))

As it can be seen in the morphology images, in the blends containing more than 10% modifiers, the interface around the PET particles would be very thick. This fact would not only be costly for the study to add more compatibilizers, but also can reduce the mechanical properties of the sample due to the agglomeration of the compatibilizers on the surface which can be easily break at the interface by applying force. The mechanical properties versus concentration of the interfacial agents are provided in Figure B.9. The results also prove the mentioned phenomena. The mechanical properties like elongation at rupture and tensile strength drops after 10% PP-g-MAH (Wyser et al., 2000).

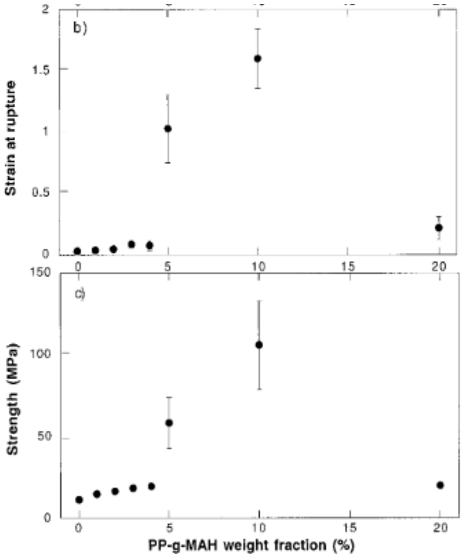


Figure B.9 Mechanical properties of the recycled PP/PET film (reprinted with the permission from (Wyser et al., 2000))

Compatibilization recycling of the post-consumer recycled oil pouches was investigated by Choudhury et al. the films containing LDPE/LDPE/PET were reactively compatibilized using PE-g-MA (Fusabond) and Surlyne ionomer. Before recycling, the recycled multilayer oil pouches (RMOP) were washed using detergent, NaOH, and hot water to remove oil and contaminations and dried before reprocessing in single screw extruder. Melt viscosity, thermal stability, and mechanical properties of the RMOP with or without compatibilizer were improved using 5 wt.% compatibilizers. The MFI of the compatibilized samples were lower due to improved interfacial adhesion between the phases and also higher molecular weight of the compatibilized blends.

Mechanical properties of the reprocessed RMOP samples with and without Fusabond and Surlyne ionomer compatibilizers showed that due to higher Surlyne crystallinity comparing with Fusabond, the mechanical strength of its samples was slightly better (Choudhury et al., 2006b).

2.3.3. Recycling additives

To elaborate the recycling process and the recyclability of the plastic packaging items, some additives should be added and also some additives must be avoided or limited as much as possible. Inclusion of additives must be analyzed to demonstrate that they do not impair the first service life of the polymers as well as their further applications in future.

Firstly, to have the polymers with durability and stable quality, incorporation of the degradable additives (bio, oxo, photo) must be avoided since they are detrimental to the recycled products' quality and shorten the effective life of them. These additives should be separated from the plastic packaging wastes or have no adverse impact on the recycled product. So, inclusion of degradable additives should be minimized to limit the possible contamination and reduce the separation costs. In addition, optical brighteners can be detrimental to recycling which are used specially in PET bottles for better appearance. Presence of this additive creates an unwanted fluorescence in the recycled products and they just can be identified after recycling in the final products when it is too late for removing them and this impairs the value of the recycled PET (A. o. P. Recyclers, 2018).

On the other hand, there are some additives that can enhance the recyclability of the polymers and help the materials to keep their properties over the lifetime and reprocessing. These additives, however, are required to be tested to meet the appropriate recyclability standards like APR recyclability standards (A. o. P. Recyclers, 2018). De-nesting, anti-static, anti-blocking, anti-fogging, anti-slip, UV barrier, stabilizer and heat receptor agents and lubricants are of the additives that can enhance the performance of the recycling and up take their quality (Hahladakis et al., 2018). For example, MFI of the HDPE increases after reprocessing due to heat degradation and chain scission of the materials. This phenomenon compromises the mechanical properties since the molecular weight of the rHDPE decreases by re-extrusion and this limits the application of the recycled polymers. By use of heat stabilizers it was concluded that the recycled HDPE material can maintain its original MFI by in multiple processing (Abad et al., 2004). Chain scission may be overcome using chain extenders.

2.4. Chemo-mechanical recycling

One of the methods that could be useful for multilayer polymer films recycling is delamination of the structure. The idea in this approach is to remove the interlayer or adhesive of the structure by chemical dissolution using solvent or stripers. After separation of the layers, by re-extrusion we can recover the polymers in separate processes and incorporate them in new packaging applications. A study has been published by Patrizia Cinelli et al. in 2016 (Cinelli, Schmid, Bugnicourt, Coltelli, & Lazzeri, 2016) in which they used whey protein in the interlayer which can perform as barrier layer (Schmid et al., 2012) in the structure shown in the Figure B.10. In this study the whey protein layer has been sandwiched by PET and PE layer. So, after the first life of the film we can easily wash out the interlayer by water and enzymatic detergent to recover PE and PET layers and reprocess them into new structure (Cinelli et al., 2016).

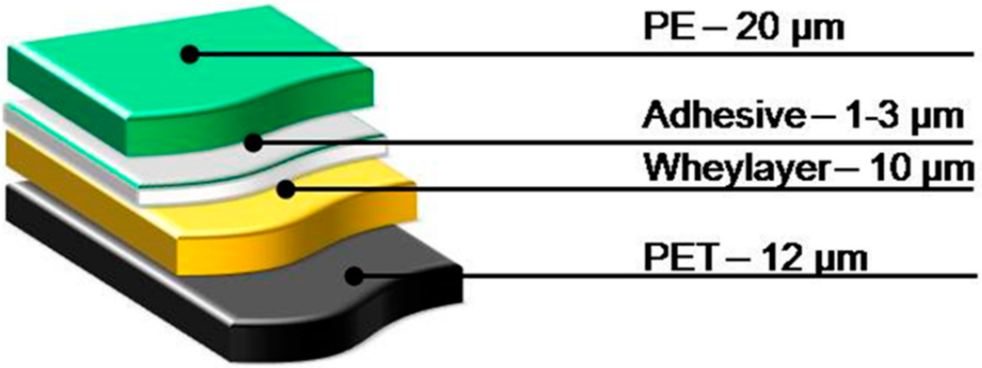


Figure B.10 Composition of multilayer film with a whey protein-based barrier layer (reprinted with the permission from (Cinelli et al., 2016))

While the idea of using whey protein in the interlayer was an interesting one, it also has major drawbacks. Firstly, the price and barrier properties of the whey protein is not comparable to the conventional barrier polymers like EVOH or PA. So, it cannot be scale up in the current industry. Furthermore, to wash the whey protein they were supposed to increase the temperature and add enzymatic detergents which are very expensive. Consequently, this method cannot be realistic for the recycling companies to follow.

There is an ongoing project based on delamination method called (TERMINUS) supported by European Union. The main idea is to develop enzymatic adhesion for lamination in multilayer packaging and through enzymes triggering the separation of layers for recycling purposes would be possible ((TERMINUS), 2019-2023).

Delamination of metal foils or paper from polymer films has been widely investigated (Bing, 2012; Olafsson, Jägerstad, Öste, & Wesslén, 1993). Usage of separating fluid with different composition for delamination of multilayer packaging is conventional (Seibt, 2013). Lovis et al. proposed a method for delamination of the multilayer structures containing at least one metal layer and polymer layer (optionally it can include paper). The separating fluid was microemulsion consisted of swelling agent (xylene, decalin, toluene), carboxylic acid (acetic acid, formic acid), water, and surfactant which can be used to penetrate the interlayer and using separation method the metal layer and polymer will be recovered for recycling purposes (Lovis, Seibt, & Kernbaum, 2017). In similar study, the effectiveness of another separating fluid mixture comprising a mixture of water, a short-chained carboxylic acid, phosphoric acid and an alkali metal hydroxide solution was reported as well (Lovis & Schulze, 2019).

3. Regulations for recycled plastic materials in packaging applications

Food packaging, as the major application of the plastic packaging, requires delicate regulations and the food safety is the reason for development and implementation of regulations on food contact materials (FCMs). European Food Safety Authority (EFSA) defines the legal framework at the European level based on the scientific studies. EFSA is the EU agency responsible to provide independent scientific advice and support on food safety issues to the European Commission, the European Parliament and EU member states. Framework Regulation (EC) No 1935/2004 regulates and covers all food contact materials including those for packaging, machinery and kitchen (European Parliament, 2004). Based on this regulation no food contact materials shall transfer components into food to the extends that endanger human health or produce impermissible changes in food composition or organoleptic properties. Specified criteria of the plastic materials and articles intended to be in contact with food have been set up in Regulation (EU) No 10/2011 and its amendment(Commission, 2011; European Commission, 2019). It specifies Positive (Union) List of authorized substances that can be used in the manufacture of food contact plastic materials and articles (EFSA should check the validity of application of new substances). The list addresses monomers, starting substances, additives and polymer processing aids and covers both mono and multi-layer plastic structures. It also establishes the rules on overall and specific migration testing for final materials or products, including testing requirements and migration limits (P. Europe, 2017). However, this directive does not address the plastic recyclates for food contact applications and a separate regulation was defined as (EU) 282/2008 and its amendment (EU) 2015/1906 (European Commission, 2015; European-Commission, 2008; Misko, 2013).

There are four possibilities to use recycled plastic in contact with food in EU regulations (P. Europe, 2017):

I. Feedstock (chemical) recyclates: plastics depolymerized into monomers or oligomers have to meet the same requirements as virgin plastic materials under Regulation (EU) No 10/2011.

II. Pre-consumer mechanical recyclates from food contact materials: offcuts and scraps from the production of plastic food contact materials that have not been contaminated yet can be re-extruded within the manufacturing site where they are generated or, alternatively, at another site where an audited quality assurance system is in place and meets the requirements laid down in Regulation (EC) No 2023/2006 (Commission, 2006). Traceability is critical in this case to verify the source of the materials and ensure that they are not affected by any kind of contaminations. Recycling of post-industrial waste (or pre-consumer) is beneficial due to their high quality as waste: they usually have a controlled and homogeneous composition and are clean waste with almost no degradation. however, there is very limited availability of this kind of plastics in the market for secondary raw materials.

III. Post-consumer mechanical recyclates from food contact materials: other possibility is to use post-consumer recycled plastics from processes verified by EFSA according to Regulation (EC) No 282/2008. In this case, the recycled plastics must be produced from waste coming from food contact materials. Traceability is therefore critical to verify the waste source and ensure the avoidance of waste contamination through a controlled closed-loop system. If a closed loop is not possible, a ‘challenge test’ must be performed to demonstrate scientifically that the recycling process is able to reduce any contamination of the plastic waste in a way that food safety risks are totally avoided. EFSA is responsible for the risk assessment of the recycling process and, taking into account its opinion, the European Commission will adopt a decision granting or refusing the authorization. Authorized recycling processes will be included in a register published on the European Commission website. At present, there are several processes with positive scientific opinions from EFSA, most of them for recycling of polyethylene terephthalate (PET), but the authorizations by the European Commission are delayed. Hence, there is no a list of authorized processes published yet, but recycled plastics from processes with positive opinion from EFSA can be used for food contact applications in the meantime in some EU member states according to their national transitional provisions.

IV. Post-consumer mechanical recyclates from non-food contact materials: other approach is to use recycled materials behind a functional barrier layer according to Regulation (EU) No 10/2011. In a multilayer structure, the functional barrier layer prohibits the migration of non-authorized substrates from recycled layer into food more than the permitted value as Specific Migration Limit (SML). To avoid set-off migration of non-authorized substances from recycled layer into the food contact layer during stacking of packaging items like cups or trays or film rolls, a symmetrical multi-layer structure can be employed. Even though, in this scenario recycled plastics might originate from non-food contact applications and it incorporates more options, there are some forbidden substances such as mutagenic, carcinogenic or toxic to reproduction, as well as nanoparticles. There are key parameters to evaluate the effectiveness of a barrier including concentration and diffusion coefficient of contaminants, chemical nature and thickness of the barrier layer, application, storage time and condition. Consequently, the new barrier structures should be scientifically tested and/or simulated case-by-case to demonstrate that a given thickness of a virgin polymer works as an effective barrier to the migration of contaminants.

Food and Drug Administration (FDA) regulates the packaging of food and drug in the US to ensure no packaging materials contaminate food. In addition, the FDA evaluates the environmental impact of the packaging materials during service life and disposal. Guidelines for using of recycled plastics in food packaging have been also established by FDA stating that the use of recycled polymers is permissible if it is of a type previously permitted for food-contact, has been kept free of contaminates during the recycling process, and the recycled material has been tested to establish suitable purity for reuse in food packaging (FDA, 2008; Qorpak, 2019). Recyclers must be able to demonstrate that contaminant levels in the reformed plastic have been reduced to sufficiently low levels to ensure that the resulting packaging is of a purity suitable for food contact. They may ask FDA to review their recycling process and issue a no objection letter for that to produce plastic recyclates for food packaging (Misko, 2019). In the recycling process additional antioxidants, processing aids, or other adjuvants may need to be added to the recycled polymer to enhance the product quality and the type and quantity of these additives must comply with existing authorizations by FDA.

FDA concluded that products of chemical recycling of PET and PEN are of suitable quality to come into contact with food, based on the evaluations conducted for the mentioned polymers. The polyesters obtained from these processes are clean enough of residual surrogates to be in contact with food. For recyclers of these two polymers via feedstock recycling, it is no longer necessary to submit data to FDA for evaluation and confirmations, while recyclers who wish to employ chemical recycling for other types of polymers are recommended to submit data for evaluations. Unlike chemical recycling, FDA recommends mechanical recyclers to demonstrate the effectiveness of their process to ensure the purity of the finished products and keep the surrogates' migration into food below Estimated Daily Intake (EDI) limit which is 1.5 micrograms/person/day.

While the consumers' exposure to the chemical contaminations migrated into food from recycled materials in packaging might be low, there is a potential that a very low steady-state concentration of certain toxins endangers consumers' health over the long term (FDA, 2019). In essence, FDA hase three main concerns about recycled plastic including:

- Contaminants from post-consumer material may appear in the final food-contact product made from the recycled material.
- Recycled post-consumer material not regulated for food-contact use may be incorporated into food-contact packaging.
- Adjuvants in the recycled plastic may not comply with relevant regulations for food-contact use.

To demonstrate the effectiveness of the recycling process for decontamination, FDA recommends testing method in which the virgin polymers are intendedly contaminated by surrogates. These surrogate contaminants represent the common gamut of chemicals that may be present in the plastic wastes which may incorporate volatile polar organic substances, volatile non-polar organic substances, non-volatile polar organic substances, non-volatile non-polar organic substances, and heavy metal salts (Clark, 2018; FDA, 2019). The contaminated polymers ('Challenged' polymers) are then entered the recycling process. If the recycled polymers do not have meaningful concentrations of the contaminants after processing, the efficacy and safety of the recycling process can be said to be confirmed. Otherwise, several alternatives are available including migration testing that simulates the actual use conditions for the recycled materials, blending the recycled material with virgin polymer to dilute the level of the contaminants, limiting the end uses, or using the recycled materials behind a functional barrier layer to prevent migration of the contaminants to the food (Clark, 2018). To demonstrate that a given thickness of a virgin polymer functions as an effective barrier to the migration of contaminants, FDA recommends that the recycler subject intentionally contaminated polymer to the recycling process and incorporate the recycled polymer into a non-food-contact layer of a finished article, using virgin polymer as the barrier layer. The migration studies should be performed as it is described in "Preparation of Food Contact Notifications and Food Additive Petitions for Food Contact Substances: Chemistry Recommendations" (FDA, 2018). Chemical composition of polymer, thickness, storage and use condition as well as time should be considered to have an effective barrier. FDA has determined that virgin PET is an effective barrier to contaminants that could potentially migrate from a recycled plastic inner layer under certain conditions (a thickness ≥ 25 µm (~0.001 in) at room temperature and below / a thickness ≥ 50 µm (~0.002 in) at higher temperatures; provided that only food containers are used in the feedstock to manufacture the recycled layer) (FDA, 2019).

4. Future trends and perspective:

Currently, only 14% of the plastic packagings are recycled and the rest 86% are lost with a value of 80 to 120 billion dollars each year. About 1/3 of the plastic packages leak into the ecosystem which can remain in the environment for hundreds of years. By this trend in 2050, it is expected to have more plastic items than the fishes in the sea (ELLENMCARTHOR_Foundation, 2019). This reveals the environmental significance of the circularity in plastic packaging industry. A new initiative was introduced which entitled New Plastic Economy with the vision supported by three key actions: elimination (of unnecessary plastics), innovation (of reusable, recyclable, and compostable plastics), circulation (of all plastics needed). The goal of this initiative is to fundamentally change global flows of plastic packaging material by 2025, setting the global economy on an irreversible path towards a circular economy (Foundation, 2017). According to this initiative, circular economy characterizations for plastic packaging incorporate different items as:

eliminating of problematic and excessive packaging, reusing and limiting the demand for single-use packaging, redesigning for 100% recyclable packaging (or composability and reusability), recycling all plastic packaging in practice (avoiding landfilling, incineration and energy recovery), decoupling plastics production from finite resources, removing hazardous chemicals in packaging structure which endangers health and safety (UN-Environment-Programme, 2018). European recyclability target is to ensure that all plastic packaging is recyclable by 2030 (Commission, 2017). Also, The Plastics Division of the American Chemistry Council (ACC) also set their goals to recycle or recover all plastic packaging by 2040 (Facts, 2019). Based on what have been discussed over this review, there should be certain modifications and scenarios to follow by manufacturers, organizations, governments and also customers (awareness raising, and modified legislations are also essential but are out the scopes of this manuscript)

- Design for recyclability in plastic packaging
- Increased, quality collection and sorting
- State-of-the-art recycling approaches
- Uptake of recyclates in new articles

4.1. Design for recyclability in plastic packaging

According to the objectives of circular economy and the sustainability, the packages should be reengineered towards recyclable structure. There exists definitions for recyclability for plastics by APR, PRE, RECOUP, and EPBP (EPBP, 2020; RECOUP, 2020). Firstly, based on the infrastructures and demands in the North America, according to APR a plastic item is recyclable if (APR):

- At least 60% of consumers or communities have access to a collection system that accepts the item.
- The item is most likely sorted correctly into a market-ready bale of a particular plastic meeting industry standard specifications, through commonly used material recovery systems, including single-stream and dual stream Municipal Recovery Facilities (MRFs), Plastic Recovery Facilities (PRF's), systems that handle deposit system containers, grocery store rigid plastic and film collection systems.

- The item can be further processed through a typical recycling process cost effectively into a postconsumer plastic feedstock suitable for use in identifiable new products.

In addition, according to the Global Plastics Outreach Alliance definition which is based on the European facilities and demands, a product is considered recyclable if it meets the following conditions (P. P. R. Europe, 2018):

- The product must be made with a plastic that is collected for recycling, has market value and/or is supported by a legislatively mandated program.
- The product must be sorted and aggregated into defined streams for recycling processes.
- The product can be processed and reclaimed/recycled with commercial recycling processes.
- The recycled plastic becomes a raw material that is used in the production of new products.

So, the first step is to ensure a recyclable plastic packaging. Plastic Recyclers Europe (PRE) and Association of Plastic Recyclers (APR) both have introduced design guidelines, features, and test methods for specific plastic flexible and rigid packaging including Polyethylene, Polypropylene, Polyethylene terephthalate, etc (APR, 2020; R. b. PRE, 2019). PRE created RecyClass with the aim of improving the design of packaging so that it is easily recyclable into high-quality recyclates which can then be used in a new plastic product. It also provides an online tool to test the recyclability of a plastic packaging and show to which extent it is suitable for recycling, and rate it with a class system from A to F (R. b. PRE, 2019). The packaging should provide the products with safety, shelf life, marketing and branding, however, the new challenge in designing is to put recyclability on top of other requirements and balance them (PRE, 2018b).

Design for recyclability must overcome the major challenges including:

- Increasingly complex packaging, barriers and coatings; using a mixture of different polymers or differing materials in the packaging impede the recyclability. Barrier structures enhance the shelf life of the products which reduces food waste (Dilkes-Hoffman et al., 2018). However, since recyclers are not able to separate these components effectively, the quality of their recycled products would be inferior. Polyamide (PA), Ethylene Vinyl Alcohol (EVOH), Polyvinylidene chloride (PVDC) and Polyvinyl chloride (PVC) are the main polymers which are employed as barrier layer from which PA, PVC, and PVDC should be prohibited and using EVOH is conditional due its thermally unstable. Other barrier components are foaming agents, aluminum foils or metalized coating which degrade the quality of the recycled materials (PRE, 2019a). Mono-material packaging is more recyclable, however, attaining the acceptable properties is challenging. Currently, manufacturers are trying to have different properties with one polymer for instance the full PE laminate pouch (Peter Niedersuess, 2016; polymers, 2020), or PP film and poches (Aishwarya, 2019). There seems also a trend in elimination of some polymers in packaging such as polystyrene which cannot be recycled (McArthur, 2019).

- Colorants and pigments; using die and pigments in the plastic packages although gives a good appearance for the first service life, it will downgrade the products after recycling. Specially with the dark colors the application of the recycled materials will be limited. It also reduces the sorting for recycling (e.g. carbon black is not visible to NIR sorting machine and the products containing this pigment will not be sorted for recycling) (Rebecca Briedis, 2019).
- Ink and direct printing; inks should be avoided as much as possible and where needed, it must be non-toxic, non-hazardous and non-bleeding (EuPIA, 2018). In addition, extensive printing (more than 50% of the packaging) is not compatible for recycling causing downgraded quality of the recycled materials and formation of gels (PRE, 2019a).
- Adhesive, labels, and sleeves; adhesives are used for labels and laminations, but they must be removable during washing step (in warm water), otherwise it disrupts the quality of the final products. Labels and sleeves, which are mostly plastics, papers, should be redesigned since papers and incompatible polymers contaminate the recycling materials. Furthermore, it may impact the sorting process (PRE, 2019a; Rebecca Briedis, 2019).
- Additives; different chemical additives are used to enhance the quality of the packaging, however, it may deteriorate the recyclability of them (e.g. chalk, talc powder or marble, which are added to the PE films, change the density of the polymer and cause the loss of them during density separation) (PRE, 2019a).

4.2. Increased, quality collection and sorting

Even though all overall plastic recycling is on the way out and the its sector has been developing all over the world particularly in developed countries, it demands further scaling up on all levels including collection and sorting statistics which is a key parameter in efficiency of the waste management system (PRE, 2019a). Advanced, automatized sorting installations and technologies guarantee for financially viable processes by upgraded output material. In collection process, however, the most problematic items are the ones with light weight which incorporate flexible packaging and films.

There are strategies to augment collection of the plastic packaging for recycling purposes and reduce the material loss into incineration or landfilling including:

- Enhancing the awareness of the consumer for recycling plastic packaging specially the flexible packaging. Media may step forward to help in this area using advertisements, social media, campaigns. Advancement of technology can also make it possible to detect an item using smart phones and Internet of Things and provide the consumer with the information on how to collect them for recycling (Niaounakis, 2019). In addition, a critical solution can be the How2Recycle label which provide the directives for recycling of the packages ("How2Recyle," ; Recycling, 2017).
- Store drop-off and establishing schemes to encourage customers to bring back their packaging after using (deposit and return system) (McArthur, 2019).
- Increased manufacturers' responsibility beyond the design and use of their packaging and contributing towards it being collected and recycled in practice (UN-Environment-Programme, 2018).
- Effective collection infrastructure, facilitating the establishment of related self-sustaining funding mechanisms, and providing an enabling regulatory and policy landscape should be provided by governments (UN-Environment-Programme, 2018). Segmented collection and sorting systems should be avoided in all the regions and standard guidelines and harmonized measures must be applied to accomplish increased collection targets (PRE, 2019b).

Sorting also limits the quality of the final recycling products particularly for the materials intended to come into contact with food which should possess of great purity to meet the regulations discussed in section 3 of this manuscript (PRE, 2019a). Furthermore, multilayer polymer structures and coated polymers are usually discarded as loss in the major sorting plants. To address the mentioned challenges there are promising technologies such as advanced NIR optical sorter to detect multi-component items, ID tags or smart labels which can be attached to the packaging for better detection by the sorter, digital and robotic sorter combining with optical and visual sensors combining with artificial intelligent, etc (Niaounakis, 2019).

4.3. Innovate and develop recycling approaches

The next stage that should be enhanced is the recycling approaches. Currently mechanical recycling is the major approach in large scale for plastic recycling. But not every plastic solid waste can be recycled mechanically. The limitations of this approach (e.g. temperature sensitive plastics, poor quality due to impurity and contamination, composites and multilayers, etc.) make this approach suitable for selected polymers like PET and Polyethylene, which totally represents 46% of the annual plastic produced. Recent research trends show advancements in the area of compatibilization of the mixed plastic wastes in the mechanical recycling to overcome the multilayer structures in plastic packaging particularly (Garcia & Robertson, 2017).

For the chemical recycling on the other hand, the main obstacle is low efficiency and energy intensity and the research in this area points the way to address them. Enhancing the chemical and enzymatic degradation as well as developing catalysis cracking will assure a higher share for chemical recycling in the years ahead. However, Chemical recycling should be seen as a complementary solution to mechanical recycling; where the mechanical recycling is inefficient for the challenging material streams (multilayer plastic packaging and highly contaminated plastics)(PRE, 2018a).

Furthermore, bio-based polymers (derived from renewable resources) impose no problem for mechanical recycling since they have been designed to keep their properties for a long time. However, the bio-degradable polymers lose their properties due to degradation of their organic portions which downgrades the quality of the recycling. So, incorporation of the bio-degradable polymers in plastic packaging waste recycling stream should be avoided (P. R. Europe, 2013).

4.4. Uptake of recyclates in new articles

While the advancements in recycling and sorting technologies have greatly improved in the past years more investments as well as research & development is needed to continuously enhance the quality of recycled material (PRE, 2019a). Statistics show that incorporation one ton of recycled plastic can save up to 130 million kJ energy and the annual energy potential saving achieved by recycling of all plastic packaging is approximately equivalent to 1.4 billion barrels of oil (Garcia & Robertson, 2017). All the effort in sorting, collection, and recycling is meaningless if no demand for recycled plastic exists to use them in new structure. Based on the circularity concept the ideal case is to keep the materials in the same market and loop and plastic packaging is not an exception. Therefore, the quantity and also quality of the recycled materials in plastic packaging must grow. Based on the predictions, packaged goods companies and retailers are targeting an average of 22% post-consumer recycled (PCR) content by 2025 which is five times their current average of 4.4% (UN-Environment-Programme, 2018). Certain measures should be applied (e.g. tax incentives for packages with share of PCR) to ensure a stable market for plastic packaging recyclers to invest and develop their technologies in the years ahead. The ability of the recyclers to upgrade the quality of the PCR products as well as the available demand for them from packaging manufacturers guarantee the sustainability of the plastic packaging recycling value chain and fulfill the increased targets for creating a truly circular economy (P. R. Europe, 2015).

Consequently, the market should expect researches to be conducted on up taking the PCR content in the plastic packaging in the future and the most delicate sector would be food packaging as the most health sensitive and major plastic packaging application.

Current application of the PCR in packaging is low and the reason behind that is the inferior (mechanical and visual) quality and also negative health image associated with the recycled content in packaging. However, a part of polymers can be reprocessed multiple times without losing the original properties and also increased quality sorting, collection and recycling advancements will lead to increasing quality of the PCR. Furthermore, the food safety authorizations have concise measures and standards to ensure minimum health risks imposing by incorporation of PCR plastics in items coming in contact with food. Still there is a demand for harmonized legislations regarding the use of PCR in food packaging to reduce the confusion and uncertainty among the market and consumers (P. R. Europe, 2018).

5. Conclusion

Incorporation of the plastics in the packaging applications benefits in both environmental and economic sides, since such materials in packaging demand lower level of energy (renewable and non-renewable energy sources), consume less water during production, emit fewer amounts of GHG, and produce lighter weight solid wastes compared to other alternatives. However, this sector must be developed in a more sustainable model in which less pressure is applied to the environment for taking the resources and also disposing the wastes of plastic packaging. Recycling is the solution that requires more advancements in different stages to limit the landfilling of incineration of plastic packaging wastes. This includes both mechanical (maintaining polymer structure) and chemical (breaking down polymer structure into more basic building blocks then building up again into new materials) recycling processes and each of them has its own advantages and disadvantages. Wates collection and sortation, shredding and grinding, cleaning and decontamination are among the pretreatments followed by the recycling process and production of the recycled plastic for using in the next applications instead of raw materials. Since the major market of the packaged products is food applications, the food safety regulations for inclusion of the secondary raw (recycled) materials must be respected to prevent any possible health issues.

Even though the market of recycling and using recycled contents in the packaging is rising, more advancements are required in different stages of this process including recyclability engineering, sorting and collection, recycling technologies, as well as the promising demand for recycled contents by incorporation of such materials in new applications as a substitute to virgin materials.