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Current Topics in Plastic Recycling

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Abstract

This chapter presents an overview of current trends in plastic recycling and focuses on specific topics of interest. Firstly, there are presented all methods used for plastic recycling, along with the advantages and disadvantages of each method. Extra attention is paid to chemical recycling and especially, pyrolysis (thermal and catalytic), which is an environmentally friendly method that results in the formation of value-added products. Emphasis is given on three case studies where there are difficulties as regards the recycling of the plastic part: *polymeric blends*, since the existence of mixed plastic wastes may be challenging for their recycling; *plastics originating in multilayer packaging*, since the multilayer packaging consists of various materials, including plastics, paper, and metals that may be an obstacle for the recycling of the plastic part; and *brominated flame-retarded plastics from waste electric and electronic equipment (WEEE)*, since in this case safe handling is required in order to avoid environmental contamination and a pretreatment step before recycling may be of paramount importance. These three case studies along with the mentioned difficulties and suggestions in order to overcome them are presented here, with the aim of offering insights for future studies on the management of plastic materials.

Keywords: plastics recycling, pyrolysis, polymeric blends, multilayer packaging, WEEE, BFR

1. Introduction

Undoubtedly, plastics play a major role in our everyday life, since plastic parts are used in numerous applications, such as packaging (for instance, food containers), automotive industry, electric and electronic equipment (EEE), etc., due to their unique properties [1]. Some of their most important characteristics that necessitate their use in these applications are lightness, ease of processing, resistance to corrosion, transparency, and others. Nevertheless, their wide use in various applications in combination with the short life span of many plastic products leads to large amounts of end-of-life plastics. Taking all these into account, along with plastic nonbiodegradability, research has focused on exploring environmentally friendly approaches for their safe disposal [2]. Plastic handling involves collection, treatment, and afterward recycling. Unfortunately, finding environmentally friendly approaches for their disposal is no mean feat (**Figure 1**); due to the variation in types of plastics, which are often of unknown composition, the existence of polymer blends, or composites, multilayer structures with other materials apart from polymers, as well as the wide range

Figure 1.
Difficulties encountered during end-of-life plastic handling.

of additives (such as UV and thermal stabilizers, antistatic agents, (brominated) flame retardants, colorants, plasticizers, etc.) they may contain [3, 4].

The disposal of post-consumer plastics occurs via landfilling, primary recycling, energy recovery, mechanical recycling, and chemical recycling [2]. Although landfilling is an undesirable, non-recycling method, since it results in serious environmental problems, such as soil and groundwater contamination, until now large amounts of end-of-life plastics still end up in landfilling [5, 6]. With a view to eliminating plastic landfilling, research has focused on recycling methods (**Figure 2**) that can be applied, which are primary recycling, recycling without quality losses, energy recovery-quaternary, mechanical or secondary recycling-downcycling into lower qualities and chemical or tertiary recycling-recovery of chemical constituents [7]:

- In primary recycling (re-extrusion), the plastic scrap is reinserted in the heating cycle of the processing line in order to increase the production [8]. It remains a very popular method, because of its simplicity and low cost. However, it can be applied only in case of clean, uncontaminated single-type waste [2].
- Mechanical recycling involves reprocessing and modification of plastic waste using mechanical-physical means with the aim of forming similar, plastic

Figure 2.
Recycling methods for post-consumer plastics.

products, at nearly the same or lower performance level when compared with the original products [6]. Since mechanical recycling can be used only in case of homogeneous plastics, heterogeneous plastics require sorting and separation before their recycling. In mechanical recycling, the presence of brominated flame retardant (BFR) incorporated in plastics must be identified before its application, in order to avoid the possible formation of toxic substances, such as polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) [9, 10]. Its main drawback is the fact that product's properties are deteriorated during every cycle [2]; and it should be underlined that each polymer can endure only a limited number of reprocessing cycles [11]. An additional challenge is the existence of mixed plastic waste (polymer blends), since different polymer types have different melting points and processing temperatures. In such cases, the processing temperature is usually set to the highest melting component. Nevertheless, this may result in overheating and possible degradation of the lower melting components and so, in reduced final properties [12].

- In chemical or feedstock recycling, plastic wastes are converted into lower-molecular-weight products, such as: fuels, monomers, or secondary valuable products that can be used as feedstock for refineries. Conversion takes place through chemical reactions in the presence of solvents and reagents [10]. It is an environmentally friendly method, since, as mentioned previously, it results in the formation of valuable products or monomers [9].
- During energy recovery, plastics are incinerated in a boiler or in other industrial equipment, taking advantage of their high energy value; for energy production in the form of heat and electricity. Nevertheless, if incomplete incineration takes place, then toxic substances, such as dioxins, furans, and others, may be formed and released into the atmosphere, resulting in environmental issues [2, 8–10].

In conclusion, during chemical recycling, plastics are converted into smaller molecules (mainly liquids and gases), which can be used for the production of new, valuable products; and that is why it is considered as an environmentally friendly and economically feasible technique. Furthermore, chemical recycling seems to be more advantageous than the other existing methods; taking into account, for instance, the fact that during chemical recycling, both heterogeneous and contaminated polymers can be treated, only with a limited pretreatment. Moreover, the energy consumption of the process is very low, if compared with that of mechanical recycling or energy recovery [6].

Chemical recycling comprises two processes: solvolysis and thermolysis. During solvolysis, polymers are dissolved in a solvent and treated with or without catalysts and initiators. *Solvolysis* can also be applied as a pretreatment before thermochemical processes (such as pyrolysis). During *thermolysis*, polymers are heated in an inert atmosphere (e.g., N₂ atmosphere) in the absence of air or oxygen. It consists of various processes including (thermal and catalytic) pyrolysis, gasification, and hydrogenation (**Figure 3**) [13–14].

Thermal pyrolysis involves polymer cracking in an inert atmosphere (usually nitrogen atmosphere), at high temperatures, and in the absence of catalysts. During this, plastic waste is converted into liquids (pyrolysis oil), gases, and solid residues (chars) [6]. Various temperatures within the range of 300–900°C as well as different heating rates varying from 4 to 25°C/min and different retention times have been investigated in literature in order to find the optimal conditions [15]. When pyrolysis of brominated flame-retarded plastics occurs, the liquid fraction usually

Figure 3.
Chemical recycling routes.

contains many brominated compounds that inhibit their reuse. In such cases, a pretreatment step before or during pyrolysis is of paramount importance, in order to obtain bromine-free products.

Catalytic pyrolysis involves polymer cracking in an inert atmosphere (usually nitrogen atmosphere) and in the presence of catalysts. It offers many advantages if compared with thermal pyrolysis, such as the fact that there are required lower temperatures and shorter reaction times; and so, in this case, less energy is consumed. Furthermore, the selectivity of the products is increased, since catalysts enhance the formation of high commercial value and quality products; and in the meantime, the formation of undesired products (e.g., brominated compounds) can be suppressed [15, 16]. As a consequence, various catalysts have been explored for pyrolysis of various types of plastics, including silica-alumina, zeolites (HZSM-5, etc.), mesoporous catalysts (MCM-41), metal-based catalysts, fluid catalytic cracking (FCC) catalysts, and minerals [9]. Among them, zeolites are the most widely investigated in case of nitrogen-containing polymers such as poly(acrylonitrile-butadiene-styrene) (ABS), since they promote the formation of aromatics [13]; but of course, their properties vary depending on the zeolite type.

Gasification includes partial oxidation or indirect combustion of polymers at high temperatures (up to 1600°C) and in the presence of oxygen. It results in the formation of two main products: CO and H₂ (synthesis gas – syngas). Syngas can be used either in order to run a gas engine or it can be converted into hydrocarbon fuels via the Fischer-Tropsch process. More often than not, it is preferable to gain condensable liquids or petrochemicals as the main products; and that is the reason why pyrolysis is favored over gasification, since the latter requires multiple steps in order to obtain liquid products [13, 14].

Hydrogenation entails the conversion of large hydrocarbon molecules into lower-molecular-weight products. It takes place in hydrogen atmosphere, high pressure (approximately 100 atm), and at moderate temperatures between 150 and 400°C [14].

Generally, it should be underlined that pyrolysis can be considered as one of the best options for plastics recycling, since its advantages are aplenty. Specifically, pyrolysis enables material and energy recovery from polymer waste, as a very small amount of the energy content of waste is consumed for its conversion into valuable hydrocarbons. Furthermore, pyrolysis products are valuable, since they can be used as fuels or chemical feedstock. Last but not least, in case that flame retardants are present in plastic waste, via pyrolysis the formation of toxic substances may be restricted, due to the fact that it takes place in the absence of oxygen [17]. Of course, catalyst's presence, as mentioned previously, plays a vital role. Apart from catalysts, various other parameters, including temperature, heating rate, residence time, operating pressure, etc., can strongly affect the quality and distribution of pyrolysis products [6].

2. Difficulties in plastics recycling

As mentioned previously, many obstacles can be found during the end-of-life plastic recycling. In this unit there are presented in detail three case studies, including: polymeric blends (difficulties due to the coexistence of mixed plastic wastes), plastics originating in multilayer packaging (challenging because of the coexistence of different materials, such as plastics, paper, and metals), and brominated flame-retarded plastics from WEEE (possible formation of undesirable, toxic substances due to the BFR's presence), along with suggestions on how to overcome these difficulties.

2.1 Polymeric blends

Polymer blends are mixtures of two or more polymers in concentration greater than 2%wt. The blends can be miscible or immiscible, a parameter that depends on the thermodynamics of the system and molecular structure, weight, and polymer concentration. More information on the complicated thermodynamics that govern polymer blend miscibility can be found in the Polymer Blends Handbook [18, 19]. Miscible polymer blends are also known as homogeneous blends and are monophasic while immiscible blends with morphologies that differ such as, spheres, cylinders, fibers, or sheets (Figure 4) [12].

Subject to polymer compatibility, polymer blends can exhibit synergistic, antagonistic, or additive behavior. A common method used to assuage the immiscibility of polymers blends is the inclusion of compatibilizers—a polymeric surface tension reduction agent that promotes interfacial adherence—in the blend. The three most common types of compatibilizers are reactive functionalized polymers, nonreactive polymers containing polar groups, and block or graft polymers [12, 19, 20].

The difficulty during polymer blend recycling lies in the different properties presented by its component parts such as melting points and processing temperatures between polymers [12]. Most recycling efforts are concentrated on the procedure of pyrolysis to extract energy through the oils, wax, char, and gasses produced. Furthermore, research in recent years has focused on the use of various, different catalysts in order to lower the energy consumption of the whole process and increase the exploitable yield. Along with those some novel methods of polymer blend recycling will be explored.

Figure 4. (a) and (b) are a visual representation of the differences between miscible and immiscible Polymer Blends. Images (c), (d), and (e) show the spherical, fibrous, and cylindrical morphologies of immiscible Polymer Blends, respectively. Image inspired by Ragaert et al. [12].

2.1.1 Production of composite materials

Polymer composites are made up of two or more elements resulting in a multi-phase, multicomponent system that exhibits superior properties compared with the constituent materials due to a synergistic effect. It comprises two parts:

- A polymeric matrix that can be either thermoplastic polymers such as polypropylene (PP), polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and poly(ethylene terephthalate) (PET) or thermoset polymers such as epoxy, vinyl ester, and polyester.
- A reinforcing filler such as glass, carbon, and aramid [21].

One way that polymer blend can be recycled is by acting as the matrix for secondary elements creating composite materials. In this way it is possible to unite the two components in a form that reinforces the secondary materials and reuses the polymer blends. This method can be adapted to use natural fillers or fibers as the reinforcing fillers. Those can be added along with a coupling agent to optimize the interaction of the fillers with the matrix further and have the positive side effect of making the whole process environmentally friendly. It is important, however, that these fillers have the capacity to be chemically treated.

In a research conducted by Choudory et al., [22], Low-density polyethylene (LDPE)/Linear low-density polyethylene (LLDPE) blend extracted from milk pouches was used as a matrix for coir fibers. The result was composites with properties only slightly lacking from the virgin material ones. In case a maleated styrene pretreatment was applied, the mechanical properties and thermooxidative stability were drastically increased [23].

In another research conducted by Lou et al., [24], PET/PP blend and bamboo charcoal were used to create extruded or injection-molded composite materials. A great increase in mechanical properties was observed in the injection-molded composites, which maintained their mechanical properties even after three rounds of processing. The percentage of total mass of PET in the blend plays a particularly significant role in the product's final behavior [23].

2.1.2 Pyrolysis

Pyrolysis is a promising choice as regards the recycling of polymer blends. With pyrolysis, high levels of conversion of the polymer blend into oil and gas with high calorific values can be attained. These can be used afterward to either fuel the process, or they can be utilized elsewhere [25]. This can be an invaluable asset to the petrochemical industry and a green way for the recycling of plastic waste [26].

Another advantage of pyrolysis is that a sorting process is not needed in contrast to other recycling methods that are extremely susceptible to contamination. This can of course save money and time when recycling polymer blends. Lastly, with the use of the pyrolysis procedure, waste management becomes easier as it is a cheap and environmentally friendly method. In the meanwhile, it allows for minimization of landfill capacity—a serious contemporary difficulty [5]. As the combination of polymers that make up polymer blends is wide, with every blend presenting different properties and pyrolysis behavior, it would be impractical to analyze each one of them. Instead, this chapter will focus on the pyrolysis route taken for the most common polymer blends by examining the research conducted by scientists in the field.

In general, the pyrolysis process can be either thermal or catalytic. In practice, however, the latter is widely preferred by the industry as it demands lower

operating temperatures—and thus cost is minimized—that produce a more satisfactory yield of pyrolytic oils, if the correct catalyst has been elected [5].

In a study conducted by Vasile et al., [26], a blend with a composition similar to that originating in municipal waste—24%wt high-density polyethylene (HDPE), 39%wt LDPE, 21.5%wt isotactic polypropylene (IPP), 10%wt PS, 4%wt ABS, and 1.5%wt PET—was investigated. The blend underwent the process of catalytic pyrolysis two separate times each with a different catalyst—HZSM-5 in the first batch and PZSM-5 zeolite catalyst in the second batch, in order to find which catalyst led to better results. It was concluded that the PZSM zeolitic catalyst was characterized by higher selectivity and stability. The optimal temperature for the pyrolysis was found to be 450–480°C, and the gas produced increased sixfold in comparison to the non-catalytic process. Furthermore, the liquid products were found to contain high concentrations of aromatic hydrocarbons. As such, both the liquid and the gas phase can be utilized by the petrochemical industry. Lastly, the pyrolysis oil could be useful as petrochemical feedstock [26].

A novel research conducted by Bober et al. [27] proposed a way to produce hydrogen gas from the catalytic pyrolysis of different consistency HDPE/ poly(methyl methacrylate) PMMA polymer blends. After trial and error, the optimal temperature for maximum hydrogen production was found to be 815°C, a temperature where the catalyst used, Ni/Co, operated the best for hydrogen production. It was also found that, the higher the HDPE content in the blend, the bigger the hydrogen output. In contrast, when PMMA was the dominant polymer in the blend, CO was produced at a greater rate than the previous procedure. The research team proposed that the best ratio for HDPE/PMMA in the blend is 4:1 [27].

It must also be noted that concerning the production of hydrogen from pyrolysis of polymer blends, a popular option is the co-pyrolysis of the polymer blends with biomass [28].

A largely untapped potential of Polymer Blends is their recycling as feedstock for the chemical industry. A study presented by Plastics Europe [29], displays that only 2–3% of the collected plastic waste in Europe is utilized as feedstock (**Figure 5**).

Figure 5.
The fate of the European collected plastic waste. Image inspired by Donaj et al. [30].

A possible procedure for the creation of feedstock from pyrolysis of Polymer Blends on the group of polyolefins was suggested by Donaj et al., [30]. For the purposes of the process, the researchers used a blend of polyolefins—46% LDPE, 30% HDPE, 24% PP- taken from MSW/plastic waste. The collected material was firstly reduced in size to about 3 mm pieces and then pyrolysis ensued under temperatures of 600–700°C in a fluidized bed reactor and with the use of steam and a catalyst if that was deemed feasible as the latter materials increase the yield of olefins. To optimize the procedure, Ziegler-Natta catalyst was used.

The research noted that after the procedure's conclusion, plastic pyrolysis had directly yielded 15–30% gaseous olefins that can then be channeled directly into a polymerization plant. The residue produced consists of a naphtha-like consistency. To be used, this residue must undergo reformation via petrochemical technologies to be upgraded into olefins. Also, as in the previous cases of pyrolysis, the products of the process can be used to fuel the procedure itself. However, work still needs to be done on this field as the process described is not as cost-effective as desired [30].

2.1.3 Melt processing

A last noteworthy method for the utilization of immiscible Polymer Blends is their direct melting processing into fibers with good mechanical properties proposed by Shi et al. [31]. The blend used in this research was PS/PP while fibers were chosen due to two distinct reasons: (a) The fiber spinning technique is known to endow improved properties to polymer blends. (b) Fibers from polymer blends may display new properties in comparison to pure polymers. This method is widely cost-effective for preparing strong fibers for the industry, and it is expected to see great development in the coming years [31].

2.2 Multilayer packaging

In this age of climate change and overall pollution, it has been the priority of policymakers to ensure the viable and sustainable future of human development. An example of this is the EU with the European Plastic Strategy dictating that all packaging used should be reusable or recyclable by 2030 [32].

A prime example of the challenges the industry faces to reach this standard is Tetra Pak, a multilayer packaging used mostly in the food, medicine, chemical, and commodities industry. Tetra Pak most usually consists of three elements: paper cardboard, aluminum, and LDPE.

As stated by the Tetra Pak company, its composition is as follows: (a) 71% paper-board, (b) 24% plastics, and (c) 5% aluminum foil (**Figures 6 and 7**).

These three make up the six layers that combined make Tetra Pak. Each layer has a particular use elaborated on below:

However, this is not an absolute rule. For example, certain products with a short shelf life have no need for the protection given by the aluminum layer. On the other hand, when the aforementioned shelf life needs to be extended, the LDPE layers can be substituted by PP providing a chance for further heat treatment of the product. HDPE, PET, and PA are also possible options for replacing the LDPE layers. Lastly, polyurethanes and EMAA are often utilized as adhesives between layers [34] while the Tetra Pak carton may also contain various chemical additives such as plasticizers, stabilizers, lubricants, fillers, foaming agents, colorants, flame retardants, and antistatic agents [35].

As Tetra Pak cartons are composed of mainly paper, the removal and recycling of the cardboard layer are of much significance. As such there are two main processing routes: recycling without hydropulping and recycling with hydropulping. The initial

Figure 6.
Raw materials used to produce Tetra Pak. Image inspired by the Tetra Pak site information.

Figure 7.
The layers of Tetra Pak. Image inspired by Georgiopoulou et al. [33].

procedure processes the cartons as a whole, while the latter uses the technique of hydropulping to first separate the cellulosic fibers from the Al-LDPE laminate.

2.2.1 Recycling without hydropulping

The main aim of those following this route is energy recovery or downcycling. Energy recovery is attained in combination with solid municipal waste through

means of pyrolysis, gasification, or incineration. However, this method comes with many downsides. Paper—the main ingredient of Tetra Pak cartons—has a low heat combustion (16 MJ/Kg), high moisture content, and a significantly high ash value. This makes the entire process inefficient, and thus it is in general not widely used [34].

2.2.2 Recycling with hydropulping

Before proceeding with the options in this category, it would be useful to briefly go over the hydropulping process. When the soon-to-be recycled material first arrives into the recycle unit, the hydropulper breaks apart the paper with rotating blades that use high pressure water and a slurry of fibers is produced. Further processing ensues in centrifugal cleaners that remove heavy materials such as sand, adhesives, staples, etc. [36]. The end result of this procedure is a pulp of cellulosic fibers and can be used as a substitute for wood pulp, in the production of brown paper and pulp board [37]. What remains after the process is the external LDPE layer and the Al-LDPE laminates. However, residual cellulosic fibers can account for up to 5% of the finished products (**Figure 8**).

2.2.3 Pyrolysis

The appeal of this method lies in its simplicity and cost-effectiveness. The pyrolysis procedure has two steps: (a) the degradation of paper (200–400°C) and (b) the devolatilization of LDPE (420–515°C) [38–40]. It should be noted that the temperature plays an important role in the composition of the final products. For example, the production of char is minimized with higher temperatures, and the opposite is true for wax.

The solid products that follow the process are aluminum, char caused by paper degradation, wax from LDPE degradation and tar. A great deal of gaseous products are also formed that mainly consist of CO₂, CO, H₂, CH₄, C₂–6 hydrocarbons, and volatile matter. Lastly, there is an aqueous phase consisting of water and phenols.

Many uses have been proposed for those pyrolytic products. The produced gases could be used to sustain the pyrolysis procedure itself or used elsewhere entirely, the char and tar can be exploited as a solid and oil fuel, respectively, while char can also act as a primal resource for the production of carbon-based materials. Lastly, the wax and aqueous phase can readily be utilized as a raw material for the chemical industry [39, 40].

Figure 8.
The main recycling routes.

A novel approach has been taken by researchers in Mexico and Spain who have used the char and the aluminum from the pyrolysis to have them act as absorbents of mercury in aqueous solutions. By means of trial and error and using thermodynamical analyses, they did conclude that char obtained from pyrolysis at 600°C at a 3 h procedure demonstrated the most promising mercury adsorption capacity at 21.0 mg/g. The field of char absorbents is still expanding with hopes of Tetra Pak pyrolysis chars acting as major absorbents for industry in the future [41].

2.2.4 Selective dissolution-precipitation process (SDP)

The basic principle of this approach is the immersion of the Al-PE laminate in a carefully selected solvent and under specific temperature conditions with the aim of the dissolution of the LDPE in the solvent. What follows is the removal by means of filtration of additives and impurities. Lastly an antisolvent is added, and as a result precipitation of the dissolved polymer follows. To maximize LDPE and pure aluminum recovery, the SDP process is repeated three times.

The LDPE produced is of quality that matches that of the virgin product while the aluminum collected is also of high purity. Along with the hydropulping process, this is a very promising option for Tetra Pak recycling. However, the procedure is not without drawbacks: firstly, because of the cost-effective energy consumption needed to separate the solvent-antisolvent mixture and secondly, due to its high environmental impact. The economic viability of this technique rests upon whether the solvent-antisolvent mixture can be separated cheaply (Figure 9) [33].

2.2.5 Acid-based delamination

This technique has been developed by researchers in China and focuses on the separation of LDPE and aluminum by means of a separation reagent, mostly aqueous solutions of organic acids or even mixtures of acids. The procedure works by breaking the mechanical bonds holding the laminate together and as such allows for recovery of the products.

The yield of the process is highly dependent on the conditions of the reaction. In the process some of the aluminum is dissolved by the acid—which is also

Figure 9.
The SDP process. Image inspired by Georgiopoulou et al. [33].

Figure 10.

The acid-based delamination process. Image inspired by Zhang Ji-fei et al. [37].

consumed—and thus losses are to be expected. However, this depends on many factors such as acid used, temperature, etc. Product purity is also correlated with those factors.

After trial and error, it has been found that methanoic acid is the best separation reagent for Tetra Pak. Lastly, there seems to be a high correlation between the separation rate, the temperature the reaction is taking place at, and the concentration of the reagent. More specifically, reaction time decreases with the rise of reagent concentration and temperature (**Figure 10**) [37].

2.2.6 Heat recovery and material recycling

Thanks to the high heating value of the Al-LDPE laminate (40 MJ/Kg), it can be used as a sufficient fuel source. This has taken precedent especially in Europe. Although the laminate can be used directly after the hydropulping process, it is most usually used in conjunction with other fuel sources. This recycling route can be considered environmentally friendly as the LDPE of Tetra Pak burns cleanly without producing fumes containing elements such as sulfur, nitrogen, or halogens.

Also, the Al_2O_3 produced during pyrolysis, by the reaction between Al and moisture in high heat conditions, is in big part exploited by the cement industry, which uses it as a desired component of cement production [36]. Lastly there is the choice of forming finished products directly by using the laminates in roof tile production, injection and rotational molding, and PE-Al agglomeration and pulverization [42, 43].

In these times that society demands a more environmental way of thinking from the industry, recycling of multilayer packaging becomes a priority for many scientists. They have developed a plethora of ways to recycle such packaging, from using it as a fuel to using its pyrolysis products as a mercury absorbent. It is most likely that this field will keep on expanding with ever more innovative and cost-effective ways to fully exploit, reuse, and transform the Tetra Pak multilayer packaging as human development is going into the future.

2.3 Brominated flame-retarded plastics originating in WEEE

The rapid technological advances along with people's need for better living conditions resulted in a global rise in the consumption of EEE over the last years and so in huge amounts of WEEE [44]. Plastics in WEEE account for ~30% of WEEE and in most cases contain BFR that necessitates careful handling [9], since BFR's presence in plastics leads to the formation of various, toxic brominated substances in the liquid fraction obtained after pyrolysis, inhibiting its further use. In such cases a pretreatment step before or during the recycling is necessary in order to receive bromine-free products. So, due to the fact that *brominated plastics from WEEE* are increasing more and more and the BFR enhances the difficulties in their recycling, this unit focuses on pretreatment methods that can be applied either before or during their recycling.

One very common pretreatment method for the removal of BFR applied before pyrolysis is *solvent extraction*. “Traditionally” it takes place using a *soxhlet* extraction apparatus. It is a very popular method until now, due to its low cost and simplicity,

although large amounts of solvents and much time are usually required [45]. For instance, Evangelopoulos et al. applied *solvent extraction* as a pretreatment before pyrolysis, via a soxhlet extraction apparatus, with the aim of reducing tetrabromobisphenol A (TBBPA) from real WEEE samples. They tried two different solvents, isopropanol and toluene, due to their different properties; and they found that isopropanol was more efficient in removing bromine from the solid fraction, whereas toluene was more efficient in removing TBBPA from the liquid fraction [46].

Apart from the typical soxhlet extraction, many advanced solvent extraction techniques have been explored over the years, including supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), ultrasonic-assisted extraction (UAE), and microwave-assisted extraction (MAE). These techniques require less time and volumes of solvents than those during soxhlet extraction [47]. Vilaplana et al. applied MAE for the removal of TBBPA and decabromodiphenyl ether (Deca-BDE) from virgin high-impact polystyrene (HIPS) and standard samples from real WEEE. They found that complete extraction of TBBPA took place when they used a combination of polar/nonpolar solvent system (isopropanol/n-hexane) and high extraction temperatures (130°C). On the other hand, in case of Deca-BDE, there were obtained lower extraction yields due to its high molecular weight and its nonpolar nature [47].

In another study [48], UAE and MAE were investigated for the recovery of TBBPA from real WEEE samples that consisted of ABS, polypropylene (PP), polycarbonate (PC), and blends of ABS/PC. From the results obtained it was proved that MAE was more efficient in extracting TBBPA than UAE, especially in case of ABS polymers. The optimal solvent media was isopropanol: n-hexane (1:1), which is a binary mixture of a polar –nonpolar solvent, whereas pure isopropanol, as a solvent, could not result in complete extraction of TBBPA [48].

As mentioned previously, SFE has also attracted a lot of attention as regards the degradation of brominated flame-retarded plastics from WEEE, because of the supercritical fluids' unique properties, such as high density, low viscosity, varied permittivity related to pressure, and high mass transfer, as well as the fact that their viscosity, density, and diffusion coefficient are very sensitive to changes in temperature and pressure. Supercritical fluids appear at temperature and pressure higher than their critical state. Supercritical CO₂ is the most widely used fluid in SFE, since it presents remarkable advantages, including: low critical point, low cost, ease of availability, non-toxicity, recyclability, and simplicity as regards its operation. Water is also, a cheap, nontoxic, and easily available fluid, but it has a relatively high supercritical point [49].

Onwudili and Williams [50] studied supercritical water ($T > 374^{\circ}\text{C}$ and $P > 22.1\text{ MPa}$) due to the fact that it presents different characteristics in comparison with organic solvents. They focused on ABS and HIPS, since they are some of the most representative brominated plastics in WEEE and degraded them in supercritical water (up to 450°C and 31 MPa) in a batch reactor. Furthermore, they investigated the effect of alkaline additives, NaOH and Ca(OH)₂, by treating the plastics both in the absence and in the presence of them. They noticed that oils, which were the main reaction products, had almost zero bromine and antimony content in the presence of NaOH additive [50]. In another work, [51] there was used subcritical water for the debromination of printed circuit boards (PCB) that contained BFR in a high-pressure batch reactor. They applied three different temperatures, 225, 250, and 275°C , and noticed that debromination increased with increase in temperature. After the debromination of the samples, they applied recycling methods, such as pyrolysis.

Apart from water, organic solvents such as acetone, methanol, and ethanol can also be used as supercritical fluids in chemical recycling of plastics from WEEE [52]. For instance, Wang and Zhang [52] used various supercritical fluids: acetone, methanol, isopropanol, and water with a view to studying the degradation of waste computer housing plastics that contained BFR. They came to the conclusion that

supercritical fluid process was efficient for the debromination and decomposition of brominated flame-retarded plastics enabling the recycling of bromine-free oil. As for solvent's efficiency in debromination, the order was the following: water > methanol > isopropanol > acetone.

It should be highlighted here that although SFE technology is considered as a green choice for resource recovery, it has some important drawbacks as well. One of the main obstacles in such technology is the fact that only equipment able to withstand high pressures and temperatures and very resistant to corrosion can be used. These demands, however, increase the cost a lot, and along with the large amount of energy that is required, prevent its industrial implementation [49].

To avoid the latter difficulties, there are other approaches that can be applied in case of flame-retarded plastics. One such approach is that of *two-step pyrolysis*. In this case pyrolysis steps affect the obtained products and by controlling the pyrolysis parameters, the formation of brominated products can be suppressed, without requiring resistant equipment. For instance, according to Ma et al. [53], who applied single- and two-step pyrolysis of waste computer casing plastics, two-step pyrolysis led to the transfer of the biggest part of brominated compounds into the liquid fraction of the first step, in comparison with that of the second step. This observation showed that high-quality oils with low bromine content can be obtained when applying two-step pyrolysis [53].

Co-pyrolysis is another worth mentioning process, in which two or more materials are pyrolyzed together, with the aim of improving the quality and quantity of the liquid fraction, without the need of a pretreatment step prior to pyrolysis. Co-pyrolysis is based on the synergistic effect of different materials that can react together during pyrolysis and leads to a reduction of the total volume of waste, since more waste (e.g., polymers) is consumed as feedstock. The mechanisms of co-pyrolysis and pyrolysis are almost the same, and it is performed at moderate operating temperatures and in the absence of oxygen [54]. Ma et al. [55] examined co-pyrolysis of HIPS, which contained decabromodiphenyl oxide (DDO) as the BFR and antimony trioxide (Sb_2O_3) as a synergist, in the presence of PP (at three different mass ratios) in order to investigate PP's effect on the bromine reduction. From the results obtained it was proved that PP's presence not only increased the yield of various, valuable products, such as toluene, styrene, etc., in the pyrolysis oil, but also led to a reduction of the bromine content [55].

As described above, during co-pyrolysis, the end-of-life brominated plastics along with other (plastic) waste are pyrolyzed together and result in bromine reduction in the derived pyrolysis oil, without any kind of pretreatment before the pyrolysis process. Another idea, in order to reduce bromine while avoiding the extra pretreatment step, is that of the *use of additives or catalysts* during pyrolysis. According to current literature data, many types of *additives*, such as NaOH, $\text{Ca}(\text{OH})_2$, CaO, scallop shell, and others, have been investigated for their effect on the reduction of bromine [56, 57]; but of course the degree of debromination depends on the types of the polymers and additives used.

During *catalytic pyrolysis*, as mentioned in the introduction, catalysts influence products' distribution. This has to do not only with favoring the formation of valuable products but also with reducing the formation of the undesirable ones, such as the brominated compounds. Here there are given some representative examples of catalysts that were examined for their debromination effect. In a recent work of Ma et al. [58], there were examined three zeolite catalysts: HY, H β , and HZSM-5 along with two mesoporous catalysts: all-silica MCM-41 and active Al_2O_3 , for their influence on products distribution. They carried out catalytic pyrolysis of brominated flame-retarded HIPS and observed that catalysts enhanced the formation of

valuable, aromatic compounds, such as toluene, styrene, etc., and, in the meantime, enhanced the debromination of the liquid fraction [58].

In another study [59], there was investigated activated Al_2O_3 for catalytic pyrolysis of waste PCB examining three different temperatures: 400, 500, and 600°C, as well as different ratios of PCB: Al_2O_3 . They noticed that higher temperatures improved the oil production; and the optimal results as regards the production of light oil and the debromination were obtained at 600°C. The catalyst's presence increased the formation of light hydrocarbons and in the meantime the debromination. Wu et al. [60] carried out catalytic pyrolysis of brominated HIPS that also contained Sb_2O_3 , in the presence of red mud, limestone, and natural zeolite, with a view to eliminating bromine and antimony from the pyrolysis oil. They found that in their presence, the total amount of bromine (and antimony) in the oil was reduced. Nevertheless, red mud was the most efficient catalyst in reducing bromine, since Fe_2O_3 present in red mud reacted with HBr that was formed during the degradation of the BFR and hindered the formation of the volatile SbBr_3 ; in the meanwhile, its zeolite property catalytically destroyed the organobromine compounds [60].

Co-pyrolysis can also take place in the presence of catalysts, known as *catalytic co-pyrolysis*. For instance, in [61], they applied catalytic co-pyrolysis of PCB in the presence of (more waste) high-density polyethylene (HDPE) and PP, with a view to reducing the brominated compounds formed. Apart from using other waste polymers as co-feeding for catalytic pyrolysis, there have been reported studies (e.g., [62]) where additives such as CaCO_3 and Fe_3O_4 were investigated along with the catalysts for their debromination efficiency in the pyrolysis oil. A two-step process (pyrolysis and catalytic upgrading) can also occur when catalysts are used and enable the conversion of e-waste plastics into high-value materials. In such cases the first step involves the pyrolysis of brominated plastics so as to decompose them; and the second one involves the catalytic upgrading of their products into valuable and bromine-free products. This two-step process is very useful when dealing with real WEEE plastics that contain impurities, etc., that may result in the catalysts' deactivation if direct catalytic pyrolysis occurs. It can be divided into two categories, based on which pyrolysis products are used as raw material; the first category includes pyrolysis vapors as raw material, and the second one includes pyrolysis oil [9].

An example that belongs in the first category is [63], in which they examined a small-scale two-stage pyrolysis and catalytic reforming of brominated flame-retarded HIPS at 500°C using four zeolites: natural zeolite (NZ), iron oxide-loaded natural zeolite (Fe-NZ), HY zeolite (YZ), and iron oxide-loaded HY zeolite (Fe-YZ). They observed that the bromine content in the oil was reduced in the presence of catalysts; however, Fe-NZ and Fe-YZ showed better debromination results, due to the reactions between the iron oxide that was loaded and the derived HBr. Compared with Fe-YZ, Fe-NZ did not greatly change the pyrolysis products and so preserved the valuable single-ring aromatic compounds. As a result, Fe-NZ was more effective and feasible for the feedstock recycling of brominated HIPS via the pyrolysis process.

Areepasert and Khaobang [64] studied pyrolysis and catalytic reforming of a polymer blend (ABS/PC) and PCB, at 500°C, using some conventional catalysts: Y-zeolite (YZ), ZSM-5, iron oxide-loaded Y-zeolite (Fe/YZ), and iron oxide-loaded ZSM-5 (Fe/ZSM-5), as well as some alternative, green catalysts: biochar (BC), electronic waste char (EWC), iron oxide-loaded biochar (Fe/BC), and iron oxide-loaded electronic waste char (Fe/EWC). They found that all catalysts increased the single-ring hydrocarbon products of the liquid fraction. As for the debromination, it was noticed that in case of ABS/PC, the most effective catalyst

was Fe/BC, whereas in case of PCB, it was Fe/EWC. Also, they concluded that the green-renewable catalysts could be a promising choice for removing bromine from the liquid fraction [64]. Ma et al. [65] investigated pyrolysis-catalytic upgrading of brominated flame-retarded ABS. The process took place in a two-stage fixed bed reactor; and the second stage included the catalytic upgrading of the vapor intermediates that were obtained from pyrolysis (first stage). The examined catalysts were: HZSM-5 and Fe/ZSM-5. Both catalysts had high catalytic cracking activities that led to an increased yield of oil and to a reduction of the bromine in the liquid fraction.

3. Conclusions

This chapter briefly presents all methods that are used nowadays for plastic recycling, including primary recycling, energy recovery, mechanical recycling, and chemical recycling. The advantages and disadvantages of each method are discussed. Emphasis though is given on chemical recycling and mainly, pyrolysis, due to its many benefits, which are fully described. Furthermore, three case studies that involve some difficulties in plastic recycling are thoroughly investigated. The first one includes the case of polymeric blends, where the coexistence of different plastic materials makes their recycling more difficult. The second one is focused on the recycling of plastics that come from multilayer packaging. The main obstacle in this case lies in the fact that multilayer packaging comprises various, different materials, such as paper and metals, apart from the plastics, so extra attention is required for their separation and recycling. The last case study that is presented here is that of brominated flame-retarded plastics from WEEE, since in such cases direct recycling is not that easy due to the formation of undesirable brominated compounds and more often than not a pretreatment step prior to their recycling is necessary. Taking into account the mentioned difficulties, the aim of this chapter is to present and analyze various recent literature data along with suggestions on how to overcome the mentioned problems.

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