We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 3

Chemical and Thermochemical Recycling of Polymers from Waste Electrical and Electronic Equipment

Dimitris S. Achilias and Eleni V. Antonakou

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/59960

1. 1. Introduction

The production of electric and electronic equipment (EEE), including personal computers, compact disks, TV sets, refrigerators, washing machines, toasters and many other daily-life items, is one of the fastest growing areas of manufacturing industry today. The rapid development in the EEE technology combined with a short life cycle and a variety of uses, at least for most of the products, poses a significant issue as far as their disposal is concerned. This has resulted in a continuous increase of Waste Electric and Electronic Equipment (WEEE) with some representative numbers: in the EU only, 9.5 million tones have been disposed in 2008 and this is expected to increase to 12.3 million tones in 2020 [1, 2]. While there is no generally accepted definition of electronic waste in most cases electronic waste consists of electronic products that were used for data processing, telecommunications, or entertainment in private households and businesses and are now considered obsolete, broken, or unrepairable (Figure 1). Despite its common classification as a waste, disposed electronics are a considerable category of secondary resource due to their significant suitability for direct reuse and material recycling. In view of the environmental problem involved in the management of WEEE, many countries and organizations have drafted national legislation to improve the reuse, recycling and other forms of recovery of such wastes so as to reduce disposal. The EU in an attempt to deal with the necessity of a meaningful recycling system and at the same time to preserve oil and fossil fuel resources has introduced 2002/96/EC directive [2], which demands 70–80% of WEEEs to be recovered in the form of energy and/or materials [2]. The directive aims at the minimization of the percentage of the solid wastes which will be landfilled or incinerated the full conversion of all waste streams (including plastics) through thermal or mechanic treatment by 2020.

INTECH
open science | open minds

© 2015 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.



Figure 1. Waste electrical and electronic equipment

The necessity of the plastic wastes recycling becomes more urgent mainly due to the following reasons:

- Significant increase in plastics recycling, which leads to a successive increased volume in the final receptors.
- Significant low life cycle (less than a month for a high fraction of plastics).
- Low biodegradability and thus accumulation in the final receptors.

It should be mentioned that most of the polymers do not have a direct influence to humans due to toxicity but mainly due to their increased waste volume.

There are three main recycling methods for polymers treatment and all three find applications in the WEEEs recycling.

- primary
- secondary (mechanical)
- tertiary
- quaternary

Primary recycling is a term referring to the recycling of non-useful or problematic plastics which have not been used by the consumers and their quality has not deteriorated significantly. It is the simplest recycling method and its main advantage is the low cost, while the main disadvantage is that it cannot be used in products that have already been used.

Secondary recycling refers to the recycling of plastics that have been used by the consumers. During this form of recycling the plastics, after some form of treatment such as cleaning, decrease in size and separate into the mixture components, melt and then reform. The main

http://dx.doi.org/10.5772/59960

advantage is that the quality of the final product is lower since the macromolecular chains might be broken after the exposure to the treatment techniques mentioned above.

Tertiary recycling refers to the process of breaking the polymeric bonds which leads to the production of either the initial monomers or fractions of oligomers. It applies mainly to condensation polymers such as polyesters and polyamides. Breaking of the polymeric chains can be done either chemically (chemical recycling) or with the use of heat (thermolysis). It is considered to be the method with the higher quality and value products. It is widely applied in condensation polymers such as polyesters and polyamides.

Quaternary recycling is related to the energy recovery of the plastic wastes in general and it includes mainly incineration. The method takes advantage of the high energy value of the waste polymers and significantly reduces their volume. The degradation of waste plastics into fuel represents a sustainable way for the recovery of the organic content of the polymeric waste will also help preserving petroleum and oil resources. The disadvantage of the method is that, mainly through incineration, a series of dangerous byproducts, such as dioxins, are been emitted.

The main problems concerning polymers recycling which do not allow their large scale applications are the variability of the product composition, the presence of polymers mixtures and the use of additives. The WEEE recycling is challenging, mainly because these types of wastes consist of many and different materials: metals, glass, elastics and plastics. Plastics usually contain metals incorporated in their structure and for this reason the separation and the mechanical recycling of the WEEE waste components contains a series of technical and economic challenges [3]. A typical WEEE fraction contains 20-30 % plastics. The composition can vary, but an example of the breakdown from actual collected WEEE is: acrylonitrile-butadiene-styrene (ABS) 30%, high impact polystyrene (HIPS) 25%, polycarbonate (PC) 10%, PC/ABS 9%, polypropylene (PP) 8%, poly(phenylene ether) (PPE)/HIPS 7%, poly(vinyl chloride) (PVC) 3%, polystyrene (PS) 3%, polyamide (PA) 3%, poly(butylene terephthalate) (PBT) 2% [4, 5]. A schematic representation of a WEEE composition appears in Figure 2.

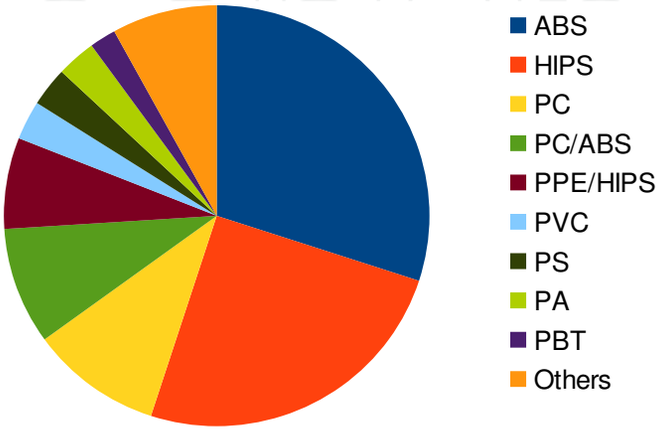


Figure 2. Typical WEEE composition

2. Mechanical recycling of WEEEs using the dissolution/reprecipitation technique

During this technique the polymer can be separated and recycled using a solvent/non-solvent system. Separating and recycling polymers by this method appear to be technologically feasible and of considerable commercial interest. The effect of different solvent/nonsolvent systems and dissolution temperatures on the % recovery of polymers from the corresponding model polymers or WEEE was investigated by Achilias et al. [6].

The main parameters affecting the dissolution/reprecipitation technique are: solvent/ non-solvent type and portion, dissolution temperature and time and polymer concentration. All of them must be optimized in order to minimize polymer degradation, cost and environmental impact of the recycling process. With respect to the dissolution, solvents used in this recycling process are selected based on the principle that polymers in general, can be dissolved in solvents having similar values of the solubility parameter, δ. A good solvent to be used in polymer recycling should combine high dissolution ability and volatility that will allow its removal with minimum chain degradation, with low cost and toxicity. The solvents used were dichloromethane, toluene, chloroform and acetone, while methanol was always employed as a non-solvent. The dissolution temperatures investigated were 25°C, 50°C and 100°C, in the cases of dichloromethane and toluene, while only 25°C and 50°C in the cases of acetone and chloroform (below their boiling point). © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E., Koutsokosta E., Lappas A. Chemical recycling of polymers from WEEE. J. of Applied Polymer Science, 2009; 114, 212-221 [6]

The effect of solvent type, dissolution temperature and polymer concentration on the % recovery of three model polymers commonly found in WEEEs (i.e. ABS, PC and PS) appears in Table 1. Polymer recoveries were high enough at all experimental conditions. An increase in dissolution temperature leads to increased polymer recovery values, while an increase in polymer concentration to slightly lower. The system dichloromethane/methanol was found to produce high PC recoveries even at low dissolution temperatures. For PS, both dichloromethane and toluene could be used as solvents with higher recoveries at increased dissolution temperatures. For ABS high recoveries were measured when using dichloromethane at 100°C but also with acetone at lower temperatures. Since acetone can dissolve ABS at room temperature, eliminating thus the risk of thermal degradation at elevated temperatures, it has been proposed as the best solvent for ABS in this recycling technique. © [2015] IEEE. Reprinted, with permission, from Achilias et al. Chemical recycling of polymers from WEEE. J. of Applied Polymer Science, 2009; 114, 212-221 [6].

Apart from model polymers, the recovery of the specific polymer from the plastic part of several WEEEs was also investigated. Results under different experimental conditions appear in Table 2. The recovery of PC from compact disks was high enough (98 wt.-%) at the specific conditions used, in accordance with results of the model polymer. Concerning the system acetone/methanol, although it resulted in good recoveries when used in model ABS it was not effective in WEEEs based on ABS (i.e computer monitor and electronic toy). For all different

Solvent/Nonsolvent	Temperat (°C)	Polymer concentration (g/100 mL)	Polymer		
			ABS	PC	PS
Dichloromethane/Methanol	25	5	86	98	92
Dichloromethane/Methanol	50	5	89	98	94
Dichloromethane/Methanol	100	5	96	98	98
Dichloromethane/Methanol	25	10	84	95	
Dichloromethane/Methanol	50	10		97	
Acetone/ Methanol	25	5	90		
Acetone/ Methanol	50	5	94		
Chloroform/Methanol	25	10		95	
Chloroform/Methanol	50	10		96	
Toluene / Methanol	25	5			93
Toluene / Methanol	50	5			95
Toluene / Methanol	100	5			97

Table 1. Polymer recovery (wt.-%) by the dissolution/reprecipitation technique from model polymers © [2015] IEEE. Reprinted, with permission, from Achilias et al. Chemical recycling of polymers from WEEE. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

WEEEs, based on ABS the best solvent was found to be dichloromethane at 100°C with recoveries greater than 90 wt.-%. Finally, the recovery of PS from the WEEE based on this polymer was high enough at both solvents used (i.e. dichloromethane and toluene). © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from waste electric and electronic equipment. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

WEEE	Polymer	Solvent/nonsolvent	Temperature (°C)	Recovery (wt.-%)
Computer monitor	ABS	Dichloromethane/Methanol	100	91
		Toluene/Methanol	100	70
		Acetone/Methanol	25	68
TV set	ABS	Dichloromethane/Methanol	100	96
		Toluene/Methanol	100	69
		Acetone/Methanol	25	90
Electronic toy	ABS	Dichloromethane/Methanol	100	90
		Toluene/Methanol	100	61
Compact Disk	PC	Dichloromethane/Methanol	50	98

WEEE	Polymer	Solvent/nonsolvent	Temperature (°C)	Recovery (wt.-%)
Radio	PS	Dichloromethane/Methanol	100	98
		Toluene/Methanol	100	95
Vacuum cleaner	PS	Dichloromethane/Methanol	100	95
		Toluene/Methanol	100	91
Electronic toy	PS	Dichloromethane/Methanol	100	95
		Toluene/Methanol	100	97

Table 2. Polymer recovery by the dissolution/reprecipitation technique from the plastic part of different WEEE © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from waste electric and electronic equipment. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

3. Chemical and thermo-chemical recycling methods

Thermal cracking or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen (usually in a nitrogen atmosphere) to yield valuable products (e.g. monomers, or fuel-type oils). During pyrolysis at increased temperatures, depending on polymer type, the monomer can be produced in a large amount (i.e in poly(methyl methacrylate)), or a fuel-type liquid fraction, occurring mainly in polyolefins (LDPE, HDPE, PP), or other secondary useful products. An overview of the science and technology of pyrolysis of waste plastics has been recently presented in an excellent book by Scheirs and Kaminsky [7].

Thermal cracking (pyrolysis) of WEEE streams is receiving increasing attention, due to the potential recovery of either monomer(s) or secondary valuable materials, leading to a more sustainable waste management. Disadvantages of pyrolysis are related to the variable product composition and the low selectivity concerning the respective monomers and /or products of commercial value. The use of suitable catalysts in the pyrolysis process can offer the possibility to control the selectivity towards the desired products.

A significant number of electrical and electronic equipment has been studied in the recent literature. Kowalska and his team [8] reported thermogravimetric studies of two types of electronic wastes: a mixture of three types of printed circuit boards and a mixture of electronic junctions with metal wires. Despite the brominated and chlorinated flame retardants present in the two samples (which remain one of the main challenges in the pyrolysis process), preliminary HPLC analysis of the liquid fraction produced indicated that it consists of a series of two to four unsaturated ring hydrocarbons and it could potentially be used as a fuel. De Marco et al. [3] have reported the pyrolysis in an autoclave of four types of real WEEEs streams: wires of polyethylene (PE), table phones, mobile phones and printed circuit boards (PCB). They found that pyrolysis liquids vary significantly depending on the WEEE pyrolysed. Molto et al. [9] reported the pyrolysis and combustion of different parts of a mobile phone (printed circuit board, mobile case and a mixture of both materials) at 850 °C in a horizontal laboratory

http://dx.doi.org/10.5772/59960

furnace. They found the liquid fraction to consist of mainly phenols and hydrocarbons. More than 100 compounds have been detected in the liquid phase, most of them straight chain and aromatics. Acomb et al. [10] studied the pyrolysis–gasification of a plastic waste collected from a commercial WEEE recycling plant, mainly consisting from waste computer monitors and television sets, by using a two-stage reaction system in order to produce hydrogen. Hall et al., pyrolysed fire retarded high impact polystyrene using a fluidized bed reactor [11]. Although the emphasis was on the bromine distribution on the pyrolysis products, the yields and compositions of the main fractions were also reported. In a later study of the same research group, three different plastic fractions from commercial waste electrical and electronic equipment (WEEE) processing plant were collected and investigated through batch pyrolysis. The first plastic was from equipment containing cathode ray tubes (CRTs), the second from refrigeration equipment, and the third from mixed WEEE. Analysis of the pyrolysis products was provided and the pyrolysis oils were found to contain valuable chemical products while the pyrolysis gases were mainly halogen free, making them suitable to be used as a fuel [12]. Pinto et al. [13] investigated the influence of several catalysts on product distribution from plastic waste pyrolysis. The waste under study had the typical composition of Portuguese municipal solid wastes (68% PE, 16% PP and 16% PS) while the catalysts selected were zeolites and a series of metallic catalysts. Similar results were obtained from the catalytic and non-catalytic runs, in terms of total conversion, product yields and composition.

Advanced thermochemical methods for WEEE treatment appear to be a sustainable and promising recycling suggestion since, as it has widely been reported in the literature, not only a high percentage of the monomer can be recovered (up to 60%) but also a variety of compounds of a commercial and research interest such as low molecular weight hydrocarbons, tar (waxes and liquid with a high percentage of aromatic compounds) and carbon (elemental as well as activated carbon). Chemical recycling methods (such as solvolysis) could be interesting alternatives but they are not able to deal with the high content of additives or the mixtures of polymers which are usually present in the used WEEEs [14].

The process of pyrolysis seems as a promising alternative for the degradation of WEEEs since it can, under controlled conditions, deal with a number of organic macromolecules and decompose them into useful products (usually the polymers' monomer and other organic compounds, some of which, of a commercial value). Significant levels of lead, mercury, cadmium, chromium (VI), polybrominated biphenyls and polybrominated diphenylethers can be found in electrical and electronic waste [15]. Most of the inorganic material included (which in some cases is or can be related to a catalytic activity in the polymer's degradation) is located in the solid residue after the pyrolysis process, with a problematic exception in the case of halogenated compounds which usually lead to the formation of undesirable organo-halogenated compounds in all fractions. The problem becomes more demanding when the halogen atoms come from halogenated aromatic compounds (such as in the case of PC) since they require more energy in order for the bonds to break, not only because of the bond energy of the $C_{aromatic}$–X bond which is higher compared to $C_{aliphatic}$–X bond, but also because of the lack of favorable geometry which will have as a result an increase in the activation energy of the reaction [15].

Williams [16] in a recent review paper reported the use of pyrolysis for the treatment of wastes from electronic printed circuit boards as a recovery method for useful products such as metals, liquid and gaseous products as well as glass fibres. He also stated that the circuit boards contain significant concentrations of bromine in the form of bromine containing flame retardants, which also appears in the liquid fraction in the form of brominated organic compounds, a property which could possibly affect the the potential end uses of the produced oil. It seems that a meaningful debromination method could be a determining step which could be crucial for the economic viability of the recycling method.

Vasile et al [15] attempted to improve the quality of the pyrolysis oil produced from WEEE during catalytic hydrogenation, in order to find applications as fuel or source of chemicals. Apart from the halogen removal, the removal of nitrogen and sulphur were also among the aims of this study. The authors have introduced a conventional acidic catalyst (DHC-8) as well as a neutral catalyst in the hydrogenation process and showed that both catalysts improved the quality of the pyrolysis oil by removing oxygen, nitrogen, halogen and sulphur containing compounds and thus improving its stability. A main disadvantage of the catalytic process is that the amount of aromatics in the produced oil remained high and this could affect a possible application of the produced oil if it is to be directly used as a fuel.

Balart et al [17] investigated the thermal properties of PC-ABS mixtures obtained from WEEE by using thermogravimetric analysis (TGA). Kinetic parameters, such as apparent activation energies (Ea) were calculated by the application of the autocatalytic method, which has been successfully applied to other polymer systems. Activation energies determined from TGA data were practically independent of heating rates in the case of ABS-based mixtures, while there seems to be some influence of the heating rates in the PC-based mixtures. The authors suggest that the thermal degradation mechanism of these samples is composed of several complex processes, and that the use of a complex stabilizing system will be necessary for an efficient stabilization of these mixtures but also a limitation of the action of the main degradation processes. The same authors [18] reported a decrease on mechanical properties of the PC-ABS blends when compared to the original polymers in compositions in the range 20–80 wt% PC.

Among the polymeric materials used in electronic equipment the most important are the terpolymer of Acrylonitrile-Butadiene-Styrene (ABS), polycarbonates (PC) and High Impact Polystyrene (HIPS) and recycling methods for these type of plastics are presented next.

4. PC recycling

Polycarbonate poly(bisphenol A carbonate) (PC) is an important engineering plastic featuring good optical clarity, high impact resistance and ductility at room temperature and below. Because of these attributes, PC is used in a wide variety of applications including electrical and electronic equipment, digital media (e.g. CDs, DVDs), automobiles, glazing in the building and construction industry, sports safety equipment and reusable food and drink containers. A major concern when PC is used as plastic packaging, and especially in baby bottles, is to do with the release of the toxic bisphenol-A (BPA) into the food.

http://dx.doi.org/10.5772/59960

Recycling of polycondensation polymers, such as PC, via pure chemical routes can be summarised by the following technologies: hydrolysis (in acid, neutral or alkaline environment), glycolysis, hydroglycolysis, methanolysis and aminolysis [19-23]. These techniques have been recently reviewed [19]. Most of the depolymerisation processes lead to decomposition of PC into its original monomer, bisphenol-A. However, due to the insolubility of PC in some of these reagents (e.g., water or methanol), depolymerisation requires severe conditions, such as long reaction time and high temperature and pressure, or even take place under supercritical conditions and in the presence of a large amount of concentrated bases or acids [23]. © [2015] IEEE. Reprinted, with permission, from Tsintzou G.P., Antonakou E.V., Achilias D.S. Environmentally friendly chemical recycling of poly(bisphenol-A carbonate) through phase-transfer catalysed alkaline hydrolysis under microwave irradiation. Journal of Hazardous Materials 2012; 241-242, 137-134 [37].

Several research groups have suggested the introduction of different types of solvent systems and catalysts [24-29], such as methylene chloride with ammonia and phenol in combination with an alkali catalyst. There are two main problems with the use of an effective solvent system in the degradation process: one problem has to do with the high cost of the separation of the product (and the high content of additives included in some of the polymer blends), and the second problem is the environmental and safety issues related to the use of toxic organic solvents. Alkali-catalysed methanolysis has been used by Hu et al. [28], Pinero et al. [30], Chen et al. [31] and Liu et al. [32]. Supercritical or near-critical conditions for the recovery of the BPA monomer and DMC have been employed [14,33]. Moreover, ionic liquids have been used as catalysts during the methanolysis of polycarbonate [34], and the characteristics of depolymerisation in supercritical ethanol were also investigated [35]. As might be expected, the most environmentally friendly reagent in PC degradation is water and the chemical recycling process of hydrolysis. However, one study found that in liquid water at 573 K, polycarbonate still remained even after 50 min [5]. Therefore, high-pressure, high-temperature water, which is also referred to as supercritical water, has been used for rapid hydrolysis without a catalyst [5,36]. © [2015] IEEE. Reprinted, with permission, from Tsintzou G.P., Antonakou E.V., Achilias D.S. Environmentally friendly chemical recycling of poly(bisphenol-A carbonate) through phase-transfer catalysed alkaline hydrolysis under microwave irradiation. Journal of Hazardous Materials 2012; 241-242, 137-134 [37].

4.1. Microwave assisted chemical recycling of PC

Nowadays, recycling using some environmentally friendly degradation method is of paramount importance. To this direction, microwave irradiation was employed by Tsintzou et al. [37] to study the chemical recycling of PC in relatively mild experimental conditions that do not require large amounts of chemicals or energy. The method of hydrolysis in an alkaline (NaOH) solution was applied to poly(bisphenol-A carbonate) to depolymerize it into its starting monomer, BPA. The hydrolysis mechanism appears in Figure 3. It was found that degradation hardly occurs at relatively low temperature, except if a phase-transfer catalyst (1-hexadecyl trimethyl ammonium bromide) is employed. The combination of irradiation time and NaOH concentration resulted in similar results, meaning that increased alkaline concentrations require less time. In all conditions, degradation of PC was minimal at temperatures below 110 °C (Fig. 4). A significant increase was observed in the region from 130 to 160 °C and

degradation values more than 80% were measured at 170 °C. Since the glass transition temperature, Tg, of PC is near 150 °C, it seems that its alkaline hydrolysis under microwave irradiation, is facilitated when the reaction temperature approaches this value. A polymer at its Tg changes from a stiff (hard) to a softer rubbery state, which causes the polymer to swell more easily in response to the alkaline reagent and hence facilitates the reaction. Finally, the importance of applying the microwave irradiation during PC alkaline hydrolysis was confirmed, since at 160 °C, high PC decomposition was achieved after only 10 min of reaction with 10% NaOH as compared with conventional heating, where more than 8 h is needed for similar results.

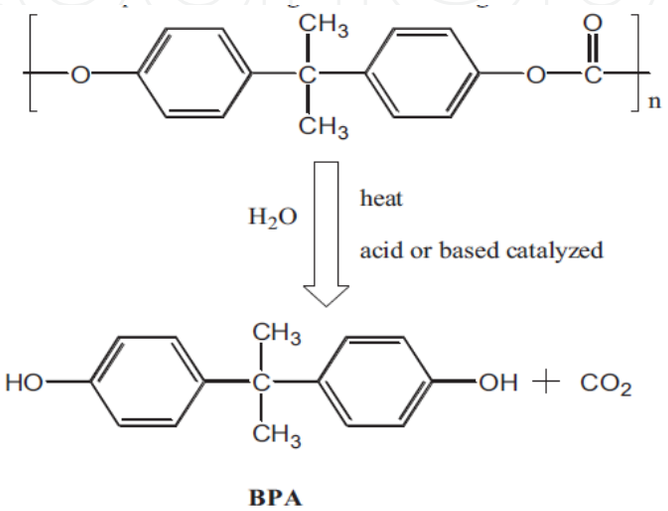


Figure 3. Mechanism of PC hydrolysis to its monomer BPA

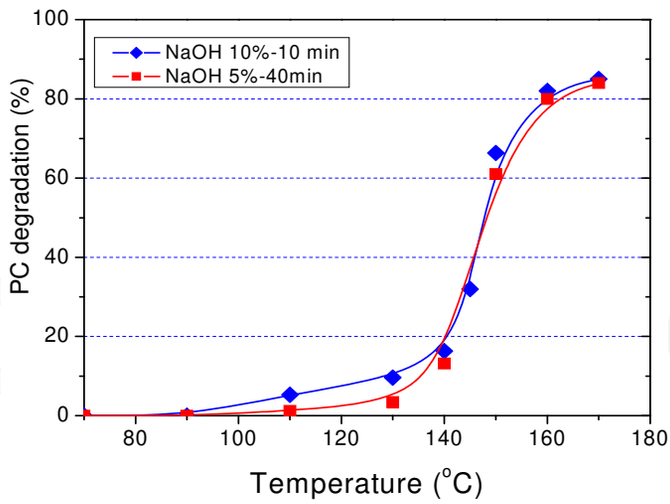


Figure 4. Effect of depolymerization temperature on the amount of polycarbonate (PC) reacted during microwave-assisted PC alkaline hydrolysis after 40 min at 5% w/v NaOH, or 10 min at 10% w/v NaOH [37]. © [2015] IEEE. Reprinted, with permission, from Tsintzou G.P., Antonakou E.V., Achilias D.S. Environmentally friendly chemical recycling of poly(bisphenol-A carbonate) through phase-transfer catalysed alkaline hydrolysis under microwave irradiation. Journal of Hazardous Materials 2012; 241-242, 137-134 [37]

In the hydrolysis products, BPA monomer was obtained and identified by FTIR measurements. However, from GPC measurements, the average molecular weight of the PC residues only

slightly decreased even after 70% degradation. These results confirm that in alkali solutions, the rate of polymer hydrolysis is so fast that the reaction occurs mainly at the surface and degradation follows a 'surface erosion' mechanism. The products, such as monomer and oligomer, are released from the surface, and the polymer mass rapidly decreases, though its number average molecular weight ($\overline{M}_N$) is almost constant. Diffusion of the reactant into the bulk phase is slower than the rate of the chemical reaction. In contrast, during the 'bulk erosion' mechanism occurring under acidic conditions, the reaction rate is so slow that the hydrolysis proceeded in the bulk phase of the polymer. The polymer mass does not change during the early stage of the reaction, while ($\overline{M}_N$) continuously decreases with the reaction time. The latter mechanism seems to be dominant during PC hydrolysis in high-pressure and high-temperature steam.In addition, the same technique was applied to the degradation of waste compact disks. Depolymerization as high as 85% was achieved at 160 °C using a 10 % NaOH solution after microwave irradiation for 10 min [37].

Nikje, 2011 [38] also studied glycolysis of PC from waste compact discs with EG using microwave irradiation in the presence of NaOH as catalyst in order to obtain the monomer BPA. The influence of various parameters, such as concentration of the alkali metal catalyst and microwave irradiation power on product yield was reported in detail. The optimum concentration of NaOH was found to be 2 wt % and the optimum microwave power was 600 W. BPA recovery was affected by the reaction time and reached to an optimum yield at 500 s [38].

4.2. Thermo-chemical recycling of PC

In this section, results are presented for the pyrolysis of waste CD's and compared to corresponding from model PC. It should be pointed out here that in order to remove the Al layer on the CD, initially it was pre-treated with a NaOH solution. The model polycarbonate used in this investigation was based on poly(bisphenol A carbonate), the same used in the electronics industry because of its desirable combination of toughness and thermal stability.

Results on the product yield from the fixed bed pyrolysis of either model poly(bisphenol A carbonate) or the compact disk appear in Table 3. The model PC pyrolysed to form a large amount of oil (i.e. 63 wt.%) a smaller amount of gas (6.6 wt.%) while leaving a rather large amount of residue (30.4 wt.%). The total degradation of poly(bisphenol A carbonate) (i.e. 70 wt.%) was slightly lower from that reported by Chiu et al. [39] (i.e. 76 wt.%) using a quartz reactor operating at 550^{o}C after 1h degradation. The pyrolysis of the CD produced a much larger amount of liquid fraction (80.4 wt.%) with almost the same gaseous fraction (8.6 wt.%) while leaving a much smaller amount of residue (11 wt.%). In the only one published paper on pyrolysis of waste CDs the amount of residue measured was much larger (i.e. 39%), while a lower liquid fraction was measured (i.e 47%) [40]. This could be due to the lower pyrolysis temperature (i.e. 450^{o}C) used by these author [40].The pyrolysis oil in both cases had a low viscosity and was brown in colour. Very recently, Hall and Williams [41], found approximately a similar composition from a mixed WEEE plastic (i.e. oil product 70.6%, gaseous fraction 7.8% and char plush ash 21.1%). © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from waste electric and electronic equipment. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

Polymer	Temperature (°C)	Gas (wt.%)	Liquid (wt.%)	Residue (wt.%)
Model PC	550	6.57	63.03	30.4
CD	550	8.64	80.36	11.0

Table 3. Product yield from the pyrolysis of model PC and a Compact Disk (wt % on polymer)

The mass composition of the pyrolysis gases (on a nitrogen free basis) is presented in Table 4. The presence of carboxyl units -COO- in the macromolecular chain of polycarbonates leads to the production of large amounts of CO_2 and CO in the gaseous fraction. Thus, the amount of carbon dioxide measured in the model PC gas released was 58% of the total fraction, while that from the CD pyrolysis was even more and nearly 66 wt.%. The amount of carbon monoxide was 21 wt.% in both cases. A smaller amount of CH_4 was also measured (17 wt.% and 6 wt.% from model PC and the CD, respectively), which is formed from the degradation of the methylene (-CH_3) branches of the polycarbonates. CO_2, CO and CH_4 consisted of 96 wt.% and 93 wt.% of the total gaseous fraction from model PC and CD pyrolysis, respectively. Pyrolysis gases from both samples investigated, contained also smaller amounts of H_2 and other C_2 – C_5 alkanes and alkenes. Very interesting was the comparison of results obtained from CD pyrolysis with those reported by Hall and Williams [41] on a mixed WEEE sample. The amounts reported by these authors on the gaseous fraction (i.e. CO_2 65 wt.-%, CO 15 wt.-% and CH_4 6 wt.-%) were very similar to those presented in this investigation. © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from WEEE. Journal of Applied Polymer Science, 2009; 114, 212-221.

	Sample	
Compound	**Model PC**	**CD**
Hydrogen, H_2	0.047	0.058
Carbon dioxide, CO_2	3.807	5.711
Carbon monoxide, CO	1.364	1.851
Methane, CH_4	1.097	0.547
Ethane, C_2H_6	0.060	0.131
Ethylene, C_2H_4	0.100	0.122
Propane, C_3H_8	0.010	0.008
Propylene, C_3H_6	0.063	0.065
Butane-Butene, nC_4	0.018	0.035
Pentane-Pentene, nC_5	0.008	0.010
Isopentane-Isopentene, iC_5	0.000	0.088
Hexanes-Hexenes, C_6	0.000	0.014
Total	*6.574*	*8.640*

Table 4. Composition of the gaseous fraction (wt % on polymer) from the pyrolysis of model PC and a Compact Disk © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from WEEE. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

http://dx.doi.org/10.5772/59960

The composition of the liquid fraction was analysed using GC-MS and the components identified are shown in Table 5. The largest component of the model PC oil was phenol (32.1%), followed by bisphenol A (16%) and cresol (12.9%). From the CD pyrolysis the monomer bisphenol A was detected in the largest amount (31.9%) followed by phenol (24.9%) and cresol (8.8%).

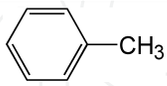
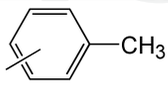
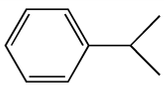
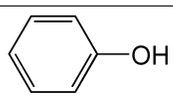
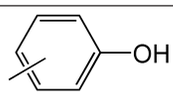
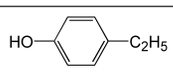
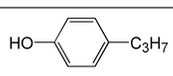
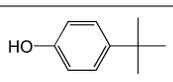
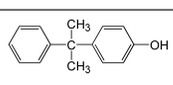
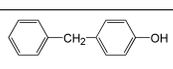
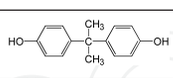
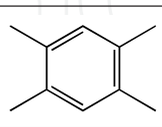
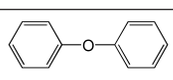
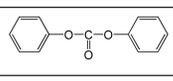
		Sample	
Compound	**Chemical formula**	**Model PC**	**CD**
Toluene		0.4	0.2
Xylene		0.4	0.1
Cumene		0.3	-
Phenol		32.1	24.9
Methyl phenol (cresol)		12.9	8.8
Ethyl phenol		2.8	5.3
Propylphenol / isopropylphenol		5.6	7.6
tert-butylphenol		0.4	0.3
4-(1-methyl-1-phenylethyl)- phenol		6.4	3.4
4-(phenylmethyl)- phenol		3.4	2.2
Bisphenol A		16.0	31.9
Other phenols		3.8	1.2
Tetramethyl benzene		9.9	9.3
Diphenyl ether		0.4	0.1
Diphenyl carbonate		0.3	0.4
Benzofuranes		0.9	0.2
Other aromatic compounds		4.0	4.1

Table 5. Compounds identified in the liquid pyrolysis fraction of model PC and Compact Disk (wt.-% on liquid produced) © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from WEEE. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

Large amount of phenols and bisphenol A in the oil fraction of PC and CD pyrolysis as well as from mixed WEEE plastic was also reported by Mitan et al. [40] and Hall and Williams [41], respectively. Other phenols, like ethyl-, propyl and tert-butyl phenols were also detected in quantifiable amounts, together with phenols having two phenyl rings in their molecular structure. Ethers and carbonates were recorded in smaller amounts, together with some benzene based compounds (i.e. tetramethyl benzene, toluene, xylene, cumene, etc.). The amount of benzofuranes was less than 1% in both samples. Increased pyrolysis temperatures may lead to increased amounts of PAHs and dibenzofuranes in the liquid fraction as it was found by Becker et al. [42]. A similar distribution of liquid products measured during pyrolysis of some polycarbonate materials has been reported in literature [43, 44, 38, 45]. © [2015] IEEE. Reprinted, with permission, from Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from waste electric and electronic equipment. Journal of Applied Polymer Science, 2009; 114, 212-221 [6]

According to Jang and Wilkie [43], the main thermal degradation pathways of PC follow chain scission of the isopropylidene linkages, rearrangement and alcoholysis/hydrolysis of carbonate linkages. Alcoholysis/hydrolysis of carbonate linkages produces alcohol compounds, such as those observed in large amounts also in this investigation (i.e. phenol, methyl phenol, ethyl phenol and isopropyl phenol), while phenyl or aliphatic end groups are primarily produced due to chain scission.[43, 44] Some carbonate linkages may react with alcohol end groups to form eventually char like structures. The presence of Bisphenol A in large amounts implies that hydrolysis/alcoholysis of carbonate linkage is the pathway for the formation of that compound.[43] Moreover, chain scission of the isopropylidene linkages and rearrangement of carbonate linkages form carbonate and ether compounds. Xanthone units and cyclic oligomers were not detected among the evolved products in nitrogen.[25] The number of liquid compounds produced from PC pyrolysis can be diminished using active metal catalysts, such as $ZnCl_2$ or $SnCl_2$ [39].

5. Recycling of HIPS

Polystyrene recycling can also be performed through a series of mechanical, chemical and thermal methods. High impact polystyrene (HIPS) is a less studied but promising material, especially for mechanical recycling technologies since its properties are not significantly affected even after multiple recovery cycles. During thermal treatment methods the liquid and gaseous products recovery depend significantly on the reaction conditions, while the catalytic methods favor the production of specific liquid and gaseous products.

High impact polystyrene (HIPS) consists of a composite material with a polystyrene base and a dispersed butadiene phase [46]. The chemical structure of HIPS appears in Figure 5. It appears to be one of the main fractions of the Waste Electrical and Electronic Equipment. It is produced through the free radicals polymerisation of the styrene polymer in the presence of butadiene aiming at a product with increased impact strength and toughness of polystyrene (PS) [47]. The properties of the produced composite material mainly depend on the percentage of the

http://dx.doi.org/10.5772/59960

butadiene in the initial polymer, which varies between 3-10 mol%. It is widely used in electrical and electronic equipment, in construction and packaging materials and in storage bottles, appliance parts, housewares, and interior parts in household electronics [48].

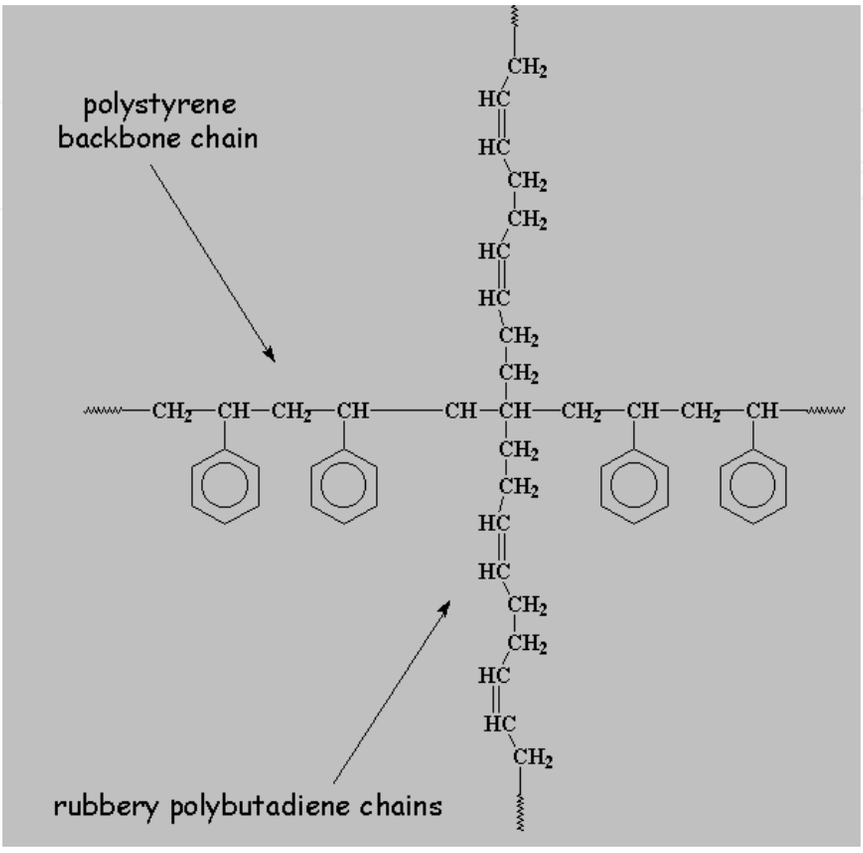


Figure 5. Chemical structure of HIPS. (www.chemsrv1.uwsp.edu)

5.1. Mechanical recycling

A recycling technique aiming at the study of the mechanical properties recycling of commercial ABS and HIPS and their mixtures has been suggested by Brennan et al. [49]. Previous studies have reported that when the polymers under study undergo multiple recycling series results are move obvious concerning properties related to impact resistance. It has also been suggested that most of the thermoplastic can be treated together with small quantities of other polymers with minimum effect on their mechanical properties, while their impact resistance can be further improved with the introduction of a suitable modifier. Recycling does not seem to have a significant effect on properties such as glass transition temperature or impact resistance concerning polymers like ABS and HIPS, while their malleability decreases significantly, especially in the case of HIPS. Generally, it is expected that the combination of small quantities of ABS in HIPS and HIPS in ABS will improve the mechanical properties that have been lost due to decomposition during recycling with an exception concerning impact resistance which can be improved with the introduction of a suitable modifier [49].

In another published work of Mural et al, mixtures of polypropylene (PP) and HIPS have been recovered mechanically from waste electronics. More specifically, mixtures of polymers have been produced with ratios PP/HIPS 30/70, 50/50 and 70/30 and their thermal properties have been studied with a variety of techniques such as DSC and TGA. Additionally, DMA analysis has shown the presence of two distinct glass transition temperatures (Tg) which correspond to PP and HIPS and are indications for the formation of a two phases morphology [50].

5.2. Pyrolysis

In one of the few studies on the thermal degradation of HIPS in the presence of a catalyst it has been reported that the introduction of a nickel catalyst results in an increased production of gases from the HIPS polymer [10]. Jakab and his team [51] have studied the thermal decomposition of four samples of HIPS in the presence of flame retardants by using methods such as TG/MS, Py-GC/MS and Py-MS. It has been found that the presence of flame retardants affects the thermal decomposition of HIPS, not as much in terms of thermal decomposition but mainly concerning the composition of the pyrolysis products. Some years later Grause and his co-workers, in an attempt to study the kinetics of the thermal decomposition reaction of HIPS [46] have used the method of thermogravimetric analysis (TGA) in samples of pure HIPS as well as HIPS in the presence of brominated flame retardant with heating rates between 2.5 and 10 K min^{-1}. The activation energy was found to be 200kJ mol^{-1}, using the Avrami-Eroféev kinetics. This value is at the range of the polystyrene decomposition activation energy so it seems that the effect of polybutadiene on the Eα is not significant. The flame retardants generally seem to reduce the activation energy value, while for higher percentages of weight loss (more than 80%) even higher values of Eα have been found, possibly due to the separate decomposition of polystyrene-polybutadiene in the presence of the retardants. Although the emphasis in both cases was on the study of the effect of the flame retardants on the pyrolysis process, a series of useful conclusions concerning the decomposition reaction kinetics could be extracted.

Marcilla and his team [52, 48] also worked on the catalytic pyrolysis of mixtures of Al-MCM-41 catalysts and a series of polymers and copolymers with a styrene base by the means of thermogravimetric analysis, and they reported that the mesoporous catalysts appear to be interesting in the process of HIPS thermal degradation. In a published paper of 2007 [52] they studied, with the thermogravimetric technique, the effect of parameters such as particle size and method of contact between polymer/catalyst in the HIPS pyrolysis. In a later study of 2009 [48] they also studied the pyrolysis of a series of polystyrene/polybutadiene copolymers in the presence of Al-MCM-41 in an attempt to compare their behaviour in the pyrolysis process with that of HIPS. Results have shown the importance of parameters such as the copolymer structure, the flow characteristics and the method of contact between the polymer and the catalyst in the pyrolysis process. Hall and Williams have studied the HIPS pyrolysis in the presence of decabromodiphenylether (retardant) in a fluidised bed reactor and they reported that the 90 wt.% of the initial polymer has been converted to a liquid pyrolysis product [11].

Jung et al [53] extensively studied the pyrolysis of HIPS in the presence of bromine containing retardants and Sb_2O_3 in a fluidised bed reactor. The pyrolysis process took place in the absence and presence of three Ca containing additives: Ca: CaO, $Ca(OH)_2$ and oyster shells. It was found that the presence of Ca affected the produced liquid fraction composition, also increas-

http://dx.doi.org/10.5772/59960

ing the concentration of the styrene produced. In a more recent study [54] the same group has studied the effect of a series of parameters such as temperature, feed rate and the type of fludising medium on the HIPS (as well as ABS) pyrolysis, also in a fluidised bed reactor. It was found that the higher feed rates and the use of product gas as a fluidising medium increased the liquid fraction production. The produced liquid fraction for HIPS reaches 87.3 wt. % and consists mainly of the styrene monomer, aromatic hydrocarbons and oligomers and could potentially be used as a fuel with no significant treatment.

5.2.1. Pyrolysis mechanism

During the thermal degradation of different forms of polystyrene with enhanced properties such as HIPS, a series of changes in the physical properties of the initial polymer have been observed, depending on factors such as the polymer density and the bead structure. Researchers have shown that the polymer structure was destroyed in temperatures between 110-120°C. The polymer particles melt in temperatures higher than 275°C, while the complete gasification takes place in temperatures between 460-500 °C [55].

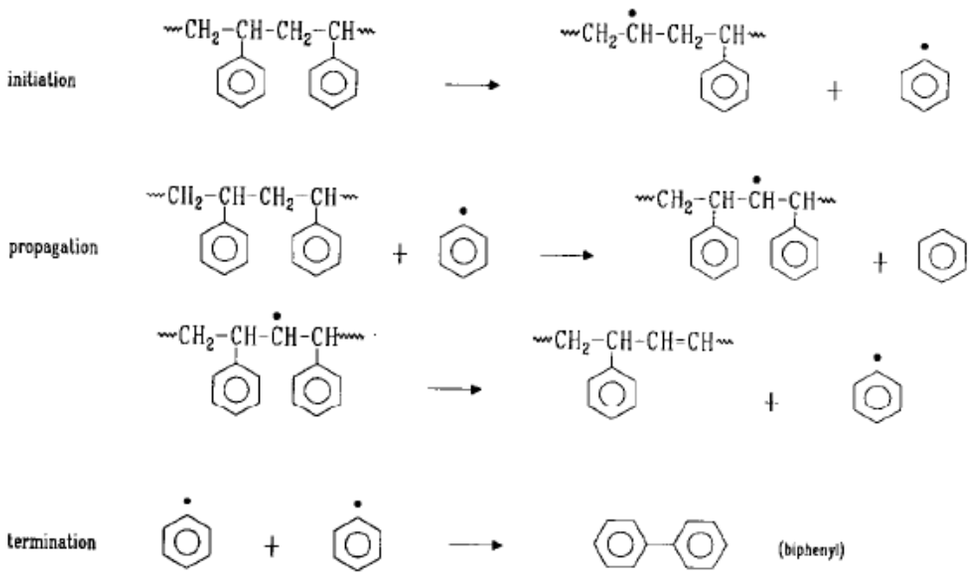


Figure 6. Thermal degradation reactions during HIPS pyrolysis

The studies on the mechanism of HIPS thermal degradation are limited but it has been suggested that the decomposition mechanism is the free radicals mechanism which takes place in three steps: initiation, propagation and termination (figure 6). A basic step of the mechanism is the formation of a phenyl free radical, which later leads to the formation of a stable biphenyl through the termination step. The determination of the benzene molecule on the pyrolysis products from many researchers leads to the hypothesis that the free radicals mechanism takes place together with some elimination reactions which possibly lead in the benzene formation. The benzene formation seems to be favored by an increase in temperature and leads to the formation of unsaturated bonds in the molecule of the remaining polymer. These bonds can

facilitate the initiation process of the free radicals mechanism acting as weak links. In fact a single C-C bond which is placed next to an unsaturated bond is more likely to participate in scission reactions through the free radicals mechanism [56].

In the case of HIPS, the polybutadiene phase can be the first step in the thermal decomposition of the polymer. As it has already been reported, the HIPS polymer is formed with the introduction of a polybutadiene phase in the polystyrene. The resulting copolymer can be structurally determined as a multiple phase system in the form of dispersed butadiene granules on a continuous polystyrene network. This phase consists of three basic isomeric units of polybutadiene: vinyl-1,2, cis-1,4, and trans-1,4 (figure 7) and the initial decomposition is related with the chemistry of these three butadiene microstructures [57]

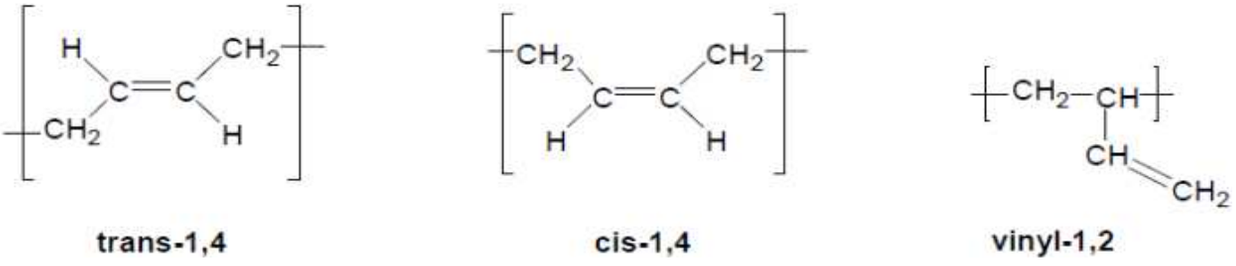


Figure 7. The three microstructures of polystyrene [57]

5.3. Photodegradation

The research team of Fernardes and coworkers [58] have studied the effect of the presence of the HIPS polymer on the photodegradation of polypropylene. The concentrations of the HIPS varied between 10 and 30 wt %. The polymer mixtures as well as the original polymers have been exposed to UV radiation for periods up to 15 weeks. After the third week of exposure to the UV radiation all the materials appear to have mechanical properties comparable to those of the initial. For time periods longer than 3 weeks, increased HIPS concentrations lead to a better photostability of the polypropylene polymer.

6. Recycling of ABS

The ABS resin is basically a terpolymer consisting of three monomers: acrylonitrile, butadiene and styrene. The ABS polymer can be of various compositions and its properties vary depending on the structure and chemical microstructure of the different phases. Generally in the more classical form of ABS the continuous phase consists of copolymers of styrene and acrylonitrile, while the butadiene usually forms the dispersed phase. ABS polymers find a variety of applications since they are tough and with enhanced resistance to heat, cold, chemicals and alteration of environmental conditions. They are widely used in construction and environmental industry, in a variety of household applications and as a thermoplastic.

http://dx.doi.org/10.5772/59960

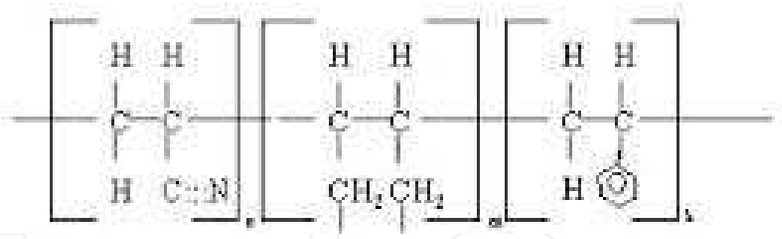


Figure 8. Chemical structure of ABS (www.cucd2011.mae.carleton.ca)

Most of the research in the area of ABS recycling is devoted in the study of ABS containing waste electronics and/or blends. Brebu et al. [59] studied the thermal and catalytic degradation of ABS polymers and the distribution of nitrogen containing compounds in the degradation products. Liu et al [60] in an attempt to upgrade recycled engineering plastics with ABS as their main component studied the possibility of blending ABS with PA, in order to maintain the advantages of both materials. They reported that the mechanical properties of ABS/PA can be upgraded with the introduction of small amounts of a compatibilizer and a core-shell impact modifier when they were working with "fresh" polymeric materials but the same technique did not apply for recycled materials.

In a study of 2003, Bhaskar et al [61] reported the thermal degradation of the ABS terpolymer which contained about 10 wt.% of a brominated flame retardant. It was found that the heating rate has a significant effect on the yields and compositions of the pyrolysis products (liquid, gas and solid residue). The solid residue consisted of the carbon residue and the wax, while the majority of the bromine was concentrated in the carbon residue. Studies to remove the bromine (as well as and nitrogen) containing products from the ABS liquid products is suggested by the researchers as the next step, if the pyrolysis oil is to find further applications and to be used as a fuel.

In a more recent study, Du et al [62] investigated the thermal degradation of ABS and denitrogenated ABS samples (DABS), by means of TGA, TGA-IR, and TGA-MS, in order to study the link between the original structure of DABS and the effect of the pyrolysis process. Degradation process of DABS was faster, initiating at a lower degradation temperature, while the amount of HCN decreases and the percentage of nitrogen in residue increases for DABS. The liquid product consists mainly of compounds of an aromatic origin. The authors suggested that effective denitrogenation of ABS before pyrolysis is beneficial for the quality of the produced pyrolysis oil, since they significantly decrease the nitrogen content and thus the HCN evolution.

In a study of 2014, Sun et al [63] in one of the few studies on the reuse of non metal parts of a real waste, investigated the co-recycling of acrylonitrile–butadiene–styrene waste plastic and nonmetal particles from waste printed circuit boards to manufacture reproduction composites (RC) in an attempt to co-recycle the two waste electronics. Results showed that the presence of nonmetal particles significantly improved the mechanical properties and the physical performance of the RC. This research suggests that this could act as a viable method to reuse waste ABS and WPCB nonmetals for manufacturing high value-added product. The composite material can find applications in panels, wall coverings and furniture.

7. Conclusion

This chapter outlines the recent advances in the area of chemical and thermo-chemical recycling of polymers from waste electrical and electronic equipments. Particularly, recycling methods were presented for polycarbonate (PC), High impact polystyrene (HIPS) and the ABS resin, a terpolymer consisting of acrylonitrile, butadiene and styrene.

The dissolution-re precipitation method which uses an appropriate solvent/non-solvent system was critically reviewed. Furthermore, pyrolysis methods were presented as a promising alternative to produce a number of secondary value-added products.

Author details

Dimitris S. Achilias* and Eleni V. Antonakou

*Address all correspondence to: axilias@chem.auth.gr

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

References

[1] Alston S., Clark A., Arnold J., Stein B. Environmental Impact of Pyrolysis of Mixed WEEE Plastics Part 1: Experimental Pyrolysis Data. Environmental Science Technology 2011; 45 9380–9385.

[2] Kantarelis E., Yang W., Blasiak W., Forsgren C., Zabaniotou A. Thermochemical treatment of E-waste from small household appliances using highly pre-heated nitrogen-thermogravimetric investigation and pyrolysis kinetics. Applied Energy 2011; 88 922–929.

[3] De Marco I., Caballero B.M., Chomon M.J., Laresgoiti M.F., Torres A., Fernandez G., Arnaiz S. 2008. Pyrolysis of electrical and electronic wastes. Journal of Analytical and Applied Pyrolysis 2008 82; 179–183.

[4] Martinho G., Pires A., Saraiva L., Ribeiro R. Composition of plastics from waste electrical and electronic equipment (WEEE) by direct sampling. Waste Management 2012 32; 1213–1217.

[5] Develop a Process to Separate Brominated Flame Retardants from WEEE Polymers UK Waste & Resources Action Programme: Banbury, UK, 2007; http://www.wrap.org.uk/recycling_industry/publications/develop_a_process__1.html; Final Report.

[6] Achilias D.S., Antonakou E.V., Koutsokosta E., Lappas A.A. Chemical recycling of polymers from waste electric and electronic equipment. Journal of Applied Polymer Science, 2009; 114, 212-221.

[7] Scheirs J., Kaminsky W., Eds. Feedstock Recycling and Pyrolysis of Waste Plastics. J. Wiley & Sons, W. Sussex, UK., 2006.

[8] Kowalska E., Radomska J., Konarski1 P., Diduszko R., Oszczudowski J., Opaliska T., Wich M., Duszyc Z. Thermogravimetric investigation of wastes from electrical and electronic equipment (WEEE). Journal of Thermal and Analytical Calorimetry 2006 86; 137–140.

[9] Molto J., Font R., Galvez A., Conesa J.A. Pyrolysis and combustion of electronic wastes. Journal of Analytical and Applied Pyrolysis 2009 84; 68–78.

[10] Acomb J.C., Nahil M.A., Williams P.T. Thermal processing of plastics from waste electrical and electronic equipment for hydrogen production. Journal of Analytical and Applied Pyrolysis. 2013 103; 320–327.

[11] Hall, W.J., Williams, P.T. Pyrolysis of brominated feedstock plastic in a fluidised bed reactor. Journal of Analytical and Applied Pyrolysis 2006 77; 75–82.

[12] Hall W.J., Williams P.T. Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment. Journal of Analytical and Applied Pyrolysis 2007 79; 375–386.

[13] Pinto F., Costa P., Gulyurtlu I., Cabrita I. Pyrolysis of plastic wastes 2. Effect of catalyst on product yield Journal of Analytical and Applied Pyrolysis 1999 51; 57–71.

[14] Grause G., Sugawara K., Mizoguchi T., Yoshioka, T. Pyrolytic hydrolysis of polycarbonate in the presence of earth-alkali oxides and hydroxides. Polymer Degradation and Stability 2009 94; 1–6.

[15] Vasile C., Brebu M.A., Karayildirim T., Yanik T., Darie H. Feedstock recycling from plastics and thermosets fractions of used computers. II. Pyrolysis oil upgrading. Fuel 2007 86; 477–485.

[16] Williams P.T. Valorization of Printed Circuit Boards from Waste Electrical and Electronic Equipment by Pyrolysis. Waste and Biomass Valorization 2010 1; 107–120.

[17] Balart R., Sanchez L., Lopez L., Jimenez A. Kinetic analysis of thermal degradation of recycled polycarbonate/acrylonitrilebutadiene-styrene mixtures from waste electric and electronic equipment. Polymer Degradation and Stability 2006 91; 527–534.

[18] Balart R., Lopez J., Salvador M.D. Recycling of ABS and PC from electrical and electronic waste. Effect of miscibility and previous degradation on final performance of industrial blends. European Polymer 2005 41; 2150–2160.

[19] Antonakou E. and Achilias D. Recent advances in polycarbonate recycling- a review of degradation methods and their mechanisms, Waste and Biomass Valorization 2012 DOI 10.1007/s12649-012-9159-x

[20] Bozzano G., Dente M. and Del Rosso R. Poly(bisphenol A carbonate) recycling: High pressure hydrolysis can be a convenient way, Material Recycling - Trends and Perspectives, D. Achilias (Ed.), 2012, ISBN: 978-953-51-0327-1, InTech, Available from: http://www.intechopen.com/books/material-recycling-trends-andperspectives/ poly-bisphenol-a-carbonate-recycling-high-pressure-hydrolysis-can-e-a convenient-way.

[21] Karayannidis G., D.S. Achilias D. Chemical recycling of PET, Macromolecular Materials and Engineering 2007 292;128-146.

[22] Liu F., Li Z., Yu S., Cui X., Ge X., Environmentally benign methanolysis of polycarbonate to recover bisphenol A and dimethyl carbonate in ionic liquids. Journal of Hazardous Materials 2010 174; 872-875.

[23] Watanabe M., Matsuo Y., Matsushita T., Inomata H., Miyake T., Hironaka K. Chemical recycling of polycarbonate in high pressure high temperature steam at 573 K., Polymer Degradation and Stability 2009 94; 2157-2162.

[24] Grause G., Sugawara K., Mizoguchi T.,Yoshioka T. Pyrolytic hydrolysis of polycarbonate in the presence of earth-alkali oxides and hydroxides, Polymer Degradation and Stability 2009 94; 1–6.

[25] Pan Z.Y., Zhen B., Chen Y.X. Depolymerization of Poly(Bisphenol A Carbonate) in Subcritical and Supercritical Toluene, Chinese Chemical Letters 2006 17; 545-548.

[26] Sato Y., Kondo Y., Tsujita K., Kawai N. Degradation behaviour and recovery of bisphenol-A from epoxy resin and polycarbonate resin by liquid-phase chemical recycling. Polymer Degradation and Stability 2005 89; 317-326.

[27] Oku A., Tanaka S., Hata S. Chemical conversion of poly(carbonate) to bis(hydroxyethyl) ether of bisphenol A. An approach to the chemical recycling of plastic wastes as monomers. Polymer 2000 4; 6749–6753.

[28] Hata S., Goto H., Yamada E., Oku A. Chemical conversion of poly(carbonate) to 11,3-dimethyl-2-imidazolidinone (DMI) and bisphenol A: a practical approach to the chemical recycling of plastic wastes. Polymer 2002 43; 2109-2116.

[29] Hu L., Oku A., Yamada E. Alkali-catalyzed methanolysis of polycarbonate. A study on recycling of bisphenol A and dimethyl carbonate. Polymer 1998 39; 3841-3845.

[30] Pinero R., Garcia J., Cocero M.J. Chemical recycling of polycarbonate in a semicontinuous lab-plant: a green route with methanol and methanol-water mixtures. Green Chemistry 2005 7; 380-387.

[31] Chen L.,Wu Y., Ni Y., Huang K., Zhu Z. Degradation kinetics of polycarbonate in supercritical methanol. Journal of Chemical and Industrial Engineering 2004 55; 1787-1792.

[32] Liu F., Li Z., Yu S., Cui X., Xie C., Ge X. Methanolysis and hydrolysis of polycarbonate under Moderate Conditions. Journal of Polymers and the Environment 2009 17; 208-211.

[33] Chiu S.J., Tsai C.T., Chang Y.K. Monomer recovery from polycarbonate by ethanolysis. E-Polymers; 2008. No. 132. Available from: http://www.e-polymers.org.

[34] Liu F., Li L., Yu S., Lv Z., Ge X. Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]. Journal of Hazardous Materials 2011 189; 249–254.

[35] Jie H., Ke H., Qing Z.,Lei C., Yongqiang W., Zibin Z. Study on depolymerization of polycarbonate in supercritical ethanol. Polymer Degradation and Stability 2006 91(10); 2307- 2314.

[36] Tagaya H., Katoh K., Kadokawa J., Chiba K. Decomposition of polycarbonate in subcritical and supercritical water. Polymer Degradation and Stability 1999 64; 289-292.

[37] Tsintzou G.P., Antonakou E.V., Achilias D.S. Environmentally friendly chemical recycling of poly(bisphenol-A carbonate) through phase-transfer catalysed alkaline hydrolysis under microwave irradiation. Journal of Hazardous Materials 2012; 241-242, 137-134.

[38] Nikje M.M.A. Glycolysis of polycarbonate wastes with microwave irradiation. Polimery/Polymers 2011; 56: 381-384.

[39] Chiu S.J., Chen S.H., Tsai C.T. Effect of metal chlorides on thermal degradation of (waste) polycarbonate Waste Management. 2006 26; 252-259.

[40] Mitan N., Brebu M., Bhaskar T., Muto A., Sakata Y., Kaji M., J. Mater. Cycles Waste Manag. 2007; 9, 62-68.

[41] Hall W., Williams P. Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment.J. Analyt. Appl. Pyrol. 2007 79; 375-386.

[42] Becker L., Lenoir D., Matuschek G., Kettrup A. Thermal degradation of halogen-free flame retardant epoxides and polycarbonate in air. Journal of Analytical and Applied Pyrolysis 2001 60; 55-67.

[43] Jang B., Wilkie C. A TGA-FTIR ans mass spectral study on the thermal degradation of bisphenol A polycarbonate. Polymer Degradation and Stability 2004 86; 419-430.

[44] Zhou W., Yang H., Zhou J. The thermal degradation of bisphenol A polycarbonate containing methyl phenyl containing additive. Journal of Analytical and Applied Pyrolysis 2007 78;413-418.

[45] Day M., Cooney J., Touchette-Barrette C., Sheehan S. Pyrolysis of mixed plastics used in the electronics industry. Journal of Analytical and Applied Pyrolysis 1999 52; 199-224.

[46] Grause G., Ishibashi J., Kameda T., Bhaskar T., Yoshioka T. Kinetic studies of the decomposition of flame retardant containing high-impact polystyrene. Polymer Degradation and Stability 2010 95; 1129-1137.

[47] Marcilla A., Gomez-Siurana A., Garcıa Quesada J.C., Berenguer D. Characterization of high-impact polystyrene by catalytic pyrolysis over Al-MCM-41: Study of the influence of the contact between polymer and catalyst. Polymer Degradation and Stability 2007 92;1867-1872.

[48] Marcilla A., Garcia Quesada J.C., Gomez-Siurana A., Berenguer, D. Characterization of styrene–butadiene copolymers by catalytic pyrolysis over Al-MCM-41. Journal of Analytical and Applied Pyrolysis 2009 85; 327–333.

[49] Brennan L.B., Isaac D.H., Arnold J.C. Recycling of Acrylonitrile–Butadiene–Styrene and High-Impact Polystyrene from Waste Computer Equipment Journal of Applied Polymers Science 2001 86; 572–578.

[50] Prasanna K. S. Mural P.K.S., Mohanty S., Nayak S.K., Anbudayanidhi K., 2011.Int J Plast Technol 15(Suppl 1):S46–S60.

[51] Jakab E., Uddin M.A., Bhaskar T., Sakata Y., 2003. Thermal decomposition of flame-retarded high impact polystyrene. Journal of Analytical and Applied Pyrolysis 68-69; 83-99.

[52] Marcilla A., Gomez-Siurana A., Garcıa Quesada J.C., Berenguer D. Characterization of high-impact polystyrene by catalytic pyrolysis over Al-MCM-41: Study of the influence of the contact between polymer and catalyst. Polymer Degradation and Stability 2007 92;1867-1872.

[53] Jung S.W., Kim S.J., Kim J.S. Fast pyrolysis of a waste fraction of high impact polystyrene (HIPS) containing brominated flame retardants in a fluidized bed reactor: The effects of various Ca-based additives (CaO, Ca(OH)2 and oyster shells) on the removal of bromine Fuel 2012 95; 514-520.

[54] Jung S.W., Kim S.J., Kim J.S.The influence of reaction parameters on characteristics of pyrolysis oils from waste high impact polystyrene and acrylonitrile–butadiene–styrene using a fluidized bed reactor. Fuel Processing Technology 2013 116; 123–129.

[55] Maharana T., Negi Y.S., Mohanty B. Review Article: Recycling of Polystyrene 2007 46(7); 729-736, DOI: 10.1080/03602550701273963.

[56] Audisio G., F. Bertini F. Molecular weight and pyrolysis products distribution of polymers I. Polystyrene. Journal of Analytical and Applied Pyrolysis, 1992 24; 61-74.

[57] Francisco Vilaplana F. Modelling the degradation processes in high-impact polystyrene during the first use and subsequent recycling. 2007 PhD Thesis, KTH Chemical Science and Engineering.

[58] Fernandes L.L., Freitas C.A., Demarquette N.R., Fechine G.J.,2011. Photodegradation of Thermodegraded Polypropylene/High-Impact Polystyrene Blends: Mechanical Properties Journal of Applied Polyners Science 2011 120; 770–779.

[59] Brebu M., Uddin M., Muto A., Sakata Y., Vasile C. The role of temperature programme on the quality of ABS degradation oil. Journal of Analytical and Applied Pyrolysis 2002 63; 43-57.

[60] Liu X.,Boldizar A., Rigdahl, Bertilsson H. Recycling of blends of ABS and polyamide. Journal of Applied Polymer Science 2002 86; 2535-2543.

[61] Bhaskar T., Murai K.,Matsui, T., Bredu M., Uddin M., Muto A. Sakata Y. and Murata K.Studies on thermal degradation of acrylonitrile butadiene styrene copolymer (ABS-Br) containing brominated flame retardantsJornal of Analytical and Applied Pyrolysis 2003 70;369-381.

[62] Du A., Zhou Q., van Kasteren J. and Wang Y. Fuel oil from ABS using a tandem PEG-enhanced denitrogenation-pyrolysis method:Thermal degradationof denitrogenated ABS. Journal of Analytical and Applied Pyrolysis 2011 92;267-272.

[63] Sun Z., Shen Z., Zhang X., Ma S. Co-recycling of acrylonitrile-butadiene-styrene waste plastic and nonmetal particles from waste printed boards to manufacture reproduction composites. Environmental Technology http://dx.doi.org/10.1080/09593330.2014.940399

IntechOpen

IntechOpen

IntechOpen