Chemical Recycling of Polymers from Waste Electric and Electronic Equipment

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ABSTRACT: This research is focused on the recycling of three types of polymers, namely polycarbonate (PC), poly(acrylonitrile-butadiene-styrene) (PABS), and polystyrene (PS) from Waste Electric and Electronic Equipment (WEEE). Initially, the chemical structure of each polymeric material in a variety of WEEE was identified by Fourier Transform Infra Red (FTIR) spectroscopy and Differential Scanning Calorimetry (DSC). The potential recycling of these polymers from these wastes was examined by employing two different approaches, the dissolution/reprecipitation method and the more challenging technique of pyrolysis. During the first, the polymer is separated and recycled through a solvent/non-solvent system. It is a simple and economic technique leading to high recovery of pure polymer. Both, model polymers and plastic parts from WEEEs were studied and optimum experimental conditions, including dissolution temperature and time, polymer concentration and type of solvent were proposed to achieve significant recovery of the polymer (>90 wt %). Furthermore, pyrolysis of waste Compact Disks (CD) was investigated and compared with model poly(bisphenol A carbonate) (PC) through a laboratory-scale fixed bed reactor. The appropriate pyrolysis temperature was selected after measuring the thermal degradation of model PC by Thermogravimetric analysis (TGA). A large amount of oil was measured, together with a smaller amount of gaseous product, leaving also a solid residue. For both samples, the gaseous fraction consisted mainly of CO_2 and CO whereas in the liquid fraction a large amount of different phenolic compounds, including the monomer bisphenol A, was measured. It seems that recycling of used CDs by pyrolysis is a very promising technique having the potential of producing useful high-value chemicals, which may find applications in the petrochemical industry. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 212–221, 2009

Key words: polymer recycling; waste electrical and electronic equipment; pyrolysis; dissolution/reprecipitation; PC; ABS

INTRODUCTION

The production of electric and electronic equipment (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. This rapidly advancing technology together with the increasingly short product life cycles have led to huge volumes of relatively new electronic goods being discarded. This has resulted in a continuous increase of Waste Electric and Electronic Equipment (WEEE) with estimates of more than 6 million tones annual production[1] or up to 10 kg per person per year (2005). It has been estimated that by 2015 the figure could be as high as 12 million tones.[2] 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 European Union is implementing a similar system described in the Waste Electrical and Electronic Equipment Directive (WEEE 2002/96/EC).[3] This Directive sets out measures for the collection, treatment, recovery, and recycling of all EE products. As a result by the end of 2006 every country has to recover up to 70% of electrical and electronic equipment (EEE). With respect to typical WEEE plastic weight percentages of 15–30%, it is obvious, that the targets cannot be fulfilled by metal and glass recycling, only. Therefore, it is imperative to provide and develop efficient methods for plastics recovery and recycling.

Recycling of WEEE involves a technological challenge due to the complex nature of electrical and electronic equipment and it constitutes an important issue not only from the point of waste treatment but

also from the recovery of valuable materials. Polymers represent approximately 20% of the total weight of EEE and are based on approximately 15 different types of engineering polymers, including ABS, HIPS, PP, PS, SAN, polyesters, etc.[4] Among them, the most important are resins of Acrylonitrile-Butadiene-Styrene (PABS), polycarbonates (PC), High Impact Polystyrene (HIPS), and different types of polyethylene (PE).[5-7] PC and mainly poly (bisphenol A carbonate) is one of the most widely used engineering thermoplastics due to the excellent physical and chemical properties, such as transparency, high heat distortion temperature, high impact strength, good thermal stability, and flame retardancy. ABS posses good impact strength and mechanical properties due to the contributing properties of each of its components. Acrylonitrile provides chemical resistance, heat resistance and toughness, whereas butadiene provides impact strength and styrene rigidity and easy processing. Although, a variety of techniques have been developed for the recycling of polymers in general[8–10] and particularly for WEEE, the high cost associated with these methods usually leads to a disposal of plastics from WEEE to sanitary landfills. The main drawback that obstructs material recovery from plastics contained in WEEE is the variety of polymers that are being used, resulting to a difficulty in sorting and recycling. Another relevant drawback in dealing with treatment of WEEE is that very often they contain brominated aromatic compounds, used as fire retardants. Thermal treatment of such chemicals is likely to produce extremely toxic halogenated dibenzodioxins and dibenzofurans.[1,11] During last years some work has been carried out on the development of different methods to recycle or give added-value to WEEE.[1,5,6,12] Processes such as extractive recycling to separate different polymer fractions and eliminate hazardous contaminants have been proposed.[4] According to these authors,[4] material recycling of WEEE plastics may be limited to certain fractions so other treatments such as pyrolysis or gasification should be considered.

In this investigation, we continue our research on the development of polymer recycling techniques[13–18] and examine the case of polymer recycling from WEEE. Thus, initially, different polymeric materials included in WEEE are determined and identified. Moreover, appropriate techniques are developed for the recycling of these polymers and possibly the recovery of secondary value-added products. For this purpose two different methods were examined: the traditional method of dissolution/reprecipitation and the more challenging technique of pyrolysis. The first belongs to the mechanical recycling techniques whereas the second to chemical/feedstock recycling. During the first technique, the polymer can be separated and recycled using a solvent/nonsolvent system.[19,20] Separating and recycling polymers by this method appear to be technologically feasible and of considerable commercial interest.[21] The effect of different solvent/nonsolvent systems and dissolution temperatures on the percent recovery of polymers from the corresponding model polymers or WEEE was investigated. Furthermore, pyrolysis was carried out in a laboratory fixed bed reactor, using either a model PC as raw material or a commercial CD. Components in the gaseous and liquid fraction from pyrolysis were identified using GC-FID/GC-TCD and GC-MS, respectively. The thermal stability of PC was also investigated using thermogravimetric analysis. It should be noticed here that very few reports have been presented in literature dealing with the pyrolysis of WEEE[12,22] and none on the pyrolysis and detailed yield and composition of the products from waste Compact Disks.

EXPERIMENTAL

Materials

Model polymers used include polystyrene ($C_6H_5CHCH_2)_n$, poly(acrylonitrile-*co*-butadiene-*co*-styrene) $(CH_2CHCN)_x$—$(CH_2CHCHCH_2)_y$—$(CH_2CHC_6H_5)_z$, and poly(Bisphenol A carbonate) (C_6H_4 $C(CH_3)_2C_6H_4O$-$C(O_2)_2)_n$, all obtained from Aldrich. Several commercial WEEE were also used (such as the plastic part from a TV set, a computer monitor, a household electric machine, an electronic toy, and a Compact Disk) made from these polymers. The solvents used (dichloromethane, acetone, toluene, chloroform, methanol) were reagent grade.

Dissolution/reprecipitation technique

In this technique, both model polymers and waste products were used. Different solvents (dichloromethane, acetone, chloroform, and toluene) were studied, whereas methanol was used as nonsolvent at a volume ratio of solvent/nonsolvent equal to 2/3. Experiments were carried out using different polymer concentrations and dissolution temperatures below the boiling point of each solvent. The experimental process comprised: the polymer (1 gm) and the solvent (20 mL) were added into a flask equipped with a vertical condenser and a magnetic stirrer. The system was heated for 30 min to the desired temperature. Then, the flask was cooled and the solution of the polymer was properly poured into 30 mL of the nonsolvent. The polymer was reprecipitated, washed, filtrated, and dried in an oven at 80°C for 10 h. The recycled polymer was obtained in the form of powder or grains.

Measurements

Fourier-transform infra-red (FTIR)

The chemical structure of the model polymers and the WEEE products based on these polymers, before and after the recycling technique was confirmed by recording their IR spectra. The instrument used was an FTIR spectrophotometer of Perkin-Elmer, Spectrum One. The resolution of the equipment was 4 cm^{-1}. The recorded wavenumber range was from 450 to 4000 cm^{-1} and 16 spectra were averaged to reduce the noise. A commercial software Spectrum v5.0.1 (Perkin Elmer LLC 1500F2429) was used to process and calculate all the data from the spectra. Thin polymeric films were used in each measurement, formed by a hydraulic press Paul-Otto Weber, at a temperature 20°C above the melting point of each polymer.

Differential scanning calorimetry (DSC)

Glass transition temperature, T_g, measurements of model polymers and WEEE products were performed using the differential scanning calorimeter Pyris 1 (Perkin-Elmer) equipped with the Pyris software for windows and calibrated for temperature and enthalpy with indium. Samples of approximately 10 mg were introduced into the appropriate position of the instrument and the heat released was recorded at a temperature interval 20 to 170°C and a scan rate of 20°C/min. T_g was calculated using the well-known procedure at the point were a change in the slope of the curve was observed.

Thermogravimetric analysis (TGA)

Dynamic thermal degradation measurements were performed on a Pyris 1 TGA (Perkin Elmer) thermal gravimetric analyzer. Samples of about 10 mg were used and they were heated from ambient temperature to 700°C at a heating rate of 10°C/min. TGA tests were carried out in alumina crucibles under a nitrogen flow rate of 20 mL/min to remove all gases evolved and avoid thermo-oxidative degradation. Sample mass versus temperature was continuously recorded and finally differentiated to produce a dTGA vs temperature plot.

Pyrolysis

A laboratory-scale fixed bed reactor was used in all pyrolysis experiments. Details of the reactor set-up can be found in Ref. 17. The reactor was filled with 0.7 g of glassbeads and the piston was filled with the polymer (1.5 g). The system was always heated in the presence of N$_2$ and, by using a temperature controller the temperature of each zone of the fur-
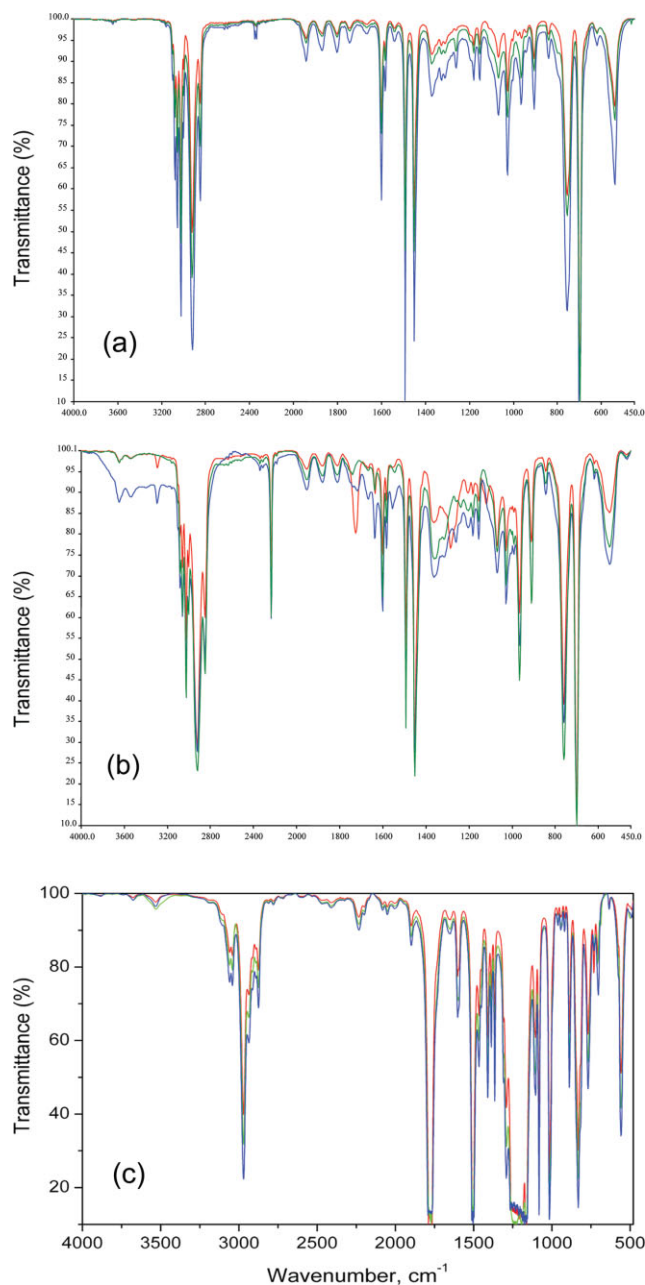
Figure 1 FTIR spectra of model polymers (red line) and commercial plastic products from WEEE based on these polymers before (green line) and after (blue line) recycling, (a) PS and part from a radio, (b) PABS and part from a TV set, (c) PC and a CD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nace was controlled. As soon as the reaction temperatures were achieved, polymer entered the reactor and the experiment started. The time of the experiment was 17 min on the basis of our previous work which showed it as the most adequate[16–18] and the reaction temperature was 550°C to ensure its completion. At the end of the experiment purging (30 min) was performed in the presence of N$_2$. The liquid products were collected in a liquid bath (−17°C)

and quantitatively measured in a pre-weighted glass receiver. The gaseous products were collected and measured by water displacement. The amount of residue was measured by direct weighting. The liquid samples were analysed by GC/MS analysis in a HP 5989 MS ENGINE. The gaseous products were analysed in a HP 6890 GC, equipped with four columns (Precolumn:OV-101; Columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30 m x 0.53 mm ID) and two detectors (TCD and FID). The chromatograph was standardized with gases at known concentrations as standard mixtures.

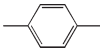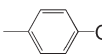## RESULTS AND DISCUSSION

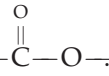### Characterization of different waste electric and electronic products

To identify the polymer in the plastic part of the particular WEEE examined, its FTIR spectrum was recorded and compared with that of the corresponding model polymer. Thus, the chemical structure of each polymer could be recognized. Indicative results of WEEE made of polystyrene, ABS, and PC together with their corresponding model polymers appear in Figure 1(a–c).

Specifically, from Figure 1(a), PS was identified from the following interpretation of the spectra. The bands at 3000–3100 cm^{-1} and the peaks at 700 and 760 cm^{-1} are characteristic of the presence of aromatic ring or substituted phenyl ring. Also, very characteristic are the peaks related to the aromatic ring stretching vibrations at 1494 and 1450 cm^{-1}, and the peak at 1600 cm^{-1} caused by the aromatic carbon double bond, C=C stretching vibration. Finally, the peaks at 2950 and 2850 cm^{-1} represent C—H stretching vibrations of the chemical functional group —CH$_2$—.

When PABS was examined three different groups were identified [Fig. 1(b)]. Initially, the styrene structural units were identified from the absorption bands at 3000–3100 cm^{-1} and the peaks at 700 and 755 cm^{-1}. Also, obvious were the characteristic peaks related to the aromatic ring stretching vibrations at 1494 and 1452 cm^{-1}, and the peak at 1602 cm^{-1} caused by the aromatic carbon double bond, C=C stretching vibration. Furthermore, a clear peak was observed at 2238 cm^{-1} attributed to the nitrile group —C≡N originated by the acrylonitrile units in ABS. The peaks at 911 cm^{-1} and 966 cm^{-1} correspond to the unsaturated groups from the butadiene phase in ABS. The peak corresponding to the cis-1,4 double bond group from the polybutadiene phase (around 730cm^{-1}) could not be identified because of the overlapping peak from the C—H out-of-plane vibration of the styrene units in polystyrene at 755 cm^{-1}. Finally, the peaks at 2920 and 2850 cm^{-1} represent C—H stretching vibrations of the chemical functional group —CH$_2$—.

Characteristic FTIR spectra of PC appear in Figure 1(c). The peaks at 1505 and 830 cm^{-1} are characteristic of the 1,4 substituted aromatic ring, —⬡— stretching. The absorption band between approximately 1160 and 1280 cm^{-1} as well as the peaks at 1010, 1080 cm^{-1} are characteristic of the presence of the para aryloxy group —⬡—o— and the peak at 2970 cm^{-1} of phenoxy aromatic. The peaks above and below 3000 cm^{-1} correspond to carbon-hydrogen stretching, while very pronounced is the peak at 1770 cm^{-1} characteristic of carbonyl stretching of the carbonate functional group —$\overset{\overset{\text{O}}{\|}}{\text{C}}$—O—.

In all WEEE samples examined, the spectra of the waste products exhibited all the characteristic peaks appeared in the corresponding model polymers.

In addition to the chemical characterization of each WEEE examined, its thermal properties were also analyzed by measuring the glass transition temperature. The values recorded appear in Table I together with corresponding T_g values obtained from model polymers. The value measured for model PC (144°C) is similar to that reported in literature[6] (146°C), whereas that for PABS (100°C) was slightly lower to other literature values (104.4°C in Ref .6 and 112°C in Ref. 21). In most waste samples examined, the T_g values did not differ significantly from the corresponding model polymer. The higher T_g measured in the TV set could be attributes to a different proportion of the three components (i.e., acrylonitrile, butadiene, styrene) in the particular resin used in the commercial sample, compared with the model polymer.

Recycling using the dissolution/reprecipitation technique

The main parameters affecting the dissolution/reprecipitation technique are solvent/nonsolvent type, dissolution temperature, polymer concentration,

TABLE I
Glass Transition Temperature (°C) of Model Polymers and WEEEs Studied

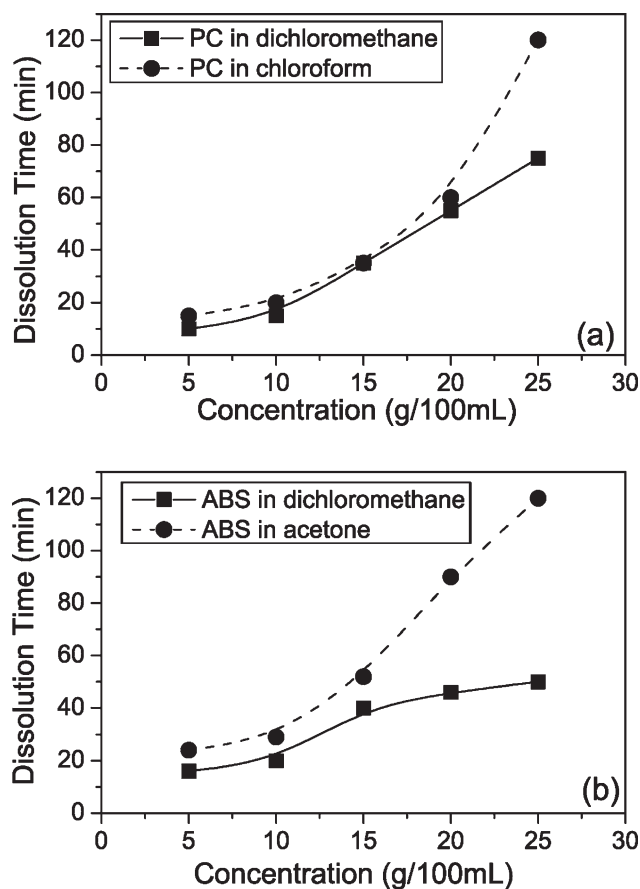| Polymer	Model		WEEE	
Polycarbonate	144	142 (Compact Disk)		
PABS	100	101 (Computer monitor)	109 (TV set)	101 (Electronic toy)
Polystyrene	95	102 (Radio)	92 (Vacuum cleaner)	

Figure 2 Dissolution time as a function of PC concentration in dichloromethane or chloroform (a) and PABS in dichloromethane and acetone (b) at room temperature (25°C).

nonsolvent/solvent portion, and dissolution time. All of them must be optimized 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. Four solvents were used, namely, dichloromethane, toluene, chloroform, and acetone, whereas methanol was always employed as a nonsolvent. Dichloromethane was a common solvent employed in the recovery of all studied polymers, while an additional solvent was used in each case, namely acetone, chloroform, and toluene for the recovery of PABS, PC, and PS, respectively. The dissolution temperatures investigated were 25°C, 50°C, and 100°C, in the cases of dichloromethane and toluene, whereas only 25°C and 50°C in the cases of acetone and chloroform (below their boiling point).

To propose values for the maximum polymer concentration that could be dissolved in each solvent, the time needed for total dissolution as a function of concentration was measured. Indicative plots for the dissolution of PC in dichloromethane and chloroform and PABS in dichloromethane and acetone at room temperature are plotted in Figure 2(a,b), respectively. Concentrations above 25 g/100 mL were not used because they resulted in too viscous solutions to be used in subsequent phases. According to literature,[10] the recycling process will be industrially feasible if the dissolution time is less than 90 min. As it can be seen from Figure 2 all concentrations in dichloromethane fulfil this criterion, whereas for PC in chloroform it is satisfied only for concentrations less than 0.25 g/mL and 0.2 g/mL for PABS in acetone. As it was expected, less concentration resulted in less dissolution times. Because, a rather abrupt increase was observed after 0.15 g/mL, only concentrations 5 and 10 g/100 mL were further investigated. Dissolution time was kept always constant to 30 min to avoid any further polymer degradation.

TABLE II
Polymer Recovery (wt %) by the Dissolution/Reprecipitation Technique From Model Polymers

Solvent/nonsolvent	Temperature (°C)	Polymer concentration (g/100 mL)	Polymer		
			PABS	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 III
Polymer Recovery by the Dissolution/Reprecipitation Technique From the Plastic Part of Different WEEE

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
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

The effect of solvent type, dissolution temperature, and polymer concentration on the % recovery of the three model polymers (i.e., PABS, PC, and PS) appears in Table II. In general, 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 PABS high recoveries were measured when using dichloromethane at 100°C but also with acetone at lower temperatures. Because acetone can dissolve PABS at room temperature, eliminating thus the risk of thermal degradation at elevated temperatures, it has been proposed as the best solvent for PABS in the dissolution/reprecipitation recycling technique.[21] In this investigation, 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 III. 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 PABS it was not effective in WEEEs based on PABS (i.e., computer monitor and electronic toy). For all different WEEEs, based on PABS 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).

Possible changes in the chemical structure of the polymer recovered with this technique could be identified by comparing the FTIR spectrum of the solid obtained after recycling with that of the model polymer. Indicative results are included in Figure 1, where the red line corresponds to the model polymer, the green to the WEEE, and the blue to the polymer recovered after the recycling technique. In all samples investigated, the characteristic bands did not change significantly after the recycling process, meaning that the polymer recovered has the same chemical structure with the corresponding model polymer. Difference between peak heights can be a consequence of the somewhat different weights of the samples.

Recycling by pyrolysis

Thermal cracking or pyrolysis, involves the degradation of the polymeric materials by heating in the
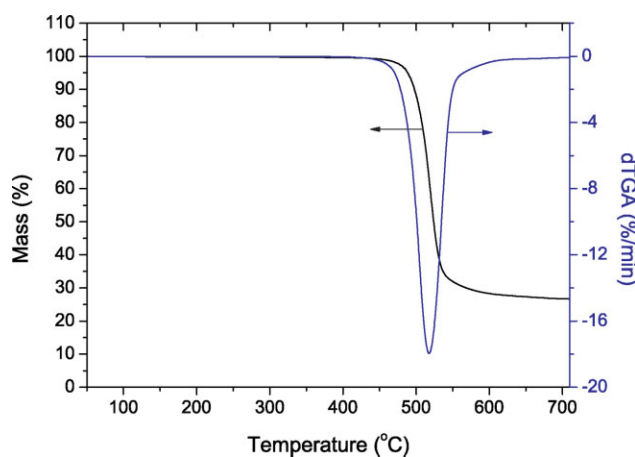

Figure 3 Thermogravimetric analysis and differential thermogravimetry curves of poly(bisphenol A carbonate) at a heating rate of 10°C/min under a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Product Yield From the Pyrolysis of Model PC and a Compact Disk (wt % on polymer)

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

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.[16–18,23] An overview of the science and technology of pyrolysis of waste plastics has been recently presented in an excellent book by Scheirs and Kaminsky.[24] In this investigation, results are presented for the pyrolysis of waste CD's and compared to corresponding from model PC. It should be pointed out here that to remove the Al layer on the CD, initially it was pretreated with a NaOH solution.

To select an appropriate pyrolysis temperature to be used in the feedstock/chemical recycling process, the thermal stability of PC was initially examined using thermogravimetric analysis. Thermal degradation of the target model polymer (PC) has been the subject of recent research.[6,25–33] The TGA and DTGA curves of model poly(bisphenol A carbonate) observed in a nitrogen flow are given in Figure 3. A negligible mass loss was observed until 450°C, whereas the major degradation occurred between 450 and 550°C and that was followed by a much slower degradation process up to 700°C. Similar results have been also reported in literature.[25,27] The temperature of 1% mass loss was 456°C, and that of 50% was 524°C. Decomposition appears to occur in one initial major fast degradation stage with a maximum rate of 18% min^{-1} (1.8 % °C^{-1}) recorded at 518°C, followed by a minor slow degradation step. The char yield at 600°C was 28.3 wt %, whereas that at 700°C 26.7%. Exactly the same temperature at maximum mass loss rate was observed by Zhou et al.[27] whereas at a slightly higher rate value (22% min^{-1}). Moreover, almost the same char yield at 700°C (27 wt %) was reported by Jang and Wilkie[25] and at 600°C (29 wt %) by Li and Huang.[32]

From the aforementioned results a temperature of 550°C was selected to carry out the pyrolysis experiments.

Results on the product yield from the fixed bed pyrolysis of either model poly(bisphenol A carbonate) or the compact disk appear in Table IV. The model PC pyrolysed to form a large amount of oil (i.e., 63 wt %) a smaller amount of gas (6.6 wt %)
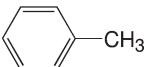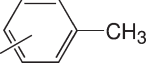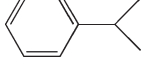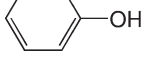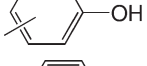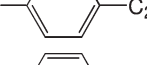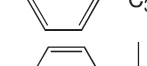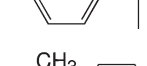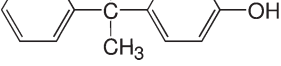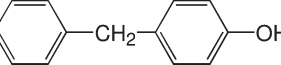
while leaving a rather large amount of residue (30.4 wt %). This finding is in keeping with the mass-loss data observed in Figure 3. The total degradation of poly(bisphenol A carbonate) (i.e., 70 wt %) was slightly lower from th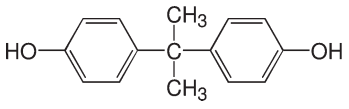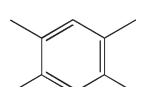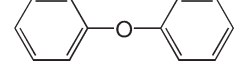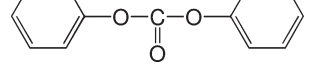at reported by Chiu et al.,[31] (i.e., 76 wt %) using a quartz reactor operating at 550°C after 1 h degradation. The pyrolysis of the CD produced a much larger amount of liquid fraction (80.4 wt %) with almost the same gaseous fraction (8.6 wt %) while leaving a much smaller amount of residue (11 wt %). In the only one published article on pyrolysis of waste CDs the amount of residue measured was much larger (i.e., 39%), whereas a lower liquid fraction was measured (i.e., 47%).[34] This could be due to the lower pyrolysis temperature (i.e., 450°C) used by these authors.[34] The pyrolysis oil in both cases had a low viscosity and was brown in colour. Very recently, Hall and Williams[12] in the only one published article on WEEE pyrolysis, 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%).

The mass composition of the pyrolysis gases (on a nitrogen free basis) is presented in Table V. 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

TABLE V
Composition of the Gaseous Fraction (wt % on Polymer)
From the Pyrolysis of Model PC and a Compact Disk

Compound	Sample	
	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 VI
Compounds Identified in the Liquid Pyrolysis Fraction of Model PC and Compact Disk (wt % on Liquid Produced)

Compound	Chemical formula	Sample	
		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

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. Similar composition was reported in Ref. 33. Pyrolysis gases from both samples investigated, contained also smaller amounts of
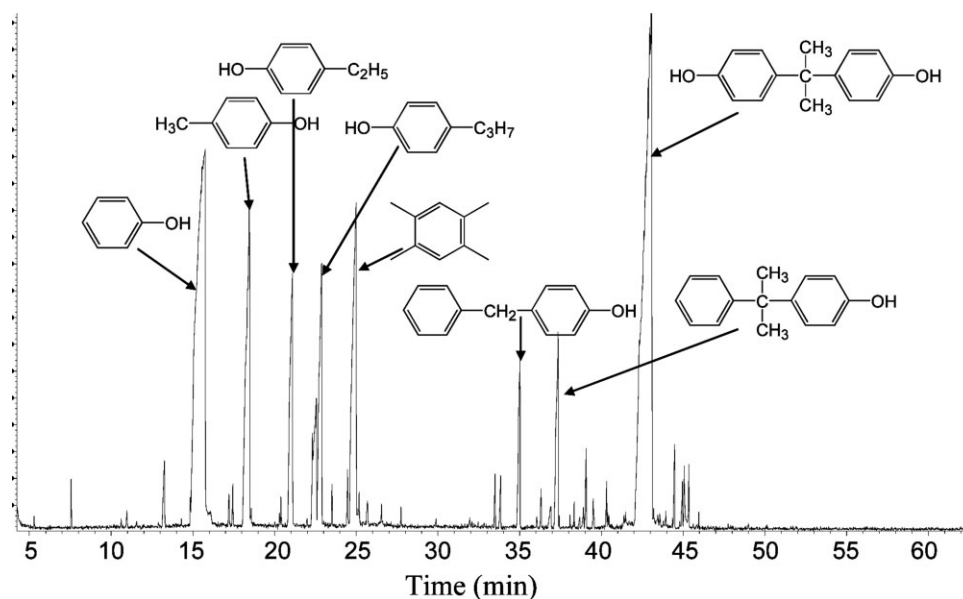
Figure 4 GC-MS chromatogram of the liquid fraction obtained from pyrolysis of a Compact Disk at 550°C.

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[12] 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.

The composition of the liquid fraction was analysed using GC-MS and the components identified are shown in Table VI. The corresponding GC-MS chromatogram of the product obtained from the CD pyrolysis is presented in Figure 4. 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%). 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.[34] and Hall and Williams,[12] 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.[30] A similar distribution of liquid products measured during pyrolysis of some polycarbonate materials has been reported in literature.[25,27,30,31,35]

According to Jang and Wilkie,[25] 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), whereas phenyl or aliphatic end groups are primarily produced due to chain scission.[25,27] 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.[25] 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 $SnCl_2$.[31]

CONCLUSIONS

This research was focused on the recycling of three types of polymers, namely PABS, PC, and PS present in WEEE. Initially, the chemical structure of each one in a variety of WEEE was identified by FTIR and DSC. Recycling of these polymers was examined by both the dissolution/reprecipitation technique and pyrolysis. The first is a simple and economic technique leading to high recovery of pure polymer with the disadvantage of using rather large amounts of, possibly toxic, solvents. Both, model polymers

and plastic parts from WEEEs were studied and optimum experimental conditions, including dissolution temperature and time, polymer concentration, and type of solvent were proposed. During the second recycling method, pyrolysis of waste compact disks (CDs) was investigated and compared with model polycarbonate. The appropriate pyrolysis temperature was selected after examining the thermal degradation of model poly(bisphenol A carbonate) by TGA. A large amount of oil was measured, together with a smaller amount of gaseous product, leaving also a solid residue. For both samples, the gaseous fraction consisted mainly of CO_2 and CO, whereas in the liquid fraction a large amount of different phenolic compounds, including the monomer bisphenol A, was measured. It seems that recycling of used CDs by pyrolysis is a very promising technique having the potential of producing useful high-value chemicals, which may find applications in the petrochemical industry. This research is continued further by examining pyrolysis of other WEEEs.

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