

Effect of brominated flame retardant on the pyrolysis products of polymers originating in WEEE

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Research Article

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Abstract

Pyrolysis is an environmentally friendly method, which is often used for the recycling of the plastics included in waste electric and electronic equipment (WEEE); since secondary valuable materials can be produced. Brominated flame retardants (BFRs) are usually added into these plastics to reduce their flammability; but they are toxic substances. The aim of this work is to examine the thermal behaviour and the products obtained after pyrolysis of polymer blends that consist of acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polycarbonate (PC) and polypropylene (PP) with composition that simulates real WEEE; in the absence and presence of a common BFR, tetrabromobisphenol A (TBBPA), in order to investigate its effect on pyrolysis products. Blends were prepared via the solvent casting method and the melt-mixing in an extruder; it was revealed that the latter method may be a better choice for blends preparation, since it didn't affect the products obtained. The chemical structure of each polymeric blend was identified by Fourier Transform Infrared spectroscopy (FTIR). Thermal degradation of the blends was evaluated by thermogravimetric (TG) experiments performed using a thermal analyser (TGA) and a pyrolyser for evolved gas analysis (EGA). It was observed that blends had a similar behaviour during their thermal degradation; and in most cases, they followed a one-step mechanism. Pyrolysis products were identified by the pyrolyser combined with a Gas Chromatographer/Mass Spectrometer (GC/MS); and comprised various useful compounds, such as monomers, aromatic hydrocarbons, phenolic compounds, etc. that could be used as chemical feedstock. Furthermore, it was found that TBBPA affected products' distribution by enhancing the formation of phenolic compounds and on the other hand by resulting in brominated compounds, such as dibromophenol.

1. Introduction

The rapid economic and technological advances along with the shorter and shorter products' lifespan have led to an increase in the production and consumption of Electric and Electronic Equipment (EEE) and so, in huge amounts of end-of-life electronic devices (Grause et al. 2015). The main difficulty as regards the recycling of Waste Electric and Electronic Equipment (WEEE) is its inhomogeneous composition; since WEEE consists of various materials, including, metals, glass and plastics that may be reused. Plastics represent a big percentage (~ 20–30%) of WEEE and include many, different types of polymers, such as acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polycarbonate (PC), polypropylene (PP), etc. as well as blends of them (Ma et al. 2016; Siddiqui et al. 2019). Another important obstacle in WEEE's recycling is the fact that plastics found in WEEE, more often than not comprise toxic additives, such as brominated flame retardants (BFRs) (Ma et al. 2016). BFRs are added into plastics in order to reduce their flammability. Among them TBBPA is the most widely used flame retardant in plastics of the electronic industry. However, brominated plastics require safe handling in order to avoid environmental contamination (Charitopoulou et al. 2020).

Until now large amounts of WEEE end up in landfilling, which causes serious health and environmental issues (Anuar Sharuddin et al. 2016). In order to eliminate landfilling, research has focused on recycling methods, which are primary recycling, energy recovery, mechanical or secondary recycling and chemical

recycling. Among these techniques, chemical recycling seems to have more advantages that limit the applicability of the other mentioned techniques, and result in its selection, as an environmentally friendly method, by many researchers (Siddiqui et al. 2019). Pyrolysis is a thermo-chemical method in which monomers can be recovered and secondary valuable chemicals can be used as fuels or chemical feedstock for the production of new products (Achilias et al. 2012; Ma et al. 2016). It takes place in an inert atmosphere, high temperatures (300–900°C) and in the absence or presence of catalysts. During pyrolysis, plastic waste is converted into liquids, gases, and solid residues (chars) (Miandad et al. 2016; Sahin and Kirim 2018). It should be highlighted that pyrolysis enables material and energy recovery from polymer waste, since only ~ 10% of the energy content of plastic waste is used in order to convert scrap into valuable hydrocarbon products (Nnorom and Osibanjo 2008; Liu et al. 2016). As regards the quality and distribution of the derived pyrolysis products, they are affected by many parameters, including pyrolysis temperature, residence time, heating rate, operating pressure, the presence of catalysts, etc. (Charitopoulou et al. 2020).

Due to pyrolysis great importance, research has focused on pyrolysis of polymers, blends or real plastics from WEEE, with the aim of finding the appropriate experimental conditions; while enhancing the formation of valuable products and eliminating the formation of undesirable ones, such as brominated compounds, that can be formed during pyrolysis (Hall and Williams 2006; Acomb et al. 2013; Caballero et al. 2016; Dias et al. 2017). For instance, Kowalska et al. (2006) applied thermogravimetric analysis (TG) on two different samples originating from WEEE (a mixture of three types of printed circuit boards and a mixture of electronic junctions with metal wires) so as to determine their appropriate degradation conditions. They found, by X-ray fluorescence measurements, that brominated flame retardant was present in the first sample, whereas chlorinated flame retardant might be present in the second one; also, the hydrocarbons formed during pyrolysis might be used as fuel. Other studies investigated printed circuit boards, mobile phones and other samples coming from WEEE by applying pyrolysis at 500°C (de Marco et al. 2008; Molto et al. 2009). In the latter work they found, by X-ray Fluorescence, that bromine was present in the samples; and after pyrolysis, some brominated compounds, such as bromophenols and dibromophenols were produced (Molto et al. 2009).

This work investigated pyrolysis of polymer blends that consisted of ABS, HIPS, PC and PP; with composition that simulates their composition in real WEEE. Firstly, attention was given on two different methods used for blends' preparation and their effect on the derived pyrolysis products. The methods applied were the solvent casting method and the melt-mixing in an extruder. The main goal of this research was to evaluate the effect of tetrabromobisphenol A (TBBPA), the most common BFR used in WEEE, on products' distribution, since more often than not WEEE comprises BFRs. So, blends were also prepared in the presence of TBBPA, applying the latter method that was found to be more beneficial. Thermal degradation of the blends was investigated using a thermal analyser (TGA) and a pyrolyser for evolved gas analysis (EGA). Pyrolysis was held at the maximum degradation temperature that was received from EGA analysis, for each blend. The composition of pyrolysis products was identified using a pyrolyser combined with a Gas Chromatography/ Mass Spectrometry (GC/MS) chromatographer.

2. Materials And Methods

2.1 Materials

The polymers used for the experiments were commercially available: ABS [(C₁₅H₁₇N)_n, FW = 211.3, batch# 01519EB, melt index: 6 g/10 min], HIPS [(C₈H₈)_x•(C₄H₆)_z, CAS 9003-55-8, lot# 02122CEV, melt index: 6 g/10 min, butadiene content 4%], PC (C₁₅H₁₆O₂, CAS 25037-45-0, lot# 07624KHV, melt index: 7 g/10 min) and PP ([CH₂CH(CH₃)]_n, CAS 9003-07-0, batch# 04227KC) supplied by Sigma-Aldrich (USA). TBBPA (3, 3', 5, 5'-Tetrabromobisphenol A, CAS 79-94-7) was also purchased from Sigma-Aldrich (USA). All polymers' pellets were ground using a mill Arthur H. Thomas Co., to reduce particle size (~ 0.2 mm) and enable the surface augmentation for the pyrolysis experiments.

2.2 Blends' Preparation

As mentioned in the introduction, there were prepared some polymeric blends, using two different methods the solvent casting method and the melt-mixing in an extruder. It should be underlined that the polymers' percentages were based on polymers' percentages in real WEEE (Yang et al. 2013). TBBPA's percentage was also based on literature data (Wäger et al. 2012; Ortuño et al. 2014) where it is referred that TBBPA in plastics in WEEE varies between 0.1–1 %.

In case of the solvent casting method, the appropriate amounts of polymers were dissolved in chlorobenzene (C₆H₅Cl, MW = 112.56) at ~ 131.6°C (boiling point) and were left for ~ 5 h in a reflux apparatus. Then, the solution was inserted into an oven (Melag) which was set at ~ 60°C, in order to let the solvent evaporate. Finally, the blend was received in the form of flakes. This blend was named as '*blend*' and consisted of 46% ABS, 39% HIPS and 15% PC.

In case of the melt-mixing method in an extruder, the appropriate amounts of polymers were inserted into a twin-screw extruder (Thermo Scientific HAAKE MiniLab) at 210°C and 30 rpm. The extrudates were further processed into thin films by hot pressing at 200°C. In this case there were prepared 6 blends: '*sample 4*' that consisted of 46% ABS, 39% HIPS and 15% PC, '*sample 5*' that consisted of 46% ABS, 39% HIPS, 15% PC and 0.9% TBBPA, '*sample 6*' that consisted of 41% ABS, 34% HIPS, 14% PC and 11% PP, '*sample 7*' that consisted of 41% ABS, 34% HIPS, 14% PC, 11% PP and 0.9% TBBPA, '*sample 8*' that consisted of 46% ABS, 39% HIPS, 15% PC and 9% TBBPA and '*sample 9*' that consisted of 41% ABS, 34% HIPS, 14% PC, 11% PP and 9% TBBPA (Table 1). The last two blends with the higher percentage of TBBPA were prepared in order to ensure better accuracy in our results.

Table 1
Composition of all blends prepared

Sample	Preparation method	ABS	HIPS	PC	PP	TBBPA*
blend	solution casting	46	39	15	-	-
sample 4	melt mixing	46	39	15	-	-
sample 5	melt mixing	46	39	15	-	0.9
sample 6	melt mixing	41	34	14	11	-
sample 7	melt mixing	41	34	14	11	0.9
sample 8	melt mixing	46	39	15	-	9.0
sample 9	melt mixing	41	34	14	11	9.0
* Amount relative to the whole polymer blend						

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of the polymer blends was confirmed by recording their IR spectra. FTIR analysis was conducted using a FTIR spectrometer, Spectrum One, from Perkin Elmer accompanied by the analogous software. All spectra were received within the range of 4000 – 600 cm^{-1} . The resolution of the equipment was 4 cm^{-1} ; and a total of 16 scans per spectrum was applied.

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric (TG) measurements were performed on a Pyris 1 TGA thermal analyzer (Perkin Elmer). Each sample weighted < 8 mg and was placed in a platinum (Pt) sample-pan. Specimens were heated from 40 to 700°C in nitrogen (99.9%) atmosphere under a 20 mL/min constant flow. The heating rate employed was 20°C/min for each experiment. Sample mass was plotted and recorded versus temperature continuously. The thermograms were treated using the Pyris Manager Software that was connected with the instrument. The sample-pan contained black residue traces when measurement was completed.

2.5 Evolved Gas Analysis (EGA) and Single Shot Analysis

EGA and Single Shot Analysis were carried out on a Pyrolyser (EGA/PY-3030D Frontier Laboratories) and in both methods the purge gas was He. The sample's mass in both cases was ~ 1 mg. EGA was applied in order to obtain information about the decomposition temperature range of each blend. During EGA there was used a metal capillary tube and samples were heated in the range of 100–700°C with a rate of 20°C/min, under satisfactory vacuum.

Single Shot Analysis was applied for the determination of pyrolysis products, after pyrolysis at a specific temperature that was chosen for each sample. During it there was used an Ultra Alloy 5% diphenyl-95% dimethyl polysiloxane capillary and the Pyrolyser (EGA/PY-3030D) was coupled with Gas

Chromatographer/Mass Spectrometer (Py-GC/MS) (QP-2010 Ultra Plus, Shimadzu, Japan). In this case it took place flash pyrolysis (0.5 min) at the maximum degradation temperature received from EGA; and in almost each case the temperature program lasted 40 min. The detailed method parameters that were finally applied after some optimization experiments are presented here. The injection temperature was 300°C and the column oven was held initially at 50°C for 1 min, then ramped to 300°C, with a heating rate of 10°C/min; and was held there for 14 min. In case of PP the column oven program was modified a little, in order to last more, since products continued to form after the total time of 40min. The chromatographs received, after each experiment, were subjected to interpretation through Shimadzu post-run software (NIST 17 Library). During post-run analysis only clear, intensive peaks were taken into account to ensure safe conclusions. Apart from applying the SCAN mode in the settings before pyrolysis, so as to scan the whole spectrum; selected ion monitoring (SIM) mode was also applied with the aim of targeting specific ions for the determination of some possible brominated compounds formed in order to indicate their presence according to the NIST 17 Library.

2.6 X-ray Fluorescence (XRF)

With a view to ensuring that bromine (from TBBPA) was present in the whole mass of our samples, X-ray Fluorescence (XRF) was also applied. XRF analysis was carried out by a S4-Pioneer (Bruker-AMS, Deutschland) wavelength dispersive spectrometer at the Scanning Electron Microscopy Laboratory of Aristotle University of Thessaloniki. Films of all blends were cut into small parts appropriate for the measurements.

3. Results And Discussion

3.1 Bromine content

The bromine content of all blends prepared by the melt-mixing method and measured via X-ray Fluorescence, is presented in Table 2. As observed, bromine was indeed present in all 'brominated' blends prepared via the extruder; in order to assure the repeatability of the blend preparation, random samples, from many, different sample-films were analysed and the mean value is presented in the Table. All values of weight percentages for each blend examined were very close, something that may be indicative of the fact that the blends were homogeneous enough, since the bromine content was almost the same in all samples of each blend examined.

Table 2
Bromine content of the tested blends

Blend's name	wt % Br measured
sample 4	0
sample 5	0.562
sample 6	0
sample 7	0.506
sample 8	5.528
sample 9	6.026

3.2 FTIR measurements

From FTIR measurements the polymers that were present in each blend were confirmed; and four representative spectra are presented here in Fig. 1, as an example. It can be noticed that blends retain characteristics of styrenics (including ABS and HIPS) and polyesters, such as PC. The former observation is based on the bands at $3000-3100\text{cm}^{-1}$ ($\nu_{\text{C-H}}$), $\sim 2236\text{cm}^{-1}$ ($\nu_{\text{C-N}}$) which is due to acrylonitrile units in ABS, $\sim 1600\text{cm}^{-1}$ ($\nu_{\text{C=C}}$), $\sim 1492\text{cm}^{-1}$ and $\sim 1453\text{cm}^{-1}$ (due to the aromatic ring stretching vibrations), $\sim 754\text{cm}^{-1}$ and $\sim 703\text{cm}^{-1}$ (due to the styrene units in HIPS). The latter observation, about PC, can be based on the bands at $\sim 1770\text{cm}^{-1}$ ($\nu_{\text{C=O}}$), $\sim 1084\text{cm}^{-1}$ and $\sim 1011\text{cm}^{-1}$ (due to the para aryloxy group) (Achilias et al. 2009; Rosi et al. 2018). TBBPA could not be identified by FTIR, because of its presence in such small amounts.

3.3 Thermal degradation via TG and EGA

For all blends tested TG and DTG curves as well as EGA curves were received so as to obtain important information, such as the degradation steps, the initial, maximum and final degradation temperature and the maximum sample loss (only from TG and DTG). Firstly, there is presented the thermal degradation of all pure polymers: ABS, HIPS, PC and PP in order to compare their degradation with that of the blends. In Figs. 2a and b there are presented the TG and DTG curves for the four mentioned polymers.

From Fig. 2 it is obvious that the thermal degradation of ABS and HIPS is quite similar since their degradation begins and ends at very close temperatures. Specifically, ABS completes its degradation at $T_{\text{fin}} = 515^{\circ}\text{C}$ (residual mass $\sim 2.3\%$) and HIPS at $T_{\text{fin}} = 509^{\circ}\text{C}$ (residual mass $\sim 1.1\%$). PP's degradation starts at a higher temperature than that of ABS and HIPS; but it is completed at a very close temperature ($T_{\text{fin}} = 499^{\circ}\text{C}$ and residual mass $\sim 3.2\%$). On the other hand, PC's decomposition starts and ends ($T_{\text{fin}} = 664^{\circ}\text{C}$, residual mass $\sim 23\%$) at higher temperatures showing greater heat endurance, due to the aromatic rings in the chain backbone. The fact that its residual mass is that much may be attributed to the char, which is formed from the aromatic parts (Vouvoudi et al. 2017). According to the DTG curves (2b), the maximum degradation of HIPS, PP and PC follows a one-step mechanism and their T_{max} are 449, 482

and 545°C respectively; whereas in case of ABS there are two maximum peaks corresponding to 448 and 461°C.

All these temperature results were confirmed from EGA analysis with only small temperature differences (for instance, $T_{\max} = 442^\circ\text{C}$ for HIPS and 530°C for PC) that are reasonable and may be attributed to the different principles of each method; in TGA there are recorded the mass losses versus temperature, whereas in EGA the relative intensity (%) versus temperature. As a result, these different, function principles governing the two techniques lead to different sensitivity.

As for the thermal degradation of the blends, in Figs. 3a and b there are presented the TG and EGA curves obtained for all of them.

From Figs. 3a and b it can be outlined that the thermal degradation of the different blends is quite similar and seems to follow a one-step mechanism. The maximum mass loss, occurs at temperatures higher than 400°C . If we compare '*blend*' (solvent casting method) with '*sample 4*' (melt-mixing in an extruder), it is noticeable that the different preparation method doesn't affect the degradation behaviour of the blends; since their T_{\max} are ~ 441 and $\sim 437^\circ\text{C}$ respectively. As regards the effect of the BFR (TBBPA) on the T_{\max} , it seems that its presence in such small amounts doesn't have an impact on the degradation behaviour of the blends, since T_{\max} remains almost the same in cases of '*sample 4*' (when TBBPA was absent), '*sample 5*' ($\sim 0.9\%$ TBBPA) and '*sample 8*' ($\sim 9\%$ TBBPA).

In Fig. 4 there is presented the EGA curve received for TBBPA. According to literature, TBBPA starts its thermal degradation at temperatures higher than 200°C ; since although its degradation begins from lower temperatures ($\sim 185^\circ\text{C}$) it becomes significant only at $T > 230^\circ\text{C}$ (Marsanich et al. 2004; Altarawneh et al. 2019). Its degradation occurs at two steps – stages, with the main degradation taking place in the range of $\sim 275\text{--}345^\circ\text{C}$, depending on the heating rate applied (M. Al-Harashsheh et al. 2018); for instance, Luda et al. 2003, found that for a heating rate of $10^\circ\text{C}/\text{min}$ the first stage ranged from $200\text{--}290^\circ\text{C}$ (Luda et al. 2003). The second stage with a significantly smaller peak occurs at higher temperatures ($T > 350^\circ\text{C}$), when the heating rate is $10^\circ\text{C}/\text{min}$ (M. Al-Harashsheh et al. 2018). Generally, during the first stage most of the sample's mass is consumed (Luda et al. 2003; Altarawneh et al. 2019). Figure 4 is in accordance with the mentioned literature data and shows that TBBPA's main degradation starts at lower temperatures than the blends ($T < 200^\circ\text{C}$), reaches the maximum loss at $T_{\max} = 273^\circ\text{C}$ and is completed at $T < 400^\circ\text{C}$ ($T_{\text{fin}} \sim 367^\circ\text{C}$). The second and extremely smaller peak (which is almost invisible in Fig. 4) appears at higher temperatures $400 < T < 500^\circ\text{C}$.

Pyrolysis of each polymer, blend or BFR was held at the maximum degradation temperature that was received from EGA analysis, which was in accordance with T_{\max} received from TGA experiments. So, in Table 3 there are presented the T_{\max} for all samples, in which flash pyrolysis took place.

Table 3
 T_{\max} for all samples examined

Sample examined	T_{\max} (°C) from EGA
ABS	428
HIPS	442
PC	530
PP	482
TBBPA	273
blend	441
sample 4	437
sample 5	437
sample 6	440
sample 7	440
sample 8	437
sample 9	433

3.4 Pyrolysis product distribution via Single Shot Analysis

In this unit there are presented the GC/MS chromatographs received after flash pyrolysis (0.5 min) at T_{\max} firstly, for all polymers and TBBPA, for comparison reasons and then for the tested blends (Figs. 5a-e and 6a-e respectively); along with the possible compounds formed during pyrolysis (Tables 4–13).

From the chromatographs above, it can be noticed that the dominant – higher peaks were received in the range of ~ 3 to ~ 25 min, with the exception of PP; whereas before and after that range only some peaks of lower intensity were received. Specifically, during the last 5 to 10 min no peaks were obtained, which is indicative of the fact that no other products could be formed after the retention time of 30–35 min; with the exception of PP, as mentioned previously, where products continued to form after the first 40min.

Comparing the chromatograph of 'blend' with that of 'sample 4', one could say that they are almost the same. But if they are compared with the chromatograph of 'sample 8', it can be noticed that the main differences are the peaks' intensity and the number of the peaks formed; since in case of 'sample 8' the relative intensity of the peaks is higher and the chromatograph is denser due to the fact that more peaks are visible now. The same trend was observed after drawing a comparison between 'sample 6' and 'sample 9'; where again in the latter case more peaks were formed and peaks' intensity became higher.

Table 4
Main products after single shot pyrolysis of ABS

Peak	Retention Time	Name	Possibility (%)
1	1.185	Hydrazine	82
2	1.658	Propenenitrile (or Acrylonitrile)	94
3	3.566	Styrene	86
4	4.739	alpha-methylstyrene	86
5	6.014	2-methylene-pentanedinitrile	95
6	9.777	Benzenebutanenitrile	94
7	10.834	3-Phenyl-2-pentenenitrile	84
8	13.550	1,3-Diphenylpropane	77
9	14.332	Cyclohexane, 1,3,5-triphenyl-	80
10	15.390	1,4-diphenyl-2-butene	78
11	15.923	2-Propen-1-amine, N-(phenylmethylene)-	78
12	16.131	2-Phenyl-1-pentene	77
13	18.360	1,3-Diphenylpropane	90
14	18.784	Hexane-3,4-dicarboisonitrile, 3,4-diphenyl-	78
15	19.058	Tetracyclo[5.2.1.0(2,6).0(3,5)]non-8-ene, 4-methyl-4-phenyl-, exo-	74
16	20.624	Cyclopentane, 1-phenyl-3-phenylmethylene-	73
17	21.160	Benzenemethanamine, N-(phenylmethylene)-	70
18	22.571	2,6-Diphenyl-1,6-heptadiene	80

Table 5
Main products obtained after single shot pyrolysis of HIPS

Peak	Retention Time	Name	Possibility (%)
1	1.429	1,3-Butadiene	96
2	2.802	Cyclohexene, 4-ethenyl-	96
3	3.648	1,3,5,7-Cyclooctatetraene	86
4	13.580	1,3-Diphenylpropane	96
5	14.450	1,2,3,4-Tetrahydro-2-phenylnaphthalene	76
6	15.214	1,3-Diphenyl-1-butene	91
7	15.436	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)-	94
8	16.163	2,5-Diphenyl-1,5-hexadiene	97
9	17.336	1,5-Diphenyl-1,5-hexadiene	90
10	21.370	Cyclohexane, 1,3,5-triphenyl-	67
11	22.117	[3-(2-Cyclopenten-1-yl)-2-methyl-1-phenyl-1-propenyl]benzene	82
12	22.523	3-Butenylbenzene	77
13	23.233	Benzene, 1,1',1''-[5-methyl-1-pentene-1,3,5-triyl]tris-	75
14	26.033	(2,3-Dibenzyl-4-phenyl-2-butenyl)benzene	72
15	26.644	[3,3-Dimethyl-1-(2-phenylethyl)-4-pentenyl]benzene	70
16	33.311	(2,3-Dibenzyl-4-phenyl-2-butenyl)benzene	66

Table 6
Main products obtained after single shot pyrolysis of PC

Peak	Retention Time	Name	Possibility (%)
1	1.26	Oxygen	87
2	5.882	p-Cresol	97
3	7.324	p-Ethylphenol	97
4	8.225	m-Isopropylphenol	84
5	9.379	p-Isopropenylphenol	90
6	15.882	4-(1-Methyl-1-phenylethyl)phenol	90
7	16.850	4-tert-Butyldiphenyl ether	77
8	19.058	Bisphenol A	86
9	26.125	2,4-Bis-[1-methyl-1-(4-hydroxyphenyl)ethyl]phenol	62

Table 7
Main products obtained after single shot pyrolysis of PP

Peak	Retention Time	Name	Possibility (%)
1	1.423	Propene	98
2	1.630	Cyclohexane	78
3	3.667	1-Undecene	88
4	4.545	4-Undecene, 7-methyl-	88
5	9.510	1-Decene, 2,4-dimethyl-	91
6	10.820	1-Undecene, 7-methyl-	90
7	11.530	(2,4,6-Trimethylcyclohexyl) methanol	88
8, 9	17.007 - 17.857	1-Undecene, 7-methyl-	90
10	19.142	1-Tricosene	89
11	20.848	1,19-Eicosadiene	86
12-14	29.360 - 30.827	1-Dodecanol, 2-octyl-	90
15	31.780	Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	86
16, 17	36.578, 37.832	1-Decanol, 2-octyl-	91
18	39.970	Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	85
19	47.428	1-Dodecanol, 2-octyl-	90
20	49.885	4-Tetradecene, 2,3,4-trimethyl-	84
21	53.543	1-Hentetracontanol	89
22	55.573	1-Cyclopentyleicosane	85
23-27	70.613 - 90.080	Cyclohexane, 1,2,3,5-tetraisopropyl-	85
28-29	90.453 - 91.883	1-Hentetracontanol	85
30	93.565	Cyclohexane, 1,2,3,5-tetraisopropyl-	82

Peak	Retention Time	Name	Possibility (%)
31–32	93.907 - 95.365	1-Hentetracontanol	84
33	97.422	Cyclohexane, 1,2,3,5-tetraisopropyl-	82
34–37	97.917 - 106.525	1-Hentetracontanol	85

Table 8
Main products obtained after single shot pyrolysis of TBBPA

Peak	Retention Time	Name	Possibility (%)
1	6.062	4-Bromophenol	94
2	10.272	2,4-Dibromophenol	93
3	13.463	1,3-Diphenylpropane	70
4	14.087	3-Methyl-benzofuran	69
5	14.280	Cyclohexane, 1,3,5-triphenyl-	82
6	17.567	2-Bromo-1-indanone	73
7	19.006	Biphenol A	92
8	21.182	Cyclohexane, 1,3,5-triphenyl-	90
9	23.572	Benzoic acid, 2-hydroxy-3-(phenylmethyl)-, methyl ester	43
10	25.732–26.259	Methyl 4-(4-bromophenyl)benzoate	48
11	27.148	9-Hexadecenoic acid, octadecyl ester, (Z)	61
12	37.051	Tetrapentacontane, 1,54-dibromo-	83

Taking into account the products mentioned in Tables 4–7 it's worth mentioning that after pyrolysis of all polymers examined there were received their monomers. In case of ABS there was produced styrene and propenenitrile (acrylonitrile), in case of HIPS butadiene, in case of PC Bisphenol A and in case of PP propylene. Pyrolysis of ABS produced benzene derivatives (in the range of C₈ – C₁₀) such as styrene and alpha-methylstyrene which are chemicals with high value since they can be used as fuels or chemicals for the production of new products (Brebu et al. 2005) as well as other aromatic hydrocarbons with one or two aromatic rings, such as 1,3-diphenylpropane (styrene dimer). It should be highlighted that styrene is one of the most important monomer building blocks in the production of plastic materials and alpha-methylstyrene is used as a co-monomer for the production of ABS (Franck and Stadelhofer 1988). Furthermore, there were formed both aliphatic (acrylonitrile and 2-methylene-pentanedinitrile) and

aromatic nitrogenated compounds (benzenebutanenitrile and 3-phenyl-2-pentenenitrile). Among them benzenebutanenitrile was formed in larger amounts (higher peak in the chromatograph) and its formation may be owed to the reaction of acrylonitrile and styrene (Brebou et al. 2005; Jung et al. 2012). Thermal degradation of ABS is radical and includes end-chain and random chain scission (Polli et al. 2009).

As regards the products obtained after pyrolysis of HIPS, they were rich in hydrocarbons both aromatic with one, two or three aromatic rings, such as 1,3-diphenylpropane (styrene dimer), cyclohexane, 1,3,5-triphenyl- (styrene trimer) which was in large amounts – the second highest peak; and not aromatic, such as 1,3,5,7-cyclooctatetraene which was the highest peak obtained. These results are in accordance with literature data (Antonakou et al. 2014) and it is worth mentioning that aromatic hydrocarbons are high added value products that can be used as chemical feedstock for the production of new products. Thermal decomposition of HIPS follows the radical chain mechanism which includes: initiation, propagation, transfer and termination. The initiation includes chain scission and the formation of primary and secondary radicals (Hu and Li 2007; Chrissafis et al. 2014). Pyrolysis of PC resulted in the formation of various phenolic compounds, either with one aromatic ring (such as p-cresol, p-ethylphenol, etc.) or with two aromatic rings (such as 4-(1-methyl-1-phenylethyl)phenol and its monomer, bisphenol A), which is in accordance with literature data (Antonakou et al. 2014). It should be mentioned that bisphenol A was obtained in large amounts, since its peak was the highest. Phenols are also valuable chemicals since they can be used for the production of phenolic resins, bisphenol A, etc. (Franck and Stadelhofer 1988). PC's thermal degradation includes chain scission reactions (Jang and Wilkie 2005).

As for the products obtained after pyrolysis of PP, they were mostly rich in unsaturated aliphatic hydrocarbons, including; alkenes, such as: propene (monomer), 1-undecene (the highest peak obtained), 7-methyl- 4-undecene, 1-tricosene, etc., cycloalkanes, such as: cyclohexane (the second highest peak) and 1,2,3,5-tetraisopropyl-cyclohexane and alkadienes. There were also formed some alcohols, such as 2-octyl-1-dodecanol, 2-octyl-1-decanol, 1-hentetracontanol, etc. These results are in accordance with literature data where it is referred that PP's degradation mainly leads to the formation of hydrocarbons (Kiran Ciliz et al. 2004; Brebou et al. 2005). PP's thermal degradation follows the free radical route and includes random chain scission reactions (Kiang et al. 1980; Ahmad et al. 2014).

In case of TBBPA there were produced some brominated phenolic compounds with one or two bromine atoms, such as bromophenol and dibromophenol (both in large amounts, especially dibromophenol - high peak in the chromatograph) as well as other brominated compounds in smaller amounts, such as 1,5,4-dibromo-tetrapentacontane (brominated hydrocarbon) etc. These results are in accordance with literature data (Marsanich et al. 2004; Ortuño et al. 2014) where again bromophenols were formed. The production of dibromophenol in large amounts may be attributed to the chemical structure of TBBPA which enables scissions between positions 4 or 4' and the propylene structure (scissions of isopropylidene bridges) (Ortuño et al. 2014; Altarawneh et al. 2014). Apart from brominated compounds there were also formed aromatic compounds with two rings, such as 1,3-diphenylpropane (styrene dimer) and bisphenol A (monomer) or three rings such as 1,3,5-triphenyl-cyclohexane and some partially oxygenated compounds, such as furan derivatives (3-methyl-benzofuran, the highest peak in the chromatograph) and others

(benzoic acid, 2-hydroxy-3-(phenylmethyl)-, methyl ester). The formation of these non-brominated compounds may be owed to the fission of aromatic-Br bonds that take place at elevated temperatures (Altarawneh et al. 2014). Thermal degradation of TBBPA is quite complicated since various competing processes and reactions occur. During its thermal degradation evaporation phenomena take place (Marsanich et al. 2004; Altarawneh et al. 2014). Also, a very important step for TBBPA's decomposition is the previously mentioned fission of isopropylidene bridges (Altarawneh et al. 2014).

Table 9
Main products obtained after single shot pyrolysis of 'blend'

Peak	Retention Time	Name	Possibility (%)
1	3.570	Styrene	92
2	4.787	alpha-methylstyrene	87
3	9.709	Benzenebutanenitrile	94
4	10.795	3-Phenyl-2-pentenenitrile	84
5,6	11.754, 12.711	2-Chlorobiphenyl	97
7	13.566	1,3-Diphenylpropane	97
8	14.354	Cyclohexane, 1,3,5-triphenyl-	80
9	15.340	1,4-Diphenylbutane	81
10	15.728	2-Propen-1-amine, N-(phenylmethylene)-	78
11	15.946	4-(1-Methyl-1-phenylethyl)phenol	88
12	18.285	Cyclohexane, 1,3,5-triphenyl-	82
13	18.699	Hexane-3,4-dicarboisonitrile, 3,4-diphenyl-	77
14	18.924	3-Phenyl-3-cyclohepten-1-ol	75
15	19.172	Biphenol A	91
16	20.470	Benzyl butyl phthalate	96
17	21.233	Cyclohexane, 1,3,5-triphenyl-	79

Table 10
Main products obtained after single shot pyrolysis of 'sample 4'

Peak	Retention Time	Name	Possibility (%)
1	1.198	Oxygen	94
2	3.548	Styrene	94
3	4.763	alpha-methylstyrene	90
4	9.708	Benzenebutanenitrile	93
5	10.790	3-Phenyl-2-pentenenitrile	84
6	13.566	1,3-Diphenylpropane	97
7	14.354	Cyclohexane, 1,3,5-triphenyl-	79
8	15.329	1,2,3,4,5,8-Hexahydronaphthalene	77
9	15.711	2-propen-1-amine,N-(phenylmethylene)	78
10	15.945	2,6-Diphenyl-1,6-heptadiene	73
11	18.279	Cyclohexane, 1,3,5-triphenyl-	81
12	18.694	Hexane-3,4-dicarboisonitrile, 3,4-diphenyl-	76
13	18.916	3-Phenyl-3-cyclohepten-1-ol	74
14	19.132	Biphenol A	91
15	20.455	Benzyl butyl phthalate	96
16	21.240	Cyclohexane, 1,3,5-triphenyl-	77

Table 11
Main products obtained after single shot pyrolysis of 'sample 8'

Peak	Retention Time	Name	Possibility (%)
1	1.236	Oxygen	90
2	2.801	2,4-Dimethyl-1-heptene	93
3	3.422	Styrene	90
4	4.731	Phenol	97
5	8.116	p-Isopropylphenol	96
6	8,988	7-Methyl-1-undecene	91
7	9.281	p-Isopropenylphenol	87
8	9.567	Benzenebutanenitrile	92
9	9.756	Phenol, 2,5-dibromo-	65
10	10.608	3-Phenyl-2-pentenenitrile	83
11	11.774	2-Hexyl-1-decanol	86
12	13.367	1,3-Diphenylpropane	95
13	14.136	4-[Benzylamino]benzo-1,2,3-triazine	79
14	14.561	1-Dodecanol, 2-hexyl-	91
15	15.592	2-Propen-1-amine, N-(phenylmethylene)-	79
16	15.742	4-(1-Methyl-1-phenylethyl)phenol	90
17	16.455	2-Octyl-1-dodecanol	90
18	18.078	Cyclohexane, 1,3,5-triphenyl-	79
19	18.723	3-Phenyl-3-cyclohepten-1-ol	74
20	19.067	3,4'-Isopropylidenediphenol	89
21	20.282	Benzyl butyl phthalate	96
22	21.012	Cyclohexane, 1,3,5-triphenyl-	74
23	21.864	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	81
24, 25, 26	22.582, 25.537, 28.829	1,2,3,5-Tetraisopropylcyclohexane	84

Table 12
Main products obtained after single shot pyrolysis of 'sample 6'

Peak	Retention Time	Name	Possibility (%)
1	3.547	Styrene	93
2	4.730	alpha-methylstyrene	92
3	9.705	Benzenebutanenitrile	93
4	10.791	3-Phenyl-2-pentenenitrile	84
5	13.566	1,3-Diphenylpropane	95
6	14.354	Cyclohexane, 1,3,5-triphenyl-	79
7	15.328	1,2,3,4,5,8-Hexahydronaphthalene	77
8	15.702	2-Propen-1-amine, N-(phenylmethylene)-	78
9	15.942	2,6-Diphenyl-1,6-heptadiene	71
10	18.276	Cyclohexane, 1,3,5-triphenyl-	81
11	18.691	Hexane-3,4-dicarboisonitrile, 3,4-diphenyl-	76
12	18.913	3-Cyclohepten-1-ol, 3-phenyl-	75
13	19.148	3,4'-Isopropylidenediphenol	92
14	20.455	Benzyl butyl phthalate	96
15	21.235	Cyclohexane, 1,3,5-triphenyl-	78

Table 13
Main products obtained after single shot pyrolysis of 'sample 9'

Peak	Retention Time	Name	Possibility (%)
1	3.390	Styrene	90
2	4.665	Phenol	98
3	8.078	p-Isopropylphenol	97
4	8.954	7-Methyl-1-undecene	91
5	9.232	p-Isopropenylphenol	88
6	9.565	Benzenebutanenitrile	93
7	9.698	Phenol, 2,5-dibromo-	84
8	10.581	3-Phenyl-2-pentenenitrile	84
9	13.350	1,3-Diphenylpropane	94
10	14.114	4-[Benzylamino]benzo-1,2,3-triazine	79
11	14.964	1,3-Diphenyl-1-butene	91
12	15.126	1,2,3,4,5,8-Hexahydronaphthalene	71
13	15.552	2-Propen-1-amine, N-(phenylmethylene)-	79
14	15.701	4-(1-Methyl-1-phenylethyl)phenol	82
15	18.052	Cyclohexane, 1,3,5-triphenyl-	80
16	18.449	4-Isopropylphenylacetonitrile	70
17	18.707	3-Phenyl-3-cyclohepten-1-ol	74
18	18.969	3,4'-Isopropylidenediphenol	90
19	20.236	Benzyl butyl phthalate	97
20	21.017	Cyclohexane, 1,3,5-triphenyl-	77
21	21.842	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	82
22	25.288	Cyclohexane, 1,2,3,4,5,6-hexaethyl-	81

The chromatographs and the main products obtained after pyrolysis of 'sample 5' and 'sample 7' are not presented here since they were exactly the same with those of 'sample 4' and 'sample 6', respectively. Furthermore, during the post-run analysis of these two samples no brominated compounds could be identified, which may be attributed to the very low bromine content. Therefore, as regards the effect of TBBPA on products' distribution, there were taken into account only 'sample 8' and 'sample 9', the blends with the higher percentage of bromine.

From Tables 9–13 it is noticeable that many of the products obtained after pyrolysis of all blends examined are the same (such as styrene, benzenebutanenitrile, etc.) appearing also at almost the same retention times. The non-brominated compounds that were formed are owed to the degradation of the polymers present in the blends. Specifically, all blends show a main peak at ~ 3.5 min that corresponds to styrene, which is a valuable chemical; and was formed because of the degradation of ABS. At ~ 9.7 min there was obtained benzenebutanenitrile, an aromatic nitrogenated compound, which was also formed because of ABS's degradation. Another important peak at ~ 13.5 min is that of 1,3-diphenylpropane (styrene dimer) which was formed due to pyrolysis of both ABS and HIPS. The formation of 1,3,5-triphenyl-cyclohexane (styrene trimer), may be attributed to the degradation of ABS and HIPS; and TBBPA as well in case of 'sample 8' and 'sample 9'. As mentioned previously these aromatic hydrocarbons are high added value products that can be used as chemical feedstock for the production of new products (Antonakou et al. 2014).

As regards the effect of the different preparation method on the products' distribution it can be concluded that after pyrolysis of 'blend' and 'sample 4' almost all products were the same, which is reasonable, since they have the same composition. Nevertheless, the main difference lies on the fact that in case of 'blend' there were received two extra peaks (at 11.754 and 12.711 min); where the product was 2-chlorobiphenyl, which isn't a desirable one. The formation of this chlorinated compound may be owed to traces of solvent that perhaps didn't evaporate completely during blend's preparation. So, the melt-mixing method (in an extruder) seems to be more advantageous than the solvent casting method, because the former has no (negative) effect on pyrolysis products.

As for the effect of TBBPA on the products' distribution, it's worth mentioning that its presence enhances the formation of phenolic compounds, which are useful products. On the other hand, it leads to the formation of brominated compounds, which are undesirable and need to be removed. Specifically, in case of 'sample 4' and 'sample 6' (absence of BFR) only one phenolic compound (at ~ 19.1 min) was obtained, bisphenol A (monomer) and 3,4'-isopropylidenediphenol, respectively, due to PC's degradation; whereas in case of 'sample 8' and 'sample 9' there were formed more phenolic compounds, such as: p-isopropylphenol, p-isopropenylphenol, 4-(1-methyl-1-phenylethyl)phenol and 3,4'-isopropylidenediphenol. The phenolic compounds formed in the latter cases are owed to PC's degradation in combination with the presence of TBBPA that according to literature (Hall et al. 2008) enhances their formation. As it is shown in Tables 11 and 13, at ~ 9.7 min there was produced dibromophenol, because of TBBPA's presence. Dibromophenol's peak was very low, which is quite expected, considering that TBBPA was added in low percentage, in comparison with the polymers that were abundant in both blends. So, in order to ensure dibromophenol's presence, SIM analysis was also performed, targeting some specific ions (250, 252, and 254) for its determination; and it was indicated that dibromophenol was indeed formed in both cases. Furthermore, for both 'sample 8' and 'sample 9' during the SCAN mode it was found that at ~ 6 min, (Bromomethyl)benzene could be obtained with 96% possibility. Nevertheless, its presence was not confirmed when applying the SIM analysis targeting specific ions (39, 63, 65, 91, 170 and 172); so further investigation may be needed.

4. Conclusions

This paper thoroughly investigated pyrolysis of polymer blends that consisted of four different polymers abundant in WEEE (ABS, HIPS, PC and PP) as well as TBBPA, one of the most common BFR used in WEEE; since their co-existence can simulate real scenarios. Polymers' presence in blends was confirmed by FTIR analysis. Pyrolysis took place using a TGA apparatus and a pyrolyser (Py-GC/MS) for EGA and flash pyrolysis. In this way important information such as the degradation steps and the maximum degradation temperature were obtained for all blends examined. TG and EGA curves showed that the thermal degradation of blends was quite similar and seemed to follow a one-step mechanism. Flash pyrolysis was held at the maximum degradation temperature and by using the post-run software all derived pyrolysis products were identified. It was found that in all cases tested there were obtained monomers along with high value products (phenols, aromatic HC, etc.) that could be used as fuels or chemical feedstock. This indicates that pyrolysis process can be applied as an environmentally friendly, recycling method for WEEE's handling.

It was proved that the preparation method didn't influence the degradation behaviour of the blends; since for instance their T_{max} were very close. Nevertheless, as regards its effect on pyrolysis products, it was found that in case of the solvent casting method there were obtained two peaks giving a chlorinated compound (2-chlorobiphenyl), due to incomplete evaporation of chlorobenzene (solvent) during the preparation. According to this observation the melt-mixing method (in an extruder) may be considered as a more advantageous method than the solvent casting, taking into account that during the former method pyrolysis products were not affected.

As for the effect of the BFR (TBBPA) on the T_{max} , it was found that its presence in such small amounts had no impact on the degradation behaviour of the blends; T_{max} in its absence and presence were very close. However, it was proved that TBBPA's presence influenced the composition of pyrolysis products, since it favoured the formation of phenolic compounds (which are useful and desirable products); however, it also led to the production of brominated compounds that are undesirable and toxic. Dibromophenol was obtained as the main brominated compound, since its presence was ensured with SIM analysis. On the other hand, more investigation is needed in order to make sure if (bromomethyl)benzene was also formed.

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Author contribution: MAC and DA contributed to the study conception, methodology and design. MAC performed material preparation, data collection and analysis. LP performed the XRF experiments and analyzed the results. Supervision: DSA. MAC wrote the first draft of the manuscript and all authors reviewed and commented on previous versions of the manuscript. All authors read and approved the final version of the manuscript.

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Figures

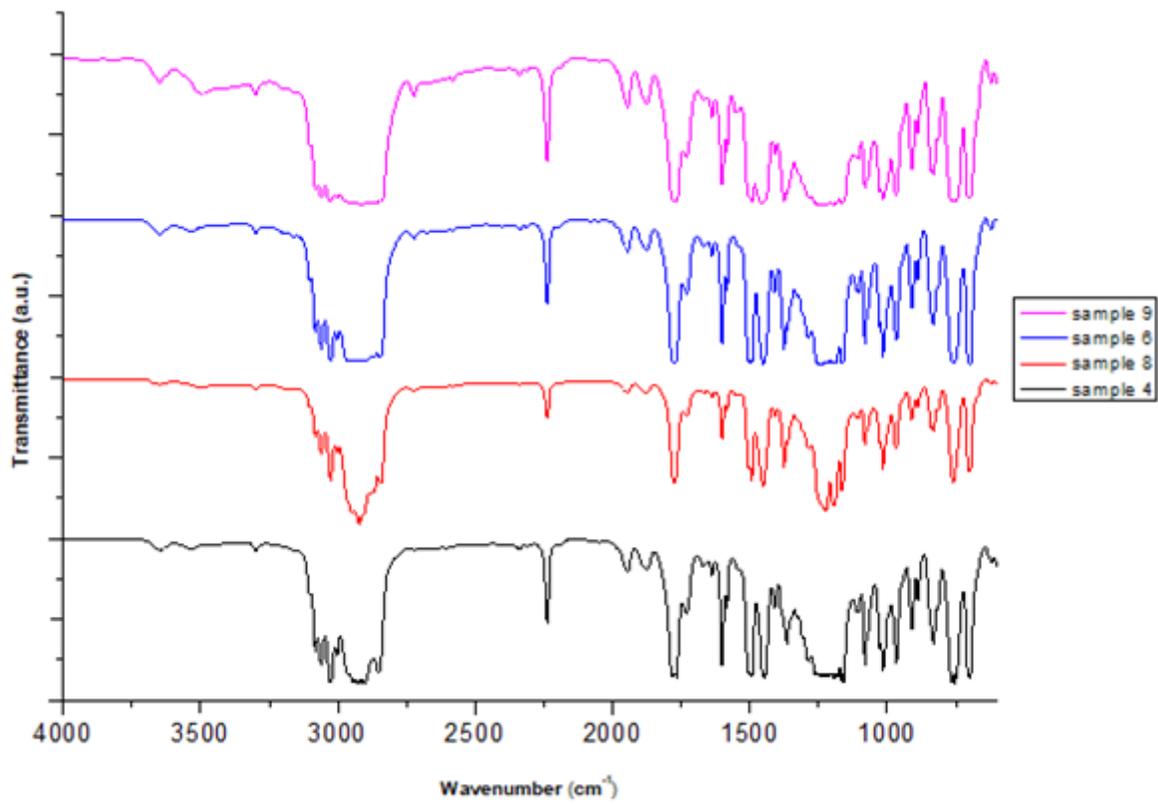


Figure 1

Representative FTIR spectra of four polymeric blends, showing the presence of all mentioned polymers

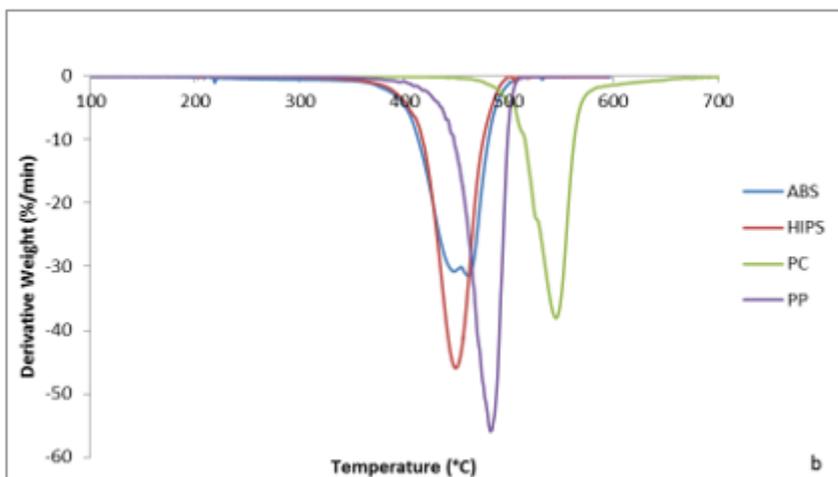
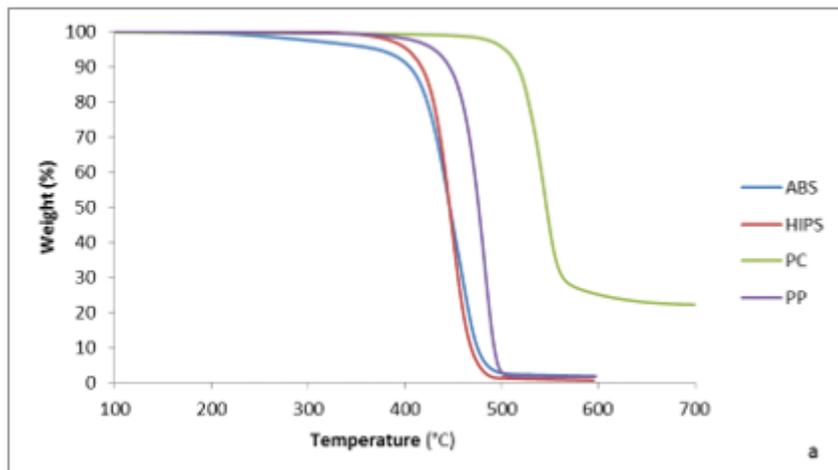


Figure 2

TG (a) and DTG (b) curves of neat ABS, HIPS, PC and PP

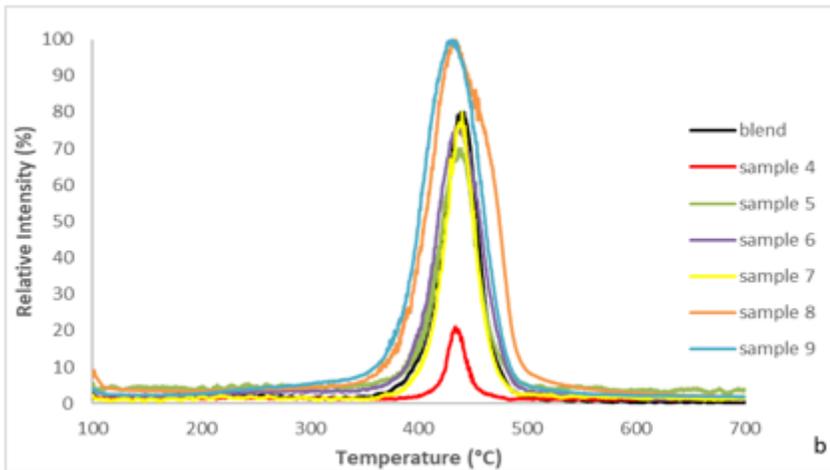
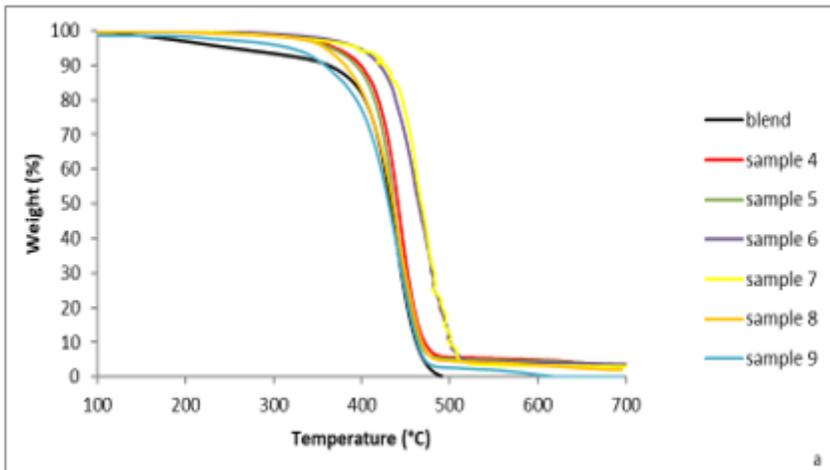


Figure 3

TG (a) and EGA (b) curves for all blends tested

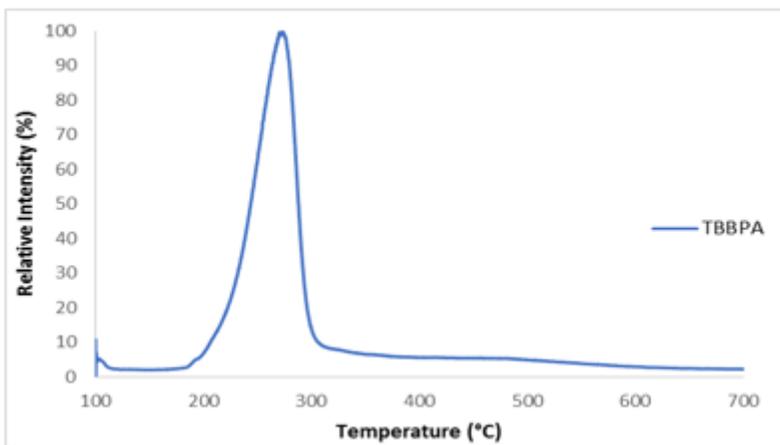


Figure 4

GA curve for TBBPA

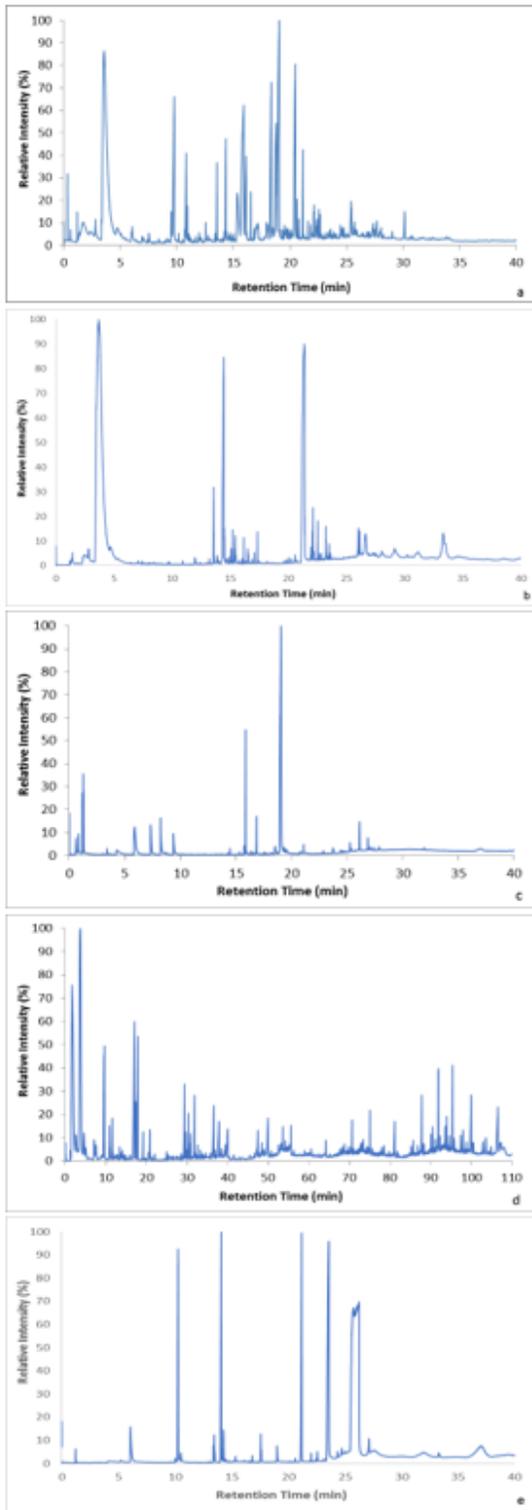


Figure 5

Chromatographs after pyrolysis at T_{max} for a. ABS, b. HIPS, c. PC, d. PP and e. TBBPA

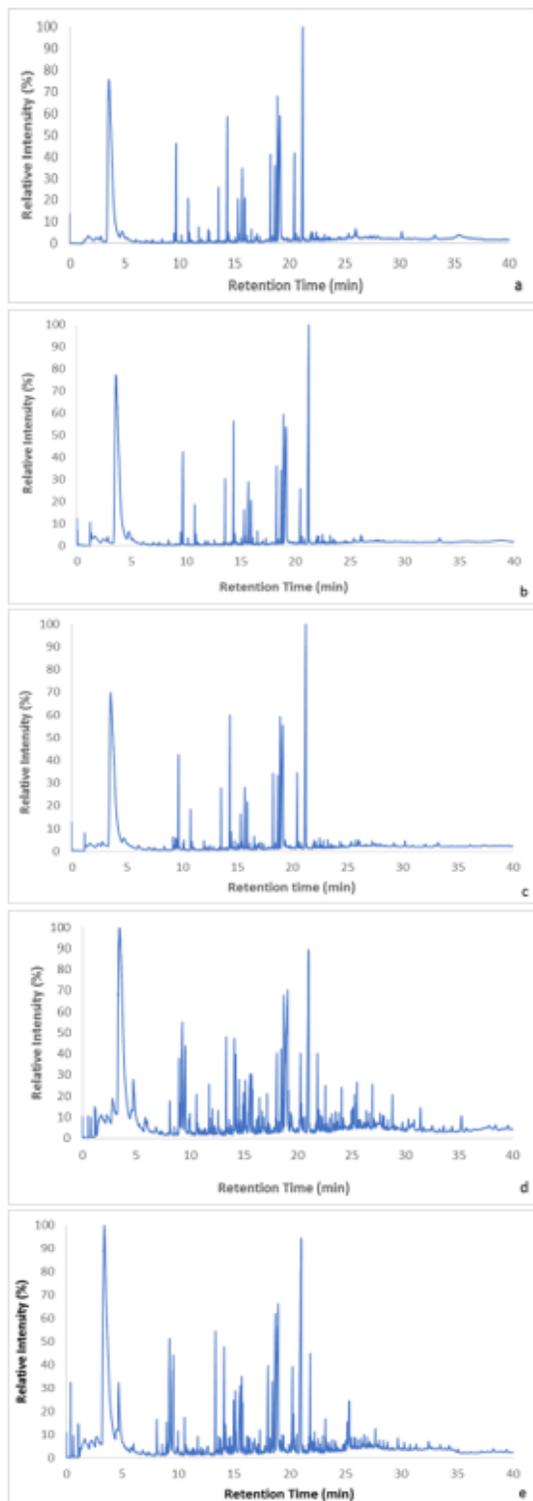


Figure 6

Chromatographs after pyrolysis at T_{max} for a. 'blend', b. 'sample 4', c. 'sample 6', d. 'sample 8' and e. 'sample