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Development of efficient techniques for the removal of brominated flame retardants from polymer blends with composition that simulates WEEE

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Abstract

Waste electric and electronic equipment (WEEE) has increased enormously because of the rapid expansion and consumption of electronic devices and their short lifespan. Recycling of WEEE is challenging, due to the presence of various materials including glass, metals and plastics (Buekens and Yang 2014). Brominated flame retardants (BFR), such as tetrabromobisphenol A (TBBPA) that are often added into plastics are toxic substances that must be removed before or during recycling (Ma et al. 2016). Pyrolysis is an environmentally friendly method, since secondary valuable materials or monomers can be recovered (Antonakou et al. 2014). In this work solvent extraction prior to pyrolysis is examined as a pretreatment method, in order to reduce the bromine content in specific brominated-polymeric blends. The blends consist of acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polycarbonate (PC) and polypropylene (PP), along with TBBPA, which is the tested BFR. Different solvents as well as different extraction times were investigated. Before and after pretreatment, blends were analysed by X-ray fluorescence (XRF) so as to estimate the bromine content; and were also pyrolysed in order to evaluate the derived products and examine if brominated compounds continue to form. XRF and pyrolysis experiments indicate that reduction of bromine can be effectively achieved.

Keywords: WEEE, pyrolysis, soxhlet extraction, brominated flame retardants, XRF

1. Introduction

The rapid economic and technological advances over the years, in combination with people's need for better living conditions have led to a global rise in the consumption of Electric and Electronic Equipment (EEE) and as a result in huge amounts of end-of-life electronic devices (Parajuly et al. 2017). Taking these into account, research has focused on finding environmentally friendly approaches for their safe disposal, while contributing to a circular economy (Achilias et al. 2012). However, recycling of Waste Electric and Electronic Equipment (WEEE) remains a challenge, since they consist of various materials, such as metals, glass and plastics that could be reused (Siddiqui et al. 2019). Different types of polymers can be identified in the plastic content of WEEE, including acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polycarbonate (PC), polypropylene (PP), etc. as well as blends of them. Plastics account for almost 30% of WEEE and usually comprise toxic additives, such as heavy metals and brominated flame retardants (BFRs) (polybrominated biphenyls (PBB), tetrabromobisphenol A (TBBPA), etc.) that enhance the difficulties in their separation and recycling (Ma et al. 2016).

At present the disposal of WEEE takes place via landfilling, energy recovery, mechanical recycling and chemical recycling. The first three have many disadvantages. For example, landfilling leads to soil and ground water pollution because of contaminants' leaching; while many years are needed for plastics degradation (Yang et al. 2013; Anuar Sharuddin et al. 2016). Instead, chemical recycling has many advantages that result in limiting the applicability of the other three mentioned techniques. Pyrolysis is a thermo chemical, environmentally friendly method since monomers can be recovered or valuable chemicals can be used as fuels or chemical feedstock for the production of new products (Achilias et al. 2012; Ma et al. 2016). Due to its paramount importance many researchers have studied various chemical recycling methods on polymers found in WEEE by using polymers or blends with composition that simulates their composition in WEEE (Ma et al. 2015; Jung et al. 2012), with the aim of finding the appropriate experimental conditions for pyrolysis, so as to form products that could be further used to produce valuable chemicals or bio-fuels.

The present investigation focuses on soxhlet extraction as a pretreatment method, prior to pyrolysis, with the aim of reducing the bromine content in some brominated-polymeric blends. Blends consist of ABS, HIPS, PC and PP, along with TBBPA (tested BFR). Different solvents and different extraction times were applied, in order to find the optimal combination (solvent-time). XRF analysis of all blends took place before and after the pretreatments, so as to estimate their debromination effect. Blends were also pyrolysed in order to evaluate the derived products and examine whether brominated compounds continue to form or not.

2. Materials and Methods

2.1 Materials

The polymers used for the blends' preparation were commercially available: ABS [(C15H17N)n, FW=211.3, batch# 01519EB], HIPS [(C8H8)x·(C4H6)z, CAS 9003-55-8], PC [(C15H16O2)n, CAS 25037-45-0] 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 purchased from Sigma-Aldrich (USA).

Blends were prepared using 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.

The solvents used for the extraction were: isopropanol, ethanol and butanol. They were chosen due to their high relative polarity and their low toxicity; since solvents' toxicity is a crucial parameter when designing a process.

2.2 Methods

Soxhlet extraction of the polymeric blends was performed with a soxhlet extractor, where ~1.3 g of blend was placed in the thimble in the soxhlet apparatus, while the spherical flask was filled with 130 ml of each solvent examined. The extraction temperature was based on the boiling point of the solvent used. Three different extraction times were applied: 3, 6 and 12hr.

Pyrolysis experiments were carried out on a Pyrolizer (EGA/PY-3030D Frontier Laboratories) that is coupled with GC/MS (QP-2010 Ultra Plus, Shimadzu, Japan). Flash pyrolysis (0.5 min) took place at 400°C applying both the SCAN mode, so as to scan the whole spectrum, and selected ion monitoring (SIM) mode so as to target specific ions (250, 252 and 254) for the determination of dibromophenol; in order to evaluate if its formation is reduced after the pretreatment.

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 were cut into small parts appropriate for the measurements and were analysed before and after pretreatment, so as to estimate the bromine reduction.

3. Results and Discussion

According to pyrolysis and XRF results, soxhlet extraction led to an important reduction of bromine in all samples tested. Specifically, during the SCAN mode, it was found that all compounds that were formed before the pretreatment, because of the polymers' degradation, continued to form (with the exception of some phenolic compounds). Nevertheless, no brominated compounds could be identified now, since they were present in very small amounts. In Table 1, there are presented some of the most important products formed after pyrolysis of a blend that consists of: ABS, HIPS, PC and TBBPA, before and after the soxhlet extraction. During the SIM mode, focusing on dibromophenol (the main bromo-compound), it was observed that in all cases examined the areas of dibromophenol peaks were significantly decreased when compared to the areas obtained before the pretreatment. These results were in agreement with those obtained from XRF, where it was confirmed that soxhlet extraction resulted in great reduction of bromine in the samples.

Table 1. Some of the most abundant pyrolysis products obtained before and after extraction of a blend with ABS, HIPS, PC, TBBPA

	Name	
Retention Time	**Before Extraction**	**After Extraction**
3.4	Styrene	Styrene
6.0	**Benzene, (bromomethyl)-**	-
8.1	p-Isopropylphenol	-
9.0	7-Methyl-1-undecene	7-Methyl-1-undecene
9.3	p-Isopropenylphenol	-
9.6	Benzenebutanenitrile	Benzenebutanenitrile
9.8	**Phenol, 2,5-dibromo-**	-
13.4	1,3-Diphenylpropane	1,3-Diphenylpropane
14.1	4-[Benzylamino]benzo-1,2,3-triazine	4-[Benzylamino]benzo-1,2,3-triazine
14. 6	1-Dodecanol, 2-hexyl-	1-Dodecanol, 2-hexyl-
15.6	2-Propen-1-amine, N-(phenylmethylene)-	2-Propen-1-amine, N-(phenylmethylene)-
15.8	4-(1-Methyl-1-phenylethyl)phenol	4-(1-Methyl-1-phenylethyl)phenol
18.1	Cyclohexane, 1,3,5-triphenyl-	Cyclohexane, 1,3,5-triphenyl-
18.4	3-Phenyl-3-cyclohepten-1-ol	3-Phenyl-3-cyclohepten-1-ol
19.1	3,4'-Isopropylidenediphenol	3,4'-Isopropylidenediphenol

As regards the effect of the extraction time on the debromination, both methods (SIM and XRF) showed that as the extraction time increased, the reduction of bromine also increased. As for the extraction solvents, it was found that butanol (applying a 6hr extraction) had the best extraction results for TBBPA; since in XRF analysis bromine was below detection limit, which was in agreement with SIM analysis in which the reduction of dibromophenol area was greater than 97%.

4. Conclusions

Pyrolysis method (applying both SCAN and SIM mode) as well as XRF analysis were used for the determination of the bromine content in polymeric blends. During the SIM mode emphasis was given on dibromophenol, which was the main brominated compound formed during pyrolysis of the brominated-polymeric blends. On the other hand, XRF was applied in order to evaluate the total amount of bromine, before and after the pretreatment. During soxhlet extraction (pretreatment), different conditions (time, solvents) were investigated as regards their effect on the extraction yield of TBBPA; and so, on bromine reduction in blends. Both methods showed that soxhlet extraction was efficient in removing bromine from the polymer blends. Furthermore, they proved that butanol was the best solvent, since in this case there was noticed the greatest bromine reduction. These results could be useful in future research on real plastics from WEEE.

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