Pyrolysis as a recycling method of polymeric blends and plastics collected from WEEE in a fixed-bed reactor

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Introduction

The production and consumption of electric and electronic devices have increased over the last years leading to large amounts of waste electric and electronic equipment (WEEE). Plastics in WEEE represent a big percentage, almost 30% of WEEE; and the most commonly used are acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polycarbonate (PC), blends of PC/ABS, etc. (Ma et al. 2016). A difficulty in the recycling of plastics from WEEE is the fact that they often contain various, toxic additives, such as colourants, plasticizers, brominated flame retardants (BFR) and others. BFR are added into plastics in order to reduce their flammability, but during the recycling of brominated flame retarded plastics careful handling is required, in order to avoid environmental contamination (Charitopoulou et al. 2021).

The disposal of WEEE occurs via landfilling, primary recycling, energy recovery, mechanical recycling and chemical recycling. Among them, chemical recycling and especially pyrolysis has many advantages and is often selected by many researchers as an environmentally friendly method. During pyrolysis the monomers can be recovered and secondary valuable materials can be produced (Ma et al. 2016). It takes place in an inert atmosphere, medium to 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).

This work investigated the thermal pyrolysis of two polymeric blends with composition similar to that of WEEE, as well as of four plastic materials gathered from real WEEE, with the aim of recovering secondary valuable products and monomers. The blends consisted of ABS, HIPS, PC and/or PP along with tetrabromobisphenol-A (TBBPA), which is a very common BFR. The plastic fractions coming from WEEE, included television, computer and printer samples. All of them were subjected to Fourier transform infrared spectroscopy (FTIR) and Evolved Gas Analysis (EGA). Then, thermal pyrolysis was conducted at 440 °C, using a bench-scale fixed bed reactor; and the liquid, solid and gaseous products were analysed. EGA analysis showed that the thermal degradation of the blends and samples followed a one-step mechanism. According to the FTIR analysis of the unknown plastics from WEEE, two strong peaks were formed within the range: 2840-3000 cm^{-1}, which are due to C-H bond; and are indicative of styrenic polymers (ABS or HIPS).

Materials and Methods

The polymers used for the preparation of the blends were commercially available: ABS [$(C_{15}H_{17}N)_n$, FW=211.3, batch# 01519EB], HIPS [$(C_8H_8)_x \cdot (C_4H_6)_z$, CAS 9003-55-8], PC [$(C_{15}H_{16}O_2)_n$, CAS 25037-45-0] and PP ($[CH_2CH(CH_3)]_n$, CAS 9003-07-0, batch# 04227KC). The BFR used was TBBPA (3, 3′, 5, 5′-Tetrabromobisphenol A, CAS 79-94-7). All of them were 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 plastic materials coming from WEEE were collected either from a recycling plant or from household appliances and included samples from televisions (T1 and T2), computers (C1) and printers (P1). After their collection, the plastic samples were firstly reduced in size, using hand cutting tools.

Both the blends and the plastic samples were analysed by various techniques. Fourier transform infrared spectroscopy (FTIR) was applied to the polymer blends in order to confirm their chemical structure; and to the plastic samples in order to recognise the polymers that were present in each device, since they were unknown. FTIR analysis was conducted using a FTIR spectrometer, Spectrum One, from Perkin Elmer, which was accompanied by the analogous software. Spectra were received within the range of 4000–600 cm^{-1}. The resolution of the equipment was 4 cm^{-1} and 16 scans per spectrum were applied. EGA analysis was applied in order to receive information about the decomposition temperature range of the samples and was carried out on a Pyrolizer (EGA/PY-3030D Frontier Laboratories), where the purge gas was He. During EGA each sample was heated in the range of 100–700°C with a rate of 20°C/min, under satisfactory vacuum. Pyrolysis experiments were performed at 440 °C, using a bench-scale fixed bed reactor heated by a 3-zone electrical furnace. The temperature of each zone was independently controlled using temperature controllers. A specially designed piston system was used to introduce the feedstock into the reactor and a constant stream of N_2 was fed from the top of the reactor for the continuous withdrawal of the products and the maintenance of the inert atmosphere

during pyrolysis. Before each measurement the reactor was filled with 0.5 g silica sand and the piston was filled with 1 g of feedstock. The liquid products were collected and quantitatively measured in the pre-weighted glass receiver, the gas products were collected and measured by the water displacement method and the amount of the solid residue formed was measured by direct weighing.

Results and Discussion

The FTIR spectra for all samples studied are shown in Figure 1. From the FTIR measurements, the polymers that were present in the blends were confirmed. As regards the FTIR analysis of the unknown plastic samples, the most important observation is the fact that for all of them two strong peaks, within the range: 2840-3000 cm^{-1}, were formed. These peaks are attributed to C-H bond and are indicative of styrenic polymers (ABS or HIPS).

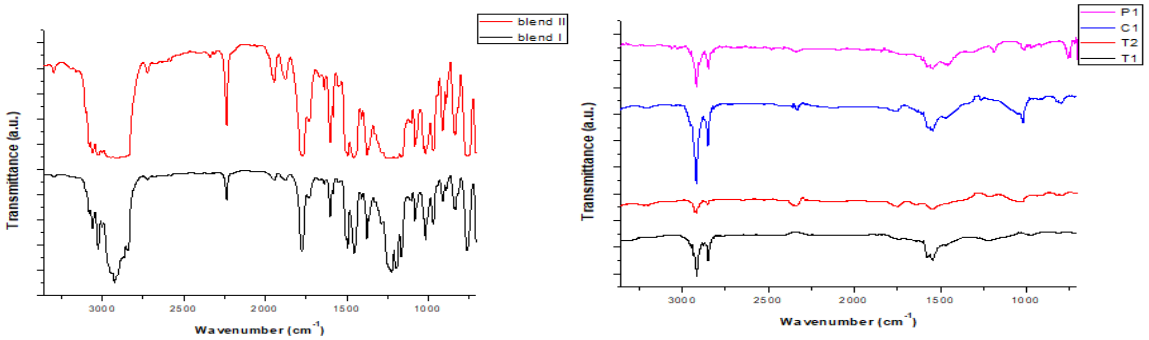

Fig. 1 FTIR spectra for blends (left) and samples collected from WEEE (right)

According to EGA analysis the thermal degradation of the blends was quite similar, since the degradation started, became maximum and ended at very close temperatures; and seemed to follow a one-step mechanism. As for the plastic samples, again the degradation followed a one-step mechanism, since one strong peak was observed, except for T1 sample, where two maximum peaks were received; but only the one of them was stronger and was considered as the main degradation peak.

As regards the pyrolysis results, as already explained in the introduction, the degradation products fall under three main categories: total liquid product, gas and solid. Their distribution is shown in Table 1.

Table 1 Analysis of products (% wt. on feedstock) for all samples examined

Sample	Liquid yield	Gas yield	Solid yield
blend I	84.2	4.9	2.8
blend II	79.7	3.7	6.0
T1	41.3	5.3	42.7
T2	89.6	1.7	2.5
C1	89.5	1.6	0.8
P1	87.5	2.7	1.2

Conclusions

In this work, two polymeric blends along with some plastic parts collected from WEEE, were analysed by various methods. Their degradation behaviour was investigated by EGA analysis and showed that the degradation of most samples followed a one-step mechanism. FTIR analysis was conducted for the identification of the polymers present in the unknown plastic samples. Both blends and plastics from WEEE were subjected to thermal pyrolysis for their recycling.

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