

# Thermal and catalytic pyrolysis of polymer blends having composition similar to that originating in WEEE

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## Introduction

Nowadays, the amount of waste electric and electronic equipment (WEEE) has increased enormously, because of the rapid expansion and consumption of electronic devices and their short lifespan. These in combination with their non-biodegradability, led to the need to explore environmentally friendly approaches for their safe disposal. Recycling of WEEE is a challenge, due to the presence of various materials, including glass, metals and plastics. Different types of polymers can be identified in the plastic content of WEEE, such as high-impact polystyrene (HIPS), polycarbonate (PC), polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), etc. Plastics originating in WEEE usually comprise many additives, such as thermal stabilizers, flame retardants (usually brominated ones), colourants, etc. (Buekens and Yang (2014)). Brominated flame retardants (BFRs) are added into plastics to reduce their flammability, but are toxic substances that need to be removed before or during pyrolysis.

At present the recycling techniques used in WEEE include landfilling, energy recovery, mechanical and chemical recycling (Ma *et al* (2016)). Among them pyrolysis, a thermo-chemical process, is often selected as an environmentally friendly and sustainable method, since secondary valuable materials can be produced and the liquid fraction can be used as fuel for energy production. Depending on the polymers used as raw-feeding materials various different products can be received in the pyrolysis oil (Antonakou *et al* (2014)).

The present investigation focuses on advanced methods for the recycling of polymer blends that simulate blends found in WEEE. Emphasis is given on the thermal behaviour and pyrolysis products of two polymer blends that consist of ABS, HIPS, PC and ABS, HIPS, PC and PP; and the same polymer blends in the presence of tetrabromobisphenol A (TBBPA), which is one of the most common BFRs in WEEE, with the aim of investigating its effect on the pyrolysis products. These polymer blends were also pyrolyzed in the presence of various catalysts, so as to evaluate their effect on the derived pyrolysis products and examine if they can enhance the reduction of the brominated compounds formed during pyrolysis. In order to investigate the degradation of the mentioned blends, thermogravimetric (TG) experiments were carried out using a thermal analyzer (TGA) and a pyrolyzer for evolved gas analysis (EGA). As regards the composition of the pyrolysis products, a pyrolyzer combined with a Gas Chromatography/Mass Spectrometry (GC/MS) was used.

## Material and Methods

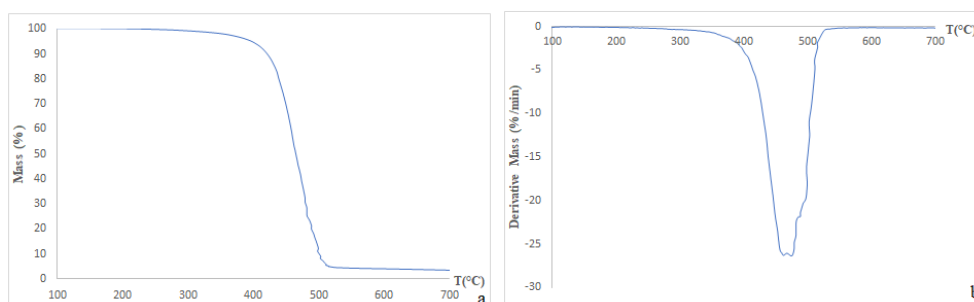
The polymers used for the blends' preparation were commercially available: ABS [(C<sub>15</sub>H<sub>17</sub>N)<sub>n</sub>, FW=211.3, batch# 01519EB], HIPS [(C<sub>8</sub>H<sub>8</sub>)<sub>x</sub>·(C<sub>4</sub>H<sub>6</sub>)<sub>z</sub>, CAS 9003-55-8], PC [(C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>)<sub>n</sub>, CAS 25037-45-0] and PP [(CH<sub>2</sub>CH(CH<sub>3</sub>))<sub>n</sub>, 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 catalysts that were studied include both acid (such as ZSM-5 and Al<sub>2</sub>O<sub>3</sub>) and basic (such as MgO) catalysts that were provided by Chemical Process and Energy Resources Institute (Centre for Research and Technology Hellas -CERTH).

TG experiments were performed on a Pyris 1 TGA (Perkin Elmer) thermal analyzer and each sample was heated from ambient temperature to 700°C, in nitrogen atmosphere with a heating rate of 20°C/min. EGA and Single Shot Analysis were carried out on a Pyrolyzer (EGA/PY-3030D Frontier Laboratories) and in both methods the purge gas was He. During EGA Analysis each sample was heated in the range of 100–700°C with a rate of 20°C/min, under satisfactory vacuum. For Single Shot Analysis the Pyrolyzer (EGA/PY-3030D) was coupled with GC/MS (QP-2010 Ultra Plus, Shimadzu, Japan) and flash pyrolysis (0.5 min) was held at a specific temperature that was chosen depending on the sample examined; the temperature program lasted ~40 min.

## Results and Discussion

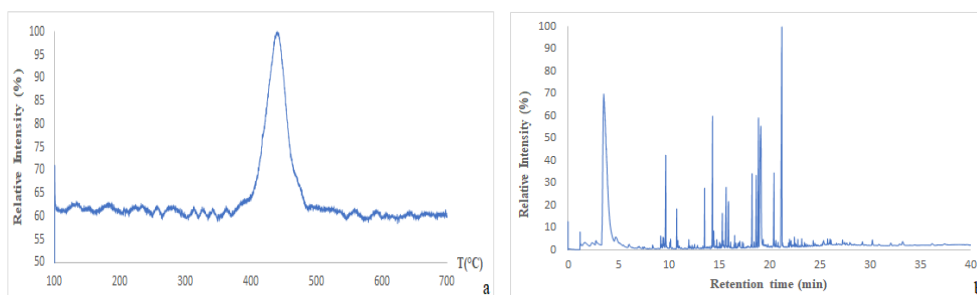
For all samples, TG, DTG as well as EGA curves were received in order to obtain important information, such as the initial, maximum and final degradation temperature and the maximum sample loss (only from TG and DTG). Then each sample was pyrolyzed so as to determine the derived products. Pyrolysis took place in the maximum degradation temperature that was received from EGA, which was in accordance with T<sub>max</sub> that was received from

DTG curves, in almost all cases. Figures 1a and 1b depict the TG and DTG curves respectively, for an indicative blend that contained ABS, HIPS, PC and PP.



**Fig. 1** Blend of ABS, HIPS, PC and PP: a. TGA curve, b. DTG curve

From Figure 1a, it is noticeable that less than 5% of the sample mass was left (residual) and from Figure 1b, that  $T_{max}=460^{\circ}\text{C}$ . Figure 2a depicts the EGA curve obtained for blend of ABS, HIPS, PC and PP; and Figure 2b depicts the chromatograph obtained after its thermal pyrolysis at the maximum degradation temperature. According to EGA curve  $T_{max}=440^{\circ}\text{C}$ . The same curves (TG, DTG and EGA) were received for all blends. For blend of ABS, HIPS, PC and PP,  $T=440^{\circ}\text{C}$  was selected as the temperature with the maximum degradation and so pyrolysis was held at that temperature (Figure 2b). In the same way  $T_{max}$  were estimated from EGA curves for the rest of the samples examined and then pyrolysis was held at those temperatures.



**Fig. 2** Blend of ABS, HIPS, PC and PP: a. EGA curve, b. Chromatograph after Single Shot pyrolysis at  $440^{\circ}\text{C}$

From Figure 2b and the use of NIST library the main products, such as styrene, benzenebutanenitrile, 1,3-diphenylpropane, etc. derived from blend's pyrolysis could be identified. Chromatographs after thermal and catalytic pyrolysis were obtained for all samples and the catalysts' effect was evaluated.

## Conclusions

TG and DTG curves provide important information, such as the initial, maximum and final degradation temperature and the maximum sample loss. These results were confirmed through EGA analysis and so pyrolysis temperature could be selected. Afterwards, the pyrolysis products could be identified and through them the effect of TBBPA on the products gained (for the brominated blends) could be specified. Furthermore, the catalysts' effect on products distribution was thoroughly investigated.

## References

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