Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 1, 137–140

THERMOGRAVIMETRIC INVESTIGATION OF WASTES FROM ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

E. Kowalska[1*], *J. Radomska*[1], *P. Konarski*[1], *R. Diduszko*[2,1], *J. Oszczudłowski*[3], *T. Opalińska*[1], *M. Więch*[1] *and Z. Duszyc*[4]

[1]Industrial Institute of Electronics, Długa 44/50 Street, 00-241 Warsaw, Poland
[2]Institute of Electronic Materials Technology, Wólczyńska 133 Sreet, 01-919 Warsaw, Poland
[3]Institute of Chemistry, Świętokrzyska Academy, Chęcińska 5 Street, 25-020 Kielce, Poland
[4]Institute of Mechanized Construction and Rock Mining, Center of Wastes Management, Kossutha 6 Street, 40-844 Katowice, Poland

Two components of electronic wastes (sample A – a mixture of three types of printed circuit boards, sample B – a mixture of electronic junctions with metal wires) were investigated using thermogravimetric analysis (TG). Thermogravimetric and derivative thermogravimetric data (TG and DTG) give information on the thermal stability of A and B samples and allows finding the correct conditions for their degradation using pyrolysis in an experimental system, built on the laboratory scale for utilization of hazardous wastes. X-ray fluorescence measurements prove that brominated flame retardant is present in sample A, whilst chlorinated flame retardant is a probable component of sample B. Preliminary liquid chromatography of oil products obtained as a result of thermal waste degradation shows that the hydrocarbons released during pyrolysis could be used as a fuel.

Keywords: *electronic waste, printed circuit boards, pyrolysis, thermal treatment*

Introduction

Due to rapid improvements in electronic manufacturing, the personal computer can be regarded as a short-life-cycle electronic product [1]. A large amount of used-up electronic equipment is sent to landfill sites for disposal [2] or incinerated with other industrial waste. Hazardous materials contained in computers [3] (i.e., various metals, fillers, flame retardants in plastics e.g., brominated flame retardants, printed circuit boards with integrated circuit including epoxy resin reinforced by glass or carbon fibre) may cause serious pollution in the environment if they are not disposed of properly. Incineration especially leads not only to toxic ash but also to toxic dust. These contain many metals, amongst other materials, and compel the use of very expensive gas purification systems in a typical plant for solid waste combustion. Therefore, methods for the safe utilization of wastes from electrical and electronic equipment (WEEE) are still sought [4]. Pyrolysis appears to be an adequate method for this purpose [5–8] due to the decomposition of the majority of organic substances to volatile compounds at elevated temperature, whilst metals, inorganic fillers and carbon or glass fibres generally should remain unchanged in the final residue. Furthermore pyrolysis limits the amount of formed dusts (lack of flame), which minimizes the adverse effects of hazardous materials adsorbed onto them. However, pyrolysis of waste plastic containing organic flame retardants (e.g. chlorinated flame retardants (CFR) or brominated flame retardants (BFR)) can lead to volatile halogenated (e.g., chlorinated, brominated) compounds, undesirable in pyrolysis gas and/or oil, because they can be precursors of toxic polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs) (or brominated analogues of dioxins and furans). Therefore this process must be performed in a specially designed instrument in which the emission of hazardous substances is limited.

One of the objectives of this research is to study the pyrolysis of electronic wastes and their thermal degradation products (oil, gas and solid residues). The main task is to develop a new technology of utilization of hazardous wastes, safe for the environment.

Experimental

We selected two samples of electronic waste to investigate:

- Sample A – a heterogenous mixture of three types of printed circuit boards: yellow, green and orange – (plastic shells – epoxy resin, reinforced by glass fibre and with added halogenated flame retardant to increase fire resistance) after dismantling of electronic components (integrated circuits).
- Sample B – a heterogenous mixture of electronic junctions (polyester resin used as electrical insulator with halogenated flame retardant) with metal wires after mechanical processing and sieve-air separation.

---

* Author for correspondence: kowal@pie.edu.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Thermogravimetric analysis of both A and B samples was performed using TA Instruments-TGA 951 at 10°C min^{-1} heating rate under helium atmosphere with the flow rate of 25 $\text{cm}^3\ \text{min}^{-1}$.

X-ray fluorescence analysis of the raw samples and solid residues of their thermal degradation were carried out using Siemens D500 powder diffractometer, equipped with high energy resolution semiconductor detector Si:Li.

Oil products obtained as the results of thermal treatment of both samples were analyzed by a liquid chromatograph (HPLC – Dionex P680 with Photodiode Array Detector PDA-100 and Fluorescence Detector RF 2000). Oils were diluted by acetonitrile, CH_3CN.

In order to perform the pyrolysis of selected electronic wastes, a laboratory experimental system for the utilization of hazardous wastes was designed and built. Our system consists of seven elements in series:

- Electrical furnace for pyrolysis, the volume capacity ~14 dm^3, maximum temperature ~850°C.
- Plasma chamber with three stainless steal electrodes, and one ignition electrode for gliding arc discharge. The gliding discharge is fed by a special 3-phase high voltage power system. All three electrodes are connected to three different phases. Plasma under oxygen atmosphere is used for combustion of the pyrolysis gas [9].
- Catalytic reactor V_2O_5–WO_3/Al_2O_3–TiO_2 employed to reduce of PCDD/Fs emission [10]. The catalytic decomposition and oxidation of dioxins/furans to CO_2, H_2O and HCl may be performed in the temperature range of 150–400°C [11]. Polyaromatic hydrocarbons (PAHs) may also be destroyed on the catalyst [12].
- Water cooler used to limit 'de-novo' reaction of PCDD/Fs and to remove the moisture from gases for protection of the carbon adsorber.
- Neutralizer based on NaOH/Al_2O_3 solid used to remove acid components from post-combustion gases.
- Adsorber (active carbon) employed to reduce of PCDD/Fs and heavy metals emission.
- Ventilator employed to keep the laboratory instrument under low pressure.

The advantage of our experimental system is its modular construction, which enables exchange of the units in order to adapt the system to various kinds of wastes.

Experiments on WEEE utilization will be run in a laboratory-scale electrical furnace with higher loads. We hope that pyrolysis followed by plasma treatment and catalytic reaction will be an environmentally friendly process and will be used as a safe utilization method of electronic wastes.

Results and discussion

TG analysis under helium atmosphere

Thermogravimetric analysis of inhomogeneous A and B samples is presented in Fig. 1 and shows that the components behave differently during thermal degradation. These effects are caused not only by dissimilar resins, being part of both samples (epoxy resin – sample A; polyester resin – sample B) but also by different flame retardants used as components.

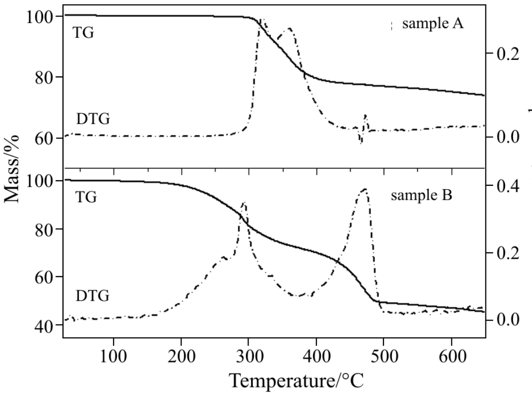

Fig. 1 TG and DTG plots of A and B samples

Sample A gave a solid residue equal to ~74 mass% of its original mass and two maxima of DTG at 320 and 356°C were observed, whilst sample B had a solid residual mass of 45% and also two maxima of DTG plot appeared at 293 and 472°C.

The two peaks registered for sample A are caused by its heterogeneity. Additional TG studies of individual types of printed circuit boards (Fig. 2) show that the yellow laminate decomposed at about 320°C whilst the orange and green laminates underwent changes at about 360°C. During the thermal degradation of epoxy resins retarded with halogenated organic compounds, flame retardants should also be decomposed. A single

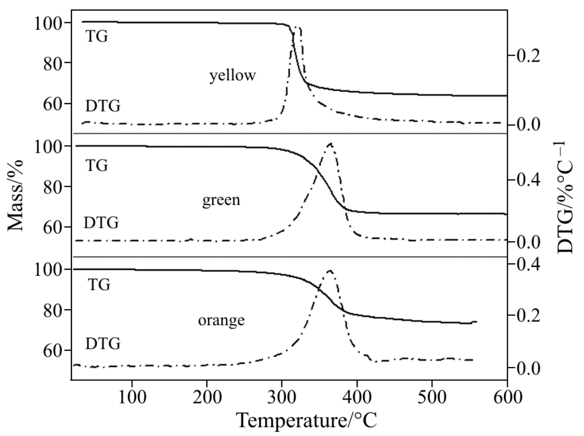

Fig. 2 TG and DTG plots of the individual components (yellow, green and orange) of sample A

DTG peak observed for all different laminates suggests that hardened plastic shells and flame retardants degrade simultaneously. Our conclusion is consistent with data presented by Blazsó [5] where analytical pyrolysis (pyrolysis-gas chromatography-mass spectrometry) of electronic scrap was described. Pyrolysis-GC/MS with thermobalance experiments (in an inert atmosphere) proved that epoxy resin (bisphenol A based epoxy resin) with brominated flame retardant (brominated bisphenol A) decomposed at around 340°C. Bisphenol A, bromobisphenol A, di- and tri-bromobisphenol A, non-halogenated compounds (phenol and its derivatives) and also CO_2, were the main volatile pyrolysis products. Discussed results are different from findings published in paper [13] where TG analysis (under nitrogen) of commercially available composites showed two peaks at around 375 and 650°C for epoxy resin with inorganic fillers (~30 mass%) and glass and carbon fibre reinforcement (~45 mass%). The differences could result from the other mechanism of the thermal degradation process of pure epoxy resin (the main gaseous product being CO_2, although hydrogen and hydrocarbons were also produced) compared with epoxy resin with halogenated additives. Authors observed that inorganic filler had a noticeable effect on gas composition and supposed that plastics based on epoxy resin decomposed in a single stage process but mass loss registered after polymer decomposition may be related to carbonization of the remaining solids.

Considering B sample, two peaks on DTG plot could also be caused by its heterogeneity but the large number of individual components did not allow studying each of them. On the other hand, the two observed peaks may be the result of a two-stage degradation process. Similar findings were published in paper [5], where mass loss during the pyrolysis of terephthalic polyester with brominated polystyrene used as electrical insulator in electronic junctions occurred at above 300 and 432°C.

It is worth stressing here that the fibre-reinforced polymer matrices (e.g. thermoset epoxy resin) can be recovered after pyrolysis. To this end, sample A was chemically washed from metals before thermal treatment. The solid residue formed after pyrolysis of sample A without metals, was easy to crumble and then the glass fibre might be separated by mechanical or chemical processes (e.g., shaking up, splitting into small pieces, crushing or chemical solution, electrochemical separation, etc.). Until then we have not determined the purity of recovered glass fibre.

X-ray fluorescence analysis

X-ray fluorescence analysis was used to estimate the main elements (with atomic mass>Ca), presented in A and B samples and to monitor the changes in composition of both materials after their thermal degradation. A Mo tube was used as the source of radiation. The fluorescence spectra are shown in Fig. 3, where we can also see effects derived from the sample holder (dotted line) and Compton scattering.

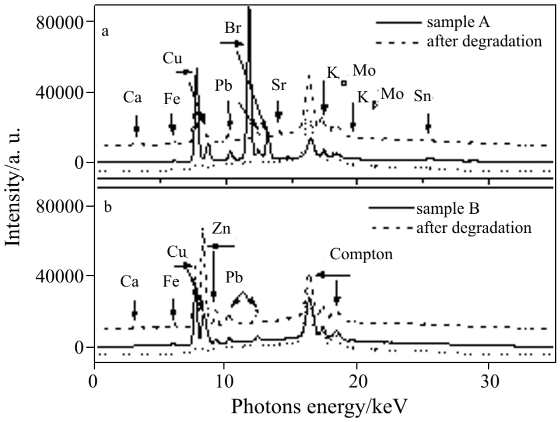

Fig. 3 Fluorescence spectra of a – the sample A —– before and –·–·– – after thermal degradation process and b – the sample B —– before and –·–·– – after thermal degradation process. The dotted line derived from the sample holder

X-ray fluorescence spectrum of sample A proves that epoxy resin – a main component of printed circuit boards includes brominated flame retardant. Br is released during the thermal degradation of plastic matrix. Preliminary elemental analysis showed that S is also released along with Br. The debromination process taking place during thermal treatment of wastes suggests that metals, glass/carbon fibre and polymeric substances could be deprived of hazardous components and thus may be safely recycled.

In case of sample B, its composition before and after thermal degradation did not change, despite the mass loss observed on TG plot. This effect leads to the assumption that sample B, during heating, loses light elements (e.g., C, Cl, S, P, N, O) unregistered by X-ray fluorescence analysis under air. Thus we can conclude that flame retardants added to plastics used as electrical insulator in electronic junctions are based on chlorinated polymers. In order to confirm our presumption we plan to perform X-ray fluorescence analysis under vacuum.

HPLC analysis

The pyrolysis of electronic wastes including polymers leads to the formation of oil, gaseous products and solid residues. Preliminary liquid chromatography analysis of the condensable products obtained as results of thermal decomposition of A and B samples indicates that the liquid oils contain the following hydrocarbons in varying proportions:

- hydrocarbons with two unsaturated rings and with a relative molar mass in the range of 128–166 (e.g. naphthalene, acenaphthene, acenaphthylene, fluorene)
- hydrocarbons with three unsaturated rings and with a relative molar mass in the range of 178–202 (e.g. phenanthrene, anthracene, fluoranthrene)
- hydrocarbons with four and more unsaturated rings with a relative molar mass in the range of 202–250 (e.g. pyrene, benzopyrene, dibenzoanthracene)

Future work planned includes the determination of the presence of aromatic (aliphatic) hydrocarbons containing Br, Cl, N, S and O, by GC-MS.

Conclusions

On the basis of results received from TG, X-ray fluorescence and HPLC measurements we conclude that the electronic wastes selected for this study undergo pyrolytic degradation in a laboratory-scale electrical furnace at temperatures up to 600°C. Under these conditions, degradation and dehalogenation (e.g. debromination) of organic materials included in wastes take place simultaneously. The volatile products of thermal degradation can be cleaned of hazardous components, by passing them through a gas purification system (plasma, catalyst, cooler, neutralizer, adsorber), enabling a safe recovery of valuable materials contained in electronic scrap. However, dismantling and separation of the metal components in the wastes should precede pyrolysis process.

Our investigation also shows that pyrolysis is a suitable method for recovering of fibre-glass present in polymer matrices. The plastics (especially epoxy resin) after thermal decomposition can be easily crumbled and thus the fibre can be separated from the solid residues. Additionally it is worth noting that the liquid hydrocarbons derived from electronic wastes may have properties enabling their use as a fuel.

Acknowledgements

This project is a part of the Multi-Year Programme PW-004 ‘Development of innovativeness systems of manufacturing and maintenance 2004–2008’ supported by the Polish Ministry of Education and Science.

References

1 www.techrecycle.com
2 C.-H. Lee, S.-L. Chang, K.-M. Wang and L.-C. Wen, J. Hazard. Mater., 73 (2000) 209.
3 C.-H. Lee, C.-T. Chang, K.-S. Fan and T.-C. Chang, J. Hazard. Mater., B114 (2004) 93.
4 P. Antonetti, Y. Flitris, G. Flamant, H. Hellio, D. Gautheir and B. Granier, J. Hazard. Mater., B108 (2004) 199.
5 M. Blazsó, Zs. Czégény and Cs. Csoma, J. Anal. Appl. Pyrolysis, 64 (2002) 249.
6 J. Heikkinen and H. Spliethoff, J. Therm. Anal. Cal., 72 (2003) 1031.
7 J. Zieliński, J. Polaczek, Z. Machowska, T. Brzozowska, B. Osowiecka and J. Machnikowski, J. Therm. Anal. Cal,. 60 (2000) 285.
8 T. Bhaskar, K. Murai, T. Matsui, M. Brebu, Md. A. Uddin, A. Muto, Y. Sakata and K. Murata, J. Anal. Appl. Pyrolysis, 70 (2003) 369.
9 M. Więch, T. Opalińska, B. Ulejczyk, T. Zieliński and S. Bartusek, Proceed of Průmyslové Technologie a Životní Prostředí, Ostrava 2002, pp. 13–18.
10 G. Wielogosiński, A. Grochowalski, T. Machej, T. Pająk and W. Ćwiąkalski, Organohalogen Compd., 66 (2004) 1098.
11 R. Weber and T. Sakurai, Appl. Catal., B, 34 (2001) 113.
12 R. Weber, T. Sakurai and H. Hagenmaier, Appl. Catal., B, 20 (1999) 249.
13 M. Cunliffe, N. Jones and P. T. Williams, J. Anal. Appl. Pyrolysis, 70 (2003) 315.

DOI: 10.1007/s10973-006-7589-z