6th International DAAAM Baltic Conference
"INDUSTRIAL ENGINEERING -
24-26 April 2008, Tallinn, Estonia

CHARACTERIZATION OF DISINTEGRATOR MILLED ELECTRONIC WASTE POWDERS FOR MATERIALS RECOVERY

**Kers, J.; Goljandin, D.; Vilsaar, K.; Tall, K; Mikli, V.;
Zuo, X.; Zhang, L. & Schuman, T.**

Abstract:
In this paper, the mechanical milling of the Printed Circuit Boards (PCB) was carried out. The new air classification stand was developed for testing the separation of lightweight particles like tinfoil stripes and plastics. The test results for separation of heavier fractions like non-ferrous metals (Al, Cu) are presented. For milled materials characterization the sieve analysis, laser diffraction analysis and a scanning electron microscope were used. The chemical composition of the PCB powders was studied by means of the energy dispersive X-ray microanalysis.
Then, the pyrometallurgical recycling PCB was executed. The mechanisms of thermal degradation and combustion are investigated using TG/DTA and MS machines with the aim of separating and recovering the organic and metallic materials. The mass loss, conversion fraction with the temperature, activation energy etc. are investigated. Some alkalis, such as Na_2CO_3, $NaHCO_3$, NaOH and $CaCO_3$ were used to control the exhausted toxic gas such as HBr and benzene.

Key words: Electronic Wastes, Printed Circuit Boards, Recycling, Pyrolysis, Combustion

1. INTRODUCTION

Printed circuit boards (PCBs) are common components of many electronic systems built for both military and commercial applications. PCBs are typically manufactured by laminating dry film on clean copper foil, which is supported on a fibreglass plate matrix. Film is exposed to the film negative of the circuit board design and an etcher is used to remove the unmasked copper foil from the plate. Solder is then applied over the unetched copper on the board [1]. Printed circuit boards are mainly produced from thermosetting resin (epoxy or phenolic resin) and reinforced with fibres such as paper, wood, textile and glass (of high performance).
Depending upon the use and design of the particular PCB, various other metals may be used in the manufacturing process, including lead, silver, gold, platinum and mercury [1].
The size reduction equipment for recycling PCBs from the end-of-life durable goods will include the following advantages: it accommodates large amounts of metal, handles tough engineering plastics in reasonable throughputs, liberates molded-in and well-adhered materials, it does not embed or encapsulate foreign materials, it produces the uniform particle shapes and sizes, requires low maintenance costs, it is easy to clean because of the switch-overs of material, it produces a low noise and has reasonable power requirements [2].
Nowadays, many mechanical recycling methods of electronic recycling have been studied [3].
In addition to traditional mechanical direct contact milling methods (ball-milling, attritor milling, hammer milling, etc.),

PCBs can be reprocessed by the collision method.

The fracture of particles in collision with the milling component of one of the rotating rotors is called disintegration. The theoretical studies on milling by the collision method, which were conducted at Tallinn University of Technology (TUT), were followed by the development of the appropriate devices, called disintegrators [4,5]. Depending on the design of the disintegrator systems the direct, separative and selective types of milling are available and useful in powder production. Milling by collision means that the mechanisms of the particle size reduction of the ductile and brittle materials are different. The milling of brittle materials by collision results in a direct fracture [6, 7]. During milling of ductile metallic materials, the metal will be hardened and the fatigue fracture will occur [6, 7].

Recycling of Electronic Wastes include mechanical recycling, which roughly separates different sections or parts (such as plastics, metals) of WEEE, metallurgical recycling, which recovers metals or high value materials from the products of mechanical recycling. Firstly, this study focuses in mechanical recycling of PCB-s and separation technique of ferrous and non-ferrous metals. Metallurgical recycling includes pyrometallurgical recycling separating metals and non-metals. This can be followed by hydrometallurgical recycling which chemically separates different metals.

2. EXPERIMENTAL METHODS

2.1. Reprocessing technology

PCB scrap was recycled by using mechanical and pyrometallurgical methods.

The reprocessing technology of the PCBs by disintegrator milling devices consisted of the following stages:

- the preliminary size reduction of the PCB plates by the experimental DSL-158 disintegrator (up to 2 times);
- the intermediate milling for the size reduction in the semi-industrial disintegrator DSA-2 (up to 6 times);
- the final milling by the DSL-115 disintegrator system in the selective milling conditions to separate the plastic and metallic components

2.2. Separation methods

Based on earlier experimental results new air separation stand was developed for the separation of metallic fraction from organic fraction of the milled PCB (See Fig.1).

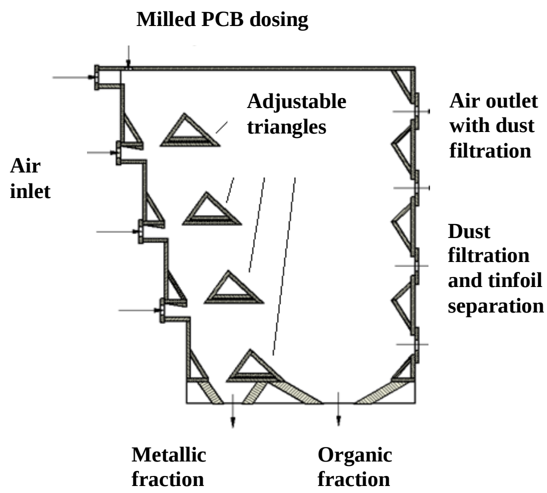

Fig. 1. Air separation stand for PCB powder

2.3. Characterization of the milled material

The particle size and distribution in the powders were examined with the help of two methods:

- Sieve analysis (particle size more than 100 μm)
- Laser diffraction analysis by Laser particle sizer Analysette 22 Compact (max particle size 300 μm)

The chemical composition of the PCB powders was studied by means of the energy dispersive X-ray microanalysis (EDS) with the Link Analytical AN10000 system. The X-ray mapping technique was used to evaluate element distribution inside powder particles.

2.4. Pyrometallurgical recycling methods

For pyrolysis process, PCB waste could be degraded to some fuel oil and gas. Combusting PCB waste is able to generate heat energy. PCB powders without screening were pyrolyzed and combusted in a thermo-gravimetric analysis and differential thermal analysis (TG/DTA), and exhausted gases were analyzed by mass spectrometer (MS). $CaCO_3$ NaOH, Na_2CO_3 and $NaHCO_3$ were mixed with PCB powders with as weight ratio 1:5 in order to absorb some emission toxic gases such HBr and benzene. Argon gas was employed as carrier gas in pyrolysis experiment, and synthetic air (20% O_2 and 80% N_2) in combustion experiment. Synchronously, 15 °C/min heating rate, 150 mL/min gas flow rate, 900 °C top temperature and 120min holding time at top temperature were also adopted in pyrolysis experiments,

3. RESULTS AND DISCUSSION

3.1. Size reduction of the PCB wastes

The results of the preliminary size reduction and intermediate milling is given in Fig 2. The particle size of the plastic component from PCB after a 2-stage milling is about 5-10 mm, after 1-2 times of milling in the disintegrator DSA-2 it is around 1 mm. The powder particles from PCB after the preliminary size reduction were mainly lamellar after preliminary milling and they stay lamellar after the milling in the disintegrator DSA-2.

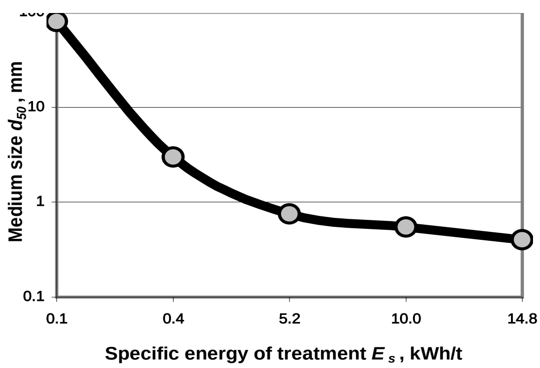

Fig. 2. The size reduction of milled PCB particle during the multi-stage milling

3.2. Results of materials separation

The milled material was divided into 7 different fractions (0-0.125 mm; 0.125-0.315 mm; 0.315-0.630 mm; 0.630-1.250 mm; 1.250- 2.500 mm; 2.500-5.600 mm and 5.600-11.200 mm) by Sieving. The ferrous metals were separated in every fraction by magnet (except fraction 0-0.125 mm). The magnetic separation of the ferrous metals gave sufficiently good results (1.2-5. wt.%) for fractions with larger particle size, but for fractions less than 0.63 mm the separation is less effective because the particles are adhering to each other.

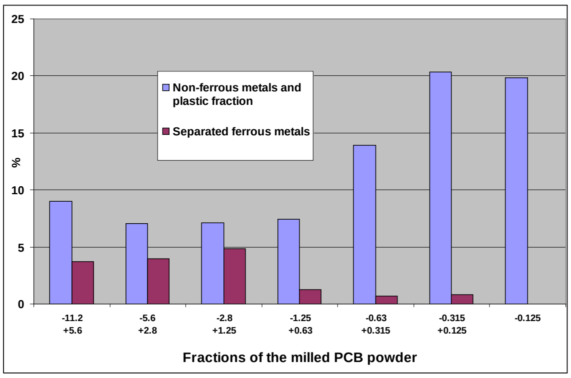

Fig. 3. Results of magnetic separation

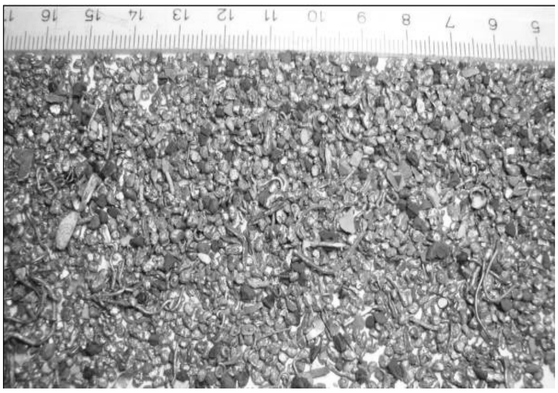

Fig. 4. Separated metallic fraction <2mm

The best air separation results gave the milled PCB powder <2mm. During the first separation the light-fraction of tin-foil stripes were collected in air outlet by dust filtration unit. As the air was re-circulating in the stand, the tin-foil stripes had to be removed. After the two times air separation the separated metallic and organic materials were weighed. The obtained powder (See Fig. 4.) had 80 wt.% of metallic content and 20 wt.% of organic materials. (See Fig. 5).

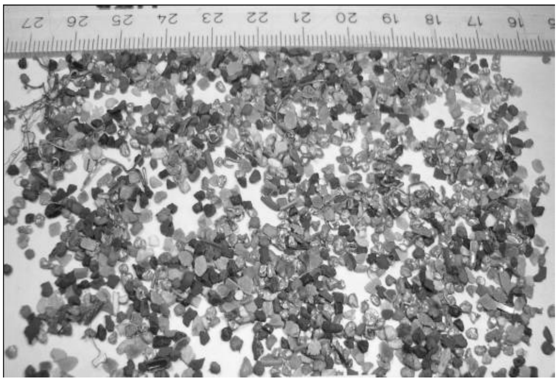

Fig. 5. Separated organic fraction <2mm

3.3. EDS study of PCB milled powders

The sample of the PCB milled powder was separated into plastic and metallic fractions and weighed. The powder contained 29 wt.% of metallic content. The micro polish of the non-metallic fraction sample was made for further EDS analysis. Then the X-ray microanalysis was performed. Oxygen was calculated by the difference of 100% with the results given in weight percentages. Most of the plastic particles contained different metallic crystals or grains inside the matrix. In Fig. 6 black plastic matrix containing Al, Si, Ca and fibers is presented. Plastic particles reinforced with fibres contained mainly carbon (60%) and oxygen (35%) and metals (5%)

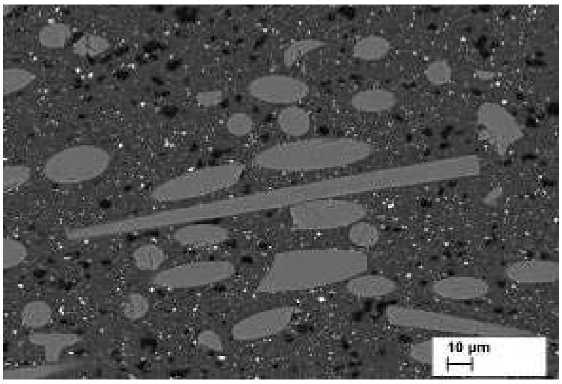

Fig. 6. Black plastic matrix with fibers

EDS analysis showed that most of the separated organic particles are composite materials, with plastic matrix and metallic, ceramic or fibre reinforcements. The precious metals like Au, Ag and Pt were not detected in milled PCB powders.

The milled PCB powders consisted in larger amounts of non-metallic elements C, O Cl. S followed by metals (Cu, Al, Zn, Fe, Sn). In minor amounts alkali earth metals (Mg, Ca, Ba), alkali metals (K, Na) and non-metallic elements (Br, P, F, S) were detected. EDS analysis is useful for determining the elementary consistence of milled PCB powders.

3.4. Pyrolysis of PCB wastes

TG curves are shown in Fig 7. As the mixture of PCB and $CaCO_3$ was pyrolyzed, 42.85% residue left in the crucible. Considering that $CaCO_3$ decomposed at high temperature and reacted with HBr, polymer residue is 35.02%. The sample PCB+$CaCO_3$ could be fully pyrolyzed at 100 min and 900 °C.

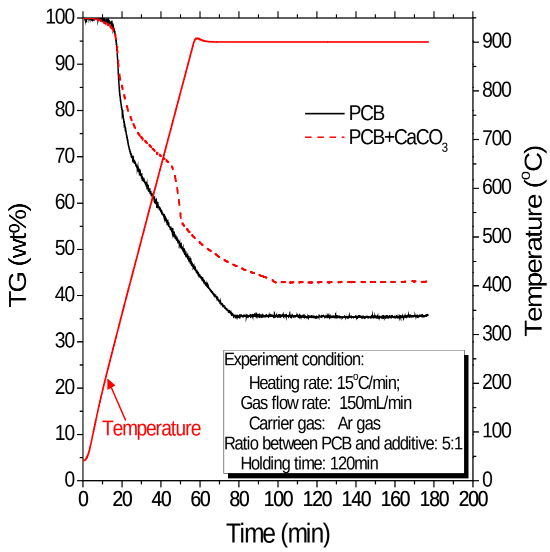

Fig. 7. TG Curves and measured temperature in pyrolysis

$CaCO_3$ could make benzene signal stronger than pyrolysis experiment without additive, which meant that $CaCO_3$ had little effect on enhancing the pyrolysis process, as shown in Fig 8. $CaCO_3$ also could remove HBr gas evolved from pyrolysis experiment effectively.

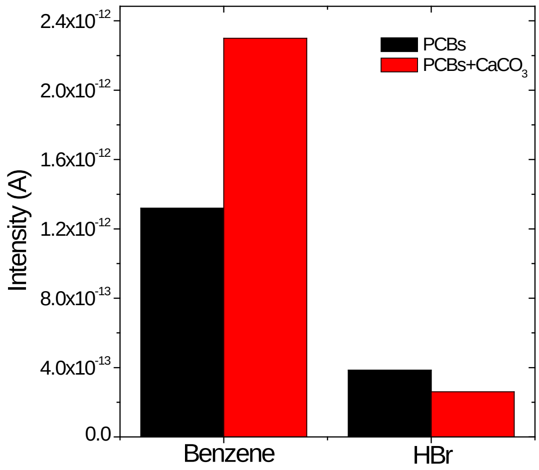

Fig. 8. Benzene and HBr MS signal peak intensity in pyrolysis

3.5. Combustion of PCB wastes

The TG curves of PCBs+$CaCO_3$, PCBs+$NaCO_3$, PCBs+$NaHCO_3$, PCBs+ NaOH and pure PCBs were shown in Fig 9. Acidic exhaust gases mainly reacted with $CaCO_3$ to form CO_2 and calcium salts. $NaHCO_3$ was decomposed Na_2CO_3, CO_2 and H_2O. Acidic gases could be removed by reacting with Na_2CO_3. Mass loss mainly generated from the degradation of PCB and the reaction between acidic exhaust gases and $NaCO_3$. No mass change could be found as the pure NaOH was heated. Main mass loss was from the degradation of PCB and the reaction between acidic exhaust gases and NaOH.

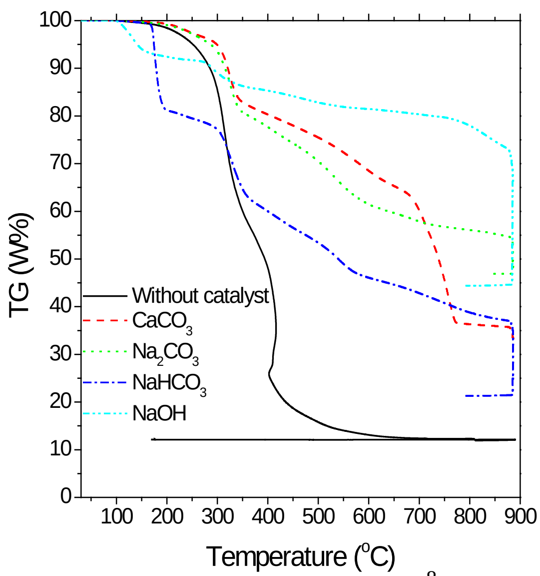

Fig. 9. TG curves in combustion [8]

For the intensity of MS signal peak investigation, as shown in Fig. 10, as the $CaCO_3$ was adopted the intensities of HBr and benzene MS signal peaks close to zero. Benzene gas was hardly controlled by adding NaOH. Na_2CO_3 and $NaHCO_3$ also had a certain effect on removing HBr and benzene.

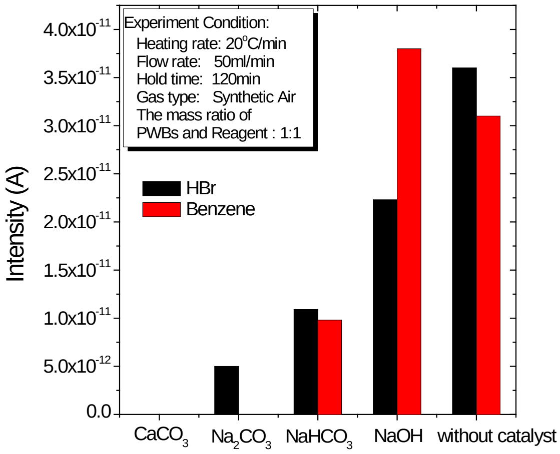

Fig. 10. Benzene and HBr MS signal peak intensity in combustion

4. CONCLUSION

The best results of reprocessing the PCB waste by disintegrators will enable a remarkable size reduction after 2 stages of intermediate milling. The bigger metal particles and tinfoil stripes can be separated by sieving. The ferrous metallic components of coarse fractions can be separated with magnets. For fine fractions (0-0.630 mm) the magnetic separation is poor.

The developed air separation stand is useful for separation of smaller than 2mm fractions of the metallic and organic particles. These test are good basis for determining the optimum milling parameters and designing of new air or wet classifiers accounting for the densities of plastic and metallic particles.

The study of the chemical composition of the PCB powder particles showed that organic particles (polymers) are having metallic grains or crystals in the matrix and because of that they are difficult to be separated by air-classification system. EDS analysis is useful determining the elementary consistence of the selected particles, but for analyzing the powdered material consistence other methods should be considered.

In pyrolysis experiment, $CaCO_3$ could effectively remove HBr from the exhausted gases, but not benzene. In combustion experiment, $CaCO_3$ is also the best candidate for green recycling PCB.

5. REFERENCES

1. *Printed Circuit Board Materials Handbook*, McGraw-Hill Professional, 1997, 784 p.

2. I.B. A. Bernardes, and D. Rodriguez, "Recycling of printed circuit boards by melting with oxidising/reducing top blowing process in Proc. Sessions and Symposia Sponsored by the Extraction and Processing Division, TMS Annual Meeting, B. Mishra, Ed., Orlando, FL, Feb. 9–13, 1997, pp. 363–375.,"

3. Cui, J. and Forssberg, E., "Mechanical recycling of waste electric and electronic equipment: A review," Journal of Hazardous Materials, Vol. 99 (3), 2003, 243– 263.

4 Tamm, B., Tymanok, A., Impact grinding and disintegrators, *Proc. Estonian Acad. Sci. Engin.*, 1996, 2, 2, pp. 209-223.

5. Tymanok, A., Kulu, P. Treatment of different materials by disintegrator systems. *Proc. Estonian Acad. Sci. Eng*., 1999, 5, pp. 222-242

6. Kulu, P.; Mikli, V.; Käerdi, H.; Besterci, M. (2003). Characterization of disintegrator milled hardmetal powder. Journal of Powder Metallurgy Progress, 3(1), 39 - 48.

7. Kers, J;, Kulu, P.; Goljandin, D.; Mikli, V. Reprocessing technology of composite plastic scrap and properties of materials from recycled plastics. Proceedings of the Estonian Academy of Sciences. Engineering, 1997, 13(2), 105 – 117

8. Zuo, X.J. and L.F. Zhang, Green Combustion of Waste Printed Circuit Boards, *in TMS 2009 Annual Meeting*. February 15-19, 2009, EPD Congress: San Francisco, CA, USA. p. 1063-1068.

ACKNOWLEDGEMENTS

The study of mechanical recycling of PCB powders was supported by Estonian Science Foundation grant ETF-7705.

The work of the pyrometallurgical recycling of electronic wastes in the current study is supported by the National Science Foundation of the US (Grant: CBET-0853458).

6. ADDITIONAL DATA ABOUT AUTHORS

Dr. Jaan Kers
Department of Materials Engineering
Tallinn University of Technology
Ehitajate tee 5, Tallinn 19086, Estonia
e-mail: jaan.kers@ttu.ee