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Thermal decomposition of three types of copper clad laminates considering the influence of an iron-clay catalyst in the production of pollutants

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ABSTRACT

Metal recovering through decomposition in the presence of steam of different wastes has been demonstrated to be an effective method. In the present work, three different types of copper clad laminates (FR4, CEM3 and ROGERS) were subjected to high temperature decomposition, analyzing their performance. Firstly, the samples were analyzed by thermogravimetry, both in the absence and in the presence of oxygen in the atmosphere; FR4 and CEM3 showed a very strong interaction with oxygen, in contrast to ROGERS. Secondly, the laminates underwent oxidative pyrolysis in the presence of steam at 900 °C in a horizontal laboratory furnace; the experiments °were carried out in the presence and in the absence of an iron-clay catalyst, in order to evaluate its effect on the production of pollutants. Analyses of the produced gas and semivolatile species are shown, including polycyclic aromatic hydrocarbons (PAHs), bromophenols (BrPhs) and brominated dioxins and furans (PBDD/Fs). The gaseous emissions are almost limited to methane, hexane, toluene and xylene, and the production of PAHs and other semivolatile compounds is considerably reduced with the use of the iron-clay catalyst. The emissions of BrPhs and PBDD/Fs are also very limited. Comparing among the behavior of the three types of laminates, the emission of brominated compounds is much lower in the gasification of ROGERS, compared to FR4 and CEM3.

1. Introduction

Nowadays a rapid technological development is observed in all kinds of sectors. For this purpose, engineers design composite materials which provide superior quality and long life span. The features of these materials contribute to many applications: electrical and electronic, defense and aerospace, automotive industries, … Some of the most commonly used are laminates based on reinforcement of glass fiber, such as FR-4, CEM-3 and ROGERS4003 [1].

FR-4 are mainly composed of glass fiber combined with epoxy resin and with outer layers of copper, and are mainly used as a base of printed circuit boards in all types of electrical and electronic equipment, especially in mobile phones [2]. CEM-3, which are very similar to the most commonly used FR-4 ones, consist of a core of vitreous felt (non-woven glass fiber) with an outer layer of woven glass impregnated with epoxy resin, and coated copper on the base plates [3]. However, the amount of brominated epoxy resins (BERs) is lower compared to FR-4. The structure and composition of ROGERS4003 are also similar to FR-4, but consist of a woven glass reinforced hydrocarbon resin with ceramic filler, without brominated flame retardants (BFRs). Worldwide, there is a huge generation of scrap laminates from obsolete and discarded equipment, which are mainly landfilled, with the increasing problems associated to this practice [1]. Additionally, due to its heterogeneous structure and the presence of BFRs, waste printed circuit boards are problematic to recycle. Consequently, appropriate treatment approaches are being sought for these types of materials.

The process of thermal decomposition of laminates composed of multilayer plastics, resins and metals has been studied with the objective of extracting the metals without melting the system [4,5]. Decomposition in the presence of steam enables almost complete elimination of char from metals/inorganic structure and reduction (by catalytic conversion) of condensing oils and tars content in the product gas. PVC cables have been studied in this sense, presenting a good recovery of copper through decomposition of plastics at high temperature [6].

Currently, other methods to transform e-waste are being considered, but attention is mainly focused on thermal methods, which have been developed with printed circuit boards (PCBs) that mainly consist of FR-4 laminates with TBBPA (tetrabromobisphenol-A) acting as binder and flame-retardant [7–9]. Some researchers conducted conventional combustion process and others used pyrolysis for the treatment of waste PCBs [10–15], focusing mainly on the characterization of solid residue

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and liquid.

Quan et al. [10] investigated the characterization of two products: pyrolytic oil and solid residue after pyrolysis of PCB waste, performed on a fixed bed reactor at 700 °C. De Marco et al. [11] conducted a pyrolysis process in an autoclave at 500 °C with four different electronic devices. Solid and liquid yields were also determined. They noticed polymer-free metals could be separated and recycled, and the liquids may be used as fuels or chemical source. Guo et al. [12] reported a thermogravimetric analysis and kinetic study on plastic particles of printed circuit boards. A fluidized bed reactor was also used for the pyrolysis of the samples, analyzing gas, liquid and solid residue yields. Hall et al. [13] achieved the separation of the organic, metallic, and glass fiber fractions of PCBs by means of pyrolysis in a fixed bed reactor at 800 °C. When heated, the organic fraction decomposed to form volatile oils and gases, whereas the metal and glass fiber fractions remained in the pyrolyzed residue, and were easy to separate. Vasile et al. [14] carried out runs with PCBs from obsolete computers using combined procedures of thermal and catalytic pyrolysis. Pyrolysis was performed by semi-batch operation at 300–540 °C. Two catalysts were used: $CaCO_3$/cracking catalyst or $CaCO_3$/cracking catalyst/Red Mud in 2.5:1 and 2.5:1:1 wt ratios, respectively. They noticed that catalytic pyrolysis decreased the amount of all heteroatoms (Br, Cl, N and O) in PCB oils. Besides, Guan et al. [15] investigated the co-pyrolysis of PCBs with calcium-basic compounds. The authors noticed that adding various calcium based waste, the copper foil was not corroded and the additive absorbed the HBr generated during the process.

Other authors focused on the pollutant production during the thermal decomposition of these materials. Tue et al. [16] pointed out the importance of avoiding uncontrolled recycling processes, due to the formation of hazardous dioxin-related compounds. Duan et al. [17] studied the formation of chlorinated and brominated dibenzo-*p*-dioxins and furans associated with the low temperature thermal processing of scrap printed circuit boards (PCBs). An important formation of brominated dioxins and furans (PBDD/Fs) was found at 250 and 275 °C, both under N_2 and air atmospheres. Further research was reported by Ortuño et al. [7], who analyzed the pollutant emissions during pyrolysis and combustion of PCBs (without and with metal) at high temperatures: 600 and 850 °C. The extensive research provided information on the generation of halogen gases and hydrogen halides, gases and volatile compounds, semivolatile compounds (including bromophenols and PAHs) and PBDD/Fs.

Nowadays, studies on elimination of e-waste concentrate on decomposition in the presence of steam, which has been used for biomass either without catalyst [18,19] or with various kinds of catalyst: Ni catalyst [20], Fe/olivine [21], dolomite [22–24], untreated olivine [22], clay catalyst with precursors [6,25]. Based on this knowledge, recycling methodologies of waste electrical and electronic equipment (WEEE) are being developed. Potential technology should aim to obtaining valuable solid residue with metals in its original form, the reduction of tars, oils and volatile compounds and production of a clean gas enriched with hydrogen.

Mońka et al. [26] dealt with the steam decomposition process of RAM memory waste under a steam flow at high temperature (750 °C for 1 h, 790 °C for 20 min). The treatment was carried out on solid residue in its original form. The study showed that this process may be considered as a promising technology for WEEE recycling.

Salbidegoitia et al. [27] carried out the pyrolysis of phenolic boards in the presence of LNK–carbonate mixture (Li_2CO_3, Na_2CO_3 and K_2CO_3 plus nickel powder) at different temperatures (550, 600 and 675 °C) to produce clean hydrogen. They observed that the addition of metal powder lead to a decrease of the organic matter content in the solid residue. Moreover, rates of hydrogen formation were accelerated when nickel powder was used.

Zabłocka-Malicka et al. [6] discussed the copper recovery from PVC multi-wire cable waste during thermal decomposition in steam atmosphere. They found that the organic fraction was completely removed from the wires after the treatment. Furthermore, copper was preserved in unmodified form and the rate of copper recovery was close to 100%.

In the present study, three laminates: FR4, CEM3 and ROGERS4003 were analyzed in the thermobalance in order to characterize their thermal decomposition. Then, the samples were subjected to thermal decomposition, without and with iron-clay catalyst. This procedure has been demonstrated to be effective in the recovery of metals, but the pollutant production has not been considered so far. For this purpose, the gases, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), brominated phenols (BrPhs) and brominated dioxins and furans (PBDD/Fs) were analyzed, with special attention to examine the influence of the presence of catalyst in the emissions of pollutants.

2. Materials and methods

2.1. Laminates

Three types of laminates were studied in the present work, FR4, CEM3 and ROGERS4003, supplied by an international company. To homogenize them, the samples were crushed by a vibratory disc mill by Herzog, HSM 100 (Osnabruch, Germany).

A CHNS analyzer (FlashEA 1112 Series, ThermoFinnigan) was used for elemental analysis, and the oxygen was obtained by difference. Also, the heating values of the samples were measured, using an AC-350 calorimetric bomb from Leco. Table 1 presents these results.

Equally, a semi-quantitative X-Ray fluorescence analysis was also performed using a Philips PW2400 X-ray fluorescence (XRF) Spectrometer. The results are shown in Table 2. In all materials, the main elements found were silica, calcium, aluminum and copper.

In order to obtain information about the content of halogens in FR4, CEM3 and ROGERS4003, EPA Method 5050 [28] was used, analyzing the obtained solutions by ion chromatography (Dionex DX-500). The amount of bromine (Br) was: 5.28, 3.77 and 0.004 wt%, for chlorine (Cl): 0.054, 0.035 and, 0.003, and fluorine (F): 0.038, 0.036 and 0.010, respectively. As expected, the amount of bromine is much higher in FR4 and CEM3, because of the presence of brominated flame retardants.

2.2. Catalyst

Natural alumino-silicate was gained from a small, local deposit in Dzierżoniów County (south-west Poland). Original raw clay was dried at ambient temperature and pulverized below 0.25 mm, and this was used for the formation of wet granules followed by drying and calcination. Preparation procedure was based on the one described by Miao at al. [29]. The clay and precursor powder: iron (III) oxide, Fe2O3, CAS 1309-37-1, pure POCH S.A. Poland (fractions below 0.25 mm) were mixed with polyethylene glycol (Carl Roth GmbH, ROTH 600, molar mass: 570–630 g/mol) and distilled water in weight proportions of 22/44/12/22. The mixture was homogenized and granules with 5–6 mm diameter were formed and dried for 24 h at 105 °C, then heated (in Nabertherm GmbH N 150 furnace) from ambient temperature to 950 °C for 9 h, calcined for 3 h at 950 °C and cooled down gradually to ambient temperature. Weight losses during drying and calcination were equal to 20% and 30%. The characterization of iron-clay granules (elemental

Table 1
Ultimate analysis of each type of laminate.

wt%	FR4	CEM3	ROGERS4003
C	24.5	25.1	12. 6
H	2.1	3.1	1.4
N	0.6	1.1	nd
S	nd	nd	nd
O and ash (by difference)	72.8	70.7	86.0
HHV (MJ/kg)	10.48	9.68	5.94

nd: not detected.