Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Delamination mechanism study of large size waste printed circuit boards by using dimethylacetamide

Himanshu Ranjan Verma *, Kamalesh K. Singh, Tilak Raj Mankhand

Department of Metallurgical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India

ARTICLE INFO

Article history:
Received 3 January 2017
Revised 3 April 2017
Accepted 3 April 2017
Available online xxxx

Keywords:
Waste printed circuit board
Mechanism
Separation
Dissolution
Delamination
Cracking

ABSTRACT

Present work investigates the recycling of waste printed circuit boards (PCBs) by cracking of its multi-layered structure by using dimethylacetamide (DMA). The study shows that cracking and separation of layers of PCBs increases as the temperature increases; and decreases as the surface area of PCBs increases. After separation of layers, the used solvent was analyzed by proton and carbon nuclear magnetic resonance spectroscopy (NMR) to understand the dissolution phenomenon of resin. Further, NMR and Fourier transform infrared spectroscopy analysis of DMA sample after 1 h, 2 h, 3 h, 4 h and 8 h of reaction with PCBs at 433 K and PCB:DMA ratio (wt/vol) of 3:10 has been carried out to investigate the mechanism of dissolution of resin. These studies revealed that hydroxyl group of PCBs polymeric chain participates in hydrogen bonding with parent carbonyl group of DMA molecule that results in the solvation of resin. Possible chemical reaction based on the above finding has been discussed. Using this technique, separation of the metallic fraction without application of any energy intensive mechanical pre-processing is possible.

1. Introduction

Electronic waste (e-waste) handling became a global issue due to its high pace of generation, low recycling rates, great intrinsic values and hazardous contents. In the current scenario, 13% of total e-waste is recycled by the formal sectors and anticipation shows that the global e-waste generation will reach to 50 million tons soon (Baldé et al., 2015; Zeng and Li, 2016). Printed circuit boards (PCBs) are the prime constituent of e-waste having high copper and precious metals (Chen et al., 2015) along with hazardous halogenated hydrocarbons and heavy metals (Shibayama et al., 2013). Although, many recycling techniques have been reported and examined by the researchers yet, most of the waste PCBs are either informally recycled or illegally landfilled (Manomaivibool, 2009; Song et al., 2012). This results in the loss of valuable metals, adverse environmental impacts and risk of cancer and genetic disorders in the livings.

Recycling of PCBs has been extensively investigated by different techniques and it may be subdivided into three major steps *viz.* – preprocessing followed by mechanical processing and ultimately the end recycling. This is because, the PCBs exhibits a heterogeneous mixture of encapsulated metal and nonmetal (Büyükbay et al., 2010) and thus, special treatment is essential to overcome the barrier of metal-nonmetal liberation and separation (Song et al., 2012; Verma et al., 2015).

Preprocessing ensures the removal of intact (reusable) and toxic components (batteries, liquid color display, cathode ray tubes, etc.). The mechanical processing includes multiple techniques for size reduction, soldered component removal, metal-nonmetal liberation and separation, etc. by using manual/automated equipment (Yang et al., 2009). It ensures the enrichment of the metal content, achievement of desirable shape and size, and significant liberation of metal and nonmetal which is quite important for successful, economical and efficient end recycling (Cao et al., 2015). Selection of various techniques for active metal liberation and separation is highly dependent on each other. *E.g.* – before electrostatic separation of metal, crushing of PCBs to −1 mm size is essential (Koyanaka et al., 1997). In spite of the availability of numerous mechanical processing methods, the maximum yield of metal liberation and separation from the nonmetallic fraction is limited to 75–80% (Sanyal et al., 2013). Further, mechanical processing unit operations are highly energy intensive, noisy, dusty and thus, associated with loss of precious metals in dust, mechanical wear and contamination of PCBs (Kan et al., 2015; Labunska et al., 2013).

End recycling is carried out by either thermal or hydrometallurgical treatment of mechanically processed PCBs. Once, end

* Corresponding author.
E-mail address: hrverma.met.iitbhu@gmail.com (H.R. Verma).

http://dx.doi.org/10.1016/j.wasman.2017.04.013
0956-053X/

recycling is the precursor of the mechanical processing, high efficiency of metal recovery is registered, but the overall economy of the recycling of PCBs is compromised (Hino et al., 2009). Contrary, exclusion of mechanical processing leads to generation of toxic and carcinogenic gases (Alabi et al., 2012; Kahhat and Williams, 2012), high lixiviate consumption, large effluent generation and poor metal recovery yields (Havlik et al., 2010; Jha et al., 2012).

Thus, it is essential to look for an alternative technique which may result in the complete liberation and separation of metal values from the PCBs, so that the uneconomical recycling scenario may be changed.

In recent years, the researchers have investigated a new technique of dissolution and separation of the brominated epoxy resin (BER) from the PCBs by using solvents (supercritical fluids, ionic liquids, organic solvents, etc.). It results in the liberation and separation of metal clad of PCBs and hence the overall economy is also improved considerably (Zhu et al., 2013a). Among the various solvents, the organic solvent found most pronounced application because of their low cost, easy operation, regeneration and negligible effluent generation. Solvent dimethylsulfoxide (Zhu et al., 2013b), N,N-dimethyl pyrrolidone (Wath et al., 2015), dimethylformamide (Verma et al., 2017a, 2016) and dimethylacetamide (DMA) (Verma et al., 2017b) have registered successful liberation of metal clad of PCBs. A comparative assessment of reported solvents has been shown in Table 1.

These studies reported the liberation of metal clad from WPCBs of size ranging from 16 to 100 mm^2. The metal liberation studies for larger size WPCBs have not investigated yet. Further, the reported research mainly focuses on the liberation of metal clad of PCBs by different solvents under optimized dissolution parameters and their relative merits. Previous studies reported that under conditions *viz*. PCB:DMA ratio of 3:10 (wt/vol), temperature 433 K; the DMA result in the most efficient dissolution of the BER of PCBs, relatively (Verma et al., 2017a, 2017b). Further, it has also been reported that the spent DMA is entirely recyclable without negligible loss in its efficiency and the dissolved solute is the BER that is recovered as residue, later. Although, research expressed some putative interpretation about the mechanism of solvent interaction with PCBs, but exact mechanism has not been investigated.

Keeping above facts in mind, present work examines the solvent-assisted recycling of large size PCBs of computer motherboards by solvent DMA with an in-depth investigation of the mechanism of interaction. Further, the delamination of different size PCBs has also been investigated in this work under optimized parameters (PCB:DMA ratio of 3:10 (wt/vol)) reported by Verma et al. (2017b). Up to the author's knowledge, the mechanism of the interaction of the solvent DMA with the BER of WPCBs has not been previously reported.

2. Material and methods

2.1. PCBs pre-processing

Waste PCBs generated from the computer motherboards were collected from local e-scrap collectors. The mounted electronic components were removed from parent PCBs mechanically and downsized into four batches of the square shape of 16 cm^2, 9 cm^2, 4 cm^2 and 1 cm^2 area. A flow sheet of mechanical processing is shown in Fig. 1.

Various analytical grade reagents used in the present investigation were - dimethylacetamide (Sisco Research Laboratories, India), bisphenol-A (Sisco Research Laboratories, India), acetone (Sisco Reserch Laboratories, India), pure ethanol (Fisher Scientific, India), chloroform-D (Sigma-Aldrich Corp.), and potassium bromide (Sigma-Aldrich Corp.).

2.2. Delamination of PCBs

To study the delamination of PCBs, the experiments were carried out in 500 mL capacity four necks, flat bottom, detachable head type flask mounted with water cooled condenser installed over a ceramic top type hot plate with an inbuilt PID type digital temperature controller (accuracy of ±1 K). The PCBs pieces of different area were charged into the flask in PCB:DMA ratio of 3:10 (wt/vol) once the DMA poured inside the flask reaches the preset temperature. Mechanical stirring by a PTFE-coated steel stirrer was provided to ignore the mass transfer effect. Once the reaction advances, representative samples at different time intervals were withdrawn and analyzed by ultraviolet–visible spectroscopy technique to estimate the amount of resin dissolved. To study the effect of temperature on PCBs of square shape (16 cm^2, 9 cm^2, 4 cm^2, 1 cm^2 area), the experiments were carried out at varying temperature (393 K, 413 K, 433 K). All experiments were repeated to observe the reproducibility of results. To study the mechanism of interaction of DMA with PCBs, 1 cm^2 PCBs were treated by pure DMA at 433 K and PCB:DMA ratio of 3:10 (wt/vol) for 8 h and representative samples were withdrawn after 1 h, 2 h, 3 h, 4 h, and 8 h, respectively.

2.3. Analysis of dissolved resin

The reaction of solvent with PCBs results in the dissolution of BER, acting as a binder to hold the various layers of PCBs together (Verma et al., 2017b). The resin is formed by curing of di-glycidyl ether of bromine substituted Bisphenol A (BPA) with suitable hardener (Luda et al., 2007). Thus, a standard concentration *vs*. absorbance plot of BPA was used to find out the concentration of resin dissolved in DMA. Pure BPA weighing 0.1 g was dissolved in 100 mL of pure ethanol and BPA solution of concentration 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 μg/mL were prepared by dilution with pure ethanol. The absorbance of the prepared solution was recorded by 'Perkin Elmer-XLS Plus' UV–VIS spectrophotometer with 1 cm matched quartz cuvette at 282 nm at which BPA shows maximum absorbance (Kang et al., 2011; Morse et al., 2010). Standard absorbance *vs*. BPA concentration curve revealed that Lambert Beer's law holds good up to 50 μg/mL (refer supplementary material Fig. 1). Thus, to analyze the amount of BER dissolved in DMA adequate dilution by using pure ethanol was done.

Table 1
Assessment of various solvents used for the separation of BER of WPCBs.

S. no.	Solvent	Parameters	WPCBs size	Reference
1.	Dimethyl sulfoxide	WPCBs:solvent – 1:2; 170 °C, 30 min	N/A	Zhu et al. (2013a)
2.	Dimethyl sulfoxide	WPCBs:solvent – 1:7; 145 °C, 60 min	16 mm^2	Zhu et al. (2013b)
3.	N,N-dimethyl pyrrolidone	WPCBs:solvent – 1:5; 100 °C, 90 min	16 mm^2	Wath et al. (2015)
4.	Dimethylformamide	WPCBs:solvent – 1:3.3; 135 °C, 240 min	100 mm^2	Verma et al. (2016)
5.	Dimethylacetamide	WPCBs:solvent – 1:3.3; 160 °C, 180 min	100 mm^2	Verma et al. (2017b)
6.	Dimethylacetamide	WPCBs:solvent – 1:3.3; 160 °C, 140–420 min	100–1600 mm^2	Present work

Please cite this article in press as: Verma, H.R., et al. Delamination mechanism study of large size waste printed circuit boards by using dimethylacetamide. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.04.013