

## A novel approach to separation of waste printed circuit boards using dimethyl sulfoxide

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**Abstract** Waste printed circuit boards are complex heterogeneous mixture consisting of organic material, metal and glass fiber, therefore, it is quite difficult for the recovery of valuable materials from waste printed circuit boards. In this study, waste printed circuit boards without electronic components (known as bare boards) are submerged into dimethyl sulfoxide solvent at 170 °C using refluxing process. Metallographic microscope shows that waste printed circuit boards produce the delamination after treated with dimethyl sulfoxide solvent for 15 min. When waste printed circuit boards are treated with dimethyl sulfoxide solvent for 30 min, the separation of waste printed circuit boards is complete to obtain metals and glass fibers. Moreover, the used dimethyl sulfoxide solvent is vaporized by the rotary decompression which obtains regenerative dimethyl sulfoxide and solid residues. Comparing two Fourier transform infrared spectroscopies, it is found that the regenerative dimethyl sulfoxide is the same as original dimethyl sulfoxide. Thermal analyses combined with Fourier transform infrared spectroscopy show that the solid residues are bromine epoxy

resins. These findings suggest that this innovative technology offers an environmental friendly process with no pollution and high efficiency for separating valuable materials from waste printed circuit boards.

**Keywords** Waste printed circuit boards · Delamination · Separation · Dimethyl sulfoxide · Dissolution

### Introduction

The production of printed circuit boards (PCBs) is the electronic industrial base as being the essential part of almost all electrical and electronic equipment. Due to the new technological innovation accelerating the replacement of equipment, the amount of waste printed circuit boards (WPCBs) had a significant increase (Zhu and Gu 2002; Guo et al. 2009).

WPCBs contain 30 % metals such as Cu, Pb, Sn, and precious metals. WPCBs contain 70 % nonmetal materials such as glass fibers and polymers (such as bromine epoxy resins, known as flame retardants). But separation and recycle of WPCBs are very difficult because they are the mixture of polymers, glass fibers, and metals (Nusruth et al. 2007; Gu et al. 2008; Zhu et al. 2009; Havlik et al. 2010; Kim et al. 2011).

Hydrometallurgy is usually employed to extract precious metals (such as Au, Ag, Pt) and base metals (such as copper) from WPCBs. Zhu separated gold from metal powders using high selective acid reagent of  $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$  (Zhu and Gu 2002). Kinoshita leached gold and silver from WPCBs using acid thiourea solution (Kinoshita et al. 2003). Kim and Zhu leached copper by electro-oxidation from the metal powders separated from WPCBs (Kim et al. 2010; Zhu et al. 2009). Havlik et al. (2011)

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leached metals using hydrochloric acid from solid residues which were obtained from vacuum pyrolysis. Oishi et al. (2007) leached copper directly from the mixture of crushed WPCBs using alkaline reagent of  $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{Cl}$ , and then the pure copper was obtained from the leaching solution using the process of extraction–electrodeposition. Recently, Ma and Li (2010) and Chuan-jin et al. (2011) tried to dissolve bromine epoxy resin of WPCBs using nitric acid, but its leaching rate was too low. From the above-mentioned hydrometallurgical process, it can be obviously seen that the use of aqueous solvents such as strong acid and alkaline produce a large amount of waste acid, alkaline liquid and sludge to cause secondary pollution. In addition, hydrometallurgical process is usually combined with other pretreatments such as pyrolysis and mechanical processes indicating the lack of independence. Thus, continued study on the recycling of WPCB is necessary, and non-aqueous solvent substituting for aqueous solvent is used to separate WPCBs.

Dimethyl sulfoxide (DMSO) is known to be an excellent non-aqueous solvent with the formula  $(\text{CH}_3)_2\text{SO}$ . DMSO is a polar, less-toxic, odorless and an aprotic solvent, which acts as both soft base (sulfoxide sulfur) and hard base (sulfoxide oxygen). DMSO has a high boiling point (189 °C), slightly high viscosity (2.2 mPa s, 20 °C) and high thermal stability with effective ability to dissolve numerous organic and inorganic chemicals, but it does not corrode metals. Due to the excellent safety characteristics of DMSO, its application covers a wide range of purposes, notably as a cleaning agent for electronic components, a reaction solvent for pharmaceuticals and agricultural chemicals (Chen et al. 2000; Dean 1991).

In this study, WPCBs are cut into small pieces and put into DMSO solvent, and then heated using refluxing process. DMSO dissolves the polymer materials of WPCBs, which makes the separation of WPCBs to obtain glass fibers and metals. This process is independent, which does not produce waste solution to cause secondary pollution. DMSO can be reused to reduce cost. To the best of our knowledge, there is no study about the separation of WPCBs using DMSO solvent. The objectives of the research are to establish a recycle technology for DMSO reuse and develop a highly efficient and environmental friendly process for separation and recovery of value materials from WPCBs.

## Materials and methods

### Materials

WPCBs for this study were collected from the solid waste disposal center in Shanghai of China. WPCBs were computer motherboards (main metal was copper), and electronic components on the WPCBs were removed by the method of manual operation. Bare board consisted of glass fiber, flame retardants containing organic bromide, inorganic fillers, copper and some other metals, and its compositions were analyzed by XRF (X-ray Fluorescence, XRF-1800, SHIMADZU LIMITED, Japan), shown in Table 1. Bare boards were broken into pieces (15–20 mm<sup>2</sup>) before the experiment. DMSO was used as the heating medium and solvent for dissolving bromine epoxy resins, and was A.R. grade products from Shanghai of China.

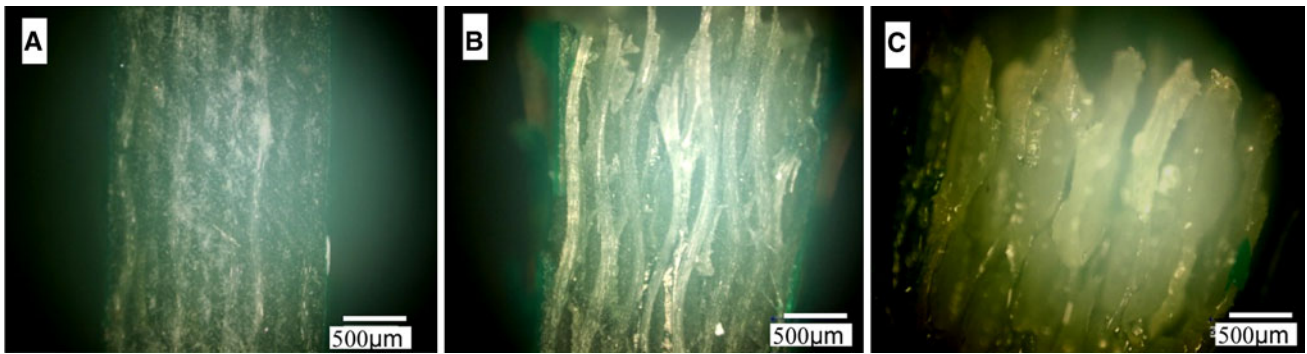
### Methods

The experiment of treating WPCBs was carried out in a four neck flask fitted with a refluxing tube, thermometer, agitator and nitrogen input. The flask was placed in a heater. First, DMSO was put into the flask at the volume of 0.5 L. Then, WPCBs were submerged into the DMSO solvent, and solid–liquid ratio of WPCBs to DMSO solvent was 1:2. The heating process started at 25 °C with the ramping rate of 5 °C min<sup>-1</sup>, then kept at 170 °C for a duration of 30 min. Finally, the used DMSO was treated by rotary decompression vaporization, which makes it regenerate.

The treated WPCBs were taken pictures using metallographic microscope (EPLPHOT 300) and digital camera. Fourier transform infrared spectroscopy (FR-IR) measurement was carried out using IFS 55 (Bruker Company, Switzerland). Thermal analysis was examined by TG–DTG–DTA (thermogravimetry–derivative thermogravimetry–differential thermal analysis, STA 449C, Germany). Sample weighed for 5.000 mg was put into a Pt-Rh crucible and heated at a rate of 8 °C/min from 25 to 800 °C. The second derivative differential thermal curve was used for determination of peak temperature. EDS (energy dispersive spectrometer) analysis was conducted using a SU-1510 scanning electron microscope (Japan) at an accelerating voltage of 20 kV.

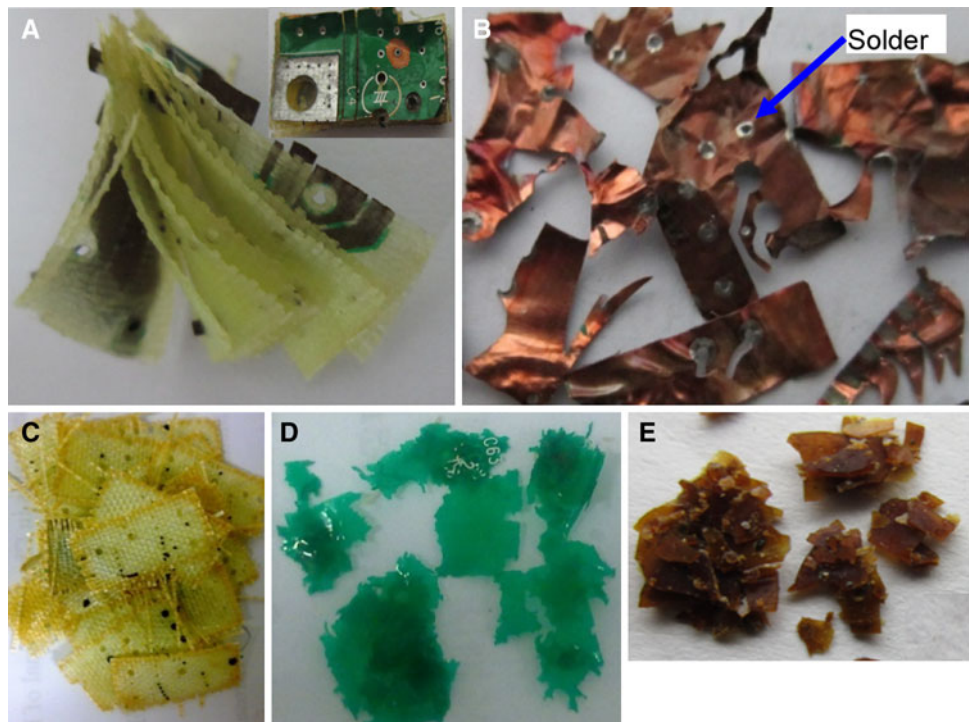
**Table 1** WPCBs main metal compositions by mean of XRF

Elements	Cu	Al	Sn	Pb	Ca	Fe	Na	Sr
Content (wt%)	14.000	4.647	1.857	0.004	3.314	0.081	1.318	0.378
Elements	Br	Si	S	Cr	Cl	P	K	Ba
Content (wt%)	16.246	24.061	17.624	0.051	3.317	0.056	0.108	12.938

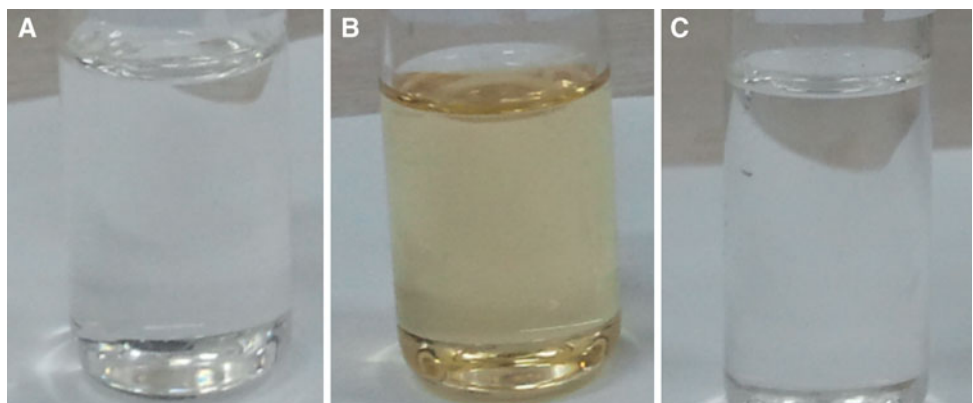


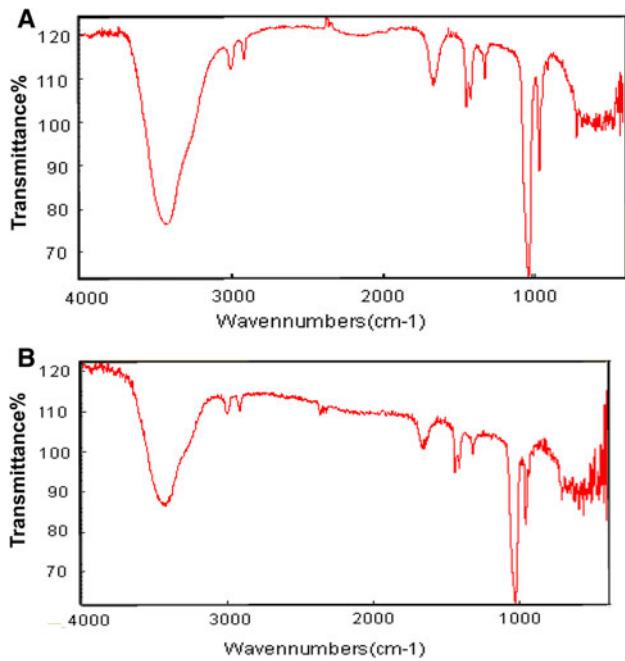
**Fig. 1** Metallographic photographs of untreated and treated WPCBs; **a** untreated WPCBs; **b** WPCBs treated by DMSO for 15 min; **c** WPCBs treated by DMSO for 30 min

**Fig. 2** Photographs of WPCBs treated in DMSO at 170 °C using digital camera; **a** WPCBs delamination; **b** Copper foil and solder; **c** Glass fibres; **d** Liquid photo solder resist; **e** Solid residue

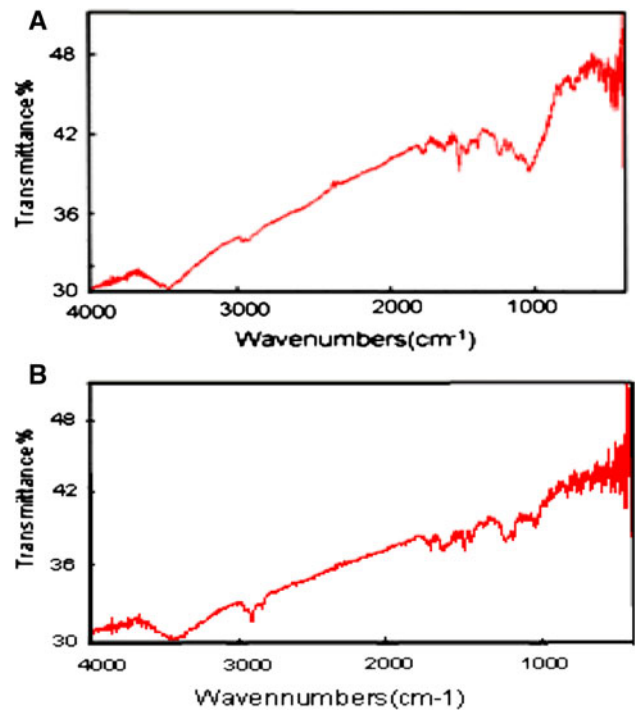


**Fig. 3** Photographs of original DMSO (**a**), used DMSO (**b**), and regenerative DMSO (**c**)

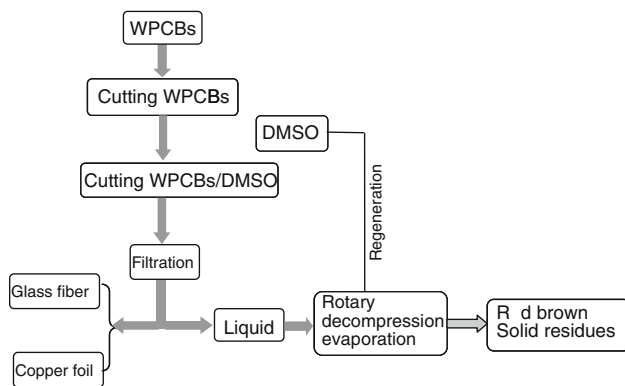




**Fig. 4** FT-IR spectra of original DMSO (a) and regenerative DMSO (b)



**Fig. 6** FT-IR spectra of epoxy resin base material (a) and solid residue (b)

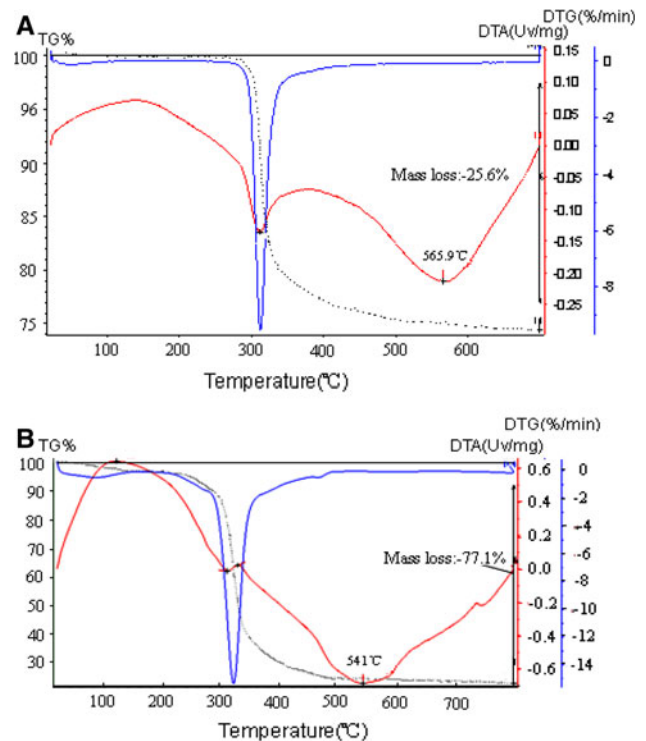


**Fig. 5** A flowchart for dissolution of the epoxy resin and regeneration of DMSO

**Results and discussion**

Figure 1a–c shows metallographic photographs of untreated WPCBs, treated WPCBs for 15 min, and treated WPCBs for 30 min, respectively. Comparing Fig. 1a, b, it can be seen that WPCBs produces the delamination when they are treated by DMSO for 15 min. With treating time increasing from 15 to 30 min, the separation of WPCBs is complete, as shown in Fig. 1c.

Figure 2a–e shows the digital photographs of the WPCBs treated by DMSO. As shown in Fig. 2a, DMSO solvent dissolves the polymer materials of WPCBs to cause the delamination of WPCBs. Figure 2b shows that metals are separated completely from the delaminated WPCBs,



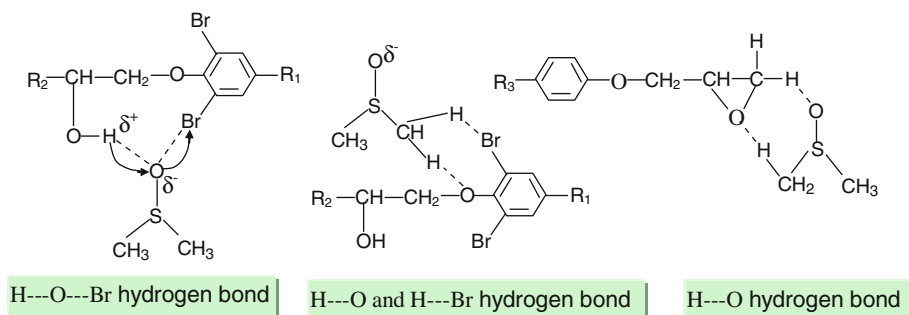
**Fig. 7** TG–DTA curve of WPCBs (a) and the solid residues (b)

and solders are adhesive on copper foil. Figure 2c, d shows that glass fibers and liquid photo solder resists are separated from WPCBs, which indicates that DMSO solvent

does not react with them. In addition, used DMSO solvents are treated by the rotary decompression evaporation, and remaining solid residues are red brown as shown in Fig. 2e.

Figure 3 shows photographs of original DMSO (a), used DMSO (b), and regenerative DMSO (c). From these figures, it is seen that original DMSO (a) and regenerative DMSO (c) are colorless, and used DMSO is yellow. This phenomenon explained that the DMSO dissolves the polymer materials of WPCBs to cause DMSO to change color. By the treatment of decompression evaporation, the color of recovery DMSO changes from yellow to colorless again. Figure 4a, b shows FT-IR spectra of original DMSO (a) and regenerative DMSO (b). Comparing Fig. 4a, b, it is seen that FT-IR spectrum of regenerative DMSO (b) is almost the same as that of original DMSO (a). From the view point of protect environment and cost reduction, it is very important that DMSO can be regenerated after it is used to treat WPCBs. Figure 5 shows a schematic flow-chart for the process involving separation of WPCBs and regeneration of DMSO solvent.

Figure 6a, b shows FT-IR spectra of WPCBs substrate (a) and red brown solid residues (b). Comparing Fig. 6a, b,



it is seen that FT-IR spectrum of WPCBs substrate is the same as that of red brown solid residues. This indicates that the structure of red brown solid residues is similar to that of WPCBs substrate, which contains hydroxyl group in molecules chain, phenyl group in the middle of the chain molecule and ether group. Figure 7a, b shows TG-DTA-DTG curves of WPCBs and solid residues. It is seen that significant weight losses for both WPCBs and solid residues are at temperature ranging 300–380 °C, This indicates that pyrolyzing temperature of solid residues is the same as that of the bromine epoxy resins of WPCBs (Guo et al. 2010). EDS of Fig. 8 shows solid residue including carbon, oxygen, and bromine with the contents of 59.12, 21.71, and 15.2 %. The above results of FT-IR and thermal analysis indicate that solid residues are the dissolved bromine epoxy resins, which does not volatilize to cause second environmental pollution during dissolving process.

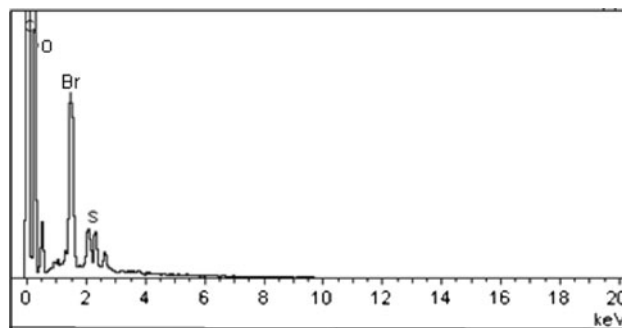


Fig. 8 EDS of the solid residues

The bromine epoxy resin of WPCBs dissolved into the DMSO may be explained as follows: one reason is the formation of hydrogen bonds between the hydroxyls and O-S-group of DMSO, and the bromine of the epoxy resin pulls electron towards itself. Meanwhile, hydrogen of methyl group in DMSO may form hydrogen bonds with bromine and oxygen of bromine epoxy resins. The bromine epoxy resins go into solution due to the minimization of this hydrogen bonding as follows: .

The other one is that the DMSO with the characteristic of strong polarity enhances dissolving polar polymer of bromine epoxy resin. On the contrary, polar DMSO does dissolve aliphatic hydrocarbons except for acetylene, and liquid photo solder resist (acrylate oligomer) is not been dissolved into DMSO because it is a kind of aliphatic hydrocarbon polymer (Prafulla et al. 2008; Östlund et al. 2009; Yaun et al. 2010).

Based on the mass balances of WPCBs treated by the DMSO shown in Table 2, the loss of DMSO is about 2 % and all materials of the WPCBs can be recovered. The content of copper in WPCBs is about 14 % and most of glass fibers are recovery materials. The cost and environmental benefits using this process are analyzed quantitatively as shown in Table 3. It is assumed that the cost of WPCBs is 1,300\$/ton, DMSO is 1,600\$/ton and the price of waste copper is 30,000\$/ton. Moreover, the power of electric heating equipment is

**Table 2** Mass balance of WPCBs treated by DMSO

Item	Mass balance (g)
Raw material mass before experiment	
DMSO	50
WPCBs	25
Mass of various components of WPCBs after experiment	
Copper	3.5
Glass fiber	17.0
Epoxy resin	4.0
Solder resist	0.5
DMSO mass after experiment	49

**Table 3** Cost and environments benefits by using this process

Item	Price
Raw materials cost (\$)	
WPCBs	1,300
DMSO loss	$1,600 \times 2 \% = 32$
Cost of electric power (\$)	11
Total cost	1,343
Environmental effects	None
Copper income (\$)	$1 \times 14 \% \times 30,000 = 4,200$
Gross profit (\$/ton)	2,857

184 KW/h, and it costs 0.12\$/KW h (in Shanghai). It is seen from Table 3 that the process is reasonable.

## Conclusion

It can be concluded that DMSO used as solvent is highly efficient to dissolve the bromine epoxy resins of WPCBs at 170 C using refluxing process, which makes the delamination of WPCBs. The delaminated WPCBs are easily separated to obtain metals and glass fibers, and the bromine epoxy resins dissolved in DMSO are recycled by rotary decompression evaporation. Metal materials, organic materials, and glass fibers from the WPCBs are all recovered, while the loss of DMSO is very low in this process. Moreover, this new process does not volatilize bromine to cause second environmental pollution which complies with the principle of sustainable development by decreasing the manufacturing cost of recycling WPCBs to achieve complete recovery of reusable resources.

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