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Separation and Recovery of Copper Foil and Fabric from Waste Printed Circuit Boards by Decomposing Brominated Epoxy Resin Using Near Critical Water

Hongjun Kang,[1] Qian Shao,[2] Xingkui Guo,[2] Alexandra Galaska,[3] Yuyan Liu*[1] and Zhanhu Guo*[3]

Waste printed circuit board (WPCB), a heterogeneous mixture of brominated epoxy resins (BERs), glass fibers and metals, has the challenge to separate and recover valuable materials. In this paper, an effective and benign near critical water (NCW) method was applied to decompose BERs to recover the glass fabric and metals. The effects of parameters including temperature, reaction time, feed ratio, acid-base catalyst, and size of WPCBs on the decomposition ratio of BERs were investigated. The results showed that the decomposition ratio of BERs reached a maximum value of 98.7% under the optimum conditions at 320 °C, reaction time of 150 min, feed ratio of 5 mL/g, HCl catalyst, and the size of 5×5 mm^2. The gas chromatography–mass spectrometry (GC/MS) result showed that the main components of liquid decomposition product were phenol (69.8%) and its derivatives (17.8%). A probable mechanism of the decomposition reaction of BERs was proposed. After NCW treatment, the glass fabric and copper foils in the residue were easily recovered by a simple artificial screening separation. The surface of recovered fabric was very clean and no damages were observed. Meanwhile, the purity of copper foil reached 97.86%. This study provides a green technology to recover valuable materials from WPCBs.

Keywords: Near critical water; waste printed circuit boards; brominated epoxy resin; decomposition ratio; separation; recovery

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1. Introduction

Printed circuit boards (PCBs), the base of electronic industry, are an essential part of electrical and electronic equipment (EEE). Recently, new technological innovations continue to accelerate the upgrade and replacement of EEE, resulting in large quantities of waste printed circuit boards (WPCBs) and polymers that need to be disposed.[1–4] WPCBs are a mixture of glass fibers or cellulose paper reinforced resin and multiple kinds of metals. The common WPCBs are made of glass fibers reinforced brominated epoxy resins (BERs), which are referred to as commercial FR-4.[5,6] For WPCBs without mounted electronic parts, the material composition is about 28 wt% metals (main copper) and 72 wt% non-metallic materials (glass fiber, BERs and some additives).[7] However, WPCBs contain plenty of toxic materials, such as heavy metals and brominated flame retardants (BFRs), which will cause huge damages to the environments if they are not properly discarded.[8–10] Therefore, the recycling of WPCBs becomes an urgent global issue and it is helpful to conserve scarce resources, to establish a reuse of e-waste, and to eliminate hazardous materials from the environment.[11,12]

Currently, some recycling methods for WPCBs have been reported, including physical method,[13] thermal treatment[14] and chemical methods.[15,16] For physical method, it can only preliminary separate metals and nonmetals, leading to relatively high loss ratio of precious metals. However, for thermal treatment, higher temperature (500~1000 °C) and longer reaction time are its disadvantages, which can cause the increase of energy consumption.[17]

In recent years, near or super critical water treatment is introduced as an environment-friendly method for chemical recycling of WPCBs. Super critical water is high temperature and high-pressure water over the critical point of 374°C and 22.1MPa, different from those of water at room temperature and atmospheric pressure. For the near critical water (NCW, T = 250~350 °C), it offers opportunities both as a benign solvent and as a self-neutralizing catalyst. In near critical condition, the dissociation constant of water is increased 3 orders of magnitude, which can provide abundant protons (H^+) or hydroxyl ions (OH^-), and thus can play a certain degree of acid or base catalysis in the hydrolysis reaction of waste polymers.[18,19] Our previous study reported the chemical decomposition of epoxy resin in the NCW condition by an acid or base catalytic method and the decomposition mechanism was proposed based on the decomposition products.[20,21] The aforementioned common WPCBs are made of glass fibers reinforced brominated epoxy resins (BERs), and some heavy metals.

[1] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 92 Xidazhi Street, Harbin 150001, China. E-mail: liuyy@hit.edu.cn
[2] College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, PR China
[3] Integrated Composites Laboratory (ICL), Department of Chemical & Bimolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA.
E-mail: nanomaterials2000@gmail.com, zguo10@utk.edu

Therefore, the valuable glass fibers and metals would like to be recycled effectively, which must decompose the BERs in WPCBs. Based on our previous works, it is adequately proved that the NCW water is an effective method for decomposing the BERs in WCPBs to recycle the valuable materials, due to its extraordinary properties, such as green media, high diffusivity and high solubility for organics.[22,23]

In the present study, NCW was used to decompose BERs of WPCBs and recover materials of glass fabric and metal copper. The aims of this study were to investigate the effects of various parameters on the decomposition ratio of BERs, such as temperature, reaction time, feed ratio, acid-base catalyst, and size of WPCBs and to optimize the operation parameters of BERs decomposition by NCW. Meanwhile, the components of liquid decomposition products were analyzed by gas chromatography–mass spectrometry (GC/MS) and a probable mechanism of the decomposition reaction of BERs was proposed in the NCW condition. The results showed that the treatment temperature was lower (320°C) and the reaction time was relatively short (150min). Besides, high purity of phenol (69.8%) in the main components was obtained, which could be further purified to synthesize some other compounds (i.e. phenolic resin). Finally, high purity copper foil was recovered and the surface of recovered glass fabric was very clean, which could be reused directly.

2. Experimental

2.1. Materials

The WPCBs disassembled from discarded computers were provided by Gigabyte Technology Co., Ltd, which were composed of glass fabric (GF), brominated epoxy resins (BERs), and metals. First, the electronic components (ECs), such as capacitors and relays, were dismantled. Then, WPCBs were cut into small fragments with areas of 400, 100 and 25 mm^2 prior to conducting the experiment. All regents used in this experiment were A.R. grade.

2.2. Methods

The whole recovery process of valuable materials from WPCBs includes ECs dismantlement, NCW treatment and artificial separation. Fig. 1 shows the schematic diagram of valuable materials recovery process. The NCW treatment of WPCBs was conducted by using a 100 mL high pressure reactor made of stainless steel, which was connected to a pressure gauge, a temperature controller and a heating furnace with salt bath. The decomposition temperature and pressure could be adjusted. The experiment process was as follows. Certain feed ratios of WPCBs, distilled water and catalyst were added in the reactor, and when the system temperature reached the set temperature, it was held at that temperature for a period of time. The treatment conditions of each experiment are described in Table 1. In each experiment, because of Br_2 production at high temperature, 0.02g NaOH was added and used as bromine absorbent to prevent the vaporization of bromine. After the treatment, the removable reactor was put into cold water and cooled down to room temperature. The solid and liquid mixtures were filtrated through a preweighted filter paper for separation. The liquid decomposition product was collected and analyzed by gas chromatography-mass spectrometry (GC/MS). The solid residue was dried at 60 °C for 12 h in a vacuum oven and weighted to calculate the decomposition ratio using Equation (1):

$$x = \frac{M_i - M_t}{M_i \times \omega} \times 100\% \tag{1}$$

where x is the decomposition ratio of BERs, M_i is the original mass of WPCBs sample, ω is the mass percentage of BERs in WPCBs and M_t is the mass of the solid residue after NCW treatment. At last, the glass fibers and metals could be readily separated from the solid

Table 1 The conditions of near critical water treatment.

No.	T (°C)	Feed ratio (mL/g)	Time (min)	Catalyst	Size (mm^2)	Pressure (MPa)
1	260	10	150	--	20×20	4.0
2	280	10	150	--	20×20	4.0
3	300	10	150	--	20×20	5.0
4	320	10	150	--	20×20	4.5
5	300	10	30	--	20×20	5.5
6	300	10	60	--	20×20	4.0
7	300	10	90	--	20×20	5.0
8	300	10	120	--	20×20	6.0
9	300	5	90	--	20×20	5.0
10	300	15	90	--	20×20	7.0
11	300	20	90	--	20×20	7.0
12	300	10	60	HCl	20×20	7.0
13	300	10	60	Na_2CO_3	20×20	6.0
14	300	10	60	NaOH	20×20	5.0
15	300	10	60	--	20×5	6.0
16	300	10	60	--	5×5	5.0

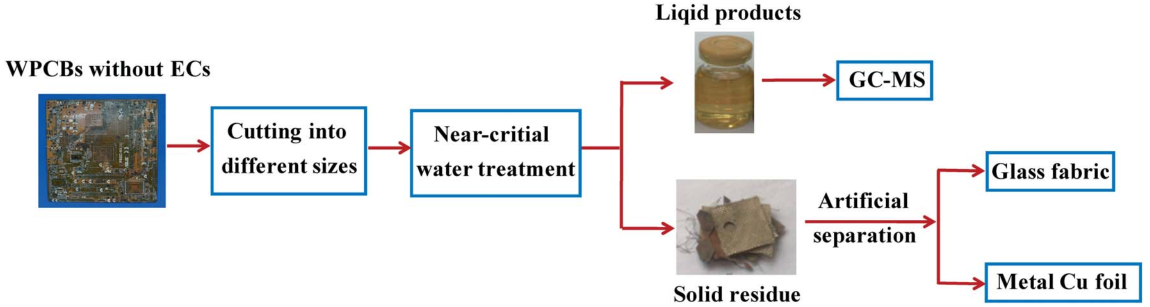


Fig. 1 The schematic diagram of valuable materials recovery process.

residue by simple artificial screening separation. Each experiment was repeated three times and only the mean values were reported.

2.3. Characterization

Thermo-gravimetric analysis (TGA, Netstal 209 F3, Germany) was carried out under a nitrogen atmosphere with the temperature ranging from 25 to 900 °C. Fourier transformed infrared spectra (FT-IR, Vertex 70, Germany) were recorded on a Nicolet Magna-IR 750 spectrometer with KBr pellets at room temperature to analyze the main structure of WPCBs matrix. The composition of the collected acetone liquid after brominated epoxy resin decomposition was analyzed by a gas chromatograph equipped with mass selective detector (GC/MS, Agilent 6890/5973N, USA). The morphological properties of the recovered glass fibers and the compositions of the recovered metal were examined by scanning electron microscope with energy-disperse X-ray analysis (SEM/EDS, FEI, Sirion 200, USA).

3. Results and Discussion

3.1. Thermo-gravimetric Analysis of WPCBs

In order to analyze the content of resin matrix in the WPCBs, the TGA test was carried out in the nitrogen atmosphere. Fig. 2 shows the typical TGA curve of the samples. The WPCBs show a weight loss of ~38.7 wt% in the temperature range of 25 to 900 °C, which is attributed to the thermal decomposition of resin matrix in the WPCBs. Accordingly, the mass percentage (ω) of BERs in the WPCBs is about 38.7 wt%, and other main components are glass fabric and metals, respectively. Meanwhile, the weight loss of WPCBs at 320 °C is only 2.2 wt%, indicating negligible effects of thermal decomposition process on the decomposition ratio of WPCBs. The NCW treatment plays a significance role in the WPCBs decomposition.

3.2. FT-IR Analysis of Resin Matrix in WPCBs

Fig. 3 shows the FT-IR spectrum of resin matrix in the WPCBs. The peak band around 600 cm^{-1} stems from the C-Br stretching vibration and the bands around 1625 and 3300 cm^{-1} are the vibration of C=C and O-H bonds, respectively.[24] In addition, the peak at 3060 cm^{-1} is the stretching vibration of the C-H bond in the benzene ring. Therefore, the main component of WPCBs matrix is brominated bisphenol A type epoxy resin (BERs).

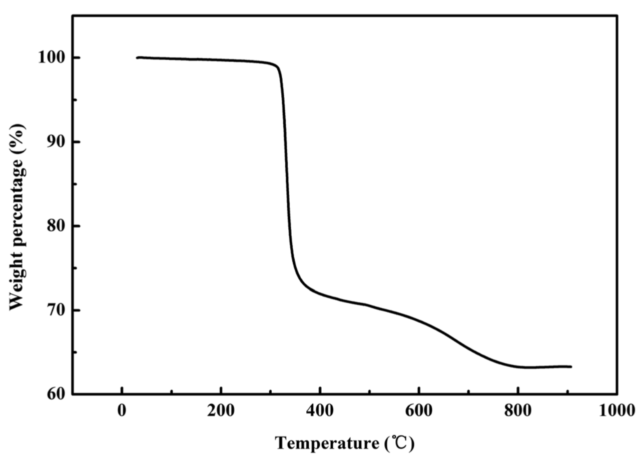


Fig. 2 TGA curve of WPCBs sample.

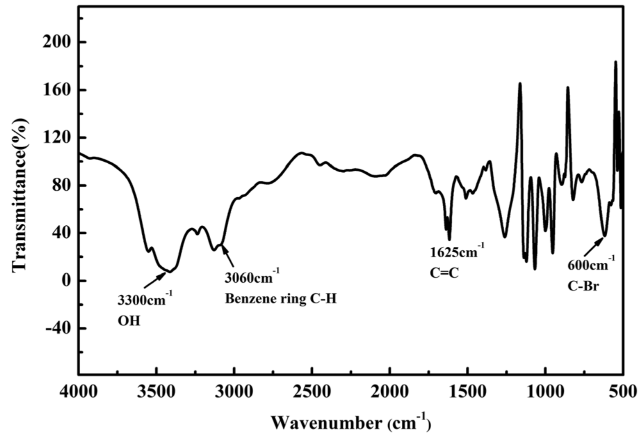


Fig. 3 The FT-IR spectrum of resin matrix in WPCBs.

3.3. Effects of Various Parameters on the Decomposition Ratio of BERs

It has been reported that temperature is the most important parameter in near critical water treatment. Fig. 4a shows the effect of temperature on the decomposition ratio of BERs. It can be seen that the decomposition ratio increases rapidly with the increase of temperature below 300 °C, i.e., increases from 12.5% at 240 °C to 95.7% at 300 °C. When the temperature exceeds 300 °C, the decomposition ratio of BERs presents a slight increase and reaches its maximum value of 98.9% at 320 °C. The result indicates that high temperatures can provide enough energy to break down the chemical bonds of BERs, which makes BERs decompose more effectively in the near critical water condition.[25]

The reaction time also plays an important role in the decomposition ratio of BERs. Fig. 4b shows the effect of reaction time on the decomposition ratio. The result indicates that the decomposition ratio increases with the increase of the reaction time. The decomposition ratio increases rapidly from 5.9% to 64.4% with the increase of reaction time from 30 to 60 min. After 60 min, the decomposition ratio increases slowly and reaches a maximum value of 97.6% at 150 min. Hence, BERs can be almost completely decomposed and the main residues are the glass fabric and metal copper foils, which can be separated and recycled easily by simple artificial screening.

Fig. 4c demonstrates the effect of feed ratio on the decomposition ratio. The feed ratio (mL/g) is defined as the ratio of medium water volume (mL) to the WPCBs mass (g). As shown in Fig. 4c, the overall trend is that the smaller the feed ratio is, the greater the decomposition rate of BERs is. When the feed ratio is 5 mL/g, the decomposition ratio of BERs reaches a maximum value of 90.9%.

The dissociation constant of water increases 3 orders of magnitude in the near critical water condition,[18,19] which provides much more hydronium or hydroxyl ions for acid or base catalysis reactions. Fig. 4d shows the effect of acid or base catalysts on the decomposition ratio. The results indicate that the addition of hydrochloric acid (HCl) is more beneficial for the decomposition of BERs and the

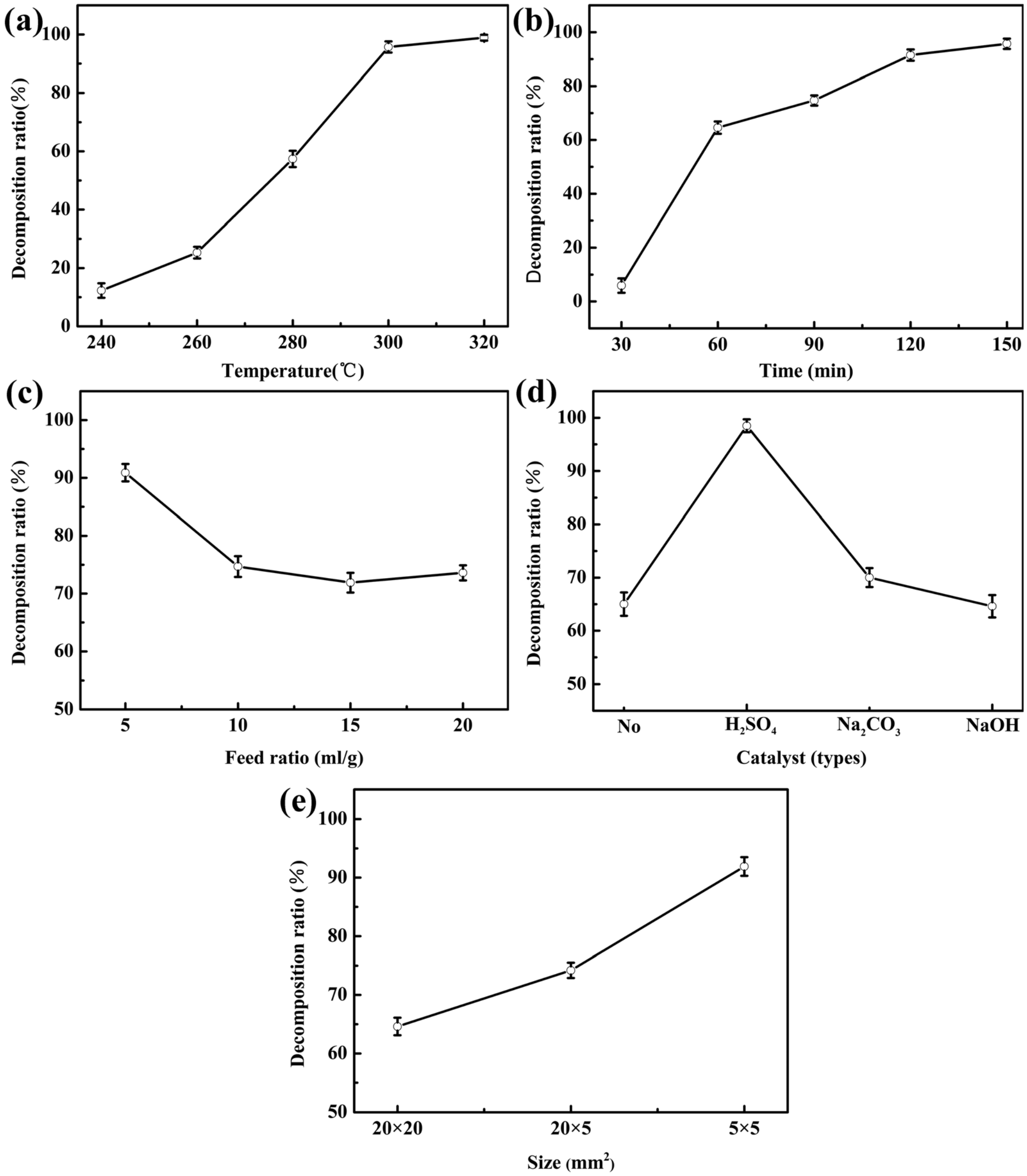


Fig. 4 Effects of various parameters on decomposition ratio of BERs: (a) temperature, (b) reaction time, (c) feed ratio, (d) acid-base type and (e) size of sample.

decomposition ratio reaches 98.5%. Without any catalysts, the decomposition ratio of BERs is 65%. However, when the catalysts of sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) are added in the near critical water reaction system, the decomposition ratios of BERs are 70.9% and 65.6%, respectively, indicating that the base catalyst has little impact on the decomposition ratio. Accordingly, it comes to the conclusion that the acid catalysis reaction plays a major role in the decomposition ratio of BERs during the process of NCW treatment.

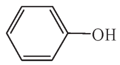
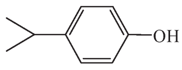
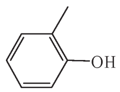
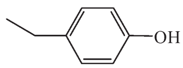
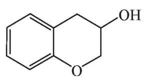
Meanwhile, as we know, the smaller the size of cut WPCBs is, the larger the contact area in the reaction medium. Therefore, the effect of cut WPCBs size on decomposition ratio of BERs is investigated in detail, as shown in Fig. 4e. It is obviously found that the smaller the size of WPCBs is, the higher the decomposition ratio is. The decomposition ratio of BERs is 92.9% with the size of 5×5 mm^2, while the decomposition ratios of BERs with the sizes of 20×5 mm^2 and 20×20 mm^2 are 74.6% and 64.6%, respectively, which is due to the larger reaction contact area with smaller sample size.

In conclusion, considering the decomposition ratio, it is recommended that the optimum decomposition conditions of BERs are the temperature of 320 °C, reaction time of 150 min, feed ratio of 5 mL/g, HCl catalyst and the size of 5×5 mm^2 during the process of NCW treatment.

3.4. The Components Analysis of Liquid Decomposition Products of BERs

Under the optimum decomposition conditions, the liquid decomposition product of BERs is brown, and is further analyzed by GC/MS to understand the organic components. Table 2 presents the main components and the relative peak area of the liquid decomposition products. As indicated in Table 2, the major components of liquid

Table 2 The main components and relative peak areas of liquid decomposition products after nearcritical water treatment (the optimum decomposition conditions: 320°C, 150min, 5ml/g, HCl catalyst and 5×5mm^2).

No.	Components	Structure	The relative peak area (%)
1	phenol		69.8
2	*iso*-propylphenol		15.3
3	*o*-cresol		1.11
4	4-ethylphenol		1.46
5	3-hydroxy benzopyran		2.40

decomposition products are phenol and its derivatives, such as phenol, *iso*-propylphenol, 4-ethylphenol and *o*-cresol, whose relative peak areas are 69.8%, 15.3%, 1.46% and 1.11%, respectively. Meanwhile, another organic component of 3-hydroxy benzopyran is also detected, and its relative peak area is 2.40%. This indicates that BERs of WPCBs are completely decomposed into small molecular substances, and it is found that by using NCW method, the main product content of phenol increased (about 19.3 %) than reported by Zhang and coworkers.[17,26]

3.5. Mechanism of Decomposition Reaction of BERs

According to the identified decomposition products of phenol and iso-propylphenol, the decomposition mechanism of the BERs is investigated. Some previous works[26–29] have proved that the decomposition of polymer belongs to a free radical reaction at high temperatures. On the basis of bond-energy theory, it needs much more energy to break down the bonds of polymer so as to produce free radicals. However, the polymer hydrolysis actually is the process of ionization, which becomes even more obvious at low temperature. In this paper, the near critical water method is employed to decompose BERs of WPCBs and the reaction temperature is controlled at 320 °C compared to traditional pyrolysis at high temperatures. In the near critical region, although this temperature cannot break down the higher energy bonds, the ion product of water is

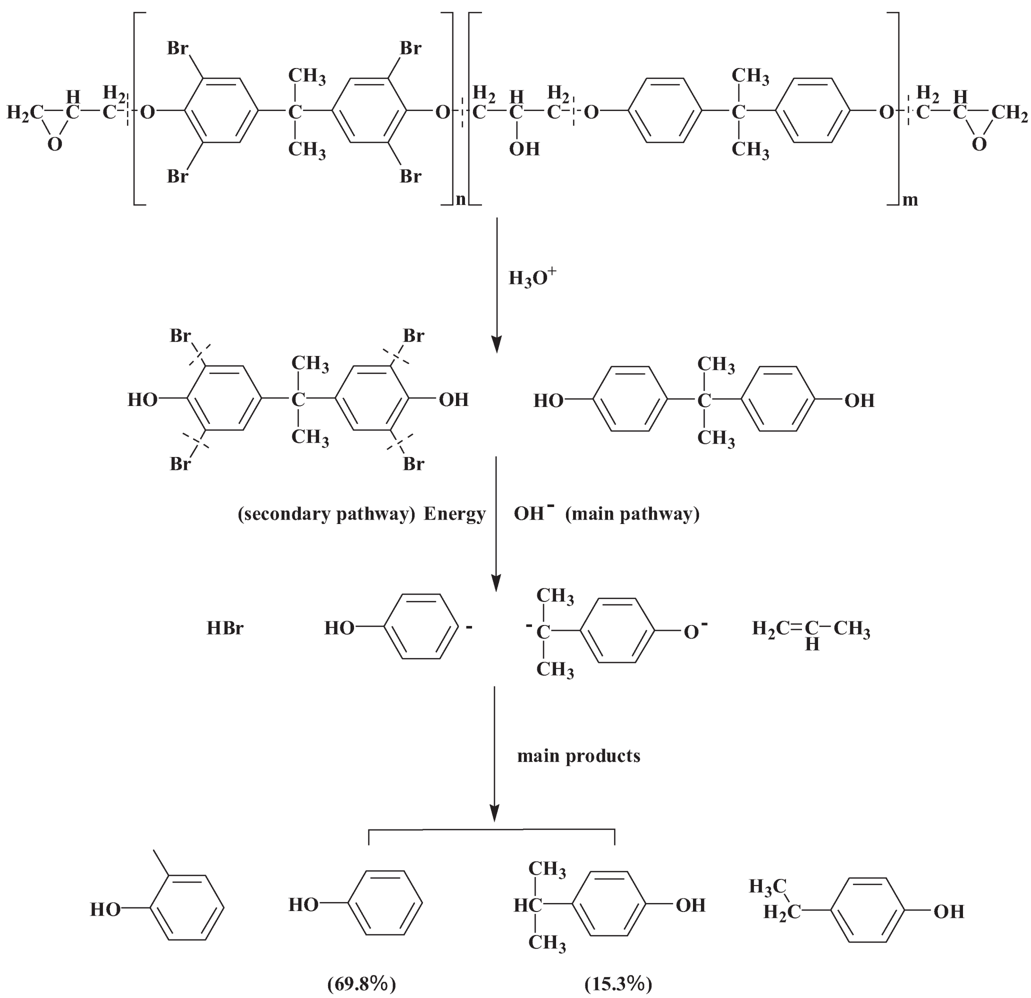


Fig. 5 A probable decomposition mechanism of BERs during NCW treatment condition.

higher than that in the ambient conditions, meaning that it acts as an acid-base catalyst precursor. Therefore, because of the existence of hydronium or hydroxide ions, hydrolysis effect plays an important role in the decomposition of BERs,[30] as shown in Fig. 5. Firstly, the ether bonds in the main chain are attacked by the hydronium and decomposed into tetrabromobisphenol A, bisphenol A monomer and other oligomers. After that, tetrabromobisphenol A and bisphenol A monomer can be further decomposed to phenol, isopropylphenol, 4-ethylphenol, o-cresol and other substances with the action of hydroxide ion and energy supplied by the reaction system.

3.6. Separation and Recovery of Metal Copper and Glass Fabric

After near critical water treatment, the BERs in WPCBs can be decomposed completely and the main residues are metal foils and glass fabric, respectively. Fig. 6a shows that the copper foil is the main metallic component in WPCBs, which can be easily recovered by artificial screening separation and is superior to the previously reported works.[25,31–33] For example, the metal copper was remained in the solid residue[31] and did not achieve valuable materials. While mechanical equipment was used for the recovery of glass fibers and copper foils,[25,33] resulting in lots of energy consumption. Meanwhile, the recyclable fibers present short fibers, limiting their application fields. The SEM is conducted to investigate the surface morphology of recovered glass fabric. Fig. 6b presents the surface of recovered glass fabric is very clean and the glass fibers are arranged compactly without any damages. Meanwhile, compared with works by Zhang et al [25] and Li et al [33], it can be seen in Fig. 6c that the surface of single fiber in the glass fabrics is much cleaner and no damages can be observed in single fibers, indicating that the recovered glass fabric can be reused directly by using NCW treatment. The recovered copper foil is further analyzed by EDS and its mass percentage reaches about 97.8wt%, Fig. 6d.

3.7. Comparison of different studies on WPCBs treatment using near- or supercritical fluids method

A comparison of different studies undertaken on WPCBs treatment during near or super critical water conditions is given in Table 3. Overall, near or super critical water method has been proven to be a great alternative for WPCBs treatment. In the present work, near critical water is also applied for the WPCB treatment. Compared with other related studies, the advantages of the near critical water treatment could be demonstrated as follows. First, the treatment temperature is lower and the reaction time is relatively short. Second, it is significant for improving the decomposition ratio of BERs by using novel HCl catalyst, and high purity phenol (69.8%) in the main components can be obtained, which can be further purified to synthesize some other compounds (i.e. phenolic resin). Finally, the glass fabric and copper foils can be recovered easily by only simple artificial separation. Meanwhile, the surfaces of glass fabric and single fiber are very clean, which can be reused directly, and the purity of recovered copper foil is very high.

4. Conclusions

Near critical water (NCW) is an efficient method for the decomposition of BERs and simultaneously recovering valuable materials of glass fibers and metals from WPCBs. During the process, the

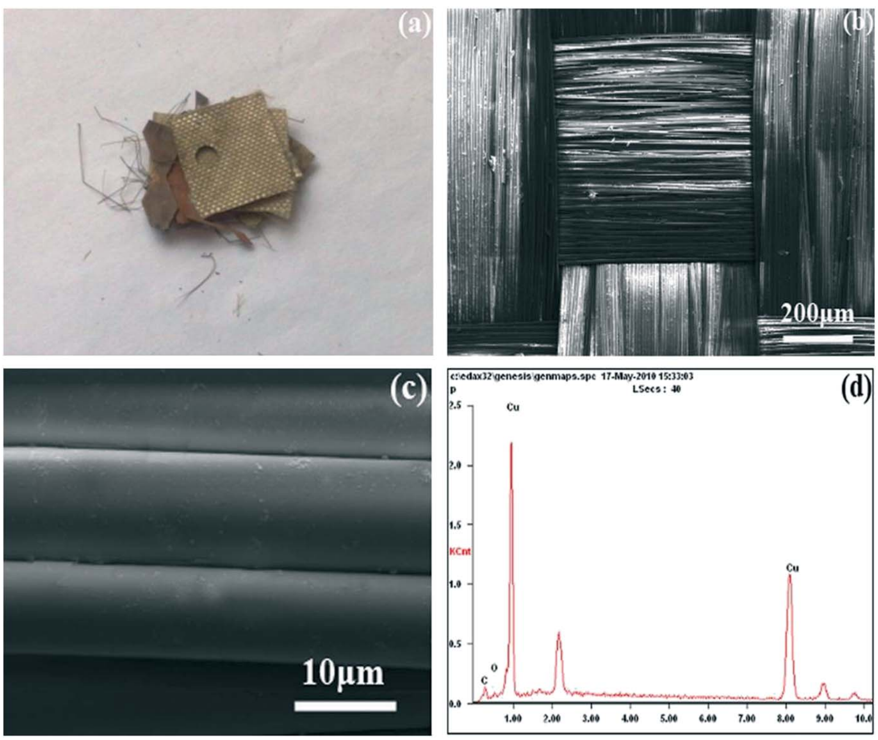


Fig. 6 The characterization of recovery solid residue: (a) the photograph of recovery glass fabric and metal copper foil, (b) and (c) SEM of glass fabric surface (d) EDS spectrum of copper foil.

Table 3 A comparison of different studies on WPCBs treatment in near or super critical water conditions.

Sources	Treatment conditions	Results
Chien[31]	Super critical water T=420 °C, t=10 min Additive: NaOH	The resin conversion ratio: 99%; The main components are not detected; Copper is remained in the solid residue.
Zhang[17]	Super critical water T=400 °C, t=120 min Water amount: 40 mL	The debromination ratio: 97.8%; The main components: phenol (58.5%) and 4-(1-methylethyl)-phenol (21.7%); It needs to crush for liberation and recovery of the glass fibers and copper foils. The surface of short glass fibers is not very clean.
Xu[33]	Near critical water T=4 °C, t=305 min P=33 MPa	Yield of residue: 69.24%; The main components: phenol, 4-(1-methylethyl)-phenol, etc; Mechanical separation is needed to recover glass fibers and copper foils.
Li[32]	Near or super critical water T>300 °C, t>30 min	The decomposition ratio of BERs: >80%; The main components: phenol (42.05%) and iso-propylphenol (22.95%). Surface of single glass fiber is not very clean
Xiu[34]	Near-critical water T=350°C t=60min Feed ratio: 9 ml/g	The decomposition ratio of BERs: about 100% Cu and Pb recovery ratio : 98.9% and 80% Decomposition products and fiber were not studied
This work	T=320 °C, t=150 min Shape: 5mm×5mm Feed ratio: 5 mL/g Additive: HCl	The decomposition ratio of BERs: 98.7%; The main components: phenol (69.8%) and iso-propylphenol (15.3%). Glass fibers and copper foils can be recovered easily by only artificial separation. The surfaces of glass fabric and single fiber are very clean.

temperature, reaction time, feed ratio, acid-base catalyst, and sizes of WPCBs are important factors to influence the decomposition ratio of BERs in WPCBs. The optimum decomposition conditions are 320 °C, reaction time of 150 min, feed ratio of 5 mL/g, HCl catalyst, and the size of 5×5 mm^2 and the decomposition ratio of BERs reaches a maximum value of 98.7%. The GC/MS result shows that the main components of liquid decomposition product are phenol (69.8%) and its derivatives (17.8%). Based on the components of liquid decomposition product, it is concluded that the hydrolysis reaction plays a main role in the BERs decomposition during the process of NCW treatment. After NCW treatment, the glass fabric and copper foils in the residue can be easily recovered by artificial separation. The surface of recovered fabric is very clean and no damages are observed. Meanwhile, the purity of copper foil reaches 97.86%.

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