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RESEARCH PAPER

Preparation of porous carbons from non-metallic fractions of waste printed circuit boards by chemical and physical activation

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Abstract: Non-metallic fractions of FR-3 type waste printed circuit boards were pyrolyzed at high temperatures. The resultant char at 600 °C was used to prepare activated carbons by physical and chemical activation. The influence of pyrolysis temperature on char yields, and activation conditions on the burn-off and porous properties of the activated carbons were investigated. Results show that char yields decrease with pyrolysis temperature. A granular activated carbon with a surface area of 1 019 $m^2 \cdot g^{-1}$ and a pore volume of 1.1 cm3·g^{-1} can be obtained by moulding, pyrolysis and physical activation using H_2O as an activation agent. An activated carbon powder with a surface area of 3 112 $m^2 \cdot g^{-1}$ and a pore volume of 1.13 $cm^3 \cdot g^{-1}$ can be achieved by KOH activation.

Key Words: Non-metallic fractions; Waste printed circuit boards; Activated carbon

1 Introduction

Printed circuit boards (PCBs) are the typical and fundamental component for almost all electronic products, which contain various metals *e.g.* Cu, Al, Fe, Sn, Sb, Pb, et al. and nonmetals *e.g.* thermosetting resins, reinforcing materials, brominated flame retardants (BFRs) and other additives. It has been reported that 20–50 million tones of waste electrical and electronic equipment (WEEE) are generated worldwide each year due to product replacement. As one of the most important branches of WEEE, waste PCBs have drawn much attention from the public and researchers because plenty of toxic materials including heavy metals and BFRs can cause huge damage to the environment if they are not treated properly [1–3]. Currently, the metallic fractions of waste PCBs can be effectively recycled through mechanical separation methods [3]. The non-metallic fractions (NMFs), which take up almost 70 mass% of waste PCBs, are generally treated by incineration or land filling. However, incineration of the NMFs could cause the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) [4], while land filling of the NMFs leads to secondary pollution caused by heavy metal residues and BFRs leaching to the groundwater [5]. Therefore, recycling of the NMFs environmental friendly from waste PCBs remains a huge challenge.

It has been reported that NMFs of waste PCBs can be recycled using physical or chemical method [6]. In the physical method NMFs are used as fillers or reinforcing fillers for various products, such as construction materials, decorating agent, adhesives and insulating materials [7–9]. For example, Xu *et al.* [8] have prepared phenolic molding compound using NMFs from paper-based waste PCBs as fillers to replace wood flour. Shen et al. [9] found that both tensile and flexural properties of the NMFs/polypropylene composites can be significantly improved by adding the NMFs into the polypropylene. Whereas, NMFs are recycled by pyrolysis, gasification, depolymerization with supercritical fluids and hydrogenolytic degradation in the chemical method[10–14]. Among these methods, pyrolysis as a promising recycling method has been widely investigated [13,14]. Pyrolysis of organic materials contained in waste PCBs leads to the formation of gases, oils and chars, which can be used as chemical feedstocks or fuels. A process called "Hloclean" pyrolysis process has been developed by 10 European partners from industries, universities and research centers to transform materials like waste PCBs into fuel oils and to recover bromine from brominated flame retardants in PCBs. Although a number of researches have been carried out for handing NMFs in waste PCBs using pyrolysis, few research focused on the use of residue chars. In the present work activated carbons with high porosity were prepared from chars derived from pyrolysis of NMFs in waste paper-based PCBs by using chemical and physical activation methods. The optimum conditions for preparing high porosity activated carbons are recommended.

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2 Experimental

2.1 Materials

The NMFs of wasted PCBs in FR-3 type (kraft mat impregnated with epoxy resin) were provided by Vary Science and Technology, Ltd., corporation, Hunan, China with particle sizes less than 0.07 mm after separating metals.

2.2 Pyrolysis

A laboratory-scale fixed bed tubular reactor was used to carry out the pyrolysis of NMFs. The sample was heated in a nitrogen flow (20 mL·min^{-1}) at a ramping rate of 5 ºC·min^{-1} from ambient temperature to the desired temperature *i.e.* 500, 600, 700, and 800 ºC, and held at the desired temperature for 2 h. Liquid products evolved during pyrolysis were collected by a cold trap maintained at 0 ºC by an ice/water bath. The resulting chars were collected for chemical and physical activation. The obtained samples were denoted as C500, C600, C700, and C800, where the numbers refer to pyrolysis temperatures.

2.3 Preparation of granular activated carbon by physical activation

The granular activated carbon was prepared according to the following procedure. The char powder derived from the pyrolysis of the NMFs at 600 ºC for 2 h was formed in an extruder under a pressure of 20 MPa using coal-tar pitch as binder. The addition amount of the binder is 30 mass%. The resultant granules were heated at a rate of 5 ºC·min^{-1} to 800 ºC in nitrogen (20 mL·min^{-1}) in the same tubular furnace, and carbonized at 800 ºC for 30 min. Then, the granular carbon was activated at 850 ºC in a mixed stream of N_2 (20 mL·min^{-1}) and H_2O (2.8 mL·min^{-1}) for different times *i.e.* 1, 2, 3, 4 h to achieve different burn-offs. The obtained activated carbons were denoted as PA1, PA2, PA3, and PA4, where the numbers refer to physical activation temperatures.

2.4 Preparation of powder activated carbon by chemical activation

The same char as above was milled to 200 mesh size (US standard sieve) using a grinder. Then, the char powder was mixed with solid KOH (KOH/char = 4/1, w/w) and activated in N_2 atmosphere at 600 and 900 ºC for 2 h. After activation, the sample was first washed with 1 mol/L HCl to dissolve ash in the samples, and then washed with distilled water until the pH value of the residual solution was 7. The resultant products were collected and dried at 120 ºC overnight. The obtained samples were denoted CA600 and CA900, where the numbers refer to chemical activation temperatures.

2.5 Characterization

The surface areas and the pore size distributions (PSDs) of the activated carbons were obtained from N_2 (77 K) adsorption measurement using a Micromeritics ASAP2020M system. The PSDs were calculated using density functional theory (DFT), and the surface area was calculated by BET method. The micropore surface area S_{mi} was obtained by the *t*-plot method. The average pore diameter (D) was estimated from the S_{BET} and total pore volume (V) according to the equation $D = 4V/S$. Powder X-ray diffraction (XRD) was performed on a Rigaku D/MAX-ⅢI X-ray diffractometer (35 kV, 40 mA) using a Cu $K\alpha$ source. Infrared spectra were recorded on a Bruker EQUINX55 FTIR spectrometer using KBr disc method. Thermogravimetric (TG) measurement was performed on a TGA analyzer (TA-Q600SDT, USA) with a heating rate of 10 ºC·min^{-1} under a flow of N_2. The scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) were performed on a Philips-FEI Quanta 200 microscope at 20 kV.

3 Results and discussion

3.1 Characterization of the precursor

Table 1 shows the elemental compositions of the NMFs. FT-IR spectrum of the NMFs is shown in Fig. 1a. The bands in the spectrum can be assigned according to the literatures [15,16]. The peak at 3 440 cm^{-1} corresponds to O—H stretching. The peaks at 2 921 and 2 855 cm^{-1} correspond to C—H stretching in benzene ring skeleton. The peak at 1 773 cm^{-1} is assigned to C═O stretching in carboxymethyl cellulose of kraft paper. The characteristic stretching vibration of C═C double bonds in benzene ring skeleton appears at 1 605, 1 504, 1 454 cm^{-1}, C—H deformation vibration of methyl appears at 1 375 cm^{-1}. The band at 1 251 cm^{-1} corresponds to P—O—Ar stretching in triphenyl phosphate. The bands at 1 165, 1 109, 1 024 cm^{-1} correspond to C—O stretching vibration of aryl- and aryl ester-based ethers in epoxide resin. The peak at 813 cm^{-1} is due to the absorption of epoxy group. The peak at 609 cm^{-1} can be assigned to C—Br stretching. The results indicate that the NMFs mainly contain brominted epoxide resin, together with triphenyl phosphate as fire retardant.

Table 1 The elemental compositions of the samples obtained by EDAX

Samples	C /mass%	O /mass%	Al /mass%	Cu /mass%	Ca /mass%	P /mass%	Br /mass%	Others /mass%
NMFs	72.29	17.06	0.18	0.83	0.11	0.42	6.56	1.33
C600	91.19	6.05	0.25	1.54	0.25		0.72	0.25
PA3	88.39	6.34	0.26	2.31	0.62			2.09
CA900	89.91	7.93	0.25	0.46	0.25			1.20