Journal of Hazardous Materials 179 (2010) 203–207

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Performance and thermal behavior of wood plastic composite produced by nonmetals of pulverized waste printed circuit boards

Jie Guo, Yinen Tang, Zhenming Xu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

ARTICLE INFO

Article history:
Received 7 December 2009
Received in revised form 5 February 2010
Accepted 24 February 2010
Available online 3 March 2010

Keywords:
Printed circuit boards
Wood plastic composite
Screw withdrawal strength
Thermogravimetric analysis

ABSTRACT

A new kind of wood plastic composite (WPC) was produced by compounding nonmetals from waste printed circuit boards (PCBs), recycled high-density polyethylene (HDPE), wood flour and other additives. The blended granules were then extruded to profile WPC products by a conical counter-rotating twin-screw extruder. The results showed that the addition of nonmetals in WPC improved the flexural strength and tensile strength and reduced screw withdrawal strength. When the added content of nonmetals was 40%, the flexural strength of WPC was 23.4 MPa, tensile strength was 9.6 MPa, impact strength was 3.03 J/m^2 and screw withdrawal strength was 1755 N. Dimensional stability and fourier transform infrared spectroscopy (FTIR) of WPC panels were also investigated. Furthermore, thermogravimetric analysis showed that thermal degradation of WPC mainly included two steps. The first step was the decomposition of wood flour and nonmetals from 260 to 380 °C, and the second step was the decomposition of HDPE from 440 to 500 °C. The performance and thermal behavior of WPC produced by nonmetals from PCBs achieves the standard of WPC. It offers a novel method to treat nonmetals from PCBs.

1. Introduction

Recycling of waste printed circuit boards (PCBs) is an important subject not only from a standpoint of the protection of the environment but also from the recovery of reusable materials. The UN Environmental Programme estimates that the world generated 20–50 million tonnes of electronic waste each year, while PCBs formed about 3% by weight of the total amount of electronic waste [1,2]. Mechanical–physical process is drawing more attention compared with hydrometallurgy and pyrometallurgy [3,4]. The mechanical–physical approach involves first a crushing process, aiming to strip metal from the base plates of waste PCBs. The extreme differences in properties such as the density and electrical conductivity between metals and nonmetals provide an excellent condition for the separation of them. Various techniques including density-based separation, jigging and corona electrostatic separation are used to separate metals from nonmetals [5,6]. Metals such as Cu, Al and Sn, are sent to recovery operations. However, significant quantities of nonmetals in PCBs (up to 70%) present an especially difficult challenge for recycling. The nonmetals of PCBs consist of thermoset resins powder and glass fibers [7]. The kind of thermoset resins varies with different PCBs. Common resins include difunctional epoxy resins such as bisphenol A, multifunctional epoxy resins such as phenol and creosol based epoxy novolacs and BT epoxy blends [8]. Thermoset resins cannot be remelted or reformed due to their network structure. Incineration is not the best method for treating nonmetals because of inorganic fillers such as glass fiber, which significantly reduce the fuel efficiency. In addition, the combustion of electronic waste in the presence of copper from PCBs may lead to higher emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) into the environment, causing even worse environmental pollution [9]. Disposal in landfill is the main method for treating nonmetals of PCBs, but it may cause secondary pollution and resource-wasting. To obtain the resource utilization of nonmetals, many researchers have carried out many studies on the recycling of nonmetals for molding electronic components [10], phenolic compound [7] and modifying asphalt [11].

Wood plastic composite (WPC) is a kind of composite materials, consisting of thermoplastic resins, wood flour and small amounts of additives. Among the thermoplastic resins used, virgin and recycled polyethylene are the most common with an estimated 83% market share followed by polyvinyl chloride (9%) and polypropylene (7%) [12]. WPC is durable and low maintenance compared to wooden products, and hence ideal for nonstructural applications. Currently, most WPC is made with polyethylene for use in exterior building component, including decking, fencing, industrial flooring, landscape timbers and railing [13]. Wood flour is the most

---

* Corresponding author. Tel.: +86 21 54747495; fax: +86 21 54747495.
E-mail address: zmxu@sjtu.edu.cn (Z. Xu).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.02.080

common organic filler used in WPC, with the aim to decrease cost and enhance performance of WPC. Demand for WPC has been steadily increasing in the past decade, with a market demand of 1.95 billion kg in 2006 [14]. Thus, WPC producers are forced to seek other nonwood sources to supply the increasing raw material requirement and protect timber resources. Bourne et al. studied the effects of cotton gin waste as a lignocellulosic substitute on the mechanical properties of WPC. It was found that mechanical properties of extruded cotton gin waste WPC were within the range of reported values for commercial WPC products [15].

To our knowledge, there is little published information about reusing nonmetals reclaimed from PCBs as a filler of WPC. The objective of this study is to investigate the possibility of using nonmetals in WPC production. Mechanical properties and dimensional stability of WPC with nonmetals were investigated. Furthermore, FTIR spectroscopy and thermal degradation of WPC were also studied.

2. Materials and methods

2.1. Materials and formulations

Thermoplastics used in the study were a kind of recycled high-density polyethylene (HDPE). Wood flour used in the study was derived from various scrap wood from wood processors. The moisture content of wood flour was about 8%, and the particle size was less than 0.15 mm. The nonmetals were obtained from two step crushing and corona electrostatic separating [6]. The particle size of the nonmetals was less than 0.07 mm. WPC were prepared by mixing recycled HDPE (35%), wood flour, nonmetals and additives (5%). Based on our previous experiments, three batches of WPC were produced, and the nonmetals were added to the raw materials mixture at a weight fraction of 0%, 15% and 40%. Define WPC with different nonmetals content as follows: “N-0-WPC” means WPC without nonmetals, “N-15-WPC” means WPC with 15 wt.% nonmetals, and “N-40-WPC” with 40 wt.% nonmetals. The additives included silane coupling agents KH-550 (2%), wax (1%), zinc stearate (0.5%) and iron oxide red (1.5%). The function of coupling agent is to promote adhesion and dispersion of fillers, and improve mechanical properties of WPC panels. Both wax and zinc stearate are lubricants, aiming to increase melt flow and reduce viscosity and friction between resin and process equipment. Iron oxide red is the pigment.

2.2. Preparation of the WPC

The recycled HDPE, nonmetals, wood flour and other additives were compounded and pelletized to composite granules. Then, the granules were used for profile extrusion by a conical counter-rotating twin-screw extruder (TSE). Along with the conical counter-rotating TSE, the die was an important part of the WPC product extrusion system. The die was heated using cartridge heating elements. After the die came the cooling tank, which was used to “freeze” the extruded profile in its linear shape. After the cooling tank, the WPC profile went through a cutoff saw that can cut the WPC panels to the desired lengths.

Average temperatures in the extruder barrel and die were maintained at 175 °C and 180 °C. The extruder pressure was maintained at approximately 9.5–11.5 MPa. The speed of the extruder was set at approximately 600 mm/min.

2.3. Measurement of properties

The mechanical properties like flexural strength, tensile strength and charpy unnotched impact strength were tested. Flexural strength is maximum bending stress developed in a specimen just before it cracks or breaks in a flexure test. Tensile strength measures the force required to pull a specimen to the point where it breaks, and is measured in units of per unit area or pascals (Pa). Charpy unnotched impact strength is defined as the amount of energy absorbed in fracturing an unnotched specimen at high velocity and is expressed as kilojoule per square meter. Flexural, tensile and Charpy impact tests were performed on the WPC composites according to ASTM D 790, ASTM D 638 and ISO 179-1982, respcetively.

Screw withdrawal strength is defined as the peak load required to pull a standard screw from the panel specimen. Face screw withdrawal strength was tested according to EN 320-1993. Specimens’ shapes for screw withdrawal strength were 150 mm × 50 mm × 30 mm. The screws used in the study are a kind of cross recessed pan head tapping screw with diameter of 4.2 mm and length of 38 mm. A 2.7 mm diameter pilot hole was predrilled 19 mm into each specimen. Then a screw was hand-driven 15 ± 0.5 mm into the specimen. The screws were perpendicular to the face plane.

Field emission scanning electron microscopy, FEI SIRION 200, was used to analyze the dispersion of fillers into the resin matrix using fractured surfaces. Prior to the analysis, the fractured surfaces of the specimens were sputter coated with a thin layer of gold.

Water absorption and thickness swelling tests were conducted in accordance with ASTM D 570-98, in which the specimens were immersed in water for 2 h and 24 h at a temperature 23 ± 1 °C. The weight gain and thickness increase were then measured 20 min after being removed from the water.

Fourier transform infrared spectroscopy (FTIR) spectroscopy was conducted on a Shimadzu IRP restige-21 spectrometer to provide knowledge of functional groups.

Thermogravimetric analysis (TGA) measurements were conducted using a TGA2050 TA instruments. The thermograms were obtained under nitrogen atmosphere, at a constant heating rate of 10 °C/min, from 80 to 600 °C for the samples.

3. Results and discussion

3.1. Mechanical properties of WPC

The mechanical properties of WPC panels were shown in Table 1. Values of flexural strength and tensile strength of WPC with nonmetals (N-15-WPC and N-40-WPC) were slightly greater than those of control specimens (N-0-WPC). This is because the glass fibers in nonmetals reinforced the properties of composites. In addition, N-15-WPC possessed the highest flexural property, with a flexural strength of 25.8 MPa. This result is expected because the nonmetals and wood flour in N-15-WPC are better encapsulated by HDPE resin which is evident from the SEM study in the forthcoming section. Unlike the flexural or tensile strength of composites, a balance in

Table 1
Mechanical properties of WPC panels.

Sample	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)	Screw withdrawal strength (N)
N-0-WPC	21.6	9.1	3.3	2072
N-15-WPC	25.8	9.8	3.4	1568
N-40-WPC	23.4	9.6	3.0	1755

properties between the matrix and fiber is required to obtain good impact strength [16]. N-40-WPC showed the worst impact strength as shown in Table 1. The 40 wt.% nonmetals content contributed to high content of glass fibers. The addition of many glass fibers in the N-40-WPC increased the probability of filler agglomeration that create regions of stress concentrations. Cracks travelled around the stress concentrations and required less energy to elongate the crack propagation.

The WPC products need to be fastened by screws when they are used for deck boards, landscape timbers and park benches in the exterior environment. The addition of nonmetals in the WPC decreased the screw withdrawal strength as shown in Table 1. This is likely because the nonmetals consist of many glass fibers and possess worse compatibility with HDPE resin compared with wood flour. Poor compatibility lowers the friction between the screw and the panels thus causing a lower withdrawal load. However, the values of screw withdrawal strength for all the WPC panels were higher than 1000 N which was the lowest value according to the industrial standard.

WPC is a kind of composites with fillers as reinforcing materials. Generally, the strength of fiber-reinforced composites depends on the interface interaction. The SEM photographs of different WPC panels after flexural fracture are shown in Fig. 1(a) showed the SEM photograph of N-15-WPC. Fillers including wood flour and nonmetals were well encapsulated by resin matrix, and dispersed homogeneously in the composite. However, wood flour and glass fibers in N-0-WPC and N-40-WPC were not well encapsulated by the matrix as shown in Fig. 1(b) and (c), respectively. Fig. 1(c) showed poor interfacial adhesion between glass fibers and resin matrix in N-40-WPC. The amount of short glass fibers in WPC increased as the increasing content of nonmetals. The increasing amount of glass fibers decreased the flow ability of composite and reduced dispersion of ingredients, leading to poor interfacial adhesion.

3.2. *Moisture absorption and thickness swelling*

Results of density, moisture absorption and thickness swelling are given in Table 2. It is found that the density of the WPC panels ranges from 1280 for N-0-WPC to 1340 kg/m^3 for N-40-WPC. The water absorption decreased with increasing nonmetals content in the composites for the 2 h water immersion tests. The different performance is caused by the large difference between the wood flour and nonmetals. The moisture absorption in wood flour is mainly due to water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water [17]. In addition, nonmetals consisting of resin powder and glass fibers are water repellent and have much lower water sorption capability than wood flour. However, after 24 h immersion, N-15-WPC showed the largest water absorption. The reasons may be complex and explained by the presence of lumens, fine pores and hydrogen bonding sites in the wood flour, the gaps and flaws at the interfaces, and the microcracks in the matrix formed during the compounding process [18]. N-40-WPC possessed best thickness swelling. The thickness swelling values of N-40-WPC are only 0.05% after 2 h and 0.12% after 24 h immersion in water. It indicates that WPC sam-

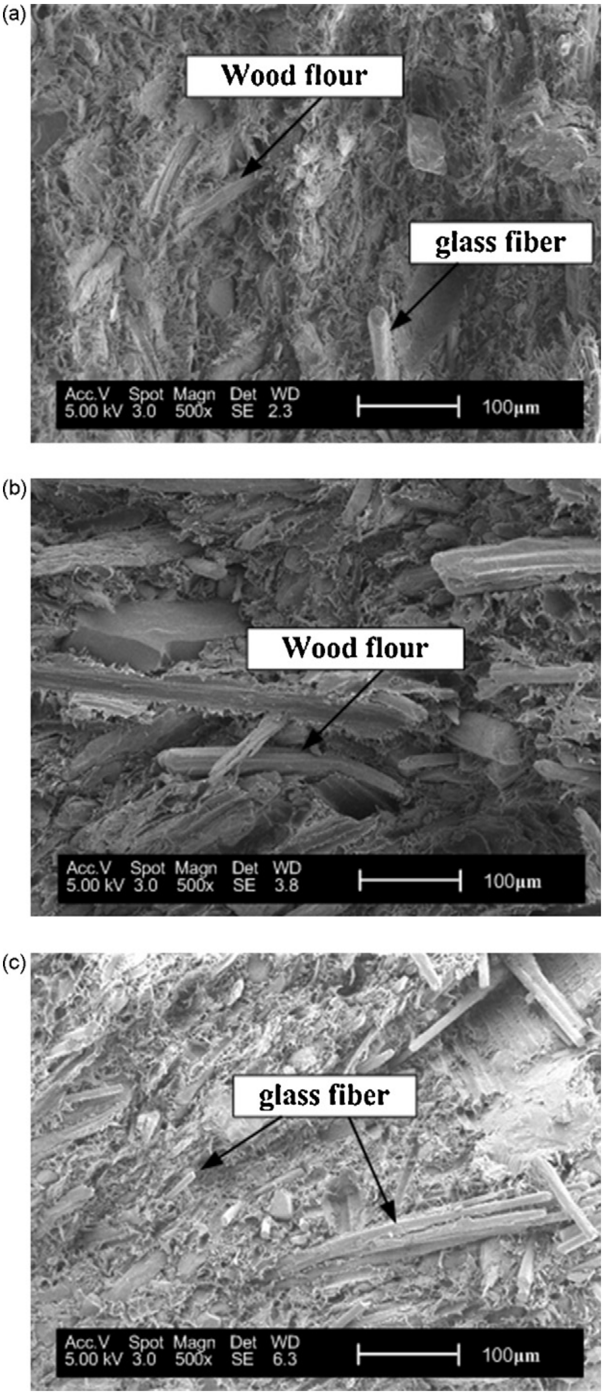

Fig. 1. SEM photographs of different WPC: (a) N-15-WPC, (b) N-0-WPC and (c) N-40-WPC.

Table 2
Water absorption and thickness swelling of WPC.

Sample	Density (kg/m^3)	Moisture absorption (%)		Thickness swelling (%)	
		2 h	24 h	2 h	24 h
N-0-WPC	1280	0.52	2.40	0.17	1.11
N-15-WPC	1320	0.40	2.71	0.16	1.38
N-40-WPC	1340	0.12	0.34	0.05	0.12

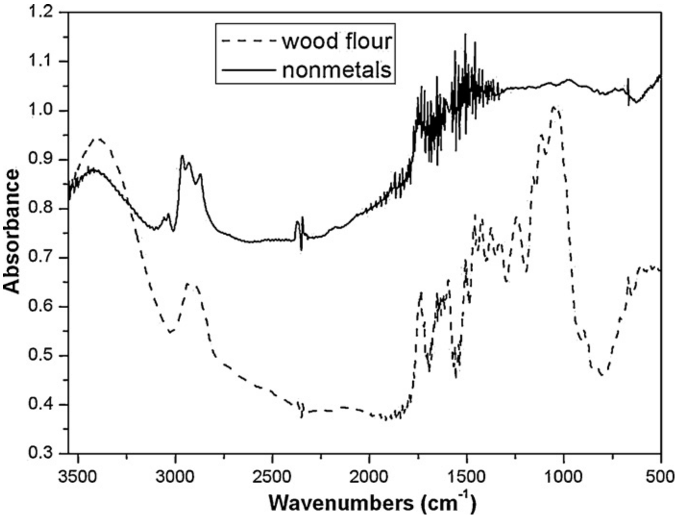

Fig. 2. FTIR spectra of wood flour and nonmetals.

ples made with higher content of nonmetals have lowest thickness swelling.

3.3. Fourier transform infrared spectroscopy

FTIR spectroscopy was used to verify the functional group in wood flour, nonmetals and WPC panels. Fig. 2 showed the FTIR spectra of wood flour and nonmetals. The spectral region between 3500 cm^{-1} and 3250 cm^{-1} has been assigned to hydroxyl groups originating mainly from cellulose of wood flour [19]. The spectral region between 1050 cm^{-1} and 1023 cm^{-1} has been assigned to C–O groups in wood cellulose [20]. Within the fingerprint region (1800–600 cm^{-1}), the peaks of FTIR spectra for the nonmetals were overlapped due to the complex ingredients in the nonmetals. So the characteristic peaks cannot be analyzed.

The FTIR spectra for the surfaces of N-0-WPC, N-15-WPC and N-40-WPC are shown in Fig. 3. Compared with the spectrum of wood flour (Fig. 2), the band peaks at 2920 cm^{-1}, 2850 cm^{-1} and 720 cm^{-1} in WPC panels are assigned to the–CH_2 from long-chain of HDPE. In the carbonyl region (1750–1700 cm^{-1}), a peak at 1718 cm^{-1} with a shoulder peak at 1735 cm^{-1} corresponding to carboxylic acid and ester groups [21]. A decrease in absorbance intensity is observed as the nonmetals content increased.

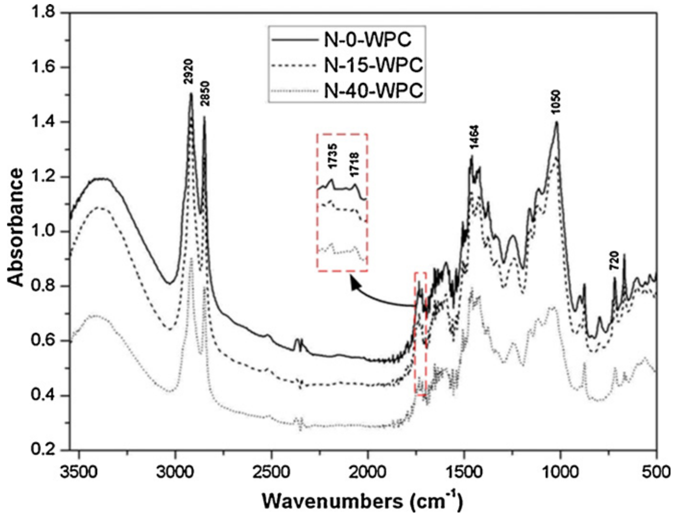

Fig. 3. FTIR spectra of different WPC panels.

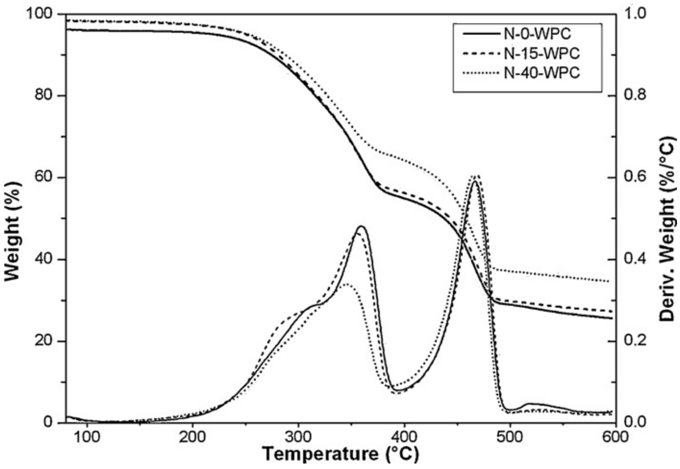

Fig. 4. TGA and DTGA thermograms of WPC.

3.4. Thermogravimetric analysis

Fig. 4 shows TGA and DTGA thermograms of WPC samples, and different data can be obtained in Table 3. It can be noticed that all thermograms represented in Fig. 4 are of similar shape. The thermal degradation of mechanism of WPC included two stages. The first step was from 260 to 380 °C, and it included the decomposition of wood flour and resin powder in nonmetals. The results illustrated in Table 3 show that the samples have a different decomposition onset temperature (T_d) at the first stage. It decomposed from 295 °C, 289 °C and 277 °C for N-0-WPC, N-15-WPC and N-40-WPC, respectively. WPC with more nonmetals decomposed more easily than WPC without nonmetals. This can be explained by the fact that the mixture of wood flour and nonmetals induces "defects" in the form of aggregates and heterogeneities in the polymer matrix. Temperatures with maximum rate of decomposition (T_{max}) were also different for three kinds of WPC. The second decomposition curves of three samples were of similar shape, with nearly the same T_d, T_{max} and weight loss. The stage began around 446 °C with a weight loss of about 28%. The weight loss was due to the decomposition of recycled HDPE. The thermal degradation step was in agreement with the results reported in the literature for degraded HDPE [22]. When the temperature reached 600 °C, the weight of WPC became relatively stable, with residue of 25.6%, 27.3% and 34.6% for N-0-WPC, N-15-WPC and N-40-WPC, respectively.

3.5. Economic evaluation

In China, the profit from recycling of PCBs is attained by selling recycled metals, and the profit can offset the cost of the recycling system, which includes management policies, a chain from production to consume, and behavior concepts. In addition, China's demand for WPC has grown at a fast pace in the past decade. In the next five years, both production and demand will continue to grow. Economic benefit of using nonmetals in WPC production was caused by different prices of nonmetals and wood flour. PCBs waste recycling enterprises have to pay treating fee when nonmetals are sent to the landfill or incineration plant, so it will be happy to convey nonmetals to WPC producer if the price of transportation is less than treating fee. So the price of nonmetals is zero when accounting the production costs. The price of wood flour is about 800 Yuan/t according to the market price in China. Therefore, long-term cooperation between producers of WPC and recycling enterprises of PCBs will attain economic benefits for both sides.

Table 3
Values of temperatures and weight loss during thermal degradation of WPC.

Sample	Stage I			Stage II			Residue (%)
	T_d (°C)	T_{max} (°C)	Weight loss (%)	T_d (°C)	T_{max} (°C)	Weight loss (%)	
N-0-WPC	295	359	41.5	445	467	27.8	25.6
N-15-WPC	289	355	42.1	447	469	28.4	27.3
N-40-WPC	277	346	33.7	442	464	28.7	34.6

4. Conclusions

A study was conducted to test whether the nonmetals from PCBs could be a feasible substitute of wood flour in the production of WPC. The addition of nonmetals in WPC improved the flexural strength and tensile strength, and reduced screw withdrawal strength. N-40-WPC showed best dimensional stability. The thickness swelling and thickness swelling of N-40-WPC were only 0.34% and 0.12%, respectively and after 24 h immersion in water. Thermal degradation of WPC mainly included two steps: the first stage was the decomposition of wood flour and nonmetals and the second stage belonged to degradation of HDPE. It is thus concluded that the nonmetals, a by-product of recycling PCBs, can be utilized as a filler in WPC production.

Acknowledgments

This work was supported by the National High Technology Research and Development Program of China (863 program 2006AA06Z364), Shanghai Tongji Gao TingYao Environmental Science & Technology Development Foundation.

References

[1] M. Bruke, The gadget scrap heap, Chem. World 6 (2007) 45–48.

[2] A. Bernardes, I. Bohlinger, D. Rodriguez, H. Milbrandt, W. Wuth, Recycling of printed circuit boards by melting with oxidising/reducing top blowing process, TMS Annu. Meet. (1997) 363–375.

[3] W. He, G. Li, X. Ma, H. Wang, J. Huang, M. Xu, C. Huang, WEEE recovery strategies and the WEEE treatment status in China, J. Hazard. Mater. 136 (2006) 502–512.

[4] H.M. Veit, A.M. Bernardes, J.Z. Ferreira, J.A.S. Tenoĭrio, C.d.F. Malfatti, Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy, J. Hazard. Mater. 137 (2006) 1704–1709.

[5] J. Cui, E. Forssberg, Mechanical recycling of waste electric and electronic equipment: a review, J. Hazard. Mater. 99 (2003) 243–263.

[6] J. Li, H. Lu, J. Guo, Z. Xu, Y. Zhou, Recycle technology for recovering resources and products from waste printed circuit boards, Environ. Sci. Technol. 41 (2007) 1995–2000.

[7] J. Guo, Q. Rao, Z. Xu, Application of glass-nonmetals of waste printed circuit boards to produce phenolic moulding compound, J. Hazard. Mater. 153 (2008) 728–734.

[8] W.J. Hall, P.T. Williams, Separation and recovery of materials from scrap printed circuit boards, Resour. Conserv. Recycl. 51 (2007) 691–709.

[9] A.O. Leung, W.J. Luksemburg, A.S. Wong, M.H. Wong, Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, Environ. Sci. Technol. 41 (2007) 2730–2737.

[10] M. Iji, Recycling of epoxy resin compounds for moulding electronic components, J. Mater. Sci. 33 (1998) 45–53.

[11] J. Guo, J. Guo, S. Wang, Z. Xu, Asphalt modified with nonmetals separated from pulverized waste printed circuit boards, Environ. Sci. Technol. 43 (2009) 503–508.

[12] J. Morton, J. Quarmley, L. Rossi, Current and emerging applications for natural and woodfiber–plastic composites, in: Proc. 7th Inter. Conf. on Woodfiber–Plastic Composites, Forest. Prod. Soc., Madison, WI, 2003, pp. 3–6.

[13] C. Clemons, Wood–plastic composites in the United States: the interfacing of two industries, Forest Prod. J. 52 (2002) 10–18.

[14] Inc. Freedonia Group, Composite and Plastic Lumber, Freedonia Group Inc., Cleveland, OH, 2004.

[15] P.J. Bourne, S.G. Bajwa, D.S. Bajwa, Evaluation of cotton gin waste as a lignocellulosic substitute in woodfiber plastic composites, Forest Prod. J. 57 (2006) 127–131.

[16] P.W. Balasuriya, L. Ye, Y.-W. Mai, Mechanical properties of wood flake–polyethlene composites. Part I: Effects of processing methods and matrix melt flow behaviour, Compos. A: Appl. Sci. 32 (2001) 619–629.

[17] K.B. Adhikary, S. Pang, M.P. Staiger, Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE), Compos. B: Eng. 39 (2008) 807–815.

[18] D.D. Stokke, D.J. Gardner, Fundamental aspects of wood as a component of thermoplastic composites, J. Vinyl Addit. Technol. 9 (2003) 96–104.

[19] N.M. Stark, L.M. Matuana, C.M. Clemons, Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites, J. Appl. Polym. Sci. 93 (2004) 1021–1030.

[20] J.S. Fabiji, A.G. McDonald, M.P. Wolcott, P.R. Griffiths, Wood plastic composites weathering: visual appearance and chemical changes, Polym. Degrad. Stabil. 93 (2008) 1405–1414.

[21] N.M. Stark, L.M. Matuana, Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy, Polym. Degrad. Stabil. 86 (2004) 1–9.

[22] F. Mengeloğlu, K. Karakuş, Some properties of eucalyptus wood flour filled recycled high density polyethylene polymer-composites, Turk. J. Agric. Forest 32 (2008) 537–546.