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Application of glass-nonmetals of waste printed circuit boards to produce phenolic moulding compound

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Abstract

The aim of this study was to investigate the feasibility of using glass-nonmetals, a byproduct of recycling waste printed circuit boards (PCBs), to replace wood flour in production of phenolic moulding compound (PMC). Glass-nonmetals were attained by two-step crushing and corona electrostatic separating processes. Glass-nonmetals with particle size shorter than 0.07 mm were in the form of single fibers and resin powder, with the biggest portion (up to 34.6 wt%). Properties of PMC with glass-nonmetals (PMCGN) were compared with reference PMC and the national standard of PMC (PF2C3). When the adding content of glass-nonmetals was 40 wt%, PMCGN exhibited flexural strength of 82 MPa, notched impact strength of 2.4 kJ/m^2, heat deflection temperature of 175 °C, and dielectric strength of 4.8 MV/m, all of which met the national standard. Scanning electron microscopy (SEM) showed strong interfacial bonding between glass fibers and the phenolic resin. All the results showed that the use of glass-nonmetals as filler in PMC represented a promising method for resolving the environmental pollutions and reducing the cost of PMC, thus attaining both environmental and economic benefits.
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Keywords: Waste printed circuit board; Phenolic moulding compound; Resource

1. Introduction

Printed circuit boards (PCBs) contain nearly 28% metals, including Cu, Al, Sn, etc. The purity of precious metals in PCBs is more than 10 times higher than that of rich-content minerals [1,2]. Recycling of PCBs is an important subject not only from the treatment of waste but also from the recovery of valuable materials as the amount of deserted PCBs is dramatically increasing. Mechanical–physical process is drawing more attention compared with hydrometallurgy and pyrometallurgy [3]. The mechanical–physical approach involves first a crushing process, aiming to strip metal from the base plates of waste PCBs, and then different methods to separate metals from nonmetals [4]. Metals such as Cu, Al, Sn, are sent to recovery operations. However, significant quantities of nonmetals in PCBs (up to 70%) present an especially difficult challenge for recycling. Nonmetals of PCBs mainly consist of thermoset resins and reinforcing materials. 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 reduces the fuel efficiency. Disposal in landfill is the main method for treating nonmetals of PCBs, but it may cause secondary pollution and resource-wasting. Yokoyama and Iji have carried out many studying works on recycling glass fiber-resin powder taken from PCBs [5,6]. In their studies, nonmetals reclaimed from waste PCBs could be used as fillers for other products, such as construction materials, decorating agent, adhesives and insulating materials. Peng also presented new methods that nonmetals are used to make formative models, compound boards or related products [7].

Phenolic moulding compound (PMC) is produced with phenolic resin acting as a bond, various fillers, solidifiers and colorants under high temperature and a certain pressure. Due to their ease of fabrication, high mechanical strength, heat-resistance and high dielectric strength, PMC is widely used to manufacture products like saucepan handles and electronic switches. Increasing production of PMC in recent years has

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greatly increased the need of wood flour, which is used as an organic filler in the moulding compounds. With the timber resource depletion and the increasing price of wood flour, it is an urgent assignment for producers of PMC to protect timber resource and reduce the cost of raw materials by finding alternative materials of wood flour. Kharade studied the effect of partial replacement of wood flour filler by lignin on the properties of moulding powders [8]. Hattali also studied the behavior of replacement of wood flours by Alpha grass soda lignin [9]. To our knowledge, there is little published information about using nonmetals reclaimed from PCBs as a filler of PMC.

The type of waste PCBs used in the study was made from glass fiber reinforced epoxy resin. Nonmetals reclaimed from this kind of PCBs (glass-nonmetals) were used to replace wood flour for producing PMC. Effects of adding content of glass-nonmetals on the properties of PMC were investigated. Therefore, from the use of renewable resources and environmental protection viewpoints, the study to analyze the possibility of substituting wood flour by glass-nonmetals and develop new types of PMC with lower cost and better properties than traditional PMC, can be very useful and practical.

2. Materials and methods

2.1. Crushing and separating of PCBs

In this study, the process technology for recycling PCBs contained two-step crushing and corona electrostatic separating. The waste PCBs were from a local PCBs factory (without electronic elements). The PCBs consisted of a woven fiberglass mat impregnated with epoxy resin. The PCBs were firstly pulverized in a process consisting of a coarse-crushing step and a fine-pulverizing step, using a shearing machine and a hammer grinder together. Then, an electrostatic separator was used to separate the metals from the nonmetals [10]. After being separated, the glass-nonmetals were screened by a vibrating screen. A stack of five sieves with hole widths from 0.3 to 0.07 mm were selected. Specimens were agitated for 20 min, then the mass of glass-nonmetals collected on each sieve was weighed to calculate the particle size distribution. Glass-nonmetals larger than 0.3 mm were fed back into the fine-pulverizing step for additional size reduction.

2.2. Preparation of PMC with filling of glass-nonmetals

Two kinds of PMC were prepared, one with ordinary raw materials, as a reference PMC (RP), and another PMC with glass-nonmetals (PMCGN). RP was prepared in a formulation used in one of the local industries for moulding insulating electrical apparatus. Phenolic resin was obtained as commercial grade from the Shanghai Twin-tree Plastics Factory. RP was prepared by mixing this resin (38%) with wood flour (20%), talc powder (30.6%), stearic acid (1.6%), urotropin (7%), magnesium oxide (0.6%), lime (0.6%), and nigrosine (1.6%) as coloring matter. Properties of PMC with similar relative density can be comparable. Thus, PMCGN was prepared through adjusting the content of resin and fillers. The glass-nonmetals of PCBs were added to the raw materials mixture at a weight fraction of 10%, 20%, 30%, and 40%, respectively. Some toxic components such as bromide and bisphenol were added to PMCGN. The function of them in PMCGN was in conformity with the function in PCBs. Some toxic components such as brominated flame retardants can reduce fire risk. Then, the environmental risk assessment of toxic components is needed to be further investigated. To ensure the surface smoothness, the size of nonmetals used to study effect of different contents on the properties of PMC was less than 0.15 mm.

The producing process of PMC was shown in Fig. 1. The ingredients were premixed for 30 min in a blender so as to improve the dispersion of the components in the raw materials, and then mixture of the resin, the fillers and other constituents were mixed on a single-shaft, oscillating screw kneader at 95–105 °C. Then the melt was extruded by two roll press, cooled, and grinded to a particle size of approximately 3 mm. Finally, these powders were compression-moulded to testing samples in different moulds according to corresponding standards.

2.3. Measurement of properties

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

The mechanical properties like flexural strength and charpy notched impact strength were tested. Specimen shapes for flexural strength and charpy notched impact strength were 120 mm × 10 mm × 4 mm and 120 mm × 15 mm × 10 mm,

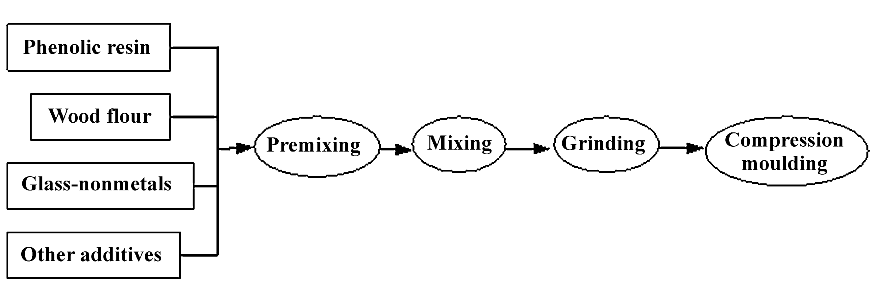

Fig. 1. Flow chart of production of PMC.

respectively. The flexural properties were determined using a Multi-purpose testing machine according to ISO 178:1993. The notched impact test was performed on a Pendulum impact-testing machine for charpy impact-testing according to ISO 179-1982. The average of the five results was reported.

Heat deflection temperature (HDT) was determined as per ISO 75-1:1993 wherein the flexural stress was 1.80 MPa. The specimens (120 mm × 10 mm × 4 mm) were lowed into an oil bath where the temperature was raised at 2 °C per min. The average of the two results was reported.

Dielectric strength was determined in accordance with IEC 60243-1: 1998. The test specimen (100 mm diameter × 3 mm thick disc) was placed between two unequal electrodes in oil at 90 °C using the step-by-step method. Voltage applied across the two unequal electrodes started at 20 kV and increased at 2 kV for 20 s until breakdown. The average of the three results was reported.

Rasching fluidity was characterized by the flowing length of stated quantity of powder in a cylindrical metal mold at a fixed pressure, temperature and time. Moulding powder (7.5 g) was filled into the mold and the temperature was increased to 160 °C. The mixture was cured at the temperature for 3 min under 30 MPa. Then the mold was opened and the length of prismoid rod was measured.

3. Results and discussion

3.1. Size distribution and shapes of glass-nonmetals

Glass-nonmetals can be attained after two-step crushing and separating process as shown in Fig. 2. Particle size distribution of glass-nonmetals was shown in Fig. 3. The particle size of glass-nonmetals smaller than 0.07 mm has the biggest portion, which amounts to 34.6 wt%. The weight percentage of glass-nonmetals with particle size from 0.125 to 0.09 mm was only 8%. The shapes and compositions of glass-nonmetals varied with different particle sizes. Microscopic observation had revealed that glass-nonmetals with particle size from 0.3 to 0.125 mm contained predominantly fiber-particulate bundles, with the majority of fibers being encapsulated in epoxy resin as shown in Fig. 4(a). Single glass fiber and powders were not seen. Glass-nonmetals from 0.125 to 0.07 mm contained both fiber bundles and single fibers as shown in Fig. 4(b). The surfaces of fiber bundles were clean for it had been liberated from epoxy resin. Lengths of fibers were more than 0.5 mm. Glass-nonmetals shorter than 0.07 mm were in the form of single fibers and resin powder as shown in Fig. 4(c). Lengths of short glass fiber were less than 0.5 mm. However, the differences of shapes and compositions among glass-nonmetals with different particle sizes are determined by intrinsic structure of PCBs and the two-step crushing process.

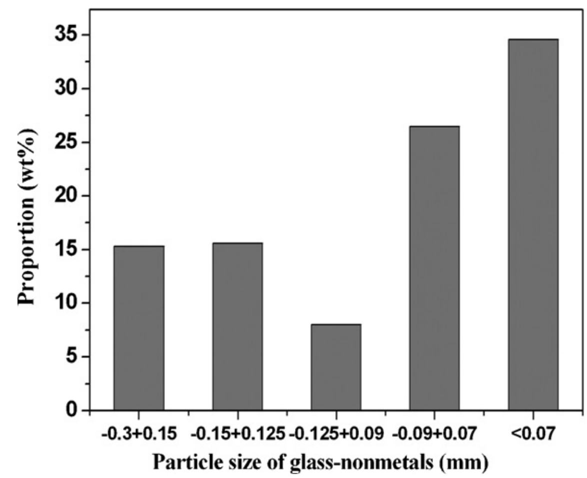

Fig. 3. Particle size distribution of glass-nonmetals.

3.2. Wetting and curing process of PMCGN

Phenolic moulding compound is a composite material with multi-phase materials. Schematic illustration of nonmetals of waste PCBs filling in the PMC was shown in Fig. 5. Preparation of PMC was divided into two stages: the first stage was the wetting process between phenolic resin and fillers. Wetting process was finished in the mixing process. The solid resin melted first under high temperature and pressure, and then the melting resin wetted the fillers through the shear force of screw shaft. Interfacial adhesion between fillers and matrix was determined by the key mixing stage. Wood flour were well coated by the matrix as shown in Fig. 6(a), glass fibers embedded into the matrix though surfaces of glass fiber were coated with little matrix as shown in Fig. 6(b); the second stage was resin curing process. Phenolic moulding powder cured into moulding product in a mould in the pressurized and heated conditions through the action of HMTA. Voids were inevitable in the curing process due to the use of

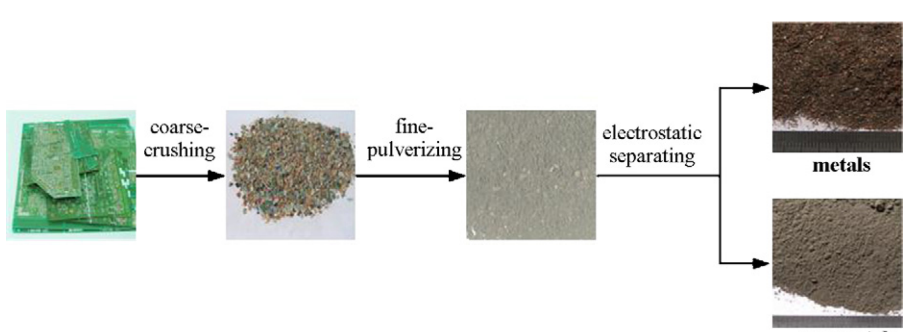

Fig. 2. Schematic illustration of crushing and electrostatic separating of PCBs.

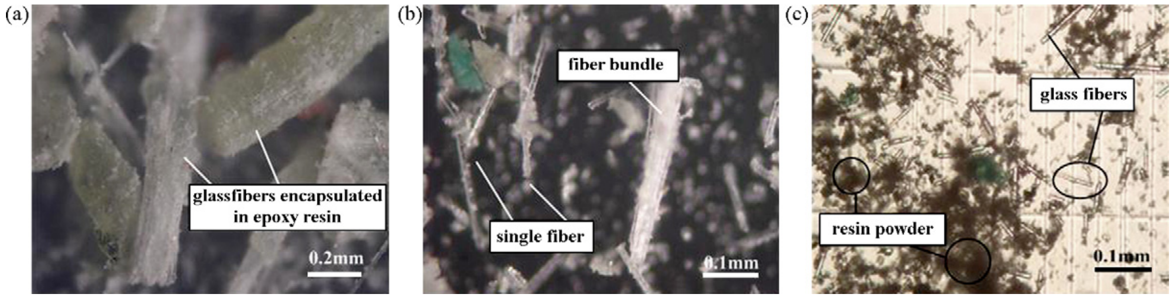

Fig. 4. Micrographs of glass-nonmetals with different particle sizes: (a) 0.3–0.125 mm; (b) 0.125–0.07 mm; (c) <0.07 mm.

Fig. 5. Schematic illustration of glass-nonmetals of waste PCBs filling in the PMC.

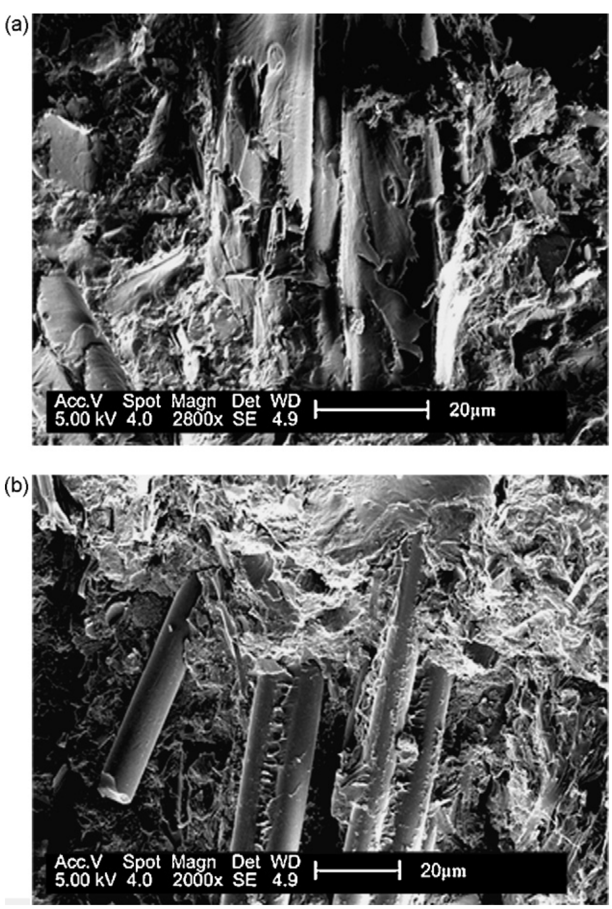

Fig. 6. Adhesive states between different fillers and resin: (a) wood flour; (b) glass fibers.

HMTA, the crosslinking reagent for phenolic resin. Typically between 5 and 15 wt% HMTA was used to produce the nitrogen containing crosslinked network. With this process a significant amount of gas was produced during the crosslinking reaction which contained at least 95% ammonia, and the cured resin might contain up to about 6% bound nitrogen. Therefore, about 75% of the nitrogen from HMTA became chemically bound in the network [11]. The volatiles released during the cure can create voids in the network as shown in Fig. 7.

3.3. Properties of PMC

The national standard of heat-resisting PMC (PF2C3) and properties of PMCGN with different contents of glass-nonmetals were shown in Table 1 [12]. All the properties of PMCGN exceeded the national standards of heat-resisting PMC (PF2C3) as shown in Fig. 8 obviously. The impact strength and

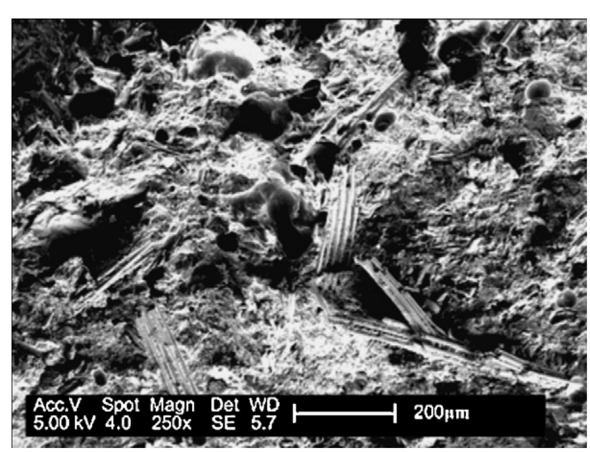

Fig. 7. Voids in PMCGN after curing process.

Table 1
Properties of RP and PMCGN with different contents of glass-nonmetals

Properties	Standard (PF2C3)	RP	PMCGN (PMCGN-*X* containing *X*% of glass-nonmetals)			
			PMCGN-10	PMCGN-20	PMCGN-30	PMCGN-40
Relative density	≤2.0	1.57	1.55	1.57	1.59	1.56
Impact strength (notched) (kJ/m^2)	≥2.0	2.3	2.3	2.3	2.8	2.4
Flexural strength (MPa)	≥60	70	78	67	82	82
HDT (°C)	≥155	175	179	177	171	175
Dielectric strength (90 °C) (MV/m)	≥3.5	3.8	3.8	3.9	3.5	4.8
Rasching fluidity (mm)	–	166	165	146	143	156

flexural strength of PMCGN were ranged at 2.3–2.8 kJ/m^2 and 67–82 MPa, respectively. PMCGN-30 showed the highest impact strength, but showed the lowest HDT and dielectric strength. The PMCGN-40 had the maximum dielectric strength of 4.8 MV/m. The reasons for the variation of properties are complex. The mechanical properties depend on the glass-nonmetals content, the wetting process and the moulding process. Dielectric strength is affected by the presence of conductive impurities that remained from the raw materials and processing of PMC. Performances of PMCGN varied with different contents of glass-nonmetals. It was hard to conclude which content was the best choice. Considering the general properties of PMCGN, the adding content of glass-nonmetals can reach 40 wt% without negatively affecting the properties of PMCGN. When adding content of glass-nonmetals was 40%, PMCGN-40 showed flexural strength of 82 MPa, notched impact strength of 2.4 kJ/m^2, HDT of 175 °C, and dielectric strength of 4.8 MV/m, all of which met the national standard data.

In addition, the rasching fluidity is also an important parameter for PMC, which indicates the ability to fill the mould when moulding powders are manufactured by injection moulding. The rasching fluidity is agreed by the two sides of supply and demand. The value of 100 mm is recommended for industrial injection production. As shown in Table 1, fluidities of PMCGN are good enough for industrial application.

3.4. Morphology after flexural fracture

Glass fibers in glass-nonmetals could be as a reinforcing material in the PMCGN. In general, the performance of rein-

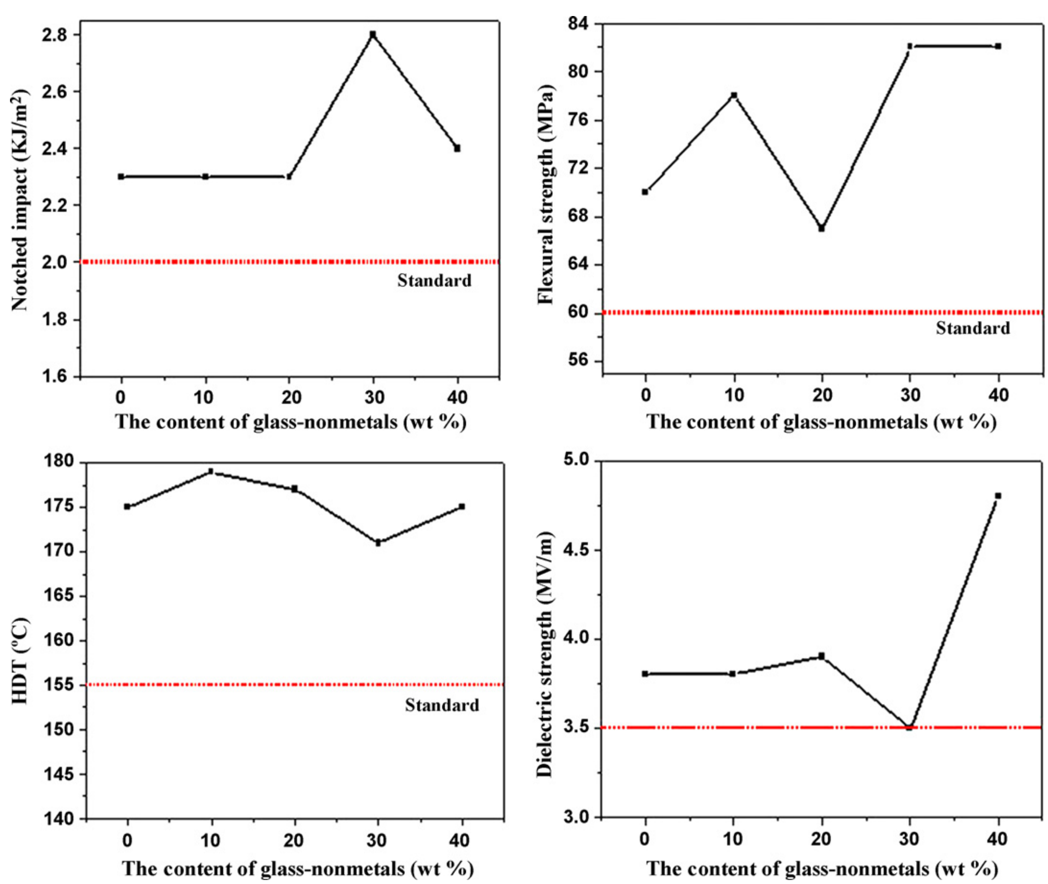

Fig. 8. Comparison of properties between RP and PMCGN.

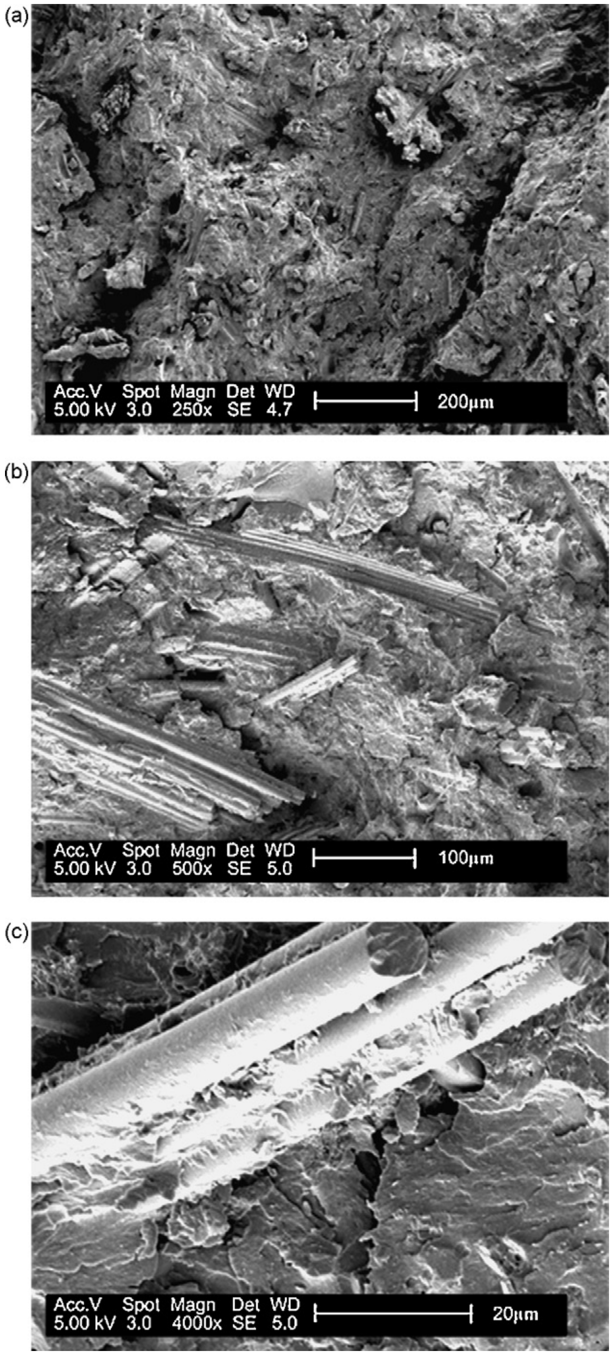

Fig. 9. SEM photographs of RP and PMCGN after flexural fracture: (a) RP; (b) and (c) PMCGN.

forcing strongly depends on the interfacial adhesion between the fillers and matrix, and the stronger is the interfacial adhesion, the more effective becomes the reinforcement. In addition, better wetting between matrix and fillers permits better dispersion of fillers in the matrix [13]. Flexural performance of PMC can be proved by comparing the fractured surface of specimens. The morphology of some flexural fractured samples are presented in Fig. 9, where the SEM microgrames of the PMCGN are compared to those of the RP composites. Fig. 9(a) showed the flexural fractured surface of RP. The surface was smooth and deep gaps were observed. Fig. 9(b) and (c) showed the flexural fractured surface of PMCGN-30. The glass fibers and smooth channels were seen as shown in Fig. 9(b). Glass fibers adhered onto or inserted into the matrix. Phenomenon of fiber pull-out and fiber/matrix interfacial debonding occurred. The adhesion between glass fibers and matrix was seen by a closer observation at a high magnification in Fig. 9(c). There was filler/matrix filled in the gap of glass fibers, which showed very strong interfacial bonding between glass fibers and the phenolic resin. Good adhesion between glass fibers and matrix can strengthen the flexural properties to some extent.

3.5. Economic analysis

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. PCBs waste recycling enterprises have to pay 2000 Yuan/t when nonmetals are sent to the landfill, so it will be happy to convey nonmetals to PMC producer if the price of transportation is less than filling fee. Therefore, the price of nonmetals is zero when accounting the production costs.

China's demand for PMC has grown at a fast pace in the past decade. In the next 5 years, both production and demand will continue to grow. Long-term cooperation between producers of PMC and recycling enterprises of PCBs will attain economic benefits for both sides. Taking a PMC producer with annual output of 10,000 t moulding powders for example, total material costs can be calculated as Eq. (1).

$$C = P_1C_1 + P_2C_2 + \cdots + P_nC_n \qquad (1)$$

where C is the total material costs, P_1, P_2 and P_n the prices of different materials, and C_1, C_2 and C_n are the contents of materials.

The economic value of saved material costs was decided by comparing material costs of PMC with different formulations. Economic benefit can be calculated as Eq. (2).

$$\text{Economic benefit} = C_\mathrm{r} - C_\mathrm{m} \qquad (2)$$

where C_r and C_m are the material cost for RP and material cost for PMCGN.

It is assumed that the adding content of glass-nonmetals is 40 wt%. The contents and prices of RP and PMCGN-40 were shown in Table 2. In addition, the price of wood flour and talc powder are 1000 and 500 Yuan/t according to the market price in China.

Economic benefit of using nonmetals in PMC production was caused by different material prices of fillers (glass-nonmetals of PCBs, wood flour and talc powder). The adding contents of other materials such as resin and additives were same between RP and PMCGN-40. So costs of resin and additives were not taken into account when accounting the economic benefit. Based on above assumption, economic benefit of 2,750,000 Yuan could be attained, which was attractive for producers of PMC.

Nonmetallic material, a byproduct of PCBs recycling industry, can be used to replace wood flour to produce qualified PMC.

Table 2
Comparison of formulations for two kinds of PMC

	Phenolic resin	Wood flour	Glass-nonmetals	Talc powder	Other additives
RP (wt%)	38	20	0	30.6	11.4
PMCGN-40 (wt%)	38	5	40	5.6	11.4
Price (Yuan/t)	–	1000	0	500	–

This would not only greatly decrease the manufacturing cost of PMC but would solve an environmental problem caused by nonmetallic materials of PCB and achieve complete recovery of reusable resources, gaining a win–win result.

4. Conclusions

The glass-nonmetals of waste PCBs with particle size from 0.3 to 0.125 mm contained predominantly fiber-particulate bundles, with the majority of fibers being encapsulated in epoxy resin. Glass-nonmetals from 0.125 to 0.07 mm contained both fiber bundles and single fibers. The surfaces of fiber bundles were clean. Glass-nonmetals with particle size shorter than 0.07 mm were in the form of single fibers and resin powder, with the biggest weight portion (up to 34.6%).

The addition of the glass-nonmetals did not negatively affect the properties of PMCGN. From the environmental viewpoint, 40% was recommended. When the adding content of glass-nonmetals was 40%, PMCGN-40 showed flexural strength of 82 MPa, notched impact strength of 2.4 kJ/m^2, HDT of 175 °C, and dielectric strength of 4.8 MV/m, all of which met the national standard data.

Economic analysis showed that the filling of glass-nonmetals would greatly decrease the manufacturing cost of PMC, which was attractive for producers of PMC.

It is thus concluded that the glass-nonmetals, produced during the recycle of waste PCBs, can be utilized as a filler in PMC production, to attain both environmental and economic benefits.

Acknowledgments

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References

[1] T. Ehner, Integrated recycling of non-ferrous metal at Boliden Ltd., in: Proceedings of the IEEE International Symposium on Electronics & the Environment, 1998, pp. 42–47.
[2] D. Bleiwas, T. Kelly, Obsolete Computers, “Gold Mines,” or High-Tech Trach? Resource Recovery from Recycling [R], United States Geological Survey, 2001, p. 7.
[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] J. Cui, E. Forssberg, Mechanical recycling of waste electric and electronic equipment: a review, J. Hazard. Mater. B99 (2003) 243–263.
[5] S. Yokoyama, M. Iji, Recycling of thermosetting plastics waste from electronic component production processed, in: Proceedings of the 1995 IEEE International Symposium on Electronics and the Environment, 1995, pp. 132–137.
[6] M. Iji, Recycling of epoxy resin compounds for moulding electronic components, J. Mater. Sci. 33 (1998) 45–53.
[7] P. Mou, D. Xiang, X. Pan, L. Wa, J. Gao, G. Duan, New solutions for reusing nonmetals reclaimed from waste printed circuit boards, in: Proceedings of the 2005 IEEE International Symposium on Electronics and the Environment—Conference Record, 2005, pp. 205–209.
[8] A.Y. Kharade, D.D. Kale, Effect of lignin on phenolic novolak resins and moulding powder, Eur. Polym. J. 34 (1998) 201–205.
[9] S. Hattali, A. Benaboura, S. Dumarçay, P. Gérardin, Evaluation of alfa grass Soda Lignin as a filler for novolak molding powder, J. Appl. Polym. Sci. 97 (2005) 1065–1068.
[10] 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 (6) (2007) 1995–2000.
[11] S. Tonogai, K. Hasegawa, H. Kondo, Influence of moisture content on curing behavior of two-step phenolic molding compounds, Polym. Eng. Sci. 20 (1980) 1132–1137.
[12] M. Shen, Y. Wang, Q. Lu, Q. Mao, Phenolic moulding materials [S], National standard of PR China, GB 1404-1995.
[13] L. Lin, M. Yoshioka, Y. Yao, N. Shiraishi, Physical properties of moldings from liquefied wood resins, J. Appl. Polym. Sci. 55 (1995) 1563–1571.