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A Plate Produced by Nonmetallic Materials of Pulverized Waste Printed Circuit Boards

Jie Guo, Bin Cao, Jiuyong Guo, and Zhenming Xu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

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Abstract:

Noble metals and Cu mainly are recycled in treating waste printed circuit boards (PCBs), and a large amount of nonmetallic materials in PCBs are disposed of by combustion or landfill, which may cause secondary pollution and resource-wasting. In this study, a kind of nonmetallic plate (NMP) has been produced by nonmetallic materials of pulverized waste PCBs. The NMP is produced by a self-made hot-press former through adding resin paste as a bonding agent. Furthermore, microshapes of nonmetallic materials and effects of the contents and particle sizes of nonmetallic materials on mechanical properties of the NMP are investigated. It has been found that the nonmetallic materials with particle size from 0.3 to 0.15 mm are in the form of fiber bundles, with the majority of fibers being encapsulated in resin. Nonmetallic materials shorter than 0.07 mm consist of single glass fiber and resin powder. When nonmetallic materials content was 20 wt %, the NMP with particle size of nonmetallic materials less than 0.07 mm, has excellent mechanical properties, which results in a flexural strength of 68.8 MPa and a Charpy impact strength of 6.4 kJ/m². This novel technique offers a possibility for recycling of nonmetallic materials of PCBs and resolving the environmental pollutions during recycling of PCBs.

Introduction

Electronic waste is becoming a global topic as quantities of electrical and electronic equipment become obsolete. Printed circuit boards (PCBs) form about 3% by weight of the total amount of electronic waste ([1](#)). Recycling of PCBs is an important subject not only from the treatment of waste but also from the recovery of valuable materials. Mechanical–physical processes are attracting more attention than hydrometallurgy

and pyrometallurgy (2, 3). The mechanical–physical approach involves disassembling, crushing, and separating processes. The aim of crushing is to strip metal from the base plates of waste PCBs. Then separating processes, such as shape separation, jigging, and density-based separation are used to separate the metals and nonmetallic materials from pulverized PCBs. Metals such as Cu, Al, Sn, are sent to recovery operations (4–6). However, significant quantities of nonmetallic materials in PCBs (up to 70 wt %) present an especially difficult challenge for recycling.

The nonmetallic materials of PCBs mainly consist of thermoset resins and glass fibers. Thermoset resins cannot be remelted or reformed because of their network structure. Incineration is not the best method for treating nonmetallic materials because of inorganic fillers such as glass fiber, which significantly reduces the fuel efficiency. Disposal in a landfill is the main method for treating nonmetallic materials of PCBs, but it may cause secondary pollution and resource-wasting.

In our previous studies, a process consisting of a coarse-grinding step and a fine-pulverizing step was used to strip metal from the base plates of waste PCBs, and corona electrostatic separating was used to separate metals and nonmetallic materials from pulverized waste PCBs (7). Then nonmetallic materials were used to produce phenolic molding compound (8). In order to take full advantage of nonmetallic materials of waste PCBs, a novel technique has been developed to recycle the nonmetallic materials of waste PCBs in this study. The nonmetallic materials were used to produce the nonmetallic plate (NMP) through adding resin paste as a bonding agent by a self-made hot-press former. Furthermore, effects of the contents and particle sizes of nonmetallic materials on mechanical properties of the NMP were investigated. The aim of this research is to develop a new technique for recycling nonmetallic materials of PCBs and resolving the environmental pollution during recycling of PCBs.

Materials and Methods

Materials. The waste PCBs used in the study are a kind of woven glass fabric copper clad laminate without electronic elements, so the metallic portion only consists of Cu. The Cu particles and nonmetallic materials after two-step crushing and electrostatic separating were shown in Figure 1. Then, nonmetallic materials were screened and ground into four size ranges: 0.3–0.15, 0.15–0.09, 0.09–0.07, and < 0.07 mm. Four size ranges of nonmetallic materials were preconditioned by acids. Then, the analysis for residual Cu content was performed by volumetric analysis.

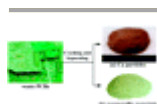


Figure 1. Cu particles (a) and nonmetallic materials (b) of pulverized waste PCBs.

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Preparation of the NMP. Table 1 shows the raw materials of the NMP. The content of nonmetallic materials of waste PCBs and CaCO₃ was kept at a constant value of 64 wt %. The nonmetallic materials were added to the raw materials mixture at weight

fractions of 0, 10, 20, 30, and 40%. Unsaturated polyester (UP) was used as a bonding agent due to its low viscosity, fast cure, excellent chemical resistance, and low cost (9). When UP was used, other additives were needed to complete the curing process of UP. Polystyrene was added as the low profile additive to eliminate the polymerization shrinkage of UP during molding and tert-butyl perbenzoate (TBPB) was added as initiators. The glass fibers used were 25 mm length.

The producing process of the NMP was shown in Figure 2. Mixture of the nonmetallic materials and CaCO_3 were premixed in a double Z-kneader. A solution composed of UP, polystyrene, TBPB, zinc stearate and pigment was stirred for 10 min with a high shear mixer. Then, the resin paste was added to the double Z-kneader. After 15 min of kneading, the glass fibers were added to the kneader. After the nonmetallic materials, CaCO_3 and glass fibers were saturated with resin, the resulting compound was called “nonmetallic dough”. Finally, the nonmetallic dough was hot-pressed into the NMP using a self-made hot-press former as shown in Figure 3. The mold was a circle with diameter of 200 mm. The initial nonmetallic dough was placed to cover 70 wt % of the mold surface to make a final plate with a thickness of 4 mm. The surface temperatures of the top and bottom molds were, respectively, 150 ± 1 °C and 145 ± 1 °C. The processing time was 5 min and the hydraulic pressure was 6 MPa.



Figure 2. Flowchart of preparation of the NMP.

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Figure 3. (a) Hot-press former and (b) the principle of the mold.

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Properties Test of the NMP. The mechanical properties of the NMP such as flexural strength, Charpy impact strength, and Rockwell hardness were tested. Flexural strength is maximum bending stress developed in a specimen just before it cracks or breaks in a flexure test. Charpy impact strength is defined as the amount of energy absorbed in fracturing a specimen at high velocity and is expressed as kilojoule per square meter. The NMP was cut into normalized samples for mechanical testing. Specimen shape for flexural strength and charpy impact strength was $80 \times 10 \times 4$ mm. The resultant five test results were averaged to determine measures of the impact and flexural strengths. Rockwell hardness testing is a method for determining the material's resistance to deformation at a prescribed load. A Rockwell hardness number is calculated from the depth of permanent deformation of the sample after application and removal of the test load. In the present experiment, Rockwell hardness was determined in accordance with ISO 2039/2 using a ball indenter.

Field emission scanning electron microscopy, FEI SIRION 200, was used to analyze the dispersion of fillers into the resin matrix using fractured surfaces of samples. Prior

to the analysis, the fractured surfaces of the specimens were sputter coated with a thin layer of gold. Olympus BX-51 was used to analyze the microshapes and particle sizes of nonmetallic materials.

Results and Discussion

Nonmetallic Materials. The particle size distribution of nonmetallic materials and residual Cu contents are shown in Table 2. Microscopic observation revealed that nonmetallic materials with particle size from 0.3 to 0.09 mm contained predominantly sheet nonmetallic materials, with the majority of fibers being encapsulated in resin as shown in Figure 4a and b. The nonmetallic materials from 0.09 to 0.07 mm consisted of fiber bundles and resin sheet as shown in Figure 4c. The surfaces of fiber bundles were clean as it had been liberated from epoxy resin. Nonmetallic materials shorter than 0.07 mm consisted of single fiber resin powder as shown in Figure 4d. A small quantity of Cu particles (1.76 vol %) existed. Lengths of short glass fiber were less than 0.2 mm. However, the differences of shapes and compositions among nonmetallic materials with different particle sizes are determined by intrinsic structure of PCBs and the two-step crushing process.



Figure 4. Micrographs of nonmetallic materials with different particle sizes: (a) 0.3–0.15 mm; (b) 0.15–0.09 mm; (c) 0.09–0.7 mm; (d) <0.07 mm.

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Production of the NMP. The NMP is a composite material with multiphase materials. UP is capable of producing very strong bonds with other materials though it is inherently weak material. Property enhancement is usually achieved by fiber reinforcement or the addition of particulate fillers (9). A schematic illustration of production of NMP was shown in Figure 5. It can be seen that the preparation of NMP was divided into two stages: the first stage was the preparation of nonmetallic dough. Nonmetallic dough was produced in the double Z-kneader. Different components such as nonmetallic materials, glass fibers, and CaCO₃ can be well coated with liquid resin paste through the shear force of Z-kneader. The resulting compound of nonmetallic dough was in a doughy form that could be separated into discrete quantities; the second stage was molding process of the NMP. Nonmetallic dough was molded into the NMP in the pressurized and heated conditions through the cross-linking of unpolymerized resin with various additives. UP consists of polar unsaturated oligomers and styrene monomer. At the initial stage of compression molding, TBPB decomposed and generated free radicals to initiate the reaction at elevated temperature. Such free radicals were generally very unstable and reacted readily to open the C=C double bonds of unsaturated oligomers and styrene monomer. The cross-linking process is very complex because of possible simultaneous reactions, i.e., styrene-UP copolymerization, styrene homopolymerization, and UP homopolymerization (10). Different authors have studied the cross-linking of the UP resin in presence of styrene monomer (11, 12). As compression continued, the melt dough flowed to the edge of mold and filled the

mold. The chopped glass fibers seemed to align to the flow direction and result in affecting the inner structure of the NMP.



Figure 5. Schematic illustration of production of the NMP.

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Figure 6 shows the inner structures of the NMP with different particle sizes of nonmetallic materials. It indicates that the matrix of the NMP with short nonmetallic materials (Figure 6b) was flatter than that with large nonmetallic materials (Figure 6a). At the same time, the filler agglomeration was seen in Figure 6a, and deep void was generated near the glass fibers. During the mixing, the liquid polyester resin was able to coat the nonmetallic materials and flow into the pores between the fillers. However, the liquid resin just spread out the surfaces of the fillers and did not fill the interstices completely when particle size of nonmetallic materials was too big. After nonmetallic dough was molded, the interstices in the matrix would lead to poor performance of the NMP. Shortest nonmetallic materials (<0.07 mm) and glass fibers were homogeneously dispersed in the matrix as shown in Figure 6b, which showed good adhesion between the fillers and resin. This may be due to that short nonmetallic materials will aid the resin ingress into the voids among the fillers. After curing, the resin is locked into the nonmetallic materials, CaCO₃ and glass fibers, providing a good mechanical bond.



Figure 6. The inner structure between filler and matrix in the NMP with different nonmetallic materials: (a) 40 wt %, 0.3–0.15 mm; (b) 40 wt %, <0.07 mm.

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Mechanical Properties of the NMP

The effects of the content and particle size of nonmetallic materials on flexural strength, impact strength, and Rockwell hardness of the NMP are shown in Figure 7. The variation trends in flexural strength and impact strength for the NMP with nonmetallic material size in 0.15–0.09 mm, 0.09–0.07 mm, and < 0.07 mm are similar. When nonmetallic material content was 20 wt %, the NMP with nonmetallic materials less than 0.07 mm has excellent mechanical properties, with flexural strength of 68.8 MPa and impact strength of 6.4 kJ/m².

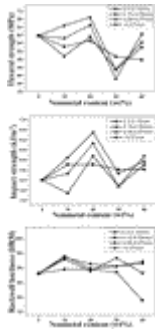


Figure 7. Variation in mechanical properties of different particle size nonmetallic materials with varying content.

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Mechanical properties are intimately related to the inner structure of the NMP. The fine nonmetallic materials with bigger surface areas enhance the adhesion between the filler and resin. The drawbacks generated in the filler/matrix and the presence of voids can affect the performances of the NMP severely. The resin was coated on the surface of large nonmetallic materials and voids existed as schematically illustrated in Figure 8a. When nonmetallic material size decreased, the resin can encapsulate nonmetallic materials entirely and voids were not easily generated as shown in Figure 8b. Therefore, mechanical properties of the NMP with fine nonmetallic materials are better than those of the NMP with large nonmetallic materials.

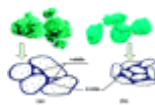


Figure 8. The wetting states of nonmetallic dough: (a) incompact dough with poor wetting and (b) compact dough with well wetting.

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The nonmetallic materials of PCBs and CaCO_3 were kept at 64 wt % during mixing. As the resin was adsorbed by CaCO_3 , the resins wetting nonmetallic materials decrease with the increment of CaCO_3 . When the nonmetallic materials of PCBs is 30 wt % and CaCO_3 is 34 wt %, the resin coating on the surface of nonmetallic materials decreases. As a result, the voids existed during mixing as schematically illustrated in Figure 8a. The voids in the NMP have influence on the flexural strength and impact strength of the NMP. Therefore, the flexural strength and impact strength of the NMP decrease at 30 wt % of nonmetallic material content in Figure 7.

Rockwell hardness is a measure of the nonrecoverable deformation of the material under a compressive stress. Rockwell hardness of the NMP varied from HRM79 to HRM94. Generally, there was no significant effect of nonmetallic material content on Rockwell hardness when particle sizes are 0.15–0.09, 0.09–0.07, and <0.07 mm. However, when nonmetallic material content was up to 40 wt %, the NMP with largest nonmetallic materials (0.3–0.15 mm) showed the lowest Rockwell hardness of HRM79. This is expected because 40 wt % large nonmetallic materials result in a reduction of cross-linking density and thus a decrease in the hardness value (13).

Table 2 shows that the residual Cu contents in the nonmetallic materials from 0.3 to 0.07 mm are less than 0.11 vol %. When the added content of nonmetallic materials is 40 wt %, the residual Cu content in the NMP is only 0.04 vol %. So the effects of residual Cu on the properties of the NMP produced with 0.3–0.07 mm nonmetallic materials are negligible. The residual Cu content in the shortest nonmetallic materials (<0.7 mm) is 1.76 vol %. When the added content of nonmetallic materials is 40 wt %, the residual Cu content in the NMP is 0.70 vol %. Meanwhile, Cu particle is in the form of globular shape as shown in Figure 4d. Therefore, Cu particles with globular shape can enhance the properties of the NMP to some extent (9).

Morphology after Flexural Fracture. It is known that the failure mechanisms of reinforcing materials are dominated by fiber debonding and fiber pull-out process. The particle size of nonmetallic materials seemed to affect the distribution of glass fibers and the adhesion between the fillers and resin. Figure 9a shows the fracture texture of the NMP without nonmetallic materials. The surface was flat and glass fibers were distributed homogeneously. Most part of glass fibers were encapsulated in the matrix, leading to a good mechanical bond. When nonmetallic material content was 20 wt % and particle size was less than 0.07 mm, the SEM photograph after flexural test was shown in Figure 9b. The adhesion between glass fibers and matrix was good. The glass fibers were mainly perpendicular to the fracture surface and this type of fiber reinforcement will lead to improvements in the flexural strength of the NMP. This observation was also in conformity with the result of flexural test. When nonmetallic materials content was 40 wt % and particle size was 0.3–0.15 mm, the deep voids appeared in the matrix of the NMP as shown in Figure 9c. The glass fibers were in the form of fiber bundles, and some matrix/fillers were coated on the surfaces of glass fibers. Bigger nonmetallic materials decrease the lubricating performance of mixture and lead to heterogeneous distribution of glass fibers. The voids in the matrix and the orientation of fiber reinforcement tended to amplify stresses concentration, and resulted in decreasing properties of the NMP.



Figure 9. SEM photographs of the specimens filled with nonmetallic materials after flexural fracture: (a) without nonmetallic materials; (b) 20 wt %, <0.07 mm; (c) 40 wt %, 0.3–0.15 mm.

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In general, the nonmetallic materials of waste PCBs, using resin as a bonding agent, can be used to produce different types of value-added products such as sewer grate, park benches, and fences. The NMP can also be used in place of wooden products since it has better mechanical performance and chemical resistance. So there is no

doubt that the technique has potential in the industry for recycling nonmetallic materials of PCBs.

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* Corresponding author phone: +86 21 54747495; fax: +86 21 54747495; e-mail: zmxu@sjtu.edu.cn.

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