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Manufacturing process of reproduction plate by nonmetallic materials reclaimed from pulverized printed circuit boards

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ABSTRACT

The aim of this study was to present a new method for resource utilization of nonmetallic materials reclaimed from pulverized waste printed circuit boards. A reproduction nonmetallic plate (RNMP) was prepared by adding resin paste, glass fiber and additives into nonmetallic materials using self-made hot-press former. Principle of manufacturing process and effects of mould temperature and moulding time on the mechanical properties of RNMP were studied. The results showed that when moulding pressure was fixed at 6 MPa, the optimum conditions for the RNMP were as follows: 140/135 °C for top/bottom mould temperature, 5 min for moulding time. The maximum content of nonmetallic materials in RNMP was up to 40 wt%. When nonmetallic material content was 20 wt%, the RNMP moulded at optimum conditions had excellent mechanical properties, with impact strength of 5.8 kJ/m^2 and flexural strength of 65.1 MPa.

1. Introduction

Electronic waste is becoming a global topic as quantities of electrical and electronic equipments are 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 process is 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 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 two-step crushing 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 moulding compound [8]. In order to take full advantage of nonmetallic materials of waste PCBs, nonmetallic materials are used to produce the reproduction nonmetallic plate (RNMP). RNMP is a kind of composite plate, consisting of nonmetallic materials of waste PCBs, bonding agent, reinforcing materials and other additives. 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 moulding and *tert*-butyl perbenzoate (TBPB) was added as initiators. The glass fibers and $CaCO_3$ are used as reinforcing materials.

In this study, RNMP is produced by a self-made hot-press former with different moulding parameters. Moulding parameters, such as moulding time, mould temperature and so on, are intimately related to the properties of RNMP. Therefore, a major concern for production of RNMP is how to control the moulding parameters, achieving better performance of RNMP. In order to investigate the effect of moulding parameters on the properties of RNMP, four different top/bottom mould temperatures and two different moulding times were used in the experiments. The aim of this research is to

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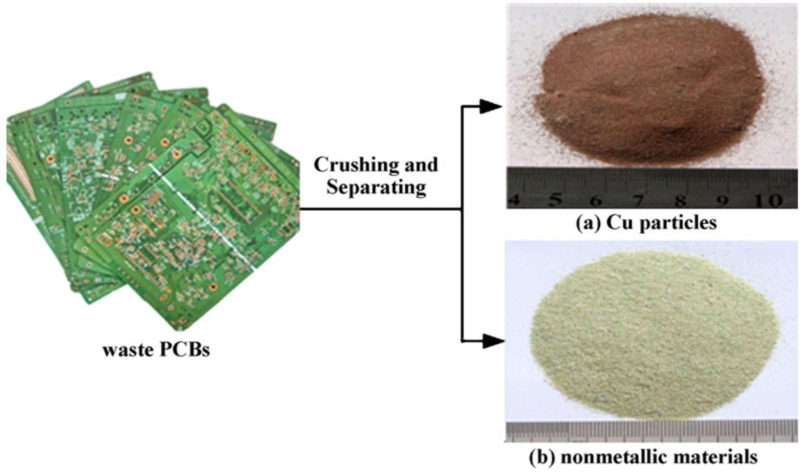


Fig. 1. Cu particles (a) and nonmetallic materials (b) of pulverized waste PCBs.

Table 1
Component of nonmetallic materials

Component	Particle size, mm	Content (wt%)
Nonmetallic materials	0.3–0.15	11.8
	0.15–0.09	22.4
	0.09–0.07	29.7
	<0.07	33.4
Residual Cu	2.7	

Table 2
Raw materials of RNMP

Ingredients	Content (wt%)
Nonmetallic materials	0, 10, 20, 30, 40
$CaCO_3$	64, 54, 44, 34, 24
Unsaturated polyester	18
Polystyrene	6
TBPB	0.2
Glass fiber	10
Zinc stearate	1
Pigment	0.8

develop a new technique for recycling of nonmetallic materials of PCBs and resolving the environmental pollutions during recycling PCBs.

2. Materials and method

2.1. Materials

The waste PCBs used in the study are a kind of woven glass fabric PCBs 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 Fig. 1. In the present experiment, a high-speed shearing machine was used as the crude crusher, and a hammer grinder was employed as the second crusher [7]. PCBs fractions larger than 0.3 mm were fed back into the second crusher for additional size reduction, and nonmetallic materials with particle size less than 0.3 mm were used in the study. The component of nonmetallic materials was shown in Table 1. The analysis for residual Cu content in the nonmetallic materials was pre-conditioned by acids, and then performed by volumetric analysis.

2.2. Preparation of RNMP

Table 2 shows the raw materials of RNMP. The content of nonmetallic materials of waste PCBs and $CaCO_3$ was kept at a constant value of 64 wt%. The producing process of RNMP was shown in Fig. 2. Mixture of the nonmetallic materials and $CaCO_3$ was premixed in a double Z-kneader. The content of nonmetallic materials of waste PCBs and $CaCO_3$ was kept at a constant value of 64 wt%. Nonmetallic materials were added to the raw materials mixture at weight fractions of 0, 10, 20, 30, and 40%. Other components included UP, polystyrene, TBPB, zinc stearate and pigment were 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 RNMP using a self-made hot-press former as shown in Fig. 3. The mould was a circle with diameter of 200 mm. The initial nonmetallic dough was placed to cover 70 wt% of the mould surface to make a final plate with a thickness of 4° mm.

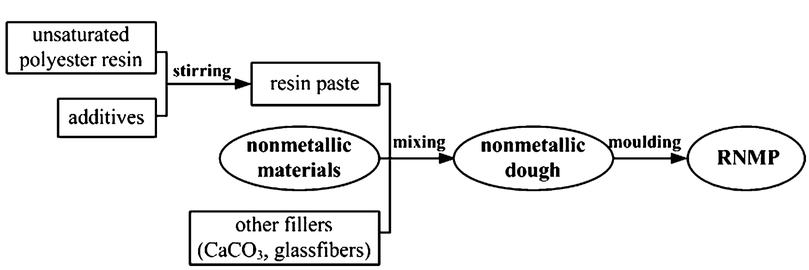


Fig. 2. Flow chart of preparation of RNMP.

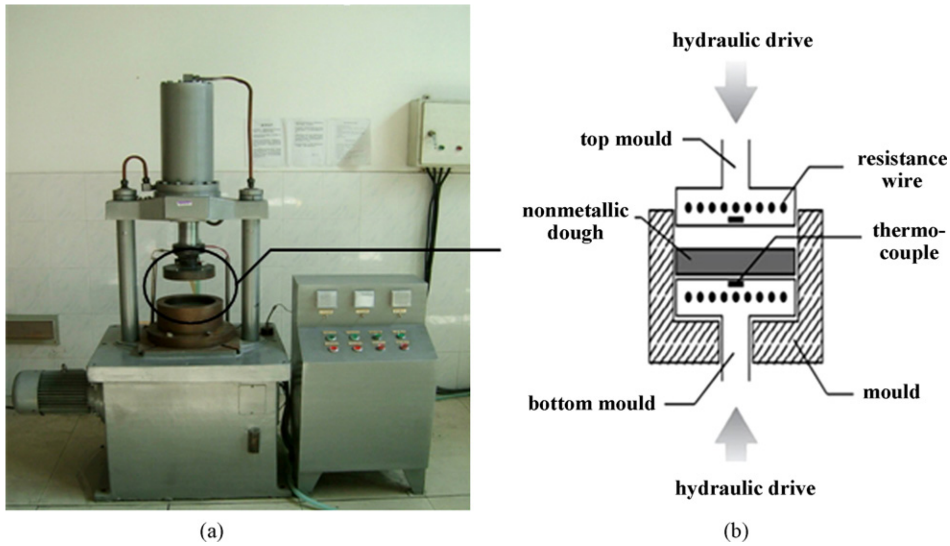


Fig. 3. (a) Hot-press former and (b) the principle of the mould.

Fig. 4. Schematic illustration of production of RNMP.

2.3. Properties test of RNMP

The mechanical properties of the RNMP such as flexural strength, flexural modulus and charpy impact strength 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 RNMP was cut into normalized samples for mechanical testing. Specimen shape for flexural strength and charpy impact strength was 80 mm × 10 mm × 4 mm. The resultant five test results were averaged to determine measures of the impact and flexural strengths.

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

3. Results and discussion

RNMP is a composite material with multi-phase materials. Schematic illustration of nonmetallic materials filling in the RNMP is shown in Fig. 4. The main process for producing RNMP includes wetting process and curing process.

3.1. Wetting process of RNMP

Preparation of nonmetallic dough included two steps: the first step was stirring of resin paste. The resin and additives were stirred by the high-speed mixing. The aim of stirring is to disperse the components of resin paste. The second step was mixing of resin paste, nonmetallic materials and glass fibers. The mixing process is the key process for the preparation of nonmetallic dough. Bonding of different components in the raw materials was fulfilled through the action of wetting between a liquid and a solid surface. The amount of wetting depends on the energies of the interfaces and the degree of wetting can be described by the contact angle. The contact angle is determined by the Young equation [10]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (1)$$

where γ_{SV}, γ_{SL}, γ_{LV}, and θ are the solid–vapour interfacial energy, solid–liquid interfacial energy, liquid–vapour interfacial energy and contact angle, respectively. The equation (1) can be also

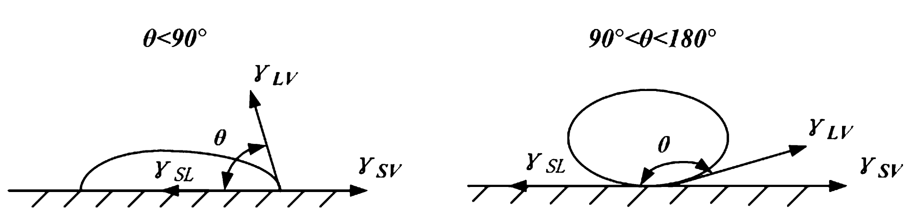


Fig. 5. Wetting of different droplets: (a) shows well wetting (a small contact angle) and (b) shows poor wetting (a large contact angle).

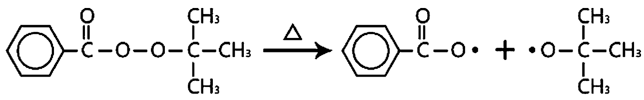


Fig. 6. Decomposition of TBPB.

described as follows:

$$\cos\,\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

When $0 < (\gamma_{SV} - \gamma_{SL}) < \gamma_{LV}$, thus $0 < \cos\theta < 1$, $0 < \theta < 90^\circ$, the solid surface is wettable and there is partial wetting as shown in Fig. 5(a); when $\gamma_{SV} - \gamma_{SL} = \gamma_{LV}$, thus $\cos\theta = 1$, $\theta = 0$, the liquid wets the solid surface completely; When $\gamma_{SV} < \gamma_{SL}$, thus $\cos\theta < 0$, $\theta > 90^\circ$, the solid surface is not-wettable as shown in

Fig. 5(b); when $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$, the wetting equilibrium is not attained and the wetting process is proceeding.

The liquid resin paste wetted the nonmetallic materials, $CaCO_3$ and glass fibers through the shear force of the double Z-kneader. Resin powders in the nonmetallic materials possessed better compatibility with resin paste compared with $CaCO_3$ and glass fibers. It is predicted that the contact angle between resin powders and resin paste will be less than 90°, and the resin paste will spread to cover most surface of resin powders. However, the exact value of contact angle cannot be measured due to technical problem. In addition, wetting performance is also related to other effects, including capillary action. Interstices among different components form microporosity. Liquid resin floats to maximize the contact surface area of solid components by action of surface tension.

3.2. *Curing process of RNMP*

After nonmetallic dough was prepared through the mixing of double Z-kneader, curing process of the RNMP only occurred under high temperature and pressure. Mould process was performed by the hot-press former through the action of resin and additives. At the initial stage of compression moulding, nonmetallic dough was heated by contact with the hot mould, and TBPB decomposed and generated free radicals to initiate the reaction at elevated temperature (Fig. 6). Such free radicals were generally very unstable and reacted readily to open the C═C double bonds of unsaturated oligomers and styrene monomer. Crosslinking occurs when the crosslinking monomer of styrene forms a bridge between two polymer chains by connecting them at C═C double bonds. It mainly contains two types of reaction: styrene homopolymerization (Fig. 7) and styrene-UP copolymerization (Fig. 8) [11–14]. After the curing process was launched by decomposing of TBPB, an increase of the resin temperature caused by the reaction exotherm may occur, which accelerated the curing reaction of UP resins. After the curing process fulfilled, the resin formed three-dimensional networks. The molecular weights of polystyrene and polyester could reach to 1000–3000 and 8000–14000, respectively [15]. Meanwhile, polystyrene and polyester forms long intertwined chains. Nonmetallic materials, $CaCO_3$ and glass fibers were inserted among the resin matrix (Fig. 9), providing a good mechanical bond.

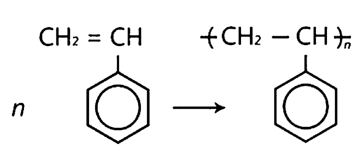


Fig. 7. Styrene homopolymerization.

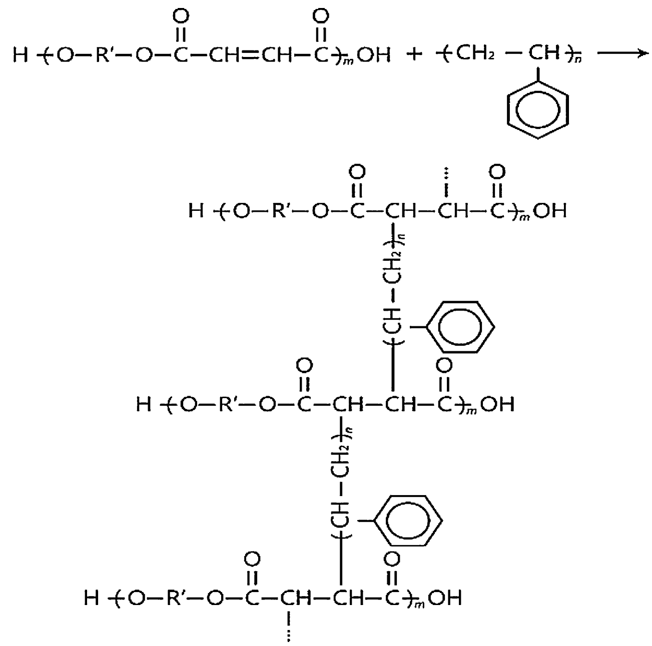


Fig. 8. Styrene-UP copolymerization.

In addition, component of nonmetallic materials was shown in Table 1. The residual copper weight percent in the nonmetallic materials was 2.7%, with a lower volume percent of 0.69%. When the added content of nonmetallic materials is 40 wt%, the residual Cu content in the RNMP is only 0.28 vol%. So the effects of residual Cu on the curing and moulding process were negligible.

3.3. *Controlling of moulding parameters*

Crosslinking transforms the dimensional molecular chains of a monomer into the three-dimensional molecular structures of a polymer. Time and heat are required when UP polymerized. The degree of crosslinking and properties of RNMP are related to the moulding parameters, such as mould temperature, moulding time and moulding pressure. In the study, the moulding pressure of the hot-former was fixed at 6 MPa, so two of the controllable parameters were mould temperature and moulding time.

3.3.1. *Effects of top/bottom mould temperatures on the properties of RNMP*

When the added content of nonmetallic materials is fixed at 20 wt% and the moulding time is 5 min, the effects of mould temperature on properties of RNMP are shown in Fig. 10. Comparing

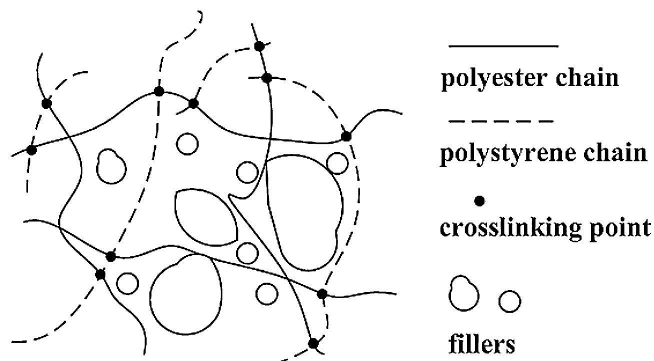


Fig. 9. Sketch of crosslinking structure of RNMP after curing.

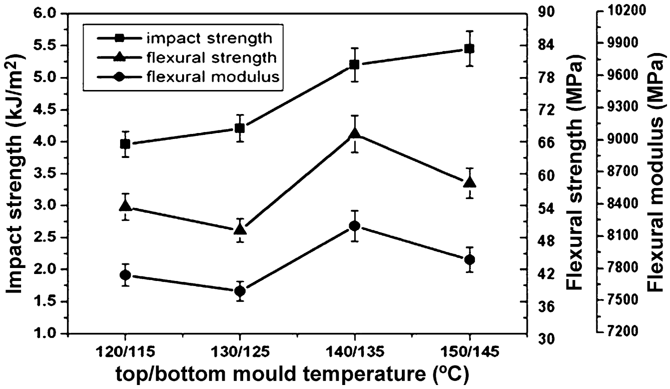


Fig. 10. Effects of top/bottom mould temperature on the properties of RNMP.

the results of RNMP cured at different mould temperature, it is observed that the impact strength increased as the increase of the mould temperature. Probably, at higher temperature the crosslinking reaction was more extensive and the inner part of the RNMP became harder and tough. For the moulding composites, when the top/bottom temperature is 140/135 °C, a sharp increase in impact strength and flexural strength is observed. The flexural strength and flexural modulus were the highest compared with other mould temperature.

Generally, if mould temperature was too low, the degree of crosslinking is likely to be lower than desired, leading to poor mechanical and physical properties. On the other hand, if mould temperature is too high, crosslinking may proceed so quickly that the nonmetallic dough did not fill the mould completely, making a drawback present in the RNMP as shown in Fig. 11. In addition, when the mould temperature was up to about 150 °C, the surface quality of RNMP decreased as some burn marks appeared. Therefore, suitable mould temperature for top/bottom mould is 140/135 °C.

3.3.2. Effects of moulding times on the properties of RNMP

Figs. 12–14 illustrate the relationship between the properties of RNMP at two different moulding times. The mechanical properties of RNMP are related to the moulding time and the amount of nonmetallic materials. It is noticeable that property values of RNMP moulded for 5 min are generally higher than those of RNMP moulded for 3 min. In other words, a length-curing process is often reach high conversion for better mechanical strength. When nonmetallic material content was 20 wt%, the RNMP moulded for 5 min has excellent mechanical properties, with impact strength of 5.8 kJ/m^2 and flexural strength of 65.1 MPa.

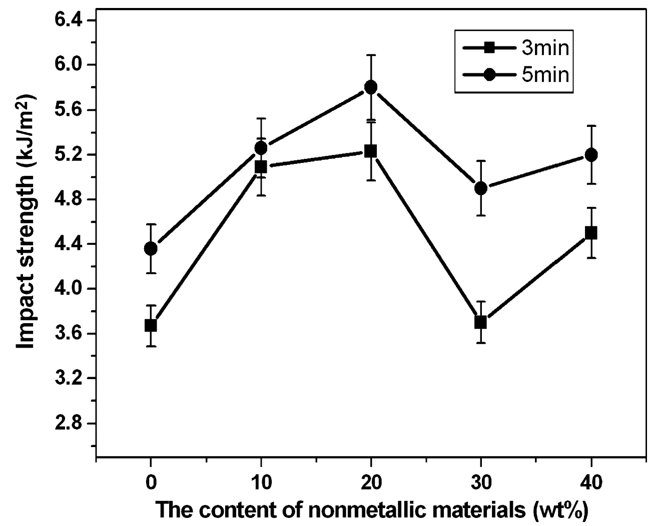


Fig. 12. Impact strength of RNMP versus nonmetallic content and moulding time.

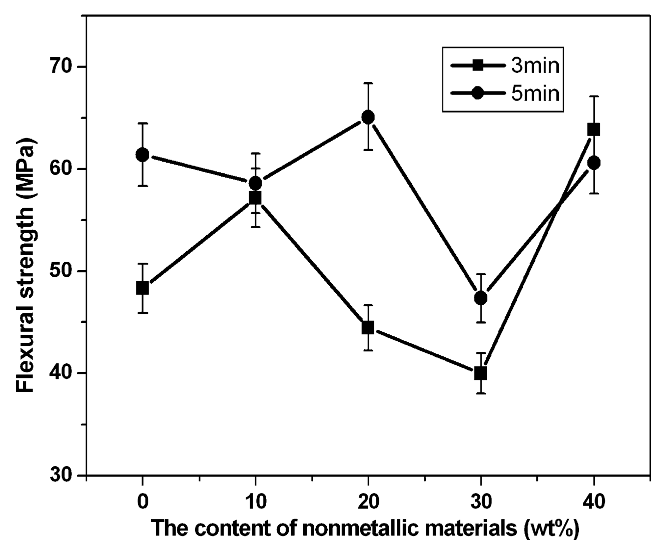


Fig. 13. Flexural strength of RNMP versus nonmetallic content and moulding time.

In addition, the variation trends in impact strength and flexural strength of RNMP with different moulding time are similar. The impact strength and flexural strength of RNMP are determined by the interfacial adhesion between the resin and fillers. Better

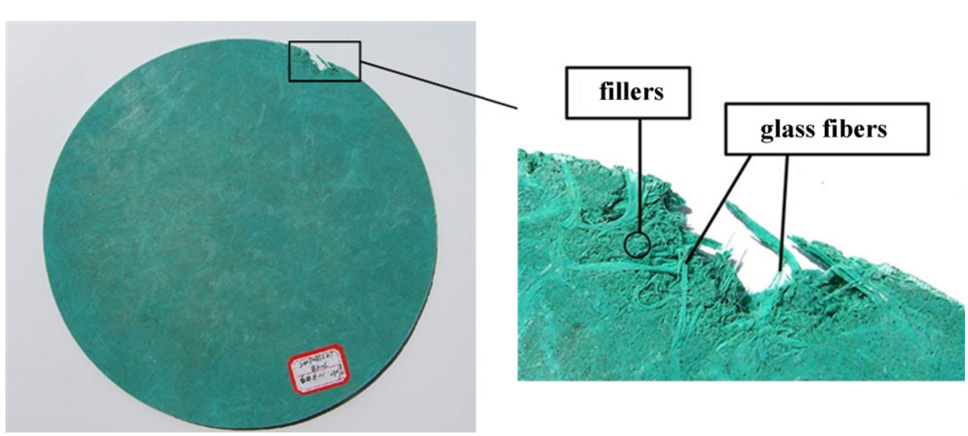


Fig. 11. Drawback in the RNMP.

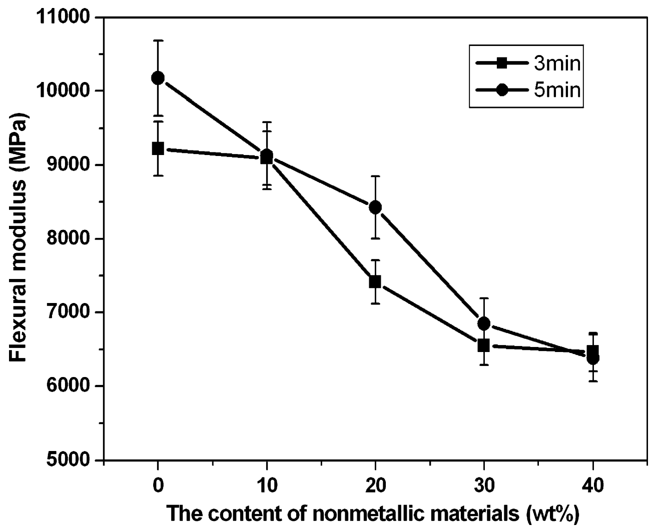


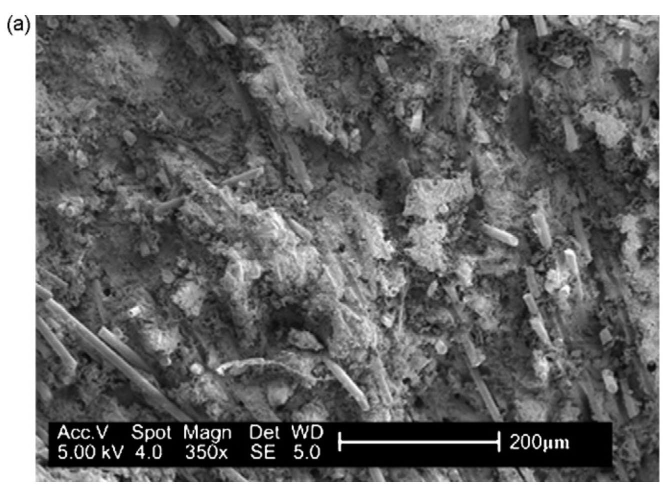
Fig. 14. Flexural modulus of RNMP versus nonmetallic content and moulding time.

adhesion inside the matrix leads to better performance of RNMP. Flexural performance of RNMP can be demonstrated by the SEM photographs. When nonmetallic materials content was 20 wt% and moulding time was 5 min, the flexural fractured surface was flat and compact as shown in Fig. 15(a), which showed strong interfacial bonding between resin and fillers. When the adding content of nonmetallic materials was 30 wt% and moulding time was 5 min, the RNMP showed the lowest performance. It can be attributed to a lack of sufficient particle bonding as shown in Fig. 15(b). Deep voids appeared in the matrix of RNMP, showing poor adhesion in the matrix.

Modulus is one of the basic properties of composites and is related to the stiffness of RNMP. Fig. 14 shows that the flexural modulus of RNMP decreased steadily with increasing content of nonmetallic materials. In the experiment, the content of nonmetallic materials of waste PCBs and $CaCO_3$ was kept at a constant value of 64 wt%. In other words, the modulus increased with increasing content of $CaCO_3$. This result is expected because $CaCO_3$ showed better stiffness than nonmetallic materials.

Surface quality of RNMP is also related to the moulding parameters. When the top/bottom temperature was 140/135 °C, and moulding time was 5 min, the RNMP with different contents of nonmetallic materials were shown in Fig. 16. The higher the contents of nonmetallic materials, the worse the surface quality was. When the content was 40%, burn marks were clearly seen on the surface of RNMP, especially in the center location of RNMP. Because nonmetallic materials consisting of resin powder possessed lower heat-resist properties compared to $CaCO_3$. It indicated that the RNMP with 40 wt% nonmetallic materials should be moulded for less time.

The value of metals contained in waste PCBs is economic incentives for the recyclers. Recyclers use different methods to reclaim metals with high purity, which can be sold at a high price. However, nonmetallic materials are generated inevitably. The amount of nonmetallic materials is enormous, but economic value of nonmetallic materials is very low. Recyclers incur additional expenses when handling and disposing of nonmetallic materials. PCBs recyclers have to pay fee when nonmetallic materials are



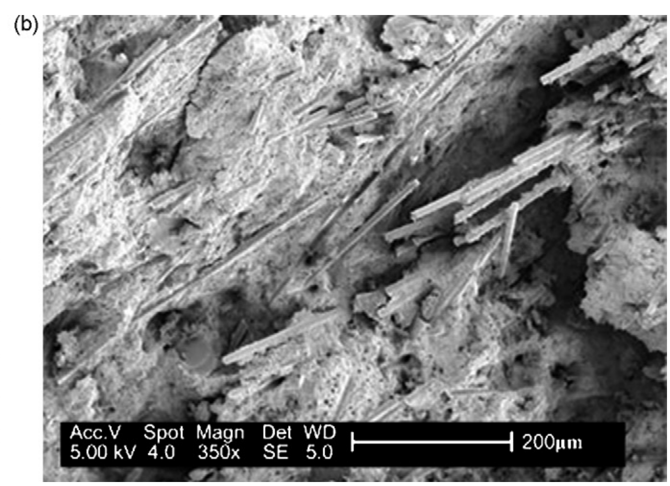


Fig. 15. SEM photographs of specimens filled with nonmetallic materials after flexural fracture: (a) 20 wt% and (b) 30 wt%.

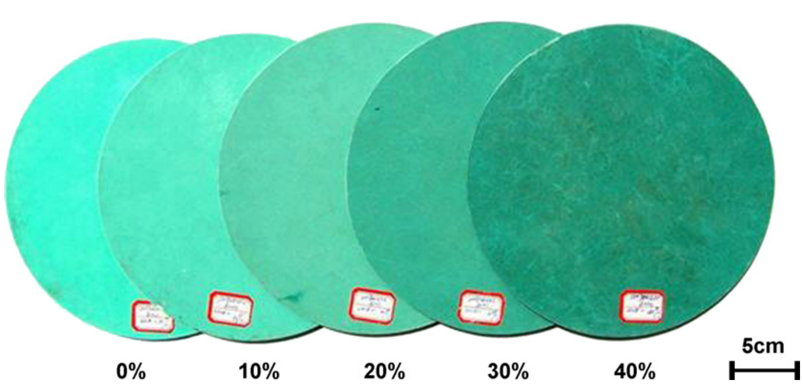


Fig. 16. Surface quality of RNMP with different contents of nonmetallic materials.

sent to the landfill sites or waste incineration plants, reducing the recycler's net revenue. In contrast, using nonmetallic materials to produce RNMP can save large amount of treating fee and generate economic value. Additionally, the Chinese government provides more incentives for resource utilization of waste. PCBs recyclers may gain subsidy to some extent. Therefore, from economic analysis viewpoints, producing RNMP is attractive for the recyclers.

4. Conclusions

Nonmetallic materials reclaimed from waste PCBs were used to produce the RNMP by a self-made hot-press former through adding resin paste as a bonding agent. This technique provided a new method for resource utilization of nonmetallic materials of PCBs.

When moulding pressure was fixed at 6 MPa, the optimum conditions using the hot-press former for the production of the RNMP were as follows: top/bottom mould temperature was 140/135 °C, and moulding time was 5 min.

The maximum content of nonmetallic materials in RNMP was 40 wt%. When nonmetallic material content was 20 wt%, the RNMP moulding for 5 min has excellent mechanical properties, with impact strength of 5.8 kJ/m^2 and flexural strength of 65.1 MPa.

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