Journal of Hazardous Materials 175 (2010) 165–171

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Effects of particle size of fiberglass–resin powder from PCBs on the properties and volatile behavior of phenolic molding compound

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ARTICLE INFO

Article history:
Received 23 June 2009
Received in revised form 1 September 2009
Accepted 26 September 2009
Available online 2 October 2009

Keywords:
Printed circuit board
Phenolic molding compound
Thermogravimetric analysis

ABSTRACT

Fiberglass–resin powder (FR powder), a mixture of resin powder and glass fibers reclaimed from pulverized waste printed circuit boards (PCBs), is used as a partial substitute of wood flour in the production of modified phenolic molding compound (MPMC). The results show that incorporation of FR powder into MPMC as a filler enhances the thermal stability represented by heat deflection temperature (HDT). MPMC with FR powder smaller than 0.07 mm shows better properties, with a flexural strength of 73 MPa, a charpy notched impact strength of 3.0 kJ/m^2, a HDT of 167 °C, and a dielectric strength of 3.7 MV/m, all of which meet the standard data. Thermogravimetric analysis shows that thermal degradation of MPMC mainly includes three steps, and over 55% weight loss of MPMC occurs between temperatures of 370 °C and 575 °C. Phenol is the main volatile compound released from molding powder during the production of molding product. After molding powder cures to molding product, low level of residual phenol is detected. All the results indicate that the MPMC can be used as a new type of molding compound.

1. Introduction

Recycling of waste printed circuit boards (PCBs) is an important subject not only from the treatment of waste but also from the recovery of reusable materials. Metals reclaimed from pulverized PCBs are sent to smelting and refining factories. However, how to deal with the significant quantities of nonmetallic materials from pulverized PCBs is becoming a hot topic. The nonmetallic materials also can be called "fiberglass–resin powder (FR powder)" as they mainly consist of glass fibers and resin powder. At present, disposal in landfill and incineration are the main methods for treating FR powder. However, incineration of FR powder is not economical or suitable because the large percent of inorganic components contained in FR powder leads to a low combustion value and the common incineration process has to be upgraded to inhibit the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) with proper tail gas treatment. Landfill will take up a mass of land, raise the cost of recycling of waste PCBs, and waste valuable resources. To resolve the environmental problem caused by FR powder, FR powder was reused as reinforcing fillers in phenolic molding compound (PMC) in our previous research [1,2].

PMC is produced with phenolic resin, various fillers, solidifiers, and colorants under high temperature and certain pressure. Typically, PMC contains 40–50 wt% resin binder, 40–45 wt% filler, and 5–10 wt% pigment and additives. Wood flour is widely used as an organic filler in molding compounds. The introduction of wood flour has been demonstrated to be extremely effective to improve the brittleness, reduce shrinkage of compounds [3]. However, with the timber resource depletion, it is an urgent assignment to protect the timber resource by finding alternative materials of wood flour. In our previous study, effects of filling content and particle size of nonmetals reclaimed from single-sided phenolic cellulose paper PCBs on the properties of PMC were studied [1]. Multi-size FR powder from epoxide woven glass fabric PCBs smaller than 0.15 mm was used to replace partially wood flour for producing modified PMC (MPMC) [2]. The effects of filling content of multi-size FR powder on the properties of MPMC were studied. Results show that the addition of FR powder did not negatively affect the properties of MPMC. However, effects of particle size of FR powder on the properties of PMC were not investigated. In order to attain better filling function of FR powder in MPMC, FR powder with different particle sizes is obtained through screening. Then effects of different particle sizes of FR powder on the properties of MPMC are investigated in the paper. Based on previous studies, the morphology of FR powder and the curing mechanism of MPMC were further studied in the paper. Furthermore, the thermal degradation and volatile behavior of MPMC have been investigated for application of MPMC.

2. Materials and methods

Fig. 1 shows a flowchart of the FR powder reusing process. The reusing process contained the recycling of FR powder and the preparation of MPMC.

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doi:10.1016/j.jhazmat.2009.09.144

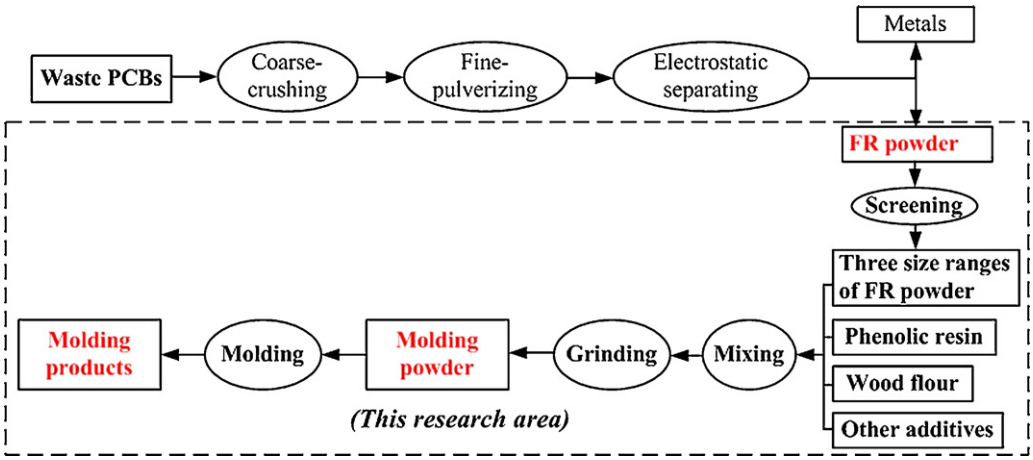

Fig. 1. Flowchart of the FR powder reusing process.

2.1. Recycling of FR powder from waste PCBs

The waste PCBs, a kind of epoxide woven glass fabric PCBs, were supplied from a local PCBs factory (without electronic elements). The FR powder was obtained from two-step crushing and corona electrostatic separating [4]. After the metals and FR powder were separated, FR powder was screened to three size ranges: 0.3–0.15 mm, 0.15–0.07 mm, and <0.07 mm. Define FR powder with different particle sizes as follows: "FR-150-300" means FR powder with particle size from 0.15 mm to 0.3 mm, "FR-70-150" means FR powder from 0.07 mm to 0.15 mm, and "FR-70" means FR powder smaller than 0.07 mm.

2.2. Preparation of MPMC

The PMC composites were divided into two types according to their composition. One was reference PMC (RP) without the filling of FR powder. The other was MPMC filled with 20 wt% FR powder. Novolac resin, a kind of phenolic resins, is used in PMC and MPMC with hexamethylenetetramine (HMTA) as the curing agent. RP was prepared by mixing novolac resin (43%) with wood flour (20%), $CaCO_3$ (25%), stearic acid (1.6%), HMTA (7.6%), magnesium oxide (0.6%), lime (0.6%), and nigrosine (1.6%). Properties of PMC with similar relative density can be comparable. MPMC was prepared by mixing novolac resin (43%) with wood flour (10%), $CaCO_3$ (15%), FR powder (20%), stearic acid (1.6%), HMTA (7.6%), magnesium oxide (0.6%), lime (0.6%), and nigrosine (1.6%). The raw materials (including FR powder after screening, novolac resin, wood flour and other additives) 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 molding powder. Finally, molding powder was compression-molded using the conditions as follows: molding temperature (160 °C), molding pressure (30 MPa), and cure time (30 s/mm thickness).

2.3. Measurement of properties

Mechanical properties (including flexural strength and charpy notched impact strength), heat deflection temperature (HDT), dielectric strength, rasching fluidity were tested as illustrated in previous study [1,2].

Thermogravimetric analysis (TGA) measurements were conducted using a TGA2050 TA Instruments. The thermograms were obtained under nitrogen atmosphere, at a constant heating rate of 20 °C/min, from 30 °C to 800 °C for all the samples. TGA of FR powder, wood flour and MPMC were tested.

A headspace solid-phase microextraction method followed by gas chromatography–mass spectrometry (HS-SPME-GC–MS) analysis method was used for the characterization of volatile aroma compounds released from molding powder and molding product. 4.0 g of sample was weighed into a vial sealed with hole-caps and silicone septa, then the vial was immersed in a water bath at 40 °C. After 20 min of sample conditioning, an activated carbon fiber was exposed to the sample headspace for 30 min and immediately desorbed for 4 min at 200 °C in the gas chromatograph.

3. Results and discussion

3.1. Morphology of FR powder

Fig. 2 shows the morphology of FR powder with different particle sizes. SEM observation revealed that FR-150-300 were in the form of fiber bundles, with the glass fibers remaining encapsulated in epoxy resin as shown in Fig. 2(a) and (b). The fibers were long and combined together through the bonding action of resin. FR-70 was stroked and milled by the high speed hammerheads of hammer grinder for longer time, so there were less resins on the surface of fibers compared with FR-150-300 as shown in Fig. 2(c) and (d). In addition, the length of glass fibers contained in FR powder was less than 1 mm, and resin powders mainly occurred in FR-70. In fact, characteristics of FR powder with different sizes were determined by intrinsic structure of PCBs and the two-step crushing process. Because of hard adhesion between resin and fibers, there were residue resins coating on the surface of glass fibers though base materials of PCBs were fiercely pulverized by crushing machines. However, fiber fragments and resin powders in FR powder could be as reinforcing materials to some extent when FR powder was used to produce MPMC.

3.2. Curing process of MPMC

PMC is a composite material with multi-phase materials. 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; the second stage was novolac resin curing process. Novolac resins cured into three-dimensional structure in a mold in the pressurized and heated conditions with HMTA as the cross-linking agent. A complex series of parallel reactions took place when molding compounds were heated. There were mainly two reaction mech-

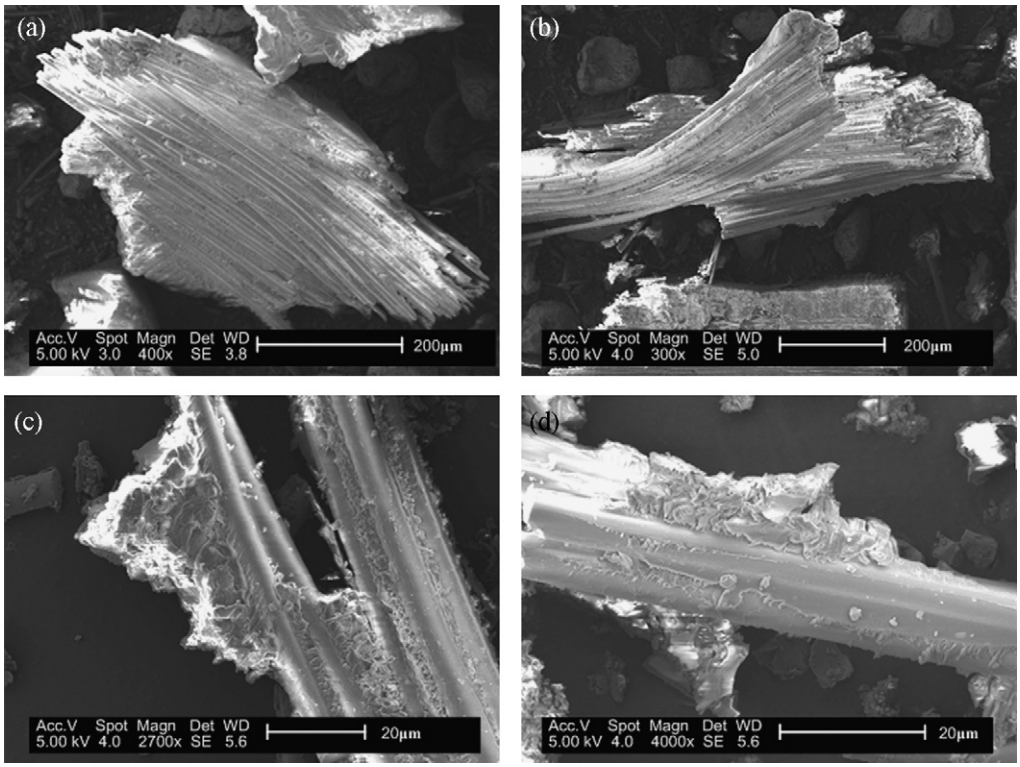

Fig. 2. Morphology of FR powder with different sizes: (a) and (b) FR-150-300; (c) and (d) FR-70.

anisms as shown in Fig. 3: (a) one mechanism assumed that the initial reactions of typical novolacs with HMTA predominantly resulted in the formation of variously substituted benzoxazines and benzylamines as intermediates. On further heating these intermediates reacted further to produce nitrogen-containing structures, and finally novolac resin became complex structure [5]; (b) the other assumed that the cleavage of N–C bond of HMTA resulted in three active sites, then reacted directly with novolac resin. Due to the bond angles and multiple reaction sites involved in the reaction chemistry, the cured novolac resin with HMTA was not a long straight chain but rather a complex three-dimensional polymer network of extreme molecular weight as shown in Fig. 3. During the cross-linking reaction, a significant amount of gas was produced, containing at least 95% ammonia. When curing process was finished, cross-linked network of molding composite contained 66–77% of nitrogen produced from HMTA [4,6]. The volatiles released during the cure can create voids in the network as shown in our previous study [2]. Regarding the filling function of wood flour, hydrophilic of wood flour arises from the hydroxyl groups of lignin and cellulose, which could easily form hydrogen bonds with phenolic hydroxyl groups [7]. So it caused the wood molecular chains to link into the cross-linked novolac chains as shown in Fig. 3. However, effects of FR powder on the curing process are needed to be studied in the future.

3.3. Mechanical properties of MPMC

The versatile PMC (PF2A2) in accordance with ISO 800:1992 and properties of RP and MPMC are shown in Table 1. Values of notched impact strength and dielectric strength of MPMC can meet standard data, but the flexural strength and HDT values of MPMC are found to be much lower than those of glass fibers reinforced PMC (GFR-PMC) produced by other researchers [8]. This is due to the high content and long length of glass fibers in GFR-PMC. The weight percent of glass fibers in GFR-PMC is up to 45%, and the length of glass fibers (1–6 mm) in GFR-PMC is much longer than that of glass fibers (less than 1 mm) in MPMC.

The impact resistance of a composite is determined by the total energy dissipated in the material before final failure occurs. The microfailure mechanisms possibly operating during impact loading include matrix cracking, fiber-matrix debonding, fiber breakage, and fiber pullout. The impact strength of MPMC is found to be higher than RP. In the case of glass fiber reinforced MPMC, frictional losses as fiber is pulled out the matrix are a major contributor to

Table 1
Properties of RP and MPMC with FR powder.

	Standard (PF2A2)	RP	MPMC (particle size of FR powder)			GFR-PMC
			MPMC150-300	MPMC70-150	MPMC-70	
Relative density	≤1.45	1.40	1.42	1.42	1.44	–
Impact strength (notched) (kJ/m^2)	≥1.5	2.1	3.0	2.4	3.0	2.9
Flexural strength (MPa)	≥70	71	68	67	73	124
HDT (°C)	≥140	154	165	165	167	198
Dielectric strength (90 °C) (MV/m)	≥3.5	3.9	4.7	3.5	3.7	–
Rasching fluidity (mm)	–	135	163	155	152	–

MPMC150-300, specimen containing FR-150-300; MPMC70-150, specimen containing FR-70-150; MPMC-70, specimen containing FR-70. GFR-PMC means glass fibers reinforced PMC (8).

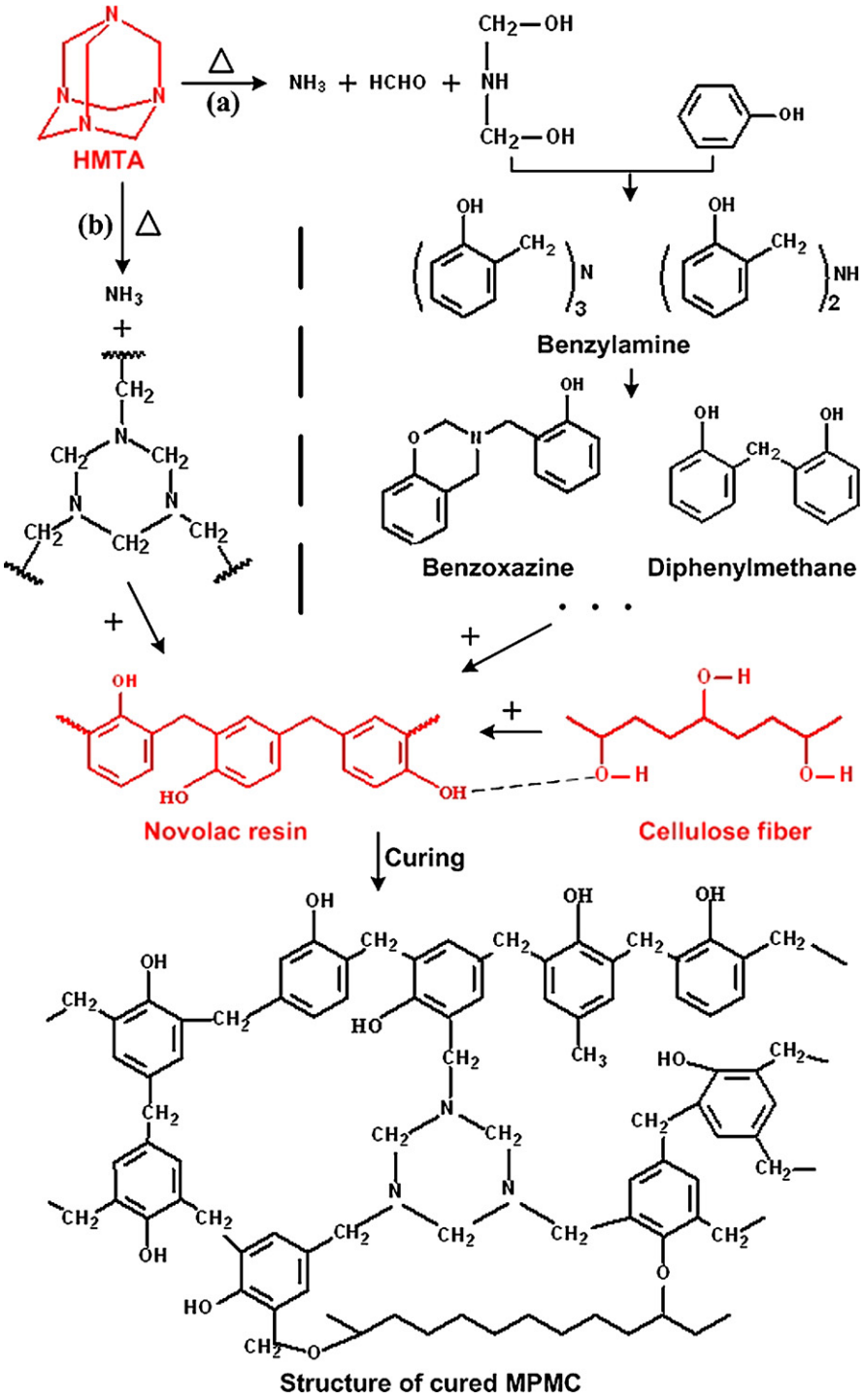

Fig. 3. Schematic illustration of MPMC curing process.

the observed toughness of the composites. This is due to the surface smoothness and regular cross-section of these glass fibers [7]. The impact results reveal that the energy-absorbing capability of MPMC increases by the addition of FR powder.

In flexural testing various mechanism takes place simultaneously. By application of flexural force, the upper and lower surface of the sample under three point bending load is subjected to compression and tension and axisymetric plane is subjected to shear stress. So there are two failure modes in the materials; bending and shear failure. The sample fails when bending or shear stress reaches the corresponding critical value [9]. The flexural strengths of MPMC150-300 and MPMC70-150 were lower than international standard. The unqualified performance of them is due to the poor interfacial adhesion between the glass fibers and resin matrix, which was evident from the SEM study in the forthcoming section. However, MPMC-70 showed best flexural strength of 73 MPa, which was higher than international standard (70 MPa). It was related to the shapes and composition of FR-70. FR-70 mainly were in the form of short glass fibers and resin powder, which improved the dispersion and bonding between FR powder and matrix.

Regarding thermal stability of composites, MPMC had HDTs of 165 °C and 167 °C, where there was an evident increase of 10 °C in

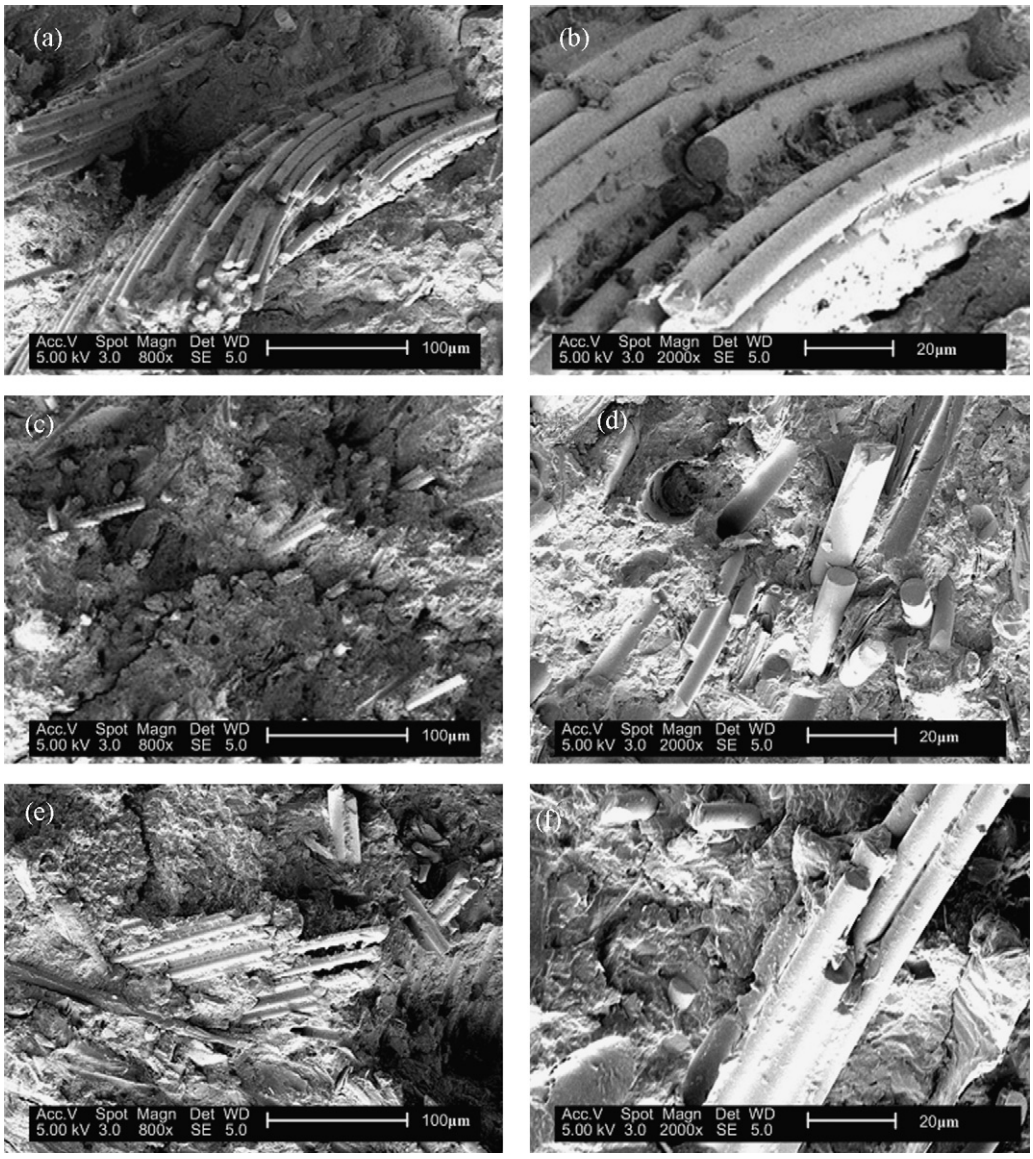

Fig. 4. SEM photographs of MPMC with different sized FR powder after flexural fracture: (a) and (b) MPMC150-300; (c) and (d) MPMC70-150; (e) and (f) MPMC-70.

HDT values compared with RP. Effects of particle size of FR powder on HDTs of MPMC were not evident. The increase in HDT of MPMC is attributed to glass fibers in FR powder. The basis of glass fibers is silica, SiO_2, which has better thermal property than wood flour, which is evident from TGA study in the forthcoming section. Generally, MPMC-70 showed better comprehensive properties, with flexural strength of 73 MPa, notched impact strength of 3.0 kJ/m^2, HDT of 167 °C, and dielectric strength of 3.7 MV/m, all of which met the international standard data.

In addition, the rasching fluidity is also an important parameter for PMC, which indicates the ability to fill the mold when molding powders are manufactured by molding. The value of 100 mm is recommended for industrial production. As shown in Table 1, fluidities of MPMC are good enough for industrial application. The rasching fluidity of MPMC had the trend of slight reducing with decrease of particle size of FR powder.

The performance of reinforcing materials strongly depends on the interfacial adhesion between the fillers and matrix. In general, better wetting between matrix and fillers permits better dispersion of fillers in the matrix [10]. Flexural performance of MPMC can be proved by comparing the fractured surface of specimens. Fig. 4 shows the fractured surface of MPMC with three size ranges of FR

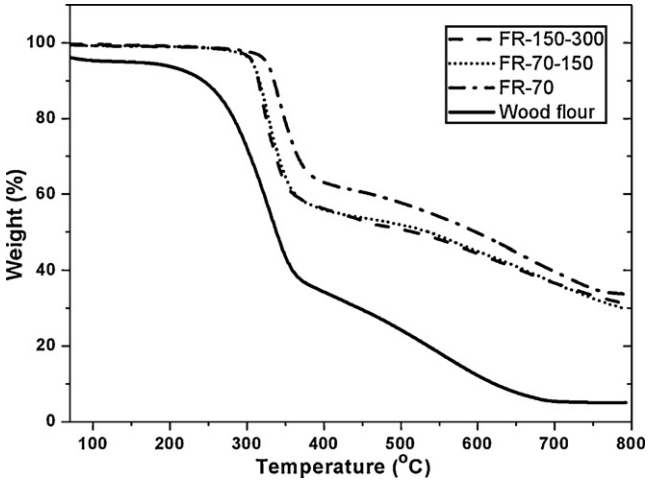

Fig. 5. Thermogram TG of FR powder with different particle sizes and wood flour.

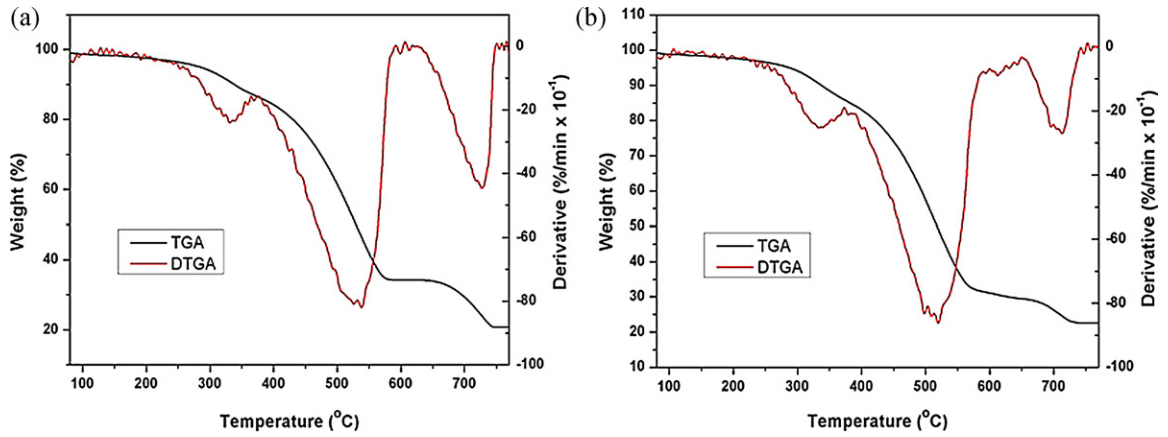

Fig. 6. TGA and DTGA curves: (a) RP; (b) MPMC-70.

powder. Glass fibers in FR-150-300 were in the form of fiber bundles as shown in Fig. 4(a) and (b). Fiber bundles were pulled out and little matrix were coated on the surface of glass fibers. Fig. 4(c) shows that the fiber bundles and single fibers were dispersed in the matrix randomly. There were deep gaps near the fiber bundles. Fig. 4(d) shows that the surface of glass fibers was smooth. Fiber pullout was observed and holes were left during composite fracture. This manifests adhesion between fiber and matrix is weak. Fig. 4(e) shows a less extensive fiber pullout and fewer holes in the matrix. This behavior is due to a better adhesion between FR-70 and phenolic resin, which is attributed to the shapes and composition of FR-70, thus leading to better mechanical adhesion. A closer observation at a high magnification in Fig. 4(f) showed that there were fillers filled among the gaps of single glass fibers after flexural fracture. This indicated that the adhesion of the glass fiber with phenolic matrix of MPMC-70 was better than MPMC150-70.

3.4. Thermal properties of FR powder and MPMC

PMC is widely used in heat-resistant area, so MPMC is of high interest in determining thermal stability. Resin powder in FR powder and wood flour are the main organic fillers in the MPMC, so thermal properties of FR powder and wood flour have influence on thermal degradation of MPMC. Fig. 5 shows a TGA of FR powder with different particle sizes and wood flour. It is obvious that FR powder shows better thermal property than wood flour. The onset temperatures of FR powder and wood flour were about 310 °C and 190 °C, respectively. Thermal properties of FR powder with different sizes varied depending on the degradable components containing in the FR powder. FR powder mainly contains resin powder and glass fibers, but the weight percents of them are different. Resin powder can be burned off and residues are inert glass fibers. When the temperature was above 800 °C, the residues were SiO_2 and carbon black. The char yields of FR powder were in a range of 30% and 35%. Wood flour is a complex and organic polymer composite made up primarily of cellulose, hemicellulose, and lignin. These three hydromxyl-containing polymers began to degrade at 200 °C. In the temperature range of 240–400 °C, major weight loss took place due to the decomposition of cellulose and lignin, and hydrocarbon structure forms through the chain scissions, or depolymerization, and breakdown of C–O and C–C bonds [11]. Above 800 °C, only less than 5% of residues were left.

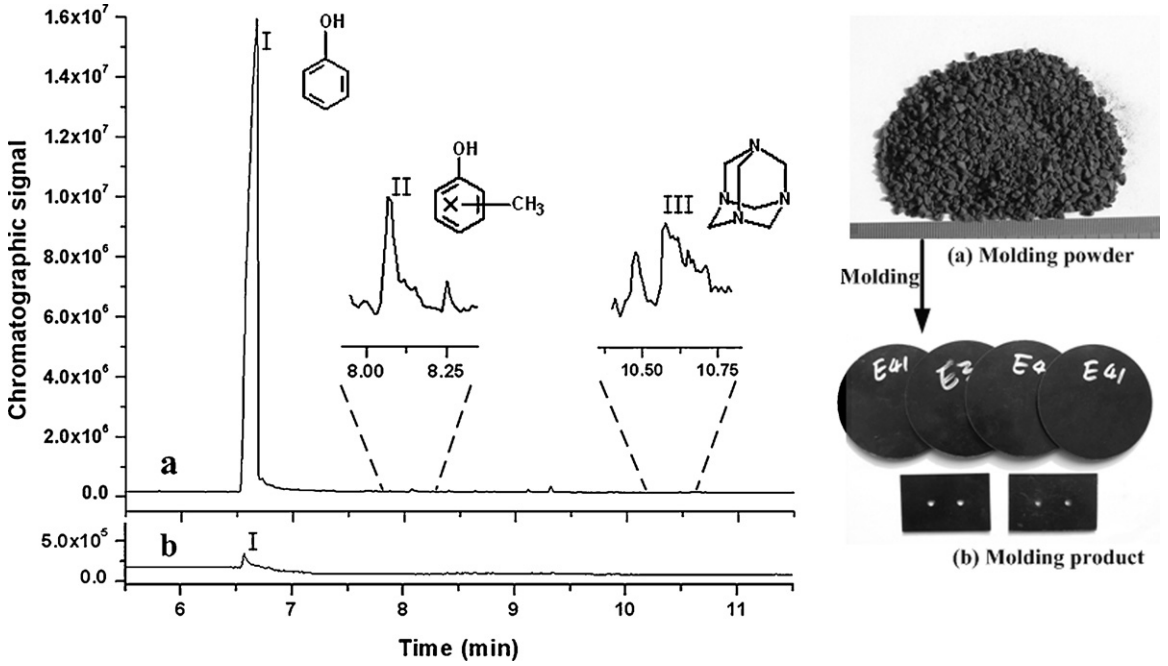

Fig. 7. A HS-SPME-GC–MS ion chromatogram of volatile aroma compounds released from molding powder (a) and molding product (b). Peak identities: (I) phenol, (II) cresol, (III) HMTA.

The TGA curves along with the derivative thermogravimetry analysis (DTGA) curves of RP and MPMC-70 are shown in Fig. 6. The thermal degradation mechanism of RP and MPMC-70 included three steps. The first step was from 200 °C to 370 °C, and it may be due to the decomposition of wood flour. The second step of thermal decomposition within the range of 370–575 °C is the result of the polymer degradation. The polymer materials are mainly from novolac resin and resin powders of FR powder. The methylene bridges decompose into methyl groups then yield both phenol and cresol homolog, and the degradation of phenol group occurs [12]. In this temperature range over 55% sample weight was lost. Weight loss is the result of formation of products such as CO, CO_2, benzaldehyde, phenol, and its polymers, with random chain scission and initial formation of char [13]. Between 575 °C and 660 °C, the sample of RP became thermally stable, and it did not lose weight in this temperature range. However, 4% sample weight loss was observed for MPMC. This result is due to the decomposition of impurity contained in FR-70. From 660 °C to 730 °C, the third decomposition stage was observed. This was mainly due to the decomposition of $CaCO_3$. The weight loss at the third stage coincided with the content of $CaCO_3$. Above 730 °C, char yield of both PMC and MPMC were about 25%, and the residues mainly consisted of oxides (such as SiO_2, CaO, etc.) and carbon black.

3.5. Volatile behavior of producing process

Regarding the environmental and healthy assessment of producing process, HS-SPME-GC–MS methodology was applied to evaluate the production of volatile aroma compounds during the preparation process of PMC. From the chromatographs, the volatile compound present at the highest levels from the molding powder was phenol, and cresol and HMTA were also detected as shown in Fig. 7a. The source of phenol detected from molding powder is phenolic resin as phenol is the monomer or raw material to make phenolic resin. Molding powder is semi-manufactured goods in the production of molding product, so the presence of phenol, cresol and HMTA is reasonable. After molding powder cured to molding product, very low level of residual phenol was detected as shown in Fig. 7b. In most cases, if an analyte peak could be detected, its GC area counts were linear with the concentration range above it [14]. So the relative concentration of volatile phenol can be compared by calculating the peak area. The concentration of phenol extracted from molding product is only 1/160 that of phenol extracted from molding powder. HMTA and cresol were not detected due to the completely curing process of components. However, further work on the quantitative amounts of volatile compounds is needed to be studied.

4. Conclusions

MPMC with FR powder smaller than 0.07 mm shows better properties, with a flexural strength of 73 MPa, a charpy notched impact strength of 3.0 kJ/m^2, a HDT of 167 °C, and a dielectric strength of 3.7 MV/m, all of which meet the standard data.

Thermogravimetric analysis shows that thermal degradation of MPMC mainly includes three steps, and over 55% weight loss of MPMC occurs between temperatures of 370 °C and 575 °C.

Phenol is the main volatile compound released from molding powder during the production of molding product. After molding powder cures to molding product, low level of residual phenol is detected.

Reusing FR powder reclaimed from waste PCBs is a new type of industry as the amount of waste PCBs increases dramatically. The method that FR powder is used in place of wood flour to produce MPMC is a promising choice. Molding powder filled with FR powder can be fabricated into different types of molding products for a variety of applications by compression, transfer, and injection molding processes.

Acknowledgments

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

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