Influence of the Recycled Glass Fibers from Nonmetals of Waste Printed Circuit Boards on Properties and Reinforcing Mechanism of Polypropylene Composites

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ABSTRACT: The feasibility of reusing the recycled glass fibers (RGF) from nonmetals of waste printed circuit boards in polypropylene (PP) composites is studied by mechanical properties, vicat softening temperature and heat distortion temperature. The influence of RGF on reinforcing mechanism of the composites is watched under scanning electron microscopy (SEM) *in situ* tensile test. The results show that the mechanical and thermal properties of the RGF/PP composites can be significantly improved by adding the RGF into PP. *In situ* SEM observation results show that the RGF are the excellent supporting bodies and can effectively lead to mass microcracks. Crack initiation, propagation, and fiber breakage dissipate tremendous energy. Therefore, the mechanical properties are reinforced. All the above results indicate that the reuse of RGF in the PP composites represents a promising way for closing the recycling loop and realizing the high added value utilization. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2914–2920, 2010

Key words: poly(propylene) (PP); recycled glass fibers; composites; mechanical properties; reinforcing mechanism

INTRODUCTION

Recycling of the glass fibers from nonmetals of waste printed circuit boards (PCBs) is of fundamental importance because of environmental, economic, and social factors. In recent years, thousands of millions of tons of nonmetals, an industrial solid-waste byproduct, are generated in the world during the recycling of waste PCBs.[1–6] A huge source of pollution, nonmetals can also be a huge resource, because those materials have abundant valuable glass fibers. In general, nonmetals recycled from waste PCBs contain 50–70 wt % glass fibers. And these glass fibers possess many excellent characteristics, such as high length diameter ratio (L/D ratio), high elastic modulus and low elongation. Recently, in our earlier publications, the valuable glass fibers could be successfully recycled from nonmetals of waste PCBs by a novel fluidized bed process technology.[7]

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Although the valuable glass fibers could be successfully recycled from the nonmetals of waste PCBs, recycling technology that was environmentally and economically viable was critical to realize their application with the aim to close the recycling loop.[8,9] Therefore, it is very important to study the application of the recycled glass fibers (RGF) to close the recycling loop for the RGF from nonmetals of waste PCBs. The RGF from SMC (Sheet molding compound) could be successfully reused in DMC (Dough molding compound) formulations and veil products, in combination with virgin glass fibers without significantly affecting the material properties, in a portion up to 50% w/w.[10] Unfortunately, in other reported cases, 100% reuse of the RGF in new thermoset composites led to mechanical property degradation.[11,12] An alternative route with a lot of promise suggested direct reuse of the RGF as reinforcement on thermoplastic matrices, such as polypropylene (PP) and polyethylene.[13,14] Remarkably, the RGF did not adversely affect the mechanical properties of the new composites.[14] But to our knowledge, there is little published information about application of the RGF from nonmetals of waste PCBs in the PP composites.

Many studies have investigated virgin glass fibers reinforced PP composite.[15–18] Because PP is one of the most important commodity plastics widely used in the packaging, textile, and automobile industries. However, its application as an engineering thermoplastic is somewhat limited because of its poor fracture behavior. In fact if it was reinforced using filler or fiber it could be used instead of other commodity thermoplastic and even engineering thermoplastics.[15–24] While the RGF recycled from nonmetals of waste PCBs still possessed inherent characteristics, such as high length diameter ratio, high elastic modulus, and low elongation.[7] Therefore, reusing of the RGF from nonmetals of waste PCBs as reinforcing fillers in the PP composites could represent a promising way for closing the recycling loop.

In this article, the objective of the research was to reuse the RGF from the nonmetals of waste PCBs in the PP composites, with the aim to close the recycling loop and recycle the resources in a more profitable and environmentally friendly way. The feasibility of reusing the RGF as reinforcing fibers in the PP composites was studied by mechanical properties, vicat softening temperature (VST) and heat distortion temperature (HDT). Meanwhile, the dynamic process of the RGF reinforcing of the PP polymer was watched under scanning electron microscope (SEM) *in situ* tensile test. All the results showed that the reuse of the RGF from the nonmetals of waste PCBs as reinforcing fibers in the PP composites represented a promising way for closing the recycling loop and realizing the high added value utilization.

EXPERIMENTAL

Materials and fabrication procedure for the RGF/PP composites

The RGF from less than 150 meshes nonmetals of waste PCBs using the fluidized bed operating at 400, 500, 600°C by the primary cyclone and 500°C by the secondary cyclone, were selected for making PP composites, respectively. The main components of nonmetals are glass fibers reinforced thermoset resins. When nonmetals were processed in a fluidized bed operating at high temperature air flow, the thermoset resins in the nonmetals were broken down and combusted. Then the glass fibers were recycled by cyclone separator. The detailed recycling process had been reported in a previous publication.[7]

To improve the dispersion of the RGF in PP matrix and the compatibility between the glass fibers and matrix, the RGF were modified with 1.0 wt % content of silane coupling agent γ-Aminopropyltriethoxysilane (KH-550, Nanjing Shuguang Chemical Group, Nanjing, China) through silanization with high speed mixer (SHR-5A, Zhangjiagang Qiangda Plastics Machinery, Suzhou, China) at 1800 rpm. Before the silanization, 40 vol% content of KH-550 was mixed and hydrolyzed in the solvent (ethanol-water, volume ratio 7 : 3) for 30 min at room temperature) (23°C) and 150 rpm in a stirrer. PP powder S1003 (Beijing Yanshan Petrochemical, Beijing, China) was used as the matrix polymer. The PP powders and the modified RGF were dried at 80°C for 2 h, respectively. Then, the RGF and PP powers were stirred and mixed by using high speed mixer. The mixtures were extruded into thread with a screw extruder [TE-35, Coperion Keya (Nanjing) Machinery, Nanjing, China] at 210°C and 220 rpm. The extrudates were pelletized, and molded in an injection machine (CJ108M3V, Chen De Plastics Machinery, Chende, China) into dumbbell-shaped tensile bars and rectangular bars. Flexural test bars and impact test bars were cut from the rectangular bars. A single-edge, 45° V-shaped notch (tip radius = 0.25 mm, depth= 2 mm) was milled in the impact test bar.

Measurements

The tensile and flexural properties of the pure PP and RGF/PP composites were measured using an electronic universal testing machine (DXLL-10000, No.4 Chemical Machinery Plant of Shanghai Chemical Equipment, Shanghai, China) at room temperature (23°C) according to ISO Standards 527–2: 1993 and 178: 1993, respectively. The notched Izod impact strengths were measured using an Izod testing machine (XJ-40A, WuZhongShi Material Tester Limited Company, WuZhong, China) at room temperature (23°C) according to ISO Standard 180: 1993. VST and HDT of the composites were measured with a HDT/Vicat testing instrument (XRW-300M, Chengde Jinjian Testing Instrument, Chengde, China) according to ISO Standards 306: 1994 and 75-1: 2003. The micrographs of the impact fracture surfaces of the composites were observed by the scanning electron microscopy (SEM, 1450, LEO, Oberkochen, Germany). The dynamic fracture process of the RGF/PP composite was observed in the system of *in situ* SEM (S-570, Hitachi, Tokyo, Japan) tensile test when external load was imposed on the composite. All of the specimens were gold-sputtered before SEM test.

RESULTS AND DISCUSSION

Mechanical properties of the RGF/PP composites

To compare the application performance of the RGF recycled at three different temperatures, the 20 wt % content of the RGF were selected and compounded in the PP composites. Figures 1, 2, and 3 show the tensile properties, flexural properties, and notched impact strength of the pure PP and RGF/PP

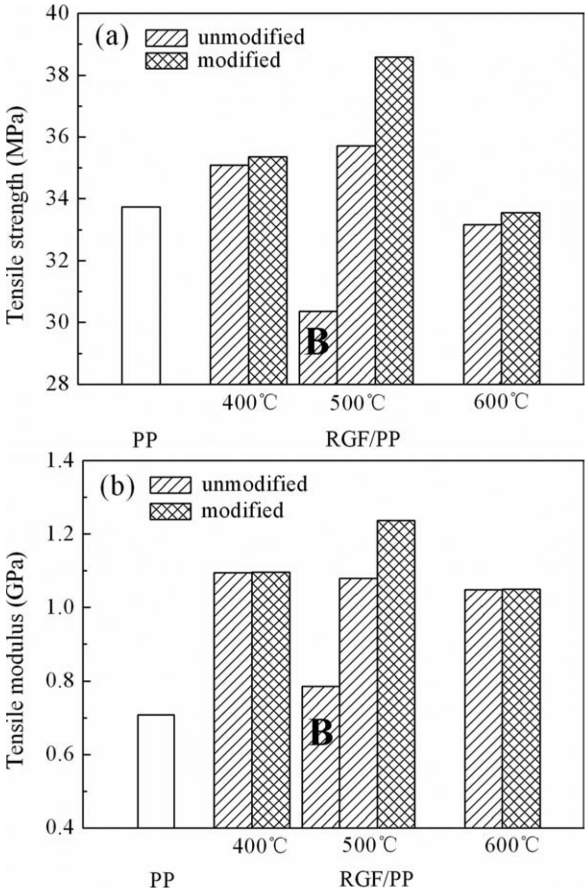

Figure 1 Tensile properties of the pure PP and RGF/PP composites (20 wt %, B: RGF by the secondary cyclone, other RGF by the primary cyclone): (a) tensile strength; (b) tensile modulus.

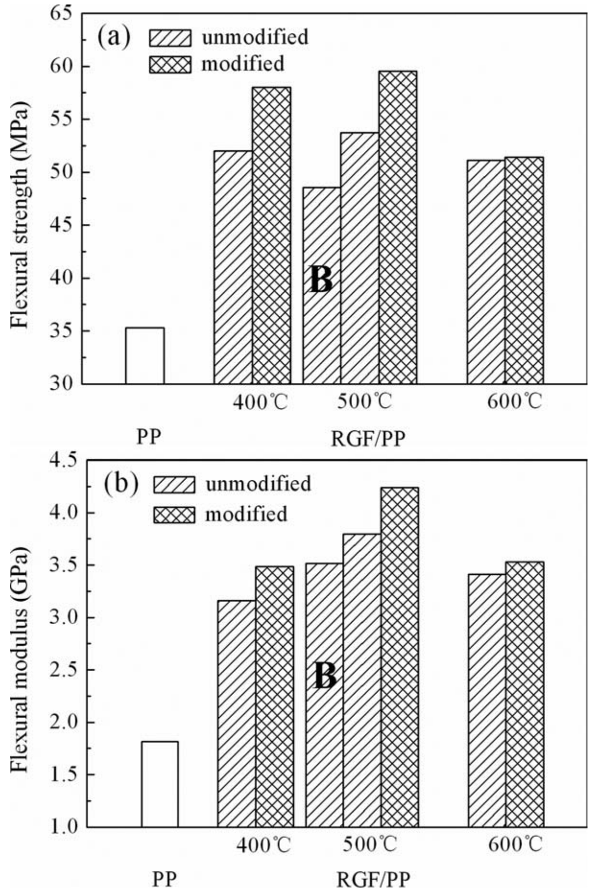

Figure 2 Flexural properties of the pure PP and RGF/PP composites (20 wt %, B: RGF by the secondary cyclone, other RGF by the primary cyclone): (a) flexural strength; (b) flexural modulus.

composites, respectively. The glass fibers were recycled from nonmetals of waste PCBs using the fluidized bed operating at 400, 500, 600°C by the primary cyclone and 500°C by the secondary cyclone. The content of the coupling agent was 1 wt %.

The fluidized bed temperatures could affect the tensile properties of the RGF/PP composites adding the RGF (unmodified) by the primary cyclone as shown in Figure 1. The tensile strength and tensile modulus of the RGF/PP composites by adding the RGF recycled at 400 and 500°C were improved. But the tensile strength the RGF/PP composite by adding the RGF recycled at 600°C was lower than that of the pure PP. That occurred mainly because the heat treatment at 400 and 500°C could not damage the silane coated cloth of the glass fibers, and this was the protective coating of the glass fibers.[7] But the heat treatment at 600°C could damage the protective coating of the glass fibers so that the strength of the glass fibers was severely weakened.[10,25,26] The surface modification of the RGF recycled at 500°C could significantly improve the tensile properties of the RGF/PP composites. But the surface modification of the RGF recycled at 400 and 600°C made no significant difference to the tensile properties of the RGF/PP composites. That occurred mainly due to the fact that the heat treatment at 500°C could effectively remove the thermoset resin in the nonmetals of waste PCBs and maintain

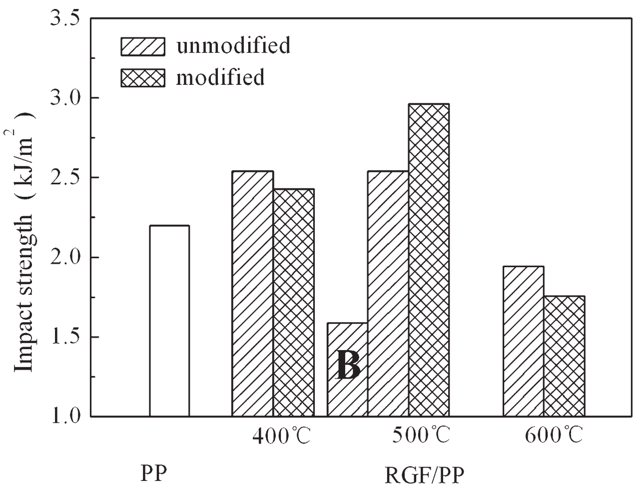

Figure 3 Notched impact strength of the pure PP and RGF/PP composites (20 wt %, B: RGF by the secondary cyclone, other RGF by the primary cyclone).

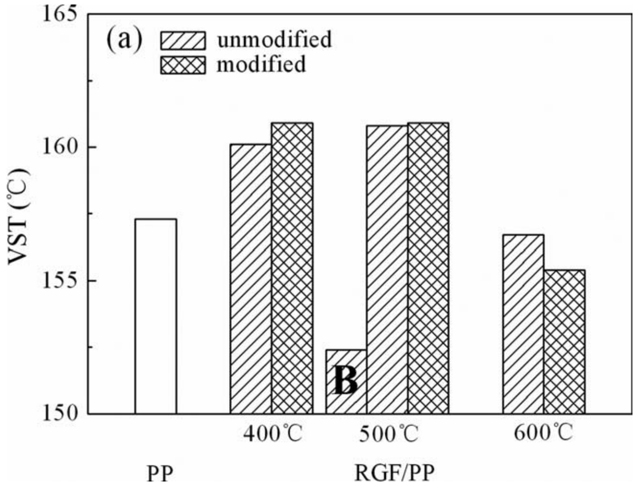

Figure 4 Vicat softening temperature of the pure PP and RGF/PP composites (20 wt %, B: RGF by the secondary cyclone, other RGF by the primary cyclone).

the strength of the glass fibers. Therefore, the surface modification gave an improved fiber to matrix interfacial bond. However, the heat treatment at 400°C could not completely remove the thermoset resin and the heat treatment at 600°C could severely weaken the strength of the RGF. In addition, the tensile properties of the RGF/PP composites adding the RGF recycled at 500°C by the secondary cyclone were significantly lower than the corresponding results by the primary cyclone. That occurred mainly because the RGF collected by the secondary cyclone were shorter than that by the primary cyclone.

Different from the tensile properties, the flexural properties of the RGF/PP composites were all improved by adding the RGF recycled at three different temperatures as shown in Figure 2. Meanwhile, the surface modification of the RGF could all improve the flexural properties of the RGF/PP composites. The maximum increments of the flexural strength and modulus of the RGF/PP composites were 69 and 133%, respectively. That occurred mainly due to the fact that the crack initiating process in the composites was different between tensile and flexural tests.

Similar to that of the tensile properties, the impact strengths of the RGF/PP composites adding the RGF recycled at 400 and 500°C by the primary cyclone were improved as shown in Figure 3. However, the impact strength the RGF/PP composites adding the RGF recycled at 600°C by the primary cyclone was lower than that of the pure PP. The surface modification of the RGF made no improvement to the impact strength of the RGF/PP composites except for them recycled at 500°C. In addition, the impact strength of the RGF/PP composites adding the RGF recycled at 500°C by the primary cyclone was significantly greater than the corresponding results by the secondary cyclone. These reasons will be discussed later in fracture surfaces of the PP composites.

In general, the changes in these properties showed that the tensile, flexural, and impact properties of the RGF/PP composites increased simultaneously by adding the RGF recycled at 400 and 500°C by the primary cyclone. And the maximum increments of the tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength of the RGF/PP composites were 14, 59, 69, 133, and 35%, respectively in comparison with that of the pure PP. But the tensile strength and impact strength of the RGF/PP composites decreased by adding the RGF recycled at 600°C by the primary cyclone and at 500°C by the secondary cyclone, respectively. In this article, based on comprehensive consideration of the mechanical properties, energy, and economy, the optimum RGF was recycled at 500°C by the primary cyclone, and the optimum application of them in the PP composites was prepared by surface modification. These were the optimum parameters for recycling glass fibers and closing the recycling loop. These showed that the RGF could be successfully used as reinforcing fibers in the PP composites.

VST and HDT of the RGF/PP composites

VST and HDT of a polymeric material are an index of its heat softening characteristics and heat resistance towards applied load, respectively. This value is particularly important for the conversion of the material into the product for their potential practical application. Figures 4 and 5 show the characteristics of VST and HDT of the pure PP and RGF/PP composites with the RGF (20 wt %) at 400, 500, 600°C by the primary cyclone and 500°C by the secondary cyclone, respectively. The VST of the RGF/PP composites adding the RGF recycled at 400 and 500°C by the primary cyclone were improved. But the VST of the RGF/PP composites adding the RGF recycled

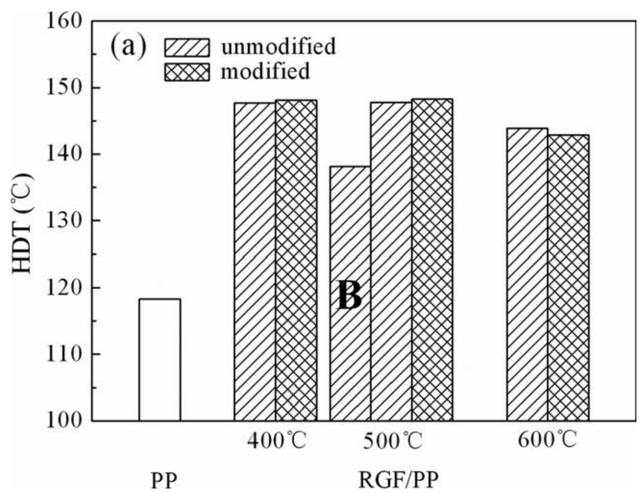

Figure 5 Heat distortion temperature of the pure PP and RGF/PP composites (20 wt %, B: RGF by the secondary cyclone, other RGF by the primary cyclone).

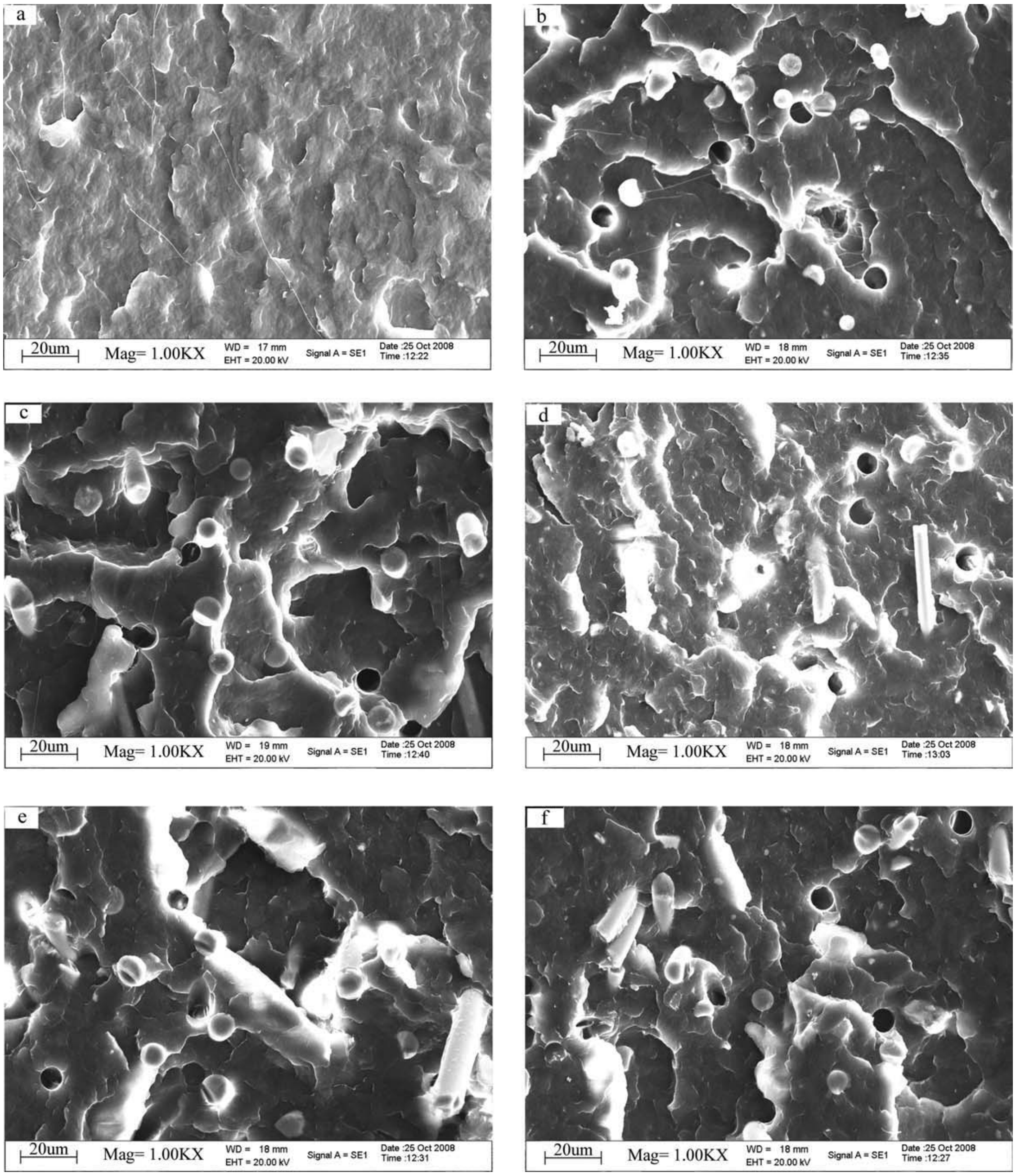

Figure 6 SEM micrograph of the impact fracture surfaces of the pure PP and RGF/PP composites (20 wt%): (a) pure PP; (b) and (c) 500°C, primary cyclone, unmodified and modified; (d) 500°C, secondary cyclone, unmodified; (e) and (f) 600°C, primary cyclone, unmodified and modified. The impact direction was vertical.

at 600°C by the primary cyclone and 500°C by the secondary cyclone were lower than that of the pure PP. The surface modification of the RGF made no improvement to the VST of the composites. In a word, the VST of the RGF/PP composites adding the optimum RGF increased 3.5°C obviously in comparison with that of the pure PP.

The HDT of the RGF/PP composites were all improved by adding the RGF (Fig. 5). In other words, the HDT of the RGF/PP composites increased 20–30°C obviously in comparison with that of the pure PP. The HDT is not actually a material property, but it is a measure of a beam bending speed. The presence of the high-modulus RGF slowed down the beam bending, thus resulting in a higher HDT. The high stiffness level of the RGF/PP composites found in Figure 2 was confirmed in Figure 5 by the high HDT values. That meant even under elevated temperatures a good bending stiffness was maintained for these RGF/PP composites.

Fracture surfaces of the PP composites

There was difference in the impact fracture surfaces of the different specimens through careful observation

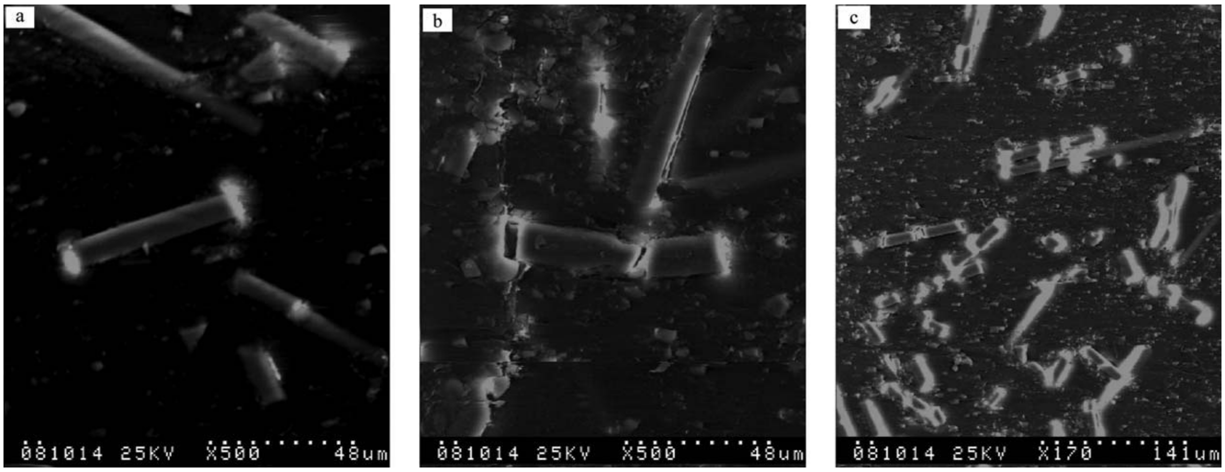

Figure 7 SEM micrograph for the in situ observation of the RGF/PP composites (modified): (a) interfacial debonding and crazes initiation; (b) crazes propagation and fibers breakage; (c) mass fibers breakage. The loading direction was horizontal.

using SEM, as shown in Figure 6. On the impact fracture surface of the pure PP specimen [Fig. 6(a)], there was a little yielding phenomenon and the topography was like a sea-wave. In addition, the direction of the waves was almost along to the impact direction. The sea-wave fracture surface topography suggested that a little yielding existed in the pure PP matrix, so that the crack propagated rapidly and the specimen fractured quickly. Therefore the pure PP specimen inclined to brittle fracture. On the impact fracture surfaces of the RGF/PP specimen with the unmodified and modified RGF recycled at 500°C by the primary cyclone, as shown in Figure 6(b,c), there were evident yielding phenomenon and a number of small pieces of the matrix with glass fibers were formed and distributed irregularly instead of a wave-shape fracture surface. Every dispersed glass fiber triggered effective stress concentrations and led to mass microcracks. A number of microcracks were initiated and increased significantly during the impact process so that the stress whitening could be clearly seen at the bright place on the impact fracture surfaces. Furthermore, the glass fibers exhibited a large extent of pullout (see the pulled out fibers and the pullout holes) and breakage in the RGF/PP composites. Thus, the impact strengths of the PP composites were improved with the addition of the unmodified and modified RGF recycled at 500°C by the primary cyclone into PP, respectively. Meanwhile, the yielding phenomenon in the RGF/PP composites with the modified RGF was better than that with the unmodified RGF. That occurred mainly due to the fact that the modified RGF showed stronger adhesion and better compatibility between the RGF and PP matrix. Figure 6(d) shows the impact fracture surface of the RGF/PP specimen with the unmodified RGF recycled at 500°C by the secondary cyclone. Although the glass fibers exhibited a certain extent of pullout and breakage in the RGF/PP composites, there was little yielding phenomenon and the topography was also like a sea-wave, similar to that of the pure PP specimen. That occurred mainly because the RGF collected by the secondary cyclone were shorter than that by the primary cyclone. Therefore, the impact strength of the RGF/PP composites adding the RGF recycled at 500°C by the secondary cyclone was significantly lower than that of the composites adding the RGF by the primary cyclone, and that of the pure PP. On the impact fracture surface of the RGF/PP specimen with the unmodified RGF recycled at 600°C by the primary cyclone [Fig. 6(e)], there was less yielding phenomenon, bigger pieces of the matrix with glass fibers and longer pulled out fibers than the corresponding results at 500°C. Meanwhile, the surface modification of the RGF made no improvement to the impact strength of the RGF/PP composites [Fig. 6(f)]. This suggested that the RGF themselves were severely weakened and there was poor interfacial adhesion between the fiber and matrix, which were responsible for the lower impact strength of the RGF/PP composites with the addition of the RGF recycled at 600°C by the primary cyclone.

In situ SEM observation and analysis

The test results showed that the strength and rigidity of the composites were improved simultaneously by the addition of the optimum RGF (500°C, primary cyclone) into PP. Although the RGF could be successfully reused as reinforcing fibers in the PP composites, influence of them on reinforcing mechanism of the composites could not be neglected. Therefore, the dynamic process of the optimum RGF (20 wt %) reinforcing of the PP polymer was observed and analyzed through *in situ* SEM tensile test.

Figure 7 shows SEM micrographs for the *in situ* observation of the PP composite by adding the modified RGF under the tensile loading. The loading direction was horizontal. Firstly, when the tensile loading was up to a certain value, partial interfacial debonding occurred between the glass fibers and matrix as it could be seen at the bright place in Figure 7(a). Meanwhile, the glass fiber acted as effective stress concentrators and initiated mass microcrazes between the glass fibers and matrix in the composite. Secondly, the interfacial debonding opening grew up and that craze was propagated along the interface between the glass fiber and matrix as the loading increased [Fig. 7(b)]. When the craze propagation met another glass fiber, the craze either was terminated or broke the fiber, and this slowed the propagation of the crack. Finally, mass broken fibers appeared as the loading further increased [Fig. 7(c)]. That occurred mainly because the glass fibers possessed high elastic modulus and low elongation, they first undertook the loading when external loads were imposed on the composite. Meanwhile, the strength of the loading was far greater than that of the single glass fibers, and there was good compatibility between the glass fiber and the matrix, so the glass fibers were first broken in comparison with the PP matrix. Subsequently, the RGF/PP composite specimen got tensile failure.

Results show that the RGF acted as effective stress concentrators and initiated mass microcrazes between the fiber and matrix in the RGF/PP composites. The craze either was terminated or broke the fiber when its propagation met another glass fiber. The process of the interfacial debonding, crack initiation, crack propagation, and fiber breakage dissipated a great amount of energy. These factors caused improvements of the tensile properties of the RGF/PP composites by adding the RGF evidently. The dominant deformation mechanism of the RGF/PP composites was crazing and the dominant reinforcing mechanism in the RGF/PP composites was the energy dissipation.

CONCLUSIONS

The mechanical properties of the PP composites were improved significantly by adding the RGF recycled at 400 and 500°C by the primary cyclone. The maximum increments of the tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength of the RGF/PP composites were 14, 59, 69, 133, and 35% respectively in comparison with that of the pure PP. The VST and HDT tests showed that the presence of the RGF could improve the thermal stability of the RGF/PP composites for their potential application.

The dynamic tensile process of the RGF/PP composite was observed with SEM. The *in situ* SEM observation results showed that the RGF were the excellent supporting bodies and could effectively lead to mass microcracks. The craze either was terminated or broke the fiber when its propagation met another glass fiber. The process of the interfacial debonding, crack initiation, crack propagation, and fiber breakage dissipated a great amount of energy. These factors could prevent and delay the crack extending into the big crack in the RGF/PP composites, and caused improvements of the strength and rigidity of the RGF/PP composites.

Based on comprehensive consideration, the optimum fluidized bed temperature for recycling glass fibers was 500°C and the optimum application of the RGF in the PP composites was prepared by surface modification. These were the optimum parameters for recycling glass fibers and realizing the closed loop recycling in a more effective and profitable way.

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