In Situ Observation of Polypropylene Composites Reinforced by Nonmetals Recycled from Waste Printed Circuit Boards During Tensile Testing

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ABSTRACT: A great amount of work has been done over the past few years to reuse the nonmetals recycled from waste printed circuit boards in polypropylene (PP) composites. This is because of the very fast generation rate of nonmetal pollution in the world each year and the very fast growing rate of PP applications in industries. This work focuses on the dynamic effects of nonmetals of different particle sizes on the tensile properties and reinforcing mechanisms of nonmetal/PP composites by *in situ* scanning electron microscopy tensile testing. The observed results show that the dominant deformation mechanism in pure PP is shear yielding. When fine nonmetals are filled into PP, mass microcracks are initiated. The glass fibers first resist the cracks and undertake the loading when they propagate. The crazes propagate slowly and then break the glass fibers. When coarse nonmetals are filled into PP, interfacial debonding and mass microcracks are initiated. A crack is either terminated when it meets another fiber–particulate bundle or branched into finer mass crazing. Interfacial debonding, crack initiation and propagation, and fiber pullout and breakage dissipate tremendous energy. These factors cause improvements in the strength and rigidity of nonmetal/PP composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1856–1863, 2009

Key words: composites; mechanical properties; poly(propylene) (PP)

INTRODUCTION

Polypropylene (PP), as one of the most important commodity polymers, is widely used in automobiles, electrical equipment, furniture, and so on because of its good processability, great recyclability, and moderate cost.[1–3] However, because of its low strength, low modulus, and high notch sensitivity, the usefulness of PP as an engineering thermoplastic is still limited. To expand the application range, the challenge of reducing the cost and enhancing the performance of the polymer by filling it with inorganic rigid particles has provoked considerable interest. Mineral fillers such as $CaCO_3$, talc, and mica are widely used in plastic products to improve the performance and to reduce the cost.[4–7] Recently, in our earlier publications, nonmetals recycled from waste printed circuit boards (PCBs) were found to greatly improve both the strength and rigidity of PP composites.[8,9] The main components of the nonmetals are thermosetting resins (epoxy resin or phenolic resin) and glass fibers. Thousands of millions of tons of nonmetals are generated in the world each year, and they are a huge source of pollution. However, they can also be a huge resource. They contain 50–70% glass fibers with high length/diameter ratios, high elastic modulus, and low elongation. Therefore, they have advantages over traditional fillers and represent a potential substitute for traditional mineral fillers or pure glass fibers. Although the nonmetals recycled from waste PCBs can be successfully reused as reinforcing fillers in PP composites, their influence on the reinforcing mechanism of the composites cannot be neglected.

To explain the reinforcing and toughening effects of inorganic rigid particles filled into brittle matrices, Lange[10] first proposed the crack-front bowing mechanism. According to this mechanism, when a crack propagates in a rigid-particle-filled composite, the rigid particles will resist it. However, the crack-front bowing theory cannot explain the relationship with changed design variables, such as the shape, size,

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aggregate size, and surface characteristics of the particles and the properties of the matrix. Then, Lee and Yee[11,12] proposed energy dissipation mechanisms in studying the toughening mechanisms of glass-bead-filled epoxies. It was thought that the various micromechanical deformations could be categorized into energy dissipation mechanisms. On the basis of this theory, the reinforcing and toughening effects on plerosphere/PP, glass fiber (GF)/PP, $CaCO_3$/PP, GB/poly(propylene oxide), and glass beads (GB)/PP composites[13–20] by inorganic particle fillers can be successfully explained.

Up to now, there have been many studies on reusing nonmetals recycled from waste PCBs in epoxy resins, polyester, and other resins.[21–24] However, the influence of nonmetals on the reinforcing mechanisms of composites was still continuing at the end of experiments and was mostly based on the results of experiments, whereas the dynamic process of particle-reinforcing mechanisms was unclear. Despite the importance of deformation mechanisms to the mechanical behavior of materials, not much attention has been paid to this subject. Therefore, understanding the influence of nonmetals on the tensile properties and fracture behavior of PP composites is of great importance. In addition, the effect of the particle size on the reinforcement of PP composites cannot be neglected. Therefore, further investigations to reveal the details of these reinforcing mechanisms in nonmetal/PP composites are still required.

The objective of this research was to study the dynamic effects of nonmetals with different particle sizes on the tensile properties and reinforcing mechanisms of PP composites by *in situ* tensile testing. In nonmetal/PP composites, crack initiation, crack propagation, fiber pullout, and fiber breakage were watched with scanning electron microscopy (SEM) *in situ* tensile testing. These changes caused by nonmetal particles supplied valid experimental evidence for the reinforcing mechanisms of nonmetal/PP composites on the basis of the energy dissipation theory.

EXPERIMENTAL

Materials and fabrication procedure for the composites

PCBs are electronic circuits created by the mounting of electronic components on a nonconductive board (nonmetals) and the creation of conductive connections between them. The creation of circuit patterns is accomplished by both additive and subtractive methods. There are three basic varieties of PCBs: single-sided, double-sided, and multilayered. The conductive circuit is generally copper. The main components of the nonmetals are thermosetting resins (epoxy resin or phenolic resin) and glass fibers. In this study, the nonmetals were recycled from waste PCBs from a local recycling factory by physical recycling. The process technology included mechanical two-step crushing and air separation. The PCBs were first pulverized in a process consisting of coarse crushing and fine pulverization. Then, an air classifier was used to separate the nonmetals from the metals. To study the effect of the particle size, nonmetals of three sizes [25–80 mesh (coarse), 80–150 mesh (medium), and <150 mesh (fine)] were selected with a vibrating screen to make PP composites. To improve the dispersion of the nonmetal particles in the PP matrix and the compatibility between the nonmetals and matrix, all the nonmetals were modified with the silane coupling agent γ-aminopropyltriethoxysilane (KH-550, Najing Shuguang Chemical Group Co., Ltd., Nanjing, China) at a 1.0 wt % concentration. PP S1003 (Beijing Yanshan Petrochemical Co., Ltd., Beijing, China; melt flow rate = 3.6 g/10 min) was used as the matrix polymer. The PP powders and the modified nonmetal particles were dried at 80°C for 2 h. Then, the dried nonmetal particles and PP powers were stirred and mixed with a high-speed mixer (SHR-5A, Zhangjiagang Qiangda Plastics Machinery Co., Ltd., Suzhou, China). The nonmetal/PP blends were extruded into threads with a screw extruder [TE-35, Coperion Keya (Nanjing) Machinery Co., Ltd., Nanjing, China] and then granulated. The extrudates were pelletized and molded in an injection machine (CJ108M3V, Chen De Plastics Machinery Co., Ltd., 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.

Mechanical property testing

The tensile and flexural properties of the pure PP and nonmetal/PP composites were measured on an electronic universal testing machine (DXLL-10000, No. 4 Chemical Machinery Plant of Shanghai Chemical Equipment Co., Ltd., Shanghai, China) at room temperature (23°C) with crosshead speeds of 50 and 2 mm/min according to ISO Standards 527-2 : 1993 and 178 : 1993, respectively. The notched Izod impact strengths were measured with an Izod testing machine (XJ-40A, Wuzhongshi Material Tester Limited Co., Wuzhong, China) at room temperature (23°C) according to ISO Standard 180 : 1993.

In situ SEM experimental setup and observation in tensile testing

To determine the reinforcing mechanisms of the pure PP and PP composites with nonmetals recycled from waste PCBs, a specially designed small-load frame (Fig. 1) was built and used to apply tensile loading.

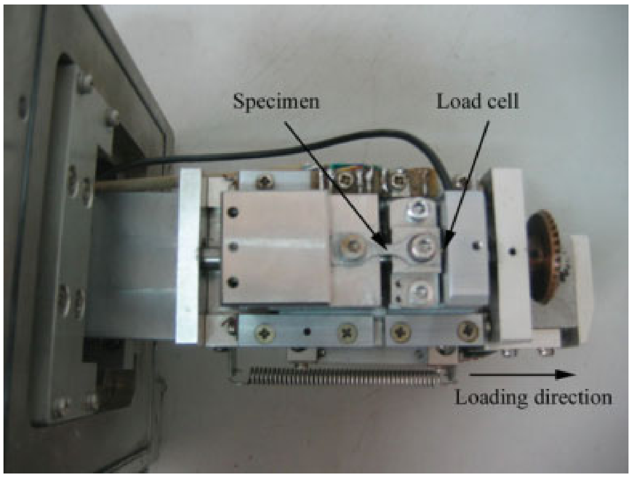

Figure 1 Load frame built for *in situ* SEM observation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The small-load frame with a specimen was examined by SEM (S-570, Hitachi, Ltd., Tokyo, Japan). The *in situ* tensile specimen shown in Figure 2 was cut from the dumbbell-shaped tensile bars. One side of the surface of the specimen was polished and coated with a thin layer of gold before microscopy to avoid charge buildup. The dynamic tensile fracture process of the pure PP and the nonmetal/PP composites was observed in the system of the *in situ* SEM tensile test when external loads were imposed on the composites.

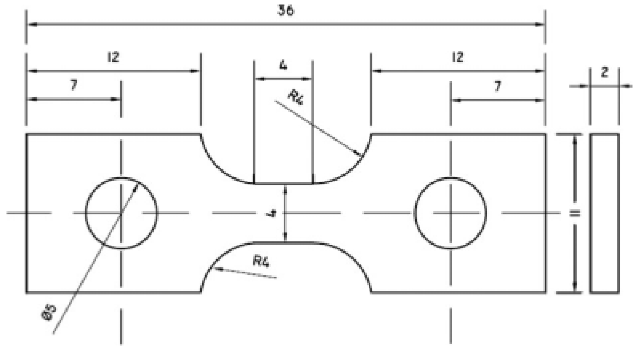

Figure 2 *In situ* tensile specimen for *in situ* SEM observation.

RESULTS AND DISCUSSION

Mechanical properties of the nonmetal/PP composites

Table I lists the mechanical properties of the pure PP and the nonmetal/PP composites filled with fine, medium, and coarse nonmetal particles (0–30 wt %). The tensile and flexural properties of the nonmetal/PP composites were improved significantly by the addition of the nonmetals. The fine and medium nonmetals were more effective than the coarse nonmetals in reinforcing the PP matrix. The surface modification of the nonmetals could also improve these properties. The maximum increments of the tensile strength, tensile modulus, flexural strength, and flexural modulus of the PP composites were 28.4, 62.9, 87.8, and 133.0%, respectively. However, the notched Izod impact strengths of the composites decreased. Some results have been reported in a previous publication.[8]

In situ SEM dynamic observation and analysis

The test results showed that the strength and rigidity of the composites were improved simultaneously by the filling of the nonmetals into PP. That occurred mainly because the glass fibers in the nonmetals possessed inherent characteristics such as high length/diameter ratios, high elastic modulus,

TABLE I
Mechanical Properties of Pure PP and Nonmetal/PP Composites

Sample	Code	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)
1	PP	34.17	0.82	35.53	1.64	2.97
2	PP-F-10	36.10	0.99	46.81	2.49	2.34
3	PP-F-20	39.73	1.16	56.08	3.13	1.98
4	PP-F-30	43.89	1.15	66.25	3.82	1.89
5	PP-M-10	36.41	1.00	50.11	2.55	1.89
6	PP-M-20	38.85	1.16	58.08	3.07	2.10
7	PP-M-30	42.79	1.34	66.71	3.82	2.13
8	PP-C-10	35.37	0.97	48.63	2.37	1.95
9	PP-C-20	37.03	1.10	55.59	3.00	2.13
10	PP-C-30	38.28	1.13	50.39	2.61	2.28
11	PP-F-20	38.77	1.14	54.50	3.10	2.04
12	PP-M-20	37.73	1.15	57.07	3.28	2.16
13	PP-C-20	36.24	1.10	49.96	2.64	2.07

F, M, and C indicate fine, medium, and coarse nonmetals, respectively; 10, 20, and 30 are the nonmetal contents (wt %). Samples 2–10 were modified nonmetals; sample 11–13 were unmodified nonmetals.

and low elongation. There were excellent supporting bodies of the glass fibers and appropriate interfacial adhesives formed between the particles and matrix. Every dispersed particle triggered effective stress concentrations and led to mass crazes, so big cracks could not be formed in the composites. Therefore, the polymer matrix properties were improved through the interaction of the nonmetal particles and matrix. In this study, the dynamic effects of nonmetals with different particle sizes on the reinforcement of PP composites were observed and analyzed during *in situ* SEM observations in tensile testing. All the results are summarized as follows.

Figure 3 shows SEM micrographs for the *in situ* observation of the pure PP under tensile loading. The loading direction was horizontal. At the beginning of the tensile loading, there was no change. Up to a certain loading, it triggered an initial microcrack nearly perpendicular to the loading direction, as shown in Figure 3(a). Subsequently, mass cracks appeared [Fig. 3(b)] but did not extend into a big crack rapidly. As the tensile loading increased, shear bands at angles ranging from 45 to 70°C with respect to the direction of the loading were evident in the pure PP in the bright region [Fig. 3(c)]. When the loading was further increased, the pure specimen suffered tensile failure along the shear bands [Fig. 3(d)]. The formation of shear bands provided evidence that the dominant deformation mechanism in the pure PP was shear yielding. This result agreed with the findings of previous scholars.[17,25–27]

Figure 4 shows SEM micrographs for the *in situ* observation of the PP composites filled with fine nonmetal particles (30 wt %) under tensile loading. The loading direction was horizontal. The nonmetals were dispersed uniformly in the matrix, as shown in Figure 4(a), under the initial conditions. At the beginning of the tensile loading, the SEM micrograph of the specimen showed no change. Up to a certain loading, partial interfacial debonding opening between the fibers and matrix could be seen in the bright region [Fig. 4(b)]. Meanwhile, every dispersed particle triggered effective stress concentrations and initiated mass crazes in the composites. As the tensile loading increased, the crazes propagated slowly perpendicularly to the loading direction. When the craze propagation met another glass fiber, it either was terminated or broke the glass fiber [Fig. 4(c)], and this slowed the propagation of the crack. That was mainly because the single glass fibers possessed high elastic modulus and low elongation. When a crack propagated in the nonmetal/PP composite, the glass fibers could resist it. Therefore, they first undertook the loading when external loads were imposed on the composite. Meanwhile, the strength of the tensile loading was far greater than that of the single glass fibers, and there was strong adhesion as well as good compatibility between the fibers and the matrix. Therefore, the glass fibers were first broken in comparison with the PP matrix. When the loading further increased, an open crack appeared and extended into the break of the composites [Fig. 4(d)]. The glass fibers exhibited a large extent of pullout on the tensile fracture surfaces of the composites. The pulled out fibers had a rough surface that showed strong adhesion and good compatibility between the fibers and the matrix. All these processes needed a great amount of additional energy to overcome the barrier. It is noteworthy that the deformation mechanism contributed to the energy dissipation before fracture. This result coincided with the findings of previous scholars.[9,11–13,17]

The effect of the coarse nonmetal particles in the nonmetal/PP composite (30 wt %) was observed during *in situ* SEM observation to research microtopography changes in particles of different sizes in the PP matrix (Fig. 5). The fillers mainly were exhibited as larger fiber–particulate bundles, and this was determined by the shape and composition of the coarse nonmetals.[8] At the beginning of the tensile loading, the SEM micrograph of the specimen showed no change, just like the nonmetal/PP composite filled with the fine nonmetals. Up to a certain loading, partial interfacial debonding opening between the bundles and matrix could be seen in the bright region [Fig. 5(a)]. Two parts of the opening, marked A and B, are enlarged on the right top and left bottom of Figure 5(a), respectively. Meanwhile, microcracks were initiated along the interface edge. As the opening grew, much crazing was propagated along the interface between the bundles and matrix as the tensile loading increased [Fig. 5(b)]. Meanwhile, the crack either was terminated when it met another bundle or branched into finer mass crazing instead of breaking the crack directly. Then, the crazes propagated along another interface, and the cracks slowly propagated [Fig. 5(c,d)]. When the loading further increased, an open crack appeared and extended into the break of the composites. All these processes also needed a great amount of additional energy to overcome the barrier.

The results of *in situ* SEM observations showed that the pure PP matrix experienced tensile failure along the shear bands in the tensile test. The dominant deformation mechanism in the pure PP was shear yielding. When the fine nonmetals were filled into the PP matrix, mass microcracks were initiated between the fibers and matrix under the tensile loading. When a crack propagated in the nonmetal/PP composite, the glass fibers first resisted it and undertook the loading. The crazes propagated slowly and then broke the fibers. The process of crack initiation and propagation and fiber breakage dissipated a great amount of energy. Meanwhile, in the process

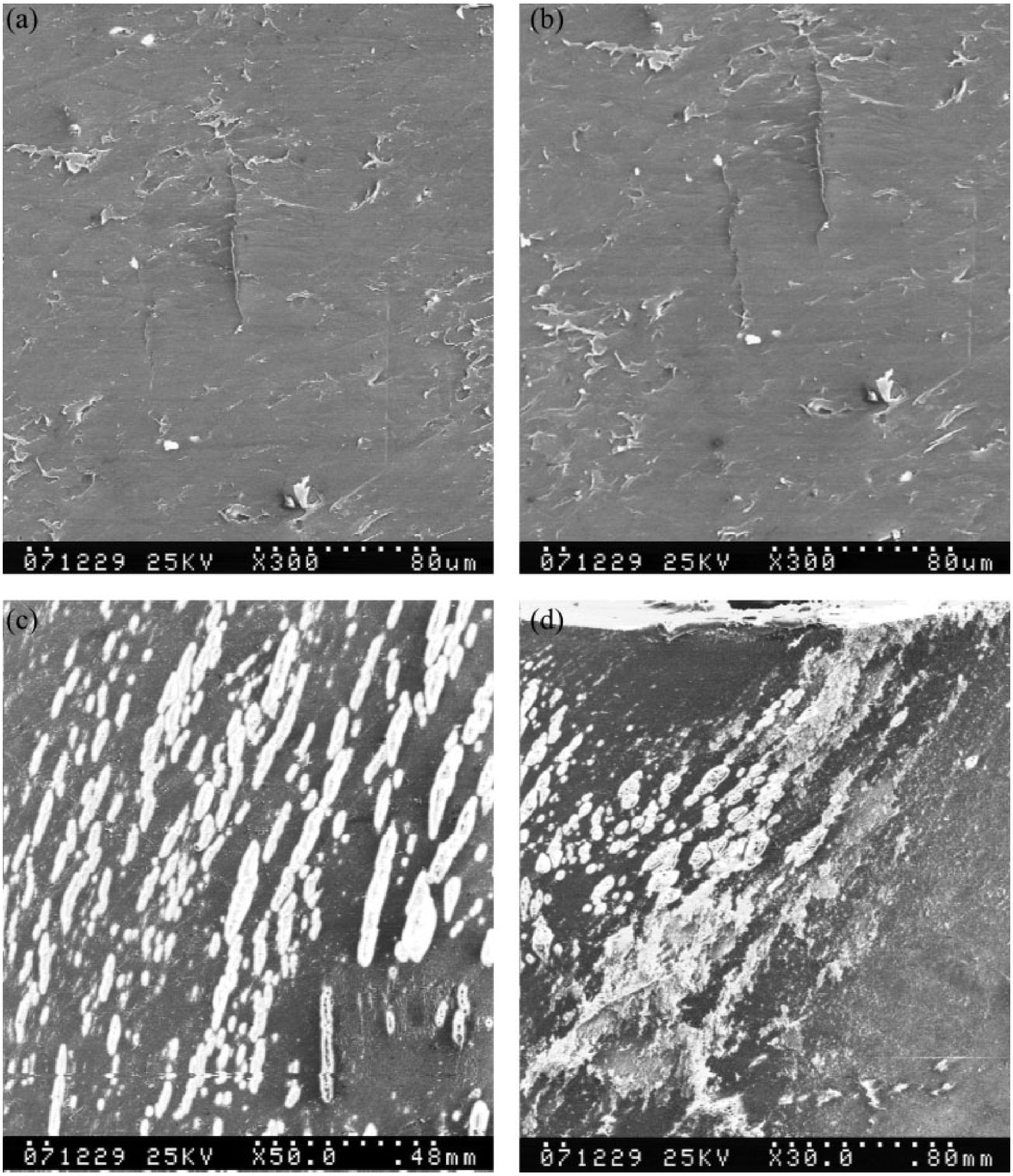

Figure 3 SEM micrographs for the *in situ* observation of pure PP: (a) triggering of the initial crack, (b) appearance of mass cracks, (c) appearance of shear bands, (d) rapid extension and then damage. The loading direction was horizontal.

of tensile loading, partial interfacial debonding and fiber pullout could also slow the propagation of the crack. These factors caused improvements in the properties of the nonmetal/PP composite with filling by the fine particles. When the coarse nonmetals were filled into the PP matrix, interfacial debonding and mass microcracks were initiated rapidly between the bundles and matrix under tensile loading. Meanwhile, the crack either was terminated when it met another bundle or branched into finer mass crazing instead of breaking the crack directly. Therefore, the cracks slowly propagated. The process

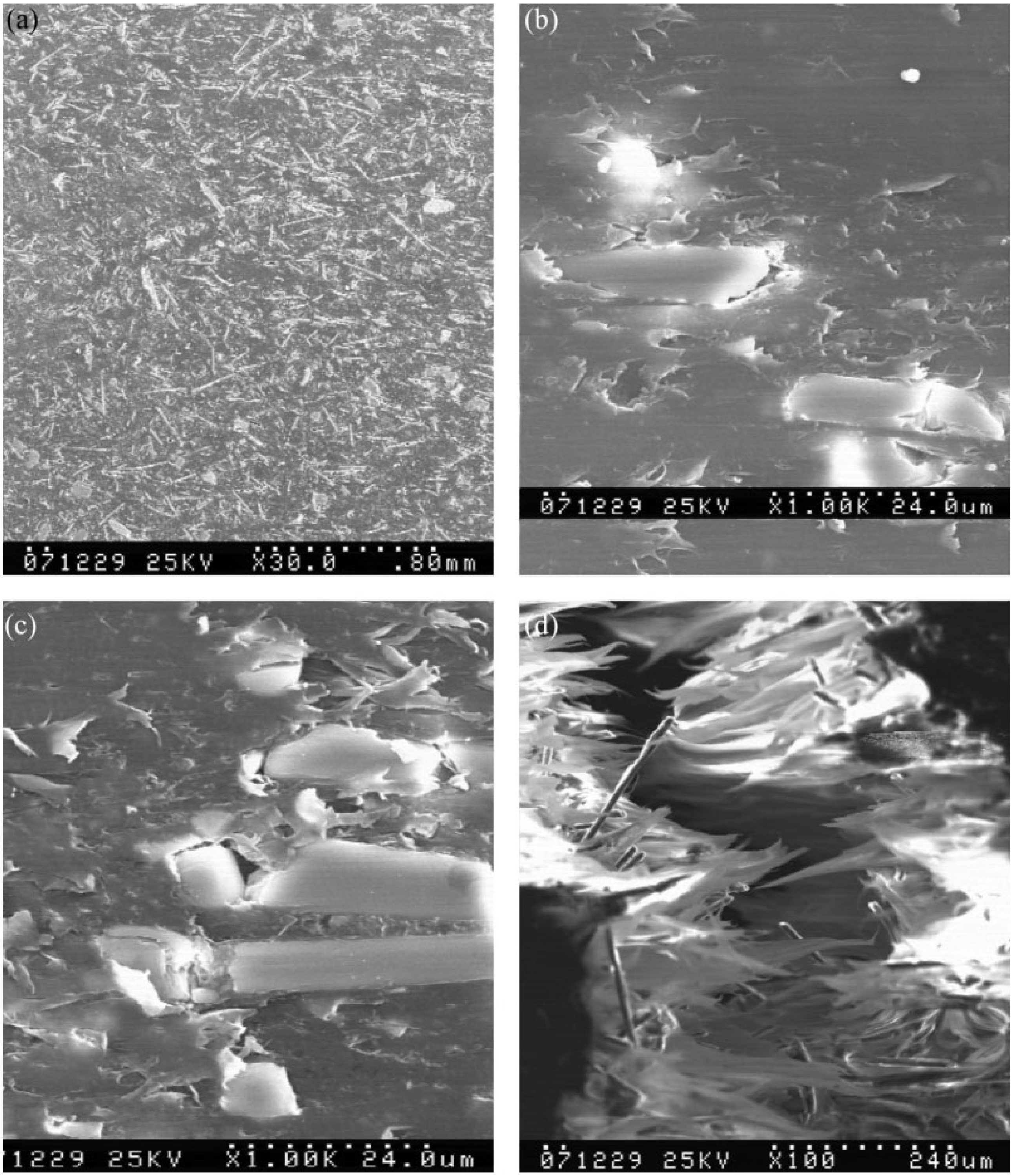

Figure 4 SEM micrographs for the *in situ* observation of a nonmetal/PP composite (30 wt %, fine): (a) initial condition, (b) interfacial debonding and craze initiation, (c) fiber breakage, and (d) appearance of an open crack. The loading direction was horizontal.

of interfacial debonding and crack initiation and propagation dissipated a lot of energy. These factors caused improvements in the properties of the nonmetal/PP composite with filling by the coarse particles. However, the presence of larger fiber–particulate particles led to the formation of larger defects (stress concentration points), so the improvements in the properties of the composite with filling by the coarse nonmetals were not greater than those for the composite with filling by the fine nonmetals.

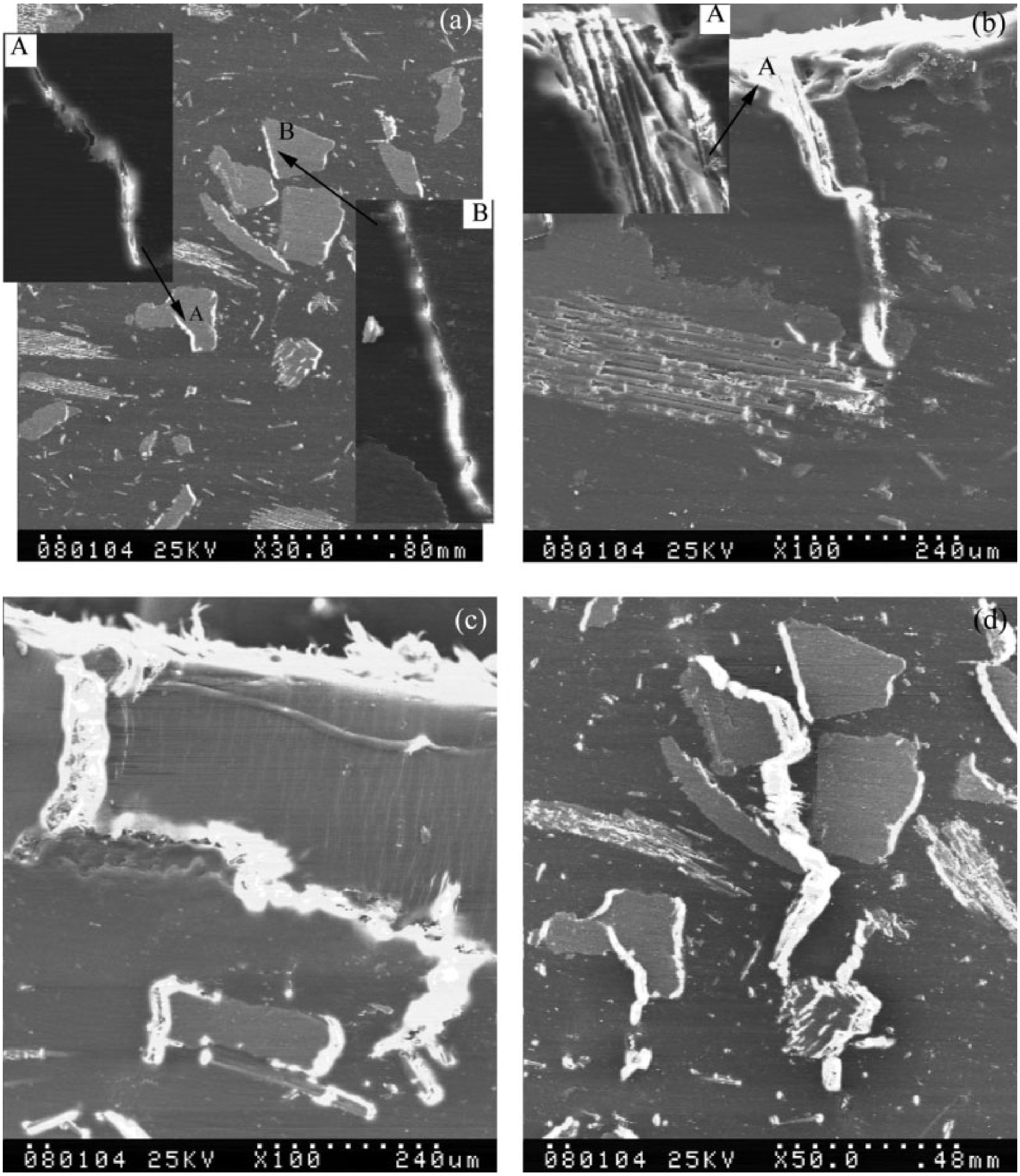

Figure 5 SEM micrographs for the *in situ* observation of a nonmetal/PP composite (30 wt %, coarse): (a) interfacial debonding and mass craze initiation, (b) craze propagation and termination, (c) craze propagation along another interface, and (d) slowing of craze propagation. The loading direction was horizontal.

The results of the *in situ* observation and analysis of the dynamic process supplied effective test evidence for the reinforcing mechanisms of the nonmetal/PP composites on the basis of the energy dissipation theory.

CONCLUSIONS

The mechanical properties of the PP composites, such as the tensile properties and flexural properties, were remarkably improved by the addition of the nonmetals. However, the impact strength of the nonmetal/PP composites decreased.

The dynamic tensile process of the pure PP and nonmetal/PP composites was observed with SEM. The *in situ* SEM observation results showed that the pure PP matrix experienced tensile failure along the shear bands during the tensile test. When the fine nonmetals were filled into the PP matrix, mass microcracks were initiated. When a crack propagated in the nonmetal/PP composite, the glass fibers first resisted it and undertook the loading. The crazes propagated slowly and then broke the fibers. When the coarse nonmetals were filled into the PP matrix, interfacial debonding and mass microcracks were initiated rapidly. The crack either was terminated when it met another bundle or branched into finer mass crazing instead of breaking the crack directly. The interfacial debonding, crack initiation and propagation, and fiber pullout and breakage dissipated a great amount of energy. These factors caused improvements of the strength and rigidity of the nonmetal/PP composites.

In situ observation and analysis of the experimental results showed that the dominant deformation mechanism in the pure PP was shear yielding, whereas the dominant reinforcing mechanism in the nonmetal/PP composites was energy dissipation.

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