In Situ Observation of Plerosphere/Polypropylene Composites in the Tensile Test

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ABSTRACT: Toughness, strength, and rigidity of the composites can be improved simultaneously by filling plerosphere particles into polypropylene (PP). The mechanism of improving the mechanical properties of the composites is studied on the basis of the energy dissipation theory. By using scanning electron microscopy (SEM), the crack initiation, propagation, and termination on the plerosphere/PP composites are investigated by *in situ* tensile test. Observation results show that the particles can effectively lead to a number of microcracks instead of the breaking crack. These microcracks formation consumes tremendous energy. As a result, the toughness and strength of the polymer can be improved. Results of the *in situ* SEM observation and analysis to the dynamic process supply effective test evidence for the toughening mechanism of the plerosphere/PP composite on the basis of the energy dissipation theory. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3736–3742, 2007

Key words: PP; composites; *in situ* SEM observation; mechanical properties; energy dissipation theory

INTRODUCTION

Reinforcing and toughening of polymers is an important part in polymer material field. Kurauchi, Inoue, and coworkers[1,2] first proposed the new conception of brittle particle reinforcing and toughening polymer, which has received increasing attention. Recently, many scientists and engineers are exploring to improve the mechanical properties of polymer by filling inorganic particles.[3–21] Mineral fillers such as $CaCO_3$ and talc[5,16–21] are widely used in plastic products to improve the performance and to reduce the costs. The using of talc has been known to improve some properties of polypropylene (PP), such as the strength and stiffness, but it has a detrimental effect on other properties, such as the impact strength and deformability. $CaCO_3$, however, can highly improve impact properties and deformability at the cost of strength.

The effects of inorganic filler on the mechanical properties of the composites depend strongly on its shape, particle size, aggregate size, surface characteristics, and the properties of the matrix.[17] Having perfect shape, particle size, aggregate size, and surface characteristics, plerosphere represents a potential substitute for these mineral fillers and can highly improve both the strength and toughness of plastic products. They have more advantages than traditional fillers.

To explain the reinforcing and toughening effects by filling rigid particles into brittle matrices, Lange[22] first proposed the crack front bowing mechanism, which has been used to explain the toughening of matrices with rigid particles.[23–25] Although, this mechanism can explain the relationship between the resistance of particles and the macroscopic fracture toughness of composites by analyzing the line tension, it failed to explain the relationship with design variables changed, such as the shape, the size, the aggregate size, the surface characteristics of particles, and the properties of the matrix. Then, Lee and Yee[7] proposed energy dissipation mechanism in studying the toughening mechanisms of glass bead filled epoxies, to explain the particle toughening of matrices more fundamentally and detailedly than the crack front bowing mechanism.

Up to now, the research of inorganic particles toughening of polymer was going on at the end of the experiment and was mostly based on the results of the experiment, while the process of the inorganic particles toughening was unclear. In this article, the objective of the research is to study the dynamic process of inorganic particles toughening of polymer. Around the inorganic plerospheres in the plerosphere/PP composites, the cracks initiation, propagation, and termination are watched under scanning electron microscope (SEM) *in situ* tensile tests. These changes caused by plerospheres supply effective experiment evidence for the toughening mechanism of the plerosphere/PP composite on the basis of the energy dissipation theory.

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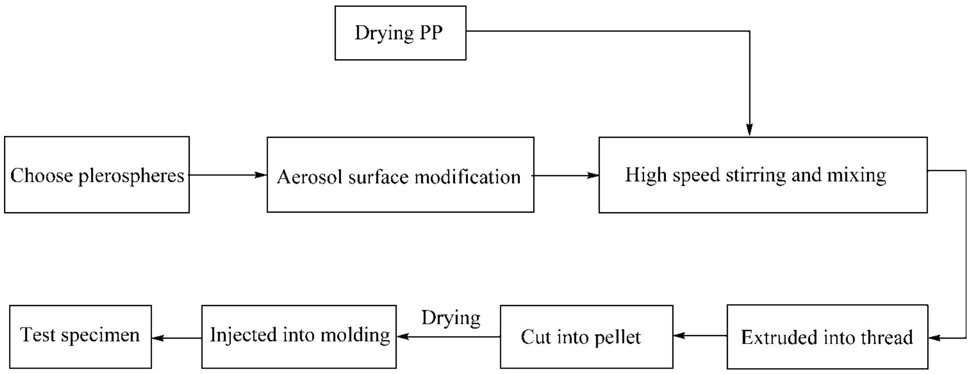


Figure 1 The process of the preparation of plerosphere/PP composites.

EXPERIMENTAL

Materials and fabrication procedure of composites

Coal fly ash,[26] an industrial solid-waste byproduct, is produced in large quantities during the combustion of coal in thermal power plants. There are many super fine spherical particles in coal fly ash. The main components of plerospheres (80–90%) are silicon dioxide (SiO_2) and alumina (Al_2O_3). The mineralogical compositions found by X-ray diffraction analysis are mullite, sillmanite, and quartz. The compression strength of plerospheres is 2000–6000 kgf/cm^2 and the surface Mohs' hardness is 6–8. Plerospheres also possess many other excellent characteristics, such as sphericity, high strength, high resistivity, and low thermal conductivity. By air classification, large quantities of plerospheres with a diameter ranging from 0.5 to 5 μm can be obtained.

The plerosphere particles, which are 2 and 5 μm in diameter with a density of (ρ) 2.4 g/cm^3 and mainly consist of 56% SiO_2 and 31% Al_2O_3, are selected for making composites. To improve the dispersion of plerospheres in PP matrix and the compatibility between the plerospheres and matrix, all the plerospheres are modified with 1.0 wt % content of silane coupling agent A-151(vinyltriethoxysilane, Beijing Chemical Reagent, China) by the aerosol method. PP 2401 (Beijing Yanshan Petrochemical, China; melt flow rate 2.8 g/10 min) is used as the matrix polymer. The PP powder is dried at 80°C for 3 h. Then, the modified plerosphere particles and dried PP powder are stirred and mixed by using a high speed mixer (GB-10A, Beijing Int Plastics Machinery General Factory, China). The plerosphere/PP blends are extruded into thread with a screw extruder (SJ-45J, Beijing Int Plastics Machinery General Factory, China). The extrudate is pelletized, dried for 2 h at 80°C, and injected into standard samples. Figure 1 shows the whole fabrication procedure of the plerosphere/PP composites.

Mechanical properties testing

The tensile and flexural properties of the pure PP and plerosphere/PP composites are measured on an electronic universal testing machine (DSS-500, Shimazu, Japan) at room temperature (20°C). The notched Izod impact strength is measured by an Izod testing machine (40/10 kg cm, German) at room temperature (20°C) and low temperature (−20°C), respectively. The dynamic process of crack initiation, propagation, and termination in the plerosphere/PP composites is observed in the system of *in situ* SEM (S-570, Hitachi, Japan) tensile test when external load are imposed on the composites. All specimens are gold-sputtered before SEM test.

RESULTS AND DISCUSSION

Mechanical properties of plerosphere/PP composites

Figure 2 shows that the effects of particle content, particle size, and temperature on notched Izod impact strength of the plerosphere/PP composites.

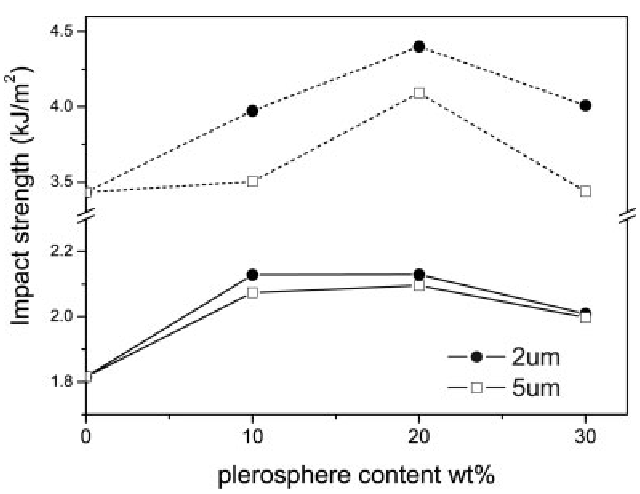


Figure 2 Notched impact strength of the plerosphere/PP composites at (- - -) 20 and (—) −20°C

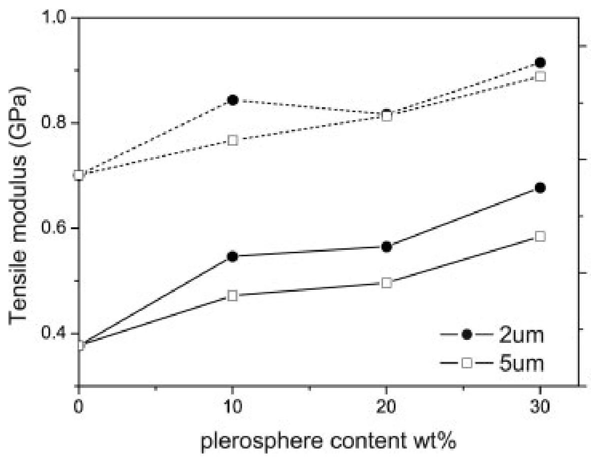


Figure 3 (- - -) Tensile strength and (—) tensile modulus of the plerosphere/PP composites.

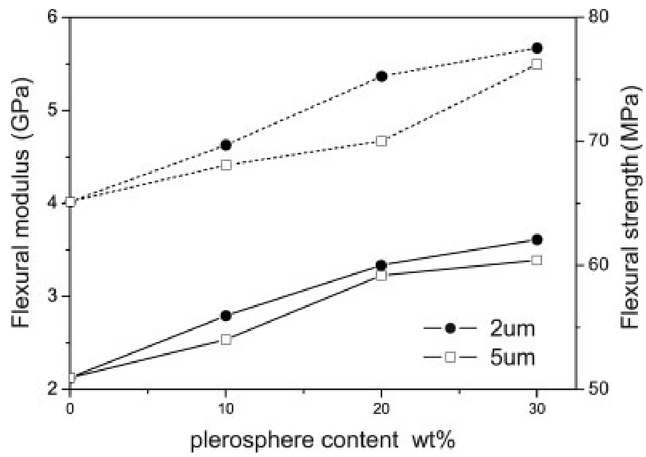
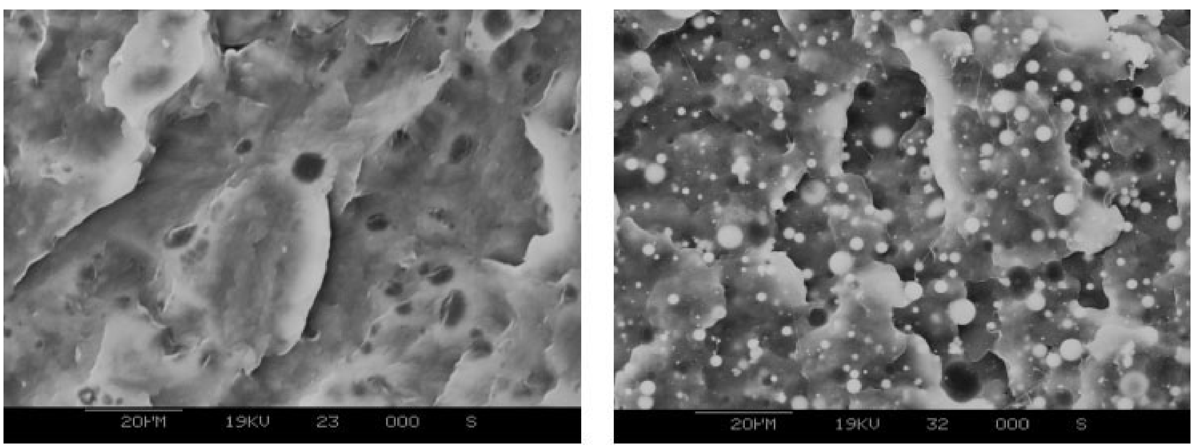


Figure 4 (- - -) Flexural strength and (—) flexural modulus of the plerosphere/PP composites.

No matter using the plerosphere particles of 2 or 5 μm, The impact strength of the composites is improved with the increase of plerosphere particles content (within 0–30 wt %) not only at room temperature(20°C), but also at low temperature(−20°C). Figure 3 shows that the tensile strength and tensile modulus of the plerosphere/PP composites are improved by adding the particles of 2 and 5 μm respectively, (0–30 wt %) at room temperature. Figure 4 shows that the flexural strength and flexural modulus of the plerosphere/PP composites are improved by adding particles of 2 and 5 μm respectively, (0–30 wt %) at room temperature. This observation has been reported in a previous publication.[26]

Fracture surfaces observation and analysis

There is difference in the fracture surface of the different specimens through careful observation on SEM. In the impact fracture surface topography of the pure PP specimen, there is a little yielding phenomenon around the prefabricated notched area. Far from the prefabricated notched area, the impact fracture surface topography is like a sea-wave, and the wave crest and trough are very clear [Fig. 5(a)]. In addition, the arrangement and direction of the waves are regular and perpendicular to the impact direction. The sea-wave fracture surface topography suggests that a little yielding exists in the pure PP matrix, so that the crack propagates rapidly and the specimen quickly fractures. So the pure PP specimen inclines to brittle fracture. On the impact fracture surface of the specimen filled with plerosphere particles of 5 μm (30 wt %), a number of small pieces of the matrix with plerospheres are formed and distributed irregularly instead of a wave-shape fracture surface. A number of microcracks are initiated and increase significantly during the impact process [Fig. 5(b)]. Furthermore, the filler particles are dispersed well in the matrix, and the spherical particles of the



(a) (b)

Figure 5 SEM photograph of the impact fracture surface of the specimens (×1000). (a) Pure PP. (b) Plerosphere/PP composite.

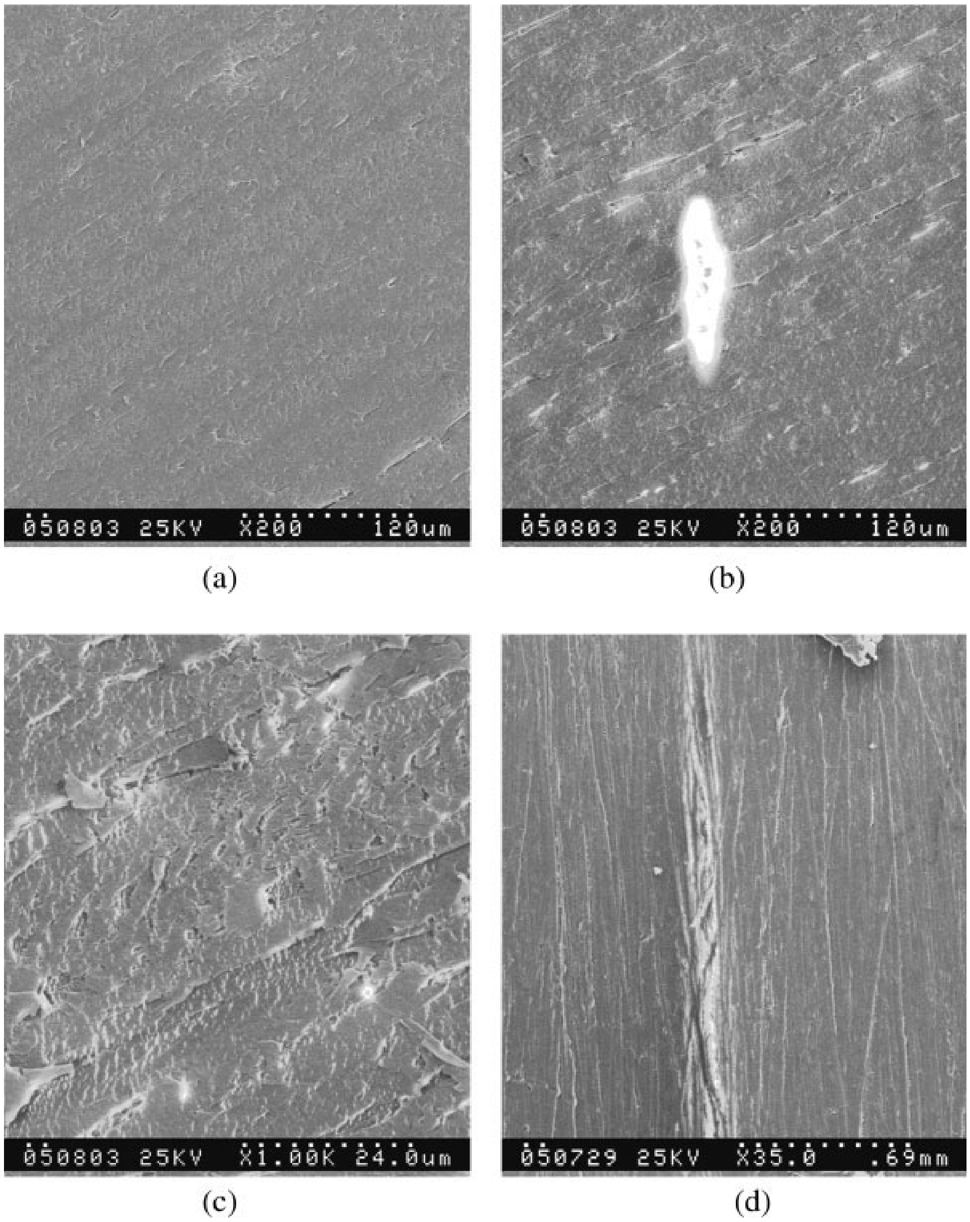


Figure 6 SEM micrograph for the *in situ* observation of the pure PP. (a) Initial condition; (b) triggering initial crack; (c) appearance of mass microcracks; and (d) rapidly extend then damage.

plerosphere are well wetted with PP material. On the other hand there is no clear separation or void at the interface of the composite.

Figure 5 shows static observation on SEM and analysis on the fracture surface of the composites. To explain the dynamic process of inorganic particles toughening of polymer, the dynamic process of the crack initiation, propagation, and termination in the composites are observed and analyzed through *in situ* SEM tensile test.

In situ SEM dynamic observation and analysis

The mechanical properties results show that toughness, strength, and rigidity of the composites are improved simultaneously when the rigid particles of plerosphere are filled into PP. That is mainly because plerospheres possess inherent characteristics such as big specific surface area, high strength, and rigidity, and the particle is super fine and its spherical rate is more than 95%. With such big specific surface area and millions of super fine particles, there is a big interfacial contact area, and appropriate interfacial adhesives are formed between the particles and matrix. Every dispersed particle triggers effective stress concentrations and lead to mass crazes so that the weak point cannot be formed in the composites. Thus, the polymer matrix properties are improved through the interaction of high strength particles

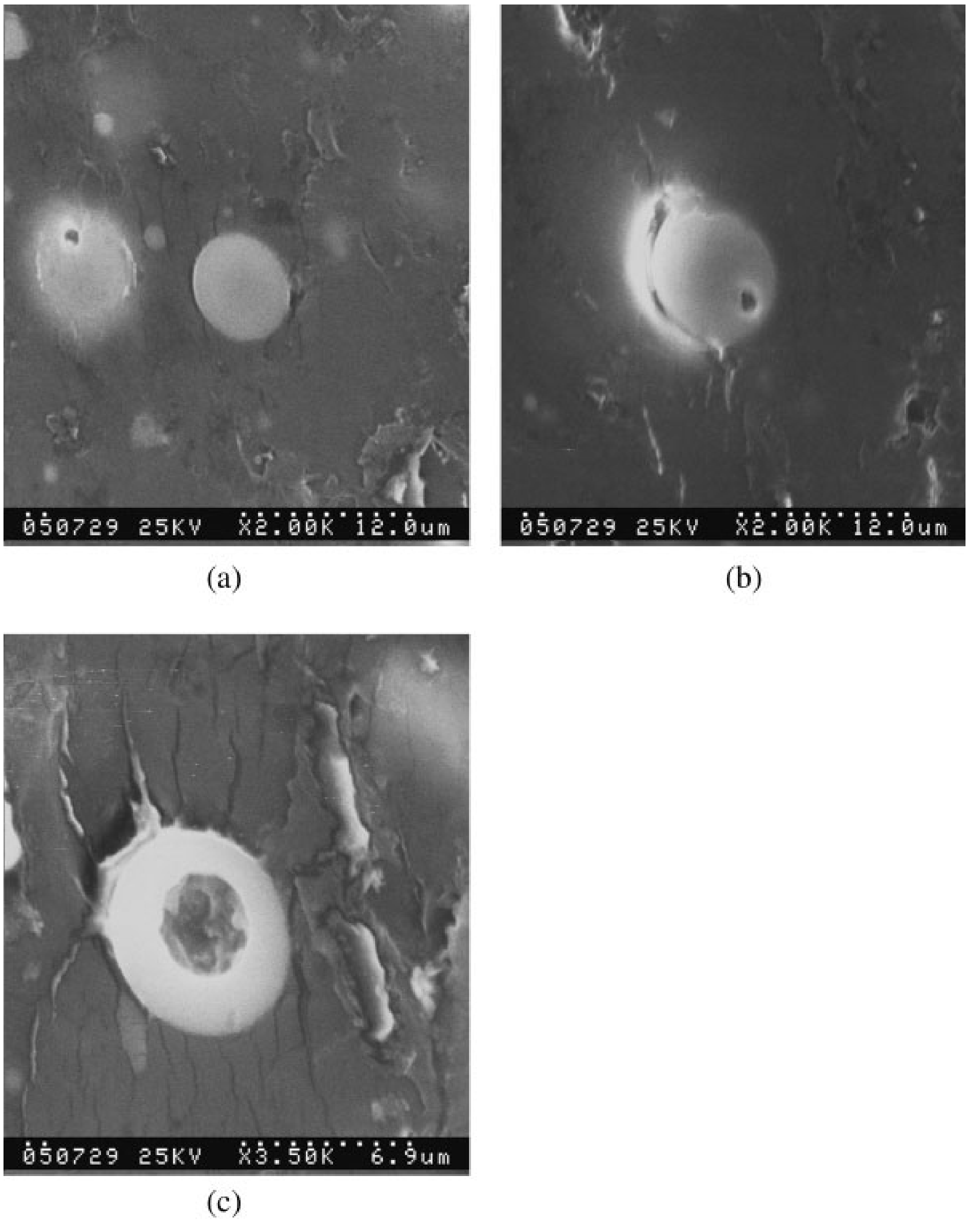


Figure 7 SEM micrograph for the *in situ* observation of the plerosphere/PP composites. (a) Triggering initial microcracks; (b) interfacial debonding; (c) growing up to bigger cracks.

and matrix. In this study, the key effect of plerospheres is analyzed during *in situ* SEM observation in the tensile test. All results are summarized as follows.

Figure 6 shows the SEM micrographs for the *in situ* observation of pure PP under the tensile loading, which shows a series of the microchange. The surface of the specimen of the pure PP is smooth without loading as shown in Fig. 6(a). At the beginning of the tensile loading, there is no change. When up to a certain loading it triggers initial crack, and the size of the crack is usually big, as shown in Fig. 6(b). Subsequently, mass cracks appear [Fig. 6(c)] and extend to the dominant crack rapidly. Then the pure PP specimen gets damaged [Fig. 6(d)].

Figure 7 shows the SEM micrographs for the *in situ* observation of the PP composites filled with 20 wt % plerospheres (5 μm). The surface of the tensile specimen of the plerosphere/PP composites is also smooth. And the particles are dispersed uniformly in the matrix. For *in situ* SEM observation, the plerosphere/PP composites get polishing treatment, and many surface-broken plerospheres expose its internal hollow structure on the surface of the composites. At the beginning of the tensile loading, the SEM micrograph of the specimen shows no change, just as pure PP. When up to a certain loading, initial microcracks are triggered and propagated around the plerosphere particles. The microcracks around the plerosphere particles are nearly perpen-

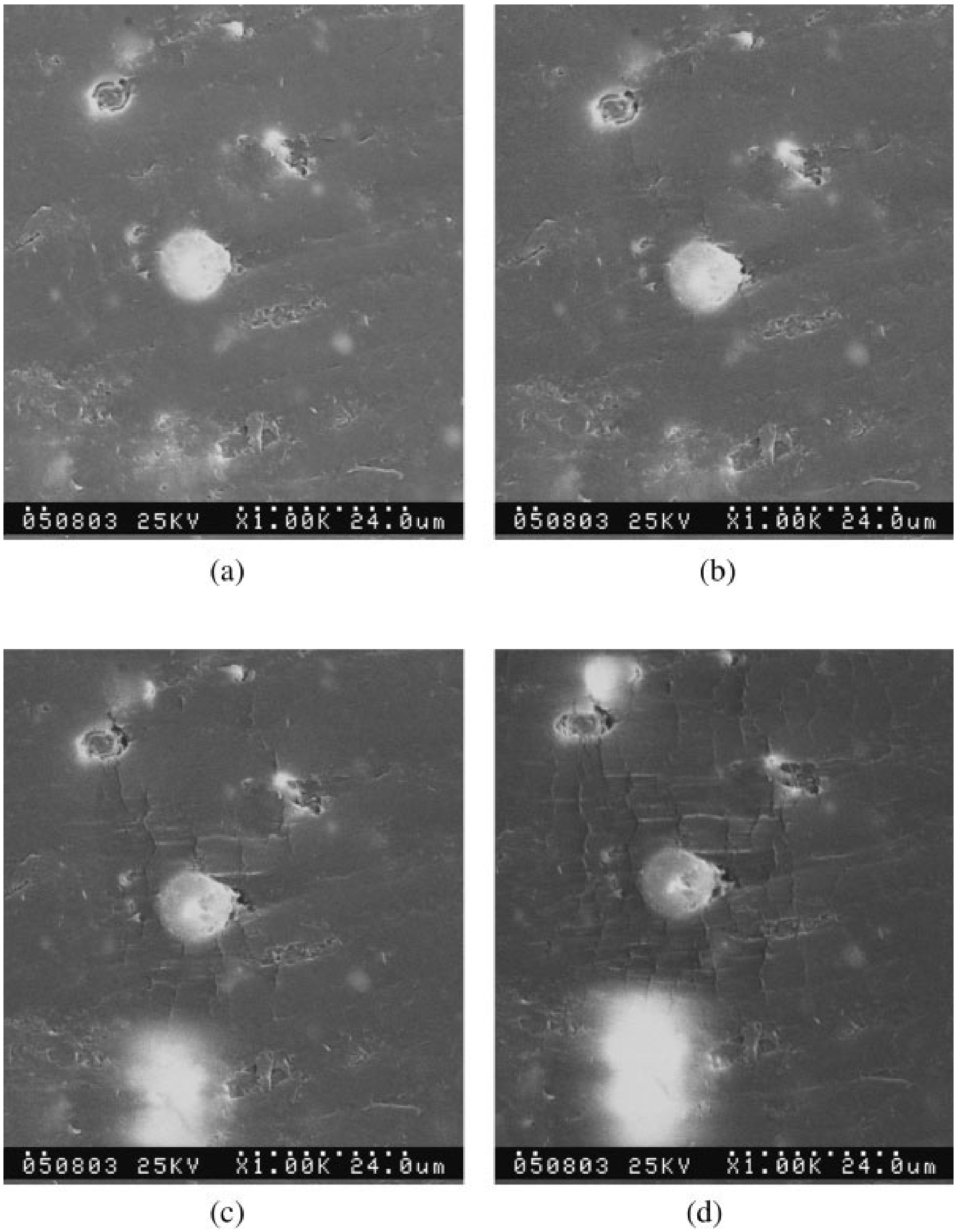


Figure 8 SEM micrograph for the *in situ* observation of the single particle in the composites. (a) Initial condition; (b) form microcracks; (c) propagating much crazing; (d) terminating to another particle.

dicular to the load direction [Fig. 7(a)]. Meanwhile, the partial interfacial debonding between the particles and matrix could be seen at the bright place around the plerosphere particles in Fig. 7[(a,b)]. The microcracks around the dispersed particles increase rapidly and grow up to bigger cracks as the tensile loading increases [Fig. 7(c)], and that many cracks are on the uniform orientation. Then the open crack appears and extends into the break of the composites.

A single particle in the plerosphere/PP composite filled with 20 wt % plerospheres (5 μm) is watched during *in situ* SEM observation to further research microtopography changes around the particles in the matrix (Fig. 8). Figure 8(a) shows the initial condition of the composite specimen without the tensile loading. When the loading reach 67 N, there is no change. When the loading is up to 105 N, there are a little debonding opening between the interface of the particle and matrix. The debonding extends along the interface and that the microcracks are formed as shown in Figure 8(b). When the loading amounts to 175 N, the opening grows up [Fig. 8(c)]. Meanwhile, much crazing is propagated around the plerosphere particles. Evidently these crazing is propagated from one particle and then terminated to another particle [Fig. 8(d)]. When the loading further increases, there is little change around the plerosphere particles. And the microcrack does not rapidly propagate to the dominant crack.

Results show that the pure PP matrix can initiate big cracks in the tensile test by *in situ* SEM observation. On increasing the loading, the bigger one of the cracks is extended into the dominant crack rapidly and then the pure PP matrix breaks. It means that the main energy absorption is in the crack initiation. While plerospheres are filled into PP matrix, mass microcracks are triggered round the dispersed particles under the tensile loading. The crack is either terminated when it meets another particle or branched into mass finer crazing instead of the breaking crack directly increasing with the test loading. The process of the crack initiation, propagation, and termination dissipate a great amount of energy. Meanwhile, in the process of the tensile loading, partial interfacial debonding between the particle and matrix can prevent the propagation of the crack and promote crack termination. These factors cause improvement of the properties of the composite evidently. The results of the *in situ* observation and analysis to the dynamic process supply effective test evidence for the toughening mechanism of the plerosphere/PP composite on the basis of the energy dissipation theory.

CONCLUSIONS

Mechanical properties of the composites, such as the notched Izod impact strength, tensile properties, and flexural properties, are remarkably improved with the addition of the surface-modified plerospheres, and the toughness, strength, and rigidity of the composites are improved simultaneously.

The dynamic tensile process of the pure PP and plerosphere/PP composites are observed with SEM. Results show that the pure PP matrix can initiate the big crack directly under the tensile loading, and extend to the breaking crack rapidly as the tensile loading increases. While plerospheres are filled into PP matrix, mass microcracks are triggered and consume tremendous energy. The crack is either terminated when it meets another particle or branched into mass crazing instead of the breaking crack directly. Meanwhile, during the process of tensile loading, partial interfacial debonding between the particle and matrix can prevent the propagation of the crack. All of these factors can prevent and delay the crack extending into the big breaking crack in the plerosphere/PP composites, and cause the improvement of the properties of the composite evidently.

In situ observation and analysis experimental results show that energy dissipation is the major factor of reinforcing and toughening mechanism. *In situ* observation and analysis to the dynamic process supply effective experiment evidence for the toughening mechanism of the plerosphere/PP composite on the basis of the energy dissipation theory.

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