JOURNAL OF MATERIALS SCIENCE **39** (2004) 3475–3478

Polypropylene composites filled with *in-situ* grafting polymerization modified nano-silica particles

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Polymeric nanocomposites consisting of inorganic nano-sized building blocks and organic polymers represent a new class of materials owing to their unique properties resulting from the nano-scale microstructure. Mechanical properties of these composites can be improved significantly at rather low filler content if the ultrafine phase dimensions of the nanoparticles are maintained [1, 2]. However, homogeneous dispersion of nanoparticles in polymers is very difficult because the particles possessing high surface energy tend to agglomerate during melt blending [3–5], the most optimum compounding technique for mass production of nanocomposites with cost-effectiveness. As a result, catastrophic failure would take place easily in the nanoparticle agglomerates when the composites are subjected to the applied force, leading to rather poor performance of the composites.

To decrease the surface energy of the nanoparticles, surface treatment of nanoparticles is necessary. Many approaches have been proposed so far, including coupling agents [6, 7] and grafting modification [8–11]. Since coupling agents can only react with the exterior particulates of nanoparticle agglomerates, the friable structure of the agglomerated nanoparticles has to be maintained in the composites, which provides neither reinforcing nor toughening effects [12]. Comparatively, modification of nanoparticles through graft polymerization is much more effective to construct nanocomposites because of (i) an increase in hydrophobicity of the nanoparticles that is beneficial to the filler/matrix miscibility; (ii) an improved interfacial interaction yielded by the molecular entanglement between the grafting polymer on the nanoparticles and the matrix polymer; and (iii) tailorable structure-properties relationship of the nanocomposites provided by changing the species of the grafting monomers and the grafting conditions as different grafting polymers might bring about different interfacial characteristics.

Considering that grafting polymerization onto nanoparticles prior to blending with polymer matrix would produce some compact agglomerates that are hard to be split by the limited shear forces offered by conventional mixers [10], the *in-situ* grafting polymerization approach is adopted in this work to solve the problem. Concretely speaking, a planetary ball mill is designed to deal with the surface pretreatment of nanoparticles. The intentions of ball milling are to make grafting monomer penetrate into the nanoparticle agglomerates covering the surfaces of nanoparticles uniformly, and to initiate slight grafting polymerization onto the particles by mechanochemical effect. *In-situ* grafting polymerization is completed together with the matrix polymer in the subsequent melt mixing process when the mixer of a torque rheometer is employed. The objective of this communication is to show how efficiently the mechanical properties of polypropylene can be improved by the above route using nano-silica as the filler.

Isotactic polypropylene (PP) homopolymer powder (type F401, melting flow index = 6.7 g/10 min) supplied by Guangzhou Petroleum Chemical Co., China, acts as the matrix polymer and precipitated SiO_2 (average diameter = 10 nm, specific surface area = 640 m^2/g) produced by Zhejiang Zhoushan Mingri Nanomaterials Ltd., China, is selected as the filler. Commercial butyl acrylate (BA) is used as the grafting monomer without further purification. Dicumyl peroxide (DCP) is used as the initiator. The nanoparticles were preheated at 140 °C under vacuum for 5 hr to eliminate the possible absorbed water on the surface of the particles. A mixture of monomer/nanoparticles and a certain amount of initiator was ground by a planetary ball mill at 500 rpm for 2 hr under atmosphere at room temperature. Then PP powder and antioxidant were added into the system and ground for an additional 1 hr. The pretreated mixture of PP and nano-silica were compounded in the mixer of Haake Rheocord 300 p torque rheometer at 180 °C for 10 min for carrying out *in-situ* grafting polymerization onto the nanoparticles. The resultant composites are denoted

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by SiO_2-g-PBA/PP in the following discussion (where SiO_2-g-PBA means poly(butyl acrylate)-grafted nano-SiO_2). For a comparitive study, two other types of composites were also manufactured. One consisted of PP and nano-silica as-received (i.e., SiO_2/PP), and the other was prepared by melt mixing PP, nano-silica, and butyl acrylate without the pretreatment in the ball mill. The specimens for mechanical tests were prepared using an injection-molding machine. Tensile testing was conducted on ASTM D638-98 Type V specimens by a Hounsfield H10K-S universal testing machine at a crosshead speed of 50 mm/min. According to ISO 179-2, notched Charpy impact strength was determined by an API advanced pendulum impact tester at a rate of 3.8 m/s. The dimensions of the specimens were 80 × 10 × 4 mm^3 and were notched with an ASN automatic sample notcher. The initial crack length of 2 mm and a span of 40 mm were selected. The fractured surfaces were studied by a JEOL-5400 scanning electron microscope (SEM).

The basic tensile properties of the composites including tensile strength and Young's modulus are shown in Fig. 1. It can be seen that the addition of untreated nano-silica results in decrease in the composites' tensile strength, while the particles modified by *in-situ* grafting are able to generate reinforcing effect (Fig. 1a). Clearly, the composites with untreated nanoparticles follow the general law of micro-particulate composites, i.e., the incorporation of the fillers always weakens the strength of the unfilled matrix due to the poor interfacial interaction [13]. It implies that the nanoparticles appear in the composites in the form of large agglomerates and cannot provide load-bearing capacity. In contrast, the *in-situ* grafted nanoparticles exhibit reinforcing ability even at a rather low filler content. The applied stress can be effectively transferred to most of the particles due to the appearance of the grafting macromolecular chains as expected. The results demonstrate that (i) the grafting treatment has brought the positive effect of the nanoparticles into play, and (ii) the pretreatment using ball milling is necessary because of the even mixing of the particles and the grating monomers. Compared to the case of strength property, the grafted nanoparticles are not as effective as their untreated version in stiffening the matrix polymer (Fig. 1b). In spite of the fact that the Young's moduli of all the composites increase with a rise in the filler content, the lower Young's moduli of the composites with the grafted nanoparticles result from the shielding effect of the grafting polymers, which build up a compliant interlayer and lower the stress transfer efficiency in the elastic deformation region. The significantly lower stiffening ability of the SiO_2-g-PBA/PP composites, prepared without ball milling pretreatment of the nanoparticles, is again indicative of the uneven distribution of the grafted nanoparticles.

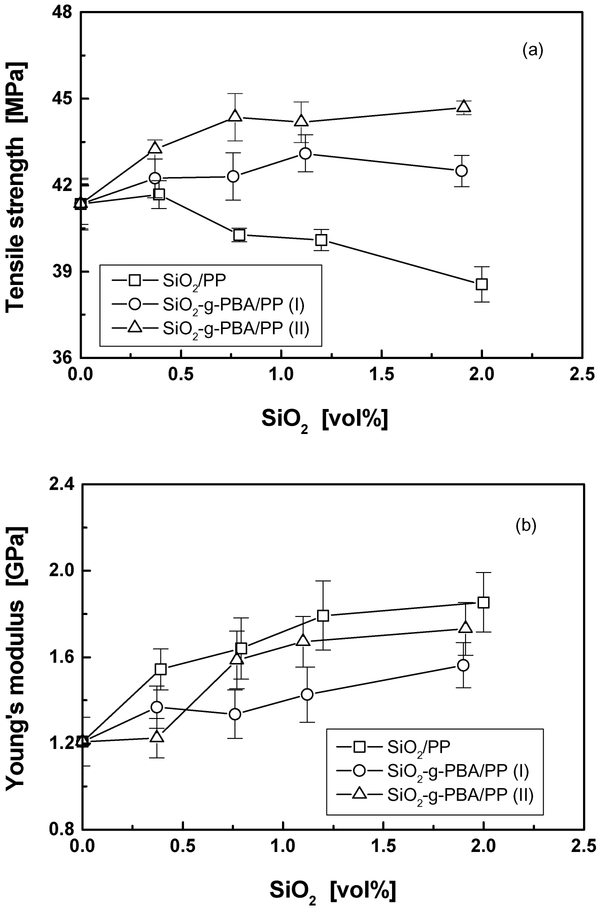

Figure 1 Tensile properties of PP composites as a function of nano-SiO_2 volume fraction: (a) tensile strength, (b) Young's modulus. SiO_2/PP denotes untreated nano-silica filled PP composites. SiO_2-g-PBA/PP (I) symbolizes the composites prepared by adding all the ingredients into the mixer of the torque rheometer, and SiO_2-g-PBA/PP (II) the composites obtained by using the ball milling pretreated nano-silica.

Besides the increase in strength and modulus, it is seen from Fig. 2 that the impact strengths of the nanocomposites can also be improved by low loading nano-silica, especially when the particles are treated by grafting. In comparison to the PP composites filled with nano-silica pretreated by irradiation graft polymerization [2, 5], which possess high notch sensitivity, the current versions prove that the methodology proposed in this work is a feasible way to improve the notch ductility of PP.

To look into the mechanism involved, SEM micrographs of the impact fractured surfaces of the composites are shown in Fig. 3. In the case of nano-SiO_2/PP composites (Fig. 3a), severe agglomeration of the nanoparticles is observed, which acts as the stress concentrator leading to the rupture of the specimen at

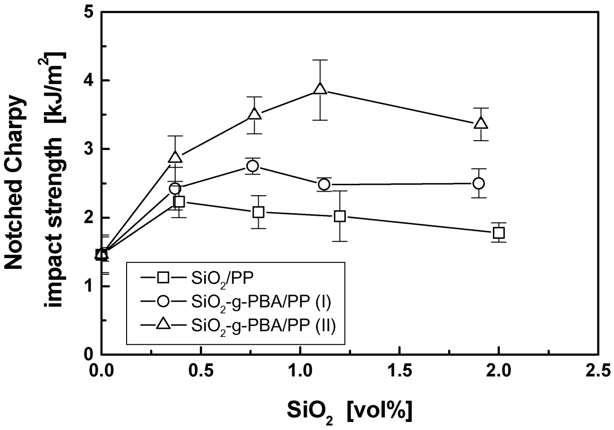

Figure 2 Notched Charpy impact strength of PP composites as a function of nano-SiO_2 volume fraction. The symbols of the composites have the same meanings as those described in the caption of Fig. 1.

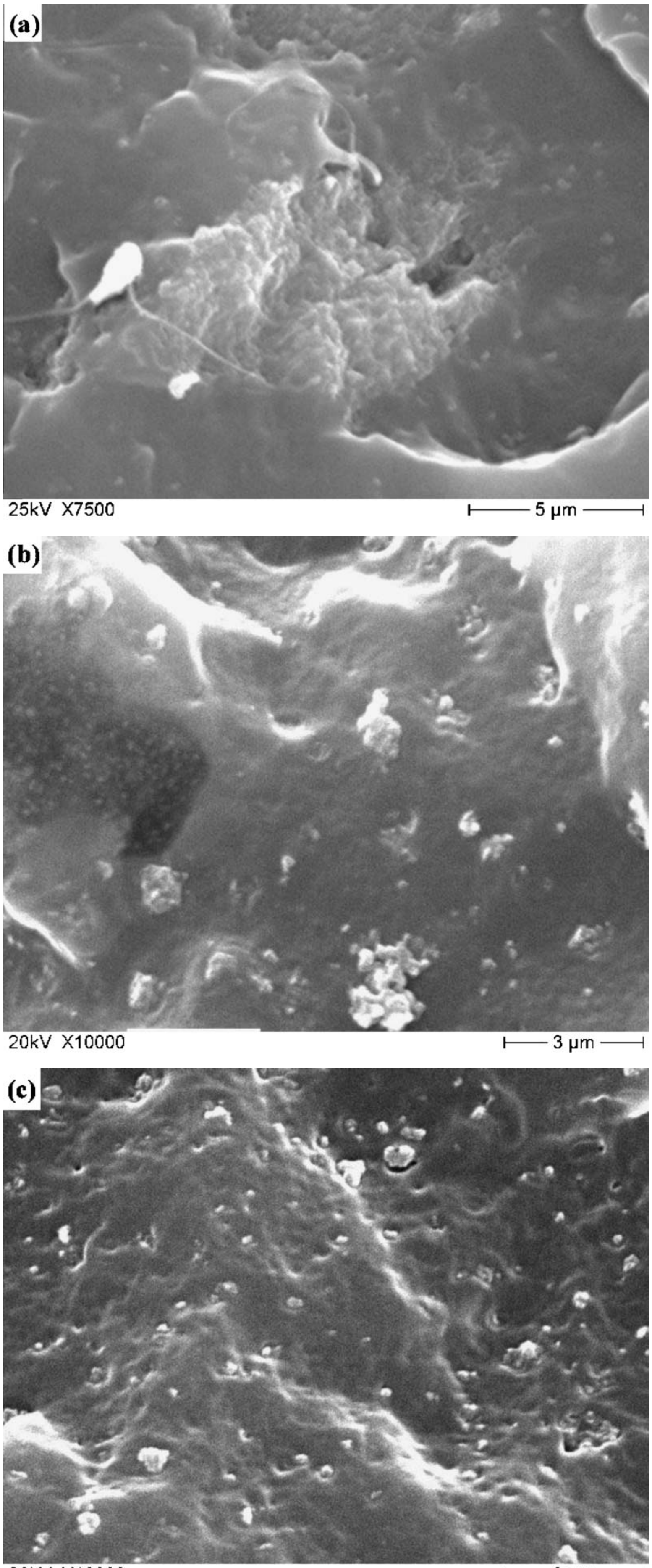

Figure 3 SEM micrographs of notched Charpy impact fractured surface of (a) SiO_2/PP (content of nano-SiO_2 = 1.20 vol%), (b) SiO_2-g-PBA/PP (I) (content of nano-SiO_2 = 1.12 vol%), and (c) SiO_2-g-PBA/PP (II) (content of nano-SiO_2 = 1.10 vol%). The symbols of the composites have the same meanings as those described in the caption of Fig. 1.

low stress level. When the nanoparticles were not pretreated with the grafting monomers in the ball mill but mixed with all the ingredients in the torque rheometer, the corresponding composites exhibit limited and localized dispersion of the particles in the matrix (Fig. 3b). The situation is greatly changed for the composites with ball milling pretreated nano-silica (Fig. 3c). It is seen that the nanoparticles are well dispersed, manifesting that the grafting monomers with low molecular weight can penetrate into the agglomerated nanoparticles during ball milling, react with the activated sites of the nanoparticles inside as well as outside the agglomerates, and eventually break down the agglomerates in the subsequent *in-situ* grafting step. These highly dispersed nanoparticles and the strong interfacial interaction between the grafted nanoparticles and the matrix are believed to favor the pinning effect in the case of crack propagation [14]. As a result, the composites acquire high impact resistance.

In conclusion, the present study demonstrates that both reinforcing and toughening effects of nano-silica on PP can be brought into play by *in-situ* grafting modification of the nanoparticles. With the help of ball milling pretreatment, the nanoparticle agglomerates are broken down and the grafted nanoparticles obtained in the subsequent melt mixing are uniformly dispersed in the matrix polymer. The proposed technical route is proved to be feasible for fabricating inorganic nanoparticles/polymer composites with cost-effectiveness.

Acknowledgments

The authors are grateful to the support of the Deutsche Forschungsgemeinschaft (DFG FR675/40-1) for the cooperation between the German and Chinese institutes on the topic of nanocomposites. Further thanks are due to the Team Project of the Natural Science Foundation of Guangdong, China (grant no. 20003038).

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Received 19 September 2003
and accepted 23 January 2004