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LETTER

Effects of reactive compatibilization on the performance of nano-silica filled polypropylene composites

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Nano-sized inorganic particles have been widely used in recent years as fillers in polymers to improve their toughness [1, 2] and tribological performance [3, 4]. However, homogeneous dispersion of the nanoparticles in polymeric matrices is very difficult because the particles with high surface energy are easy to agglomerate. In addition, the hydrophilic nanoparticles and the hydrophobic polymers are not compatible in nature, which has to result in poor interfacial bonding. All of these deficiencies obstruct effective utilization of inorganic nanoparticles in polymer composites. To lower surface energy of inorganic nanoparticles, surface pre-treatment that aims at improving dispersibility of the powders in polymers and tailoring the interfacial interaction is highly desired. Many approaches have been proposed so far, including coupling agents [5, 6] and grafting modification [7–10], whereas most of them did not consider the possibility of reactive compatibilization. As a result, physical interaction generally predominates the interfacial interaction between the treated nanoparticles and polymer matrices.

In our previous works [2, 8, 9, 11, 12], graft polymerization of polystyrene, poly(methyl methacrylate), poly (ethyl acrylate) and poly(butyl acrylate) was employed to modify inorganic nanoparticles like silica and calcium carbonate, which were then mechanically compounded with polypropylene (PP) as usual. Mechanical tests of these PP composites showed simultaneous improvement of stiffness, strength and toughness. However, it is worth noting that the grafted polymers adhered to the nanoparticles are not miscible with the matrix. The method could not induce thermodynamic compatibility in the composites. The enhancement of the grafted nanoparticles/PP composites were believed to be due to chain entanglements at the interface and amendment of the friable structure of the nanoparticle agglomerates.

It is known that two polymers would form a compatible mixture when they have functional groups capable of generating covalent, ionic, donor–acceptor, or hydrogen bonds between them. On the basis of this principle, the effect of reactive compatibilization can be obtained. That is, the addition of a reactive polymer, miscible with one blend component and reactive towards functional groups attached to the second blend component results in the ‘‘in situ’’ formation of block or grafted copolymers [13]. It has been demonstrated that reactive compatibilization appears to produce the best blend compatibilization [14]. Accordingly, to further bring the positive effects of nanoparticles into play, the authors of the present work planed to introduce the concept of reactive compatibilizing into nanoparticles filled PP composites as follows.

Firstly, nano-silica particles were chemically grafted with poly(glycidyl methacrylate) (PGMA) that possesses reactive epoxide groups. The grafted particles were then melt blended with PP and amine functionalized PP (PP-g-NH_2). The latter was applied as the reactive polymer (i.e. reactive compatibilizer) because it is able to react across the melt phase boundary during the short blending time. Taking the

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advantage of the reaction between epoxide and amine groups, chemical bonding can be built up at the filler/matrix interface. The current communication evaluates the feasibility of the above technical route in terms of mechanical properties. It is hoped that a new methodology for manufacturing nanoparticles/polymer composites can be established.

Isotactic PP homopolymer H1500 (melt flow index=10.5 g/10 min, 230 °C, 2.16 kg; number average molecular weight, $M_n = 7.9 \times 10^4$) was used as matrix and nano-sized SiO_2 (Aerosol 200, Degussa Co. Germany) with an average primary size of 12 nm and a specific surface area of 200 m^2/g was selected as the filler. Prior to the pre-treatment via graft polymerization, double bonds were introduced onto the surface of SiO_2 nanoparticles by treating the particles with a silane coupling agent (γ-methacryloxypropyl trimethoxy silane, KH570). The content of KH570 attached to SiO_2 surface was 6.20 wt% as detected by thermogravimetric analysis (TGA) (i.e. the average number of KH570 units per surface area of nano-SiO_2 was 0.66 mol/nm^2, according to the estimation method proposed in Ref. [14]). For conducting graft polymerization of glycidyl methacrylate (GMA) onto the silane treated SiO_2, the latter was mixed with toluene under sonication for 30 min. Then, the initiator, AIBN (0.018 mol/L) was added with stirring into the reactor that was kept at 80 °C and protected with N_2. The monomer GMA (0.84 mol/L) was charged into the system 5 min later, and the reaction kept for 6 h. Eventually, the nano-silica particles with 42.9 wt% (0.16 mol/nm^2) grafted PGMA (that can not be removed by solvent extraction) was used for the subsequent preparation of PP composites. Number average molecular weight of the ungrafted PGMA was 7×10^3 as determined with a Walter 208LC gel chromatograph (GPC). PP-g-NH_2 ($M_n = 5 \times 10^4$) was produced by melting amination from maleic anhydride grafted PP [15]. Thus, the average number of amine groups per PP-NH_2 chain is 5.2 as calculated from its molecular weight and grafting yield of 1 wt%.

To prepare PP composites, both SiO_2-g-PGMA and PP-g-NH_2 were directly compounded with PP at certain proportion in the mixer of a Haake Rheocord 300p torque rheometer at 180 °C for 15 min. Then the compounds were broken and injected into standard bars for mechanical tests with a Y-350 vertical injection molding machine at 200 °C. 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 XJJ-5 tester.

Tensile strengths of different PP composites are compared in Fig. 1a. Obviously, the incorporation of untreated nano-silica nearly has no effect on enhancement of PP matrix. The nanoparticles even lower tensile strength of the composites when the filler content is higher than 1.3 vol%.

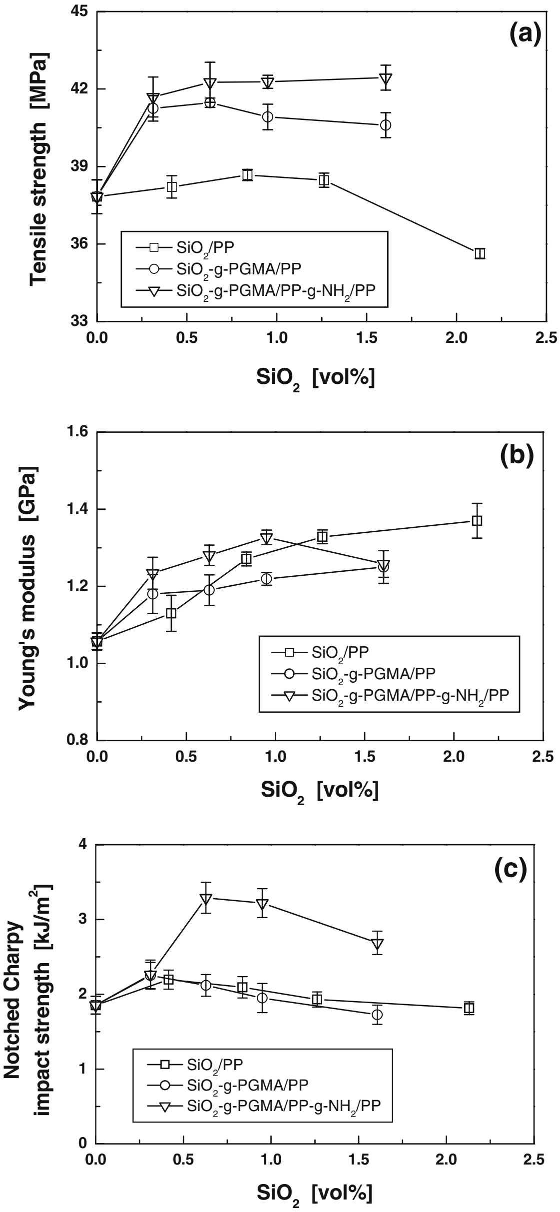

Fig. 1 Tensile strength (**a**), Young's modulus (**b**) and notched Charpy impact strength (**c**) of various PP composites as a function of nano-silica content. The content of PP-g-NH_2 is 10 vol% for SiO_2-g-PGMA/PP-g-NH_2/PP

This can be ascribed to the worse dispersion of silica with increasing filler loading [1]. In contrast, the addition of SiO_2-g-PGMA is able to strengthen PP owing to the improved interfacial interaction originating from chain entanglement between the grafted PGMA and PP molecules. In the case of SiO_2-g-PGMA/PP-g-NH_2/PP system, the highest tensile strength within the filler content range of interests can be observed. It should be related to the reaction of epoxide groups of SiO_2-g-PGMA with amine groups of PP-g-NH_2, which further enhances the interfacial adhesion as expected.

As for the stiffness, all the composites exhibit increasing trends with nano-silica content (Fig. 1b). It is noted that SiO_2-g-PGMA weakens the stiffening effect of nano-silica, while the incorporation of PP-g-NH_2 into the composites imparts a higher modulus to PP than the untreated silica. Again, this should be attributed to the covalent bonding between the grafted SiO_2 nanoparticles and PP-g-NH_2, which increases the interfacial adhesion.

Besides static tensile properties, impact toughness of the composites was also determined (Fig. 1c). It is seen that when the ungrafted nano-silica is added, a mild increase in impact strength of PP is measured up to 0.4 vol% of the filler. With a rise in filler content, however, there is a decreasing trend in impact strength, similar to the case of tensile strength (Fig. 1a). Evidently, the agglomerated nanoparticles at higher concentration are much more difficult to be broken apart by the limited shear force during compounding. For SiO_2-g-PGMA/PP composites, the treated nanoparticles cannot provide remarkable toughening effect as poly(ethyl acrylate) grafted nano-SiO_2 [11], probably due to the brittle feature of PGMA. Nevertheless, the system containing SiO_2-g-PGMA/PP-g-NH_2 performs much better than the others, demonstrating the importance of reactive compatibility in enhancing interfacial adhesion in the composites.

The FTIR spectrum of SiO_2-g-PGMA is given in Fig. 2. The absorption band at 910 cm^{-1} shows the existence of epoxide functional groups. It proves that the nano-silica particles have acquired the desired reactivity. To confirm the reaction between the components in the course of compounding, a model mixture of SiO_2-g-PGMA/PP-g-NH_2 (20/80 wt/wt) was manufactured using the same processing conditions as those adopted for preparing the aforesaid composites. Then it was extracted by toluene for 8 days to remove the unreacted PP-g-NH_2. From the FTIR spectrum of the residue of the compounds after extraction (Fig. 2), it is found that the peak of epoxide groups on SiO_2-g-PGMA becomes weakened, while the characteristic adsorptions of PP (i.e. the multiple peaks at 2820–2962 cm^{-1} corresponding to the stretching modes of C–H in $–CH_2–$, –CH– and $–CH_3$, and the peaks at 1377–1457 cm^{-1} for the bending modes of $–CH_2–$ and $–CH_3$) and SiO_2 (i.e. the anti-symmetric stretching mode of Si–O–Si at 1100 cm^{-1}) are perceivable. It means that some epoxide groups on SiO_2-g-PGMA have been consumed during the reaction with the amine groups on PP-g-NH_2. In order to identify the yield of this reaction, the same sample was measured by TGA to give the weight ratio of PGMA/PP-g-NH_2. The results indicate that weight loss of the reaction product of SiO_2-g-PGMA/PP-g-NH_2 (20/80 wt/wt) after extraction is 73%, while that of SiO_2-g-PGMA is 33%. Thereby, the weight ratio of PGMA/PP-g-NH_2 is 40/60. In other words, about 8% of epoxide groups of grafted PGMA were consumed in the reaction with PP-g-NH_2, which is consistent with the FTIR spectrum in Fig. 2. It should be pointed that the estimation might be not accurate enough, because extraction of the sample would remove some nanoparticles together with the reaction product.

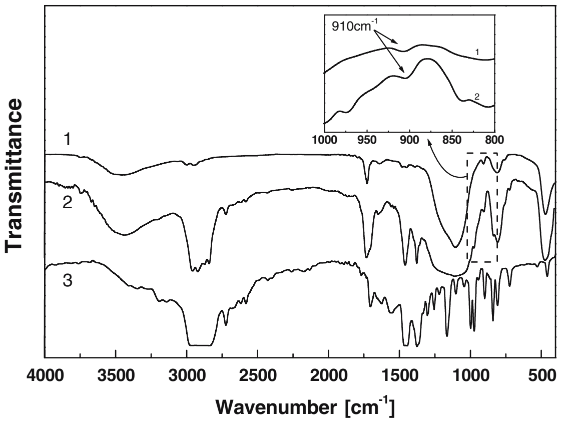

Fig. 2 FTIR spectra of (1) SiO_2-g-PGMA, (2) the residue of the model mixture of SiO_2-g-PGMA/PP-NH_2 after toluene extraction, and (3) PP-NH_2

Since reactive compatibilization has shown its importance in the above discussion, the influence of PP-g-NH_2 content should be known. As illustrated in Fig. 3, both tensile and impact strength of the composites increase with PP-g-NH_2 content up to 10 vol%, and then keep almost constants. The possible reason might be that PP-g-NH_2 tended to encapsulate the PGMA grafted nano-silica, and the extra PP-g-NH_2 cannot take effect at the interface. It should be pointed out that the amount of amine groups on the present PP-g-NH_2 is quite low (~1 wt%). Therefore, a much higher reinforcing efficiency might be attained at lower PP-g-NH_2 content according to the mechanism revealed by Fig. 3.

In conclusion, the current study demonstrated the efficiency of reactive compatibilization in improving mechanical performance of nano-SiO_2/PP by forming chemical

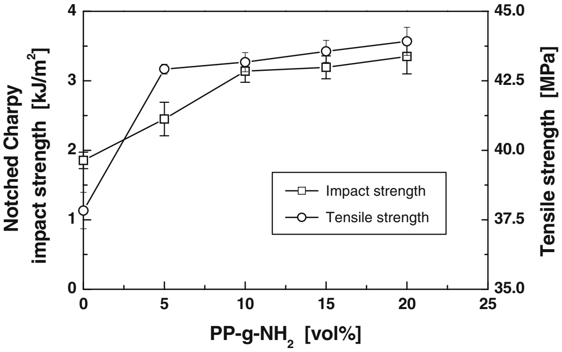

Fig. 3 Notched Charpy impact and tensile strength of SiO_2-g-PGMA/PP-g-NH_2/PP composites as a function of PP-g-NH_2 content. The content of nano-silica is 0.95 vol%

bonding between the components. Further efforts will be made to raise the reactive compatibility and hence mechanical properties of the composites. Also, the influence of different types of reactive compatibility and even cross-linking will be explored.

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