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ORIGINAL PAPER

Location of functionalized-TiO_2 nanoparticle in an immiscible PP/PA6 blends and its effect on the compatibility of the components

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Abstract Nanocomposites based on 70/30 (w/w) polypropylene (PP)/polyamide 6 (PA6) immiscible blends and functionalized-TiO_2 nanoparticles were prepared via melt compounding. The influences of TiO_2 on the morphology of nanocomposites were investigated. Scanning electron microscopy results revealed the domain size of the dispersed PA6 phase decreased in presence of functionalized-TiO_2 and the TiO_2 nanoparticles were preferentially located at the PA6 phase and at the interfacial region between PP and PA6, which were ascertained by differential scanning calorimetry. The functionalized-TiO_2 nanoparticles played the compatibilizer for the immiscible PP/PA6 blends, increasing the interaction of the two phases in certain extent. Therefore, a clear compatibiliting effect was induced by the TiO_2 in the immiscible PP/PA6 blends.

Introduction

Nanocomposites offer new technological and economical benefits. The incorporation of nanometer scale reinforcement (e.g., layered silicates of clay and nanofiber) may dramatically improve selected properties of the related polymer. Numerous researchers described polymer/inorganic nanocomposites on the basis of single-polymer matrix, including polypropylene (PP) [1], polyamide (PA) [2]. In recent

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years, there has been intense interest in multiphase polymer blends due to the potential opportunities of combining the attractive features of each blend component while at the same time reducing their deficient characteristics [3]. However, binary blends of immiscible polymers generally exhibit poor mechanical properties due to most homopolymer pairs are immiscible, they form phase-separated morphologies having poor mechanical properties, and such as in polypropylene/polyamide blends [4]. Therefore, it is essential to control and stabilize a desired type of morphology in a polymer blend in order to generate polymeric materials with favorable properties. In principle, there are two ways to overcome the phase separation in an immiscible polymer blend. The first approach is to add block or graft copolymers to immiscible polymer blend, which are covalently connected immiscible blocks, have demonstrated very effective compatibilization activity in immiscible blends [5]. A second method is addition of inorganic fillers to an immiscible polymer blend, which provides an alternative way to modify its interfacial properties. Some publications reported the compatibilization effect of organoclay on immiscible polymer blends. For example, Gelfer et al. [6] as well as Wang et al. [7] observed a drastic enhancement of the degree of dispersion in blends of PS/PMMA and PS/PP modified with organoclay. Adding of organoclay has resulted in a reduction of the micro-domain size of the dispersed phase in PS/PEMA blends [8]. Wang et al. [9] reported that Nanomer I.30 TC acted as a compatibilizer in blends of PA6 with 10 wt% PP, improving the tensile modulus and strength, but at a cost of impact strength. However, the compatibilization mechanism is not very clear. Location of nanoparticles in immiscible polymer blends remains an important topic for understanding of the mechanism of compatibilization.

Polypropylene (PP) exhibits excellent moisture barrier but poor oxygen barrier properties. On the contrary, Polyamide 6 (PA6) has good barrier against oxygen, but shows poor resistance to water and water vapor. PP and PA6 blending was attempted to achieve improvement in mechanical properties, paintability, and barrier properties [10]. The nanocomposites of either PP [2] or PA6 [3] with layered silicates have been extensively studied. Some literature reported PA6/PP blend modified by organoclay and found that the organoclay is well dispersed and preferentially embedded in PA6 phase. However, nanocomposites based on PP/PA6 blend modified by some other nanoparticles having a certain function properties were less involved in studies according to the open literature. Adding TiO_2 nanoparticles to PP/PA6 blends can generate excellent mechanical nanocomposites with high antimicrobial and anti-aging properties. Further, PP/PA6/functionalized-TiO_2 combinations form a very good model system for evaluating the compatibilization activity of the TiO_2. The compatibilizations of TiO_2 nanoparticles were investigated by SEM. Further, the possible chemical reactions between PP, PA6 and functionalized-TiO_2 were proposed.

Experimental

Materials

Polypropylene (PP) was supplied by Titan Himont Polymer (M) Sdn. Bhd. (Malaysia) and polyamide 6 (PA6) used in this study was a commercial product from Toray Nylon Resin Amilan (Japan). PP-g-MAH is Maleic anhydride grafted PP and was synthesized in our lab. TiO_2 nanoparticles were obtained from Zhoushan Mingri Nanomaterials Co., Ltd, (China) and the mean particle size is 20 nm.

Specimen preparation

TiO_2 nanoparticles were dried for 24 h at 110 °C under vacuum. The functionalization procedure was carried out as following: in a typical experiment, a mixture with 6.0 g γ-glycidoxypropy1 trimethoxysilane dispersing in 100 ml anhydrous ethanol was placed in an ultrasonic bath for 30 min, and then the solution mixed with 300 g TiO_2 nanoparticles in a high speed mixer. Melt compounding of the PP/PA6 based compounds at fixed mass ratio of 70/30 were done on counter-rotating twin screw extruder. The extrusion zone temperature ranged from 220 to 240 °C. Prior to extrusion, PA6 pellets and were dehumidified by using a vacuum oven at 80 °C for 8 h. The extrudates were pelletized with the Haake pelletizer. The pellets were injection molded into standard tensile bar using a Niigata AN 50 injection molding machine. Injection molding temperature ranged from 220 to 240 °C. Prior to injection molding, all pellets were dehumidified in vacuum oven at 80 °C for 8 h.

SEM observation and thermal analysis

The fracture surfaces of selected PP/PA6 based compounds were inspected in a scanning electron microscope (SEM, JSM-6360LV). The fracture surface was coated with a thin layer of gold to avoid electrostatic charging during examination. The crystallization behaviors of the compounds were studied under nitrogen atmosphere by differential scanning calorimetry (TA DSC Q 10), using 5–8 mg sample sealed into aluminum pans. In order to avoid any effect of moisture, all the test specimens were dried using vacuum oven at 80 °C prior to the measurements. The temperature was raised from room temperature to 250 °C at a heating rate of 40 °C/min, and after a period of 5 min it was swept back at 10 °C/min. In order to erase the thermal history, after 1 min second heating similar to the first at a heating rate of 10 °C/min was then performed.

Results and discussions

Phase morphology of PP/PA6 blends

To investigate the compatibilization of functionalized-TiO_2 on the immiscible PP/PA6 blend, the fractured samples were etched in formic acid for 24 h to distinguish the phases, which selectively removed the PA6 phase; that is, the holes in the SEM micrographs represent PA6 domains and the results are shown in Fig. 1.

Figure 1a shows the morphology of the fracture surface of PP/PA6 blend without compatibilizer. In this blend, large PA6 particles dispersed in the PP matrix can be seen and the domain size is about 10 μm. These particles debonded

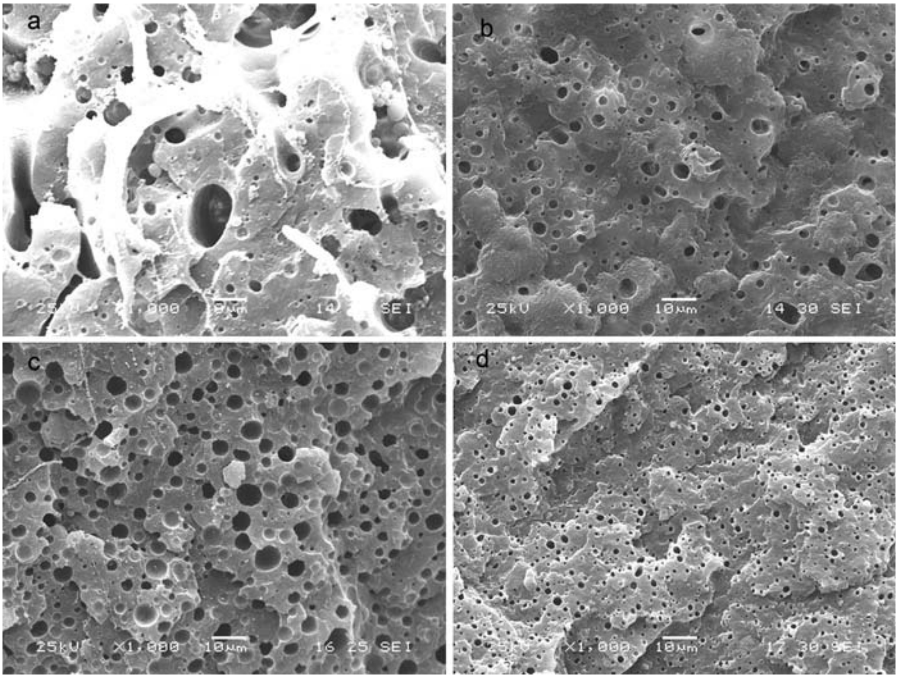

Fig. 1 SEM micrographs of PP/PA6 (**a**), PP/PA6/PP-g-MAH (**b**) PP/PA6/functionalized-TiO_2 (**c**) and PP/PA6/PP-g-MAH/functionalized-TiO_2 (**d**)

easily from the PP matrix and the slick interface was observed because of the weak interfacial adhesion. Figure 1b shows the morphology of PP/PA6 with 5.0 wt% loading of PP-g-MAH, both the interparticle distance and the size of the dispersed PA6 phase are found decrease to 2–3 μm. With the incorporation of 2.0 wt% functionalized-TiO_2 into PP/PA6 blends, the PA6 domain size reduced to about 4 μm and most of the domain shape is ellipsoidal (Fig. 1c), indicating the functionalized-TiO_2 have strong compatibilization on PP/PA6 blends. Figure 1d shows the morphology of the fracture surface of PP/PA6/PP-g-MAH/TiO_2 nanocomposite, PA6 domain dispersed in the PP matrix can be seen and the domain size is about 1 μm. The incorporation of the PP-g-MAH into the PP/PA6/functionalized-TiO_2 blends mildly affected the dispersed phase PA6 domain size. This indicates that the addition of PP-g-MAH can promote the functionalized-TiO_2 disperse uniformly in the PP/PA6 blends.

Thermal analysis of study composites

To elucidate the thermal behavior of PP/PA6 and PP/PA6 based composites, the DSC thermograms were measured. The related data and curves are shown in Table 1 and Fig. 2, respectively.

It can be seen from Table 1 and Fig. 2 that the crystallization temperature (T_c) for PP phase remained unaltered with the addition of functionalized-TiO_2.

Table 1 Thermal properties of PP/PA6, PP/PA6/gPP and their nanocomposites

Sample	Mass ratio	PP phase			PA6 phase (dispersed phase)		
		T_0 (°C)	T_c (°C)	$-\triangle H_c$ (J/g)	T_0 (°C)	T_c (°C)	$-\triangle H_c$ (J/g)
PP/PA6	70/30	126.30	122.28	83.74	189.98	186.82	35.5
PP/PA6/gPP	70/30/5	130.48	124.31	82.41	187.97	184.09	41.30
PP/PA6/TiO_2	70/30/2	126.80	122.12	87.94	192.25	188.25	46.75
PP/PA6/gPP/TiO_2	70/30/5/2	129.09	124.92	82.36	190.80	186.66	38.94

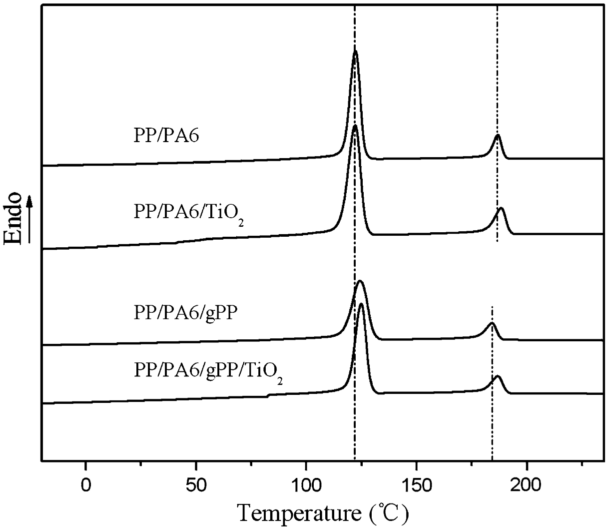

Fig. 2 DSC thermograms of PP/PA6, PP/PA6/PP-g-MAH and their nanocomposites

However, the T_c for PA6 phase slightly increased with the incorporation of functionalized-TiO_2. For instance, the T_c for PP phase in PP/PA6 blend is 122.28 °C, when 2 wt% functionalized-TiO_2 were added to the PP/PA6 blend, the T_c is 122.12 °C, i.e. remained unchanged. However, the T_c for PA6 phase was increased from 186.82 to 188.25 °C. As far as PP/PA6/PP-g-MAH blend is concerned, the T_c for PP phase is 124.31 °C and the T_c for PP is 124.92 °C, as expected the T_c for PA6 phase increased from 184.09 to 186.66 °C. These results firmly revealed that the functionalized-TiO_2 are mainly dispersed in the PA6 phase, whereas the thermal behavior of the PP matrix is practically unaffected by the presence of the functionalized-TiO_2. Moreover, functionalized-TiO_2 also affect the crystallization ability of two phases and the enthalpies for the crystallization transitions of PP and PA6 indicated the functionalized-TiO_2 have much influences on PA6 phase, which indicated a strong interaction and adhesion between the PP, PA6 and functionalized-TiO_2.

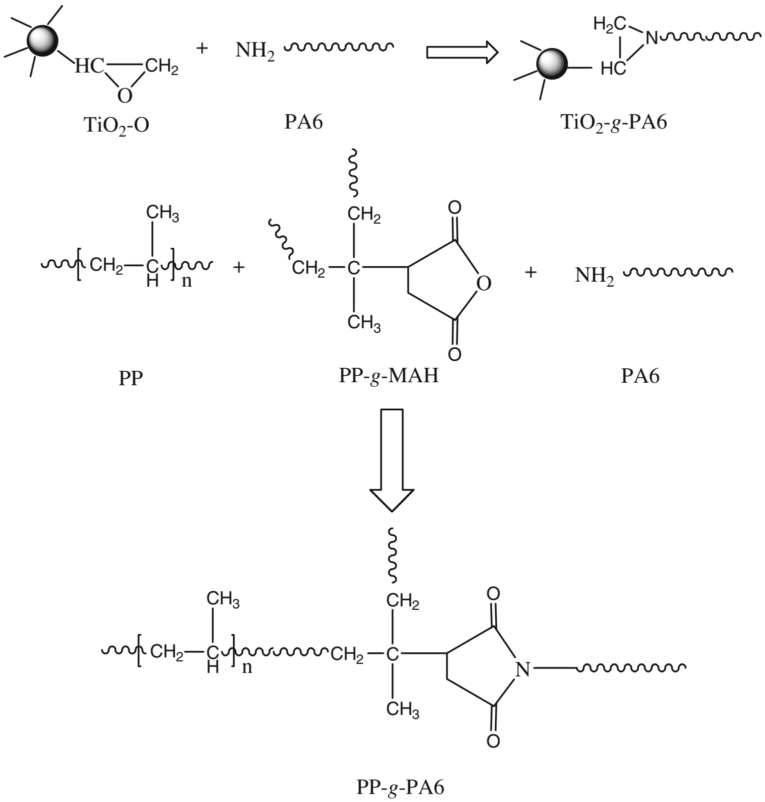

Fig. 3 Possible chemical reactions between PP, PP-g-MAH, PA6 and functionalized-TiO_2

Schematic mechanism of compatibilization

The possible chemical reactions between PP, PP-g-MAH, PA6 and functionalized TiO_2 during melt compounding are proposed in Figure 3 PA6, a polar polymer, has amino groups in its main chains, which could react with the epoxy groups at TiO_2 surfaces, resulting in a portion of PA6 grafted at TiO_2 surfaces. In the presence of PP-g-MAH, a PP-g-PA6 copolymer might have resulted. When PP-g-MAH is added to PP/PA6 blends, the anhydride group reacts with the terminal amino group of PA6 during melt mixing, resulting in the formation of PP-g-PA6 copolymer, which was in line with the founding of Chow et al. [11]. The functionalized-TiO_2 are uniformly dispersed in the PP/PA6 blends, more or less, the TiO_2 play the role of coupling species between the two homopolymers, increasing the interaction of the two phases. Besides, the TiO_2 act as barriers to the assembly of the domains, kinetically prevent the expansion of the domain. This action becomes more intense in presence of PP-g-MAH probably because the space available for domain formation becomes more limited.

Conclusions

The affinity between the PA6 and functionalized-TiO_2 was better than that of the PP and TiO_2 and the TiO_2 were preferentially located at the PA6 phase, which were consistent with the result of DSC analysis because of the epoxy groups at TiO_2 surfaces can react with the amino groups in polar PA6 chains. In the morphological studies by SEM, the sizes of the PA6 droplets were decreased in presence of the functionalized-TiO_2, which played the role of a coupling species between the two polymers, indicating the functionalized-TiO_2 have a strong compatibilization on the PP/PA6 blends.

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