

In situ compatibilization of polypropylene and polystyrene-grafted nano-sized TiO₂ in the presence of Friedel–Crafts catalyst

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Abstract

In situ compatibilization of polypropylene (PP) and polystyrene-grafted nano-sized TiO₂ (TiO₂-g-PSt) was carried out by melting compounding process in the presence of Friedel–Crafts (FC) catalyst, AlCl₃/styrene(St), to give the PP/TiO₂-g-PSt nanocomposite. The resulting materials were investigated by the Fourier-transform infrared spectra (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and ultraviolet (UV) artificially accelerated aging testing, respectively. The results show that the dispersibility of TiO₂-g-PSt in PP could be improved obviously with the help of FC catalyst, which results in a better resistance to UV aging. The PP/TiO₂-g-PSt nanocomposite containing 2.0 wt.% TiO₂-g-PSt with FC catalyst (AlCl₃/St: 1.0 wt.% /0.3 wt.%) shows a higher percentage of retention in tensile strength, 88.2%, after UV artificially accelerated aging for 15 days.

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1. Introduction

In recent years, the rutile nano-sized TiO₂ (nano-TiO₂) has been studied extensively since it can improve the resistance of polymers to ultraviolet (UV) aging greatly without the shortcomings such as toxicity and short-life compared to the organic additives [1–3]. However, it is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility at the interphase between the hydrophobic matrix and the hydrophilic oxide surface [4]. The raw nano-TiO₂ introduced into polypropylene (PP) by melting compounding process aggregates easily and the existence of agglomerates will decrease the interface area between the matrix and particles, resulting in a poor resistance to UV aging [5].

Many methods have been explored to improve the dispersibility of inorganic nanoparticles in polymer such as sol–gel

blending technique [6], in situ polymerization process [7–9], in situ forming nanoparticles process [10] and polymer encapsulation technologies [11–13] etc. In our previous studies, it was found that the dispersibility of nano-TiO₂ in PP could be improved to a certain extent through the grafting of polystyrene (PSt) at the nano-TiO₂ particles. However, it is difficult for the PSt-grafted nano-TiO₂ (TiO₂-g-PSt) to disperse further at a smaller size (<100 nm) in PP probably for the poor compatibilization at the interphase between PP and PSt.

The Friedel–Crafts (FC) catalyst, AlCl₃/styrene(St), is useful to improve compatibilization of thermoplastic blends containing PSt, because that, a hydrocarbon chain can be chemically bonded to the benzene ring of PSt through alkylation reaction. The resulting graft copolymer (polyolefin-g-PSt) located at the interphase will behave as an in situ compatibilizer for the specific polyolefin/PSt blend [14–16]. Thus, if the FC catalyst is introduced into PP during the melting compounding with TiO₂-g-PSt, the dispersibility of TiO₂-g-PSt in PP might be improved effectively through the in situ compatibilization of PP and PSt grafted at the nano-TiO₂ particles.

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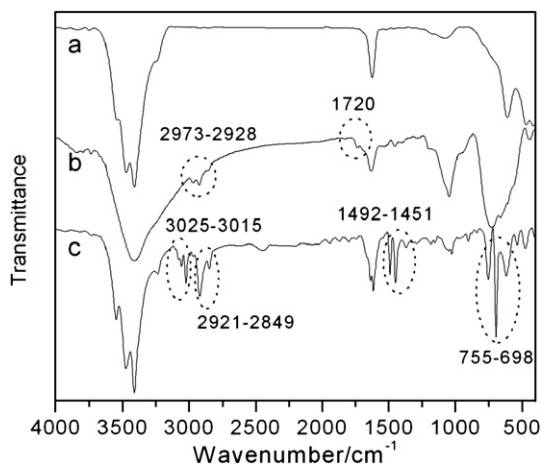


Fig. 1. FTIR spectra of samples: a. raw nano-TiO₂ b. TiO₂-g-MPS c. TiO₂-g-PSt.

In this report, the TiO₂-g-PSt sample was prepared by the dispersion polymerization of St and then introduced into PP by melting compounding process in the presence of FC catalyst to give the PP/TiO₂-g-PSt nanocomposite. The influence of FC catalyst on the dispersibility of TiO₂-g-PSt in PP and resistance to UV aging have been investigated.

2. Experimental

2.1. Chemicals

The nano-TiO₂ (rutile, 50 nm) was purchased from Zhoushan Mingri Nanometer Material Co., Ltd., China. The polypropylene (PP, F401, 2.3 g/10 min) was supplied by Sinopec Yangzi Pet-

rochemical Co., Ltd., China. The monomer, styrene from Aldrich, was purified upon distillation under reduced pressure and the initiator, 2,2'-azobis (isobutyronitrile) (AIBN) from Aldrich, was re-crystallized before use. The coupling agent, 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%) from Acros organics, used as received. Other chemicals used were of AR grade.

2.2. Materials preparation

2.2.1. TiO₂-g-PSt

The TiO₂-g-PSt was prepared according to the following procedure: MPS (4.0 g) and deionized water (0.2 g) were dissolved in 400 ml absolute ethanol, then nano-TiO₂ (4.0 g) dried was introduced and dispersed under ultrasonic irradiation for 30 min. The suspension solution was refluxed in a Wolff bottle (1000 ml) with machine stirring at 80 °C for 6 h. Subsequently, the oligomers of MPS and unreacted MPS were removed from the dispersion by centrifugation. The obtained product, TiO₂-g-MPS (3.0 g), was dispersed in 300 ml isopropanol by ultrasonic irradiation for 30 min, then St (10.0 g) and AIBN (0.2 g) were added at once in the mixture. Under nitrogen atmosphere, the polymerization proceeded with stirring at 80 °C for 20 h. The resulting dispersion was first centrifugated, then the precipitate was purified to remove the PSt homopolymer by 5 cycles of dispersion in toluene and centrifugation. The product, TiO₂-g-PSt, was dried in vacuum at 45 °C for 24 h.

2.2.2. PP/TiO₂-g-PSt nanocomposite

The PP/TiO₂-g-PSt nanocomposite (PPTPSt-10) was prepared by melting blending of 96.7 wt.% PP and 2.0 wt.%

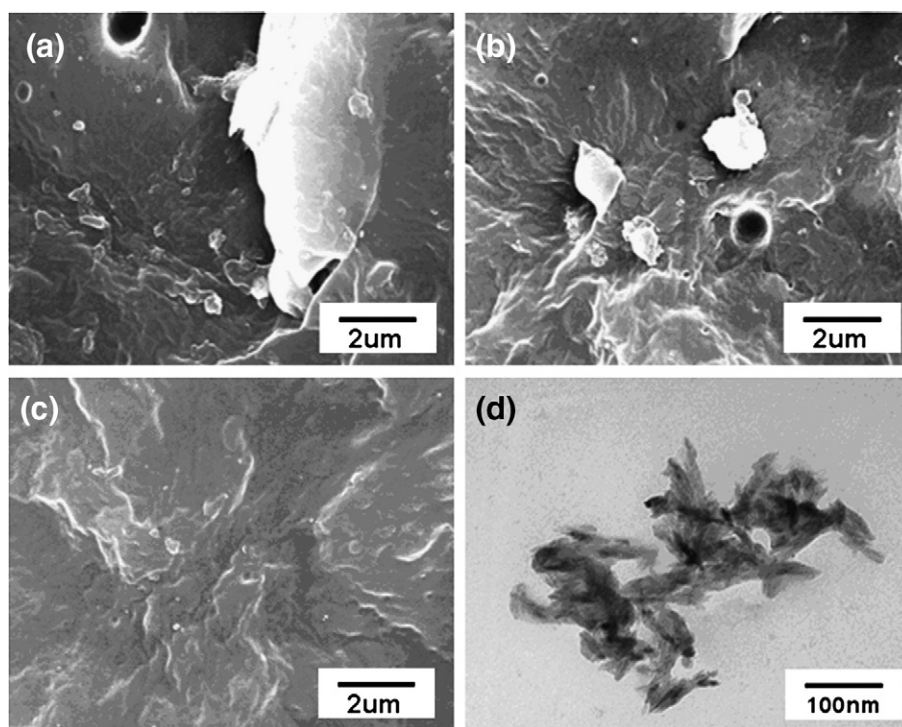


Fig. 2. Micrographs of samples: (a) SEM, PPTM-0 (b) SEM, PPTPSt-0 (c) SEM, PPTPSt-10 (d) TEM, TiO₂-g-PSt.

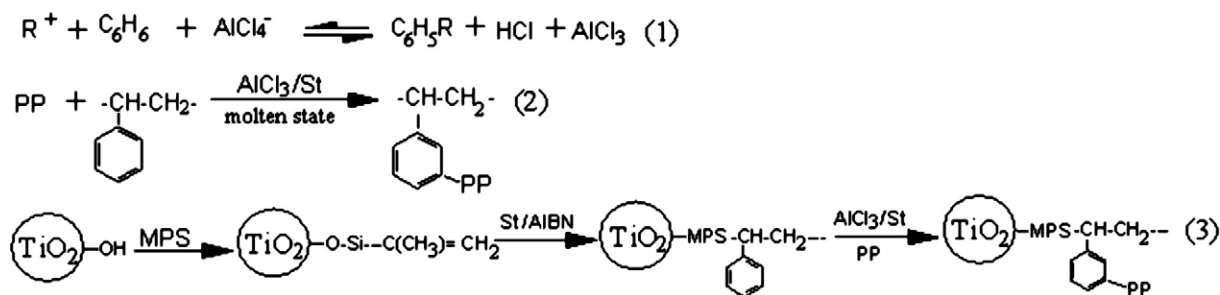


Fig. 3. Scheme for the reaction between TiO_2 -g-PSt and PP in the presence of FC catalyst.

TiO_2 -g-PSt in the presence of FC catalyst ($AlCl_3/St$: 1.0 wt.%/0.3 wt.%). Blending was carried out in a batch mixer (Haake polylab) at 200 °C, 60 rpm for 25 min. Then the resulting product was compressed into a sheet with a thick of 1 mm at 190 °C, 15 MPa for 5 min. For comparison, the PP/ TiO_2 -g-PSt (98 wt.%/2 wt.%, PPTPSt-0), PP/raw TiO_2 (98 wt.%/2 wt.%, PPT-0) and PP/ TiO_2 -g-MPS (98 wt.%/2 wt.%, PPTM-0) nanocomposites without FC catalyst were prepared, respectively, at the same conditions as used for PPTPSt-10 sample.

2.3. Materials characterization

Fourier-transform infrared spectra (FTIR) of samples were obtained from KBr pellets using a Nicolet Avatar 360 spectrophotometer. The morphology of TiO_2 -g-PSt sample was observed by transmission electron microscopy (TEM) at an accelerator voltage of 100 kv. The particles were dispersed in ethanol and then deposited on a Cu grid. The dispersibility of TiO_2 -g-PSt in PP was evaluated using scanning electron microscopy (SEM). The samples were fractured at cryogenic temperature and then coated with Au in a PELCO 91000 sputter coater. The resistance of samples to UV aging was determined by UV artificially accelerated aging testing performed in an UV accelerometer (UVB-313, 3.2 kw, 280–400 nm). Tensile test for samples were carried out on an Instron tester with crosshead speed of 50 mm/min at room temperature. Dogbone tensile specimens (ASTM D638 M, type IV) were cut from plates prepared by compression molding.

3. Results and discussion

Fig. 1 shows the FTIR spectra of raw TiO_2 , TiO_2 -g-MPS and TiO_2 -g-PSt sample. In Fig. 1(b) corresponding to the TiO_2 -g-MPS sample, the characteristic absorptions (cm^{-1}) of 2973–2928 (ν_{C-H}) and 1720 ($\nu_{C=O}$) for MPS are observed indicating that a few MPS molecules have grafted at the TiO_2 particles. For the spectrum (Fig. 1(c)) of TiO_2 -g-PSt sample purified, there are strong characteristic absorptions in the region 1451–1492, 3015–3025, 2849–2921 and 698–755 cm^{-1} , confirming the existence of PSt grafted onto the TiO_2 particles. It can be seen from Fig. 2(d) that the TiO_2 -g-PSt is composed of nano- TiO_2 particles coated by PSt domain with light grey, indicating the encapsulation of nano- TiO_2 particles by PSt is successful.

Fig. 2(a–c) shows the SEM micrographs of samples. Many aggregates with sizes of 0.5–2 μm could be observed from Fig. 2(a), indicating a poor dispersion of TiO_2 -g-MPS in PP. Moreover, the microholes present in the

continuous phase, indicating a poor compatibilization at the interphase between TiO_2 particles and PP, are also found. Elodie Bourgeat-Lami et al. reported that MPS was grafted to the TiO_2 particles under the form of oligomers rather than monomers owing to the influence of a little water in the medium [17]. If those oligomers are too big, the surface of TiO_2 particles will be hindered and grafting will be more difficult, which result in the presence of a large quantity of unreacted hydroxyl groups at the TiO_2 -g-MPS particles and consequently a poorer compatibilization. From comparison with the TiO_2 -g-MPS system, the dispersion of nano- TiO_2 in PP has been improved to a certain extent by the grafting encapsulation of PSt at the nano- TiO_2 particles (Fig. 2(b)). However, the agglomerates with sizes larger than 0.5–1.0 μm and microholes in PP phase are still observed. When the FC catalyst, $AlCl_3/St$ (1.0 wt.%/0.3 wt.%), was introduced into PP, the dispersibility of TiO_2 -g-PSt in PP is improved greatly (Fig. 2(c)). The mean size of nano- TiO_2 domain is in the range of 100–200 nm and no obvious microholes are observed. This can be attributed to the formation of PP-g-PSt copolymer at the interphase between the TiO_2 -g-PSt particles and PP through alkylation reaction. It has been suggested that the styrene monomer can form the initial carbocation in the presence of $AlCl_3$ catalyst. Then the initial carbocation attacks the PP chain, forming a PP macro-carbocation [18]. Subsequently, the PP macro-carbocation substitutes a proton on the benzene ring of PSt, forming the graft copolymer, PP-g-PSt, at the interphase. The general reaction scheme are shown in Fig. 3.

Fig. 4 shows the percentage of retention in tensile strength (PRT) of samples artificially weathered for 15 days. It can be seen that the pure PP shows a lower PRT, only 45.3%, after exposure of 15 days, indicating a severe oxidized degradation. When 2.0 wt.% raw nano- TiO_2 was introduced, the PRT of PPT-0 sample increased by about 9%

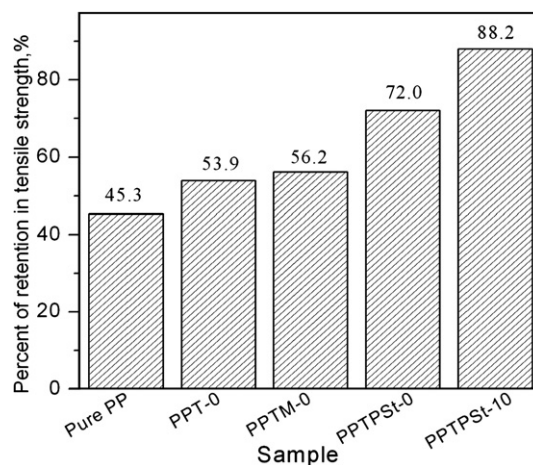


Fig. 4. The percentage of retention in tensile strength of samples weathered for 15 days.

compared to pure PP and a slight enhancement in PRT, only about 3%, is obtained after the surface modification of TiO₂ by MPS. From comparison with the raw nano-TiO₂ or TiO₂-g-MPS system, the PP containing 2.0 wt.% TiO₂-g-PSt shows a higher PRT, about 72.0%, and the PRT is enhanced further from 72% to 88.2% when the FC catalyst, AlCl₃/St (1.0 wt.%/0.3 wt.%), were introduced. This can be attributed to a better dispersion of TiO₂-g-PSt in PP with the help of the FC alkylation reaction. It is well known that nano-TiO₂ is a strong UV light absorber due to its semiconducting properties. The electrons could be promoted to cross the band gap in nano-TiO₂ particles under the action of UV light and consequently the energy of photons is absorbed [19]. A good dispersion of nano-TiO₂ in PP will result in a larger interface area between PP and nano-TiO₂ particles, and a higher resistance to UV aging is expected.

4. Conclusions

The dispersibility of TiO₂-g-PSt in PP could be improved obviously with the help of the FC catalyst and a better resistance to UV aging could be obtained. When AlCl₃/St (1.0 wt.%/0.3 wt.%) are introduced, the PP containing 2.0 wt.% TiO₂-g-PSt shows a higher percentage of retention in tensile strength, about 88.2%, after UV artificially accelerated aging for 15 days.

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