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High-performance TiO_2/polyacrylate nanocomposites with enhanced thermal and excellent UV-shielding properties

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ABSTRACT

High performance TiO_2/polymer nanocomposites with enhanced thermal and excellent UV-shielding properties have been successfully prepared by means of the anatase TiO_2 nanoparticles homogeneously dispersed in the poly (methyl methacrylate/butyl acrylate/methacrylic acid) [P (MMA/BA/MAA)] matrix *via* a miniemulsion polymerization process. Highly crystalline TiO_2 nanoparticles with 5–8 nm diameter, were synthesized by a non-aqueous process and then modified with γ-Methacryloxypropyltrimethoxysilane (A174) to improve the compatibility with polymer. FTIR, TGA and dispersity tests in monomers/water verify that the A174 is chemically bonded onto the surface of TiO_2 nanoparticles. TEM, SEM and EDS analyses indicate that the TiO_2 nanoparticles are homogeneously dispersed in the polymer matrix. TGA and DSC studies confirm that the thermal properties of the resultant nanocomposites are significantly enhanced with respect to the neat polymer. UV–vis transmission spectra results reveal that the films with TiO_2 nanoparticles has an excellent UV-shielding property, even at 1.5 wt% TiO_2 nanoparticles loading can almost block the UV light below 350 nm while still having a high visible transparency. Therefore, the resultant nanocomposite films could be used as transparent UV-shielding materials.

1. Introduction

UV light has many useful applications in human life including lamps, televisions, fluorescence, etc. However, it is responsible for some skin diseases [1,2] and degradation of various materials [3–5], such as polymers, plastics, wood, dyes and pigments. Nowadays more and more researches are focusing on transparent UV-shielding materials [6–12]. Therefore, there is a great significance to develop transparent UV-shielding materials.

Due to the intense absorbability of UV light, some inorganic particles, *e.g.* ZnO [8,9], CeO_2 [10], TiO_2 [11], and etc., are normally loaded to the polymer matrix to prepare UV-shielding materials. By incorporating these inorganic nanoparticles, the polymer matrix has been discovered the enhanced UV-shielding capacity, mechanical, optical and other properties. TiO_2 nanoparticles have attracted mostly attention because of excellent UV-shielding capacity, outstanding visible light transparency and nontoxicity [12]. The key aspect is to disperse the TiO_2 nanoparticles homogeneously into the polymer matrix in order to maintain its desired properties. However, there is a strong tendency for TiO_2 nanoparticles to agglomerate in polymer matrix, which is attributed to their high polarity and large specific surface area [13]. Surface modification of TiO_2 nanoparticles is an effective way to improve its compatibility with polymer. There are several ways to modify the surface of TiO_2 nanoparticles including grafting of silane coupling agents [13,14], capping with surface active agent [15] and absorption of polymeric dispersants [16,17]. Nevertheless, surface modification of TiO_2 nanoparticles by silane coupling agents is the most widely used way, due to the formation of chemical interactions between TiO_2 nanoparticles and polymer [18].

Numerous methods such as mechanical mixing [19,20], sol-gel technique [21–23] and *in situ* polymerization [24–33] have already been developed to prepare TiO_2/polymer nanocomposites. Although the mechanical mixing technique is simple and attractive in industry, it usually produces inhomogeneous nanocomposites with massive agglomeration of TiO_2 nanoparticles. The nanocomposites obtained by sol-gel technique are homogeneous without phase separation. However, sol-gel technique is limited by the strict operation condition and the complicated process. Mallakpour et al. [23] investigated the TiO_2/Polyimide nanocomposites by sol-gel

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technique. However, the obtained TiO_2 nanoparticles in polyimide matrix were amorphous, which limited the optical applications. *In situ* polymerization approach is also used frequently. Inkyo et al. [25] synthesized the transparent TiO_2/PMMA nanocomposites *via in situ* bulk polymerization, assisted by a new type of bead mill technology to improve the dispersity of TiO_2 nanoparticles in MMA. Although a good dispersity of TiO_2 nanoparticle in PMMA was obtained and the nanocomposites were more thermally stable than the pure PMMA, the new type of bead mill technology is energy-consuming and expensive. Džunuzović et al. [26] encapsulated TiO_2 nanoparticle with PMMA by *in situ* free radical polymerization, whereas a large amount of toluene was used, which is poisonous and non-ecofriendly. Nguyen et al. [27] successfully prepared TiO_2/P(MMA-BA) hybrid emulsions *via in situ* RAFT polymerization using macro-RAFT agents. However, the preparation process of macro-RAFT agents was complicated and the macro-RAFT agents may affect the molecular weight distribution of the emulsions [10]. Recently, miniemulsion polymerization has been found to be a very useful method to synthesis nanocomposites because of the droplets nucleation mechanism. In comparison with other polymerization technique, miniemulsion polymerization has the advantages of higher monomer conversion, higher solid content and higher encapsulation efficiency of inorganic nanoparticles [34,35]. Erdem et al. [29–31] studied the encapsulation of TiO_2 nanoparticles with PS by using stabilizer OLOA370 (polybutene–succinimide pentamine) *via* miniemulsion polymerization. A relative high encapsulation efficiency (83% TiO_2 and 73% PS) was achieved, unfortunately, the morphology of the final hybrid latex and the films properties were not presented. What is more, it was required to remove the mineral oil diluent from OLOA 370. This process is time-consuming. Yang et al. [32] prepared TiO_2/PMMA nanocomposite latex by miniemulsion polymerization. The properties of the self-cleaning coatings were improved, but some TiO_2 nanoparticles agglomerates could be observed from the TEM images yet. Jin et al. [33] systematically synthesized TiO_2/polystyrene nanospheres, where TiO_2 nanoparticles assembled to 30 nm clusters and had a good dispersity in the polystyrene matrix, the methodology is scalable to industrial production because of the straightforward process and non-strict operation condition.

As discussed above, the preparation of homogeneous TiO_2/polymer nanocomposites without agglomeration and phase separation *via* a straightforward method is a great challenge. In this work, highly crystalline TiO_2 nanoparticles with an average diameter of 5–8 nm were firstly synthesized by a non-aqueous process and then modified by A174. The A174-modified TiO_2 nanoparticles contained vinyl groups on its surface, which could improve the compatibility between the TiO_2 nanoparticles and the monomers, and further copolymerize with the monomers. Then the A174-modified TiO_2 nanoparticles were successfully incorporated into P (MMA/BA/MAA) matrix with an excellent homogeneous dispersion *via* miniemulsion polymerization. The procedure has some similarities with the strategy reported by Jin et al. [33], while the application background is completely different. The purpose of this report is to fabricate nanocomposites films with outstanding UV-shielding capacity and high visible light transparency. The morphology of the resulted nanocomposite latex was examined by TEM. The dispersion state of the TiO_2 nanoparticles in the nanocomposite films was verified by SEM and EDS. These results shown that TiO_2 nanoparticles were mainly primary, dimer and trimer in the nanocomposites and well dispersed in polymer matrix. The improvement of thermal and UV-shielding properties as well as the transparency of the nanocomposite films were analyzed by DSC, TGA and UV–vis transmission spectra.

2. Experimental

2.1. Raw materials

Titanium (IV) chloride ($TiCl_4$) was obtained from Tianjin Fuchen Chemical Reagent Co., Ltd. (China). Anhydrous benzyl alcohol and diethyl ether was offered by Tianjin Damao Chemical Reagent Co., Ltd. (China). Absolute ethanol (AR, 99.7%) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (China). Silane coupling agent (γ-Methacryloxypropyltrimethoxysilane, A-174) was obtained from Union Carbide Co., Ltd. (America). Commercial methyl methacrylate (MMA, 99%), butyl acrylate (BA, 99%), and methacrylic acid (MAA, 99%) were purified to remove the inhibitors before used. Sodium dodecyl sulfate (SDS), polyoxyethylene sorbaitan monolaurate (Tween-20), hexadecane (HD) and potassium persulfate (KPS) were offered by Aladdin Reagent Co., Ltd. (China).

2.2. Synthesis of TiO_2 nanoparticles

The synthesis of TiO_2 nanoparticles was based on literature method [36]. In details, 5 mL of $TiCl_4$ was slowly added to a 250 mL round-bottomed flask containing 25 mL of anhydrous ethanol under vigorous stirring, producing a transparent yellow slurry. 100 mL of anhydrous benzyl alcohol was introduced, followed by stirring for 9 h in an 80 °C oil bath until the slurry turned slightly opaque. The slurry was then precipitated in 400 mL of anhydrous diethyl ether, after which the TiO_2 precipitate was separated from solvent by centrifuge (10 min at 4000 rpm), and then washed with anhydrous ethanol for three times.

2.3. Modification of TiO_2 nanoparticles with A174

The above TiO_2 precipitate was dispersed in the mixed solution of 195 mL anhydrous ethanol and 5 mL distilled water, and then 1.8 g of A174 was added to the system. The suspension was ultrasonicated in an ice bath for 30 min (600 W output power, 2 s work time, 2 s pause time) and was then stirred in a 60 °C oil bath for 3 h, while kept refluxing. Finally, the suspension was centrifuged at 8000 rpm for 10 min to separate from the solvent, and then the precipitate was washed with anhydrous ethanol for three times.

2.4. Preparation of TiO_2/P (MMA/BA/MAA) nanocomposite latex

The wet modified TiO_2 nanoparticles were dispersed into the mixture (13.5 g of MMA, 13.5 g of BA, 3 g of MAA, 1.2 g of HD) with the aid of ultra-sonication for 30 min (600 W output power, 2 s work time, 2 s pause time). The amount of TiO_2 nanoparticles was changed in the different mixture to obtain final loadings of 1.0%, 1.5%, 2.0% (wt). The dispersion was introduced into nonionic surfactant solution (0.3 g of Tween-20, 40 mL of deionized water), followed by stirring for 30 min. Then the dispersion was transferred to another anionic surfactant solution (0.3 g of SDS, 40 mL of deionized water), and was stirred for 30 min again. After that, the mixture was ultra-sonicated in an ice bath for 15 min (600 W output power, 2 s work time, 2 s pause time) to obtain the pre-miniemulsion. The pre-miniemulsion was then poured into a 250 mL three-neck round-bottomed flask equipped with reflux condenser and stirrer in an oil bath. The polymerization started with 0.3 g of KPS initiator at 75 °C and finished within 3 h. To compare, the neat P (MMA/BA/MAA) latex was synthesized similarly to that of the preparation of TiO_2/P (MMA/BA/MAA) nanocomposite latex, only without TiO_2 nanoparticles. The fabrication process of TiO_2/P (MMA/BA/MAA) nanocomposite latex is shown in Scheme 1.