Preparation and Characterization of Titanium Dioxide/ Poly(methyl methacrylate) Composites by *in-situ* Polymerization†

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Anatase titanium dioxide (TiO₂) particles were obtained by sol-gel method and modified with silane coupling agent. TiO₂/poly(methyl methacrylate) composites were prepared *via in situ* bulk polymerization of methyl methacrylate, in which modified TiO₂ particles were dispersed uniformly. SEM micrographs showed that TiO₂/poly(methyl methacrylate) composites exhibited favourable miscibility behaviour, even at high content of TiO₂ (0.7 wt %). Moreover, incorporation of TiO₂ particles can improve mechanical and thermal stability of poly(methyl methacrylate) significantly.

Key Words: Titanium dioxide, Poly(methyl methacrylate), *In situ* copolymerization.

INTRODUCTION

Recently, polymer/metal oxides composites have attracted much attention both in the industry and academia. As an inorganic material, TiO₂ has been widely used in various applications due to its excellent optical properties, chemical stability and relatively low production cost. Generally, incorporating TiO₂ particles into polymer matrix have a significant improvement in thermal^{1,2} and optical properties³ compared with the corresponding pure organic polymers.

However, nanoscale particles typically possess a strong tendency to aggregate because of the high surface energy. In order to attain high-quality composites, a homogeneous dispersion of TiO₂ in the polymer matrix is required. Surface modification of TiO₂ particles with coupling agents is recommended⁴. In this study, we synthesized TiO₂/poly(methyl methacrylate) composites by *in situ* bulk copolymerization. Typically, TiO₂ particles synthesized *via* a sol-gel method were modified with the silane coupling agent. Covalent bonds between poly(methyl methacrylate) and *m*-TiO₂ were helpful for improving the miscibility behaviour of composites. The effect of TiO₂ on properties of TiO₂/poly(methyl methacrylate) composites, such as miscibility behaviour, thermal and mechanical stabilities, was especially investigated.

EXPERIMENTAL

After tetrabutyl orthotitanate (13.6 mL) was dissolved in ethanol (16 mL) completely, a mixture of water (2.4 mL),

ethanol (8 mL) and glacial acetic acid (1.5 mL) was added dropwise under continuous stirring for 2 h. After that, dilute hydrochloric acid was added to adjust the pH value of the mixture to 3. The mixture was dried at 60 °C in a vacuum oven and then calcined at 500 °C for 5 h. TiO₂ particles were collected as white powder after grinding and dispersed in a mixture of water, ethanol and silane coupling agent (KH-151) under reflux for 8 h at 80 °C. Subsequently, the modified TiO₂ slurry was washed with ethanol and dried under vacuum at 50 °C for 24 h. TiO₂/poly(methyl methacrylate) composite were prepared by dispersing various amounts of *m*-TiO₂ particles into methyl methacrylate monomer and sonicated for 0.5 h. Then *in situ* copolymerization was initiated by azodiisobutyronitrile under constant stirring at 80 °C for 20 min. Afterwards, the mixture was poured into a glass mould and kept at 50 °C for 5 h and additional 2 h at 100 °C.

RESULTS AND DISCUSSION

The XRD technique was employed to determine the crystallinity and structure of the as-prepared TiO₂ and *m*-TiO₂. Fig. 1 showed that both TiO₂ and *m*-TiO₂ particles are anatase-type. Notably, the crystalline nature of *m*-TiO₂ particles didn't undergo any changes after silane grafting onto the surface of the as-prepared TiO₂ particles.

Fig. 2(a), (b) shows the SEM micrographs of as-prepared TiO₂ and *m*-TiO₂ particles, respectively. It is observed that unmodified TiO₂ particles tended to aggregated in larger size,

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whereas modified ones exhibited a lower agglomeration tendency and a more uniform size distribution due to the lower surface energy by the saline coupling. Additionally, Fig. 2(c) and (d) showed that no larger size aggregations were observed even the amount of *m*-TiO₂ in the composites was as high as 0.7 wt %.

Fig. 1. XRD patterns of pure TiO₂ and *m*-TiO₂ particles

Fig. 2. SEM photographs of TiO₂ (a), *m*-TiO₂ (b), TiO₂/poly(methyl methacrylate) 0.3 % (c), TiO₂/poly(methyl methacrylate) 0.7 % (d)

Fig. 3 presented TG/DTG profiles of pure poly(methyl methacrylate) and TiO₂/poly(methyl methacrylate) composites in nitrogen atmosphere. Apparently, they were thermally stable up to 180 °C and began to degrade in three-steps. Moreover, incorporation of TiO₂ particles can improve thermal stability of poly(methyl methacrylate) significantly. As shown in DTG curves, the thermal degradation of the TiO₂/composites shifted to higher temperature comparing with pure poly(methyl methacrylate), especially at high content of *m*-TiO₂ (0.9 wt %), confirming the enhancement of thermal stability of poly(methyl methacrylate) by *m*-TiO₂ particles.

Fig. 3. TGA/DTA curves of pure poly(methyl methacrylate) and poly(methyl methacrylate)/TiO₂ composites

Fig. 4 showed the dependence of tensile strength on *m*-TiO₂ content. The tensile strength of composites increased with the content of *m*-TiO₂ to a maximum peak at 35 MPa and then decreased. It should be noted that all composites with contents of *m*-TiO₂ lower than 0.7 % possessed higher tensile strength than that of pure poly(methyl methacrylate) because of the covalent bonding induced uniform dispersion of *m*-TiO₂ particles in poly(methyl methacrylate) matrix. However, composites with higher *m*-TiO₂ contents (higher than 0.7 %) exhibited lower tensile strength, which was attributed to excessive aggregation of *m*-TiO₂ particles in poly(methyl methacrylate) matrix.

Fig. 4. Effect of *m*-TiO₂ content on the tensile strength of composites

Conclusion

TiO₂/poly(methyl methacrylate) composites with a favourable miscibility behaviour were successfully obtained by *in situ* bulk copolymerization. Incorporation of *m*-TiO₂ particles can improve mechanical and thermal stability of poly(methyl methacrylate) significantly. The tensile strength of composites could be increased by 74 % compared with that of poly(methyl methacrylate) when the content of *m*-TiO₂ was 0.3 wt %.

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