Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5640-5642

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH48

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

MENG LI, BENHONG YANG*, YUN WU and TONGZHONG YU

Department of Chemistry and Materials Engineering, Hefei University, Hefei 230601, P.R. China

*Corresponding author: E-mail: yangbh@hfuu.edu.cn

AJC-13288

Anatase titanium dioxide (TiO_2) particles were obtained by sol-gel method and modified with saline coupling agent. TiO_2/poly(methyl methacrylate) composites were prepared *via in situ* bulk polymerization of methyl methacrylate, in which modified TiO_2 particles were dispersed uniformly. SEM micrographs showed that TiO_2/poly(methyl methacrylate) composites exhibited favourable miscibility behaviour, even at high content of TiO_2 (0.7 wt %). Moreover, incorporation of TiO_2 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, TiO_2 has been widely used in various applications due to its excellent optical properties, chemical stability and relatively low production cost. Generally, incorporating TiO_2 particles into polymer matrix have a significant improvement in thermal[1,2] and optical properties[3] 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 TiO_2 in the polymer matrix is required. Surface modification of TiO_2 particles with coupling agents is recommended[4]. In this study, we synthesized TiO_2/poly(methyl methacrylate) composites by *in situ* bulk copolymerization. Typically, TiO_2 particles synthesized *via* a sol-gel method were modified with the silane coupling agent. Covalent bonds between poly(methyl methacrylate) and *m*-TiO_2 were helpful for improving the miscibility behaviour of composites. The effect of TiO_2 on properties of TiO_2/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 ºC in a vacuum oven and then calcined at 500 ºC for 5 h. TiO_2 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 ºC. Subsequently, the modified TiO_2 slurry was washed with ethanol and dried under vacuum at 50 ºC for 24 h. TiO_2/poly(methyl methacrylate) composite were prepared by dispersing various amounts of *m*-TiO_2 particles into methyl methacrylate monomer and sonicated for 0.5 h. Then *in situ* copolymerization was initiated by azodiisobutyronitrile under constant stirring at 80 ºC for 20 min. Afterwards, the mixture was poured into a glass mould and kept at 50 ºC for 5 h and additional 2 h at 100 ºC.

RESULTS AND DISCUSSION

The XRD technique was employed to determine the crystallinity and structure of the as-prepared TiO_2 and *m*-TiO_2. Fig. 1 showed that both TiO_2 and *m*-TiO_2 particles are anatase-type. Notably, the crystalline nature of *m*-TiO_2 particles didn't undergo any changes after saline grafting onto the surface of the as-prepared TiO_2 particles.

Fig. 2(a), (b) shows the SEM micrographs of as-prepared TiO_2 and *m*-TiO_2 particles, respectively. It is observed that unmodified TiO_2 particles tended to aggregated in larger size,

---

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

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*-TiO_2 in the composites was as high as 0.7 wt %.

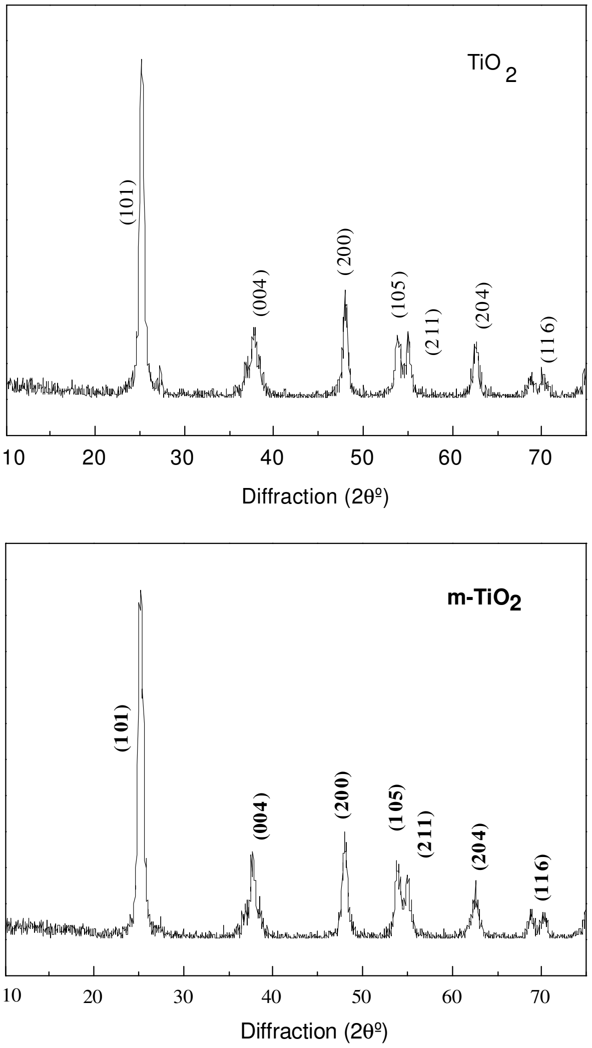

Fig. 1. XRD patterns of pure TiO_2 and *m*-TiO_2 particles

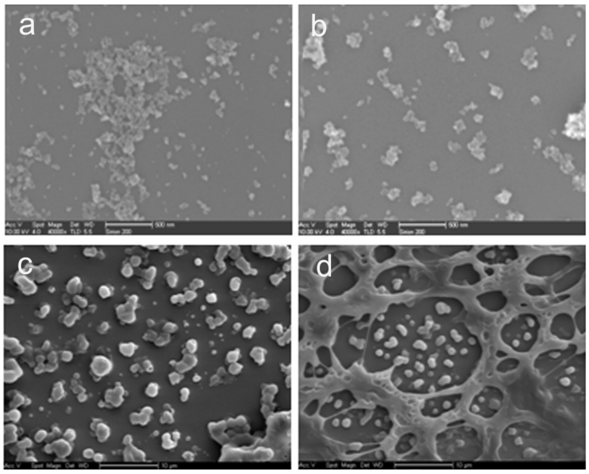

Fig. 2. SEM photographs of TiO_2 (a), *m*-TiO_2 (b), TiO_2/poly(methyl methacrylate) 0.3 % (c), TiO_2/poly(methyl methacrylate) 0.7 % (d)

Fig. 3 presented TG/DTG profiles of pure poly(methyl methacrylate) and TiO_2/poly(methyl methacrylate) composites in nitrogen atmosphere. Apparently, they were thermally stable up to 180 ºC and began to degrade in three-steps. Moreover, incorporation of TiO_2 particles can improve thermal stability of poly(methyl methacrylate) significantly. As shown in DTG curves, the thermal degradation of the TiO_2/composites shifted to higher temperature comparing with pure poly(methyl methacrylate), especially at high content of *m*-TiO_2 (0.9 wt %), confirming the enhancement of thermal stability of poly(methyl methacrylate) by *m*-TiO_2 particles.

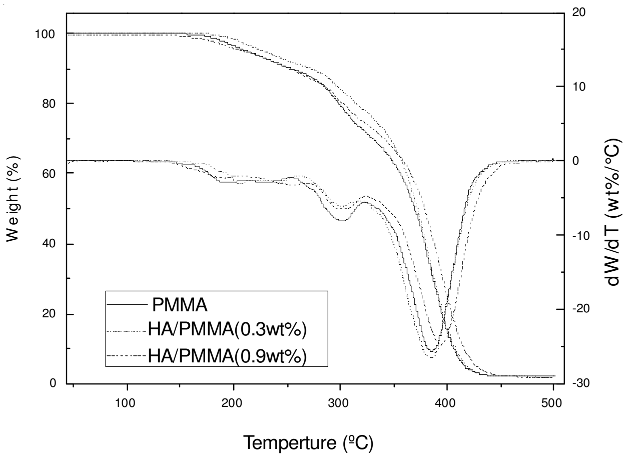

Fig. 3. TGA/DTA curves of pure poly(methyl methacrylate) and poly(methyl methacrylate)/TiO_2 composites

Fig. 4 showed the dependence of tensile strength on *m*-TiO_2 content. The tensile strength of composites increased with the content of *m*-TiO_2 to a maximum peak at 35 MPa and then decreased. It should be noted that all composites with contents of *m*-TiO_2 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*-TiO_2 particles in poly(methyl methacrylate) matrix. However, composites with higher *m*-TiO_2 contents (higher than 0.7 %) exhibited lower tensile strength, which was attributed to excessive aggregation of *m*-TiO_2 particles in poly(methyl methacrylate) matrix.

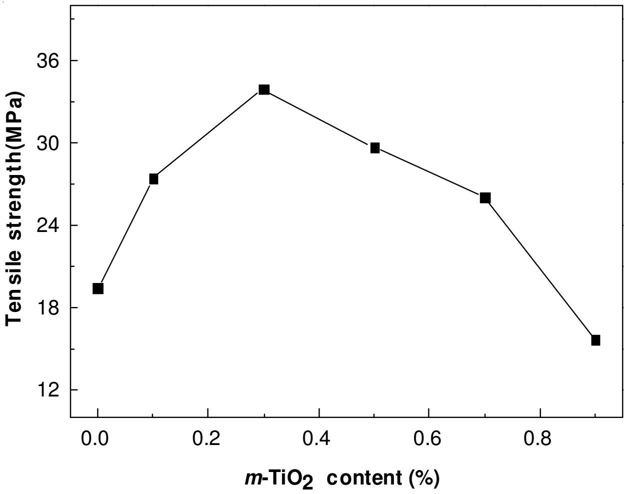

Fig. 4. Effect of *m*-TiO_2 content on the tensile strength of composites

Conclusion

TiO_2/poly(methyl methacrylate) composites with a favourable miscibility behaviour were successfully obtained by *in situ* bulk copolymerization. Incorporation of *m*-TiO_2 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*-TiO_2 was 0.3 wt %.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the Natural Science Foundation of Anhui Educational Department (No. KJ2011A247), the Natural Science Foundation of Anhui Province (No. 1208085MB24) and the Natural Science Foundation of Hefei University (No.11KY01ZR).

REFERENCES

1. Y.C. Huang, W.C. Yen, Y.C. Liao, Y.C. Yu, C.C. Hsu, M.L. Ho, P.T. Chou and W.F. Su, *Appl. Phys. Lett.*, **96**, 123501 (2010).
2. S.M. Graja, J. Blömer, J. Bertling and P.J. Jansens, *Chem. Eng. Technol.*, **33**, 2029 (2012).
3. J.M. Liu, L.X. Cao and G. Su, *Curr. Appl. Phys.*, **11**, 1359 (2011).
4. S.M. Khaled, R.H. Sui and P.A. Charpentier, *Langmuir*, **23**, 3988 (2007).