



Synthesis and Characterization of ZnO/Poly(methyl methacrylate) Composites by *in situ* Polymerization†

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AJC-11311

A simple approach for *in situ* preparation of transparent ZnO/poly(methyl methacrylate) nanocomposite films was developed. Scanning electron microscope images revealed that zinc oxide nanocrystals were homogeneously dispersed in poly(methyl methacrylate) matrix. The TGA and ultraviolet-visible absorption measurements displayed that ZnO/poly(methyl methacrylate) nanocomposite films possessed better thermal stability and optical property than pristine poly(methyl methacrylate) films.

Key Words: Composites, Poly(methyl methacrylate), Nanoparticles, Polymerization.

INTRODUCTION

The development of polymer-based nanocomposite materials has been attracting immense interest from researchers in a large range of applications, such as light-emitting devices (LEDs)¹, solar cells², biological labels³, nonlinear optical devices, *etc.* This compositing approach represents a cost-effective way to create new materials with unusual combinations of optical, mechanical, physical and chemical properties of each component. However, the most vital challenge in preparing these nanocomposite materials is to achieve a uniform distribution of nanopaticals in the polymer matrix. It has being reported that nanoscale particles tend to agglomerate in a polymer matrix because of the high surface energy. Hence, a number of strategies have been employed to avoid the agglomeration of nanoparticles in the host matrix. It starts from modifying the nanopaticals by organic coupling agents, following by good dispersing in the monomer and then *in situ* copolymerization⁴. This has been realized as a simple, fast and cost-effective way to achieve nanocomposite films with a good dispersion of inorganic nanoparticles.

In this study, we presented a simple approach for preparing transparent ZnO/PMMA [PMMA = poly(methyl methacrylate)] nanocomposite films *via* the *in situ* copolymerization. Firstly, rod-like ZnO nanoparticles were synthesized by hydrothermal method using cetyltrimethyl ammonium bromide (CTAB) as a surfactant. Then these nanoparticles were treated with the coupling agent of triethoxyvinyl silane (KH-151) to

ensure them dispersing uniformly in the monomer, followed by radical grafting copolymerization to graft poly(methyl methacrylate) (PMMA) chains onto the surface of ZnO nanoparticles. Notably, the treatment of particles with KH-151 is necessary to prevent undesired aggregation. Additionally, the terminal double bonds (C=C) in the modified nanopaticals allow the copolymerization of methyl methacrylate with ZnO nanopaticals to improve the miscibility behavior, optical and thermal properties of the ZnO/PMMA nanocomposites.

EXPERIMENTAL

In this study, ZnO/PMMA films were synthesized as follows. Zinc acetate (AR, 99.9 %) was dissolved into deionized water. And then, ammonia solution was added into zinc acetate solution to precipitate zinc cations with constant stirring. The obtained precipitates, cetyltrimethyl ammonium bromide and deionized water-ethanol mixture were introduced into a Teflon lined stainless steel autoclaves, sealed and maintained at 160 °C for 10 h in an electric oven. The resulting solid products were washed alternately by centrifugation with distilled water and ethanol twice and finally dried at 60 °C in air for 10 h. ZnO nanoparticles were hydrophobized by treatment with silane coupling agent (KH-151). Various amounts of *m*-ZnO nanoparticles 0, 0.1, 0.3 and 0.7 % (wt %) were dispersed into methyl methacrylate monomer and sonicated for 0.5 h in a three-neck flask. Then AIBN (5 mg) as initiator was added into the flask under constant stirring at 80 °C for 0.5 h. Afterwards, the solution in the flask was transferred into the glass

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

plate mould and kept at 80 °C for 4 h in an electric oven. After that, a 3 mm thickness of poly(methyl methacrylate) sheets was separated from the glass plate moulds. Using ultraviolet-visible absorption spectra (UV-VIS, UV-2550, Shimadzu) to study on the UV absorbance properties of nano-ZnO/PMMA composites. Morphology of ZnO nanoparticles is examined by field-emission scanning electron microscope (FE-SEM, Sirion200, FEI). Thermal properties of ZnO/PMMA nanocomposites (TGA, STA 409PC, NESTCH) were carried out with a heating rate of 10 K/min under nitrogen.

RESULTS AND DISCUSSION

The SEM images of ZnO and *m*-ZnO particles are shown in Fig. 1(a) and (b). It is observed that the morphology of the obtained ZnO particles is rod-like with a diameter of about 100 nm and a length of about 600 nm. As seen in Fig. 1(c) and (d), it is clearly found that ZnO nanocrystals are homogeneously dispersed in the PMMA matrix and no large ZnO agglomerations are observed. The free-radical polymerization of MMA and *m*-ZnO allows introducing well-dispersed nanoparticles into PMMA matrix due to the graft of PMMA polymer chain onto *m*-ZnO nanoparticles.

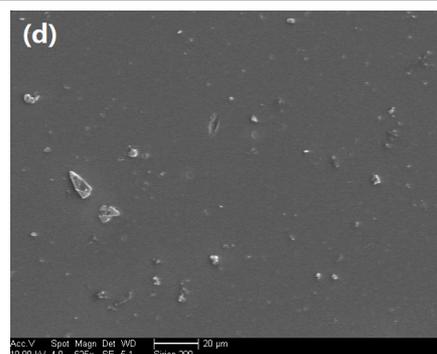
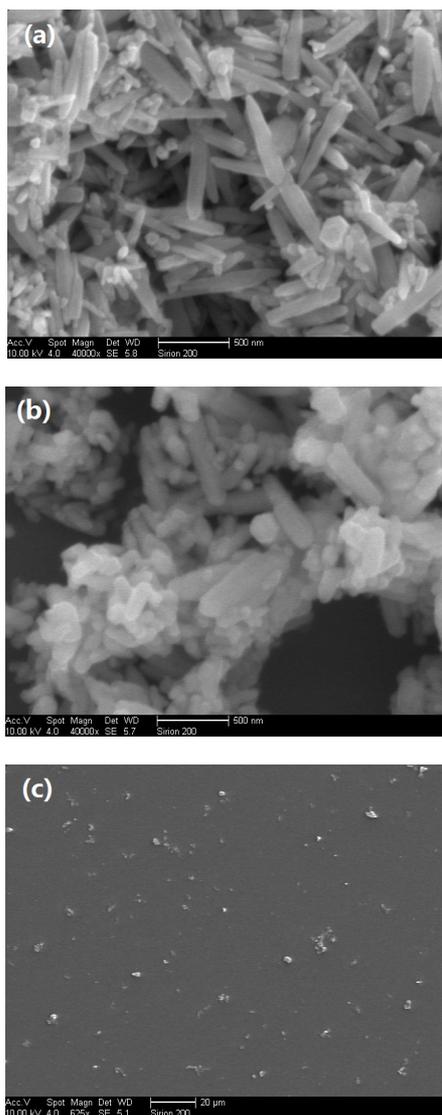


Fig. 1. SEM photographs of original ZnO (a), *m*-ZnO nanoparticles (b), ZnO/PMMA 0.3 % (c) and ZnO/PMMA 0.7 % (d)

Thermal stability of the PMMA and ZnO/PMMA nanocomposite is investigated *via* thermo-gravimetric analysis in Fig. 2. Comparing with the TGA curve of PMMA, the thermal degradation of the ZnO/PMMA nanocomposite becomes more difficult in the temperature range from 350–450 °C because of the interfacial interaction between PMMA and ZnO nanocrystals resulting from free-radical polymerization. Moreover, the homogeneous dispersion of ZnO nanocrystals in PMMA matrix also results in higher thermal stability.

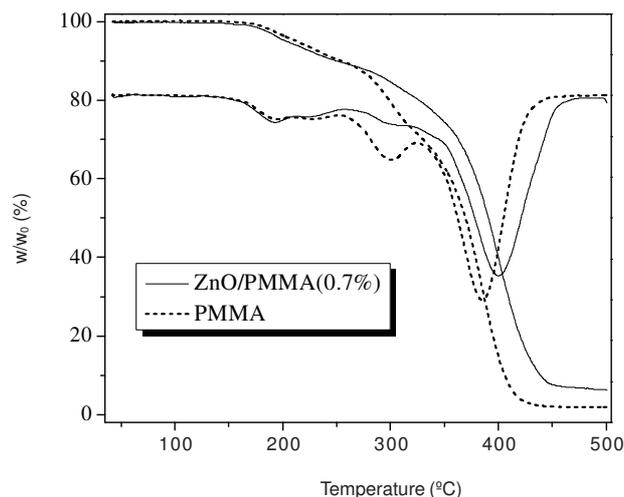


Fig. 2. TGA and DTG curves of pristine poly(methyl methacrylate), ZnO/poly(methyl methacrylate) (PMMA) 0.7 % (wt %)

The effect of ZnO nanoparticles on the optical properties of ZnO/PMMA nanocomposite films are investigated in detail. UV-VIS absorption spectra of pristine PMMA and ZnO/PMMA nanocomposite are shown in Fig. 3. Comparing with the UV absorption of pristine PMMA, the absorption band of ZnO/PMMA nanocomposites is red-shift significantly due to the presence of ZnO nanoparticles, which has a high-absorption effect in the UV region. Additionally, UV absorption of ZnO/PMMA nanocomposites is improving with an increase in ZnO content.

Conclusion

We have successfully prepared rod-like ZnO nanoparticles with a uniform morphology *via* a simple hydrothermal method. ZnO/PMMA nanocomposites were synthesized by *in situ*

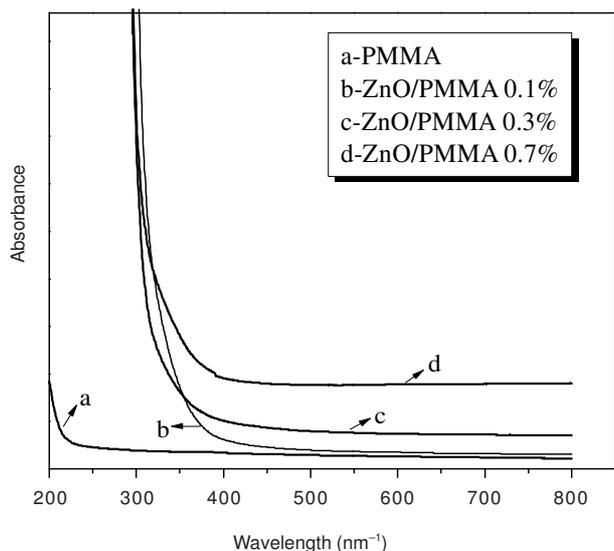


Fig. 3. UV-VIS spectra of ZnO/PMMA nanocomposites with different amounts of ZnO

polymerization process using ZnO modified with KH-151. The *in situ* polymerization of methyl methacrylate in the presence of nanosized ZnO particles gives access to composite materials, which improved thermal stability and UV resistance in comparison to pristine PMMA.

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).

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