



Preparation and Properties of ZnO:Ce/Poly(methyl methacrylate) Nanocomposites *via in situ* Copolymerization†

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Novel inorganic/polymer nanocomposites were prepared by using *in situ* copolymerization of the modified inorganic nano-ZnO:Ce and methyl methacrylate. X-ray diffraction and SEM were employed to characterize the structure and morphology. Tensile test and TGA show that the incorporation of ZnO:Ce nanoparticles into poly(methyl methacrylate) matrix can significantly improve the mechanical and thermal properties of the composite.

Keywords: ZnO:Ce, Poly(methyl methacrylate), Nanocomposites, Properties.

INTRODUCTION

Inorganic/polymer nanocomposite materials are different from those conventional inorganic/polymer filler systems. The former is formed by the inorganic and organic phases which integrate together in the nanometer scale or on a molecular level, so that the resultant composite materials could combine the strong points of both polymeric materials like excellent processability, toughness and low-cost and inorganic materials such as good heat resistance, antioxidation, mechanical properties and even some special functions. Nanocomposites have become one of the most attractive research areas of materials sciences¹⁻⁴.

Zinc oxide as a direct wide bandgap ($E_g = 3.37$ eV) semiconductor material, has a larger exciton binding energy at room temperature (60 meV)⁵. The exciton emission at room temperature can be achieved, resulting in near UV shortwave light emission. With those unique optical and electrical properties, ZnO has found a wide range of applications. Rare earth-doped ZnO materials can effectively improve the luminescent properties, thus further widening the application scope of ZnO^{6,7}.

This article aims to explore the method of preparation of ZnO:Ce/PMMA nanocomposites. The nano-ZnO:Ce was synthesized by hydrothermal process and modified with a silane coupling agent to make its surface contain vinyl groups.

The modified ZnO:Ce (m-ZnO:Ce) was mixed with methyl methacrylate monomers and undergone free radical copolymerization to form ZnO:Ce/PMMA nanocomposites.

EXPERIMENTAL

ZnCl₂ and Ce(NO₃)₃·6H₂O were mixed together in a molar ratio of 50:1 and dissolved in alcohol. Under vigorous agitation, a NaOH solution was added in dropwise to adjust pH value to 8. The mixture was poured to a Teflon-lined autoclave and maintained at 160 °C for 12 h. The solid product was filtered out and washed alternately with distilled water and alcohol three times, dried at 60 °C for 24 h. The resultant ZnO:Ce particles were treated with vinyltriethoxysilane (VTES) *via* a sol-gel process to graft vinyl groups on the surface of ZnO:Ce.

ZnO:Ce/PMMA nanocomposites with different content of ZnO:Ce were prepared by *in situ* bulk copolymerization between m-ZnO:Ce and MMA monomers. The m-ZnO:Ce particles were dispersed into MMA monomer and sonicated for 0.5 h and *in situ* copolymerization was initiated by benzoyl peroxide (BPO) under constant stirring at 80 °C for 0.5 h. Then, the mixtures were poured into a glass mould and kept at 50 °C for 5 h and another 2 h at 100 °C to form sample bars. The pure PMMA was polymerized under the same condition. Pure PMMA and ZnO:Ce/PMMA nanocomposites were characterized by SEM, TGA and tensile test, respectively.

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RESULTS AND DISCUSSION

X-ray diffraction technique was employed to determine the crystallinity and structure of the ZnO:Ce and *m*-ZnO:Ce particles. As is seen in Fig. 1, *m*-ZnO:Ce displays a same XRD pattern as ZnO:Ce, meaning that surface-modification did not change the crystal structure of ZnO:Ce. ZnO:Ce indicates a similar XRD pattern as pure ZnO, showing characteristic diffraction peaks at $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.7^\circ, 56.5^\circ, 62.8^\circ$ and 68.0° , respectively corresponding to (100), (002), (101), (102), (110), (103) and (200) crystal planes and consistent with the JCPDS card 36-1541 for hexagonal crystal of ZnO, revealing that Ce has been doped into the lattice of ZnO. Sharp peak pattern indicates that the sample has a high degree of crystallinity.

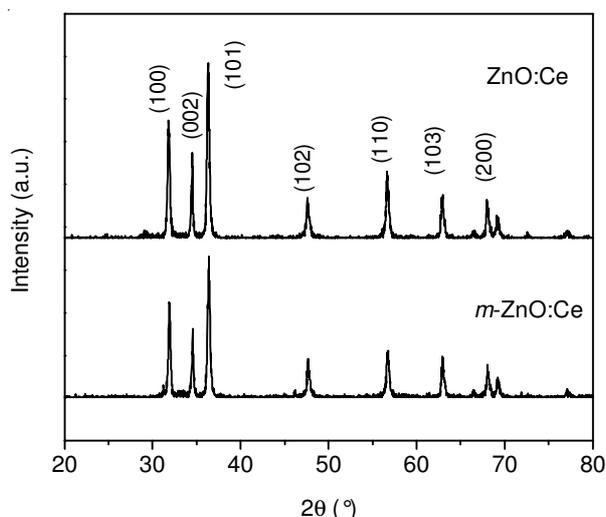


Fig. 1. XRD patterns of ZnO:Ce and *m*-ZnO:Ce particles

Fig. 2a-b indicate the SEM images of ZnO:Ce particles. ZnO:Ce shows a rod-like morphology with average 150 nm long and 50 nm wide in size, which is accordant with XRD analysis. Fig. 2c-d display the SEM images of ZnO:Ce/PMMA nanocomposites. When ZnO:Ce content is lower than 0.3 wt %, ZnO:Ce nanoparticles were evenly dispersed in PMMA matrix because of the covalent bonding between ZnO:Ce particles and PMMA chains. When ZnO:Ce content is as high as 0.7 wt %, aggregation of ZnO:Ce was observed. Even though, the aggregated particles are still well dispersed in the PMMA matrix and no sharp interfaces were sighted, implying the success of saline coupling strategy in making ZnO:Ce/PMMA composites.

Fig. 3 shows the effect of ZnO:Ce content on the tensile strength of ZnO:Ce/PMMA composites. When ZnO:Ce content is less than 0.5 wt %, the tensile strength of ZnO:Ce/PMMA composites indicates a increasing trend with the increase of the content of incorporated ZnO:Ce due to the strong interaction between nanoparticles and polymer chains. When ZnO:Ce content goes higher than 0.5 wt %, however, it shows a decreasing tendency, probably resulting from the aggregation of ZnO:Ce nanoparticles, which weakens the interaction. But, the tensile strength is still larger than that of pure PMMA when ZnO:Ce content is less than 0.9 wt %, meaning that ZnO:Ce particles with several micrometers in size still have positive

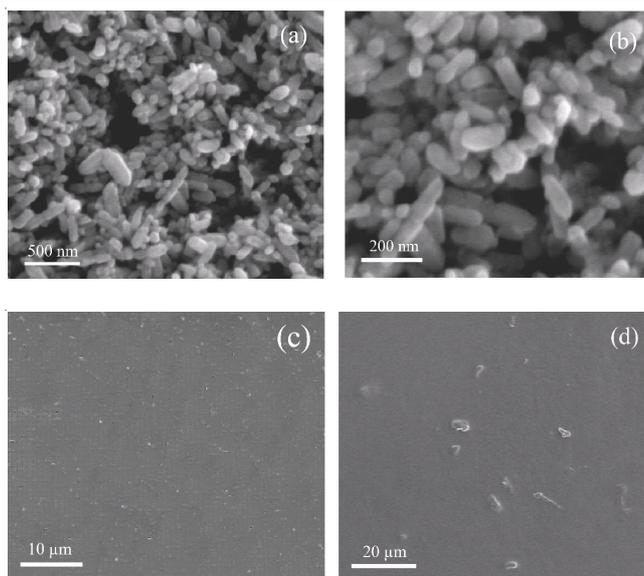


Fig. 2. SEM images of ZnO:Ce particles (a) and (b), ZnO:Ce/PMMA 0.3 % (c) and ZnO:Ce/PMMA 0.7 % (d)

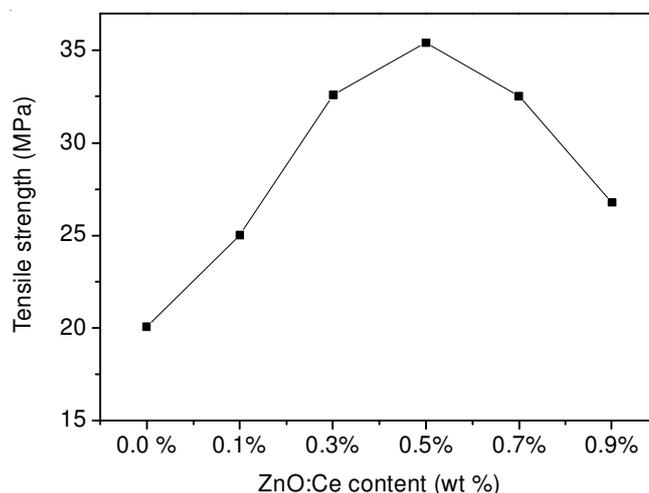


Fig. 3. Effect of ZnO:Ce content on the tensile strength of ZnO:Ce/PMMA composites

effect in reinforcing polymers if they are evenly dispersed in the polymer matrix (Fig. 2d).

Fig. 4 displays the TGA thermographs of pure PMMA and ZnO:Ce/PMMA composites. ZnO:Ce/PMMA composites all show three-step degradations like pure PMMA, hinting that the incorporation of nano-ZnO:Ce particles did not change the thermal behaviour of PMMA. Table-1 suggests the trend that the decomposition temperature (T_d) increases with the increase of ZnO:Ce content when less than 5 wt %, possibly owing to the strong interaction between nanoparticles and PMMA chains, which hindered the chain motion and delayed the polymer from decomposition.

Conclusion

ZnO:Ce/PMMA nanocomposites were prepared *via* an *in situ* copolymerization method. SEM images show that the surface-modified ZnO:Ce nanoparticles were evenly dispersed in PMMA matrix, which play a role of anchoring points, hindering the free motion of PMMA chains, thus significantly

TABLE-1
THERMAL AND MECHANICAL PROPERTIES OF ZnO:Ce/PMMA AND PMMA

Sample	ZnO:Ce content (wt %)	T _{d1} (°C)	T _{d2} (°C)	T _{d3} (°C)	Tensile strength (MPa)
PMMA	0.0	172.1	283.0	340.4	20.09
ZnO:Ce/PMMA-1	0.1	173.7	286.3	342.8	25.00
ZnO:Ce/PMMA-2	0.3	179.8	288.8	346.1	32.60
ZnO:Ce/PMMA-3	0.5	204.7	291.2	353.3	35.40
ZnO:Ce/PMMA-4	0.7	198.9	281.4	331.5	32.53
ZnO:Ce/PMMA-5	0.9	–	–	–	26.79

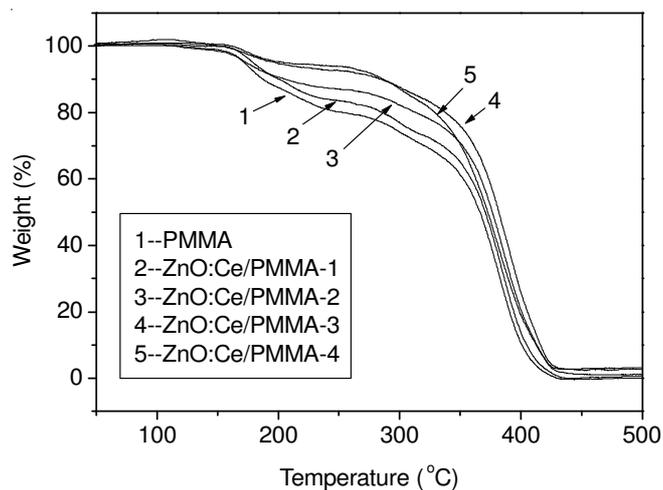


Fig. 4. TGA thermographs of pure PMMA and ZnO:Ce/PMMA composites

improved the thermal and mechanical properties of the nano-composites.

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REFERENCES

1. W. Qiang, Y. Wang, P. He, H. Xu, H. Gu and D. Shi, *Langmuir*, **24**, 606 (2008).
2. J.Y. Kim, Y.H. Ohn, K.J. Ihn and C. Lee, *J. Appl. Polym. Sci.*, **119**, 2002 (2011).
3. Y. De Hazan, M. Wozniak, J. Heinecke, G. Müller and T. Graule, *J. Am. Ceram. Soc.*, **93**, 2456 (2010).
4. A.K. Mishra, S. Bose, T. Kuila, N.H. Kim and J.H. Lee, *Prog. Polym. Sci.*, **37**, 842 (2012).
5. M. Willander, O. Nur, Q.X. Zhao, L.L. Yang, M. Lorenz, B.Q. Cao, J. Zúñiga Pérez, C. Czekalla, G. Zimmermann, M. Grundmann, A. Bakin, A. Behrends, M. Al-Suleiman, A. El-Shaer, A. Che Mofor, B. Postels, A. Waag, N. Boukos, A. Travlos, H.S. Kwack, J. Guinard and D. Le Si Dang, *Nanotechnology*, **20**, 332001 (2009).
6. S. Geburt, D. Stichtenoth and S. Müller, *J. Nanosci. Nanotechnol.*, **8**, 244 (2008).
7. X. Zeng, J. Yuan and L. Zhang, *J. Phys. Chem. C*, **112**, 3503 (2008).