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Size effect of added LaB_6 particles on optical properties of LaB_6/Polymer composites

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ABSTRACT

Modified LaB_6 particles with sizes ranging from 50 nm to 400 nm were added into polymethyl methacrylate (PMMA) matrix in order to investigate the effect of added LaB_6 particles on optical properties of LaB_6/PMMA composites. Method of in-situ polymerization was applied to prepare PMMA from raw material—methyl methacrylate (MMA), a process during which LaB_6 particles were dispersed in MMA. Ultraviolet–visible–near infrared (UV–vis–NIR) absorption spectrum was used to study optical properties of the as-prepared materials. The difference in particle size could apparently affect the composites' absorption of visible light around wavelength of 600 nm. Added LaB_6 particles with size of about 70 nm resulted in the best optical properties among these groups of composites.

1. Introduction

It is advantageous to add nanoparticles into a polymer matrix to produce a nanocomposite with excellent properties brought by the additive [1].

LaB_6 nanoparticle was recently proved to be effective in near-infrared absorption and visible transmittance, bringing its applications in reduction of solar heat gain [2]. Polymers containing LaB_6 are considered by more and more scientists because of their excellent properties in optical application. Stefan and Smith [3] successfully prepared LaB_6-doped polyvinyl butyral (PVB) laminates using the method of extrusion at 190 °C. They also studied the laminates' optical properties around the wavelength of 300–2400 nm, finding effective absorption of near infrared (NIR) and good transmittance of visible radiation (VIS). Hu et al. [4] obtained polymethyl methacrylate (PMMA) laminates containing LaB_6 through melt extrusion and they proved that PMMA with a higher content of LaB_6 was beneficial for rejecting solar heat while good transmittance of VIS was guaranteed.

In this report, the method of in-situ polymerization was applied to prepare PMMA from methyl methacrylate (MMA), during which LaB_6 particles in different sizes were separately dispersed in MMA solution. Size effect of added LaB_6 particles on optical properties of LaB_6/PMMA composites was demonstrated.

2. Experimental procedure

LaB_6 particles were successfully prepared via a solid state reaction in vacuum [5]. These particles were treated with acid cleaning and purification. And then 0.4 ml silane coupling agent was added into 20 ml alcohol solution containing these particles to finish the surface modification of LaB_6 particles. They were then dispersed in distilled water under supersonic vibration. Particles at the lower bottom after sedimentation were dried at 60 °C for 10 h. LaB_6 particles with sizes of 50 nm, 70 nm, 150 nm and 400 nm were then obtained.

MMA was pretreated in alkaline solution containing 5 wt% NaOH in order to get rid of polymerization inhibitor. Then anhydrous Na_2SO_4 was poured into pretreated MMA to absorb residual water.

After pretreatment of MMA, 0.01 g modified LaB_6 particles with sizes of 50 nm, 70 nm, 150 nm and 400 nm were added into 50 ml MMA separately. Then pre-polymerization of MMA was carried out, accompanied by supersonic vibration and mechanical mixing. Not until the viscosity of MMA equated that of glycerol should this process be stopped. After pre-polymerization, the mixture was poured into a mold and was then kept at 45 °C in vacuum for 20 h. The mold was actually a 10 mm × 12 mm × 80 mm glass colorimetric ware, which was broken at last to get final product. Molds and final products were shown in Fig. 1.

X-ray diffraction (XRD) analysis of LaB_6 materials was performed on Japan Rigaku D/max-RB X-ray diffractometer ($\lambda = 1.5406$ Å). Field emission scanning electron microscopy (FESEM) images of LaB_6 particles were taken on a JSM-6700F scanning electron microscope at a 3.0 kV acceleration voltage.

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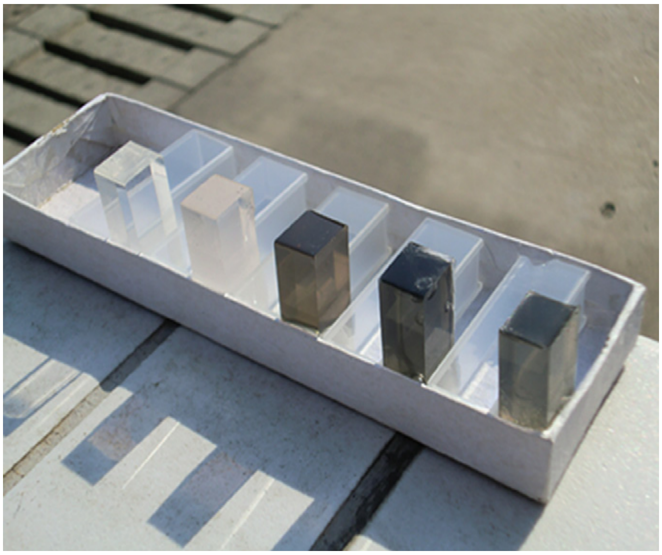

Fig. 1. Molds and final composites' samples. The left sample was made of pure MMA without LaB_6 added in; the others were made of mixture of MMA and LaB_6 particles.

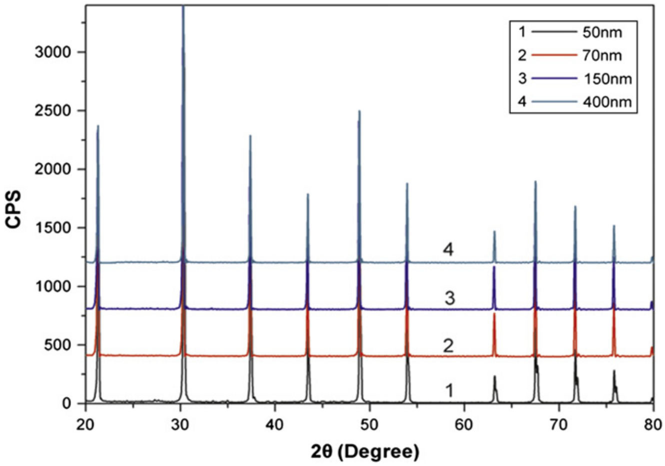

Fig. 2. XRD results of LaB_6 particles in different sizes.

Ultraviolet–visible–near infrared (UV–vis–NIR) absorption spectrum of the products was recorded on UV–vis–NIR spectrophotometry (U-4100).

3. Results and discussion

3.1. Formation of LaB_6 particles in different sizes

The formation of LaB_6 particles in different sizes was ascertained through XRD analysis and FESEM characterization, as shown in Figs. 2 and 3.

It could be seen from Fig. 2 that all samples were pure LaB_6. There was a trend of narrowing in peaks from line 1 to line 4, indicating an increase in grain size. This tendency was further proved in Fig. 3, which also clearly showed that most particles were elliptical or cubic shaped.

3.2. Modification of LaB_6 particles

Previous work [4] has proved that LaB_6 particles were successfully modified by the added silane coupling agent.

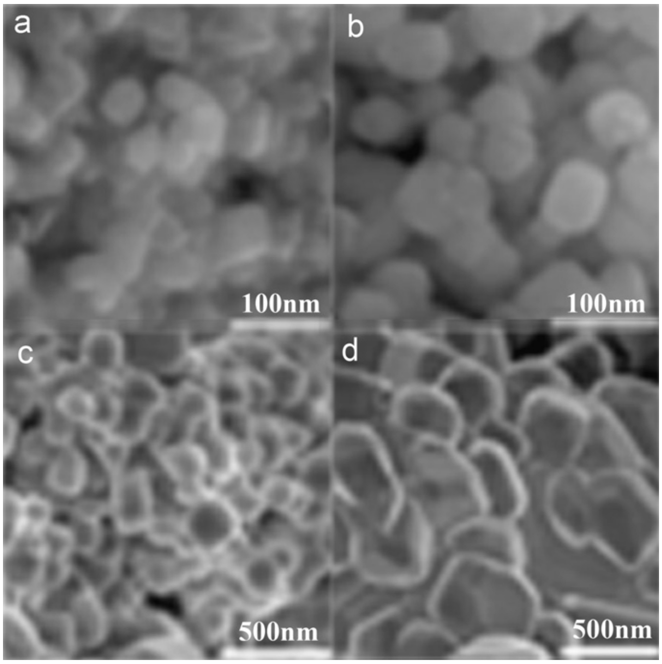

Fig. 3. FESEM images of LaB_6 particles in different sizes. (a), (b), (c) and (d) show particles with size of 50 nm, 70 nm, 150 nm and 400 nm, respectively.

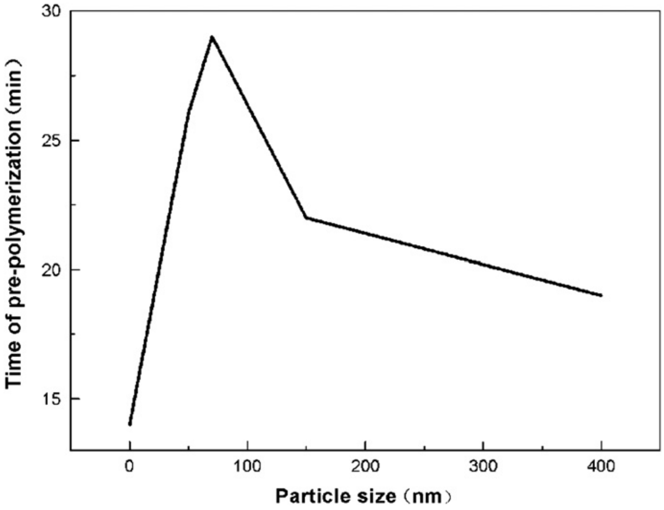

Fig. 4. Size effect on time needed for pre-polymerization of MMA. 0 nm stood for pure MMA without LaB_6 particles.

3.3. Size effect on time needed for pre-polymerization of MMA

Fig. 4 shows that the pre-polymerization process was apparently prolonged by the added LaB_6 particles. 0 nm stood for pure MMA without LaB_6. Added particles of 50 nm size prolonged this process by 12 min. 70 nm LaB_6 particles had the most obvious effect, changing the time to 29 min. With particle size increasing from 70 nm to 400 nm, pre-polymerization of MMA was gradually shortened to 19 min.

Reason for this trend lied in nano-size effect of LaB_6 material. Added particles retarded the process of pre-polymerization because of the role they played as polymerization-inhibiting particles by hindering MMA from forming new C–C bonds. So the process was prolonged by LaB_6 particles in any size. The key point was that when grain size was below 70 nm, surface atoms, which carried lots of unsaturated bonds and were active to accelerate the process of pre-polymerization, took a large part of all added LaB_6 atoms. So decreasing particle size from 70 nm to 50 nm meant a larger part taken by surface atoms, which could accelerate the process to some extent. With particle size increasing from 70 nm to 400 nm, nano-size effect of added particles declined and was exceeded by the polymerization-inhibiting effect. Considering that weight percentages of LaB_6 in different samples were the same, there were fewer dispersed LaB_6 particles in bigger case in MMA, indicating weaker obstruction on pre-polymerization.

3.4. *Size effect on optical property of LaB_6/PMMA composites*

Fig. 5 shows the distribution of LaB_6 particles in different sizes in PMMA matrix. It could be seen that added LaB_6 particles of 50 nm size and 70 nm size were not well dispersed in matrix and presented in agglomeration to some extent. With size increasing to 400 nm, agglomeration of LaB_6 particles in PMMA gradually disappeared.

Fig. 6 shows the result of UV–vis–NIR absorption spectrum of the products. PMMA doped with LaB_6 had stronger light absorption than pure PMMA. The peaks appearing around 1150 nm and 1380 nm were those of PMMA. It was notable in Curve 2 that absorption of light around 600 nm decreased apparently. Composites containing 50 nm and 150 nm LaB_6 particles also had a similar but weaker tendency around 600 nm. On increasing LaB_6 particle size to 400 nm, there was hardly any drop of light absorption around 600 nm, and absorption of NIR decreased. Reason for the latter might lie in two facts. First, LaB_6 particles in bigger case were less than those in smaller case, and this could also account for the decreasing tendency in absorption peak around 1000 nm, which was initially not there but is now weak. Besides, scattering peak of LaB_6 was also around 1000 nm and its scattering efficiency increased with particle size, so this could also partly affect absorption of NIR, resulting in decreasing NIR absorption peak. So in contrast to pure PMMA, PMMA doped with LaB_6 nanoparticles had an increased absorption of all light from 400 nm to 1600 nm. VIS around 600 nm was absorbed less than NIR, and this was especially obvious concerning PMMA doped with LaB_6 particles of 70 nm size. With particle size increasing beyond nano-scale, the remarkable lower absorption of VIS than that of NIR gradually disappeared.

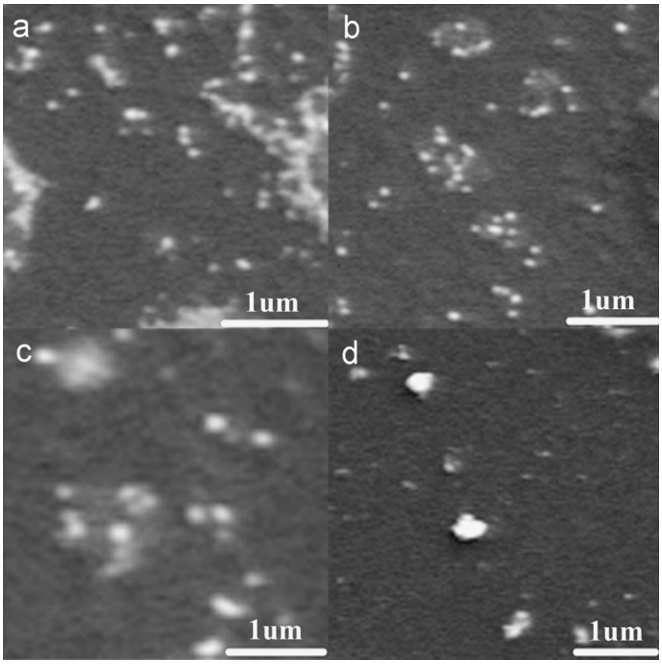

Fig. 5. FESEM images showing distribution of LaB_6 particles in PMMA matrix. (a), (b), (c) and (d), respectively, depict distribution of particles with sizes of 50 nm, 70 nm, 150 nm and 400 nm.

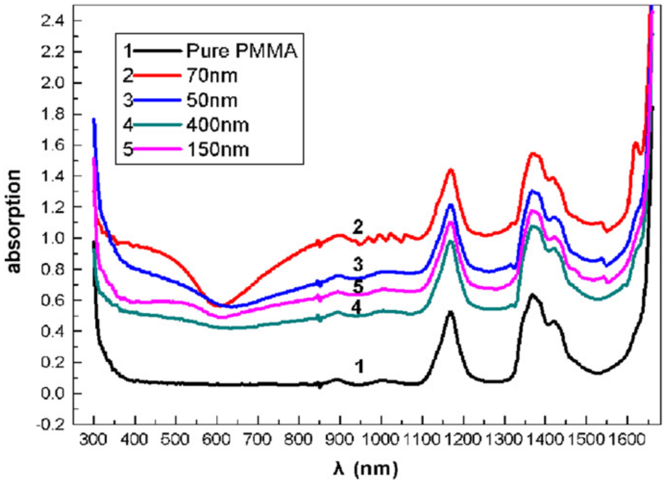

Fig. 6. Absorption spectrum of LaB_6/PMMA composites from 300 nm to 1600 nm.

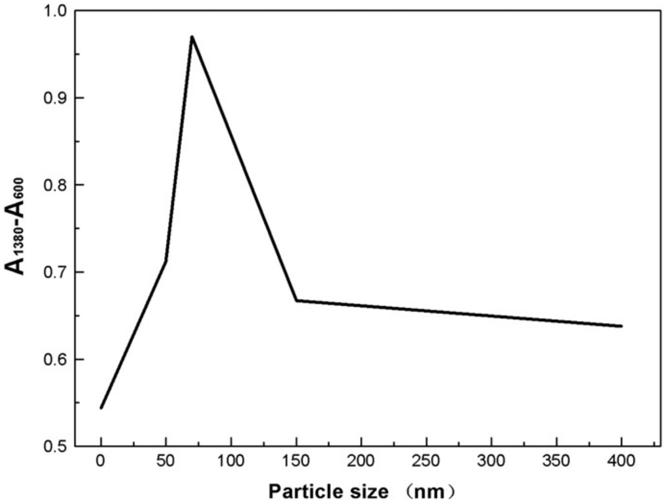

Fig. 7. Relative strength of light absorption concerning composites containing LaB_6 particles in different sizes. 0 nm stood for pure polymer without LaB_6 particles.

Here, the value of $(A_{1380}-A_{600})$ was viewed as the relative strength of light absorption and was used to measure the performance of these composites in NIR and VIS absorption, where A_{1380} meant absorption strength at wavelength of 1380 nm, so did A_{600} at 600 nm. Fig. 7 shows the values of $(A_{1380}-A_{600})$ based on the five curves in Fig. 6, where 0 nm also stood for pure polymer. Considering that satisfying composites should absorb NIR as much as possible and VIS as little as possible, it could be concluded that the composite with 70 nm LaB_6 particles had the best performance in NIR and VIS absorption.

4. Conclusion

Pre-polymerization process of MMA was apparently prolonged by the added LaB_6 particles.

Added LaB_6 particles increased the light absorption strength of composite as a whole. The difference in particle size could affect absorption of VIS and NIR. The composites containing LaB_6 nanoparticles, especially with size of 70 nm, resulted in the best performance in NIR and VIS absorption, which could not be achieved by the composites containing LaB_6 particles beyond nano-scale.

Acknowledgments

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References

[1] D.I. Mitsugi, T. Yusuke, T. Takashi, Ind. Eng. Chem. Res. 47 (2008) 2597–2601.
[2] S. Stefan, G.B. Smith, Appl. Phys. Lett. 82 (2003) 4346–4348.
[3] S. Stefan, G.B. Smith, J. Appl. Phys. 97 (2005) 124314-1–124314-8.
[4] L.J. Hu, G.H. Min, X. Yang, Adv. Mater. Res. 150 (2011) 703–706.
[5] Y.F. Yuan, L. Zhang, L.M. Liang, K. He, R. Liu, G.H. Min, Ceram. Int. 37 (2011) 2891–2896.