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Hydrothermal synthesis of ZnO@polysiloxane microspheres and their application in preparing optical diffusers

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Abstract:

In this study, the optical diffusers based on the fillers of ZnO@polysiloxane microspheres were successfully prepared by solvent-free UV curing process. ZnO@polysiloxane microspheres had been synthesized via high efficient and facile hydrothermal synthesis method. The microscope analysis revealed that the ZnO@polysiloxane microspheres were about 6~8 μm in diameter. The optical properties of the diffusers were also measured for the first time. The results suggested that the novel diffuser based on the fillers of ZnO@polysiloxane microspheres possessed suitable light transmittance, good diffusion capacity, and low incident angle dependence. In addition, the tunable optical diffusing capacity relied on the amount of ZnO@polysiloxane microspheres fillers. When the concentration of ZnO@polysiloxane microspheres was up to 15 wt%, the diffusing properties of novel diffusers can reach the level of diffuser on market. Therefore, the new fillers can be widely used for preparing multifunctional diffusion materials such as touch-panel functions, monitors, military projectors, TVs, etc.

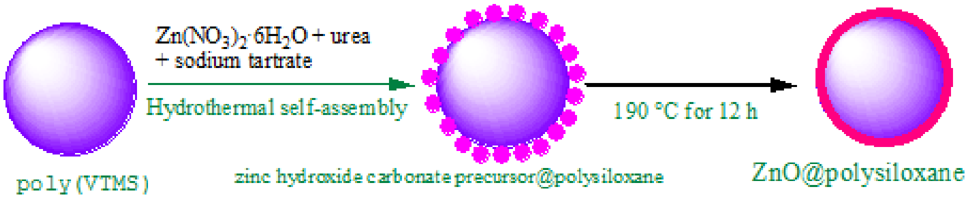
Keywords: Optical diffuser; ZnO; Photoluminescence; Core-shell structure

1. Introduction

There is a requirement for better light diffusion for liquid crystal displays (LCDs) in order to meet the development of them to become larger and thinner[1]. Optical diffuser is the key component in backlight unite (BLU) for LCDs, which plays the role of smoothing the illumination profile behind the LCD and making it more uniform[2, 3]. In early studies, the properties of optical diffusers were enhanced through a careful design of the diffusion particles and manufacturing conditions, respectively[4, 5]. Quite recently, the development of sophisticated surface patterning techniques has led researchers to explore the feasibility of improving the light diffusing effect of diffusers by patterning optical micro-structures on the upper surface of the film[6-8]. Besides, our group have proposed hybrid optical diffusers in which various functions were combined[9, 10].

Although the cost of the prepared diffusers via coating organic light-diffusing particles was relatively low, there were still drawbacks with the coated optical materials, including dispersion of particles, the low thermal stability, single function, complex process for particles preparation, etc.[11-15] In particular, since the research progress of optical diffusers was mainly protected in the form of patents, the literatures were very limited and it was needed to be explored and to get up breakthrough earlier[2].

Core-shell hybrid microspheres have become one of the most effective sources for fabricating advanced materials due to their special structure different from common particles. Besides, the structure, size, and composition of the particles can be altered in a controlled synthesis route over a broad range to tailor a variety of novel properties (e.g., electrical, themal, mechanical, optical, and magnetic)[16-22]. The methods developed to produce core-shell microspheres include seed polymerization, macromonomer method, self-assembly method, and gradually heterogeneous condensation method[23-25]. However, those methods were not simple and convenient enough and can not satisfy the demands of atomic economics. Herein, we reported a facile, efficient, simple and green approach for obtaining ZnO@polysiloxane core-shell microspheres via hydrothermal assembly process. The synthesis route was shown in Scheme 1. Moreover, the novel diffusers based on the fillers of ZnO@polysiloxane were prepared by facile UV curing process. The optical properties and diffusing abilities were characterized for the materials to show the feasibility as an optical material. Besides, a series of optical performances was also first investigated.



Scheme 1. The synthesis route of ZnO@polysiloxane core-shell microspheres.

2. Experimental procedures

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.5%), urea ($CO(NH_2)_2$, 99.5%) and sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$, 99.5%) were obtained from Shanghai Chemical reagent Company. Poly(VTMS) microspheres were prepared by ourselves via sol-gel method (seen in Electronic Support Information). Tri(propylene glycol) diacrylate, photoinitiator 184, and polyurethane acrylate were obtained from Guangzhou Sadoma Chemical Co., Ltd. PET films with a thickness of 50 μm were obtained from Shenzhen Shenli Optical Film Co., Ltd.

2.2. Preparation of ZnO@polysiloxane sample

In a typical synthesis process, 2 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 4 mmol urea ($CO(NH_2)_2$) and 0.15 mmol sodium tartrate were dissolved in 70mL deionized water to forming clear solution, then 2 g polysiloxane microspheres (self-preparation, seen in Electronic Support Information) were added to the above solution with stirring for 10 min. The mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 110 °C for 4 h. The precipitate was centrifuged and washed several times with deionized water and absolute ethanol, and then dried at 190 °C for 12 h. Then, ZnO@polysiloxane microspheres was obtained.

Took down a few of the product sample, and then calcined at 300 °C for 2 h, only for investigating the structure of synthesized microspheres. In order to compare the structure of samples in XRD analysis, ZnO particles were prepared by hydrothermal method as described in literatures[26].

2.3. Preparation of optical diffuser sample

Subsequently, the complex films were prepared by solvent free UV curing. 5 g Tri(propylene glycol) diacrylate, 0.4 g photoinitiator 184, and 15 g polyurethane acrylate were mixed in dark space. The concentration of relative particles with 5—20 wt% were added to the above. The film samples were obtained by double-sided coating in 50 μm PET. Then, the film was placed in 100 w UV lamp (365 nm) for 10 min each side. Finally, it was placed in an oven at 60 °C for 24 h. The market diffuser for comparison derived from Dong Xucheng Chemical Co., Ltd. (DXC Diffusion 50-BDN).

2.4. Characterization

The structure of ZnO@polysiloxane was examined by FT-IR, powder transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA), shown in Electronic Support Information. UV-vis-NIR spectra of the optical diffusers were measured on a Shimadzu UV 3600 spectrometer, and the sample was made in the form of film via precision coater. The transmittance haze meter (WGT-S) was used for measuring the properties of optical diffusers. Optical diffusing properties were measured by light intensity distribution measuring instrument (WGZ-III).

3. Results and Discussion

3.1 Diffusing fundamentals

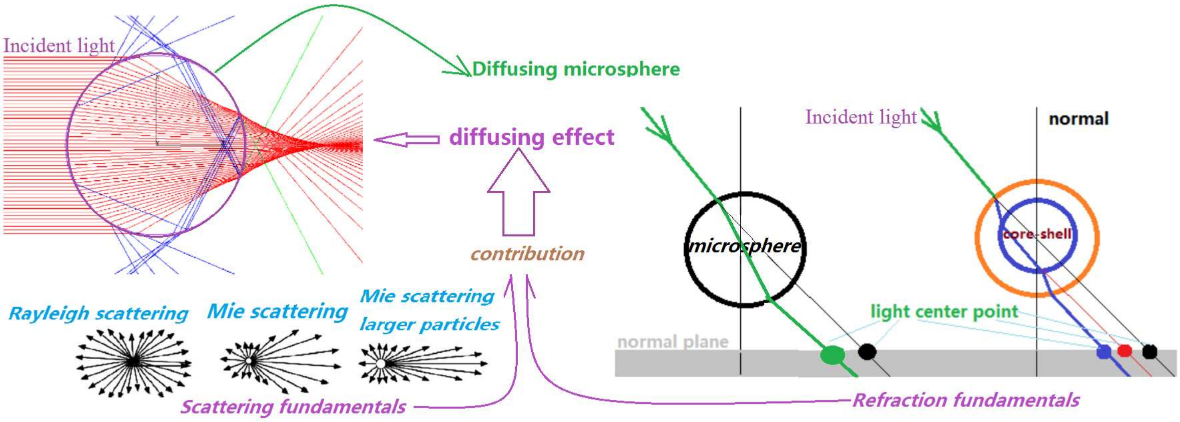


Figure 1. Light-diffusing phenomenon and relative fundamentals.

Light-diffusing phenomenon and relative fundamentals are very important for the light-diffusing study and the design of light diffusion agent. Fig. 1 displayed the diffusing effect based on diffusing microspheres. As can be seen, light-diffusing originated from scattering and refraction. The former contained Rayleigh scattering and Mie scattering, and the distinction between them was the size of diffusing particles. When the diameter of diffusing particles was much smaller than the wavelength of visible light, Rayleigh scattering occurred. Mie scattering appeared in the diffusing particles whose diameter was as much as the wavelength of visible light. In addition, the scattering effect would decreased continuously with the size of particles increasing. From the above analysis, it indicated that the size of diffusing particles for optimal diffusers should be concentrated in the range of 1~10 μm. The latter mainly relied on the shape and internal structure of particles, and the spherical structure can obtained excellent diffusing effect[9]. Besides, the inner structure of particles played more important role in light-diffusing effect than size-distribution of diffusing particles. Compared to common spherical, the core-shell structure can make better light-diffusing effect due to multi-scattering.

3.2 XRD analysis

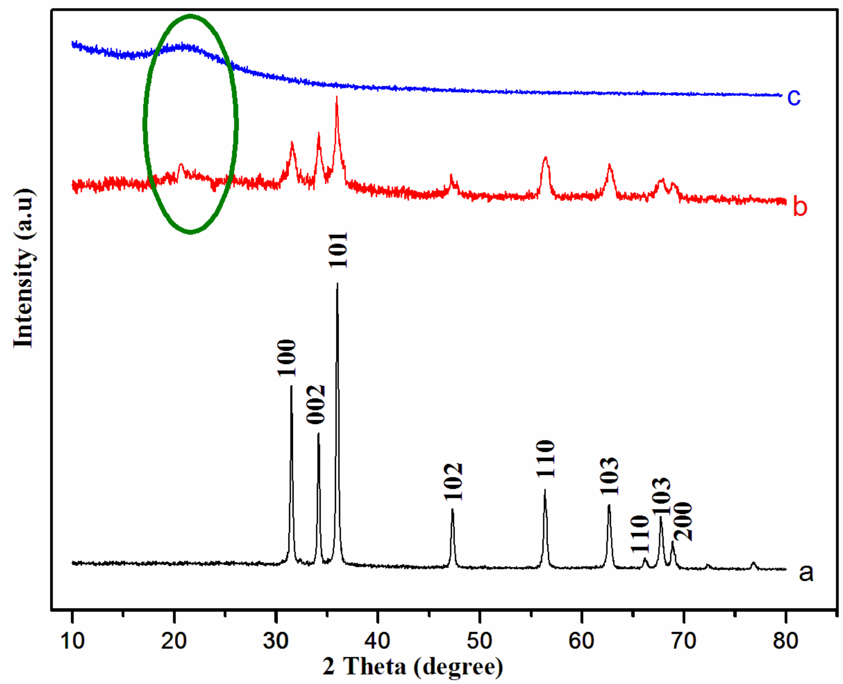


Figure 2. X-ray diffraction (XRD) patterns of (a) bare ZnO; (b) the product prepared by hydrothermal method; (c) poly(VTMS).

The X-ray diffraction (XRD) patterns of synthesized composites were shown in Fig. 2. The XRD pattern (2 θ>25°) of synthesized composite powders agreed well with the peaks of standard ZnO (Joint Committee on Powder Diffraction Standards (JCPDS) File Card No. 36-1451), which confirmed that the synthesized products contained ZnO. In addition, it formed a small broad peak in the hydrothermal product (shown in XRD curve b), which was corresponding to the poly(VTMS) XRD pattern.

Comparing the peak intensities of curve (a) with curve (b), it can be observed that the XRD pattern of hydrothermal product presented weak ZnO peaks and poly(VTMS) peak, which indicated the structure of the product took on the decreasing crystallinity. It suggested the composites of hydrothermal product experienced chemical Assembly other than the physical blend of poly(VTMS) microspheres and formed ZnO particles.

3.3 SEM analysis

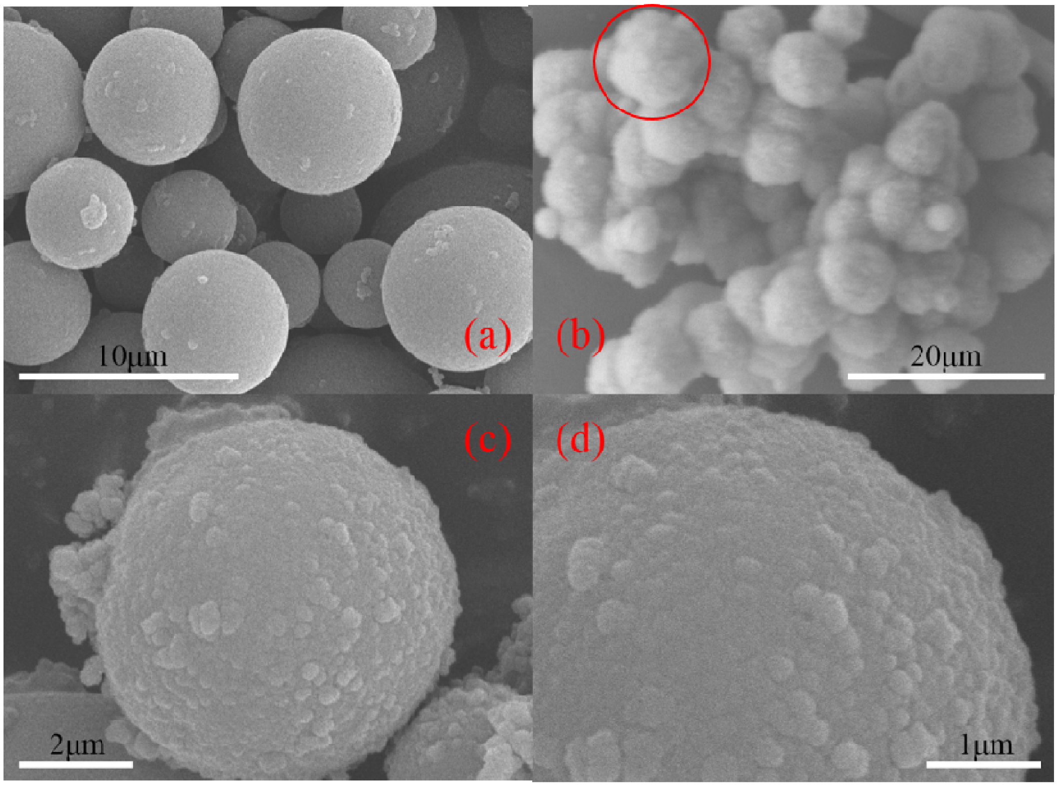


Figure 3. SEM photomicrographs of (a) poly(VTMS) microspheres; (b) ZnO@polysiloxane; (c) and (d) enlarged view within the red circle of (b).

Dimensions and morphological features of synthesized particles were observed by SEM shown in Fig. 3. The poly(VTMS) particles were prepared via sol-gel process, and the morphology was obtained in Fig. 3(a). The particles took on smooth regular spherical, and the size of them mainly focused on 5~8 μm. Then, the morphology of hydrothermal product was displayed in Fig. 3(b), 3(c) and 3(d), which presented the rough spherical. Fig. 3(c) and 3(d) were the enlarged view of red circle of Fig. 3(b), which displayed clearly the surface morphology of the target product. The size of final product was about 5~8 μm , and the morphology of the product was regular spherical shape. From the above analysis, it suggested that the rough of the product would not increase the thickness of Fig. 3(a) microspheres obviously.

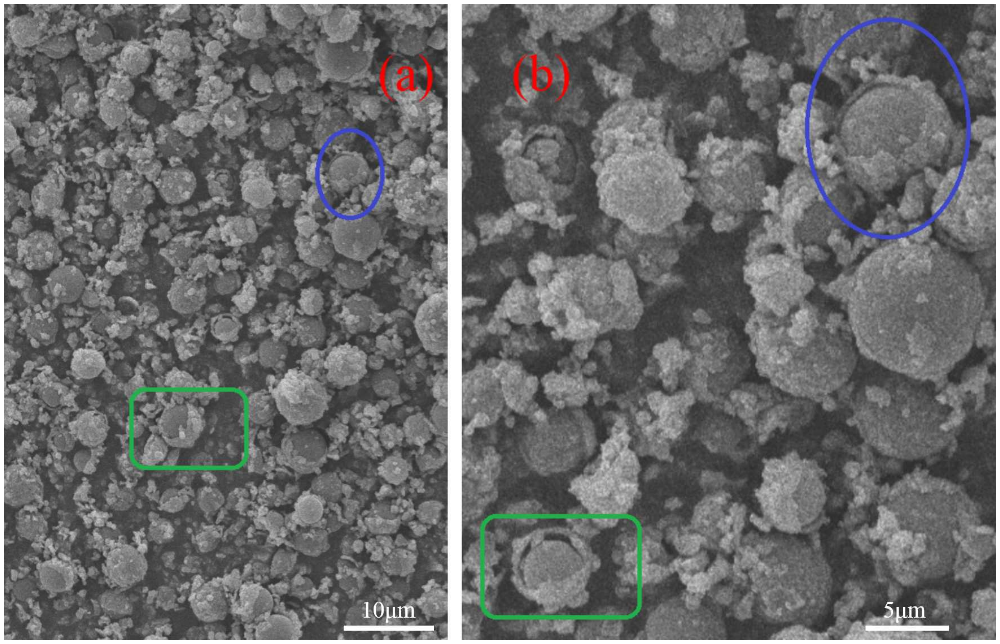


Figure 4. SEM photomicrographs of (a) the compared sample via hydrothermal process and then being calcined at 300 °C for 2 h; (b) enlarged view of (a).

To investigate the internal structure of the microspheres, the calcined sample was measured by SEM (shown in Fig. 4). Fig. 4(b) was the enlarged view of Fig. 4(a). As can be seen in the delineated boxes of Fig. 4, the broken structure of final product obviously revealed the core-shell structure of the microspheres. Compared with the SEM photomicrographs mentioned, it was suggested that the inner layer of final product was poly(VTMS) microspheres and the outer layer was ZnO. In addition, the microscope analysis revealed that the core-shell microspheres were about 5~8 μm in diameter and with a shell thickness of approximately 400~800 nm. Therefore, the core-shell structure with nanometer size shell layer made it owning special physical and chemical properties different from solid particles due to its refractive index difference, larger specific surface area, and nanostructured wall, as well as their potential applications of these materials for example controlled delivery, artificial cells and light-weight filler.

3.4 **Light Diffusion Phenomenon**

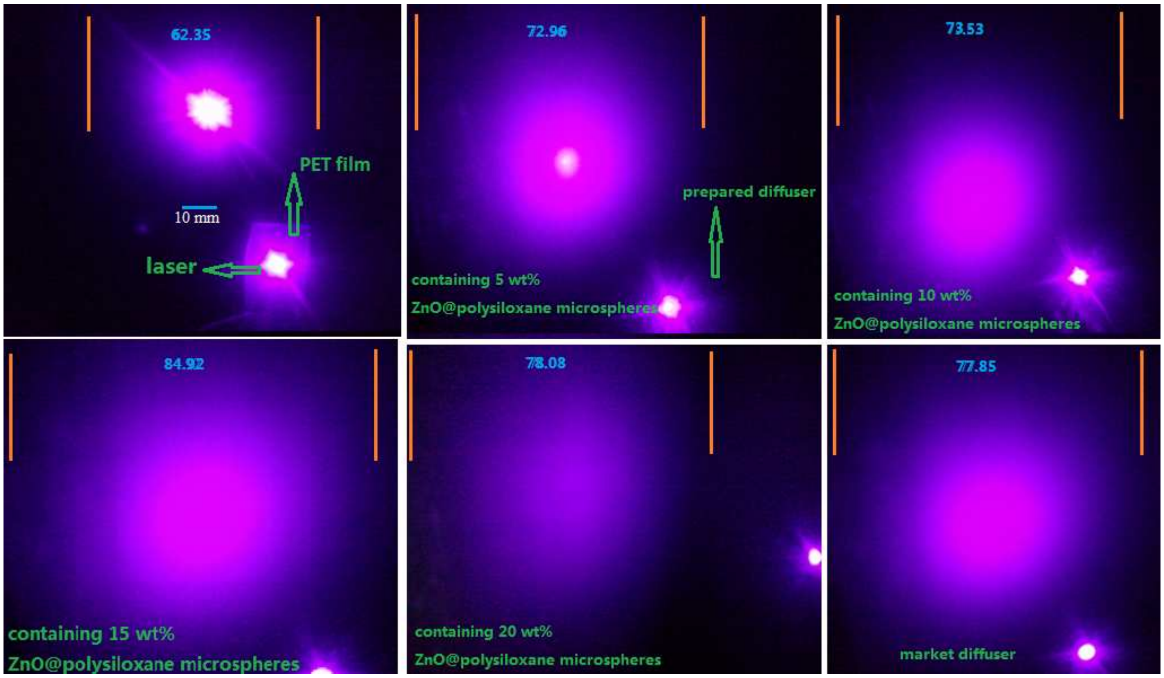


Figure 5. Diffusing images with 405nm laser.

The novel optical diffusers were examined to understand the effect of diffusing ability for the concentration of diffusing fillers. The quantity of ZnO@polysiloxane microspheres was modulated, including 5, 10, 15 and 20 wt %. A laser with 405 nm wavelength was used to illuminate directly on diffusers and the optical pattern was recorded by digital camera (shown in Fig. 5). It was clear that diffusion range gradually increased with the concentration of ZnO@polysiloxane microspheres increasing. Moreover, the prepared diffusers had good visible light transmittance, and the tunable optical diffusing capacity relied on the amount of ZnO@polysiloxane microspheres fillers. When the concentration of ZnO@polysiloxane microspheres was up to 15 wt%, the diffuser possessed good light-diffusing effect, similar to optical diffusers on market.

3.5 **Light Diffusing properties**

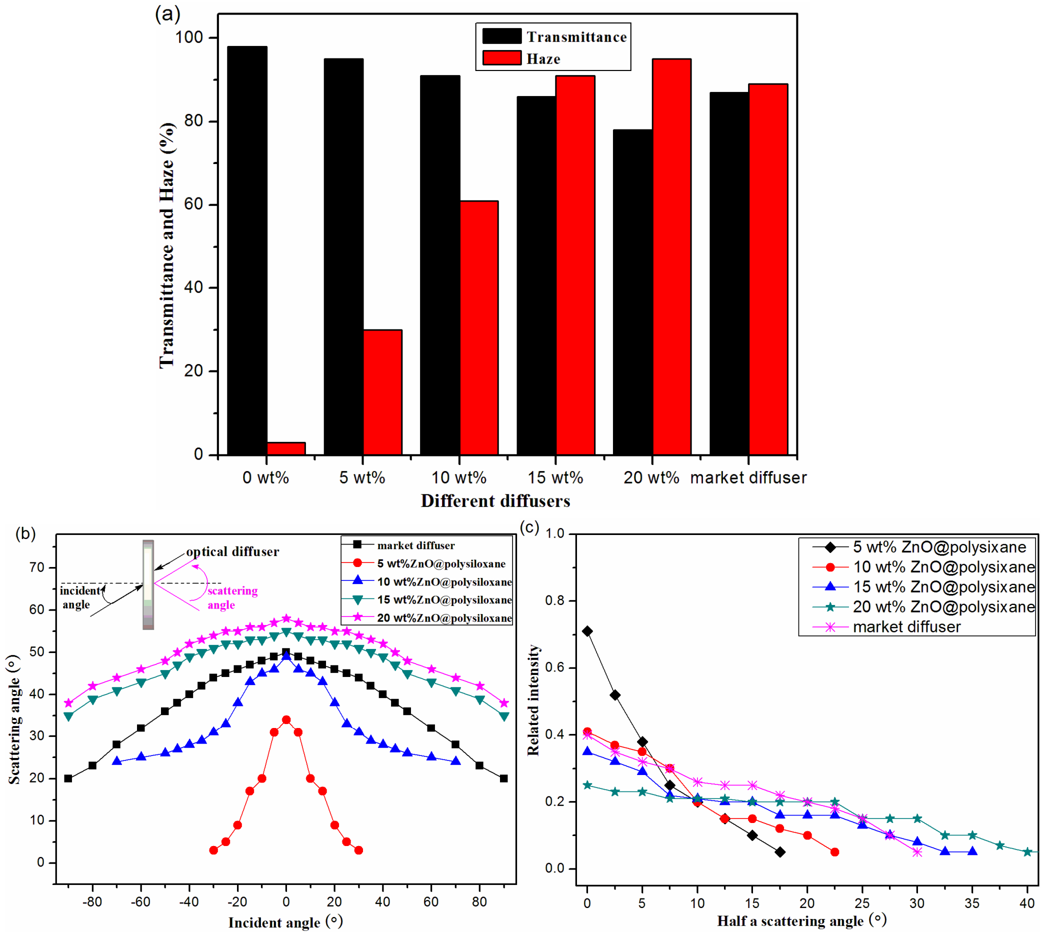


Figure 6. (a) the impact of transmittance and haze on the concentration of ZnO@polysiloxane microspheres; (b) the relationship between incident angle and scattering angle based on diffusing films with different fillers; (c) The related brightness for different ZnO@polysiloxane addition as a function of half a scattering angle.

The transmittance and haze of new diffusers with different concentration of ZnO@polysiloxane microspheres were measured by the transmittance haze meter. Fig. 6 (a) showed the transmittance and haze of the diffusers. The transmittance of the diffusers slightly decreased with the concentration of ZnO@polysiloxane microsphere increasing while the haze increased. When the concentration of ZnO@polysiloxane microspheres was up to 15 wt%, the haze of new diffusers can exceed the optical diffusers on market. Fig. 6 (b) showed the relationship between incident angle and scattering angle based on diffusing films with different concentration fillers. It can be observed that the scattering angle, also named as scattering range, increased with the concentration of ZnO@polysiloxane microspheres increasing. Due to multi-scattering derived from ZnO@polysiloxane microspheres structure, the new diffuser presented low incident angle dependence. In other words, all different angles of incident light can be scattering through the new diffuser when the concentration of novel diffusing fillers was certain value. When the concentration of ZnO@polysiloxane microspheres was up to 15 wt%, light scattering properties of new diffusers can reach the level of optical diffusers on market.

Fig. 6 (c) showed the related brightness as a function of half a scattering angle, wherein the related brightness was defined as the measured flux divided by the maximum flux. Thus, the percentage of the 0th order beam, defined as the flux in the center of diffusing beam divided by the overall flux of a laser beam, was also evaluated. It was observed that the intense of the 0th order beam decreased with the amount increasing of ZnO@polysiloxane, and it revealed that the scattering angle and the percentage of the 0th order beam could be modulated by the concentration of ZnO@polysiloxane microspheres. Therefore, various diffusing performance of optical diffusers can be obtained via adding the certain amount of ZnO@polysiloxane.

4. Conclusions

In conclusion, we explored an innovative and cost-effective optical diffusing filler with good optical properties. ZnO@polysiloxane microspheres were prepared by facile hydrothermal method, and the diffusers based on the fillers of them can be manufactured via solvent-free UV curing process. The optical properties of the new diffusers were also measured for the first time. The new diffuser based on the fillers of ZnO@polysiloxane microspheres possessed suitable light transmittance, good diffusion capacity, and low incident angle dependence, which were critical and necessary for excellent optical diffusers. In addition, the tunable optical diffusing capacity relied on the amount of ZnO@polysiloxane microspheres fillers. When the concentration of ZnO@polysiloxane microspheres was up to 15 wt%, the diffusing properties of the novel diffusers can reach the level of diffuser on market. Thus, ZnO@polysiloxane microspheres were quite suited to being as optical fillers and such microspheres can be widely used for preparing different multifunctional optical diffusers.

Acknowledgements

The authors are grateful to the financial supports of National Natural Science Foundation of China (Grant no. 21306023, 21376051, 21106017 and 51077013), Fund Project for Transformation of Scientific and Technological Achievements of Jiangsu Province of China (Grant no. BA2011086), Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant no. 20100092120047), Key Program for the Scientific Research Guiding Found of Basic Scientific Research Operation Expenditure of Southeast University (Grant no. 3207043101) and Instrumental Analysis Fund of Southeast University.

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