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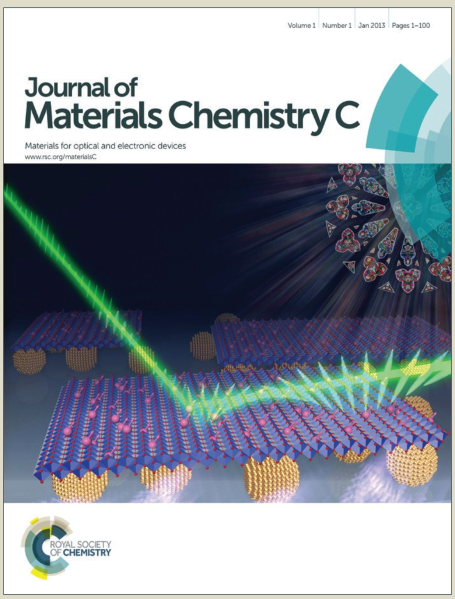

Optical diffusers with enhanced properties based on novel fillers of polysiloxane@CeO_2@PMMA

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Abstract: Multifunctional optical diffusers based on hybrid microspheres of polysiloxane@CeO_2@PMMA were successfully prepared by UV curing process. The novel diffusing microspheres can be synthesized via facile one-pot method, and the structure was proved by FT-IR, TEM, SEM, XRD, and TGA. The diffusers based on polysiloxane@CeO_2@PMMA were found to have greater properties than the diffusers using organic diffusing microspheres in heat resistance, mechanical, UV-shielding, fluorescence, and anti-aging ability. Moreover, the new diffuser exhibited a strong NIR absorption, which had a potential application in absorbing materials and night vision LCD monitor products. In addition, it obtained good diffusing effect via using the new diffuser, and the light-diffusing mechanism had also been illustrated. Besides, anti-aging ability of diffusers can be gradually improved with the fillers concentration of polysiloxane@CeO_2@PMMA increasing. Compared to moist-heat aging, the novel diffusers based on polysiloxane@CeO_2@PMMA possessed stronger effect for resisting UV aging. Hence, this study firstly introduced hybrid microspheres to optical diffusers, which can be except for preparing different multifunctional diffusing materials such as touch-panel functions, monitors, military projectors, novel LCD, etc.

Keywords: Optical diffuser; Anti-aging; CeO_2; Multifunctional materials.

1. Introduction

Optical diffusers are now widely used in backlight systems of various liquid-crystal display (LCD) devices such as TVs, overhead projectors, handheld game consoles, mobile phones, etc.[1] As well known, the constituent materials of optical diffusers are polymer materials with super optical characteristics, i.e., polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), or polycarbonate (PC)[2-4]. However, these materials have the disadvantage of high thermal sensitivity, poor UV-shieling effect and low NIR absorption, which limited the diffusers in the application of such as monitors, military projectors, night vision LCD, etc.[5-6]

At present, there were mainly two types diffusers to achieve a good optical diffusers for LCD[7]. The One depended mainly on microstructures of surface layer, such as microlenses, pyramids, rough surfaces and other microstructures, which was called surface-relief diffusers[8-10]. The other relied on adding transparent micro beads or fillers inside the plates to scatter light, which was called volumetric diffusers[11]. Conventional diffusing plates and films often coated the mixed solutions on substrate, in which it contained glass, polystyrene beads, poly(methyl methacrylate) (PMMA), $CaCO_3$, SiO_2, core-hell microspheres, and etc.[11-14] Organic-inorganic hybrid materials were fast-growing materials that may exhibit novel optical, nonlinear optical, mechanical, electronic, magnetic, photovoltaic, and conductive properties[15]. In particular, polymer-inorganic hybrid nanocomposites have been considered as excellent candidates for multifunctional materials, which possessed properties of both inorganic nanoparticles and polymers[16-19]. The hybrid materials also had enhanced dispersion property which was beneficial for processing[20]. Besides, incorporation of a small amount of inorganic nanoparticles can dramatically improve the bulk performance of polymer matrix in optical, thermal, mechanic and other properties[21-27]. Cerium dioxide (CeO_2), a typical rare-earth oxide, can be used as a component of multifunctional materials because of its special properties. Moreover, due to its good thermal and chemical stability, photoluminescence, low cost, etc.[27-28], it had potential applications as fillers for preparing multifunctional diffusers.

In the published literatures, the researches related to the hybrid fillers of optical diffusers were very limited. Current research on optical diffusers mainly foucsed on exploring and studying anisotropic materials. Haider Butt et al.[29] reported a devitrite-based optical diffuser with good diffusing effect. Takuya Ohzono et al.[30] proposed a tunable optical diffuser based on deformable wrinkles. The above novel materials presented good optical diffusion properties, which were based on the matericals with anisotropic properties. Another aspect, the results of conventional researches about optical diffusers (such as 3M, LG, Samsung Company) indicated the filler's microspherical structure can exhibit superior optical properties in optical diffusers[11, 13]. However, hybrid light-diffusing microspheres, to the best of our knowledge, has not been referred in any form relative research.

In this study, polysiloxane@CeO_2@PMMA microspheres were successfully synthesized by controllable one-pot process (seen in Electronic Support Information). Photoluminescence, thermal stability, mechanical, and UV-shielding properties of the target product were investigated in detail. The diffusers based on polysiloxane@CeO_2@PMMA were found to have greater properties than the diffusers using organic diffusing microspheres in heat resistance, mechanical, UV-shielding, fluorescence, and anti-aging ability. Therefore, the modification of PMMA microspheres with multiple structures has important theoretical significance and application value, and it can be expectable that the novel materials have a great potential application for preparing novel multifunctional materials.

2. Experimental procedures

2.1 Preparation of tunable optical diffusers

Polysiloxane@CeO_2@PMMA core-hell microspheres were synthesized by a convenient one-pot method (shown in Fig. 1). The experimental details can be presented in Electronic Support Information. 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.

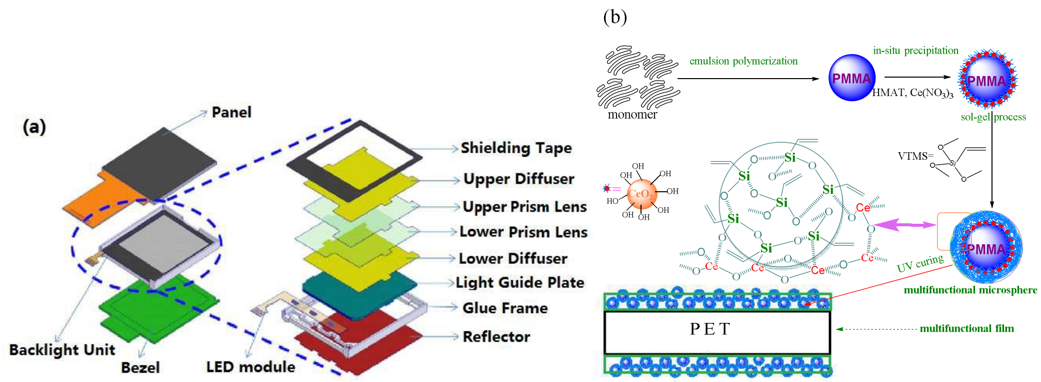

Figure 1. (a) the structure of backlight systems in LCD; (b) the synthetic route of polysiloxane@CeO_2@PMMA microspheres.

2.2 Performance Testing

The structure of polysiloxane@CeO_2@PMMA 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. The fluorescence property of the hybrid microspheres was measured using a Fluoromax-4 spectrofluorometer (Horiba, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). 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); 3NH NH310 color difference meter was used for measuring aging properties; HDZW-P UV aging test box and KJ-2091 moist-heat aging test machine were used; mechanical properties were tested by tensile machine KJ-1066B.

3. Results and discussions

3.1. Morphology and diffusing mechanism

The morphology of diffusers are fundamentally important for the light-diffusing study. The SEM images of the new diffuser were presented in Fig. 2. It displayed cross-sectional view of the new diffuser in Fig. 2(a). As can be seen, the top layer of cross-sectional view was the forming diffusion structure via UV curing, and it took on rough surface containing diffusion microspheres. Fig. 2(b) was the SEM image of the top surface of this new diffuser, and its enlarged view of the surface SEM image was listed in Fig. 2(c). It can be clearly found that the obtained polysiloxane@CeO_2@PMMA had been uniformly dispersed in the light-diffusing coating. The size-distribution of polysiloxane@CeO_2@PMMA had been shown in Fig. 2(d). It took on normal distribution approximately, and the size of them mainly foucsed on 700 nm. Besides, the inner structure of diffusing particles played more important role in light-diffusing effect than size-distribution of diffusing particles. The relative light-diffusing mechanism had been listed in Fig. 2(e). It can be seen that the direct cause of light-diffusing derived from special structure of the rough surface[3, 4]. The spherical scattering particles scattered light as light illuminated on the certain 3D space[29]. Compared to common spherical, the core-shell structure can make better light-diffusing effect due to multi-scattering.

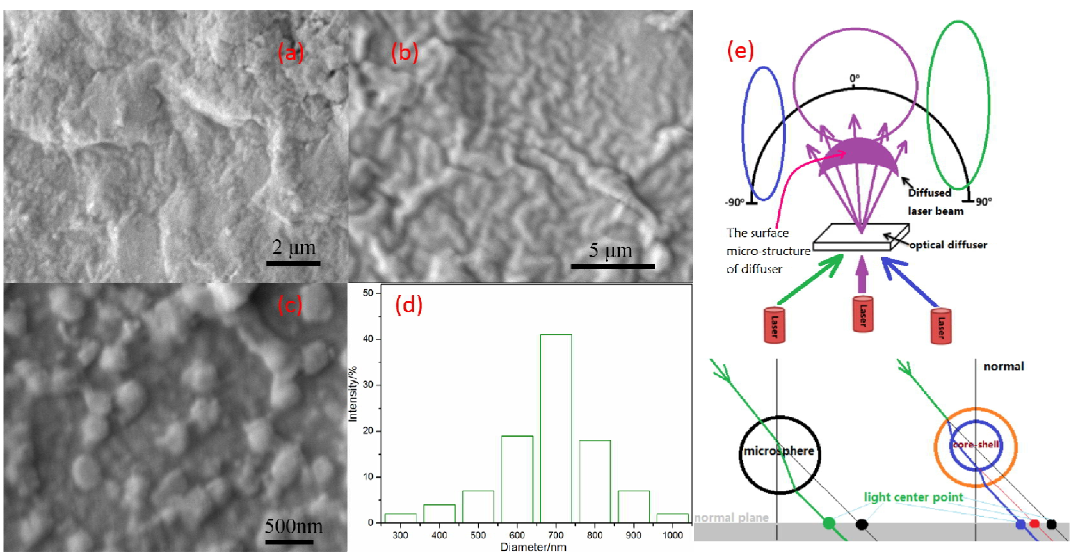

Figure 2. (a) Cross-sectional view of the new diffuser; (b) SEM image of the top surface of the new diffuser; (c) Enlarged view of the surface SEM image; (d) size-distribution of polysiloxane@CeO_2@PMMA; (e) light-diffusing mechanism.

3.2. TG-DSC Analysis

The TG-DSC curves of related compounds were shown in Fig. 3. As can be seen from TG curves, it presented a distinguishing thermal degradation process. The thermogravimetric data of these polymers were summarized in Table 1. The temperature of 5 % and 10 % weight loss (T5, T10) of the polymers had been calculated by means of thermograms and used as criterion for evaluation of thermal stability of the polymers. As can be seen in Fig. 3(a), the initial decomposition temperatures of composites were higher than the initial decomposition temperature of pure PMMA, which suggested that the precipitation of nano-CeO_2 in the surface of PMMA microspheres can improve the thermal stability of the polymer effectively. Moreover, the initial decomposition temperature can continue to improve via forming a cross-linked siloxane hybrid structure. Combined with the corresponding DSC curves and Fig. 3(b), it can be indicated that the weight of composites decreased with increasing calcination temperature, and then gradually approached a constant value. In addition, these weight losses possessed two reaction stages, including the removal of trace adsorbed water and surface hydroxyl, and the thermal decomposition of polymer components successively. Interestingly, the TGA curve of polysiloxane@CeO_2 @PMMA showed a continuous weight loss in the range 440~560 °C (orange box in Fig. 3 (b)), while the organic ingredients of polysiloxane evidently can be completely decomposed at or below 440 °C. The above fact suggested that only the rest of Ce-O-Si hybrid framework can be damaged by calcination. Ce-O-Si hybrid framework started to destroy at 440 °C, and it almost collapsed at T´ (shown in Fig. 3(b)). T´ can be defined as collapse temperature of hybrid framework, and the collapse temperature of hybrid framework was obviously higher than organic components. Thus, the strategy of forming Ce-O-Si hybrid framework can improve the thermal stability of polymer material effectively.

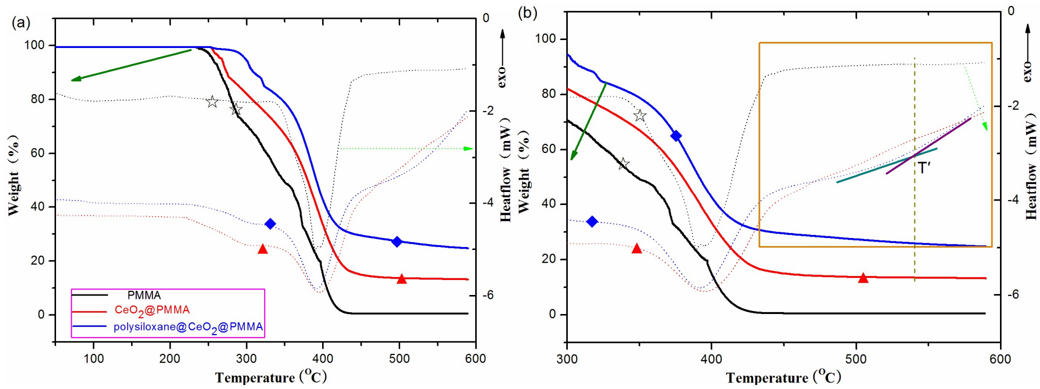

Figure 3. TG-DSC curves of related compounds.

Table 1. Thermal properties of polymers.

Polymer	Decomposition temperature (°C) T5	Decomposition temperature (°C) T10
PMMA	**255**	**265**
PMMA@CeO_2	**268**	**274**
Polysiloxane@CeO_2@PMMA	**299**	**310**

3.3. Photoluminescence properties

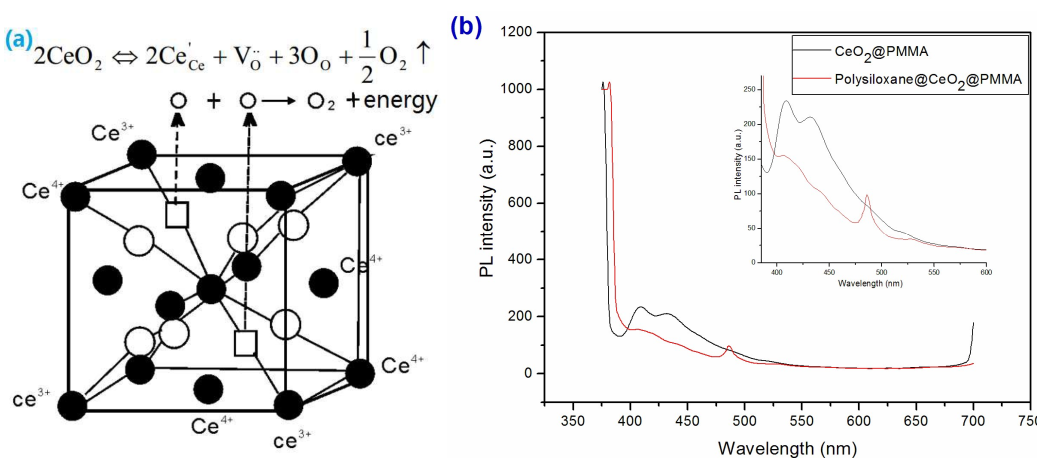

Figure 4. Photoluminescence emission spectrum of the samples at λex=375 nm.

As well-known, two form of Ce^{4+} and Ce^{3+} existed in CeO_2 particle, and then the resulting cystal defects of Cerium(IV) dioxide led to photoluminescence (PL) properties (shown in Fig.4 (a)). Thus, CeO_2 particle can form two types of optical centers depending on whether their surrounding environment was composed mainly of Ce^{3+} or Ce^{4+} ions and the latter was observed to emit a shorter PL wavelength than the former[31]. As can be shown in Fig. 4(b), typical broad peaks of CeO_2 appeared in PL spectrum, which were corresponding to the peaks centered below 460 nm. In addition, a new peak was clearly detected in the PL spectra of polysiloxane@CeO_2@PMMA at 487 nm. Combined with the analysis results of FT-IR and TG-DSC, the existence of Ce-O-Si caused a change in the lattice structure of CeO_2. So, it can be inferred that the PL peak at 487 nm mainly originated from Ce-O-Si in hybrid matrix. Thus, the novel PL properties had centain potential for application in biological labeling, heavy metal ion sensing, and etc.[32, 33]

3.4. Optical Properties

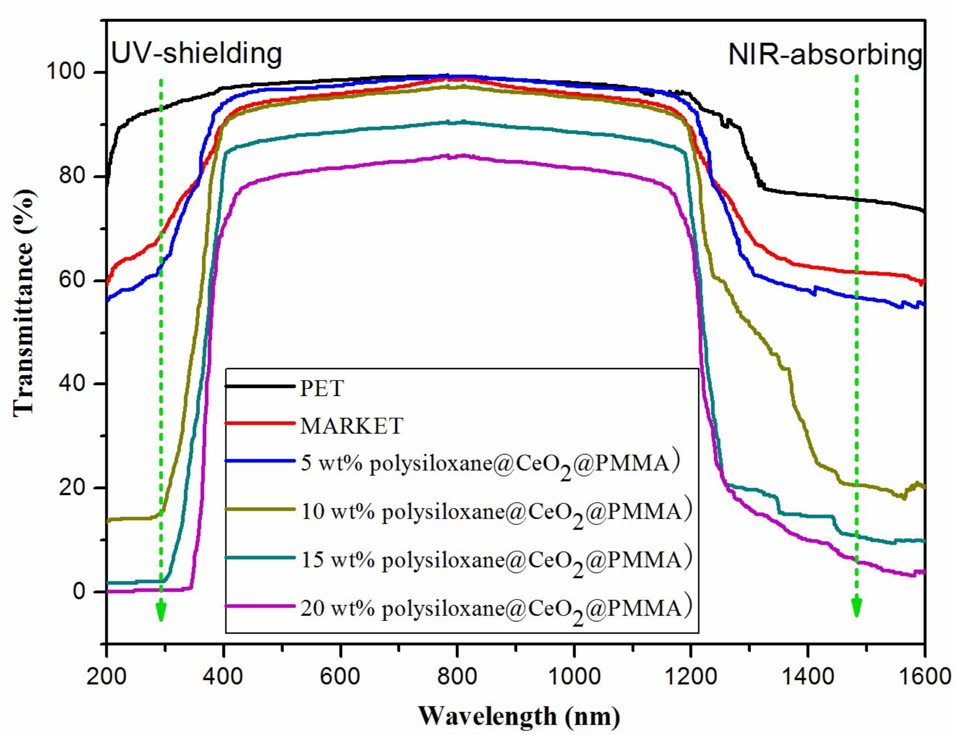

Figure 5. UV-vis-NIR spectroscopy of multifunctional films with different fillers.

The transmittance of novel diffusing film with different amount of polysiloxane@CeO_2@PMMA was measured by UV–vis-NIR spectrometer. Fig. 5 showed the transmittance of relative materials as a function of incident wavelength ranged between 200 and 1600 nm. The experimental result revealed that the novel diffusers had almost no absorption in the visible range, and the transmittance of visible light slightly decreased with the amount increasing of polysiloxane@CeO_2@PMMA. Nevertheless, the novel diffusers had a strong absorption in the ultraviolet region, significantly better than conventional diffusion film. When the amount of polysiloxane@CeO_2@PMMA microspheres was up to 15 wt%, the novel diffusers can almost block all UV light. It can be mainly attributed to CeO_2 accession[34]. Besides, the novel diffuser exhibited a strong NIR absorption, which had a potential application in absorbing materials and night vision LCD monitor products.

3.5. Light Diffusion Effect

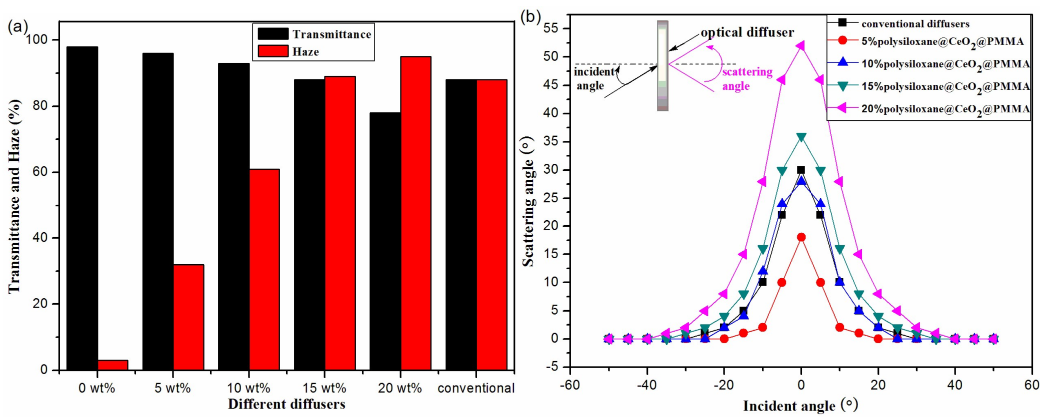

Figure 6. (a) the effect of polysiloxane@CeO_2@PMMA concentration on transmittance and haze; (b) the relationship between incident angle and scattering angle based on diffusing films with different fillers.

Optical diffusion properties can be characterized by haze measuring. Tunable optical diffusers with different amount of polysiloxane@CeO_2@PMMA microspheres were measured, shown in Fig. 6(a). It was easily found that the haze increased with the amount increasing of polysiloxane@CeO_2@PMMA. When the concentration of polysiloxane@CeO_2@PMMA microspheres was up to 15 wt%, the haze of novel diffusers can exceed the conventional LCD diffusers on the market. Fig. 6(b) presented the relationship between incident angle and scattering angle based on tunable optical diffuser with the fillers of different amounts. It was clear that the scattering angle, also named as scattering range, increased with the amount of polysiloxane@CeO_2@PMMA increasing. Due to the multi-scattering derived from polysiloxane@CeO_2@PMMA core-hell structure, the novel optical diffuser presented great diffusing effect. When the concentration of polysiloxane@CeO_2@PMMA microspheres was up to 15 wt%, light diffusion effect of novel diffusers can reach the level of conventional LCD diffusers on the market.

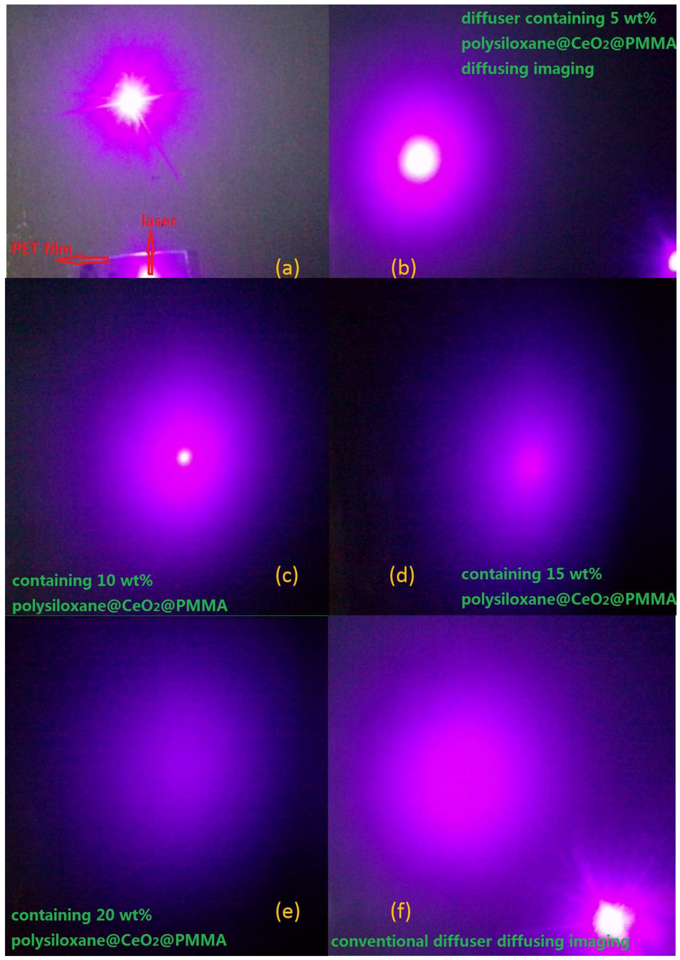

Figure 7. The light diffusing images of different films (a) PET; (b) diffuser containing 5 wt% polysiloxane@CeO_2@PMMA; (c) containing 10 wt%; (d) containing 15 wt%; (e) containing 20 wt%; (f) conventional diffuser diffusing imaging.

The tunable optical diffusers were examined to understand the effect of diffusing ability for the concentration of diffusing fillers. The quantity of composite 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. Fig. 7(a)–(f) showed the optical images of diffusion pattern, and it was clear that diffusion range gradually increased with the concentration of polysiloxane@CeO_2@PMMA microspheres increasing. Due to red and violet light being similar in human visual perception, the presented took on the similar color with purple. However, the image of diffuser containing 20 wt% polysiloxane@CeO_2@PMMA appeared out of blue color. Thus, it can be inferred that photoluminescence generating the light of 487 nm wavelength had produced a significant impact on laser imaging. In addition, when the concentration of polysiloxane@CeO_2@PMMA microspheres was up to 15 wt%, the diffuser possessed improved light diffusing effect exceeding the conventional LCD diffusers on the market.

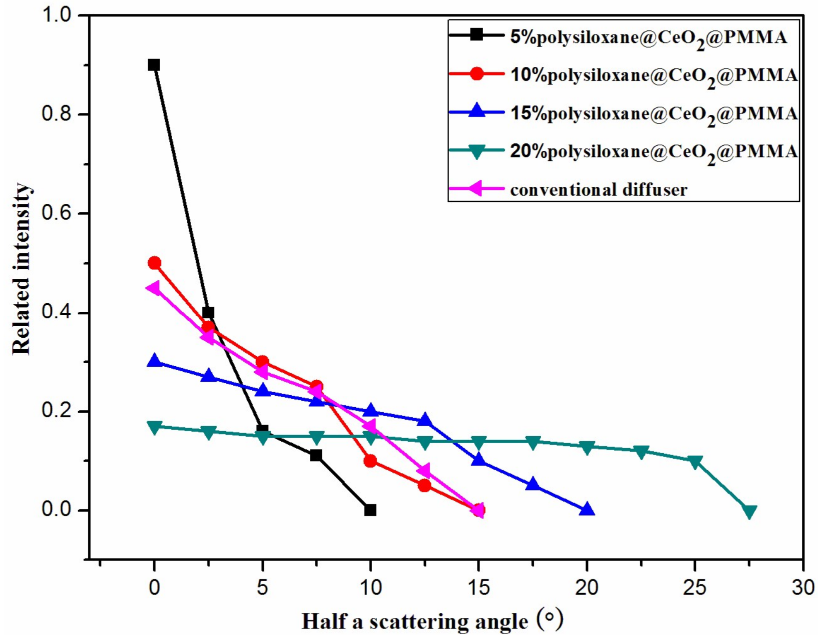

Figure 8. The related brightness for tunable diffusers as a function of half a scattering angle.

Fig. 8 showed the related brightness for Fig. 7(b)–(f) 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 polysiloxane@CeO_2@PMMA, and it revealed that the scattering angle and the percentage of the 0th order beam could be modulated by the concentration of polysiloxane@CeO_2@PMMA microspheres. Therefore, various diffusing performance of optical diffusers can be obtained via adding the certain amount of polysiloxane@CeO_2@PMMA.

3.6. Enhanced mechanical properties

Fig. 9 showed the mechanics properties of the multifunctional films containing tensile strength and breaking elongation. As can be seen, when the mass fraction of the light scattering agent adding to PMMA was from 0% to 20%, the film containing polysiloxane@CeO_2@PMMA core-shell microspheres had increasingly breaking elongation which was higher than the breaking elongation of the film containing PMMA microspheres. It indicated that the synthesized hybrid microspheres can improve the ductile fracture of PET substrate effectively. In addition, the variety of tensile strength presented different situations with the light scattering agent increasing. The film containing PMMA microspheres displayed the slightly decreasing tensile strength with the light scattering agent increasing, while the film containing polysiloxane@CeO_2@PMMA displayed the increasing and then decreasing tensile strength. The results both tensile strength and breaking elongation strongly suggested that the diffuser containing polysiloxane@CeO_2@PMMA core-shell microspheres was more and more toughness with the quantity increasing.

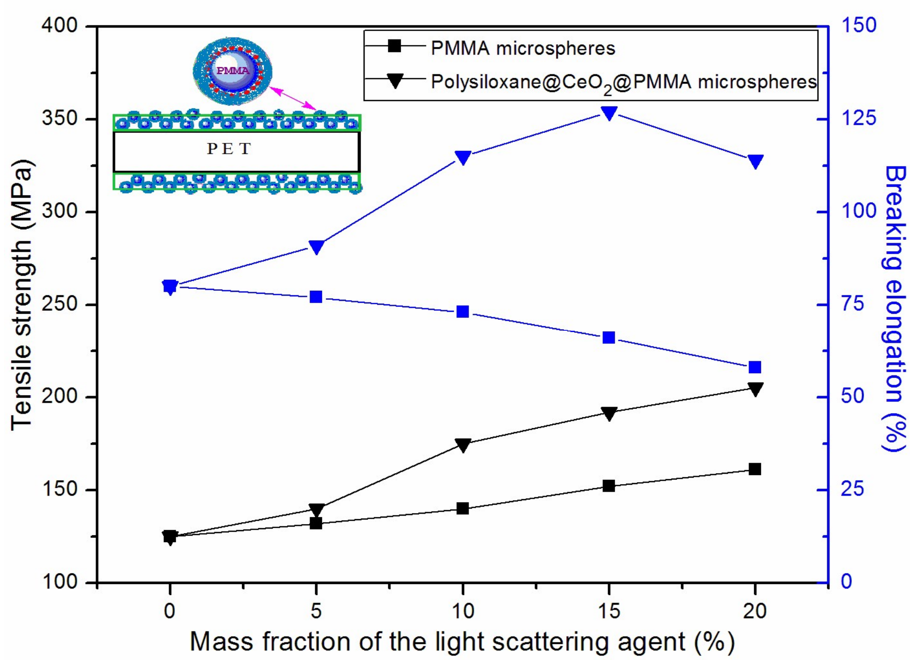

Figure 9. The mechanics curves of multifunctional films with different fillers.

3.7. Enhanced anti-aging properties

Table 2. Aging performance comparison of different addition amount with polysiloxane@CeO_2@PMMA.

Moist-heat aging	△E	Yellowness Index	UV aging	△E	Yellowness Index
0 wt% amount	16.58	2.62	0 wt% amount	21.32	2.97
5 wt% amount	14.35	2.25	5 wt% amount	18.15	2.62
10 wt% amount	11.43	1.86	10 wt% amount	14.93	2.13
15 wt% amount	8.56	1.48	15 wt% amount	10.76	1.75
20 wt% amount	5.76	1.02	20 wt% amount	6.27	1.17

Anti-aging properties of the optical diffusers were very important, which directly affected their quality and application field. The evaluation of aging properties can be used as indicators of the nature of diffusers. Aging resistance can be divided into moist-heat aging and UV aging, which are inevitably occurred in the material of the organic component in the practical application. Therefore, the study of diffusers in moist-heat and ultraviolet radiation aging properties had important significance. Color deviation(ΔE) and yellowness index is the most common and most important indicators of anti-aging evaluation. Table 2 listed aging performance comparison of different addition amount with polysiloxane@CeO_2@PMMA. As can be seen, the film without adding polysiloxane@CeO_2@PMMA had a poor anti-aging ability. ΔE and yellowness index possessed a large value after aging process. It was easily found that ΔE and yellowness index obviously decreased with the fillers concentration of polysiloxane@CeO_2@PMMA increasing. In other word, anti-aging ability of diffusers gradually improved with the fillers concentration of polysiloxane@CeO_2@PMMA increasing. Compared to moist-heat aging, UV aging decreased more quickly with the concentration of polysiloxane@CeO_2@PMMA increasing, which was due to that the fillers of polysiloxane@CeO_2@PMMA possessing a very strong ability to absorb ultraviolet.

Conclusions

In summary, multifunctional optical diffusers based on hybrid microspheres of polysiloxane@CeO_2@PMMA were prepared by convenient solvent-free UV curing process, and the novel diffusing microspheres can be synthesized via facile one-pot method. The novel diffusers had an enhanced UV-shielding effect, heat resistance, mechanical, fluorescence, and anti-aging properties. Moreover, the novel diffuser exhibited a strong NIR absorption, which had a potential application in absorbing materials and night vision LCD monitor products. It confirmed that novel diffusers had a good diffusing effect and transmittance. Thus, it can be expected to a wide application in optical diffusers. Besides, anti-aging ability of diffusers gradually improved with the fillers concentration of polysiloxane@CeO_2@PMMA increasing. Compared to moist-heat aging, the novel diffusers based on polysiloxane@CeO_2@PMMA possessed stronger effect for resisting UV aging.

Acknowledgements

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Supporting Information

The synthesized details of polysiloxane@CeO_2@PMMA was presented. Then, the physical and chemical properties of multifunctional microspheres of polysiloxane@CeO_2@PMMA were examined by FT-IR, powder transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray diffraction

(XRD).

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