Nano-silica reinforced hybrid light-diffusing films with enhanced mechanical and thermal properties

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Ultraviolet-curable hybrid light-diffusing films with good optical, mechanical and thermal properties were prepared by involving vinyl-silane-modified nano-silica into light-diffusing films. The light-diffusing films were two-phase materials consisting of UV-curable matrix and light-diffusing agent. The effect of three different light-diffusing agents, viz. inorganic layered particle ($CaCO_3$), spherical acrylic resin (MR-7HG) and organosilicone resin (KMP-590) and their contents, on the optical properties of light-diffusing films was studied. The results showed the light-diffusing film exhibited good optical properties (the transmittance was 90.7% and the haze was 95.5%) when KMP-590 was a light-diffusing agent and its content was 25%. It was because that KMP-590 showed good transparency, good dispersion in the UV-curable matrix and the greater difference in refractive index with UV-curable matrix and polycarbonate substrate. Furthermore, the effect of nano-silica on the optical, mechanical and thermal properties of the hybrid light-diffusing films was investigated. Compared to that of the light-diffusing films without nano-silica, the haze of the hybrid light-diffusing films containing nano-silica was lightly enhanced to above 98%, while their transmittance basically remained unchanged at a high value (above 89%). Additionally, scratch and abrasion resistance of the hybrid films were obviously improved by nano-silica especially with the particle size of 10–15 nm. Furthermore, the mechanical property and thermal stability of the hybrid films were improved as the content of nano-silica with the particle size of 10–15 nm increased. The enhanced mechanical property and thermal stability of the films could be attributed to the dense structure induced by the increase in network density with the addition of vinyl-silane--modified nano-silica.

Keywords: optical materials and properties, nanocomposites, light-diffusing films, sol-gel preparation, nanoparticles.

1. Introduction

Light-diffusing film is a material with high light transmittance and high haze. It can diffuse a point or line light source, or adjust the angle of emergent light to achieve homogeneous surface lighting. Recently, it has been widely used in the fields of lighting and display, *e.g.*, LCD backlight, transmission type screen and lighting equipment [1–3]. Based on different diffusing principles, light-diffusing film can be classified into two types: the surface-relief type and the particle-diffusing type [4].

The surface-relief type film mainly depends on microstructures on the surface to scatter light, such as microlens [5], pyramids [6], hemisphere [7] and other microstructures [8]. These microstructures are often fabricated via complicated processes and expensive equipment.

The particle-diffusing type films are prepared by coating a mixture of light-diffusing particle (LDP) and binder resin on optical plastics. Diffusing principle of this film type mainly depends on the difference in refractive index between the resin and LDP. When light passes the interface of the resin and the particles, a refraction event occurs to achieve light scattering. Accordingly, there are many factors that will influence the optical performance of the films such as the type of binder resin/LDP, dispersion of a LDP in binder resin, particle diameter, coating thickness, and so on [9–11]. KUO *et al.* [9] firstly investigated the correlations between light transmittance/haze of the films and the coating thickness/particle diameter ratio and beads/resin weight ratio and gave a general guide for the design engineers. Subsequently, many types of LDP, including organic LDP (polymethylmethacrylate, polystyrene, acrylic resin), inorganic LDP (SiO_2, silicate microspheres, TiO_2), and organic/inorganic composite LDPs (polysiloxane@CeO_2-PMMA, poly(methylmetharylate-co-3-(trimethoxysilyl)propyl-methacrylate) hybrid particle) were studied to obtain the light-diffusing film with good optical properties [4, 9, 12–16]. Besides optical properties, mechanical and thermal properties of the films are also very important for their application.

Herein, we report a facile approach that can be used to conveniently prepare UV-curable hybrid light-diffusing films with good mechanical and thermal properties as well as excellent optical performance. First, the influence of three different light diffusing agents, viz. inorganic layered particle ($CaCO_3$), spherical acrylic resin (MR-7HG) and organosilicone resin (KMP-590) on the optical properties of light-diffusing film was studied. Next, a vinyl-silane-modified nano-silica/1,6-hexanedioldiacrylate (HDDA) dispersion was prepared and introduced into the light-diffusing film to form organic/inorganic hybrid light-diffusing films. The effect of nano-SiO_2 with two different particle sizes on the optical and mechanical properties of the films was investigated. Finally, the influence of nano-silica contents with the particle size of 10–15 nm on the mechanical and thermal properties of the films was studied.

2. Experiment

Silane-modified nano-silica was prepared by adding γ-methacryloxypropyltrimethoxysilane (KH570) and vinyltrimethoxysilane (VTMS) into a colloidal suspension of silica (Nissan Chemical Industries, Ltd.) based on the molar ratio of KH570/VTMS = 1 and (KH570 + VTMS)/SiO_2 = 0.1. Then the mixture was sonicated at 0°C for 30 min and heated at 50°C for 3 h in a water bath with magnetic stirring. Afterwards, HDDA (Jiangsu Sanmu Corporation, China) was added to the mixture and then sonicated at 0°C for 30 min, followed by vacuum distillation at 45–60°C to get SiO_2/HDDA dispersion with the weight ratio of silane-modified nano-silica and HDDA of 1.
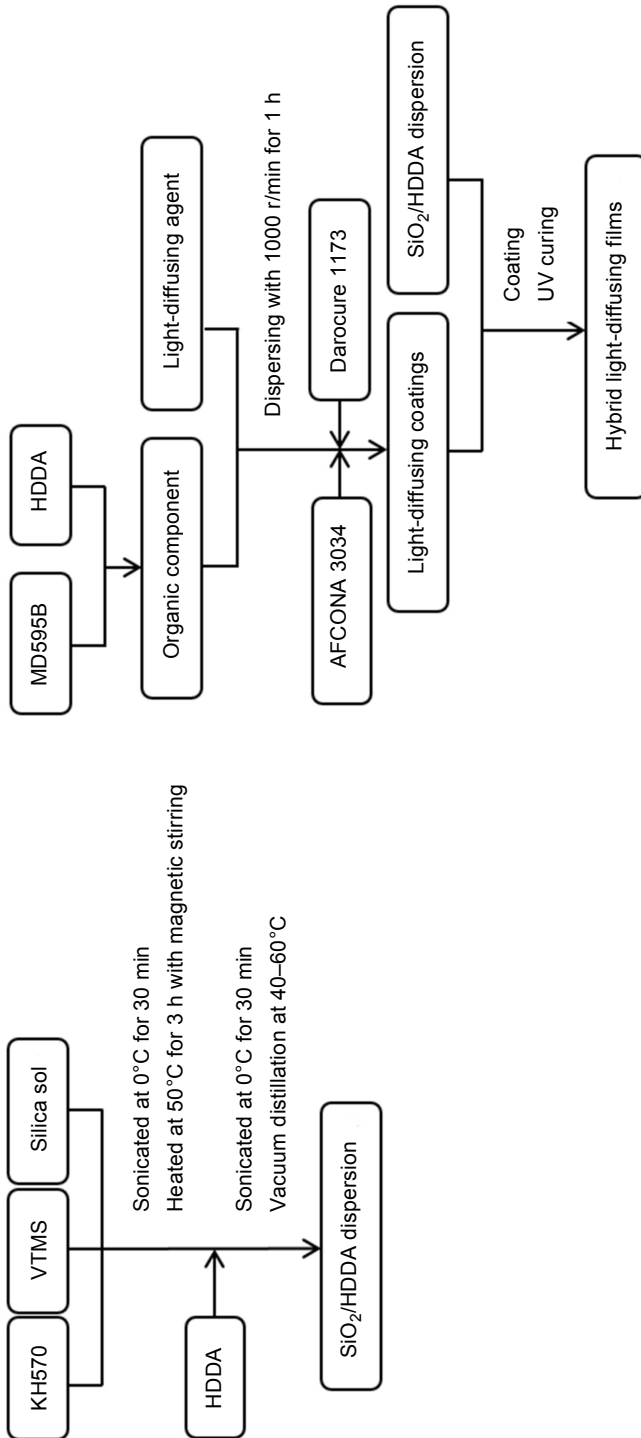
Fig. 1. Procedure for the preparation of light-diffusing films.

The light-diffusing coating was obtained by mixing organic component and light-diffusing agent. Organic component was a mixture of polyurethane acrylate (MD595B, Shanghai Miaoda Polymer Materials Co., Ltd., China) and HDDA with the weight ratio of 3:2. Three different kinds of light-diffusing agents have been investigated, viz. $CaCO_3$ (Foshan Yuanlei Powder Co., Ltd., China), MR-7HG (Suzhou Soken Chemical Co., Ltd., China) and KMP-590 (Shin-Etsu Chemical Co., Ltd., Japan). The coatings were designated as LDC-X, where LDC stands for a light diffusing coating and X stands for a light-diffusing agent. Light-diffusing agents were dispersed in the organic component with 1000 r/min for 1 h. Afterwards, 3 wt% leveling agent AFCONA 3034 and 4 wt% of photoinitiator Darocure 1173 were added to get UV-curable light-diffusing coating materials.

The as-prepared SiO_2/HDDA dispersion was dispersed in LDC-KMP to get the hybrid light-diffusing coatings. Two different particle sizes of SiO_2, *i.e.*, 10–15 nm and 100 nm were chosen. The corresponding hybrid light-diffusing coatings were labeled as HLDC-10 (containing 10–15 nm SiO_2) and HLDC-100 (containing 100 nm SiO_2), respectively. The hybrid coatings were further cast on PC substrates using a 25 μm wire-gauged bar applicator at room temperature and then exposed to a UV cross-linking apparatus (maximal peak: 365 nm) to get the hybrid films. The above synthetic procedure is shown in Fig. 1.

The dispersion of KMP-590 and SiO_2 nanoparticles in light-diffusing coatings was characterized by a transmission electron microscope (TEM, JEM-2010F, Japan). The transmittance and haze of the films were measured with a haze meter (Diffusion Systems EEL57D, UK). The refractive index was measured with an Abbe refractometer (2W (WZS-1), China). FTIR spectra were recorded on an AVATAR 370 FTIR apparatus (Nicolet, US) in the wave number range of 4000–400 cm^{-1}. The crystal phases of the films were identified by a D/max-2200/PC X-ray diffractometer (Rigaku, Japan). The abrasion resistance was carried out by subjecting the coated substrate to a standardized Taber abrasion test. The CS-10 rubber wheel was used in conjunction with 500 g load on each wheel. Pencil hardness was tested by a PPH-I pencil hardness tester according to ASTM D3363. The microhardness of the UV-cured films was measured with a nanoindenter (Tribo Indenter, USA) equipped with a diamond Berkovich indenter. Finally, thermogravimetric analysis (TGA) of the films was carried out with Q500 equipment (TA company, USA) from 40 to 700°C at heating rate of 10°C/min under nitrogen atmosphere.

3. Results and discussion

3.1. The effect of light-diffusing agents on the optical properties of light-diffusing films

The optical properties of the light-diffusing films with three different light-diffusing agents are presented in Fig. 2. As seen graphically, LDC-KMP shows the better optical
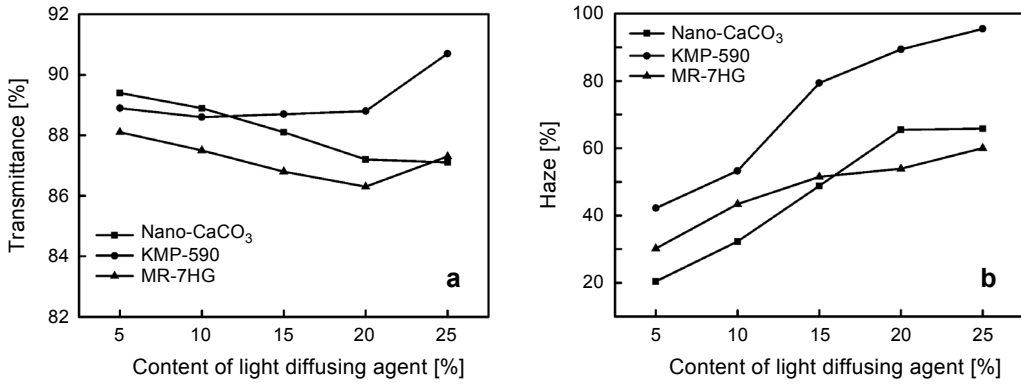
Fig. 2. The transmittance (**a**) and haze (**b**) of films as a function of the content of light-diffusing agent.

property. The reason is that KMP-590 is the organosilicone resin with good transparency and dispersion in the UV-curable matrix. In addition, light on the smooth spherical surface of KMP-590 has regular behaviors, such as reflection and refraction. At the same time, the refractive index between KMP-590 ($n = 1.43$) and PC substrate ($n = 1.59$), UV-curable matrix ($n = 1.48133$), is not matched. MR-7HG is PMMA power which also has a spherical structure. However, it appears that the difference in the refractive index between MR-7HG ($n = 1.49$) and PC substrate, UV-curable matrix, is less than KMP-590 ($n = 1.43$). Therefore, both the transmittance and the haze of the film are at a relatively lower level. $CaCO_3$ ($n = 1.49$) is an irregular layered solid particle, which allows the initial light source to pass through the layers with more loss and messy scattering. So the light diffusion effect is not good. From Fig. 2, it can be found that as KMP-590 content increases, the transmittance and haze of LDC-KMP increase. When the content is 25%, the transmittance and haze reach 90.7% and 95.5%,
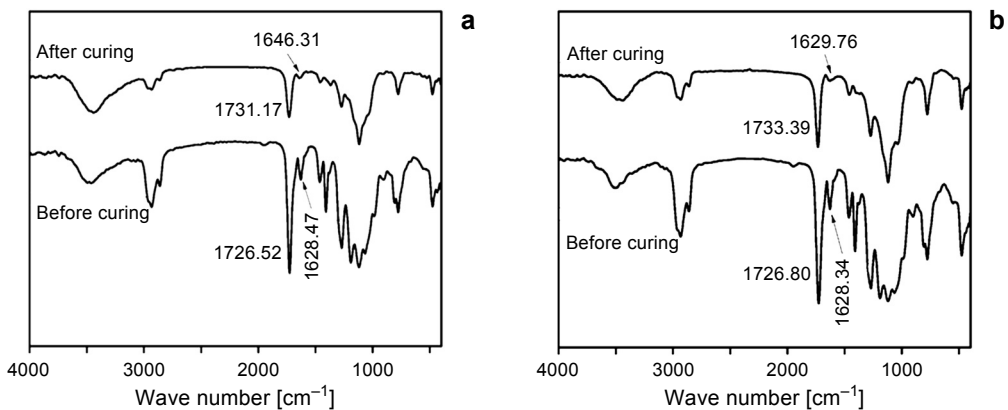

Fig. 3. FT-IR spectra of HLDC-10 (**a**) and HLDC-100 (**b**).

respectively. However, when the content is more than 25%, the viscosity of the coating will become very high, which is not-suitable for application. Thus, 25% KMP-590 is chosen in the following experiment.

3.2. The characterization of organic/inorganic hybrid light-diffusing films

The FTIR spectra of HLDC-10 and HLDC-100 are presented in Fig. 3. It can be found that their spectra are similar. The peak at 1628 cm^{-1}, which is assigned to the symmetric stretching vibration of C=C, has disappeared dramatically after the coatings are cured, meaning the polymerization reaction occurs and has a high double bond conversion rate. XRD analysis is employed to investigate the crystal phases of HLDC-10 and HLDC-100. The typical XRD patterns in Fig. 4 contain a broad feature at about $2\theta = 21°$ due to an amorphous SiO_2 without the diffraction peaks of other crystalline components.

3.3. The optical performance of organic/inorganic hybrid light-diffusing films

The transmittance and haze of the hybrid films with different particle sizes of nano-SiO_2 coated on PC substrate are presented in Fig. 5. It can be found that the transmittance
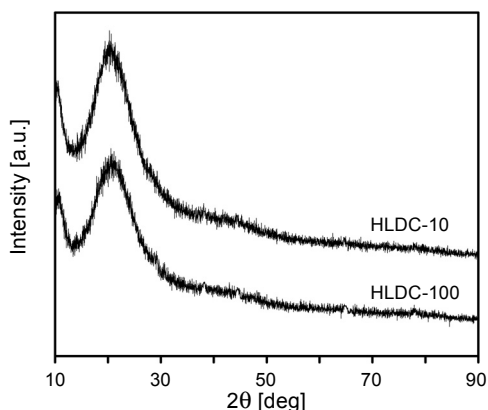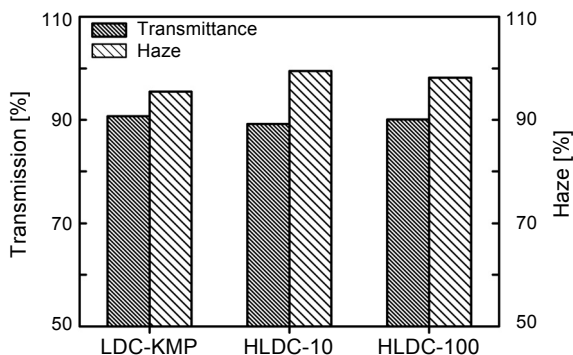

Fig. 4. XRD patterns of HLDC-10 and HLDC-100.

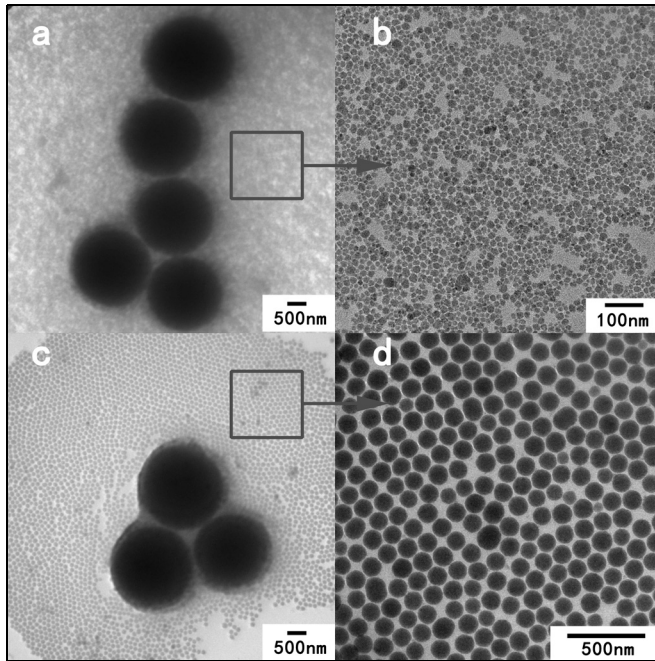Fig. 5. The transmittance and haze of LDC-KMP, HLDC-10 and HLDC-100.

Fig. 6. TEM micrograph of HLDC-10 (**a**), SiO$_2$ nanoparticles (10–15 nm) in HLDC-10 (**b**), HLDC-100 (**c**) and SiO$_2$ nanoparticles (100 nm) in HLDC-100 (**d**).

of the light-diffusing films remains unchanged at high value (above 89%) with the incorporation of nano-SiO$_2$. The reason is that SiO$_2$ nanoparticles with a small particle size hardly block light. In addition, nano-SiO$_2$ modified with KH570 and VTMS can be evenly dispersed in the polymer matrix and have no aggregated morphology due to the steric barrier of the organic chains from the coupling agents (Fig. 6) [17]. Furthermore, we can see that the hybrid light-diffusing films containing nano-silica have a little higher haze than the films without nano-silica, which is attributed to the difference in the refractive index between the SiO$_2$ (10–15 nm)/HDDA dispersion (n = 1.44696), SiO$_2$ (100 nm)/HDDA dispersion (n = 1.44605) and LDC-KMP (n = 1.48020) [16].

3.4. The mechanical properties of organic/inorganic hybrid light-diffusing films

The abrasion and scratch resistance of the hybrid films with different particle sizes and contents of nano-SiO$_2$ were measured to reveal the efficiency of mechanical improvement by nano-SiO$_2$.

As seen from Fig. 7, LDC-KMP has a mass loss of about 8.70 mg after 400 wear cycles. On the other hand, HLDC-100 and HLDC-10 have a mass loss of about 7.50 mg and 2.65 mg. It means that the abrasion resistance of the films can effectively increase with the addition of nano-SiO$_2$, which is attributed to the Si–O–Si backbone of inorganic network. In addition, the abrasion resistance of HLDC-10 has more improve-
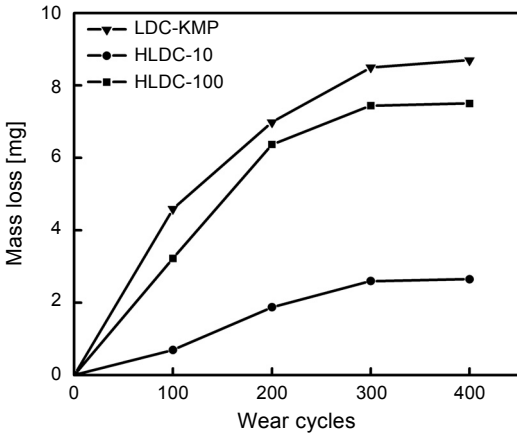
Fig. 7. The abrasion resistance as a function of the number of wear cycles for LDC-KMP, HLDC-10 and HLDC-100.

ment than that of HLDC-100. It is very likely that the amount of grafted silane coupling agent is greater due to a larger number of surface hydroxyl groups in nano-SiO_2 with a smaller size. It helps to achieve a high crosslinking density and form the denser network structure.
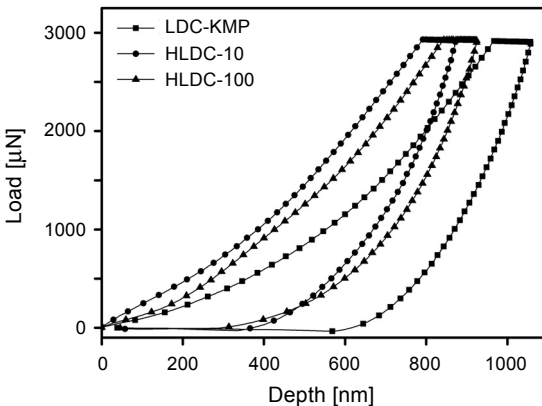

Fig. 8. Load *versus* displacement curves obtained for LDC-KMP, HLDC-10, and HLDC-100.

The load-displacement curves of LDC-KMP, HLDC-10 and HLDC-100 obtained by nanoindentation tests are shown in Fig. 8. As seen graphically, the addition of nano-SiO_2 in the light-diffusing films causes a decrease in indentation depth at the same load. Accordingly, the hardness of LDC-KMP, HLDC-10 and HLDC-100 is 0.12, 0.17 and 0.15 GPa, respectively. These results show the higher hardness of the hybrid films compared to that of LDC-KMP, indicating better mechanical proper-ties of the hybrid light-diffusing films.
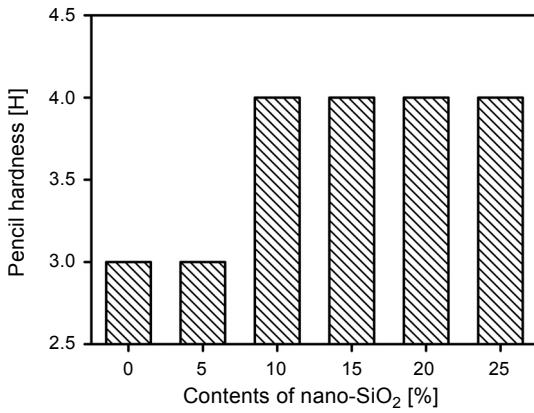
Fig. 9. The pencil hardness as a function of different contents of nano-SiO$_2$ with the particle size of 10–15 nm.
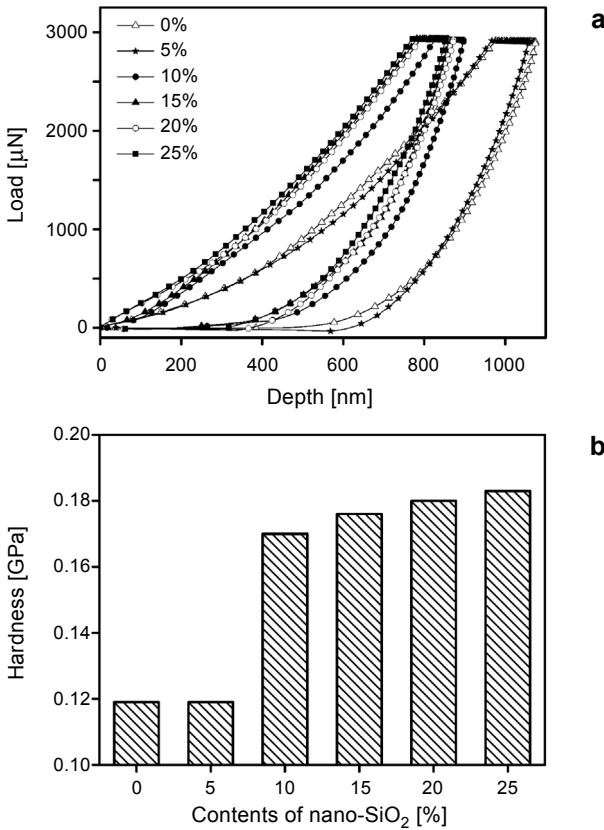

Fig. 10. Load *versus* displacement curves (**a**) and the hardness obtained for the films containing different contents of nano-SiO$_2$ with the particle size of 10–15 nm (**b**).
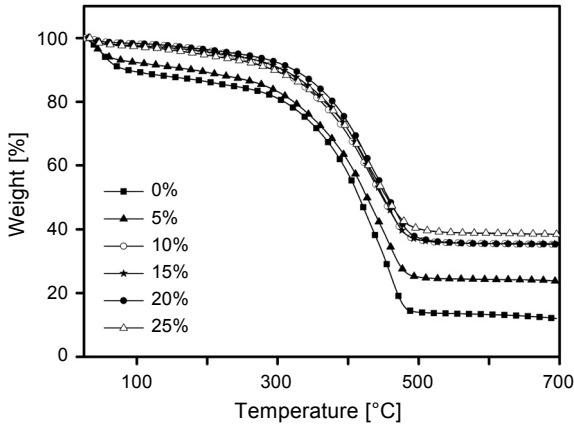
Fig. 11. TGA curves of hybrid light-diffusing films with different SiO_2 contents.

From the above analysis, it is clear that scratch and abrasion resistance of the hybrid films are obviously improved by nano-SiO_2 especially with the particle size of 10–15 nm. Based on this understanding, our interest moved to how the contents of nano-SiO_2 with the particle size of 10–15 nm would affect the mechanical properties of the hybrid light-diffusing films. To confirm it, the pencil hardness of the films was first tested. As seen from Fig. 9, it can be found that the pencil hardness of the films is 3H when nano-SiO_2 content is 0 and 5%, while the pencil hardness increases to 4H when nano-SiO_2 content is ≥10%. Furthermore, the mechanical properties of the films containing nano-SiO_2 with different contents are measured by nanoindentation. The load-displacement curves and the hardness of the hybrid films are shown in Figs. 10**a** and 10**b**, respectively. It shows the hardness obviously increases as the nano-silica content increases. The results of nanoindentation experiment are in accord with those of the pencil hardness tests.

3.5. The thermal stability of the films containing different contents of nano-SiO_2

The TGA curves of the films with various contents of nano-SiO_2 with the particle size of 10–15 nm are shown in Fig. 11. It is clearly seen that the temperature with a 5% weight loss significantly increases from 51°C for the film without nano-SiO_2 to more than 229°C for the hybrid films with ≥10% nano-SiO_2 content and tends to be stable as the nano-SiO_2 content increases. In addition, the residual mass at 700°C of the hybrid films is higher than that of the film without nano-SiO_2 and increases with the increase in nano-SiO_2 content. This indicates that the thermal stability of the hybrid light-diffusing films can be improved by the incorporation of nano-SiO_2 [18].

4. Conclusions

UV-curable hybrid light-diffusing films were prepared by the involving of vinyl-silane-modified nano-silica/1,6-hexanedioldiacrylate (HDDA) dispersion into the light-

diffusing films composed of UV-curable matrix and light-diffusing agent. The transmittance and haze tests showed that the light-diffusing film exhibited good light-diffusing effect when KMP-590 was as light diffusing agent and its content was 25%. The hybrid light-diffusing films containing nano-SiO_2 showed higher haze (98.2%) than the light-diffusing film without nano-SiO_2 (95.5%), while their transmittance remained unchanged at a high value (above 89%). What is more, scratch and abrasion resistant properties of the hybrid films were obviously improved by nano-SiO_2 especially with the particle size of 10–15 nm and the mechanical property of the hybrid films increased as the nano-silica content increased. Furthermore, the hybrid light-diffusing films had higher initial decomposition temperature and residual mass than the light-diffusing film without nano-silica, demonstrating improved thermal stability. The synergistic effect of light-diffusing agent KMP-590 and nano-silica induced the excellent optical, thermal stability and mechanical properties of hybrid light-diffusing films, which made them suitable for anti-glare LED application.

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