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**Facile fabrication of light diffuser films based on
hollow silica nanoparticles as fillers**

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Abstract

A light diffuser film based on hollow silica nanoparticles as fillers was facilely fabricated by coating suspension of the particles in a UV-curable acrylate monomer solution on a cleaned glass substrate. The amount of the particles in the films was varied from 5 to 20 vol%. The optical properties and the light diffusing ability of the films were then studied and further compared to those of the cleaned glass. The result revealed that the films become opaque when the amount of the particles increases. The increment of the particles also leads to the formation of aggregated particles with a larger size and homogeneous dispersion as the FE-SEM images had been presented. Although the films exhibit the opacity, their total transmittance is still high and close to the cleaned glass transmittance. Moreover, the improved diffuse transmittance of the films is obtained from the increased amount of the particles. The increment of the particles also provides the different scattered light image sizes with a homogeneous light resulting in a distinct light diffusing ability. Those results indicated that the films based on the hollow silica nanoparticles as fillers are probably applied for light diffuser films in the LCD industry.

Keywords: Optical diffuser films, Hollow silica nanoparticles, Light diffusing ability, Light scattering

1. Introduction

Light diffuser films have both high total and diffuse transmittance since they are able to diffuse a point or line of light source; for instance, adjusting the angle of incident light [1-2]. Consequently, the light diffuser films have a **homogeneous** of the light penetration. This efficiency of the light diffuser films; therefore, have attracted a lot of interest during recent years for applying in the backlight systems of several liquid crystal display (LCD) devices [2-5]. At present, two types of the light diffuser films are widely achieved as good optical diffusion in the LCDs. The first type is called surface-relief diffuser films, which are mainly dependent to microstructures of the surface layers [6-9]. Most of the microstructures are fabricated by complicated processes and expensive equipment [2-3]. Another type, namely volumetric diffuser films, is simply prepared by coating a mixture of filler and binder resin on an optical material. According to the production of those two light diffuser film types, the study of volumetric diffusers has been conducted by many researchers. Moreover, the volumetric diffusers provide a uniform light scattering throughout fillers, which play an important role on optical properties of the volumetric diffusers [1, 4-5, 10-12]. There are many kinds of the fillers; for example, organic particles [1], inorganic particles [2, 5, 13-14] and organic/inorganic composite particles [3-4, 15]. Principally, the filler-diffuser type films are related to the difference of refractive indices between the filler and the resin. When light passes through the interfaces of the filler and the resin, a formation of refraction occurs as resulting in light scattering [2, 4-5].

In particular, polymer-inorganic hybrid nanocomposite materials are considered as excellent option for multifunctional materials [16-17]. These are attributed to their properties that possess both polymers and inorganic nanoparticles. Moreover, such hybrid materials are capable of enhancing dispersion property, which is advantageous for mixing fillers and binder resins [18]. In addition, an aggregation of a small amount of inorganic particles is able

to improve the bulk performance of polymer matrix for thermal, mechanical, and especially optical properties [2, 5, 13-14, 19-20]. Those properties significantly affect the application of the filler-diffuser films [2]. Meanwhile, microspherical structure of fillers is widely used for optical diffuser films in the LCD industry [3, 21-22]. However, fillers having cubic structure applied for fabricating polymer-inorganic hybrid light diffuser films have not been reported in any involved research. **Hollow silica nanoparticles** comprise of nano-sized hollow interior and a solid shell with unique properties of a low density, high specific surface area, thermal insulation, optical properties, for instance, light-weight filler [1, 5, 23-24]. With these properties, the **hollow silica nanoparticles** have much appealingly used as fillers light diffuser films. By considering their hollow structures, it can be expected to obtain critical importance for light scattering as more light can penetrate into their hollow interior resulting in increasing light scattering [25].

In this study, a facile fabrication used to prepare a light diffuser film is coating mixed suspension of **hollow silica nanoparticles** and a UV-curable acrylate monomer solution by a bar coater. The UV-curable acrylate monomer has good mechanical and thermal properties; for instance, excellent optical properties [2, 26-28]. The composition of the **hollow silica nanoparticles** was initially investigated in order to eradicate any unexpected result, which may affect optical properties of the light diffuser films. The optical properties of the films containing different amount of the particles were then analyzed by a UV-visible spectrophotometer and compared to those of the cleaned glass in the visible region (400-800 nm). The quantitative effect of the hollow particles on the optical properties of the films was also investigated.

2. Material and methods

2.1 *Hollow silica nanoparticles* (HSiNPs)

The composition of HSiNPs was investigated using a thermogravimetric analysis (TGA, Thermo Plus TG-8120, Rigaku) measurement. The sample was placed in a platinum crucible for each analysis and then heated in the air to 800 °C at a heating rate of 10 °C/min. The TGA result was used to specify a certain temperature to eliminate some contamination. The morphologies of HSiNPs before and after calcination were observed using a field emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL Ltd.) at an acceleration voltage of 15 kV with secondary electron image (SEI) and transmission electron diffraction (TED). The samples were dispersed in ethanol (EtOH, 99% Wako Pure Chemical Industries, Ltd.) by an ultrasonication. Then, the suspensions were dropped on a microgrid (STEM150Cu, Oken Shoji) and dried in the air. The density of the powder samples was further measured by a helium pycnometer (Ultrapycnometer 1000T, Quantachrome Instruments). The helium pycnometer was run in the multimode with a standard deviation of 0.05%. The samples were dried under vacuum at temperature of 180 °C for 3 days in order to eradicate any error caused by some remaining air. The calcined HSiNPs preserving morphologies same as the raw material was used to prepare a light diffuser film.

2.2 *Facile fabrication of light diffuser films based on HSiNPs as fillers*

An amount of the desired HSiNPs in the light diffuser films was studied as listed in the first column of Table 1.

Table 1 Amount of the HSiNPs in the light diffuser films

Amount of the HSiNPs in light diffuser films (vol%)	Amount of the HSiNPs in suspensions (vol%)
5	1.04
10	2.17
15	3.41
20	4.76

The concentration of the suitable HSiNPs in the suspensions can be calculated using the equations on our previous study [26]. The calculated values are shown in the second column of Table 1. The known masses of the HSiNPs were dispersed in methyl isobutyl ketone (MIBK, 99.5% Wako Pure Chemical Industries, Ltd.) by the ultrasonication for 10 min. Meanwhile, UV-curable acrylate monomer supplied by the JSR Corporation was diluted by MIBK to get 10 wt% UV-curable acrylate monomer solution. Each of the HSiNPs dispersions was combined with the 10 wt% monomer solution. Suspensions of the HSiNPs were obtained and then coated on cleaned glass substrates using a commercial bar coating machine (K101 Control Coater; RK PrintCoat Instruments, Ltd.) to obtain wet films. The cleaned glass substrates were achieved after successively cleaning in DI-water, EtOH, and acetone for 10 min in each solvent. The wet films were kept in the dark and then cured by a UV-photo surface processor (PL16-110D; SEN LIGHTS Corp.) for 5 min. This process aimed to induce photopolymerization. Consequently, the light diffuser films with different amounts of the HSiNPs as shown in the first column of Table 1 were obtained.

2.3 Characterization of light diffuser films based on HSiNPs as fillers

The morphologies of the obtained films were observed with the FE-SEM. Before the FE-SEM observation, the films were directly dried on a hot plate at the temperature of 150 °C for 2 h since some residual solvent containing in the films may cause of unclear images. The dried samples were further coated by a thin layer of osmium tetroxide using an osmium plasma coater (OPC60A; Filagen). The optical transmittances in the visible region (400-800 nm) of the films were also studied using a UV-Vis-NIR spectrophotometer (UV3150; SHIMADZU) and compared the transmittance results of the films to those of a cleaned glass substrate. The light diffusing ability of all films was inferred by their scattered light image. The scattered light image was recorded by a digital camera performed on an apparatus together with a 532 nm laser (Z1M18B-F-532-PZ; Z-Laser). A film coated on cleaned glass substrate was placed on the apparatus in front of the laser lamp in about 15 cm length from each other. Subsequently, a scattered light image of the film exhibits on the dark background, which has the distances between them about 26 cm.

3. Results and Discussion

3.1 Characterization of HSiNPs

3.1.1 Composition of HSiNPs

The result of the composition of the raw HSiNPs was investigated using TGA and the result is shown in Fig. 1. It reveals two regions of weight loss. The first region of weight loss is observed in the range of 40-150 °C because of the removal of bound water (5%). Another region of weight loss about 25% (300-520 °C) is considerably ascribed to the dehydration of Si-OH on the silicates or the loss of some residual reagent such as surfactant, which is used to produce the HSiNPs [29-30]. Moreover, the incombustible residue can be assumedly silica.

The results are consistent with other previous studies involving TGA for silica nanoparticles [31].

Fig. 1. TGA curve of the raw HSiNPs.

According to its TGA result, the raw HSiNPs was further calcined at temperature of 400 and 600 °C in order to eliminate some contamination which could lead to a flocculation of the HSiNPs. This flocculation possibly forms via the contamination that is an undesirable in the preparation of highly loaded HSiNPs suspensions for a resulting film [32].

3.1.2 Morphologies of HSiNPs

The morphologies of HSiNPs before and after calcination were observed using the FE-SEM with and TED modes. In Fig. 2 (a), the morphologies of the particles before calcination (raw) that clearly exhibits cubic shapes is shown. Furthermore, the cubic shapes are also observed from the FE-SEM image obtained from SEI mode of the particles after calcination at temperature of 400 °C as seen in Fig. 2 (b). However, no cubic shape is obtained from the particles after calcination at temperature of 600 °C that is visibly shown in Fig. 2 (c). Meanwhile, the FE-SEM images obtained from TED mode of all particles were presented in Fig. 2 (d-f). The particles after calcination at temperature of 400 °C (Fig. 2 (d)) still consist of hollow interior as same in the raw particles (Fig. 2 (e)). On the other hand, the morphologies

of the particles after calcination at temperature of 600 °C (Fig. 2 (f)) contain a little hollow structure. These results indicate that the calcination at temperature of 600 °C possibly changes hollow forms of the particles to dense forms. This is due to the growth of mesoporous silica that increases condensation of silicon [33]. It results in a larger degree of Si-O-Si bonds and fewer Si-OH groups involving to typical nonporous Stöber particles. Therefore, the calcination at temperature of 600 °C is not proper for preserving cubic shapes consisted of hollow interior of the HSiNPs. It can be concluded that the particles calcined at temperature of 400 °C were desirably used to prepare a light diffuser film because they still exhibit the morphologies of the HSiNPs.

Fig. 2. FE-SEM images obtained from SEI and TED modes of HSiNPs before calcination for (a) and (d) and after calcination at temperature of 400 °C for (b) and (e), including to at temperature of 600 °C for (d) and (f).

3.1.3 Density of HSiNPs

To enhance more understanding of the effect of the calcination temperature on the morphologies of the HSiNPs, the density of all samples was further measured by the helium pycnometer.

Table 2 Density of HSiNPs before and after calcination.

Sample	Density (g/cm ³)
Raw HSiNPs	1.6704
HSiNPs calcined at 400 °C	1.6599
HSiNPs calcined at 600°C	1.7802

Table 2 illustrates the density of the HSiNPs before and after calcination. It reveals that the density of the HSiNPs calcined at 400 °C is quite lower than that of the raw HSiNPs which is attributed to the contaminant removal. Meanwhile, the density of the HSiNPs calcined at 600 °C is obviously higher than that of the raw HSiNPs. Interestingly, the density of the HSiNPs at 600 °C is close to that of fumed silica nanoparticles (2.2 g/cm³) [34-35]. Therefore, the temperature of 400 °C is much more suitable than that of 600 °C when removing the contamination in HSiNPs.

3.2 Morphologies and optical properties of the light diffuser films based on the HSiNPs as fillers

3.2.1 Morphologies of the light diffuser films based on the HSiNPs as fillers

The HSiNPs calcined at 400 °C were used to fabricate the light diffuser films by coating their suspension on the cleaned glass substrates, then curing with the UV-photo surface processor.

Fig. 3. Optical images of the light diffuser films containing different amounts of the HSiNPs such as (a) 5 vol%, (b) 10 vol%, (c) 15 vol% and (d) 20 vol%.

The optical images of obtained films were presented in Fig. 3. It distinctly shows that the obtained films were uniformly fabricated by the bar coating machine. Apparently, the films slight became opaque when the amount of the HSiNPs was increased from 5 to 20 vol%. The opacity in the films is attributed to a high amount of fillers [36]. Moreover, the aggregated particles on the film surfaces probably occur because of the solvent removal during the photopolymerization [37].

The FE-SEM with SEI mode was used to observe the morphologies of the light diffuser films based on the HSiNPs as fillers in order to study an effect of those particles.

Fig. 4. FE-SEM images with (inset) high magnification of the light diffuser films containing different amounts of the HSiNPs such as (a) 5 vol%, (b) 10 vol%, (c) 15 vol% and (d) 20 vol%.

In Fig. 4, the FE-SEM images with (inset) high magnification of the light diffuser films containing different amounts of the HSiNPs are presented. The film surface containing 5 vol% the HSiNPs shown in Fig. 4 (a) has a small size of aggregated particles with a random dispersion. The size of about 1 μm of the aggregated particles can be roughly estimated by the high magnified FE-SEM image of the film as shown in inset Fig. 4 (a). From the enlarged FE-SEM image shown in the inset Fig. 4 (b), the film surface containing 10 vol% the HSiNPs

exhibits a larger size of aggregated particles ($\sim 2\ \mu\text{m}$). Moreover, this film surface observed from the low magnified FE-SEM image (Fig. 4 (b)) shows a good dispersion of the aggregated particles. Fig. 4 (c) displays the film surface containing 15 vol% the HSiNPs that exhibits a high amount of aggregated particles. The aggregated particles observed are quite larger than $2\ \mu\text{m}$ (as seen in inset Fig. 4 (c)) with a better dispersion when comparing to the films containing lower amount of the HSiNPs. Meanwhile, the film surface containing 20 vol% the HSiNPs in Fig. 4 (d) illustrates the highest amount of aggregated particles when being compared to the other films. The inset Fig. 4 (d) further reveals that the aggregated particles closely contact with the neighboring aggregated particles leading to a larger size ($> 3\ \mu\text{m}$), which possess the entire film surface. When the film containing 20 vol% the HSiNPs was compared to the other films containing lower amounts of the HSiNPs, it suggests that the dispersion of aggregated particles on the film containing 20 vol% the HSiNPs exhibits the highest amount of the particles with a **homogeneous** dispersion. All the results of the FE-SEM correspond to an order of the opacity of the film as being shown in the Fig. 3. The results also indicate that the high amount of the HSiNPs could probably provide higher amount of those particles on the film surfaces with their high dispersion [18]. In addition, it can be concluded that both the size and dispersion of fillers are the main factors, which have an influence on the optical performance of light diffuser films [2, 18].

3.2.2 Optical properties of the light diffuser films based on the HSiNPs as fillers

3.2.2.1 Total transmittance of the light diffuser films based on the HSiNPs as fillers

The total transmittance of the light diffuser films based on the HSiNPs as fillers was measured by the UV-Vis-NIR spectrophotometer in the visible region (400-800 nm), then compared to the cleaned glass substrate.

Fig. 5. Total transmittance spectra of the cleaned glass (a) and the light diffuser films containing different amounts of the HSiNPs such as (b) 5 vol%, (c) 10 vol%, (d) 15 vol% and (e) 20 vol%.

The results are demonstrated in Fig. 5. It can be found that the transmittance spectra of every coated glass are over than 87%, which approaches to that of the uncoated glass (cleaned glass) [38]. The results indicate that the highly transparency of the light diffuser films coated on the glass substrate were fabricated. Interestingly, the transmittance spectra of the film containing 20 vol% the HSiNPs (Fig. 5 (d)) is over than that of the cleaned glass (Fig. 5 (a)) at the wavelength longer than 450 nm. Therefore, the film containing 20 vol% the HSiNPs probably has an anti-reflection property [38]. Moreover, the total transmittance of the light diffuser films slightly decreases when the amount of the HSiNPs as fillers in those films also decreases. These results disagree with the optical images of the films as shown in Fig. 4 as the result of the difference of refractive indices between particles and films [10]. Larger aggregated HSiNPs with a high refractive index probably lead to the optical scattering and opacity of material.

3.2.2.2 Diffuse transmittance of the light diffuser films based on the HSiNPs as fillers

The diffuse transmittance of the light diffuser films containing different amounts of the HSiNPs was measured using the spectrophotometer equipped with an integrating sphere, then compared to that of the cleaned glass.

Fig. 6. Diffuse transmittance spectra of the cleaned glass (a)

and the light diffuser films containing different amounts of the HSiNPs
such as (b) 5 vol%, (c) 10 vol%, (d) 15 vol% and (e) 20 vol%.

In Fig. 6, the diffuse transmittance spectra of the films and the cleaned glass are demonstrated. It was found that the diffuse transmittance of the films is over than that of the cleaned glass. The results reveal that the films based on the HSiNPs dramatically improve diffuse transmittance of the glass substrate. The diffuse transmittance of the films gradually increases when the amount of the particles in those films also increases [3-5]. The enhancement of diffuse transmittance relates to the different refractive indices between particles and homogeneous film, which can be explained by the Rayleigh scattering [4]. This

result can be explained by the Rayleigh scattering which is defined that the light scattering depends on the size of the particles, which is very small in relation to the wavelength of incident light. And the intensity of the scattering is inversely proportional to the fourth power of the wavelength. Also, the Rayleigh scattering has a significantly influence on the longer wavelength of the light. This relates to the abrupt reduction of the diffuse transmittance at the longer wavelength, which can be seen in all diffuse transmittance of the films (Fig. 6 (b)-(e)). The results can be inferred that almost aggregated particles inside the films are smaller than the wavelength of the incident light and the size of the observed aggregated particles on the film surfaces (as can be seen in the FE-SEM images of the film surfaces in Fig. 4) [10]. Meanwhile, the aggregated particles on the film surfaces probably occur throughout the Rayleigh scattering interfering with the Mie scattering. In the case of the Mie scattering, the size of the particles is comparable or larger than the wavelength of the incident light [10, 39]. The intensity of the light scattering is independent to the size of the particles. Moreover, the direction of the light scattering is towards that of the incident light. The light scattering on the film surfaces significantly has an influence on the enhancement of the total and diffuse transmittance of those films. It is evidently confirmed by the sequence of the diffuse transmittance the films, which corresponds to the order of the total transmittance of those films.

3.2.2.3 Light diffusing ability of the light diffuser films based on the HSiNPs as fillers

The Mie scattering not only play a key role in the transmittances of the films but also influences on homogenization of the incident light. The homogenization is one of the main factors to achieve the good light diffuser films [2]. The homogenization of the light penetrated throughout the light diffuser films containing different amounts of the HSiNPs can

be examined using the apparatus. The results are shown in the scattered light image of the films as exhibited in Fig. 7, which can be implied the light diffusing ability of those films.

Fig. 7. The scattered light images of the cleaned glass (a) and the light diffuser films containing different amounts of the HSiNPs such as (b) 5 vol%, (c) 10 vol%, (d) 15 vol% and (e) 20 vol%.

When comparing the scattered light images in Fig. 7, it reveals that the size of the scattered light images of the films is larger than that scattered light image of the cleaned glass. The films can diffuse the point and the line light source resulting in **homogeneous** surface lighting [2]. It can be implied that the films exhibit their high light diffusing ability. These are due to the production of the scattered light by the particles. The scattered light is only occurred by the particles, when the polymer matrix is assumed to be transparent and **homogeneous** [40]. Consequently, the high amount of particles loaded in the films probably provides a greater light scattering leading to a high diffuse transmittance. As could be seen in

Fig. 7 (b)-(e), the size of the scattered light image of the film dramatically increases with the increment of the amount of the HSiNPs. The scattered light images of the films also display a uniform pattern. This suggests that the HSiNPs used as fillers leads to the uniform pattern of the scattered light [4, 11-12]. In addition, the aggregated particles on the film surfaces (as observed from the FE-SEM images in Fig. 4) do not have a sufficient separation; therefore, they probably occur multiple scattering based on the Mie scattering [40]. The multiple scattering usually occurs in the film containing aggregated particles because the scattered light of each particle or cluster is supposed to be dependent on each other. Consequently, the film containing the highest amount of aggregated particles (20 vol% the HSiNPs) continually provides more the scattered light which leads to both high transmittances and **homogeneous** light. These properties play significant role in a high performance of a light diffuser film [2]. Therefore, the films containing high amount of the HSiNPs have a great potential to be light diffuser films, especially manufactured multifunctional light diffuser films in the LCD industry. A schematic illustration of applying the light diffuser film based on the HSiNPs as fillers in the LCD is shown in Fig. 8.

Fig. 8. Schematic illustration of applying the light diffuser film based on the HSiNPs as fillers in the LCD.

4. Conclusion

The light diffuser films based on HSiNPs as fillers were facilely fabricated by coating the suspension of the HSiNPs calcined at temperature of 400 °C and the UV-curable acrylate monomer solution. The films became opaque when the amount of the HSiNPs was increased. Meanwhile, the films containing different amounts of the particles exhibit a various total transmittances and they are also close to the cleaned glass. While the diffuse transmittance of the films increases with increasing the amount of the particles that are also obviously higher than that of the cleaned glass. Moreover, the films gave a larger size of the scattered light image which can be implied that the films are able to diffuse the point or the line of the light source. Additionally, the size of the scattered light images increases when the particle loading was increased. Therefore, it can be concluded that the films containing the high amount of the HSiNPs have a high light diffusing ability. In conclusion, the films containing the high amount of the particles have both the high transmittances and the light diffusing ability; therefore, the films based on the HSiNPs as fillers are potentially applied for light diffuser films in LCDs.

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References

- [1] S. Song, Y. Sun, Y. Lin, B. You, A facile fabrication of light diffusing film with LDP/polyacrylates composites coating for anti-glare LED application, *Appl. Surf. Sci.* 273 (2013) 652-660.
- [2] X. Sun, N. Li, J. Hang, L. Jin, L. Shi, Z. Cheng, D. Shang, Nano-silica reinforced hybrid light-diffusing films with enhanced mechanical and thermal properties, *Opt Appl* 46 (2015) 393-404.
- [3] J. Hu, Y. Zhou, X. Sheng, Optical diffusers with enhanced properties based on novel polysiloxane@CeO₂@PMMA fillers, *J. Mater. Chem. C* 3 (2015) 2223-2230.
- [4] J. Hu, Y. Zhou, M. He, X. Yang, Novel multifunctional microspheres of polysiloxane@CeO₂-PMMA: Optical properties and their application in optical diffusers, *Opt. Mater.* 36 (2013) 271-277.
- [5] J. Hu, Y. Zhou, T. Zhang, The novel optical diffusers based on the fillers of boehmite hollow microspheres, *Mater. Lett.* 136 (2014) 114-117.
- [6] J.-H. Wang, S.-Y. Lien, J.-R. Ho, T.-K. Shih, C.-F. Chen, C.-C. Chen, W.-T. Whang, Optical diffusers based on silicone emulsions, *Opt. Mater.* 32 (2009) 374-377.
- [7] T.C. Huang, J.R. Ciou, P.H. Huang, K.H. Hsieh, S.Y. Yang, Fast fabrication of integrated surface relief and particle-diffusing plastic diffuser by use of a hybrid extrusion roller embossing process, *Opt. Express* 16 (2008) 440-447.
- [8] S.J. Liu, Y.C. Huang, Manufacture of dual-side surface-relief diffusers with various cross angles using ultrasonic embossing technique, *Opt. Express* 17 (2009) 18083-18092.

- [9] D. Sakai, K. Harada, S. Kamemaru, M.A. El-Morsy, M. Itoh, T. Yatagai, Direct fabrication of surface relief holographic diffusers in azobenzene polymer films, *Opt Rev* 12 (2005) 383-386.
- [10] S. Guo, S. Zhou, H. Li, B. You, Light diffusing films fabricated by strawberry-like PMMA/SiO₂ composite microspheres for LED application, *J. Colloid Interface Sci* 448 (2015) 123-129.
- [11] H. Butt, K.M. Knowles, Y. Montelongo, G.A.J. Amaratunga, T.D. Wilkinson, Devitrite-Based Optical Diffusers, *ACS Nano* 8 (2014) 2929-2935.
- [12] S. Ahn, G.H. Kim, An electrosprayed coating process for fabricating hemispherical PMMA droplets for an optical diffuser, *Appl Phys A* 97 (2009) 125-131.
- [13] L.E. Mcneil, R.H. Franceh, Multiple scattering from rutile TiO₂ particles, *Acta mater.* 48 (2000) 4571-4576.
- [14] Y. Zhao, P. Ding, C. Ba, A. Tang, N. Song, Y. Liu, L. Shi, Preparation of TiO₂ coated silicate micro-spheres for enhancing the light diffusion property of polycarbonate composites, *Displays* 35(2014) 220-226.
- [15] K. Shin, H. N. Kim, J. C. Cho, S. J. Moon, J. W. Kim, K. D. Suh, Fabrication of monodisperse polymer/silica hybrid microparticles for improving light diffusion properties, *Macromol Res* 20 (2012) 385-390.
- [16] T. Wang, T. T. Isimjan, J. Chen, S. Rohani, Transparent nanostructured coatings with UV-shielding and superhydrophobicity properties, *Nanotechnology* 22 (2011) 265708.
- [17] M. H. Tsai, C. J. Chang, P. J. Chen, C. J. Ko, Preparation and characteristics of poly(amide-imide)/titania nanocomposite thin films, *Thin Solid Films* 516 (2008) 5654-5658.

- [18] M. E. Calvo, J. R. Castro Smirnov and H. Míguez, Novel approaches to flexible visible transparent hybrid films for ultraviolet protection, *J. Polym. Sci. Pol. Phys.* 50 (2012) 945-956.
- [19] Y. Tu, L. Zhou, Y. Z. Jin, C. Gao, Z. Z. Ye, Y. F. Yang, Q. L. Wang, Transparent and flexible thin films of ZnO-polystyrene nanocomposite for UV-shielding applications, *J. Mater. Chem.* 20 (2010) 1594-1599.
- [20] L. Qi, A. Sehgal, J. C. Castaing, J. P. Chapel, J. Fresnais, J. F. Berret, F. Cousin, Redispersible hybrid nanopowders: Cerium oxide nanoparticle complexes with phosphonated-peg oligomers, *ACS Nano* 2 (2008) 879-888.
- [21] H. P. Kuo, M. Y. Chuang, C. C. Lin, Design correlations for the optical performance of the particle-diffusing bottom diffusers in the LCD backlight unit, *Powder Technol.* 192 (2009) 116-121.
- [22] L. Mingyan, W. Daming, Z. Yajun, Z. Jian, Optimization and design of LCD diffuser plate with micro-semisphere structure, *Procedia Eng.* 16 (2011) 306-311.
- [23] Y. Liao, X. Wu, H. Liu, Y. Chen, Thermal conductivity of powder silica hollow spheres, *Thermochim. Acta* 526 (2011) 178-184.
- [24] Y. Du, L.E. Luna, W.S. Tan, M.F. Rubner, R.E. Cohen, Hollow silica nanoparticles in UV-visible antireflection coatings for poly(methyl methacrylate) substrates, *ACS Nano* 4 (2010) 4308-4316.
- [25] M.C. Tsai, J.Y. Lee, P.C. Chen, Y.W. Chang, Y.C. Chang, M.H. Yang, H.T. Chiu, I.N. Lin, R.K. Lee, C.Y. Lee, Effects of size and shell thickness of TiO₂ hierarchical hollow spheres on photocatalytic behavior: An experimental and theoretical study, *Appl. Catal., B* 147 (2014) 499-507.

- [26] W. Suthabanditpong, R. Buntem, C. Takai, M. Fuji, T. Shirai, The quantitative effect of silica nanoparticles on optical properties of thin solid silica UV-cured films, *Surf. Coat. Technol.* 279 (2015) 25-31.
- [27] A. Milinavičiūtė, V. Jankauskaitė, P. Narmontas, Properties of UV-curable hyperbranched urethane-acrylate modified acrylic monomer coatings, *Mater. Sci. (Medžiagotyra)* 17 (2011) 378-383.
- [28] C.J. Chang, M.H. Tsai, P.C. Kao, H.Y. Tzeng, Optical and mechanical properties of jet printed and UV cured blue pixels with phosphated epoxy acrylate as the curing agent, *Thin Solid Films* 516 (2008) 5503-5507.
- [29] H. Wanyika, E. Gatebe, P. Kioni, Z. Tang, Y. Gao, Synthesis and characterization of ordered mesoporous silica nanoparticles with tunable physical properties by varying molar composition of reagents, *Afr. J. Pharm.* 5(2011) 2402-2410.
- [30] D. Das, Y. Yang, J. S. O'Brien, D. Breznan, S. Nimesh, S. Bernatchez, M. Hill, A. Sayari, R. Vincent, P. Kumarathan, Synthesis and Physicochemical characterization of mesoporous SiO₂ nanoparticles, *J. Nanomater.* (2014) Article ID 176015.
- [31] R.V.R. Virtudazo, M. Fuji, C. Takai, T. Shirai, Fabrication of unique hollow silicate nanoparticles with hierarchically micro/mesoporous shell structure by a simple double template approach, *Nanotechnology* 23 (2012) 485608.
- [32] A. Liberman, N. Mendez, W. C. Trogler, A. C. Kummel, Synthesis and surface functionalization of silica nanoparticles for nanomedicine, *Surf Sci Rep.* 69 (2014) 132-158.
- [33] Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng, J. Shi, Hollow/rattle-type mesoporous nanostructures by a structural difference-based selective etching strategy, *ACS Nano* 4 (2009) 529-539.

- [34] S. Rimdusit, K. Punson, I. Dueramae, A. Somwangthanaroj, S. Tiptipakorn, Rheological and thermomechanical characterizations of fumed silica-filled polybenzoxazine nanocomposites, *ENGINEERING JOURNAL* 15 (2011) 15 27-38; doi:10.4186/ej.2011.15.3.27.
- [35] V. M. Gun'ko, L. S. Andriyko, V. I. Zarko, A. I. Marynin, V. V. Olishkevskyi, W. Janusz, Effects of dissolved metal chlorides on the behavior of silica nanoparticles in aqueous media, *Cent. Eur. J. Chem.* 12 (2014) 480-491.
- [36] T. Otsuka, Y. Chujo, Poly(methyl methacrylate) (PMMA)-based hybrid materials with reactive zirconium oxide nanocrystals, *Polym. J.* 42 (2010) 58-65.
- [37] T. Ribeiro, A. Fedorov, C. Baleizão, J.P.S. Farinha, Formation of hybrid films from perylenediimide-labeled core-shell silica-polymer nanoparticles. *J. Colloid Interface Sci.* 401 (2013) 14-22.
- [38] J. W. Leem, Y. Yeh, J. S. Yu, Enhanced transmittance and hydrophilicity of nanostructured glass substrates with antireflective properties using disordered gold nanopatterns, *Opt. Express* 20 (2012) 4056-4066.
- [39] R. Barchini, J.G. Gordon II, M.W. Hart, Multiple light scattering model applied to reflective display materials, *Jpn. J. Appl. Phys.* 37 (1998) 6662-6668.
- [40] A. Rastar, M.E. Yazdanshenas, A. Rashidi and S.M. Bidoki, Theoretical review of optical properties of nanoparticles, *J. Eng. Fiber Fabr.* 8 (2013) 85-96.