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**The quantitative effect of silica nanoparticles on optical properties of
thin solid silica UV-cured films**

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Abstract

A thin solid silica UV-cured film was prepared by coating the dispersion of commercial silica nanoparticles in a UV-curable acrylate monomer on a glass substrate using a bar coater. The silica UV-curable acrylate resin was stored for 24 h in the dark for film formation and then transformed into the thin solid silica UV-cured films upon exposure to UV light at the wavelength of 254 nm for 5 min at ambient temperature. The amount of silica nanoparticles in the UV-cured films was varied from 1 to 30 vol % and then the optical properties of the coated glass were compared with the bare glass. The result revealed that the total transmittance of all the films is insignificantly different when the amount of silica nanoparticles increases. The total transmittance of all the coated glasses is similar to that of the bare glass indicating the transparency of the film. Although the total transmittance of the films is independent of the amount of particles, the improved diffuse transmittance of the films is obtained as the amount of particles increased. This is due to the enhanced multiple scattering that occurs in the film. The increased amount of silica nanoparticles also leads to the formation of the aggregated particles with a larger size and homogeneous dispersion as evidenced from the FE-SEM images. These indicated that the amount and distribution of the silica nanoparticles strongly affect the improved optical properties of the thin solid silica UV-cured film.

Keywords: Silica nanoparticles, UV-cured polymer, Optical materials, Thin films, Coating

1. Introduction

The diversity of UV-curable monomers and oligomers, including acrylates, acrylated urethanes, epoxies and vinyl ethers, allow the UV-coating formulator many choices in achieving the desired properties [1]. A liquid resin rapidly transforms into a solid material under intense UV illumination within seconds at ambient temperature by the formation of a highly crosslinked polymer [2]. Due to its high crosslink density, the UV-cured polymer exhibits a better adhesive property [3], hardness [4, 5], mechanical property [5, 6], elastic property [6] and excellent abrasion resistance [5]. Consequently, the UV-cured polymer has been used in various industries as adhesive materials [3], jet-printed ink [7] and hard transparent coatings for optical materials [5, 8].

So far, optical materials have been extensively used in our daily life for various applications such as lens, automobile parts, and screen panel displays in many electronic devices [9-12]. The brightness and resolution are needed for achieving highly effective images. However, the issues of contrast ratio, resistance capacitance (RC) time delay, pixel resolution, reflection, glare and transmittance (or brightness) are crucial problems especially when the liquid crystal display (LCD) panel size is enlarged. Due to the low quality of the final image, the transmittance and glare of the LCD panel must be improved in order to achieve both a higher brightness and better resolution. To solve these problems, the coating technology using various materials has been developed to increase the transmittance and reduce the glare of the LCD. Recently, a light diffusing film, a material with a high transmittance and light diffusivity [13], has been extensively investigated. This type of film has also an excellent anti-glare property so it is widely applied in LED light systems. The organic/inorganic hybrids have been extensively used for fabricating light diffusing films because of their unique and enhanced mechanical, thermal, electrical and optical properties [14, 15]. A variety of inorganic colloidal particles including titanium dioxide, copper oxide, aluminum hydroxide, alumina and silica have been combined with an organic polymer [15, 16] to produce the hybrid materials. Among these materials, organic-silica hybrid materials are of great interest due to their high transmission, low refractive index, easy preparation and low cost [14, 17-18]. Konjhodzic et al. were able to produce a low refractive index film using mesoporous silica and a nonionic triblock copolymer, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ [19]. This hybrid film with a sufficient thickness showed an ultralow refractive index and birefringence. Yu et al. prepared a polyimide-silica hybrid thin film using a soluble fluorine-containing polyimide and

monodispersed colloidal silica [20]. This film had an excellent optical transparency in both the UV and visible regions. Its refractive index and thermal stability were controlled by the silica content. Early attempts to fabricate an optical coating using nanoparticles resulted in fragile surfaces [21], but researchers recently tried to develop optical thin film coatings using nanoparticles and a UV-cured polymer to enhance the abrasion resistance. Krogman et al. studied the refractive index of sub-100 nm thin films by varying the metal oxide nanoparticle loading in an aqueous colloidal solution and UV-curable monomer [22]. The mechanical and optical performances of the resulting anti-reflective films coated on the plastic substrates were investigated. The results revealed that the thin films prepared by silica and ceria nanoparticles dispersed in a UV-curable monomer exhibited an optical transparency and anti-reflective property. Similarly, a high quality image through the light diffusing film of a display requires a quantitative description of light scattering in a high amount of dispersed particles in the colloid [15]. It is due to the polymer matrix that is assumed to be transparent and homogeneous [23]. Therefore, the light scattering is assumed to be only due to the particles. When the light travels through a large amount of particles, the light scattering more readily occurs [23]. However, the particles usually tend to appear in aggregated cluster forms. The particles also do not have enough separation, thus the scattered light of each particle or cluster is dependent on the other ones, and multiple scattering occurs. The multiple scattering affects the increasing diffuse transmittance in the film. It should be concluded that the enhanced optical properties of the polymer film with particles is attributed to the amount, dispersibility and aggregated size distribution of the particles [14]. Especially, preparation of an optical film using a colloid of dispersed particles in a polymer must control the stability of the dispersant to force the particles to remain separated and, in turn, on the sign and magnitude of the total interparticle potential energy, V_T [24]. The general equation for describing V_T can be expressed as [25]:

$$V_T = V_{vdW} + V_{elect} + V_{steric} \quad (1)$$

where V_{vdW} is the attractive potential energy due to long-range van der Waals interactions between the particles, V_{elect} is the repulsive potential energy resulting from electrostatic interactions between the like-charged particle surfaces, and V_{steric} is the repulsive potential energy resulting from long-chain molecules adsorbed onto the particle surface. The stability of the dispersion is achieved when the repulsive forces are high enough to overcome the attractive van der Waal attractive forces [24]. The parameters involved in the electrostatic repulsion are well described by the DLVO theory (as developed by Derjaguin,

Landau, Verwey and Overbeek). The electrostatic repulsion between the particles depends on the dielectric constant of the medium, therefore, it is less effective in the majority of nonaqueous media than in water because of the lower ionic concentration and the lower dielectric constant [24]. Steric barriers between particles and dispersing medium are also another way to induce a colloidal stability [25]. The long-range van der Waals interactions between particles must be mitigated during colloidal processing to achieve the dispersion stability [26]. One approach is to render this force negligible by matching the refractive index of the dispersed particles and media. This has been previously demonstrated for nanosilica and UV-curable acrylate monomers [25]. The results show that minimization of the Van der Waals forces and affinity of the monomer end group for the silica surface (for example hydrogen bonding) are the main parameters allowing high loading dispersions in the appropriate monomer and highly transparent dispersions having curing depths on the order of 10 mm in the UVA range. According to the V_{vdW} attraction, the interparticle attraction for two spherical particles of radius a separated by the distance h can be expressed by the effective Hamaker constant (A) [25]:

$$V_{vdW} = \frac{-Aa}{6\pi h} \quad (h \ll a) \quad (2)$$

The effective Hamaker constant is given by

$$A = a \left(\frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m + \varepsilon_p} \right)^2 + b \frac{(n_m^2 - n_p^2)^2}{(n_m^2 + n_p^2)^{3/2}} \quad (3)$$

where ε is the dielectric constant, n is the refractive index and a and b are constants [25]. The subindices m and p refer to the dispersing medium and the dispersed particles, respectively. Equation (3) reveals that the dielectric constant and refractive index differences contribute to the Hamaker constant. Meanwhile, the dielectric constant depends on the complex refractive index (n_c) through Equation (4). Hence, the refractive indices of the interacting media are matched, i.e., when $n_m = n_p$, the second term in Equation (3) vanishes as a result of reducing the Hamaker constant to a minimum.

$$\varepsilon = n_c^2 \quad (4)$$

The complex refractive index is defined by Equation (5) [27].

$$n_c = n + Ki \quad (5)$$

The real part of n_C , namely n , is the same as the normal refractive index [27]. The imaginary part of that, namely κ , is called the extinction coefficient. κ is directly related to the absorption coefficient α of the medium which is very low in a transparent material. The first term in Equation (3) may also become negligible when both the real and imaginary parts of the complex refractive indices (n_C) are matched [27] leading to a zero value of the Hamaker constant. Thus, the result of matching the refractive index in a colloidal system is effectively a minimization of the Van der Waals attraction. These form the base of our research which pertains to the possibility of silica nanoparticles (silica NPs) dispersion in a UV-curable monomer and its optical properties after the UV-cured film process.

In this study, highly loaded commercial silica NPs dispersions in a UV-curable monomer were prepared using a UV-curable acrylate monomer because its refractive index is close to that of silica NPs at the wavelength of 500 nm [22]. The dispersion of the silica NPs was coated on the glass substrate using a bar coater to prepare a thin solid silica-UV-cured film. The optical properties of the resulting films were then analyzed by a UV-visible spectrophotometer and compared with the uncoated substrate in the range of 300-800 nm. The effect of the silica loading on the optical properties of the films was also investigated.

2. Experimental

2.1 Materials

All solvents and chemicals were of reagent grade and used without further purification. The chemical formula of the used compounds are shown in Fig. 1. Commercial silica nanoparticles, SO-C1, were purchased from Admatechs, Japan. An SEM image of the silica NPs used in this study is shown in Fig. 2. The particles have a spherical shape, and their size is in the range of 150-300 nm. The bulk density of silica NPs is 2.1 g/cm³ as measured by a helium pycnometer. The UV-curable acrylate monomer was composed of two major components, dipentaerythritol penta-/hexa acrylate as an acrylic monomer and Irgacure 184 (1-hydroxycyclohexyl phenyl ketone) as a photo initiator supplied by the JSR Corporation, Japan. Methyl isobutyl ketone (MIBK; 99.5%) was purchased from Wako Pure Chemical Industries, Japan. The density of the MIBK is 0.802 g/cm³. It was used as a reactive diluent in the composite monomer to adjust the viscosity and dispersibility.

Fig. 1. Chemical formulas of the compounds used.

Fig. 2. FE-SEM image of the silica NPs as received.

2.2 Instrumentation

An Ultrapycnometer 1000T (Quantachrome Instruments) was used for measuring the bulk density of the silica NPs. Helium gas was used to precisely control the pressure of the pycnometer. The helium pycnometer was run in the multimode with a standard deviation of 0.05%. A Branson digital sonifier 450DA (Branson Ultrasonic Corp., JP) was used to disperse the silica NPs in the monomer solution. The digital sonifier was carried out using an ultrasonic horn. A planetary centrifugal deaeration mixer (ARE-930 Twin THINKY Mixer, JP) at a revolution speed of 1000 rpm under a vacuum of 20 kPa was used for removing air bubbles from the dispersions after the ultrasonic process. The particle size distribution of the silica NPs dispersions was determined by dynamic light scattering performed using a Malvern Zetasizer nano (Sysmex Company, JP). A VIBRO Viscometer SV-10 (A&D Co., JP) using the tuning fork vibration method equipped with small sample cup was used for measuring the viscosity of the dispersions. A 30 cm³ volume of the dispersion was placed in the cup for measuring at 25°C. A refractometer (Multi-wavelength Abbe refractometer DR-M2; ATAGO Co., JP) with a 589 nm interference filter was used to determine the refractive index of the dispersions. The refractometer is capable of measuring in the range of 1.3000-1.7100 with a precision of ± 0.0002 . A bar-coating machine (K101 Control Coater; RK PrintCoat Instruments, Ltd., UK) with a standard meter bar having the wire diameter of 0.76 mm and a constant speed of 2.0 cm/s was used to prepare the wet silica film. The wet silica film was cured by a UV-photo surface processor (PL16-110D; SEN LIGHTS Corp., JP) with a UV emission wavelength in the range of 254 nm and output of 110 W. The thicknesses of the wet and dry films were measured by a confocal laser scanning microscope (CLSM; LEXT 3D Measuring Laser Microscope CLS-4000; Olympus, JP) at a magnification of 5X. The surface morphology of the silica UV-cured films was examined using a field emission scanning electron microscope (FE-SEM; JSM7600F; JEOL, JP) equipped with COMPO detectors. The silica UV-cured films were directly dried on a hot plate at the temperature of 150°C for 2 h before being coated with osmium tetroxide in order to eradicate any unclear images caused by some residual solvent. A thin layer of the osmium tetroxide was coated on the dried sample by an osmium plasma coater (OPC60A; Filagen) prior to the imaging. It should be noted that the films were observed in the COMPO mode which uses back-scattered electrons [28]. They are a reflection from the sample due to elastic scattering. The intensity of the back-scattered electrons corresponds to the atomic number (Z) of the specimen. The optical properties of the prepared silica UV-cured films were measured by a UV-Vis-NIR

spectrophotometer (UV3150; SHIMADZU, JP). The measurements were made in the wavelength range of 300-800 nm.

2.3 Preparation of silica UV-curable acrylate monomer dispersion

Dispersions containing 0.2-8.0 vol% of silica NPs were prepared by ultrasonication of the mixtures between the known masses of the silica powder and 20 wt% UV-curable monomer solutions by a digital sonifier at the amplitude of 40% and pulse on/off of 1 sec for 10 min in an ice bath to prevent polymerization throughout the dispersion process. The desired volume percentage of the silica NPs in the dispersion can be calculated by dividing the measured volume of the 20 wt% acrylate monomer solution (V_{sol}) by the volume of silica NPs (V_s). The calculated value is then converted to a percentage by multiplying by 100 and appending a percentage sign to the result.

$$Vol\% \text{ of silica NP in dispersion} = \frac{V_s}{V_s + V_{sol}} \times 100 \quad (6)$$

Using the average density of silica NPs and Equation (7), the volume of the silica NPs can be calculated.

$$V_s = \frac{M_s}{\rho_s} \quad (7)$$

where M_s is the mass of the silica NPs and ρ_s is the average density of the silica NPs, which was determined by the helium pycnometer. The calculated values are shown in the first column of Table 1.

Table 1 Amount of silica NPs in the dispersion and in the thin solid silica UV-cured film.

Amount of silica NPs in 20 wt% UV-curable acrylate monomer (vol%)	Amount of silica NPs in thin solid silica UV-cured film (vol%)
0.20	1
1.04	5
2.17	10
3.41	15
4.76	20
6.25	25
7.89	30

The second column of Table 1 lists the percentage volume content values of the silica NPs in the UV-cured films. The dry film basically consists of silica NPs dispersed throughout the continuous UV-cured acrylate film. The percentage volume content of the silica NPs in the UV-cured films can be calculated by dividing the volume of the silica NPs by the total volume of all the solids. The calculated value with a decimal point is converted to a percentage by multiplying by 100 and appending a percentage sign to the result.

$$\text{Vol\% of silica NP in UV - cured film} = \frac{V_s}{V_s + V_M} \times 100 \quad (8)$$

To know the volume of the acrylate resin (V_M) in the monomer solution, the measured volume of the acrylate monomer solution is multiplied by its density ($\rho_{sol} = 0.855 \text{ g/cm}^3$) and then divided by the density of the acrylate monomer ($\rho_M = 1.18 \text{ g/cm}^3$). It can be expressed as

$$V_M = V_{sol} \times \frac{\rho_{sol}}{\rho_M} \quad (9)$$

The air bubbles in the dispersions were removed by a planetary centrifugal deaeration mixer for 5 min in order to eliminate their effects on the optical properties of the resulting films. Dynamic light scattering (DLS) studies were conducted to measure the particle size distributions of the silica NPs in the dispersions. The viscosities of the dispersions were then measured by a viscometer. A refractometer was used to determine the refractive index of the dispersion. All the measurements were performed at 25°C.

2.4 Fabrication of thin solid silica UV-cured films on glass substrate

A clean glass substrate was coated by the silica dispersion using a commercial bar-coating machine to obtain a wet silica film. The glass substrate was ultrasonically cleaned successively in DI-water, ethanol and acetone for 10 min in each solvent. The wet silica film was initially dried at room temperature in the dark for 24 h before being further cured by a UV-photo surface processor for 5 min to remove any organic compounds. The thin solid silica UV-cured film was then obtained with the solid content yield shown in Table 1. The thickness of both the wet and dry films was measured by CLSM. The quantitative effect of the silica NPs on the optical properties of the thin solid silica UV-cured films was studied using a UV-Vis-NIR spectrophotometer. The transmittances of the coated substrates were then compared to that of the uncoated substrate in the wavelength range of 300-800 nm. The

particle distributions on the film surfaces were also observed by a field emission scanning electron microscope.

3. Results and Discussion

3.1 Physical properties of silica UV-curable acrylate monomer dispersion

The dispersions of the silica NPs in UV-curable acrylate monomer were successfully prepared. The amounts of the silica NPs in the dispersions were varied and the refractive indices of all the dispersions are illustrated in Fig. 3.

Fig. 3. Refractive indices of the modified UV-curable acrylate monomers for different amounts of silica NPs.

It can be seen that the presence of silica NPs in the UV-curable acrylate monomer significantly affects the refractive indices of the dispersions. Adding MIBK ($n=1.3952$ at 589 nm) to the UV-curable acrylate monomer solution makes its refractive index lower and closer to the refractive index of the silica NPs. The value of the refractive index of the silica NPs at 589 nm is about 1.4584 [29]. When the refractive indices of the dispersed particles and dispersing media are matched, it provides a transparent dispersion and allows a highly loaded dispersion [30-32]. To confirm the stability of the dispersion from the resultant of the matching refractive indices in a colloidal system, various amounts of the silica NPs in the dispersions at different times were studied. Fig. 4 shows images of the dispersions at the different times. The figure clearly reveals that the colloid dispersions with removed air

bubbles (0 h) became turbid without any precipitation when the amount of the silica NPs increased from 0.20 to 7.89 vol%. Turbidity in the dispersions is caused by a high amount of dispersed particles. Besides, the stability of these colloidal dispersions during dark storage can be maintained for several hours by matching the refractive indices of the silica NPs and UV-curable monomer solution. However, a precipitate in the dispersions can be observed after 24 h as seen in Fig. 4 (c).

Fig. 4. Stability of silica UV-curable acrylate monomer dispersions at different times such as (a) 0 h, (b) 1 h and (c) 24 h.

The results suggest that the amount of MIBK in the dispersions of the silica UV-curable acrylate monomer may be sufficient to modify the interaction between the silica NPs resulting in the dispersion stability. This is consistent with some previous studies, which reported that the selected monomer with refractive index matching to the dispersed particles reduces the particle-particle attraction forces, especially the Van der Waals forces [25]. This leads to the dispersion containing a large amount of particles and having a long-term stability. The dispersion properties (like viscosity, pH and ionic strength), the dispersed particle properties (like particle size, particle volume fraction and specific surface area) and the presence of soluble polymers or surfactants [25] affect the particle interactions in the dispersion. To further understand the interaction of the particles in the dispersions, the silica loading effect on the viscosity of the dispersions was investigated. The results are shown in Fig. 5.

Fig. 5. Influence of silica loading on the viscosity.

The viscosity of the silica NPs dispersion gradually increases as the amount of the silica dispersed in the UV-curable acrylate monomer is increased corresponding to a previous study [33]. In a nonaqueous solution, the viscosity of a concentrated colloidal dispersion significantly depends on the interactions between the particles. Therefore, the lower the viscosity, the lower the interaction and the better is the given dispersant [34]. This is due to the structure of dipentaerythritol penta-/hexa acrylate that is OH terminated as shown in Fig. 1. This monomer is then able to form hydrogen bonding with the hydroxyl groups present on the silica surface and thereby increase the surface compatibility to the monomer which leads to particle aggregation [25, 35]. This is evident by the cumulative size distribution curve of

the silica NPs dispersions as plotted on a log scale in Fig. 6. A larger size of the particles with a narrow distribution was obtained when the amount of the silica NPs in the UV-curable acrylate monomer was increased to 3.41 vol%. However, the larger size with a wider particle distribution was obtained when the amount of the silica NPs was higher than 3.41 vol%. These may be due to the fact that the silica NPs used here is hydrophilic and contains excess –OH groups on its surfaces [36]. The silica NPs also has a high surface area to volume ratio and therefore possesses a high surface energy. Consequently, it tends to aggregate so as to minimize the surface energies [37].

Fig. 6. The cumulative size distributions curve of silica NPs dispersed in 20 wt% UV-curable acrylate monomer.

3.2 The optical properties of the thin solid silica UV-cured films

3.2.1 Optical transmittance of the thin solid silica UV-cured films

The dispersion of silica NPs in the UV-curable acrylate monomer was coated on a cleaned glass. The coated glass was then kept in the dark at room temperature for 24 h to prevent any premature polymerization. The wet silica film was exposed to 254 nm UV light for 5 min to induce the crosslinking polymerization. A thin solid silica UV-cured film was eventually obtained. The silica content in the films related to the final dry mass is shown in Table 1. To confirm the solvent removal by the UV-curing process, the thickness of the wet and dry silica films were measured by CLSM. The results are shown in Fig. 7 which shows that the average thicknesses of the UV-cured acrylate films doped and undoped with silica NPs are lower than those of the wet films. It indicates that the UV-curing process is capable for removing the solvent corresponding to the results from the COMPO mode in the FE-SEM

characterization as will be shown later in Fig. 10. Besides, the increase in the amount of the silica NPs produces both thicker wet and dry films. This is due to the increasing amount of the particles that affects the increasing viscosity of the dispersion (as seen in Fig. 5) corresponding to more formed silica aggregates [33].

Fig. 7. Comparison of thicknesses of wet and dry films with different silica NPs

contents.

Therefore, the dispersion having a high silica loading possibly contains a high number of particles with a bigger size and various shapes leading to the increased film thickness. In terms of the total transmittance, all the hybrid films were examined by UV-VIS in the wavelength range of 300-800 nm and the result is shown in Fig. 8.

Fig. 8. Total transmittance of the modified UV-cured films with silica NPs

coated on glass substrate.

In the visible region, the total transmittance of every coated glass is about 90% which is close to that of both the bare glass substrate [16] and the UV-cured acrylate film. These results confirmed that the highly transparent silica UV-cured films on the glass substrate were produced. A sharp absorption edge in the ultraviolet region due to the absorption of the glass substrate [16] was also observed. Interestingly, the edge shifts to a longer wavelength (red shift) for the pure UV-cured film. This behavior was also found in the UV-cured films containing silica NPs. This indicates that the UV-cured acrylate film may absorb light at a wavelength longer than the uncoated substrate.

3.2.2 Diffuse transmittance of the thin solid silica UV-cured films

The total light transmittance (T_t) and diffuse light transmittance (T_d) are usually used as indicators for estimating the light diffusing properties of diffuser plates in an LCD system [38]. The films with a high total transmittance and high diffuse transmittance tend to achieve a relatively excellent anti-glare and other optical properties [13]. They are thus suitable for a higher performance LCD in order to obtain the better final images. In this study, the thin solid silica UV-cured films with both a high total transmittance and high diffuse transmittance were prepared with various amounts of silica NPs. The diffuse transmittance spectra of the films containing different amounts of silica NPs are shown in Fig. 9. They were measured using a spectrophotometer equipped with an integrating sphere. When compared to the bare glass, the samples containing silica NPs lower than 15 vol% showed slight increases in their diffuse transmittances, while those with 20 and 25 vol% silica NPs showed moderate increases.

Fig. 9. Influence of silica quantity on the diffuse transmittance spectra of the thin solid silica UV-cured film coated on glass substrate.

The highest diffuse transmittance of 20% was obtained at the 30 vol% level of silica NPs. However, the red shift was observed when the amount of silica NPs was greater than 20 vol%. The diffuse transmittance at a longer wavelength is decreased due to a lower interaction between the light and particles when the wavelength is greater than the particle size. These results reveal that the diffuse transmittance of the film is attributed to the particle loading. When the polymer matrix is assumed to be transparent and homogeneous, the only scattering entity is then assumed to be the particles [39]. Therefore, the high number of particles in the film possibly provides a greater light scattering leading to a high diffuse transmittance. The refractive index of the film is evidence to confirm the light scattering occurrence. The average refractive index for cleaned glass substrates and UV-cured acrylate films is about 1.5232 and 1.5198, by, respectively. However, the refractometer cannot measure the refractive index of the UV-cured acrylate film containing the silica NPs due to the significant refractive line. The refractive line is quite difficult to visually focus the light as a result of an error in visual acuity. Thus, the refractive index for the thin solid silica UV-cured films cannot be defined. These results also support that a large amount of silica NPs in the UV-cured acrylate film may provide light scattering leading to the light refraction. Based on the Mie theory, when the light interacts with the high amount of particles with a size smaller than or comparable to the wavelength of the light, each particle is more illuminated by both the incident light and the secondary scattering than from other particles resulting in the increased diffuse transmittance of the film. This behavior is called multiple scattering which usually occurs in the film containing aggregated particles. If the aggregated particles in the media do not have a sufficient separation, the scattered light of each particle or cluster is assumed to be dependent on each other. At longer wavelengths, the diffuse transmittance drops because the interaction of the light with the particles decreases when the wavelengths become greater than the particles [40].

3.2.3 Morphology of the thin solid silica UV-cured films

To gain a better understanding of the quantitative effect of the silica NPs on the optical properties of the thin solid silica-UV-cured films, the surface morphology of the films were analyzed by FE-SEM. As could be seen in Fig. 10, the polymer surfaces containing carbon (C) atoms with a lower atomic number (as compared to silicon atom in silica) exhibit a dark background emission. This evidence confirms the existence of the silica NPs in these films. The films containing 5 and 10 vol% silica NPs as shown in Figs. 10 (a) and (b) have low amounts of particles on the surface and have a random distribution. The observed

particle size of the silica NPs is approximately 150 nm which is similar to that of the received particles (as seen in Fig. 2). These results suggest that only a small aggregation of particles occurs. However, the number of particles is increased in the film when the amount of silica NPs is increased to 20 vol% as illustrated in Fig. 10 (c). The size of the aggregates is in the range of 300 to 400 nm. It may be attributed to the strong interaction and strong adhesion between the particles [13]. The size of the aggregates corresponds to the cumulative size distribution of the silica NPs nanoparticles dispersed in the UV-curing resin as shown in Fig. 6. Interestingly, the thin solid silica UV-cured film with 30 vol% silica NPs exhibits a high particle distribution.

Fig. 10. FE-SEM surface images of the silica UV-cured film with different amounts of silica NPs (a) 5 vol%, (b) 10 vol%, (c) 20 vol% and (d) 30 vol%.

The distribution is homogeneous and the particles form a greater aggregation as seen in Fig. 10 (d). Its diffuse transmittance is the highest (about 20%) as shown in Fig. 9. This indicates that the increased amount of silica NPs effectively improves the particle dispersion in the polymer film, and influences the morphology of the films corresponding to the increased optical properties of the films [13]. The reasonable explanation is the influence of multiple scattering. The multiple scattering occurs if the particles in the media are not sufficiently separated, thus the scattered light of each particle or cluster is dependent on each other [39]. In this case, both the incident and the secondary scattered light cause the

illumination of each particle. Thus, the higher number of aggregated particles on the substrate more continuously traps the scattered light resulting in both high total and diffuse transmittances. In addition, the increased silica NPs in the film exhibits a wide particle size distribution which improves the diffuse transmittance of the film at the longer wavelengths. The larger size of the aggregates allows the light with longer wavelengths to pass through.

4. Conclusion

A thin solid silica UV-cured film was successfully prepared by coating the silica NPs dispersion on a glass substrate, followed by UV exposure to induce crosslinking polymerization. The total transmittances of the films are close to the bare glass indicating the films transparency. Although the increased amounts of the silica NPs in the UV-cured films do not significantly affect their transmittances, the presence of silica NPs in the UV-cured films produces a significant difference in the diffuse transmittance. The thin solid silica UV-cured film containing 30 vol% silica NPs exhibits the diffuse transmittance of 20% which is higher than other films and the uncoated glass substrate. This is due to the increase in the multiple scattering by the particles in the film. The increased silica NPs in the UV-cured films also provides a good compatibility and good dispersion of the particles which is one of the main roles to improve the optical properties of the films. Therefore, the optical property of the thin solid silica UV-cured film depends on the amount and distribution of the silica nanoparticles.

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