Surface & Coatings Technology 279 (2015) 25–31

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

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

W. Suthabanditpong [a], R. Buntem [b], C. Takai [a], M. Fuji [a,*], T. Shirai [a]

[a] *Advanced Ceramics Research Center, Nagoya Institute of Technology, Nagoya, Japan*
[b] *Department of Chemistry, Faculty of Science, Silpakorn University, Nakhon Pathom, Thailand*

ARTICLE INFO

Article history:
Received 27 April 2015
Revised 27 July 2015
Accepted in revised form 29 July 2015
Available online 31 July 2015

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

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.

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, $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O_{20})H$ [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

---

[*] Corresponding author.
E-mail address: fuji@nitech.ac.jp (M. Fuji).

http://dx.doi.org/10.1016/j.surfcoat.2015.07.068
0257-8972/© 2015 Elsevier B.V. All rights reserved.

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 are 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]:

$$V_T = V_{vdW} + V_{elect} + V_{steric} \tag{1}$$

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]:

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

The effective Hamaker constant is given by

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

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. Eq. (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 Eq. (4). Hence, the refractive indices of the interacting media are matched, i.e., when $n_m = n_p$, the second term in Eq. (3) vanishes as a result of reducing the Hamaker constant to a minimum.

$$\varepsilon = n_C^2. \tag{4}$$

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

$$n_C = n + Ki. \tag{5}$$

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 Eq. (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/cm^3 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/cm^3. It was used as a reactive diluent in the composite monomer to adjust the viscosity and dispersibility.