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Strength of the interactions between light-scattering particles and resins affects the haze of anti-glare films

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ABSTRACT

In this study we evaluated the effects of the surface functional groups of light-scattering particles (LSPs) and the nature of the resin on the haze of anti-glare (AG) films. We fabricated LSPs with amino groups on their surfaces from commercial crosslinked polystyrene microbeads, and LSPs presenting aliphatic chains through reactions of these amino groups with stearic acid. X-ray photoelectron spectroscopy and contact angle analysis revealed that these surface-modified LSPs had different elemental compositions on their surfaces and different wettabilities, respectively. To fabricate AG films, we incorporated the LSPs presenting the different surface functional groups into resins having various affinities. At the same LSP concentration and with the same resin, the AG films incorporating LSPs with aliphatic chains exhibited greater outer haze than did those featuring amino groups. The outer haze increased upon decreasing the ratio of the viscosity of the mixture of LSPs and resin to that of the resin. We speculate that the outer haze was affected by the interactions between the LSPs and the resin.

1. Introduction

Optical thin films are indispensable components in optoelectronic products (e.g., optical apparatuses, displays, solar cells, biosensors) because of their special properties and functions. To ensure superior or different characteristics, transparent colloidal particles (TCPs) are often incorporated in optical thin films to vary the degrees of reflection, light scattering, and light interference and alter the band gap by virtue of refractive index, size, morphological, and quantum effects [1–10]. When the diameters of TCPs are greater than the wavelength of incident light, diffraction effects are suppressed and refraction and scattering become obvious. Such TCPs are regarded as light-scattering particles (LSPs). When the LSPs have higher refractive indices, more LSPs or a larger particle size will result in increased haze. A higher haze value makes thin films more efficient at homogenizing the transmitted or reflected light and avoiding locally concentrated light, which deteriorates visibility. This light-scattering technology has been applied successfully in liquid crystal display diffusers [11] and anti-glare (AG) films [12,13].

AG and anti-reflective (AR) [14–18] films are usually applied in displays or touch panels to ensure comfortable visibility. Because AG films are cheaper than AR films, they are more popular in practical applications. The effect of the composition of the AG film on the haze value has been widely explored, including the ratio of the LSPs to binding resin, the difference in refractive index of the LSPs and binding resin, the average diameter of the LSPs, and the thickness of the AG coatings [19,20]. When the LSP-to-binding-resin ratio or the thickness of the coating is changed, we would expect the surface roughness to be affected and, consequently, so too the haze value. It remains unclear, however, whether other factors can affect the haze value at the same composition of an AG coating. Few studies have investigated the variation in the distribution of particles in a coating layer after drying a particle/resin/solvent suspension [21]. In an earlier study [22] we found that the amount of surfactant located on the surfaces of LSPs significantly affects the distribution of the LSPs in the AG coating layer and, thereby, the ratio of the outer haze to the inner haze. LSPs presenting less surfactant on their surfaces are less hydrophilic and tend to aggregate when the affinity of the solvent to both the resin and the LSPs decreases gradually during the evaporation of the solvent, resulting in larger aggregates and larger outer haze values. For practical applications, LSPs may be obtained from several manufacturers (e.g., Soken Chemical and Engineering, GE-Toshiba Silicones, Nippon Shokubai, and Admatechs), but the amount of surfactant on their surfaces is difficult to control, raising a new question: Are there other factors that affect the distribution of LSPs in AG coating layers?

In this study, we built upon our earlier findings to evaluate the effects of the surface functional groups of LSPs on the haze values of AG films. We positioned amino (NH_2) groups and aliphatic chains

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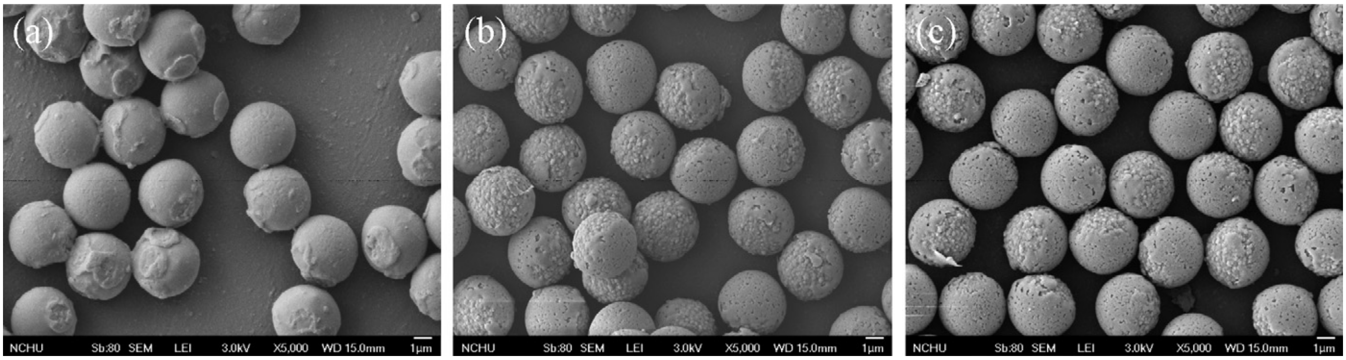

Fig. 1. SEM images of LSPs: (a) PS, (b) PS–NH_2, and (c) PS–SA.

on the surfaces of commercial LSPs and then examined the corresponding structures and haze values of AG coating layers prepared using the modified LSPs.

2. Materials and methods

2.1. Materials

Polystyrene microbeads (PS, SX-350H) were obtained from Soken Chemical and Engineering. Stearic acid (SA, Sigma–Aldrich), pentaerythritol triacrylate (PETA, Sartomor), trimethylolpropane triacrylate (TMPTA, Sartomor), 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba-Geigy), tin (Sn) pellets (Santoku Chemical), sulfuric acid (H_2SO_4, 95–97%, Sigma–Aldrich), nitric acid (HNO_3, 65%, Sigma–Aldrich), hydrochloric acid (HCl, 37%, Sigma–Aldrich), sodium hydroxide (NaOH, reagent grade, Shimakyu's Pure Chemical), isopropanol (IPA, 99.8%, Sigma–Aldrich), and toluene (99.5%, Katayama Chemical) were used as received. Deionized water (DI water, >18 $M\Omega$ cm) was used in all experiments. 90 wt% HNO_3 was obtained after vacuum distillation of HNO_3/H_2SO_4 (1:1, v/v) at 80 °C.

2.2. Preparation of LSPs with special functional groups on surface

LSPs presenting NH_2 groups were synthesized using a procedure reported previously [23]. First, 90% HNO_3 (50 mL) was added dropwise to PS (12 g) in a four-neck reaction vessel immersed in an ice-water bath and then left to react at ca. 0 °C for 24 h. The mixture was then warmed to 25 °C and kept at that temperature for 1 h before being vacuum-filtered. The filter cake was washed with DI water to remove residual HNO_3 then it was redispersed in DI water through ultrasonication; this washing process was repeated several times. The filter cake was dried in a vacuum oven at 60 °C for 24 h. The dried filter cake (9 g) was redispersed in HCl (45 mL) through ultrasonication. Sn pellets (25.2 g) were added and then the suspension was heated under reflux at 90 °C for 24 h. Next, HCl (45 mL) was added to oxidize the remaining Sn pellets. The modified LSPs were filtered, washed sequentially with HCl, NaOH, and DI water, and then dried in a vacuum oven at 60 °C for 24 h, resulting in LSPs presenting NH_2 groups on their surfaces (PS–NH_2).

Stearic acid (30 g) was heated in a vessel at 80 °C and then PS–NH_2 (3 g) was dispersed in the melted stearic acid under ultrasonication. The vessel was placed in an oil bath and heated at 100 °C for 24 h. The modified LSPs were filtered off, washed with EtOH, and then dried in a vacuum oven at 60 °C for 24 h, resulting in LSPs presenting aliphatic chains on their surfaces (PS–SA).

2.3. Fabrication of AG films

The AG coating consisted of LSPs, a UV-curable monomer, a photoinitiator, and solvent. Using ultrasonication, the LSPs (PS–NH_2 or PS–SA) were dispersed in a mixture of IPA and toluene (1:1, v/v; 2 g). The suspension was then mixed with Irgacure 184 (0.15 g) and either PETA or TMPTA (2.5 g). Using a wire-wound rod, the mixture was coated onto a glass substrate that had been washed with EtOH and DI water. The coated film was dried at 70 °C for 3 min and then UV-cured at 500 mJ/cm^2.

2.4. Measurements

The particle size and coating morphology were examined using a field-emission scanning-electron microscope (JSM-7401F, JEOL). The viscosities of the mixtures of LSPs and resin were evaluated using a viscometer (DV-II, Brookfield). Elemental analysis and the binding energy of the surface of the LSPs was performed using X-ray photoelectron spectroscopy (PHI 5000 VersaProbe, ULVAC-PHI) at a take-off angle of 90°. The wettability of the surface-modified LSPs was determined from water contact angle measurements (CA-D, Kyowa Interface Science). At four points on each sample, the haze and transmittance of the AG films were measured using a haze meter (NDH-500W, Nippon Denshoku) under standard illuminant D65 and in compliance with JIS specification K 7361. The haze values of the pristine AG samples, as measured by the haze meter, were regarded as the total haze values. A polystyrene layer was coated on the surfaces of the pristine AG samples to ensure level surfaces. The inner haze values were measured from the smooth AG samples. The outer haze values were determined by subtracting the inner haze values from the total haze values. The samples were qualified by controlling the haze values at the four points to within an error of 5%.

3. Results and discussion

To increase the practical applicability of our approach and to minimize the number of factors influencing the haze of AG films, in this study we employed commercial uniform spherical cross-linked PS microbeads. Fig. 1a reveals that the particle size of the PS beads was uniform (ca. 3.5 μm), but some large protrusions appeared on the surfaces. After surface-modification with the NH_2 groups or aliphatic chains, no observable change occurred in the particle sizes of the microbeads, but the protrusions had disappeared. The modified microbeads featured raspberry-like and/or porous surfaces (Fig. 1b and c). Because PS–NH_2 and PS–SA had similar sizes and configurations, we could ignore the effects of the morphologies of the microbeads in our subsequent experiments.