Double-Sided Nanowrinkle Structure for Anti-Glare Film Prepared by Controlling Inhibition Reactions of Radical Photopolymerization

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A microwrinkle surface made of UV-curable resin is known to reduce the regular reflection or glare of light because the wrinkle structure diffuses the incident light. However, the regular reflection cannot be reduced completely because the back side of the film or substrate reflects light as well. To achieve greater reduction in regular reflection, we developed a double-sided nanowrinkle film prepared on a water surface. A mixture of dipentaerythritol penta-/hexa-acrylate (DPHA), 1,6-bis(acryloyloxy)hexane, and 1-hydroxycyclohexyl phenyl ketone (HCK, photoinitiator) was spread on a water surface containing an inhibitor (Cupferron), and exposed to UV light. The photopolymerization reaction shrunk the liquid film, and solidification occurred simultaneously in the core of the liquid film. However, the top and bottom interfaces contacted air and water, respectively, and the oxygen in air and the inhibitor in water retarded photopolymerization. The difference in photopolymerization rates results in a mismatch of shrinking speed between the core and each interface, and forms a double-sided wrinkle film. The size of the wrinkles within 0.7 μm of air interface was obtained by changing the concentration of DPHA. The double-sided wrinkle film reduced the regular reflection of laser light (λ = 520 nm) more than the single-sided nanowrinkle film.

Keywords: Oxygen inhibition, Wrinkle structure, Nanowrinkle

1. Introduction

The number of monitors in a car increases with increasing number of cameras outside the car. For example, the rear camera, front camera, and side cameras. The images are transmitted to monitors from the cameras and used for assisting driving the car without psychological stress and eventually automated cruising in the future. At intersections or hilly roads, the headlights of other cars transmit light, which reflects on the monitors in your car. The reflected light is transmitted to the driver’s eye, which can be dangerous. The reduction in light reflection is important for the protection of the human eye in a car.

Recently, a wrinkle structure has attracted attention for the application of light extraction from organic light-emitting diodes. Moon et al. prepared a wrinkle structure for energy efficient organic light-emitting diodes (OLEDs) [1]. A UV-curable prepolymer was cast on a substrate and exposed to UV light, which spontaneously formed the wrinkled structure. The effect of the formulation of two bifunctional monomers was investigated, and the details of the wrinkle formation condition were elucidated [2]. They changed the types of monomers and their ratios in further investigations [3]. The application of a wrinkled structure to an OLED is currently widely studied [4-7].

The wrinkle structure is also widely studied for reducing light reflection. Nixon et al. elucidated that the wrinkle structure can reduce the regular reflection and enhance diffuse reflection by studying dragonflies [8]. Hou et al. showed that the wrinkle structure prepared by photo-curing exhibits a high transmittance of over 90% and low reflection of below 5–8%, with an anti-reflection efficiency of 4–7% compared to the flat blank coating [9]. The wrinkle structure can diffuse the incident light and
reduce the regular reflection.

The mechanism of wrinkle formation was proposed for various materials: rocks [10], metal thin films on silicone rubber [11], polyethylene sheets and human skin [12], and titania [13]. They indicate that a thin film compressed in the in-plane (horizontal) direction will undergo buckling deformation and eventually create the wrinkle structure.

The in-plane compression occurs in the UV-curable resin spontaneously as mentioned above [1]. The top surface shrank more than the inner resin, and the mismatch in shrinkage caused by photopolymerization between the top and bulk layers led to the formation of a wrinkle surface [14, 15]. A hierarchical wavy (wrinkle) structure with 10–20 μm line width wrinkles on relatively large wrinkles of 400–500 μm line width have been studied using another methodology [16]. That study built a contact-and-detach UV resin between two plate devices. Initially, primary wrinkles were formed by detaching the two plates; then, small wrinkles were formed by photo-curing. Chandra and Crosby prepared a wrinkle structure using the oxygen inhibition reaction [17]. Zhao et al. investigated the effect of substrate reflecting conditions and prepared a wrinkle structure by weak photo-curing and complete thermal curing [18]. Currently, the wrinkle surface can be formed reversibly by photo irradiation [19].

However, the wrinkled film is prepared on a substrate in most studies. A film with a wrinkle structure on both sides has not yet been formed. As the reflection from the substrate is difficult to reduce, creating a double-sided wrinkle structure is a possible strategy to attenuate that reflection. Regarding the self-compression behavior of UV resin, if a mismatch in shrinkage could occur on both sides of the film, a double-sided wrinkle structure would possibly be produced.

In this study, we created a wrinkle structure on both film sides with the aid of inhibition reactions of radical polymerization, as shown in Fig. 1. The wrinkle structure formed on both sides of a UV-curable resin—the water interface and surface exposed to air. On the surface exposed to air, oxygen in the air inhibited the photopolymerization [20,21], and the inhibition reaction produced wrinkles according to a previous study [17]. A water-soluble inhibitor, Cupferron, is promising to reduce the polymerization rate on the water surface. The core of the liquid UV-curable resin photopolymerized first and formed wrinkles on both sides.

2. Experimental

2.1. Materials

A mixture of dipentaerythritol penta-/hexa-acrylate (DPHA, containing ≤ 650 ppm MEHQ as inhibitor, 407283, Merck), 1,6-bis(acryloyloxy)-hexane stabilized with MEHQ (B2936, Tokyo Chemical Industry, Japan), and 1-hydroxycyclohexyl phenyl ketone (HCK, Irgacure 184, BASF) was used as the UV-curable resin. The formulation was changed as shown in Table 1. The mixture was stirred at approximately 23 °C and stored for at least 24 h to increase the homogeneity. The water-soluble inhibitor of polymerization, ammonium N-nitroso-N-phenylhydroxylamine (Cupferron, Wako Pure Chemical, Japan) was added at 1 wt% to ion-exchanged water.

| wt%  | 1,6-bis(acryloyloxy)-hexane | DPHA | HCK |
|------|-----------------------------|------|-----|
| DPHA 1 wt%  | 98                          | 1    | 1   |
| DPHA 7 wt%  | 92                          | 7    | 1   |
| DPHA 10 wt% | 89                          | 10   | 1   |

2.2. Preparation of double-sided nanowrinkle films

A high-pressure mercury lamp (OmniCure S2000, ExFo, Canada) was used as the light source and UV intensity was measured using a photometer (UIT-150, Ushio, Japan) with maximum sensitivity at 365 nm. A nanowrinkle preparation device is shown in Fig. 2. The UV light was transmitted to a concave lens to collimate. The UV-curable resin was gently spread on the water surface and exposed to UV light for 30 s at the different UV intensities, where the first and second exposures were 5 and 20 mW/cm², respectively.

2.3. Evaluation

The surface of the wrinkle structure was observed using a scanning electron microscope (JSM-7610F, JEOL, Japan) with an acceleration voltage of 5 kV after coating with palladium and gold.
Fig. 2. Schematic of the nanowrinkle preparation device.

A lab-made light reflectometer, as shown in Fig. 3, was used to measure the angle dependence of reflectivity of the 520-nm incident laser. The integration sphere collects the light passed through the pinhole (3 mm). The intensity of the reflected light on the film was measured using a silicon diode sensor. The sensor signal was recorded as $P$. The intensity distribution was plotted as a function of angle $\theta$ and $P(\theta)$. The angle of the integration sphere was changed to measure the reflection angle dependence from $-25^\circ$ to $90^\circ$.

3. Results and discussion

Figure 4 shows two optical images of the sample films prepared with and without the radical polymerization inhibitor, Cupferron, in water. Figure 4 (a) shows the film without Cupferron. The film was largely bent upwards. Photopolymerization was not inhibited at the interface between the water and the UV-curable resin, while it was inhibited on the surface of the UV-curable resin exposed to air. The difference in the degree of shrinkage between the surface and interface caused inhomogeneous shrinkage and bending of the film.

The film with Cupferron (Fig. 4(b)) was not bent, i.e. a flat film was obtained. Cupferron inhibited polymerization at the interface of water and UV-curable resin appropriately; therefore, the surface and interface shrank together. In fact, the concentration of Cupferron was adjusted and 1 wt% in water was optimal to obtain a flat film.

The effect of DPHA concentration on the microstructure of the film is shown in Fig. 5. The low- and high-magnification views are shown in the top and bottom rows, respectively. The scale bars are all 10 $\mu$m. As shown in Fig. 5, winkle structures were formed, although the detailed microstructures of different DHPA concentrations are different. DPHA at 1 wt% tends to have sharp wrinkles, DPHA at 7 wt% has wrinkles with particles, and DPHA at 10 wt% shows a hierarchical wrinkle pattern where microwrinkles exist on the macro wrinkles. The magnified view of Fig. 5(c) (Fig. 6) shows that the pitch of the wrinkles is 860 nm. A part of the wrinkle structure is less than 1 $\mu$m.

![Fig. 3. Lab-made light reflectometer.](image)

![Fig. 4. Effect of photopolymerization inhibitor Cupferron on film shape: (a) without and (b) with Cupferron.](image)

![Fig. 5. Low- and high-magnification views of the film with 1 wt% DPHA.](image)

![Fig. 6. Magnified view of Fig. 5(c).](image)

![Fig. 7. The angle dependence of light reflection was measured using a lab-made light reflectometer for the 7 and 10 wt% DPHA films.](image)

The effect of DPHA concentration on the pitch size of the wrinkle structure was measured based on the micrograph and is shown in Fig. 7. The wrinkle size is between 0.5 and 1.5 $\mu$m. No clear trend was obtained; therefore, the developed preparation process is still immature. Spreading the UV-curable resin on the water is difficult and requires skill. The thickness of the UV-curable resin is possibly different every time, even though the same amount of UV-curable resin was supplied with an accurate pipette.

The angle dependence of light reflection was measured using a lab-made light reflectometer for the 7 and 10 wt% DPHA films, as shown in Fig. 8. The dashed line represents the ideal regular reflection direction. A strong reflection was observed for the film with 7 wt% DPHA, which is caused by the regular reflection of the film.
Fig. 5. Effect of DPHA concentration on the microstructure of films. (a) DPHA 1 wt%, (b) DPHA 7 wt%, and (c) DPHA 10 wt%. The scale bar is 10 μm for both the normal and magnified images.

Fig. 6. Magnified view of the image of DPHA 10 wt% in Fig. 5 (c) film. The scale bar is 1 μm.

The direction of the experimental data is different from the ideal direction because of the uneven bulk film surface, as shown in Fig. 4 (b) (top view). It was limited by our ability to obtain a smooth and flat surface in our preparation process. Even though the direction of regular reflection is different from the ideal direction, Fig. 8 shows that the DPHA 7 wt% film gives a stronger regular reflection than
that of 10 wt% DPHA. The 10 wt% film reflects the incident light isotropically and gives no strong regular reflection.

![Graph](image1)

**Fig. 7.** Effect of DPHA concentration on the pitch of the wrinkles. The error bar indicates the standard deviation of the pitch.

![Graph](image2)

**Fig. 8.** Light-reflectance of the film prepared with different concentrations of DPHA. The dashed straight line is the ideal regular reflection angle ($\theta = 45^\circ$).

To determine the relationship between the light reflection and microstructure, Fig. 9 shows the SEM images of the front and back sides of the film. There are micro and nanowrinkle structures on the front sides of the films with 7 wt% and 10 wt% DPHA, respectively (Figs. 9 (a) and (b)). However, the back side of the 7 wt% film shows a relatively larger structure, which is no longer a wrinkle structure. On the back side of DPHA 10 wt% film, a dense nanowrinkle structure exists.

Our preliminary hypothesis on the regular reflection of a film with a dense wrinkle structure is shown in Fig. 10. In the film with a wrinkle structure only on the front side, the regular reflection from the back side is prominent. The film with the wrinkle structure on both sides can reduce the regular reflection on both sides. Therefore, the net effect of regular reflections is reduced.

![Graph](image3)

**Fig. 9.** SEM micrographs of the front and back sides of microstructures of films. (a) DPHA 7 wt%, (b) DPHA 10 wt%.

![Graph](image4)

**Fig. 10.** A model of light reflection from both the front and back sides of films with wrinkle structure.

### 4. Conclusion

A new process for the preparation a film with a nanowrinkle structure on its front and back sides was developed with the aid of two different inhibition reactions: oxygen inhibition and the water-soluble inhibition of photopolymerization. Both sides of the film shrank uniformly and a wrinkle structure was formed. The smallest pitch of the wrinkle was 860 nm for the film with 10 wt% DPHA. The regular reflection of incident light was successfully reduced by the wrinkle structure on both sides of the DPHA 10 wt% film.

The process developed herein has three advantages. (1) the wrinkle structure is formed on both sides, (2) the pitch of the wrinkle structure is reduced to less than 1 μm, and (3) the wrinkle structure of both sides can effectively reduce the regular reflection. This self-standing film can reduce regular reflection and car accidents at night.
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