

# Antiglare Layer Formation on Polycarbonate Sheet Using UV-Curable Resin-induced Crystallization and Subsequent CO<sub>2</sub> Gas Foaming

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A low-reflectance film was used to reduce the reflection of light from the displays of electronic devices (personal computers, televisions, smartphones, etc.). In this study, an ultraviolet (UV)-curable resin was used to form a nano/microstructure by organic-solvent-induced crystallization and to fill the cracks in the polycarbonate plate. Two different processes were examined: Process 1: the surface of the polycarbonate plate was crystallized at 40, 60, 80, or 100 °C for 10 min and thoroughly rinsed with isopropyl alcohol; and Process 2: the surface of the polycarbonate plate was crystallized at 40 °C for a desired time. The excess UV-curable resin was removed by UV-induced curing and CO<sub>2</sub> foaming during UV exposure using high-pressure CO<sub>2</sub> equipment. CO<sub>2</sub> pressures of 4.5, 5.5, and 6.5 MPa and CO<sub>2</sub> impregnation times of 80, 160, 240 s were investigated to optimize the microstructure. It was clarified that spherulites of polycarbonate existed on the surface by differential scanning calorimetry and scanning electron microscopy. The surface prepared with Process 2 had a relative reflectance that was about 600 and 30 times lower than those of the untreated polycarbonate plate and a commercially available low-reflectance film, respectively.

**Keywords:** Antiglare, Solvent-induced crystallization, Spherulites

## 1. Introduction

Antiglare coatings or films are used to diffuse the reflection of light from the displays of electronic devices (personal computers (PCs), televisions (TVs), smartphones, etc.). Antiglare coatings could be realized by dispersing nanoparticles in a polymer matrix. Liu and Teng fabricated an antiglare film by controlling the aggregation of polystyrene particles with an acid or base treatment [1], and Muzalev et al. prepared a nanocomposite by dispersing silver nanoparticles in poly(methyl methacrylate) [2]. Moreover, Chang et al. prepared a highly hardened antiglare coating by the ultraviolet (UV) curing of 3-(trimethoxysilyl)propyl

methacrylate and fluoroalkylsilane modified silica particles in dipentaerythritol hexaacrylate (DPHA) [3]. Askar et al. assembled close-packed 110 nm silica nanoparticle monolayers on both sides of a glass substrate as high-quality antiglare coatings [4], and Song et al. fabricated a light-diffusing particle (LDP)/polyacrylate composite via in situ radical polymerization with sulfuric acid and vinyl triethoxysilane (A-151) [5]. Sul and Song developed a theoretical framework that quantitatively evaluates the dispersion state of the silica beads of a polyethylene terephthalate (PET)-based antiglare film [6]. Hu et al. used nanocarbon in swollen poly(methyl

methacrylate) particles for a UV-curable antiglare coating [7]. These previous studies used nano/microparticles to reflect incident light in arbitrary directions. The hemispherical shape of the dispersed particles is efficient for reducing the specular reflection of light. However, it is challenging to disperse nano/microparticles on a substrate uniformly as it is necessary to modify the particle surface to attain uniform dispersion.

In this study, a novel preparation method is proposed to create a hemispherical surface using spherulites of polycarbonate crystals. Polycarbonate is a well-established polymer for display applications. Generally, polycarbonate is not crystallized by cooling it from the molten state; however, it could be crystallized by contact with certain solvents [8-11]. Polycarbonate spherulites could be produced by solvent-induced crystallization (SIC). When certain solvents come in contact with polycarbonate in the amorphous state, the mobility of the polymer chains increases, and crystallization begins. The crystallization of these polymer chains forms a spherical lump of crystals, which is a spherulite.

Generally, SIC results in a solvent-induced crack because the density of the crystalline phase is higher than that of the amorphous phase. The shrinking of the crystallized amorphous phase causes a gap between the crystalline and amorphous phases, which is the location of the onset of cracking [8]. If the gap could be filled with a UV-curable resin while inducing crystallization, the spherulite surface will help disperse the incident light for an antiglare film.

In this study, a UV-curable resin was used to induce the crystallization of a polycarbonate surface and fill the gaps between the crystalline and amorphous phases to prepare an antiglare surface. This study is divided into two experimental parts: (1) the realization of UV-curable resin-induced crystallization and (2) the preparation of a crack-free antiglare surface.

## **2. Experimental**

### **2.1. Materials**

An acryl-type UV-curable resin and a 1-mm-thick polycarbonate plate for a display were supplied by HiTEC, Japan and used as received. The details of the UV-curable resin

are confidential. The resin was clear and tuned for good adhesion to polycarbonates. Isopropyl alcohol was used to remove the UV-curable resin in Process 1.

### **2.2. Processes**

Two different processes were utilized. Process 1 was used to crystallize polycarbonate by the UV-curable resin. Process 2 was used to crystallize and remove the excess UV-curable resin on the plates to form a crack-free antiglare surface.

#### **2.2.1. Process 1**

A polycarbonate plate was coated with the UV-curable resin maintained at temperatures of 40, 60, 80, or 100 °C on a hot plate for 10 min. Then, the surface was thoroughly rinsed with isopropyl alcohol to remove the resin completely.

#### **2.2.2. Process 2**

A polycarbonate plate was coated with the UV-curable resin, and the surface of polycarbonate plate was crystallized at 40 °C for a desired time. The plate was placed in a high-pressure CO<sub>2</sub> apparatus developed in our previous study [12] and exposed to UV light. This apparatus could maintain the CO<sub>2</sub> gas pressure at 6.5 MPa or less at 40 °C. The UV-curable resin dissolves the surface of the polycarbonate plate, and the CO<sub>2</sub> gas dissolved in the resin and plate. Both the CO<sub>2</sub> and UV-curable resin were used to promote the crystallization of polycarbonate. Then, the excess UV-curable resin was removed by UV-induced curing and subsequent CO<sub>2</sub> foaming during UV exposure. CO<sub>2</sub> pressures of 4.5, 5.5, and 6.5 MPa and CO<sub>2</sub> impregnation times of 80, 160, and 240 s were investigated to optimize the microstructure of the polycarbonate crystals.

### **2.3. Characterization**

The crystallization of polycarbonate was analyzed with a differential calorimeter (DSC, 8500, Perkin-Elmer) at a heating rate of 10 °C/min. The surface structure was observed with a field-emission scanning electron microscope (SEM, S-4500, Hitachi) at an acceleration voltage of 5 kV. The relative reflectance was measured with a three-dimensional variable-angle photometer

(GP-200, Murakami Color Research Laboratory, Japan). The angle of the incident light and observed light was 5°. The relative reflectance is the magnitude of reflectance relative to the piece of polycarbonate plate of which reflectance is 4%.

### 3. Results and discussion

#### 3.1. Process 1

Figure 1 shows SEM images of the surfaces of polycarbonate plates annealed at 40, 60, 80, and 100 °C for 10 min on a hot plate. Several 2–3 μm spherulites formed at 40 °C. Spherulites with a diameter of 6–8 μm were formed at temperatures greater than 60 °C. The spherulites merged and aggregated with each other. Interestingly, a 100-nm-scale fibrous lump sprouted on the spherulites.

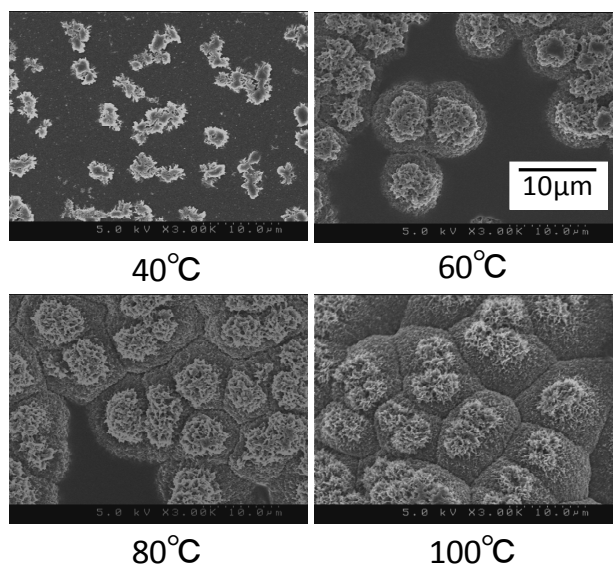


Fig. 1. SEM micrographs of the UV-curable resin-induced crystallization of polycarbonate at different annealing temperatures.

The crystallized polycarbonate plate was subjected to DSC thermal analysis to determine the melting temperature. Figure 2 shows the DSC heat profiles of the annealed plates. The reflection point is around 148 °C, which indicates the glass transition temperature of polycarbonate. Melting peaks were observed in the temperature range of 208–215 °C for the samples processed at 60, 80, and 100 °C. This indicates that the crystalline phase of polycarbonate was formed by the UV-curable resin-induced crystallization.

The sample annealed at 40 °C shows no

peaks in the range of 208–215 °C, while the crystalline phase was identified in the SEM micrograph in Figure 1. Crystallization only occurred on the surface of the polycarbonate plate, and the amount of the crystalline phase was too small to detect by the DSC analysis.

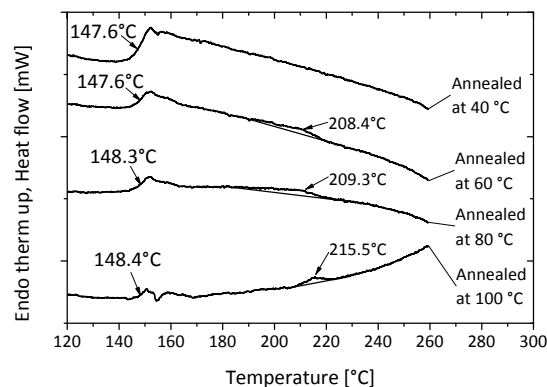


Fig. 2. Thermograms obtained by differential scanning calorimetry of the samples prepared in Process 1.

Figure 3 shows an SEM micrograph of a sample annealed at 50 °C. Cracks are observed, as indicated by the arrows around some spherulites. These cracks caused catastrophic destruction when the sample was deformed.

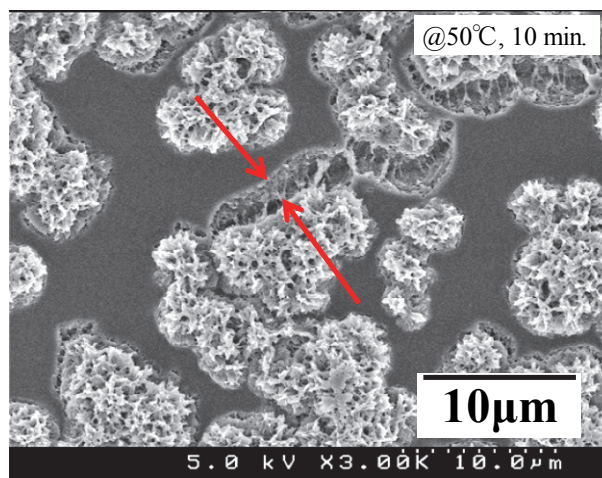


Fig. 3. Surface of a sample annealed at 50 °C for 10 min.

The relative reflectance of the samples annealed at four different temperatures in Process 1 is shown in Fig. 4. The magnitudes of the relative reflectance at 40 and 50 °C are higher than those at 80 and 100 °C because the amount of the hemispherical and fibrous structure of the crystalline phase that could diffuse/reflect the incident light was

relatively low. A similar relative reflectance was obtained at 80 and 100 °C because the crystallization on the surface matured and similar microstructures were obtained.

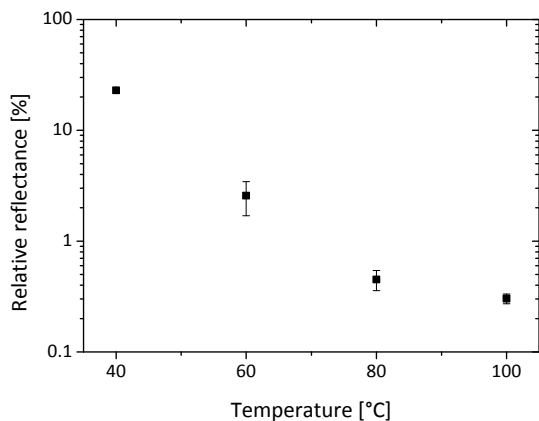


Fig. 4. Relative reflectance of samples prepared with Process 1. The error bars indicate the standard deviation of two samples.

### 3.2. Process 2

In Process 1, the cracks caused by crystallization could not be avoided. To realize a crack-free antiglare surface by UV-curable resin-induced crystallization, Process 2 was performed. Process 2 is the same as Process 1 in that the UV-curable resin dissolves the surface of the polycarbonate plate, and polymer chains are crystallized to form spherulites. If the surface is exposed to UV light, the UV-curable resin is cured on the spherulite surfaces, and the UV-cured resin/air interface reflects incident light. Diffusive reflection is not realized.

To expose the spherulites to incident light, Process 2 employed CO<sub>2</sub> gas foaming of the UV-cured resin [13]. When the UV-curable resin that coated a polycarbonate plate was placed in a high-pressure atmosphere, CO<sub>2</sub> gas dissolved in the resin. The dissolved CO<sub>2</sub> gas forms gas bubbles during UV-light irradiation because of the heat of irradiation and polymerization [13]. UV curing and CO<sub>2</sub> gas foaming occurred simultaneously.

Figure 5 shows a cross-section of CO<sub>2</sub> gas-foamed UV-cured resin. The several 10 μm order pores are observed in the region of 30 μm from surface. The expansion of these pores during the gas-foaming warped and peeled off surplus UV-cured resin. Fortunately, the gas foaming exposed the

spherulites by removing the UV-cured resin. Moreover, the UV-curable resin infiltrated and repaired the cracks.

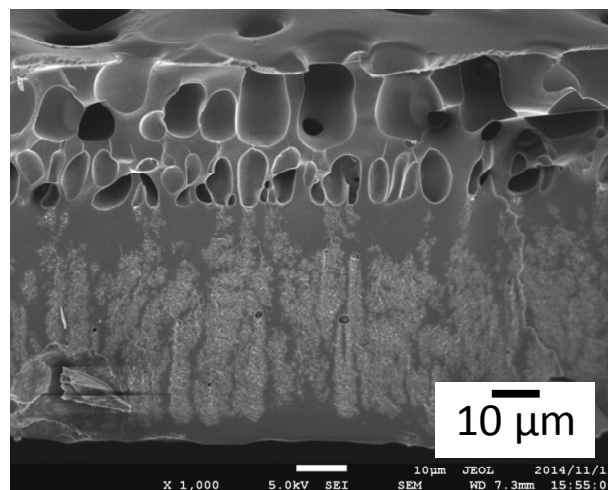


Fig. 5. Gas-foamed UV-cured resin which had covered on the spherulites.

Figure 6 shows an SEM micrograph of the surface of a polycarbonate plate prepared with Process 2. A hemispherical microstructure is observed, which could be formed by crystallization and subsequent UV curing. No cracks were observed with UV-curable resin-induced crystallization. The UV-curable resin filled in the gaps in the spherulites.

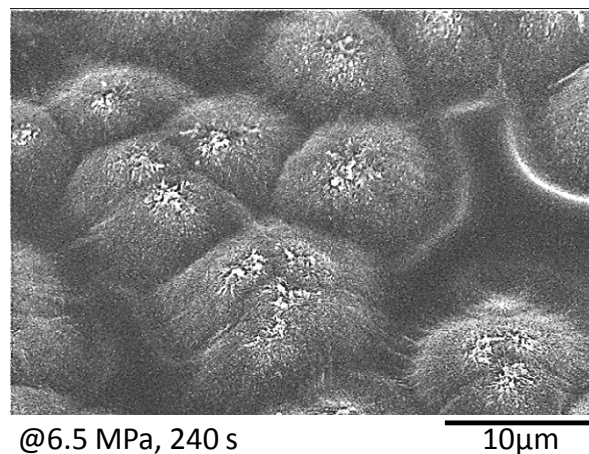


Fig. 6. Surface of a sample prepared at a CO<sub>2</sub> pressure of 6.5 MPa for an impregnation time of 240 s.

Figure 7 shows a series of microstructures obtained for different CO<sub>2</sub> impregnation times and pressures. A hemispherical shape was formed for every set of the impregnation time

and pressure. Moreover, the density of spherulites increased with the impregnation time and pressure. These spherulites were partially filled with the UV-cured resin and were no longer in the molten state by heating. Thus, it was not possible to analyze the crystallinity with the DSC.

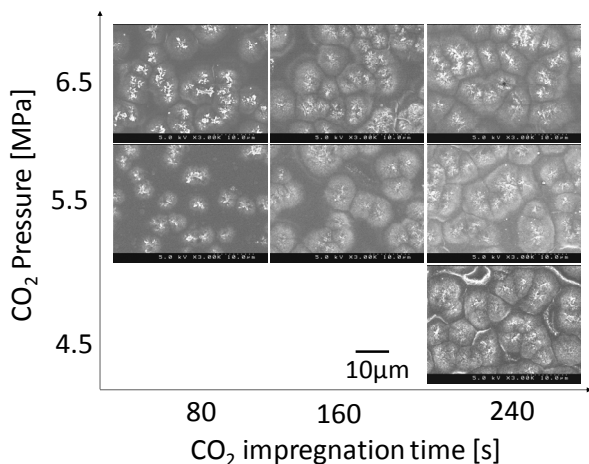


Fig. 7. Effects of the CO<sub>2</sub> impregnation time and pressure on the surface microstructure.

Figure 8 shows the surface crystallinity of samples prepared with Process 2 at different CO<sub>2</sub> pressures and impregnation times. The surface crystallinity was calculated by dividing the area of the crystalline phase by that of the SEM micrograph. Although the surface crystallinity for 4.5 MPa and 240 s is higher than that for 5.5 MPa and 240 s, the surface crystallinity generally increased as the CO<sub>2</sub> pressure and impregnation time increased. The plasticization effect of CO<sub>2</sub> on polycarbonate facilitated crystallization [14,15]. Thus, the plasticization effects of both CO<sub>2</sub> and the UV-curable resin could promote crystallization.

The relative reflectance is shown in Fig. 9 and decreased as the CO<sub>2</sub> pressure and impregnation time increased. This corresponds with the trend for the surface crystallinity in Fig. 8. The increase in the surface crystallinity reduced the reflectance.

The hemispherical microstructure reflects the incident light at every angle. Therefore, the magnitude of the reflected light at the observation angle (5°) became relatively small. Thus, the relative reflectance was reduced. The role of the crystalline phase for reducing the relative reflectance is elucidated. Further, the relative reflectance at 6.5 MPa

and 240 s for the sample fabricated with Process 2 was ~600 times lower than that of the untreated polycarbonate plate and 30 times lower than that of a commercially available low-reflectance film (HiTECH, Japan). However, the film was not transparent. Its haze value was 93.8% (6.5 MPa, 120 s), which was relatively higher than the commercially available antiglare film.

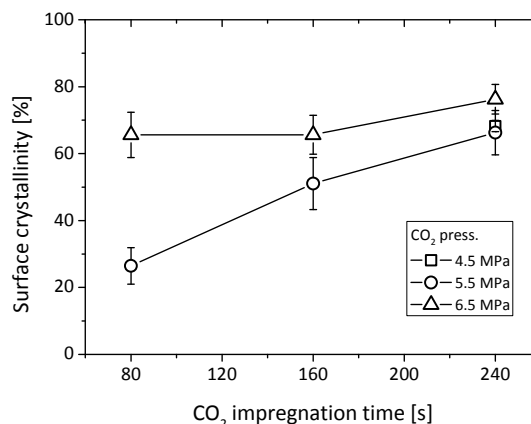


Fig. 8. Effects of the CO<sub>2</sub> impregnation time and pressure on the surface crystallinity. The error bars indicate the standard deviation of three samples.

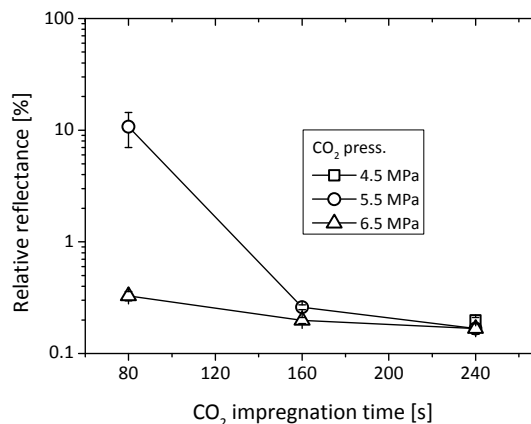


Fig. 9. Effects of the CO<sub>2</sub> impregnation time and pressure on the relative reflectance for samples prepared by Process 2. (squares: 4.5 MPa, circles: 5.5 MPa, triangles: 6.5 MPa)

#### 4. Conclusion

A hemispherical microstructure on a polycarbonate plate was successfully prepared by a sequential process using UV-curable resin-induced crystallization, photopolymerization, and CO<sub>2</sub> gas foaming of

a UV-cured resin to reduce the reflectance. The obtained relative reflectance was 600 times lower than that of the untreated polycarbonate plate because the hemispherical microstructure realized diffuse reflection of the incident light.

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