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Reliability of liquid crystal cell and immiscibility between dual-curable adhesives and liquid crystal

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ABSTRACT

The dual-curable adhesive used to attach thin film transistors (TFTs) to color filters in the construction process of liquid crystal display (LCD) panels requires fast curing by UV irradiation and strong bond strength after thermal-curing. In addition, it is necessary to consider the immiscibility of the dual-curable adhesives with the liquid crystal, because they come directly into contact with the liquid crystal without curing process in the large LCD panel production. In this study, dual-curable adhesives based on partially acrylated epoxy acrylate oligomers were prepared and investigated with nematic liquid crystals using gas chromatography (GC), polarized optical microscopy and the measurement of the transmittance of the liquid crystal.

As the concentration of C=C bonds was increased, the immiscibility was enhanced due to the fast curing rate of the partially acrylated epoxy acrylate oligomers and reduced visual contamination was observed in the polarized optical microscope images. Moreover, the transmittance of the liquid crystal cells was not changed before and after the dual-curing of the adhesives and was maintained for 100 h.

1. Introduction

Since liquid crystals were first discovered by Reinitzer and Lehmann more than 100 years ago, there have been many studies on their display applications [1]. Liquid crystals are very useful for constructing a variety of electro-optical devices owing to their large optical anisotropy which is easily controlled by an external electric field or geometrical modulations.

There are various types of commercialized display such as cathode ray tubes (CRTs), plasma display panels, vacuum fluorescent displays, light-emitting diodes, electroluminescent displays, field-emission displays and LCDs [2]. Among them, LCDs are widely used for flat panel displays as a substitute for CRTs all around the world [3]. Moreover, liquid crystals are applied to many optical processing devices [4,5] and adapted for biophysical devices.

Recently, with the increasing demand for mobile devices in the digital multimedia broadcasting and ubiquitous environments, all organic displays in which all of the elements such as the substrates, integrated circuits, and electrodes are made of organic materials, have attracted much attention, since thin, lightweight, and bendable displays have several advantages including their low power consumption and simple fabrication processes [6].

Liquid crystals are important in several key areas of flat panel displays and fiber-optic communications, since their large optical anisotropy can be electrically and/or geometrically controlled in a simple way. The majority of the specific electro-optical effects of liquid crystals depend on the anisotropy of their electrical and optical properties. The basis of these effects is the reorientation of the director, which

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is described as the average axis of preferred orientation of the liquid crystal molecules, in the macroscopic volume of the materials under the influence of an externally applied field [7,8]. Also, in many application areas, the reliability of the liquid crystal devices comes to be more important, since the physical properties of the liquid crystals depend on the heat, pressure, electromagnetic field, and irradiation of light. The liquid crystal devices should be explored under a variety of environmental conditions such as outdoor and humid conditions for practical applications [9,10]. Particularly, the temperature dependence of the optical properties of the liquid crystal displays is the most important factor determining their reliability [11].

It is important to increase the aperture efficiency of the LCD panel in order to acquire a low power consumption and high luminance LCD. For this purpose, it is necessary to accurately adhere the TFT substrate and the color filter substrate and to reduce the overlap margin in order to compensate for the positional deviation [12]. Also, the production methods used for LCD panels evolve as their size increases. In the case of small LCD panels, the adhesive frame was made by putting the dual-curable adhesive on the surface of the TFT and then covering the color filter. Next, this adhesive frame was cured by a UV- and thermal-curing process. Finally, the liquid crystal was injected into the gap using capillary action in a vacuum environment. However, as the panel size is increased, the time required to inject the liquid crystal increases. Therefore, the one-drop filling (ODF) method was developed. In this method, the adhesive frame is made by putting dual-curable adhesive on the surface of the TFT and then the exact amount of liquid crystal is poured into the frame without any curing process of the adhesive. Next, the color filter is placed over the frame and the adhesive is cured by UV irradiation and thermal heating. Therefore, for the application of various electro-optical control and display devices, the immiscibility between the liquid crystal and adhesives must be considered. Many studies have been conducted on the phase behavior, morphological properties, polymerization kinetics, and electro-optical properties of liquid crystal [13–16]. However, there were no related researches to immiscibility between liquid crystal and adhesives.

The goal of this work, therefore, is to evaluate the immiscibility between the dual-curable adhesives used for the ODF method and the liquid crystal during the UV- and thermal-curing process. Their immiscibility is investigated using gas chromatography, transmittance measurements, and polarized microscopy.

Table 1
Blend ratio of dual-curable adhesives.

Epoxy acrylate oligomer	50.3 wt%
TMPTA	21.5 wt%
Photoinitiators	7.2 wt%
Latent curing agent (LCA)	10.1 wt%
Curing acceleration agent	1.0 wt%
SiO_2	10.0 wt%

2. Experimental

2.1. Materials

In order to synthesize the partially acrylated epoxy acrylate oligomers, a diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (KER 828, epoxy group content: 5260–5420 mmol/kg) was kindly supplied by Kumho P&B Chemicals, South Korea. Acrylic acid (Junsei Chemical, Japan) and triphenylphosphine (TPP, Fluka, Switzerland) were used. Also, to prepare the dual-curable adhesives, the trifunctional monomer, trimethylolpropane triacrylate (TMPTA), and two types of photoinitiators, hydroxy cyclohexyl phenyl ketone (Micure CP-4) and hydroxyl dimethyl acetophenone (Micure HP-8), were kindly provided by Miwon Commercial, South Korea. As the thermal-curing agent, a mixture of dicyandiamide type latent curing agent (Amicure® CG-1400, Air Product) and curing acceleration agent (Sunmide LH-2102) was used. Also, hydrophobic fumed silica filler (Aerosil® R 974, Degussa) was used. All

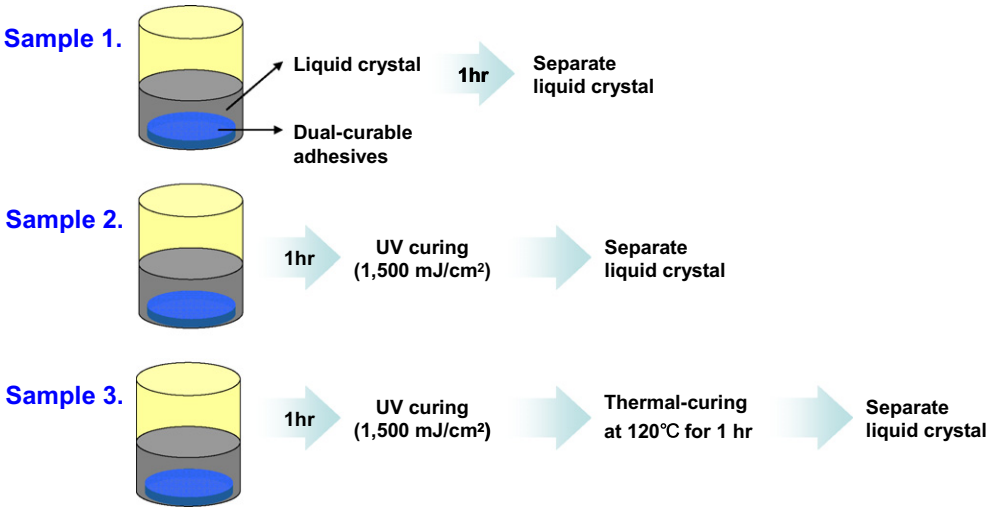
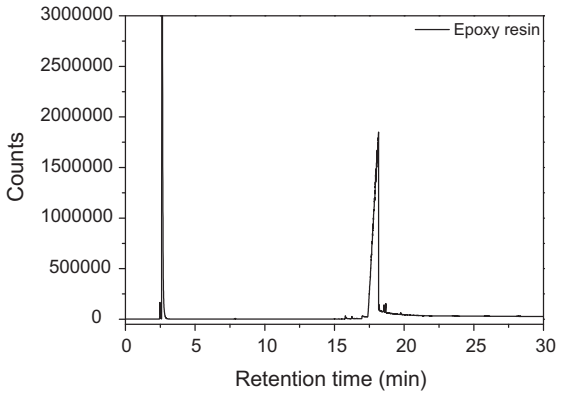
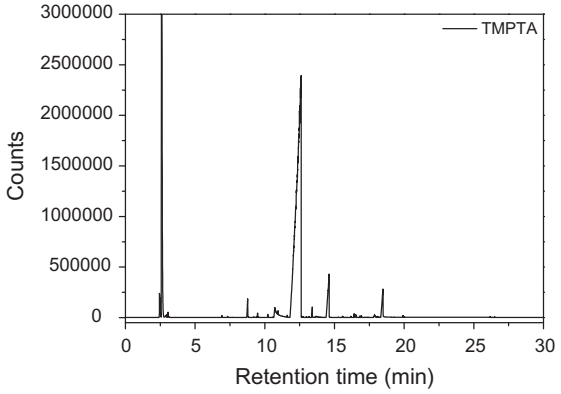


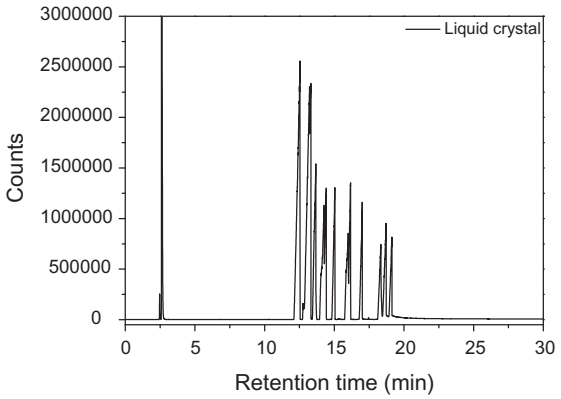
Fig. 1. Schematic diagram of sample preparation procedure of the liquid crystals designed to measure their immiscibility with the adhesive.



(a) Chromatogram of pure epoxy resin



(b) Chromatogram of pure reactive monomer, TMPTA



(c) Chromatogram of pure liquid crystal

Fig. 2. GC chromatograms of pure epoxy resin and liquid crystal.

reagents were used without further purification. Moreover, to evaluate the miscibility between the dual-curable adhesives and liquid crystal, negative liquid crystal, ZLI-5600-100 (Merck, Germany, T_{NI}: about 84 °C), was used.

2.2. Preparation of dual-curable adhesives

The epoxy acrylate oligomers containing various concentrations of carbon–carbon double (C=C) bonds, TMPTA, photoinitiators, latent curing agent, curing acceleration agent, and silica filler were blended using a paste mixer (Daewha Tech, South Korea). Table 1 shows the blend ratio of the dual-curable adhesives. The epoxy acrylate oligomers were synthesized with three different acrylic acid concentrations, viz. 0.2, 0.6, and 1.0 mol%. The blending process consisted of two steps to make a homogeneous mixture and to remove the air bubbles in the adhesives. In the first step, the revolution and rotation speeds were 1500 rpm for 20 min and, then, in the second step, the revolution speed was 1400 rpm and the rotation speed was 100 rpm for 10 min.

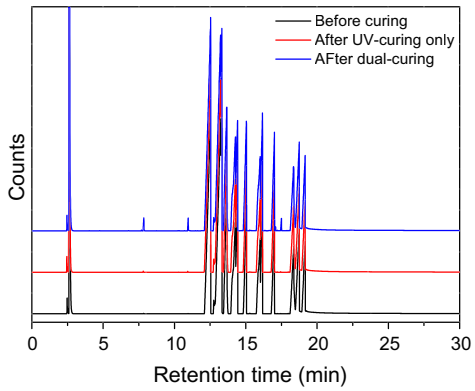


Fig. 3. GC chromatograms of the liquid crystals in contact with the dual-curable adhesive under various conditions: (a) before curing; (b) after UV-curing with a UV dose of 1500 mJ/cm^2; and (c) after UV- and thermal-curing at 120 °C for 1 h. The dual-curable adhesive used was prepared using the partially acrylated epoxy acrylate oligomer which was reacted with 0.6 mol% of acrylic acid and contained 20 phr of latent curing agent.

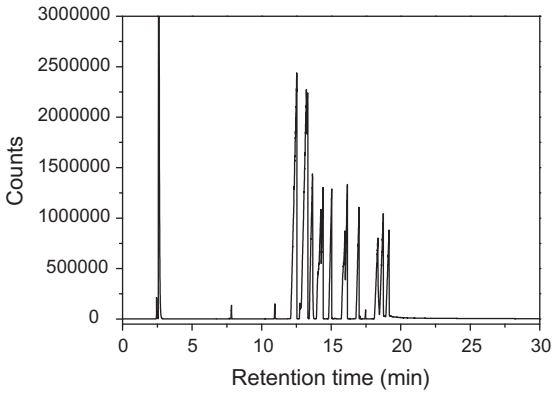
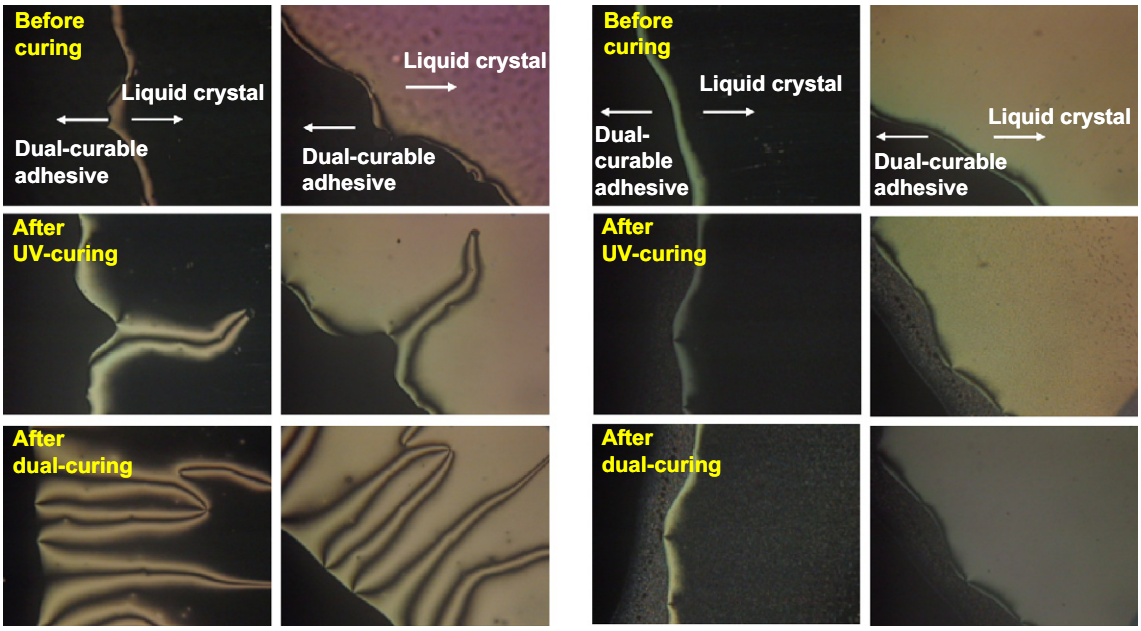


Fig. 4. GC chromatograms of the liquid crystal after UV- and thermal-curing of the dual-curable adhesive soaked in the liquid crystal. The dual-curable adhesive used was prepared using the partially acrylated epoxy acrylate oligomer which was reacted with 1.0 mol% of acrylic acid and contained 20 phr of latent curing agent.

2.3. Measurements

2.3.1. Gas chromatography (GC) analysis

Three types of liquid crystal were prepared. First, 0.1 g of the dual-curable adhesive was coated on the bottom of



(a) 0.2 mol.-% of reacted acrylic acid concentration (b) 1.0 mol.-% of reacted acrylic acid concentration

Fig. 5. Polarized optical microscope images of the liquid crystal cells in contact with the two types of dual-curable adhesives reacted with 0.2 and 1.0 mol% of acrylic acid: before curing (top), after UV-curing (middle), and after dual-curing (bottom). The UV dose was 1500 mJ/cm^2 and then thermal-curing was performed at 120 °C for 1 h.

three glass bottles, and then 1 g of liquid crystal was poured into each bottle. These three liquid crystal samples were maintained at room temperature for 1 h. Next, two samples were UV-cured with a UV dose of 1500 mJ/cm^2. Finally, one sample was thermal-cured at 120 °C for 1 h. After each treatment, the liquid crystals were separated from the dual-curable adhesives for measurement. Fig. 1 shows the schematic diagram of the sample preparation procedure.

The GC spectrometry analyses were performed using a Hewlett–Packard 6890 Series II Plus gas chromatograph. A vaporization injector operating at 250 °C in the packed split mode (1:30) was used. A flame ionization detector (FID) was used. The oven temperature was programmed to remain at 50 °C for 2 min, then increase to 320 °C at a heating rate of 15 °C/min, and then remain at this temperature for 10 min. The injection volume was 2 μl and high purity nitrogen gas was used as the carrier gas at 5 cm/s.

2.3.2. Transmittance of liquid crystal cell

Two ITO glasses coated with an alignment layer were rubbed and then attached to each other using the photo-curable precursor, NOA-65 (Norland Products, Inc.). The cell gap was controlled at approximately 6 μm. The set-up consisted of a laser beam (He–Ne, 632.8 nm) passed through a polarizer (−45°), liquid crystal cell, polarizer (+45°) and pinhole in that order. The set-up was attached to a detector which was connected to a multimeter and computer. Dual-curable adhesives were injected into the gap between the two indium-tin oxide (ITO) glasses under a vacuum and then the liquid crystal was injected on the opposite side. The transmittance was measured in three stages: before curing, after UV-curing only and after UV- and thermal-curing.

2.3.3. Polarized optical microscopy of liquid crystal

For the optical microscopy experiment, a polarized optical microscope (Nikon Optiphot2-POL) equipped with a 12 V, 100 W, filtered halogen light source was used. The magnification was 400×. Pictures were taken using a photographic program.

3. Results and discussion

3.1. GC analysis

GC is a very useful technique for the analysis of a wide variety of mixtures. In order to investigate the contamination of the dual-curable adhesive in the liquid crystal, four types of liquid crystals were examined using GC.

Pure epoxy resin and the liquid crystal were examined using GC. Fig. 2 shows the typical chromatograms of the (a) pure epoxy resin, (b) pure TMPTA, and (c) pure liquid crystals. A distinct sharp peak at a retention time of 18 min was observed for the epoxy resin and several sharp peaks were observed for the liquid crystal at retention times in the range from 12 to 19 min. In order to investigate the immiscibility of the liquid crystal, three types of liquid crystals were prepared. Before UV-curing, the chromatogram of the liquid crystal was the same as that of the pure liquid crystal, as shown in Fig. 3; however, after the UV-curing of the dual-curable adhesive, two very tiny peaks were detected at retention times of 7.8 and 10.9 min and, after the dual-curing of the dual-curable

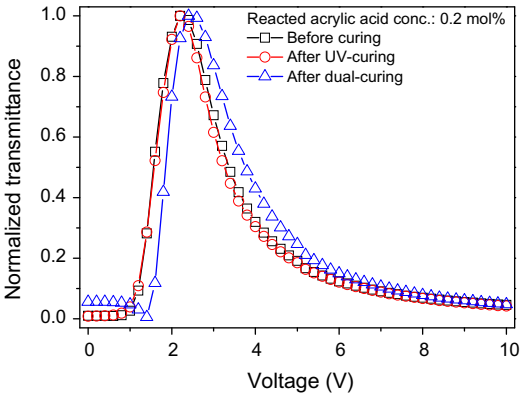
adhesives, they increased in size. These two peaks correspond to those in the chromatogram of the reactive monomer, as shown in Fig. 2(b). Also, after dual-curing, a very tiny peak was observed at a retention time of approximately 17.5 min, which is related to the unreacted epoxy resin, as shown in Fig. 2(a). Therefore, this means that the unreacted components, such as the reactive monomer and partially acrylated epoxy acrylate oligomer, after the UV-curing of the dual-curable adhesive dissolved into the liquid crystal. Also, after the thermal-curing, unreacted epoxy molecules remained in the dual-curable adhesives and affected the immiscibility of the liquid crystal. This phenomenon was clearly observed when the dual-curable adhesive was thermal-cured, because the mobility of the unreacted components was increased at high temperature.

Similarly, Fig. 4 shows the chromatogram of the liquid crystal after the dual-curing of the adhesive, when the dual-curable adhesive containing a large amount of C=C radicals was used. Compared to the chromatogram after dual-curing shown in Fig. 3, although they are not distinctly observed because of the scale of the *x*-axis, the peaks at retention times of 7.8 and 10.9 min related to the C=C radicals slightly decreased with increasing C=C radical content, due to the fast curing reactivity [17]. Also, the intensity of the peak at a retention time of approximately 17.5 min related to the unreacted epoxy resin greatly decreased, because the amount of glycidyl groups of the partially acrylated epoxy acrylated oligomer decreased with increasing acrylic acid concentration.

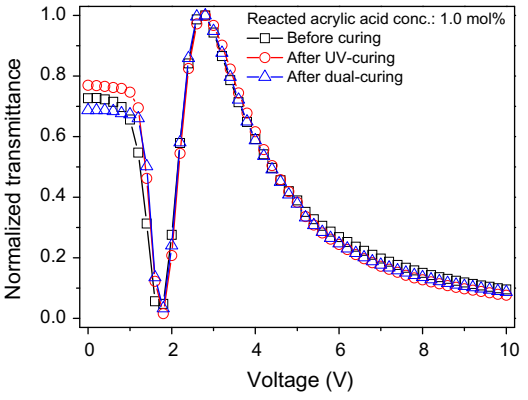
3.2. Morphology development

When the dual-curable adhesives were injected into the gap between the two ITO glasses and then the liquid crystal was injected on the opposite side, their interface was very clean without any contamination, as shown in Fig. 5(a). However, for the dual-curable adhesives prepared using the partially acrylated epoxy acrylate oligomer reacted with 0.2 mol% of acrylic acid, as mentioned in the GC analysis, unreacted components, such as the reactive monomer, partially acrylated epoxy acrylate oligomer and epoxy molecules in the dual-curable adhesive, slightly permeated into the liquid crystal phase after the UV-curing with a UV dose of 1500 mJ/cm^2, and after the thermal-curing of the dual-curable adhesives, the liquid crystal was further contaminated. As a result of the contamination of the liquid crystal, the interface between the dual-curable adhesives and liquid crystal was enlarged to approximately 300 μm.

In the case where there was a high concentration of C=C bonds in the dual-curable adhesives, as shown in Fig. 5(b), a definite interface between the dual-curable adhesive and liquid crystal was observed. Also, after the UV-curing and thermal-curing of the dual-curable adhesives, the interface was distinctly observed, due to the fast reactivity of the C=C bonds [17,18]. Therefore, the faster UV-curing rate by irradiation than that by thermal-curing strongly affects the immiscibility between the dual-curable adhesives and liquid crystal, because the cross-linked structure of the reactive monomer and C=C bonds of the epoxy acrylate oligomer are formed first by



(a) 0.2 mol.-% of reacted acrylic acid concentration



(b) 1.0 mol.-% of reacted acrylic acid concentration

Fig. 6. Normalized transmittance of the liquid crystal cell using the dual-curable adhesive prepared from the partially acrylated epoxy acrylate oligomer reacted with (a) 0.2 and (b) 1.0 mol% of acrylic acid and containing 20 phr of latent curing agent.

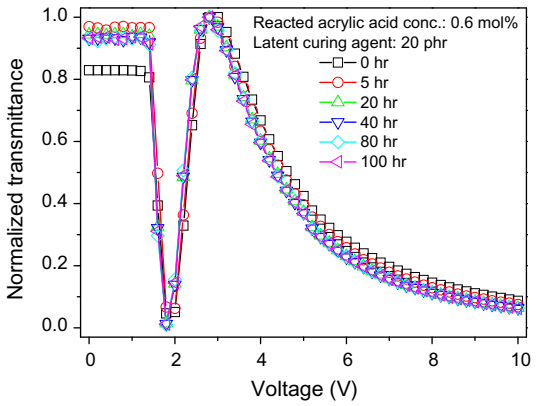


Fig. 7. Normalized transmittance of the liquid crystal cell using the dual-curable adhesive synthesized using 0.6 mol% of acrylic acid and containing 20 phr of latent curing agent as a function of time.

UV irradiation and then the unreacted epoxy resin and glycidyl groups of the epoxy acrylate oligomer form a more

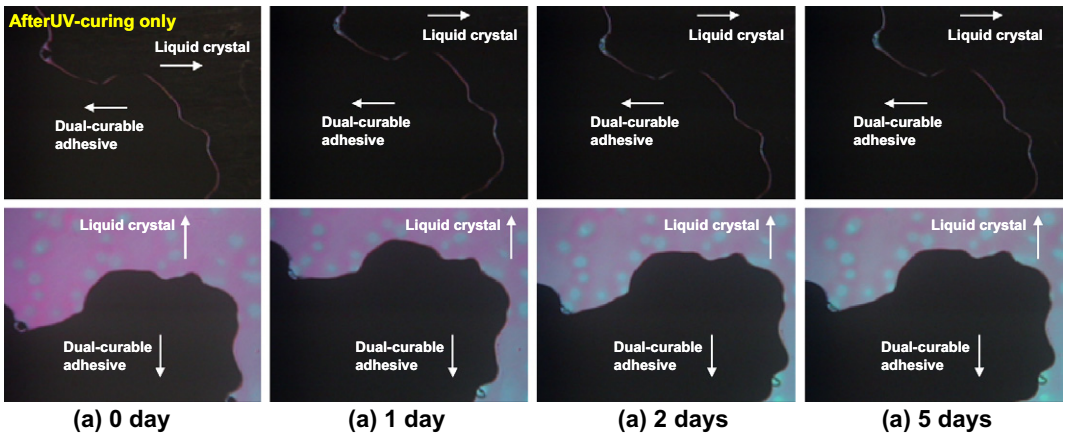


Fig. 8. After UV-curing only, the polarized optical images of the liquid crystal cell using the dual-curable adhesive which was synthesized using 0.6 mol% of acrylic acid and containing 20 phr of latent curing agent as a function of time.

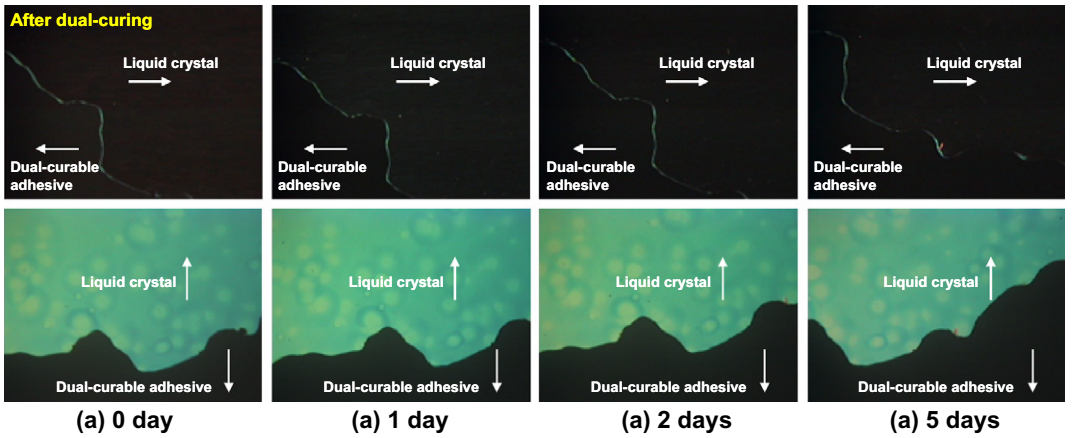


Fig. 9. After UV- and thermal-curing, the polarized optical images of the liquid crystal cell using the dual-curable adhesive which was synthesized using 0.6 mol% of acrylic acid and containing 20 phr of latent curing agent as a function of time.

tightly cross-linked structure. The photo-polymerization process depends on the temperature and the concentration of C=C bonds. However, it is difficult to achieve 100% conversion, because of the diffusion-limited propagation [19,20]. Therefore, even when the optimum conversion conditions are used, unreacted components exist in the cross-linked structures and these ingredients contaminate the liquid crystal phase.

3.3. Transmittance of liquid crystal cell

As mentioned above, the dual-curable adhesives penetrate into the liquid crystal phase during the dual-curing process. Therefore, it is necessary to investigate the physical properties of the liquid crystal that is used.

The normalized transmittances of the liquid crystal cells made using two different dual-curable adhesives are shown in Fig. 6. As the voltage is increased, the transmittance of the liquid crystal cell at low voltage is in the dark state and then it decreases after the white state is observed, because the anisotropy of the liquid crystal is gradually decreased. Therefore, for the dual-curable adhesive containing 0.2 mol% of acrylic acid, the transmittance before and after UV-curing showed the same result, because the liquid crystal was highly contaminated during the thermal-curing stage, as shown in Fig. 5(a), but it was shifted to a slightly higher voltage because of the corruption caused by the dual-curable adhesive. Conversely, for the dual-curable adhesives containing 1.0 mol% of acrylic acid, the transmittance was not changed. The difference in the transmittance at the initial stage comes from the cell gap between the ITO glasses and the measurement point. That is, the immiscibility between the dual-curable adhesives and liquid crystal was strongly affected by the curing rate of the dual-curable adhesives.

3.4. Reliability of liquid crystal cell

The dual-curable adhesives used herein contain unreacted components after dual-curing. Also, during the cur-

ing process, they contaminate the liquid crystal from the visual point of view, as shown in Fig. 5. Therefore, their reliability was evaluated using the transmittance of the liquid crystal cell as a function of time. Fig. 7 shows the normalized transmittance of the liquid crystal cell using the dual-curable adhesive containing 0.6 mol% of acrylic acid. After the dual-curing of the adhesive, the transmittance was measured for up to 100 h. Although there exist some unreacted components, the normalized transmittance did not show any change. That is, although some unreacted components moved into the liquid crystal phase, the physical properties of the liquid crystal were not changed.

In contrast to the ODF method, the dual-curable adhesive was injected into the gap of the liquid crystal cell and then UV- and thermal-cured successively. Next, the liquid crystal was injected into the gap. The polarized optical images after UV-curing only and after the dual-curing of the injected dual-curable adhesive are shown in Figs. 8 and 9, respectively. After UV-curing only, the polarized optical images of the dual-curable adhesive cured with a dose of 1500 mJ/cm^2 did not showed any changes as a function of time, due to the reduced mobility of the uncured components induced by the cross-linked structures of the C=C bonds. Also, after dual-curing, similar results were observed. That is, although some unreacted components contaminated the liquid crystal during the thermal-curing process, there was no interaction between the adhesive and liquid crystal from the visual point of view.

4. Conclusions

The immiscibility between the dual-curable adhesives and nematic liquid crystal before and after the curing of the adhesive was investigated and the reliability of the liquid crystal cell was evaluated.

When the dual-curable adhesives came into contact with the liquid crystal, contamination was not detected using GC. However, after UV-curing, very tiny peaks corresponding to contaminants such as the reactive monomer, partially acrylated epoxy acrylate oligomer and epoxy resin were observed and then after dual-curing, these peaks increased in intensity. These unreacted components penetrated into the liquid crystal phase and were then cured. This phenomenon was controlled by adjusting the concentration of C=C bonds of in the partially acrylated epoxy acrylate oligomers. As the concentration of C=C bonds was increased, the interface between the dual-curable adhesives and liquid crystal was maintained with no contamination before and after each curing step. Therefore, the transmittance was also preserved before and after the dual-curing of the adhesives.

After the dual-curing of the adhesives, the reliability of the liquid crystal cell was maintained for 100 h. It appears that the two different phases do not interfere with each other over time. For this reason, after the dual-curing of the adhesives, the dual-curable adhesives show good immiscibility with the liquid crystal.

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