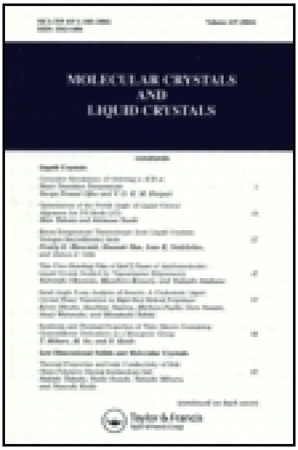

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Effects of Fatty Acids on the Transparency of OCL Materials as Revealed by NIR Spectroscopy

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The shelf life of over coating layer (OCL) materials for TFT-LCD panels prepared by mixing methacrylate copolymer and epoxy compound was improved compared with other materials consisting of a single component. However, a rough surface was formed on the OCL during the post-baking process. Previously, we reported that fatty acids with longer alkyl chains were very effective in preventing the roughing of the OCL surface [1]. In this study, the reaction of carboxy and epoxy groups was studied by using near infrared (NIR) spectroscopy. It was confirmed that the fatty acids do not accelerate the reaction, but compatibilize each component of the OCL material.

Keywords: over coating layer; positive-type photoresist; thermosetting polymer

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1. INTRODUCTION

The production and sales of liquid crystal displays (LCDs) are still increasing in the flat panel display market because of lowered prices in recent years. To provide higher-quality LCDs, many suppliers are trying to improve the manufacturing processes and materials. A thin-film transistor (TFT) array panel consists of many TFT devices in which the height of each TFT device ranges unevenly from 2 to 3 μm. The disorder of liquid crystal molecules on the TFT device areas sometimes causes poor quality of the TFT panel. Thus, overcoating layer (OCL) materials have been widely studied for the TFT panel, because the order of the liquid crystal molecules can be improved by coating OCL materials on the TFT devices [2,3] (Fig. 1). The LCD display panels with OCL films show fast response times and wide viewing angles because of well-ordered liquid crystal molecules on the device. However, current OCL materials have a short shelf life, because of a cross-linking reaction between the epoxy unit and the methacrylic acid unit during storage. In the post-baking process, cross-linked polymer networks are formed by thermal reaction of the carboxy and epoxy groups. The most usual OCL materials developed have both the units in the same polymer chain as copolymers. Therefore, we tried to extend the shelf life of the OCL materials by separating the units into two components: one is methacrylate copolymer having carboxy group, and the other is tri-functional epoxy compound shown in Figure 2. However, a decrease in the transparency of the TFT panels was observed when using modified OCL materials. The transparency

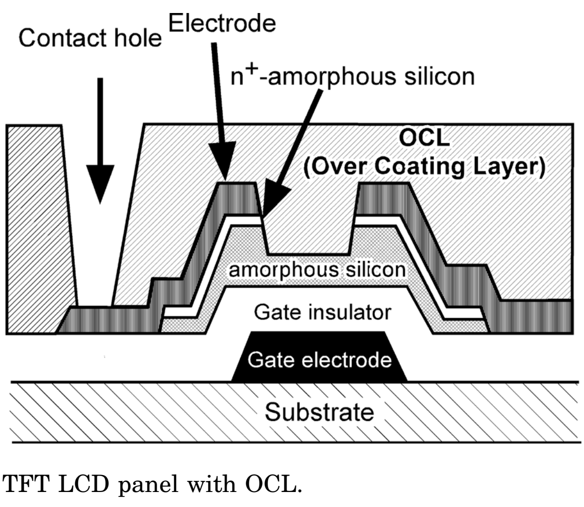

FIGURE 1 TFT LCD panel with OCL.

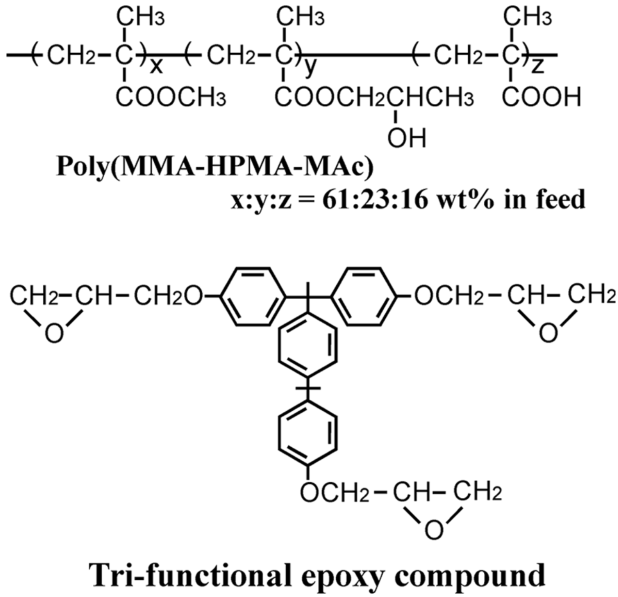

FIGURE 2 Polymers and epoxy compound in modified OCL material.

was improved by using a cross-linking accelerator, but the shelf life was extremely shortened.

We revealed that the decrease in the transparency was closely related to the roughing of the OCL materials [4] through inhomogeneous phase separation of the components, as can be seen in Figure 3. It was assumed that the phase separation was caused during the development and post-baking processes, because of a difference in affinity to the developer (tetramethyl ammonium hydroxide (TMAH) solution) for methacrylate copolymer and epoxy compound. The phase separation results in the inhomogeneous cross-linking reaction of carboxyl groups with epoxy groups in the phase-separated segments, because of inhomogeneous distribution of epoxy groups as a cross-linking agent. As a result, a difference in degree of shrinking was induced during thermal curing by post-baking, causing roughing surface for compensation of the volume difference.

Previously, we reported [1] that some fatty acids could prevent roughing surface of the OCL, leading to improved transparency of the OCL film. In this study, therefore, we investigated the reaction rate of carboxy and epoxy groups in the OCL film during the post-baking process by using near infrared (NIR) spectroscopy in order to clarify the effect of fatty acid on the improvement of the transparency.

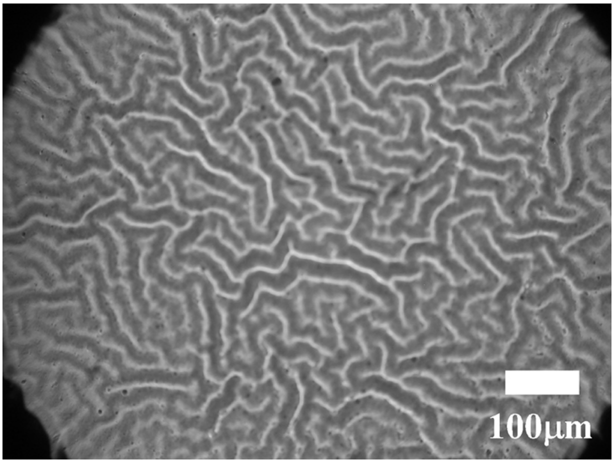

FIGURE 3 Surface of roughing OCL on glass substrate.

2. EXPERIMENTAL

OCL materials were prepared by mixing an methacrylate copolymer and an epoxy compound (Fig. 2). The methacrylate copolymer consisted of methyl methacrylate (61 wt%), 2-hydroxypropyl methacrylate (23 wt%), and methacrylic acid (16%). Its M_w value was $\sim$20,000 as measured by GPC. A tri-functional epoxy compound was used as the epoxy unit for cross-linking. The methacrylate copolymer and the epoxy compound were dissolved in 2-butanone, and amine or fatty acid was added as an additive. In this study, no other components, such as a photo-activator, were added in the OCL material to clearly observe the changes in the NIR spectrum. OCL films of 500 μm thickness were formed on a glass substrate by a casting method after drying in vacuo. For the development, the OCL films were dipped in 0.2 wt% TMAH solution for 60 s and rinsed with deionized water. After drying in air, post-baking was performed by heating on a hot-plate at 220°C for various periods. NIR spectra of the OCL films on the glass substrate were measured with a UV-VIS-NIR spectrometer (Shimadzu; UV-3100). The contents of epoxy units in the OCL films were determined from the absorbance at 4529 cm^{-1}(–O–) normalized with absorbance at 4622 cm^{-1}($C{-}H_{aromatic}$) as the internal standard [5] (Fig. 4). The amount of unreacted epoxy group was calculated by comparing the content of the epoxy units with that of the initial state at different post-baking times.

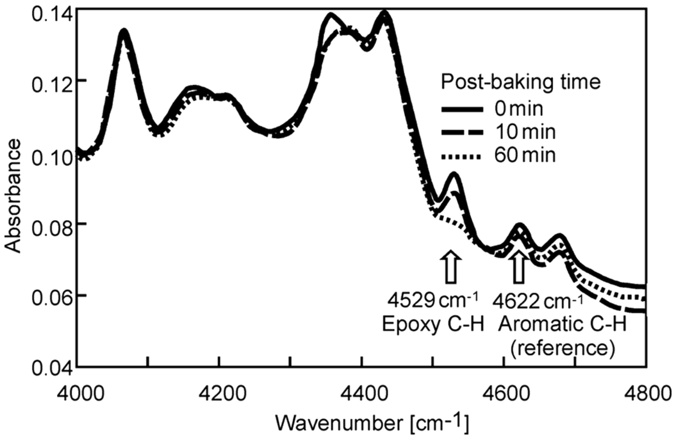

FIGURE 4 Change in NIR spectra of OCL film with post-baking time.

3. RESULTS AND DISCUSSION

The changes in the NIR spectra of the OCL films without additives were measured during post-baking. The OCL films on the glass substrate (thickness $\sim$500 μm) used were prepared from OCL material solution by the cast method in vacuo. NIR spectra of the OCL films were measured before and after the post-baking process by heating at 220°C in air. The content of the epoxy group in the OCL film decreased with post-baking time as shown in Figure 4. The reaction of the carboxy and epoxy groups was found to complete by heating at the temperature for 60 min (Fig. 5).

In the same manner, OCL films containing amines were prepared and the changes in NIR spectra were measured as a function of post-baking time at 220°C (Fig. 5). Amines are well known as accelerators for the reaction of epoxy groups such as cross-linking agents. In this study, diazobicyclo[5.4.0]undecane (DBU) octylate or DBU *o*-phthalate were added as the amine derivatives to the OCL material. The reaction rate was significantly increased by the addition of the amines, and the OCL films obtained showed good transparency. The amines act as a strong base to enhance the reactivity of the epoxy group through nucleophilic addition. Consequently, the rapid curing reaction gave a flat OCL film before forming corrugations on the surface of the film. Although amines prevented roughing during the post-baking process by an acceleration effect, the shelf life (pot life) was extremely shortened. Actually, gelation of 2-butanon solution of the OCL material with these amines was caused in one day at room temperature.

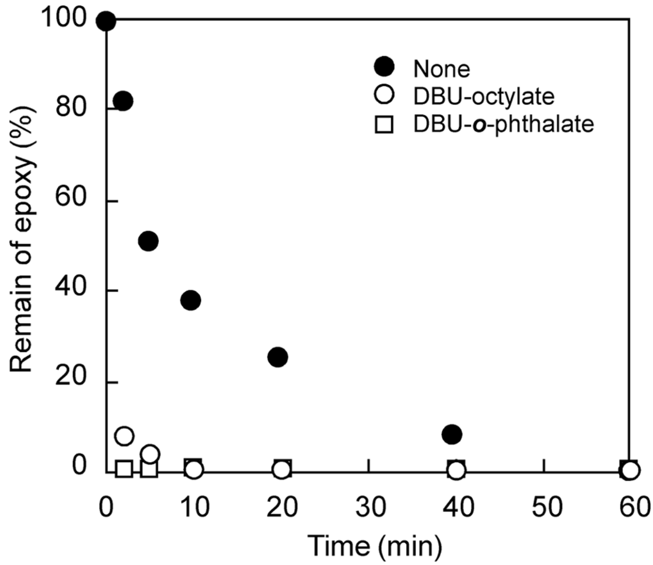

FIGURE 5 Change in remain of epoxy in OCL film with amines.

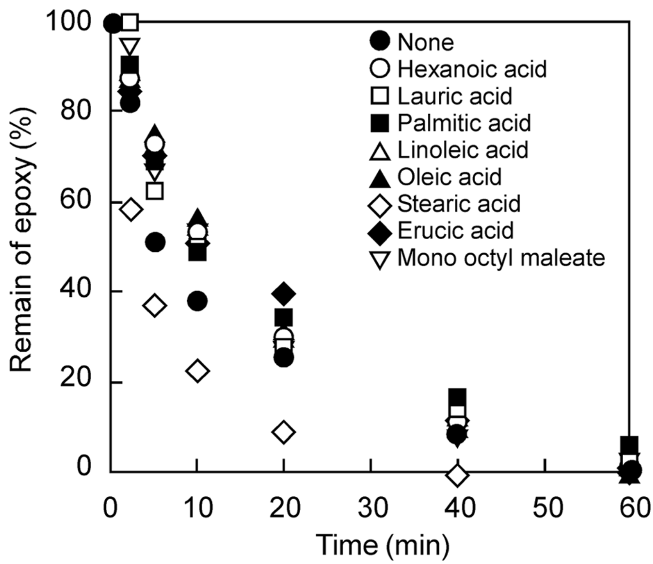

FIGURE 6 Changes in remain of epoxy in OCL film with fatty acids.

Next, the effect of fatty acids having different alkyl chains on the cross-linking rate was explored by NIR spectroscopy, because the fatty acids exhibited sufficient prevention of the roughing of the OLC materials [1]. Fatty acids such as hexanoic acid, lauric acid, palmitic acid, linoleic acid, oleic acid, stearic acid, erucic acid, and mono octyl maleate mono acid were used in this study. Figure 6 shows the time courses of residual epoxy units in the OCL films. Compared with the amines, the reaction rates with fatty acids were almost the same or less with the OCL films without any additives. Namely, all fatty acids exhibited no acceleration effect. Based on these results, it can be assumed that the ability of the fatty acids to prevent roughing contributed to the compatibilization ability to prevent the phase separation. Thus, fatty acids are more suitable additives to prevent roughing of the OCL films.

4. CONCLUSIONS

The effects of additives on the cross-linking reaction of the carboxy group with an epoxy group in the modified OCL material were investigated by NIR spectroscopy during the thermal curing reaction. Although the amines greatly accelerated the reaction rate, the fatty acids had little effect on it. The ability of the fatty acids to prevent roughing was brought about by compatibilization between the methacrylate copolymer and the epoxy compound. As a result, fatty acids are suitable for use in the modified OCL materials as a compatibilizer to prevent the roughing of the OCL film without shortening the shelf life.

REFERENCES

[1] Ogata, T., Takahashi, S., Mochida, K., Nonaka, T., & Kurihara, S. (2006). *Molecular Crystals and Liquid Crystals*, *458*, 89.
[2] Takahashi, S., Kawato, S., & Noguchi, T. (2004). *Japanese patent, Toku-kai*, 2004-287326.
[3] Takahashi, S. (2005). *Japanese patent, Toku-kai*, 2005-17666.
[4] Takahashi, S. (2005). *Electronic Display technology*, *86*, 2005.
[5] Wang, Q., Storm, B. K., & Houmoller, L. P. (2003). *J. Appl. Polym. Sci.*, *87*, 2295.