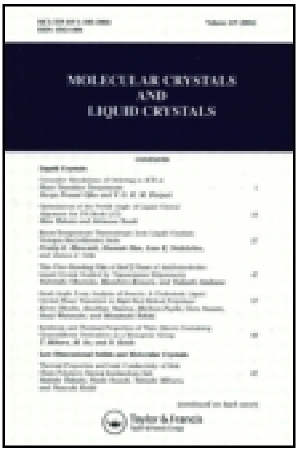

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A Study on the Morphology and Electro-optic Properties of Liquid Crystal-Polymer Composite Films

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A Study on the Morphology and Electro-optic Properties of Liquid Crystal-Polymer Composite Films

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We have studied the relationship between the morphology and the electro-optic properties of liquid crystal-polymer composite (LCPC) materials. The materials consist of the liquid crystal (80% by weight) and the polymerizable mixture (20% by weight) composed of the monofunctional monomer, the oligomer, and the multifunctional acryl monomer. The results show that the electro-optic properties such as the driving voltage and the transmittance depend strongly on the polymer species used.

When the solubility between the liquid crystal and the growing polymers formed during the polymerization process is low and the speed of phase separation is fast, the morphology shows a 'Network' type, the liquid crystal exhibits a continuous phase through the sample, and such a film scatters light strongly in the off state. The maximum transmittance in the on state depends primarily on the polymer morphology and secondly on the solubility between the polymers and the liquid crystal in the 'Network' type LCPC film.

The morphology of the optimum sample chosen from the experimental results shows an intermediate morphology between the 'Swiss Cheese' and the 'Network' types.

Keywords: morphology, optical property, liquid crystal, polymer

1. INTRODUCTION

Liquid crystal and polymer composite (LCPC) materials have been studied for display application by improving the fabrication method.[1–4] There are two main types of LCPC materials based on their morphology. One is a so-called polymer-dispersed liquid crystal (PDLC) material[5–8] which is composed of micronsized nematic liquid crystal droplets dispersed in a polymer matrix and the other is a polymer network liquid crystal (PNLC) material in which the liquid crystal forms a continuously connected phase through the polymer network.[4] The two morphologies are in general observed in PDLC materials.[8] These are: (i) 'Polymer Ball' morphology and (ii) 'Swiss Cheese' morphology.

The 'Polymer Ball' morphology occurs when the growing polymer becomes insoluble in the mixture. The liquid crystal droplets thus form irregular and large shapes. In the 'Swiss Cheese' film, the liquid crystal phase separates and the sep-

TABLE I

The polymer constituents

Monofuctional monomer	Oligomer	Multifunctional Acryl monomer
2-Hydroxyethylmeth acrylate(HEMA, 1.4520)	Polyesterdiacrylate (1.4680)	1,1,1-Trimethylolpropane triacrylate (TMPTA, 1.4700)
Methylmethacrylate (MMA, 1.4140)	Urethanediacrylate (1.4650)	
2-Ethylhexylacrylate (EHA, 1.4360)	Epoxydiacrylate (1.5410)	
N-Vinylpyrollidone (NVP, 1.5120)		

* The numbers in the brackets indicate the refractive indices at 20℃.

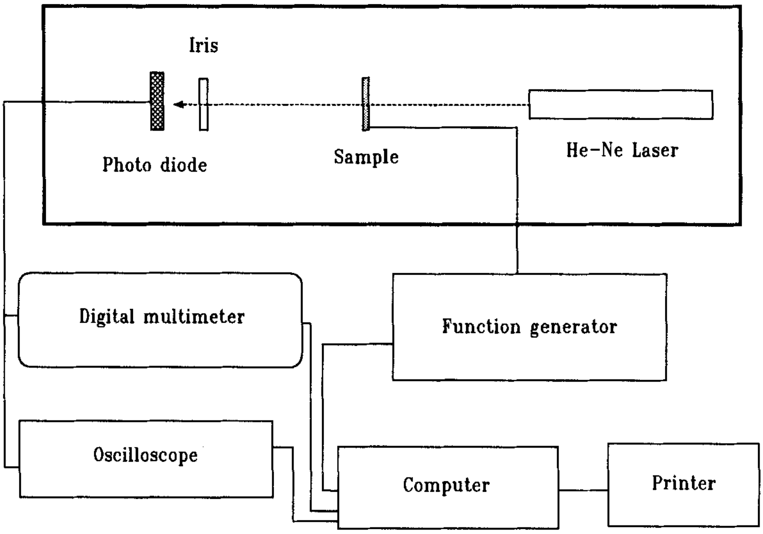

FIGURE 1 Experimental arrangement for the measurement.

arated liquid crystal droplets form small and nearly spherical shapes. The 'Swiss Cheese' morphology is generally known to exhibit stronger scattering and smaller hysteresis than that of the 'Polymer Ball' type.[8] For the 'Swiss Cheese' type of PDLC films formed initially by the spinodal decomposition mechanism from the mixture of the monomer, the oligomer, and the liquid crystal followed by exposure to ultraviolet (UV) source, the driving voltage and contrast of the films were reported to be superior in terms of display applications.[9]

The scattering mechanism of the PNLC films is known to be different from that of the PDLC films.[10–13] In a scattering state without an applied electric field in a PNLC film, the distortion of the nematic liquid crystal directors along the polymer

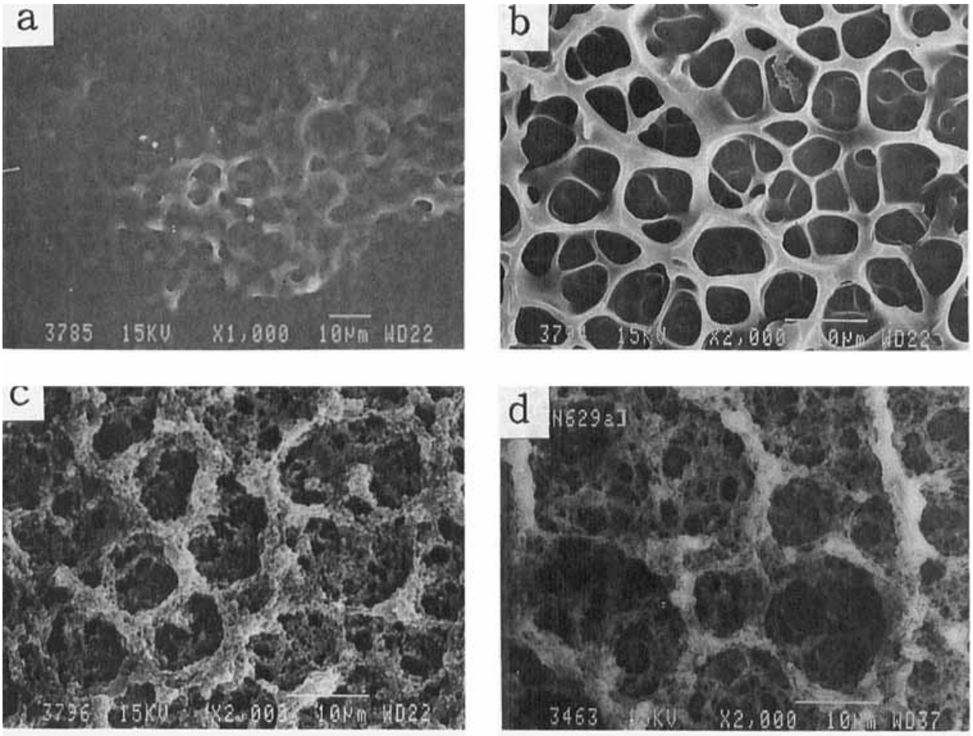

FIGURE 2 Microphotographs with different species of the monomer: (a) 2-EHA, (b) MMA, (c) NVP and (d) 2-HEMA.

surface causes light scattering and in a transparent state with an applied electric field the films exhibit a finite transmittance with little dependence on the refractive index difference between the liquid crystal and the polymer.

LCPC materials having good electro-optic properties in driving voltage, transmittance, etc., show two different morphologies: 'Network' or 'Swiss Cheese' types. There are common aspects that they consist of the liquid crystal more than 60% by weight and the UV curable acryl resin.[9,13] We have studied the LCPC morphology and the electro-optic properties of the LCPC films including some different polymers. We have achieved LCPC films which have less than 6 Vrms driving voltage, high contrast, and fast response time.

2. EXPERIMENTAL

The mixtures under study are made up of the liquid crystal (80% by weight) and the polymer (20% by weight). The polymer is composed of a monofunctional monomer, an oligomer, and a multifunctional acryl monomer. The proportion of a photoinitiator in the polymer mixture is 2% by weight. We have observed the morphology and electro-optic properties of the films as functions of the polymer

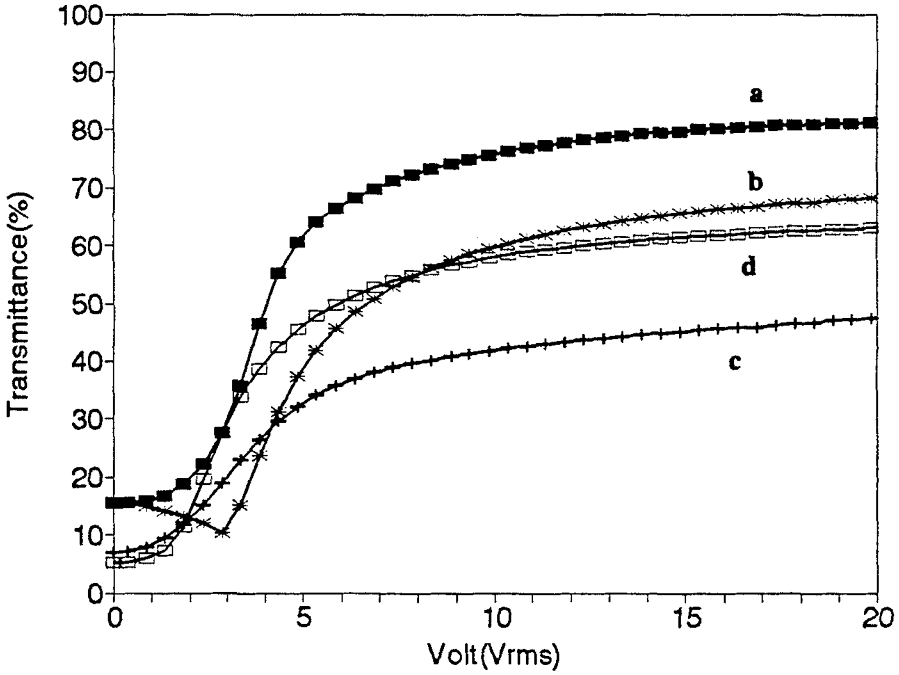

FIGURE 3 Electro-optic properties with different species of the monomer: (a) 2-EHA, (b) MMA, (c) NVP and (d) 2-HEMA.

species and their concentration. Materials, the fabrication methods, and experimental techniques are as follows.

A. MATERIALS AND FABRICATION METHODS

We have used a liquid crystal BL-001 (BDH Co., England). The UV curable polymer constituents are listed in Table I.

We have used 2-Hydroxy-2-methyl-phenylpropane-1-one (E. Merck Co., Darocure 1173) as the photoinitiator. The composite materials put in a 40°C water bath were mixed homogeneously by a mechanical mixer. The mixture was then casted on indium-tin-oxide (ITO) coated glass substrates and spherical glass spacers with 7 μm diameter size were put in to control the film thickness. Before illuminating a UV light, the sample was kept at 40°C to keep the homogeneous phase. The sample was then exposed to the UV source with 365 nm for 3 minutes.

B. ELECTRO-OPTIC MEASUREMENTS AND MORPHOLOGY

The setup is shown in Figure 1. A He-Ne laser with 632.8 nm was used. The intensity of the light transmitted through the sample at an applied voltage across the sample was detected by a photodiode. The value of the output voltage corresponding to the transmitted intensity was collected by an IBM personal computer. The transmittance according to 100% was determined from the value measured without the sample. The voltage to the sample was applied by a function generator

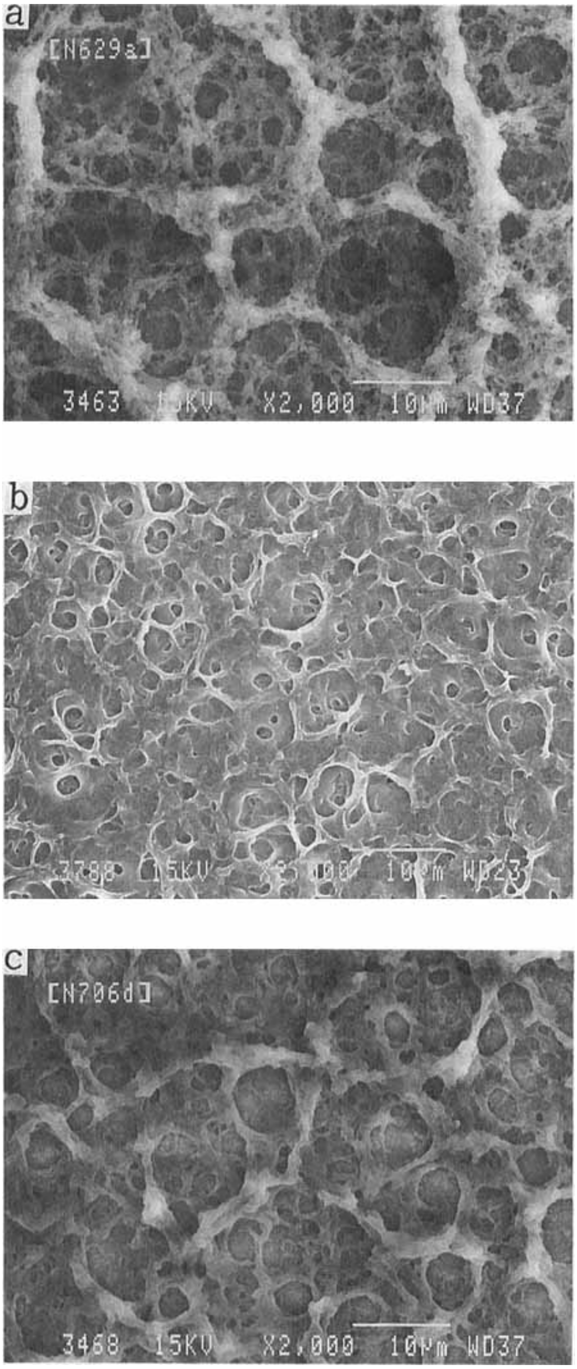

FIGURE 4 Microphotographs with different species of the oligomer: (a) polyesterdiacrylate, (b) epoxydiacrylate and (c) urethanediacrylate.

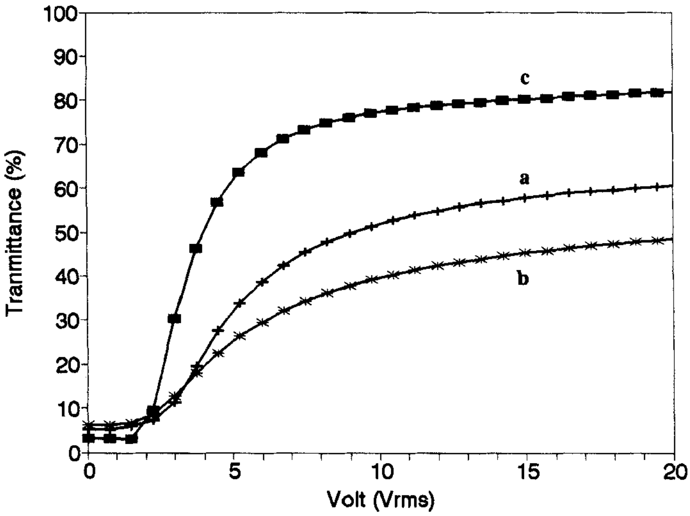

FIGURE 5 Electro-optic properties with different species of the oligomer: (a) polyesterdiacrylate, (b) epoxydiacrylate and (c) urethanediacrylate.

(HP 3245A) and the electro-optic response was measured by using a digital storage oscilloscope (Iwatsu OS-6121A) which was connected to the IBM personal computer.

The bare LCPC films were immersed in acetone solvent for 24 hours and washed out by an ultrasonic cleaning method for 30 minutes in order to remove the liquid crystal remaining in the film. The top-view of the film was taken by using a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

It has been known that one can obtain LCPC films having good electro-optic properties provided that either an oligomer or a monomer-oligomer system is properly chosen.[9,13] However, if only an oligomer is used, the high viscosity and low solubility of the oligomer in the mixture, including the liquid crystal close to 80% by weight, causes difficulty to make a homogeneous mixture and thus restriction to choose an appropriate oligomer. To overcome the disadvantages, a monomer more than 40% by weight is recommended to have a homogeneous mixture. In this case, photo-polymerization may not take place due to the weak reaction of the monomer. However, when a multifunctional acryl monomer such as 1,1,1-Trimethylopropanetriacrylate (TMPTA) is introduced into the polymer mixture, we are able to make a homogeneous polymer-liquid crystal mixture which can be photo-polymerized.

The micrographs in Figure 2 show the polymer morphology according to the species of monomers where the oligomer of polyesterdiacrylate and the monomer of multifunctional acrylate (TMPTA) were used. The corresponding transmittances as a function of applied voltage are shown in Figure 3. The weight proportions of

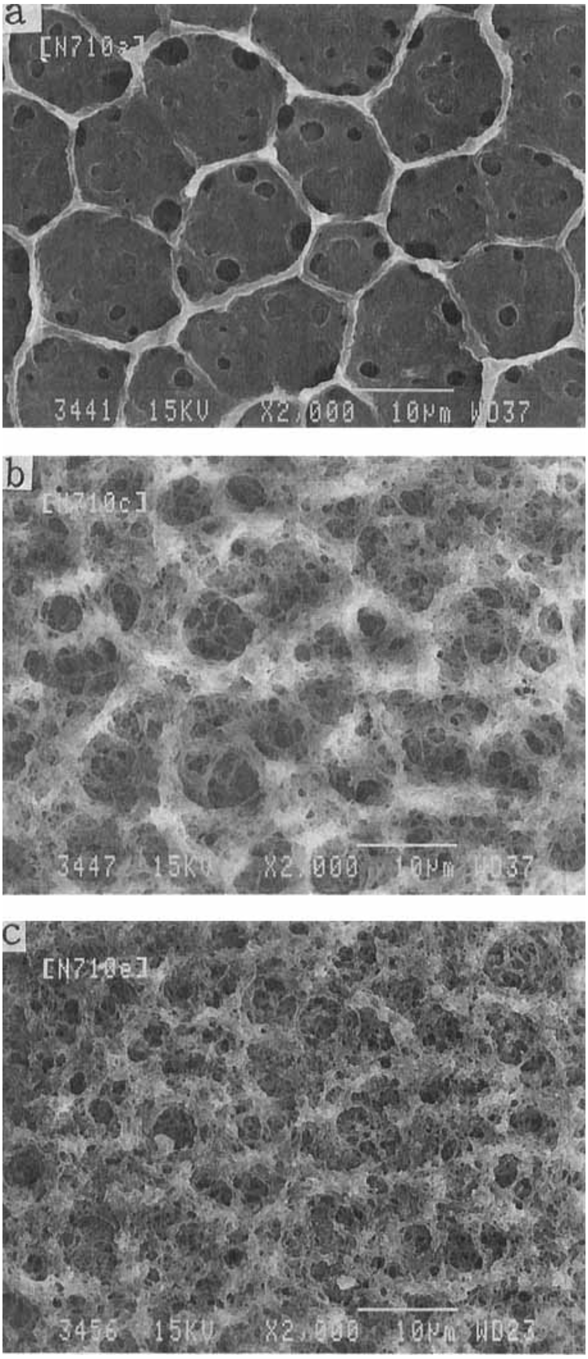

FIGURE 6 Microphotographs with different concentration of TMPTA: (a) 23 wt%, (b) 32 wt% and (c) 38 wt%.

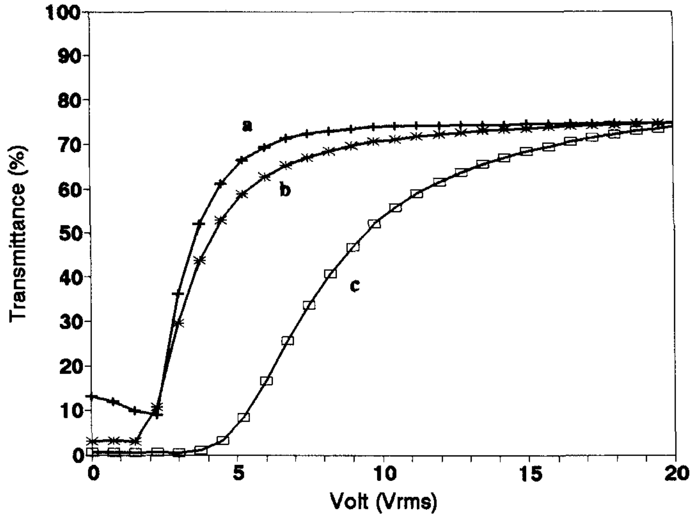

FIGURE 7 Electro-optic properties with different concentration of TMPTA: (a) 23 wt%, (b) 32 wt% and (c) 38 wt%.

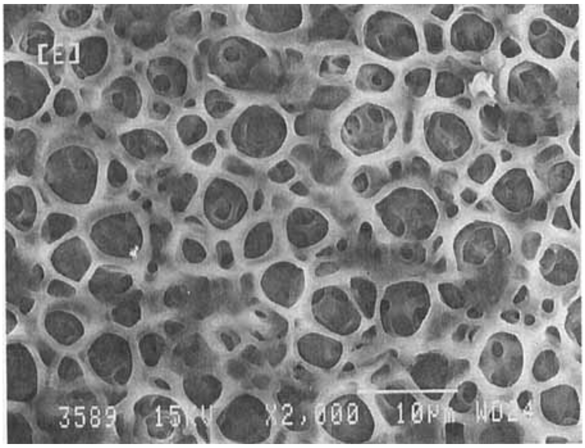

FIGURE 8 Microphotograph of the 'best' sample.

the monomer, the oligomer, and the multifunctional acrylmonomer are 30%, 40%, and 30%, respectively. The morphology shows the 'Polymer Ball' type for the 2-EHA and the 'Swiss Cheese' type for the MMA. For the mixture including the monomers of NVP and 2-HEMA, the morphologies of the 'Network' type are observed and the scattering properties in the off state are relatively better than those for the 2-EHA and the MMA. It is observed that the scattering in general becomes better in the off state as the polymer forms the 'Network' type. In the fabrication of the PDLC films, the 'Swiss Cheese' type, which is known to have relatively good electrooptic properties, is in general observed since the liquid crystal phase separates if the monomer and the polymer is soluble and the solubility of

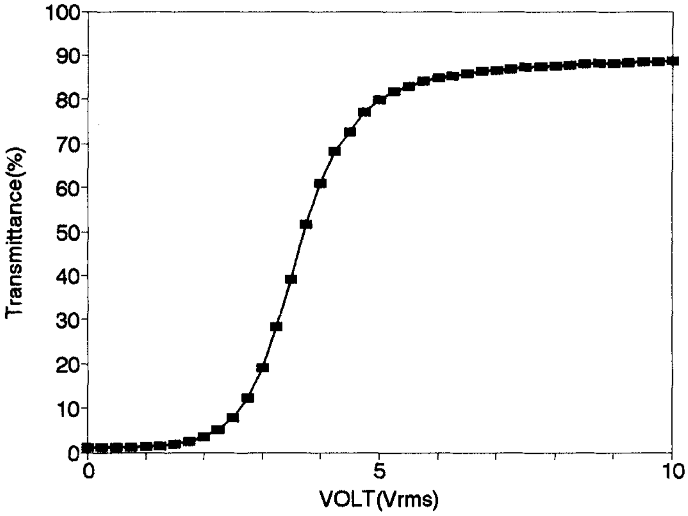

FIGURE 9 Electro-optic properties of Figure 8 sample.

the monomer and the liquid crystal is low.[8] It is thought that the monomer plays the role of a diluent and solvent so that it can lower the viscosity of the mixture and increase the solubility. The degree of the solubility between the liquid crystal and the polymer before photo-polymerization depends strongly on the species of the monomers.

We have observed clear homogeneous phases in the mixtures of the liquid crystal and the prepolymers at room temperature. When the mixtures were cooled down to 0°C, the speed of phase separation had the following order.

NVP, 2-HEMA > 2-EHA > MMA

In the above experiment where the liquid crystal occupies most of the mixture (80 wt%), we have noticed from the observed morphology that the solubility between the monomer and the liquid crystal is significant in the formation of the LCPC materials. The morphology varies depending on the speed of phase separation and the solubility between the liquid crystal and the growing polymer formed during the curing process. It is easier to form the network type when the speed of phase separation is fast and the solubility between the growing polymer and the liquid crystal is low. The speed of phase separation was inferred from the observation of the induction time of scattering state. If the separation is slow and the solubility between the growing polymer and the liquid crystal is high, the formation of PDLC type materials is easier.

Figures 4 and 5 show the morphologies and the transmittances with respect to the change of the oligomer species when we use the monomer, 2-HEMA, and the multifunctional acryl monomer, TMPTA. The weight proportions of the monomer, the oligomer, and the multifunctional acryl monomer are respectively the same—30%, 40%, and 30%, as before. After the homogeneous solutions were cooled down to 0°C, the phase separation depending on the species of oligomers took place as the following order.

urethanediacrylate > polyesterdiacrylate > epoxydiacrylate

The morphology formed from the epoxydiacrylate oligomer reveals a structure which is not well phase-separated and the transmittance exhibits poorly. On the other hand, the morphologies for the urethanediacrylate oligomer and the polyesterdiacrylate oligomer observed by SEM show the 'Network' type structure. Even though two refractive indices for the oligomers are close to each other, electro-optic properties, such as scattering and maximum transmittance, for the urethaneacrylate oligomer are observed to be better than those for the polyesterdiacrylate oligomer. It seems that the low transmittance of the polyesterdiacrylate oligomer system at the saturated voltage comes from higher solubility of the liquid crystal in the polymer than the urethanediacrylate oligomer system. In the LCPC system which contains a relatively large fraction of liquid crystals, the maximum transmittance at the saturated voltage depends mainly on the morphology and secondly on the solubility difference between the liquid crystal and the polymer.

Figures 6 and 7 show the morphology and the transmittance at different TMPTA concentrations where the monomer of the 2-HEMA and the urethaneacrylate oligomer were used. The weight proportion of the oligomer occupation is 40% among the polymers. Figure 6(a) shows the structure for 23% TMPTA concentration and (b) and (c) show the 'Network' type structures for 32% and 38% TMPTA, respectively. If the quality of the TMPTA is small, the polymerization is so slow that we can observe the PDLC type morphology due to the good solubility between the growing polymer and the liquid crystal. Otherwise, as the TMPTA concentration increases, the phase separation occurs for a very short time since the polymerization is fast and the formation of the 'Network' type is easier.

Figures 8 and 9 show the morphology and electro-optic properties of the 'best' sample obtained from the consideration of our experimental results. The contrast ratio is 120:1, the driving voltage is less than 6 Vrms, and the response times for the rising and decaying are 0.5 ms and 25 ms, respectively. The liquid crystal forms a continuous phase through the sample and the sample shows the intermediate morphology between the 'Swiss Cheese' and the 'Network' types. This type of LCPC film scatters light strongly because of relatively large distortion resulting from the increase of interface between the liquid crystal and the polymer. In order to obtain such a morphology, the solubility between the resin component and the liquid crystal should be relatively high to make homogeneous solution before the photo-polymerization, the speed of phase separation should be fast, and the solubility between the polymer and the liquid crystal should be appropriate.

4. CONCLUSIONS

We have studied the relationship between the morphology and electro-optic properties of the LCPC systems which depends on the species of the constituent components such as the monomer, the oligomer, and the multifunctional acryl monomer. The driving voltage of the LCPC films can be reduced by selecting an appropriate polymer species.

The electro-optic properties of the films are closely related to the morphology of the LCPC materials. It is possible to make LCPC materials which are applicable to a display from the information of our experimental results.

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