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# 유화법으로 제조한 PVA/E44 고분자분산액정

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# Polymer Dispersed Liquid Crystal of PVA/E44 Prepared by Emulsion Technique

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**요 약**: 유화법을 이용하여 PVA와 E44로 구성되는 고분자분산액정(PDLC)을 제조하였다. 인가 전기장 및 입사광의 파장이 막의 투과도에 미치는 영향을 연구하였다. 문턱전장의 세기는 $20V_{p-p}/\mu m$ 혹은 $7V_{rms}/\mu m$였다. 전기장 인가시 투과도는 입사광의 파장과 더불어 증가하였다. 한편, 전기장 무인가시에는 입자광의 파장이 증가할수록 투과도는 약간 증가하는 경향을 보였다.

**Abstract**: Polymer dispersed liquid crystal(PDLC) films were prepared from poly(vinyl alcohol)(PVA) and E44 using an emulsion technique. Effect of input electric field and the wavelength of incident light on the transmittance have been studied. The threshold electric field was about $20V_{p-p}/\mu m$ or $7V_{rms}/\mu m$. The transmittance of the powered film increased, rapidly at high and smoothly at low applied voltage, with increasing incident wavelength. However, for unpowered film the transmittance slightly decreased with the increasing wavelength.

*Keywords : PDLC, NCAP, PVA, E44, electrooptics.*

## INTRODUCTION

Liquid Crystal(LC) is used in a wide variety of electrooptic devices including optical display especially when relatively low power consumption and satisfactory response time are needed.[1,2] However, it is quite difficult to maintain uniform thickness over entire LC surface areas due to the fluidity of LC, and hence LC display devices have been of relatively small size.[3~5]

During the last decade, encapsulated liquid crystals have been tested for LC display devices, called nematic curvilinear aligned phase (NCAP).[6,8] Method to prepare the NCAP includes simultaneous mixing of LC and water soluble polymer in water. Then the dispersed LC phase is encapsulated by water soluble polymer to form emulsion. The emulsion is mounted on transparent electrode, which is commonly indium-tin oxide(ITO) coated glass plate, and dried until water evaporates completely. This method has been applied by Fergason[6] to obtain the polymer dispersed liquid crystal(PDLC).

When the LC forms a continuous phase (rather than the isolated droplets as in PDLC) in a spongy-like polymer matrix, the polymer/LC composite film is called polymer network liquid crystal(PNLC), where the LC molecules tend to align parallel to polymeric wall.[9,11] This type of composite film have been reported to show better electrooptic properties to include enhanced optical transmittance, higher contrast, and lower threshold voltage.[3,11~14]

We consider poly(vinyl alcohol)(PVA)/LC (E44) composite film at 40/60 composition. Electro-optic properties as a function of applied voltage and frequency at a fixed wavelength of the incident light, and the effect of the incident light wavelength have been studied throughout the UV-visible range.

## EXPERIMENTAL

**Materials and cell preparation.**[11,12] PVA (Fluka, degree of polymerization=500, degree of hydrolysis=97.5~99.5mole%, $n_p$=1.51~1.52) is used as an encapsulating medium and E44($T_{KN}$=0℃, $T_{NI}$=100℃, $n_e$=1.790, $n_o$=1.528) as an LC. The LC was mixed with 8% aqueous solution of PVA. The mixture was cast on a PET film, with its thickness controlled by an applicator. The film was dried in an oven for 10h at 40℃ to remove residual moisture. By adjusting the gap size of applicator, films with thickness of 7 $\mu$m were prepared. The film was sandwiched between two ITO-coated glass plates(measuring cell), and sealed using an epoxy-type adhesive.

**Morphology and electrooptic measurements.** Morphology of the film was studied with a scanning electron microscopy(SEM, Jeol JSM820). Micrographs were taken from the cast film surface and cryogenically fractured surface of the cast film, which were sputtered with gold before viewing.

For electro-optic measurements, a collimated beam of He-Ne laser (wavelength=632.8 nm) was passed normal to the film surface and the transmitted light intensity was measured with a photodiode. The transmittance through the cell was recorded in a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and the photodiode was 300 mm. An electric field was applied across the film. The effect of wavelength of incident light was studied using an UV-Visible spectrophotometer(Kontron, UVIKON 860).

## RESULTS AND DISCUSSION

**Effect of applied voltage.** Mechanism of transition from light scattering to transmitting state comes from the anisotropic nature of LCs. Because the LC used in this study has a positive dielectric anisotropy($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}>0$), the LC molecules will align with their long dimension parallel to the applied field to minimize their energy.[1] In order to measure the response characteristics of the film, a sinusoidal voltage at 1kHz has been supplied for a period of 50ms. An output signal was detected using a digital storage oscilloscope and the results were recorded by a laboratory computer.

Nematic director orientation within the LC domain is determined by the balance between elastic force, electric force and surface interaction.[15,16] Therefore, there exists a threshold electric field($E_{th}=V_{th}/d$), below which directors can not rotate and orient along the field direction. Fig. 1 shows a transmittance as a function of applied voltage. The transmittance is almost unchanged with applied voltage up to 10~20

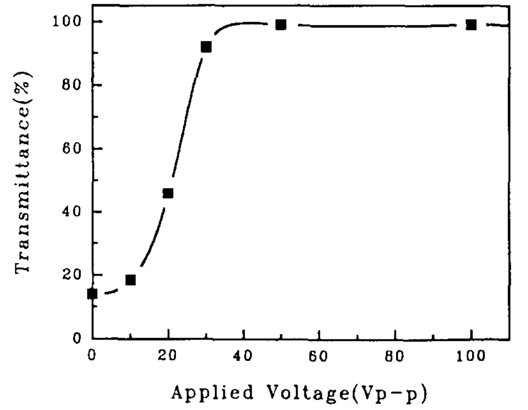


**Fig. 1.** Transmittance vs. applied voltage for PVA/E44 composite film at 1kHz, 25℃.

$V_{p\text{-}p}$, beyond which it increases abruptly with increasing voltage. A threshold electric field($E_{th} \equiv V_{th}$/film thickness) is observed at about 20 $V_{p\text{-}p}/\mu$m or, 7Vrms/$\mu$m. This is a significantly low value, which is due to the weak interfacial interactions between PVA and LC.

Figs. 2 and 3 show rise time($\tau_R$) and decay time($\tau_D$) as a function of applied voltage. The

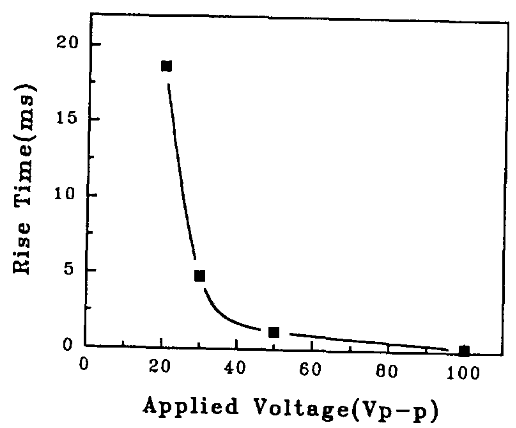


**Fig. 2.** Rise time vs. applied voltage for PVA/E44 composite film at 1kHz, 25℃.

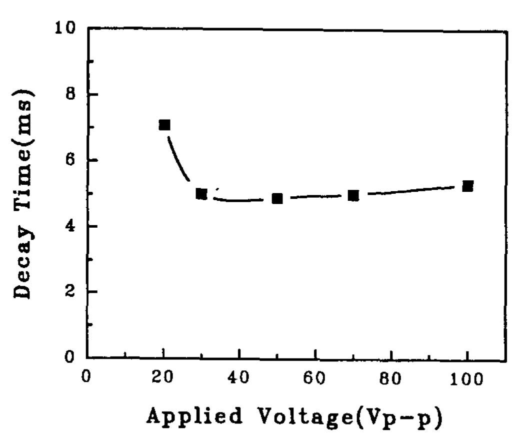


**Fig. 3.** Descay time vs. applied voltage for PVA/E44 composite film at 1kHz, 25℃.

rise time decreases rapidly above Eth and it is less than 1ms at around 100Vp-p. However, the decay time is almost constant due probably to the clean phase separation between PVA and LC. This is consistent with theoretical predictions given below :[5,17]

$$\frac{1}{\tau_R} = \frac{1}{\eta}\frac{9\varepsilon_0 \Delta\varepsilon V^2}{d^2(\rho_P/\rho_{LC}+2)^2} + \frac{K(l-1)}{\eta a^2} \quad (1)$$

$$\frac{1}{\tau_D} = \frac{\eta a^2}{K(l^2-1)} \quad (2)$$

where, $\eta$, $\varepsilon_0$, $\Delta\varepsilon$, V, d, a, $\rho$, K, and $l$ represent viscosity of LC, vacuum permittivity, dielectric anisotropy, applied voltage, film thickness, major dimension, resistivity, elastic constant, and aspect ratio(major dimension/minor dimension) of LC domain, respectively, and subscripts P and LC denote polymer and liquid crystal. Eqs. 1 and 2 state that $\tau_R$ is inversely proportional to $\sim V^2$, and $\tau_D$ depends only on the inherent properties of LC and film geometry. Thus $\tau_R$ decreases rapidly with V, whereas $\tau_D$ is independent of V. It should be noted that the response time ($\tau_R + \tau_D$) is less than 10ms at > $80V_{p\text{-}p}$, and this is much faster than that of conventional twisted nematic type display device.[2]

**Effect of applied frequency.** Fig. 4 shows a transmittance as a function of frequency. The transmittance increases with a frequency showing S-shaped curve. When the transmittance oscillates following the external field, an average between the minimum and maximum was taken to report. In most dielectric composites composed of polymer and LC, the applied external electric field is not entirely imposed on LC phase. The distribution of external field to polymer and LC phases strongly depends on the

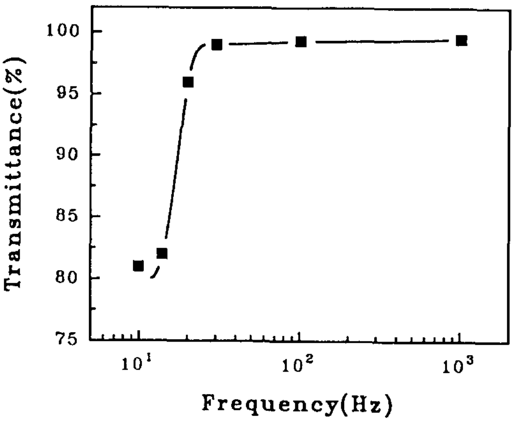


**Fig. 4.** Transmittance vs. frequency for PVA/E44 composite film at $100V_{p-p}$, 25℃.

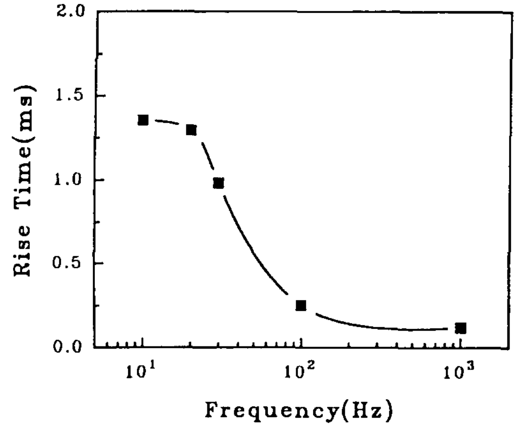


**Fig. 5.** Rise time vs. frequency for PVA/E44 composite film at $100V_{p-p}$, 25℃.

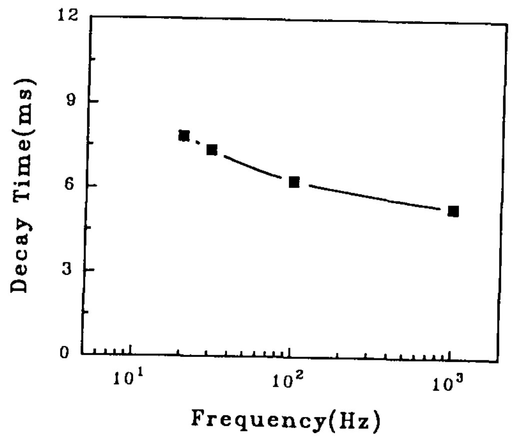


**Fig. 6.** Descay time vs. frquency for PVA/E44 composite film at $100V_{p-p}$, 25℃.

magnitude of dielectric constant and conductivity. For a series connected dielectric composite model which finds close analogy to the films of present concern, the partition of external electric field is given as :[10,12]

$$\frac{E_{LC}}{E_P} = \frac{|\varepsilon_P^*|}{|\varepsilon_{LC}^*|} = \left( \frac{\omega^2 \omega_P'^2 + \sigma_P^2}{\omega^2 \omega_{LP}'^2 + \sigma_{LC}^2} \right)^{1/2} \quad (3)$$

where E, $\varepsilon^*$, $\varepsilon'$, $\sigma$ and $\omega$ represent electric field, complex and dielectric constants, conductivity and angular frequency, respectively. This equation states that at very low and very high enough frequencies the electric field of each phase is inversely proportional to the conductivity ratio($\sigma_P/\sigma_{LC}$) and dielectric constant ratio ($\varepsilon_P'/\varepsilon_{LC}'$), respectively. Since $\varepsilon_P'/\varepsilon_{LC}'$ is generally larger than $\sigma_P/\sigma_{LC}$, the magnitude of $E_{LC}/E_P$ decreases in a frequency range near and below the relaxation frequency of the interfacial polarization.[10,11,18] It is well agreed with our results.

Figs. 5 and 6 show the rise time and decay time as a function of frequency. According to Eq. 3, $\tau_R$ decreases with applied frequency since $E_{LC}$ is larger at high frequency. $\tau_D$ is also constant in most of the frequency range measured. It seems that when interfacial interaction or anchoring strength is small, neither voltage nor frequency can affect $\tau_D$ significantly.

**Effect of wavelength.** Fig. 7 shows a transmittance as a function of wavelength at various voltages. For this particular experiment, a film of 11 $\mu$m thickness was used. For unpowered

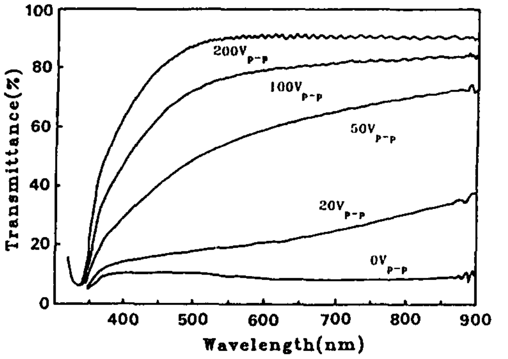


**Fig. 7.** Transmittance vs. wavelength for PVA/E44 composite film at 1kHz, 25℃ (film thickness of 11 $\mu$m).

film, the transmittance decreases slightly with increasing wavelength. However, for powered film, the transmittance increases with increasing wavelength, slowly at low applied voltage and rapidly at high applied voltage. Following Montgomery,[19] when a beam incidents to sample cell, internal reflection also occurs as well as backward and forward scattering. The magnitude of internal reflection also depends on droplet size and concentration. Drazaic et al.[20] reported multiple scattering effect is unimportant on powered films, whereas it is very important in unpowered film. The increased transmittance with decreasing wavelength in unpowered film most likely due to multiple scattering effect, that is, some lights scatter back into the original direction resulting in the increase of transmittance. However, for the powered film, the decrease of transmittance with lower wavenumber ($\lambda$) is mainly due to the increased light scattering, notably Rayleigh scattering,[21~24] which is proportional to $1/\lambda^g$ where $1<g<4$.

## CONCLUSION

The composite films prepared from polyvinyl alcohol(PVA) and E44 using an emulsion technique showed a reasonably low threshold voltage and small response times. In addition, the response times generally followed the theoretical prediction for a single LC drop.

With regard to the effect of incident wavelength, transmittance decreased with decreasing wavelength for powered films, and this was interpreted in term of increased scatterings at low wavelength.

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