

UV-Curable Silica NPs as a Reinforcing Component in Reverse Mode Polymer-Network LC Light-Scattering Device Fabricated Under Different Curing Conditions

Eriko Fukuda, Mitsuhiro Akimoto, Masahiro Miyazaki, Shunsuke Kobayashi

Faculty of Engineering, Sanyo-Onoda City University
1-1-1 Daigaku-Dori, Sanyo-Onoda, Yamaguchi, 756-0884 Japan

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ABSTRACT

Here we examine how curing condition affects the alternation of electro-optical properties of reverse-mode polymer network liquid crystal with UV-curable silica nanoparticles (UVC-NPs). It turns out that addition of UVC-NPs invariably results in the reduction of threshold and saturation voltage under all the curing condition we have examined. From the analysis of electro-optical properties, it is found that incorporation of UVC-NPs has almost the same effect as increasing the curing temperature by around +10°C.

1 INTRODUCTION

Composite materials of polymer and liquid crystal have been intensively studied as an important class of materials applied for light-scattering device in the field of advanced LC display technologies, since such composite films can be fabricated by a simpler and cost-effective procedure, do not require additional optical element including polarizers, and find a variety of applications such as see-through and/or flexible displays, light shutters, and smart windows [1]. Conventional PDLCs, referred to as normal mode PDLCs, are a representative of polymer-LC composites and show the light-scattering (high haze) state when no voltage is applied and becomes transparent under applied voltage because the LC director inside a droplet re-orientates by electric field resolving the mismatch of refractive index between LC droplets and surrounding polymer matrix. Contrary to the normal mode PDLC, the reverse mode device operates in a reverse manner; it shows a transparent off-state and becomes highly opaque under voltage application. There are various methods for preparation of a reverse mode light-scattering device based on polymer-LC composites, among which forming anisotropic polymer network by photopolymerizing reactive mesogens (RMs) in a host of low-molecular mass LC material is widely used [2]. We refer to this type of reverse mode device as the reverse mode polymer network liquid crystal (R-PNLC) film.

In our previous study [3], we have investigated a basic electro-optical property of nanoparticle (NPs) doped R-PNLC films. We used functional NP whose surface is covered with UV-curable groups such as acrylate. When

implementing these UV-curable NPs (UVC-NPs) to a PNLC based on LC and RMs, we have obtained a large reduction of the threshold and saturation voltages of the R-PNLC, especially for the case where the polymer network formed inside a cell is a “smooth” type one [4]. In another study of ours [5] have revealed that UVC-NPs enhance the polymerization induced phase separation during UV irradiation. It is indicated that UVC-NPs perform as large cross-linkers for reactive monomers. In addition, the morphology of formed polymer network is altered by adding UVC-NPs.

Recently Jeon et al., have reported that the electro-optical properties of R-PNLC is largely influenced by curing temperature [6]. They found that lowering curing temperature leads to improvement of the transparent (off) state and response time of the R-PNLC, but the saturation voltage is increased. Those effects are ascribed to the fact that polymer network cured at low temperature does not disturb the initial alignment of LC and the LC domain size is reduced. Here we examine the effect of curing conditions on the basic electro-optical properties of the R-PNLC with UVC-NPs.

2 EXPERIMENT

2.1 Sample Cell Preparation

The nematic LC material we used is MLC-2038 from Merck ($\Delta n = 0.103$ at $\lambda = 589.3\text{nm}$, $\Delta\epsilon = -5.0$ at $f = 1.0\text{kHz}$, and $\gamma = 179\text{mPa}\cdot\text{s}$ at 20°C) which has a negative dielectric anisotropy. As for reactive mesogens (RMs), we purchased 1,4-Bis [4-(3-acryloyloxypropoxy) benzoyloxy]-2-methylbenzene (RM257) which is a widely-used, diacrylate monomer from Tokyo Chemical Industry. As is the same as our previous study we used a functional silica NPs, supplied as NANOBYK-3605 from BYK-Chemie GmbH, to replace a part of RMs. NANOBYK-3605 is a silica NP dispersion with liquid 1,6-Bis(acryloyloxy)hexane (HDDA) as a carrier. The content of silica NPs is 50wt%. The surface of dispersed silica NPs is modified with acrylate groups. HDDA is a non-mesogenic difunctional, and photopolymerizable monomer with relatively simple chemical structure. The sample preparation is as follows; first, RM257, NANOBYK-3605, and MLC-2038 were mixed with

different weight ratios (RM257/NANOBYK-3605/MLC-2038 composites: 5/0/95, 3.5/1.5/95), and about 3wt% (with respect to the amount of reactive component, i.e., monomers and UVC-NPs) of a photoinitiator, Irgacure 651 from BASF was added to them. Next, the dispersion was stirred by a magnetic stirrer and then intensely sonicated at room temperature for obtaining a homogeneous mixture. A small amount of the composites was spread in an empty cell with gap of 20 μ m, which has homeotropic alignment layers of polyimide SE-4811 (Nissan Chemicals) without rubbing. The whole fabrication was done in the clean room condition.

In order to photopolymerize RM257 to form an anisotropic polymer network in a LC host, the test cells were exposed to a UV light of 365nm wavelength under a series of irradiation conditions with a couple of control parameters. The control parameters we adjust are irradiation intensity of UV light, irradiation time, and curing temperature. In the present study, we demonstrate the results obtained under two UV irradiation condition: (1) 5 mW/cm² for 60 min (referred to as 'weak and long' condition), (2) 50 mW/cm² for 10 min (referred to as 'strong and short' condition). The curing temperature was varied from -10 °C to +40 °C.

2.2 Measurement

The electro-optical properties of these light-scattering films is measured with an LCD evaluation system LCD-5200 (Ohtsuka Electronics). During an electro-optic measurement, a square wave voltage of 1kHz was applied. For measuring a voltage-dependent transmittance, an applied voltage is varied from 0V to 200V. The rise time, t_{Rise} is defined as the time required reaching from $T_{\text{min}}+0.9(T_{\text{max}}-T_{\text{min}})$ to $T_{\text{min}}+0.1(T_{\text{max}} - T_{\text{min}})$ where T_{max} is the maximum transmittance at no applied voltage and T_{min} is the minimum transmittance reaching by applying a certain voltage for response time measurement (which is usually not equal to the saturation voltage). The fall time, t_{Fall} is the time required to return to $T_{\text{min}}+0.9(T_{\text{max}}-T_{\text{min}})$ from $T_{\text{min}}+0.1(T_{\text{max}} - T_{\text{min}})$ after switching off. Here, the reference of light intensity is taken as a transmitted light without sample cells. The measurement is done without any polarizer and at room temperature. For morphological observation, we used a polarized optical microscope BX-53 (Olympus).

3 RESULTS

Figure 1 shows the voltage-dependent transmittance (V-T curve) of the R-PNLCs fabricated at different curing temperatures. UV irradiation condition is 'weak and long'. As the curing temperature is lowered, the transmittance at no bias is increased and both the threshold and saturation voltage shifts to higher voltage region. This is the same tendency reported in Ref. [6,7]. Still there is a discrepancy between our result and that of Jeon et al. [6]. That is, in our result, the transmittance at saturation voltage (high haze state) also shifts upward, while in Ref. [6] the cell

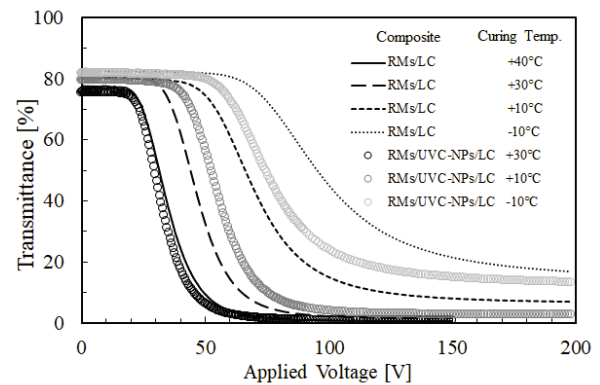


Figure 1 Applied voltage-dependent transmittance of the reverse mode PNLC films cured at different curing temperatures. UV irradiation condition is 'weak and long' (5 mW/cm² for 60 min).

cured at lower temperature marks lower transmittance (high haze). It means that the contrast ratio of the R-PNLC obtained by Jeon et al. does not get worse (or rather showing better performance) even if curing at low temperature. Our R-PNLC cured at lower temperature exhibits lower contrast ratio. But apparent degradation such as Mura was not seen by POM observation (image not present here). Contrary to Jeon et al.'s result, Ma and Yang reported the same tendency as ours [7]. They have pointed out that the low curing temperature induces slow diffusion of monomers, so that polymerization becomes slow as well and the cross-sectional diameter of a formed polymer bundle decreases when decreasing the curing temperature [7]. In other words, the mesh size (LC domain size) becomes fine at lower curing temperature which is confirmed by their SEM observation. This fine mesh of polymer network causes a higher shift of V-T curve and residual light-scattering at saturation voltage; all of those are consistent to our results. We do not do SEM observation of polymer network yet, but still it is plausible to consider that the morphology of polymer networks of our R-PNLC have similar feature. Regarding on the effect of UVC-NPs, the reduction of both the threshold and saturation voltage is always obtained when comparing the same curing temperature. Thus, the UVC-NPs works well for better performance of the R-PNLC. Additionally, the above tendency is observed even if we fabricated the R-PNLC films under different weight ratio of the photoinitiators and UV irradiation conditions; the RM/LC composites to which 10wt% (with respect to the amount of RMs) of the photoinitiators are added were irradiated the 'strong and short' condition.

One remarkable feature is found in the present study that the V-T curve of the cell without UVC-NPs cured at +40°C (solid line in Figure 1) almost traces the V-T curve of cell with UVC-NPs cure at +30°C (darkest open circles). Other data of the V-T curve shows that such a tracing behavior is clear at higher curing temperature.

This indicates that addition of UVC-NPs decreases the miscibility between LC materials and polymer network during the polymerization induced phase separation process, that can be regarded as the same effect of increasing curing temperature. This result is totally consistent with another study of ours on normal mode PDLC [5].

Figure 2 gives a summary of the response time measurement of the R-PNLC films cured at different temperatures. Figure 2(c) shows the applied voltage V10 when measuring the response characteristics of each R-PNLC cell. The R-PNLC cells show a very short t_{Rise} from sub-msec to several msec range because of their high operating voltages as shown in Figure 2(c). As can be seen from Figure 2(a,b), both t_{Rise} and t_{Fall} get faster when curing at lower temperature. When replacing a part of RMs with UVC-NPs, the response time gets slower significantly. Here it should be mentioned that the effect that incorporation of UVC-NPs can be regarded as temperature increase also emerges in the response time measurement. A systematic shift of t_{Rise} , t_{Fall} and V10 is observed when comparing the data of the R-PNLC containing UVC-NPs to that of conventional R-PNLC without NPs. This behavior can be ascribed to the change in the mesh size of polymer network as is the same as V-T curve because the response time characteristics is also affected by spatial structure of polymer network according to the bundle-fibril model of the R-PNLC [7].

Finally, the influence of intensity of UV irradiation on the V-T curve of the R-PNLC (without UVC-NPs) is presented in Figure 3. The curing temperature is -10°C and $+30^{\circ}\text{C}$. When the cell is cured under the 'strong and short' condition of UV irradiation, a small shift of V-T curve to upper voltage region is observed irrespective of curing temperature. It is the same tendency of Ma and Yang's result [7], while upper shift is more significant in their study. The alternation in the electro-optical properties by changing UV irradiation is related the activation of photoinitiators. Fewer activated photoinitiators under lower UV intensity help the polymer bundle of RMs growing largely as discussed in Ref. [7]. Therefore, the formed rough network leads to low operating voltage and large response time. In the present study, however, the effect of curing temperature is dominant, and the UV intensity has a little impact on the electro-optical characteristics of the R-PNLCs.

It is known that there are two merits of low-temperature curing of the R-PNLC according to the existing literature [6,7]. One is the realization of highly transparent state (T_{max}) at no bias voltage, because the polymer network can be formed without disturbing the initial LC alignment. The other is faster response under external voltage application due to the fine mesh size of polymer network. Meanwhile, however, the operating voltage becomes too much high. Thus, it is important to find the best

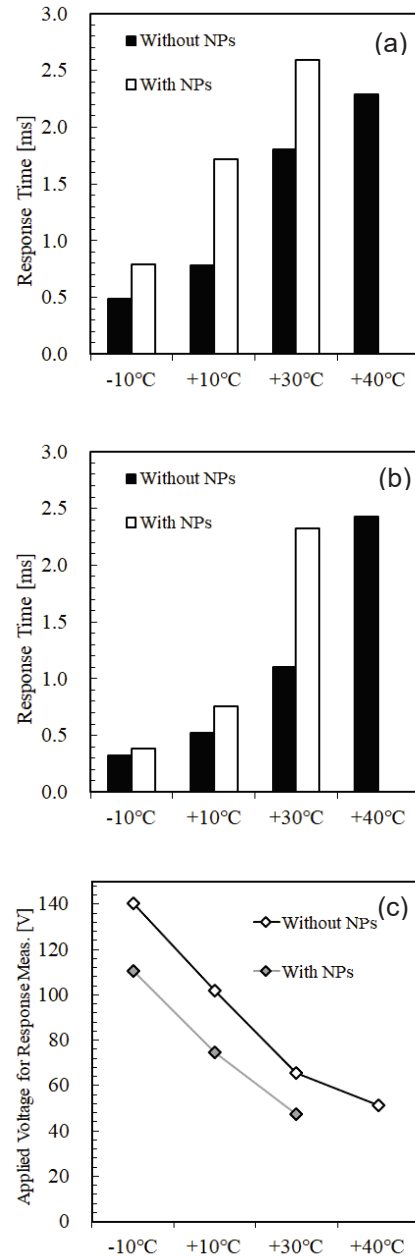


Figure 2 Total comparison of response time (a,b) and threshold voltage V10 (c) of the R-PNLC with and without UVC-NPs. (a) t_{Rise} , (b) t_{Fall} , and (c) V10 as an applied voltage for response time measurement. UV irradiation condition is 'weak and long (5 mW/cm² for 60 min)'.

compromise of electro-optical performance of the R-PNLC. We found here that the incorporation of UVC-NPs largely affects the mesh size of formed polymer network in a similar way of increasing the curing temperature. From the viewpoint of curing condition, incorporation of UVC-NPs can be regarded as an alternative method to control the curing temperature.

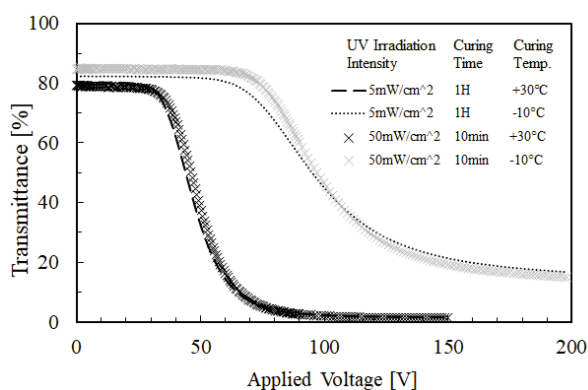


Figure 3 Comparison of applied voltage-dependent transmittance of the reverse mode PNLC films cured at different curing temperatures and UV irradiation conditions.

4 CONCLUSION

In this study, we investigate the effect of curing condition on the electro-optical properties of the R-PNLC cells with and without incorporation of UVC-NPs. It turns out that the curing temperature is the main influential factor for determining the V-T behavior and response times, as already reported in Refs. [6,7]. The novel feature we found is that the incorporation of UVC-NPs to the R-PNLC has almost the same effect as increasing the curing temperature by around +10°C. In the conventional R-PNLC, the curing temperature affects the viscosity of materials, diffusional properties of monomers, and fluctuation of LC director, and thereby the morphology of polymer network formed inside the cell. UVC-NPs give an alternative way to modify the formation of polymer network in a R-PNLC device. We believe that the incorporation of UVC-NPs may enlarge the range of choice of materials for realizing a better R-PNLC based light controlling device.

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