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Effect of SiO₂ nanoparticle doping on electro-optical properties of polymer dispersed liquid crystal lens for smart electronic glasses

Eunju Kim¹, Yang Liu¹, Sung-Jei Hong^{2*} and Jeong In Han^{1*}

Abstract

In this paper, SiO₂ nanoparticle doped polymer dispersed liquid crystal (PDLC) lenses were made from a mixture of prepolymer, E7 liquid crystal and SiO₂ nanoparticles by the polymerization induced phase separation (PIPS) process for smart electronic glasses with auto-shading and auto-focusing functions. Electro-optical properties of doped and undoped samples including transmittance, driving voltage, contrast ratio and slope of the linear region of the transmittance-voltage were measured, compared and analyzed. Driving voltage of SiO₂ nanoparticle doped PDLC lenses moderately improved. But the slope of linear region, response time and contrast ratio deteriorated, especially the latter two. It can be assumed that these doping effects were due to the mechanistic change from liquid-gel separation to liquid-liquid separation by the fast heterogeneous nucleation rate caused by the increased nucleation at the surface of SiO₂ nanoparticles. The marked deteriorations of falling response time and contrast ratio were due to well defined liquid crystal molecules in LC droplets, which induced slow and imperfect random rearrangement of LC molecules at the off state.

Keywords: Polymer dispersed liquid crystal; SiO₂ nanoparticles; PDLC; Electronic glasses; Auto-shading; Auto-focusing

1 Background

Recent studies of smart electronic glasses (E-glasses) with various functions have been reported [1-7]. E-glasses with auto-shading and auto-focusing functions have been developed for shortsighted people and applications. Auto-shading is the ability of the e-glasses to automatically increase or decrease the amount of external light, through automatic opening and closing of the aperture when the external light is strong and weak, respectively. Auto-focusing refers to the automatic modulation of the focal length with the distance from the subject. Using polymer dispersed liquid crystal (PDLC) lenses, we have studied smart electronic glasses with auto-shading and auto-focusing functions [1,2]. The electro-optical properties can be further improved. To enhance electro-optical properties of PDLC lenses, such

as driving voltage, slope, response time and contrast ratio, one of many approaches is to induce the heterogeneous nucleation for the phase separation to solid polymer and LC droplets. Through the addition of very small sized particles, initiation of heterogeneous nucleation at the surface of nano-sized particles can be expected.

Presently, doping of SiO₂ nanoparticles was done during the fabrication of PDLC lenses. These lenses were fabricated and evaluated for use in auto-shading and/or auto-focusing e-glasses. Electro-optical properties of the undoped and doped PDLC devices including transmittance, driving voltage, slope of linear region, contrast ratio, and rising and falling response time were measured to assess the potential application to auto-shading and/or auto-focusing e-glasses. Mechanisms of heterogeneous nucleation and phase separation are proposed to explain the behaviors of the electro-optical properties.

* Correspondence: hanji@dongguk.edu; hongsj@kети.re.kr

¹Department of Chemical and Biochemical Engineering, Dongguk University-SEOUL, Seoul 100-715, Korea

²Display Components and Materials Research Center, Korea Electronics Technology Institute, Gyeonggi 463-816, Korea

2 Methods

The fabrication process of PDLC lens process has been previously summarized [1-3]. The average size and purity of SiO₂ nanoparticles obtained from Sigma Aldrich were 10–20 nm and 99.95%, respectively. The concentrations of the doped SiO₂ nanoparticles varied from 0–2.0% in weight in 0.5% increments. For PDLC lens fabrication, NOA 65 (Norland Products) and nematic LC E7 were used as the pre-polymer and nematic LC mixture, respectively. NOA 65 is a mixture of trimethylpropane diallyl ether, trimethylpropanetrithiol, isophorone diisocyanate ester and a benzophenone photoinitiator [8,9], which makes it an ultraviolet (UV) curable optical adhesive. Liquid crystal E7 consists of 4-pentyl-4'-cyanobiphenyl (5CB), 4-heptyl-4'-cyanobiphenyl (7CB), 4-octyloxy-4'-cyanobiphenyl (8OCB), and 4-pentyl-4'-cyanoterphenyl (5CT) [9,10]. E7 was synthesized by homogeneous mixing of 51 wt% of 5CB, 25 wt% of 7CB, 16 wt% of 8OCB and 8 wt% of 5CT at 75°C, which is much higher than the nematic-to-isotropic transition temperature of 61.0°C. The mixing ratio of NOA 65 and E7 was 40% NOA 65 to 60% E7 LC. PDLC devices were made by sandwiching the NOA 65 and E7 mixture between two 30 × 40 mm² indium tin oxide-coated glass plates with the cell gap maintained at 30 μm using poly (methyl) methacrylate (PMMA) polymer ball spacers having a uniform diameter. For PDLC lenses, photopolymerization of the mixture of NOA 65 prepolymer and E7 LC was induced using an UV lamp. UV curing intensity was fixed as 580 μW/cm² at 365 nm. The samples were not cooled on water cooling plate during UV curing [3].

Doped and undoped PDLC surfaces were observed by optical microscopy and scanning electron microscopy (SEM). The electro-optical property of the PDLC device was measured as described previously [1-3]. A He-Ne laser with a wavelength of 620 nm and a photodetector were used as the light source and detector, respectively. A digital oscilloscope, function generator, power amplifier and digital multimeter were used for the measurements. Transmittance changes with the voltage applied to the PDLC devices, falling and rising response times and contrast ratio were measured. Slopes of the characteristic transmittance-voltage curves with the applied voltage of the PDLC lens were obtained for versions of smart e-glasses including active shutter glasses for three-dimensional high definition television, and smart glasses with auto-shading and/or auto-focusing functions. Rising and falling response times were measured at an applied voltage of 40 V using a digital oscilloscope and function generator. Contrast ratios were derived by comparing the light transmittance of the on-state with that of the off-state of PDLC lenses.

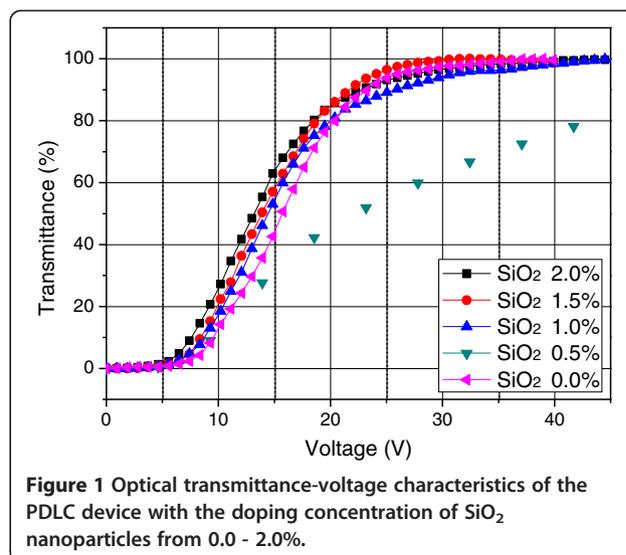
3 Results and discussion

With the concentration of SiO₂ nanoparticles ranging from 0–2.0% weight in 0.5% increments, the optical

transmittance - applied voltage curves of the PDLC devices for 40% NOA 65 - 60% E7 LC cured by UV intensity of 580 μW/cm² (Figure 1). The addition of 0% SiO₂ nanoparticles was equivalent to the PDLC lens prepared from the mixture of 40% NOA 65 - 60% E7 LC without the addition of SiO₂ nanoparticles [1,2].

The optical transmittance-voltage curves of the PDLC polymer lens were well-defined S-shaped curves (Figure 1), except for 0.5% SiO₂ nanoparticles. The driving voltage moderately shifted from 25.7 V to the lower voltage of 22.8 V with the increase of SiO₂ nanoparticle concentration from 1.0% to 2.0%. The driving voltage for the device with 0.5% SiO₂ nanoparticles displayed a voltage of 56.4 V. This sample was not good for the smart electronic glasses because it was unsaturated at the higher voltage, and thus yielded an incomplete optical transmittance-applied voltage curve. When no SiO₂ nanoparticles were added, the driving voltage was 23.3 V. Doping of SiO₂ nanoparticles into PDLC lenses moderately reduced the driving voltage to 22.8 V.

In the gel formation process, SiO₂ nanoparticles may function as heterogeneous nucleation sites (i.e., heterogeneous nuclei). As the amount of SiO₂ nanoparticles increased, the heterogeneous nucleation sites for the solidification of prepolymer would correspondingly increase. This increase of heterogeneous nuclei for gel formation of the prepolymer would accelerate polymerization. Faster polymerization seems to induce gel formation from liquid-liquid separation to liquid-gel separation, similar to the cooling that occurs during UV curing [2], resulting in the reduction of the driving voltage as the concentration of SiO₂ nanoparticles is increased. However, the driving voltage of 22.8 V for samples with 2.0% SiO₂ nanoparticles was slightly lower than the driving voltage of 23.3 V for PDLC lens without SiO₂ nanoparticles. This indicates that



the homogenous nucleation rate without SiO₂ nanoparticles in PDLC lens is almost similar to heterogeneous nucleation rate of the sample doped with 2.0% SiO₂ nanoparticles.

These results supported the view that PDLC lenses undoped and doped with SiO₂ nanoparticles differ in phase separation mechanisms. While homogeneous nucleation is the dominant mechanism for phase separation to the solid polymer and LC droplets for the undoped device, heterogeneous nucleation is dominant for doped samples.

For PDLC device with 0.5% SiO₂ nanoparticles, the amount of SiO₂ nanoparticles was too small to form pre-polymer gel by heterogeneous nucleation at the surface of SiO₂ nanoparticles. Thus, its optical transmittance-applied voltage curve was immature and exhibited no saturation region at higher voltage.

The slopes of linear region of the optical transmittance curves with the applied voltage with the concentration of SiO₂ nanoparticles are plotted in Figure 2. The slopes ranged from 9.24%/V for the undoped device to 5.85%/V for samples of 1.5% SiO₂ nanoparticles, which was the minimum value. The change of the slope with SiO₂ nanoparticles did not improve, but rather deteriorated. The slope was negatively affected by the doping of SiO₂ nanoparticles. This may have been due to the change of gel formation mechanism from liquid-gel separation to liquid-liquid separation by fast heterogeneous nucleation rate, similar to the cooling effect. For the homogenous nucleation of undoped samples, this mechanism changes from liquid-gel separation to liquid-liquid separation during cooling in the UV curing process. Homogeneous and heterogeneous nucleations with liquid-liquid separation mechanism do not enhance the slope of the linear region, but slightly improve the driving voltage.

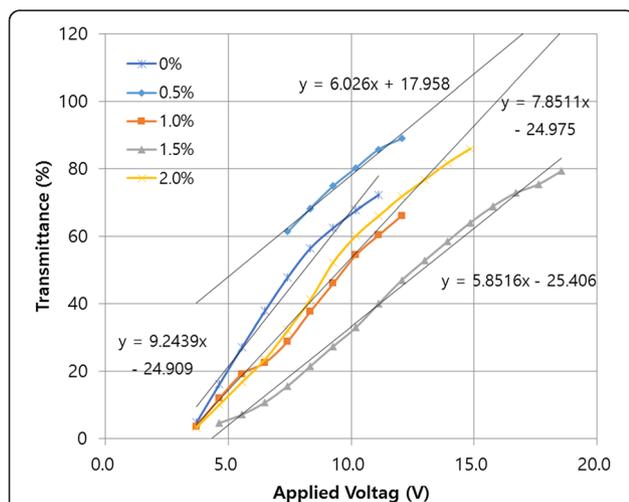


Figure 2 Variations of the slope of the linear region with the doping concentration of SiO₂ nanoparticles from 0.0 - 2.0%.

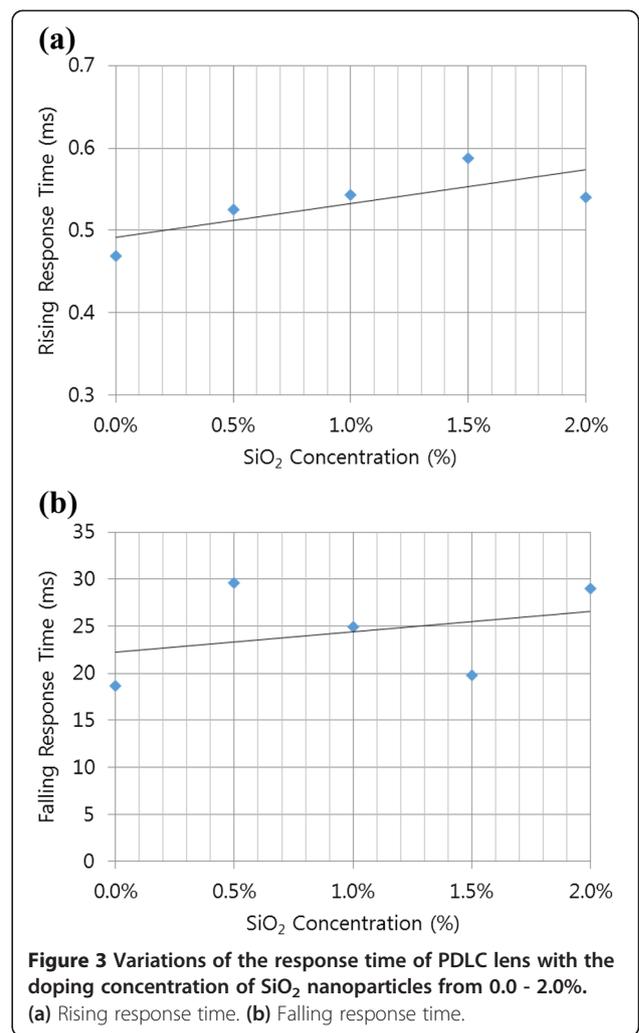


Figure 3 Variations of the response time of PDLC lens with the doping concentration of SiO₂ nanoparticles from 0.0 - 2.0%. (a) Rising response time. (b) Falling response time.

Since the gel formation of pre-polymer was sufficiently rapid, one can assume that the gel point of NOA 65 pre-polymer was reached faster and this early polymerization resulted in intensive liquid-gel separation. Thus, droplets of the heavily doped PDLC device have better molecular arrangement than lightly doped devices, which can be

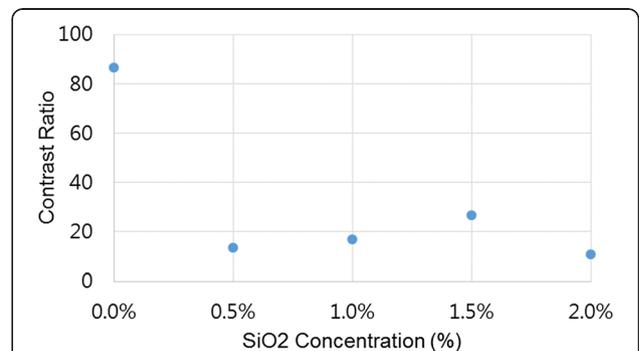


Figure 4 Variations of contrast ratio for the undoped and doped PDLC lens device.

aligned at low voltage [11]. Also, the difference in the initial separation process may explain the improvement of the driving voltage. The initial phase separation from the mixture of NOA 65 and E7 LC into LC droplets surrounded by solid polymer wall changed from a liquid-gel separation to a liquid-liquid separation by heterogeneous nucleation at the surface of SiO₂ nanoparticles. The heavier the PDLC lenses were doped with SiO₂ nanoparticles, the faster was the heterogeneous nucleation rate.

Deterioration of the slope seemed to be caused by well-aligned molecules in the LC droplets. For this alignment to occur, more opposite force and more time are needed to randomly rearrange at the off state (i.e., slow and incomplete return to the original and random arrangement of molecules in LC droplets). Slow and imperfect rearrangement of LC arrangement induced a mild slope (Figure 2).

The variations of rising and falling response time for PDLC samples doped with SiO₂ nanoparticles are depicted in Figure 3. Though the rising response times of all samples were less than 1 ms, the rising response times were moderately increased with the increasing concentration of SiO₂ nanoparticles. The falling response time varied from 18.6 ms to 29.6 ms with 0.0% to 2.0% SiO₂ nanoparticles.

These results also can be explained on the basis of a mechanism change from liquid-gel separation to liquid-liquid separation. Deterioration of falling response time seems to have been caused by well-aligned molecules in LC droplets, as discussed earlier. Well aligned LC molecules require time for random rearrangement at the off state (i.e., slow falling response time). Like the driving voltage and the slope of the linear region, the new mechanism for phase separation – liquid-gel separation – caused a slow response time.

Unlike the cooling effect on contrast ratio of PDLC device, contrast ratio of the doped sample was not improved, but rather was profoundly reduced by doping. With doping from 0.0% to 2.0%, the contrast ratio was drastically reduced from 86.4 to 10.7 (Figure 4). Cooling during UV curing of PDLC devices changed the initial phase separation from liquid-liquid separation to gel-liquid separation. The difference between the cooling and doping effect on the electro-optical properties of PDLC lens was that one is homogeneous nucleation and the other heterogeneous nucleation. In cooled and doped samples, the driving voltage improves and the slope and response times are not enhanced [3]. However, the contrast ratio improves in cooled samples. Presently, the contrast ratio was not enhanced, but rather profoundly deteriorated. This may have been due to the well-aligned molecules in LC droplets as a result of rapid polymerization. Such molecules require more external force, such as applied voltage, to return to the original random arrangement at the off state. Even though the

liquid molecules in LC droplets at the off state appear randomly arranged, the arrangement may actually not be perfectly random, increasing light scattering at the off state. There may be pronounced leakage of light at the off state due to imperfect random arrangement of molecules in LC droplets.

4 Conclusions

In this study, electro-optical properties of polymer dispersed liquid crystal lens were enhanced by doping of SiO₂ nanoparticle. Driving voltage of 22.8 V for the sample with 2.0% SiO₂ nanoparticles was moderately lower than the driving voltage of 23.3 V for PDLC lenses without SiO₂ nanoparticles. The slope of the linear region deteriorated from 9.24%/V for the undoped device to 5.85%/V for the samples of 1.5% SiO₂ nanoparticles, which was the minimum value. If conditions that improve the response time and contrast ratio are optimized, it is thought to be applied to smart electronic glasses.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Jeong-In Han planned and executed the work. Eunju Kim synthesized E7 and evaluated PDLC device. Yang Liu made PDLC devices. Sung-Jei Hong evaluated SiO₂ nanoparticles for E7. All are participated in the characterizations and discussion. All authors read and approved the final manuscript.

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