Photostability of liquid crystals and alignment layers

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Abstract — Photostability of liquid-crystal (LC) materials and surface alignment layers was evaluated using a UV lamp and a blue laser beam. Both organic polyimide (PI) and inorganic silicon-dioxide (SiO_2) alignment layers were studied under nitrogen environment. Two commercial TFT-grade LC mixtures (low-birefringence MLC-9200-000 and high-birefringence TL-216) were used for comparisons. Results indicate that SiO_2 alignment layers are much more robust than PI layers, and low birefringence LCs are more stable than the high-birefringence ones. At the He–Cd laser wavelength ($\lambda = 442 \text{ nm}$), both LC mixtures and SiO_2 alignment layers are hardly damaged. To lengthen the lifetime of an LCD projector, inorganic SiO_2 alignment layers, high-optical-density UV filter, long cutoff-wavelength blue filter, and short-conjugation (low birefringence) LC materials should be considered.

Keywords — Liquid crystals, photostability, lifetime, alignment layers, inorganic SiO_2 , LCD projector.

1 Introduction

Photostability of liquid-crystal (LC) materials and alignment layers play a crucial role in affecting the lifetime of liquid-crystal-display (LCD) devices.^{1–4} In direct-view displays, ultraviolet (UV) light is often used to seal the LC panels. In projection displays using liquid-crystal-on-silicon (LCOS),⁵ the employed arc lamp is relatively bright. Although a cold mirror and a hot mirror are used to filter out the unwanted UV and infrared contents of the lamp, residual UV light could still penetrate into the LC panels and cause performance degradation. Even if the UV contents are completely filtered out, the blue wavelength might still be harmful to the LCD panels. These high-energy photons could cause gradual degradation of the organic alignment layers and the LC molecules. Once the LC medium is decomposed or the alignment layers deteriorated, the pretilt angle is changed and the consequent electro-optic effects are altered.⁶

In this paper, we report the photostability of LC alignment layers and LC materials in the UV and blue wavelengths. Regarding the alignment layers stability, we studied the buffed polyimide (PI) and sputtered inorganic silicon-dioxide (SiO_2) alignment layers under nitrogen environment. On the LC-material stability studies, we selected two Merck LC mixtures: TL-216 ($\Delta n = 0.20$) and MLC-9200-000 ($\Delta n = 0.08$). A high birefringence LC mixture, such as TL-216, enables a thinner cell gap to be used. The advantages are twofold: (1) faster response time and (2) weaker fringing-field effect. For instance, the Philips color-sequential LCOS projector⁷ uses a $\sim 1\text{-}\mu\text{m}$ cell gap in order to achieve fast response time and minimize the fringing-field effect. On the other hand, a low-birefringence LC mixture, such as MLC-9200-000, is commonly used for three-panel LCOS projectors.

2 UV stability of LC alignment layers

The Hamamatsu UV light was delivered to the sample through a fiber bundle and collimated by a lens. The output light passed through a narrow-band interference filter centered at $\lambda \sim 365 \text{ nm}$. The light intensity at the sample position was measured to be $I \sim 350 \text{ mW/cm}^2$. Beside the UV stability, we also studied the material stability of TL-216 in SiO_2 cell at $\lambda = 442 \text{ nm}$. A He–Cd laser ($\lambda = 442 \text{ nm}$) was used as the light source to illuminate the LC cell directly. The light intensity at the sample position was controlled to be 20 W/cm^2 .

Three kinds of homogeneous LC cells were studied: two with commercial PI layers (PI-A and PI-B) and one with a SiO_2 alignment layer. These PI cells were purchased from different vendors in order to compare the PI performances.

FIGURE 1 — Transmittance of PI-A (red line), SiO_2 (blue line), PI-B (green line), and filter (gray line).

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FIGURE 2 — (a) PI-B and (b) SiO₂ alignment cells after 5 (left), 10 (middle), and 15 (right) hours of UV exposures.

Figure 1 shows the measured UV absorption spectra of these cells. Here, red, green, and blue lines represent PI-A, PI-B, and SiO₂ cells, respectively. The transmittance of the UV filter was included as reference. The transmittance of each cell at $\lambda \sim 365$ nm has the following order: PI-A > PI-B > SiO₂. In principle, SiO₂ alignment layers are highly transparent from $\lambda > 200$ nm. The absorption of the cells is mainly from the indium-tin-oxide (ITO) electrode. Different cells may have slightly different ITO thickness. As a result, their transmission in the UV region is somewhat different.

In order to compare the UV stability of LC alignment layers, the test cells were covered with a black paper and divided into two areas. The UV light passes through the center of the cell only. These empty cells were illuminated under nitrogen environment. At each stage, we inspected the cell by filling the cell with 5CB (4-*n*-pentyl-4'-cyano-biphenyl) LC. We observed the cells on a light table between crossed polarizers after 5, 10, and 15 hours of UV illumination. Results are shown in Figs. 2(a) and 2(b). Figures 2(a) and 2(b) show the photos of PI-B and SiO₂ cells, respectively. The PI-A has similar results as PI-B.

FIGURE 3 — Photos of PI-B cells after (a) 10 and (b) 15 hours of UV exposure. Photos were taken under crossed-polarizing microscope. A 5 $\times$ magnification objective lens was used.

The left, middle, and right photographs of each figure represent the cells after 5, 10, and 15 hours of UV exposure, respectively. The first and second rows of each figure show the photos when the cell rubbing direction is at 0° and 45° with respect to the polarizer, respectively. From Fig. 2(a), both PI alignment layers are damaged within 10 hours and the degradation accumulates as the UV dosage increases. Because of the alignment layer degradation, the pretilt angle increases so that light leaks through the crossed polarizers. However, the SiO₂ alignment layer [Fig. 2(b)] could withstand the UV light for more than 15 hours.

In order to see the degradation of PI alignment layer clearly, we also inspected the PI-B cell under a polarizing optical microscope. The cell rubbing direction was set parallel to the polarizer, and photos were taken after 10 and 15 hours of UV exposure. Results are shown in Figs. 3(a) and 3(b). Many lines whose axes are perpendicular to the rubbing direction appear within the illumination area. These crossed lines imply that the rubbing direction has been disturbed. As a result, the LC alignment is degraded. Figure 4 shows the photo of the SiO₂ cell under microscope (magnification, 5 $\times$) after 15 hours of UV exposure. The SiO₂ align-

FIGURE 4 — Photograph of the SiO₂ cell after 15 hours of UV exposure. The dark circle shows the edge of the illumination area. Above this line is the illumination area.

ment layers maintain excellent uniformity across the whole cell.

3 UV stability of LC mixtures

To examine the UV effects on LC mixtures, two commercial TFT-grade LC mixtures were investigated. They are TL-216 ($\Delta n = 0.20$ at $\lambda = 633$ nm and $T = 23^\circ\text{C}$) and MLC-9200-000 ($\Delta n = 0.08$). If the LC sample was exposed to the air,⁸ then oxidations would occur during UV exposure. In order to avoid the oxidation and humidity effects, the LC mixture was vacuum-filled into the cell. The UV illumination took place in a nitrogen chamber. We inspected the cell after each UV illumination and measured its voltage-dependent

FIGURE 5 — UV absorption spectra of TL-216 (red line), MLC-9200-000 (blue line), and UV filter (gray lines). LC weight % = 4×10^{-3} % in cyclohexane and cuvette gap $d = 1$ cm.

transmittance, birefringence,⁹ and visco-elastic coefficient.¹⁰ All the measurements were performed using a He-Ne laser ($\lambda = 633$ nm) at $T = 23^\circ\text{C}$.

3.1 UV absorption spectra of LC mixtures

Two mechanisms are responsible for the observed UV degradation: structural effect and absorption effect.¹¹ The structural effect is particularly apparent for the carbon-carbon double- and triple-bond linking groups. The LC mixtures we studied: TL-216 and MLC-9200-000 all consist of cyclohexane, phenyl, and biphenyl rings. These rings are quite stable. Thus, the absorption effect is the dominant degradation mechanism. We measured the UV absorption spectra of TL-216 (red line) and MLC-9200-000 (blue line) in a cyclohexane solvent. The weight percentage of LC mixture is 4×10^{-3} % and the cuvette cell gap is 1 cm. Results are plotted in Fig. 5. The edge of transmittance of the UV filter (gray line) is also included as a reference.

The two major $\pi \rightarrow \pi^*$ transitions^{12,13} of TL-216 appeared at $\lambda_1 \sim 213$ nm and $\lambda_2 \sim 255$ nm and the tail ends at ~ 318 nm. The $\pi \rightarrow \pi^*$ transitions of MLC-9200-000 appear at $\lambda_1 \sim 200$ nm and $\lambda_2 \sim 255$ nm and the tail ends at ~ 300 nm. The similar λ_2 absorption peak implies that these two mixtures contain a common compound (maybe fluorinated biphenyl), but at different percentages.

3.2 UV stability of MLC-9200-000

We evaluated each cell's stability by characterizing its voltage-dependent transmittance (V - T) curves. Figures 6(a) to 6(c) represent the V - T curves of MLC-9200-000 in the SiO₂, PI-A and PI-B cells, respectively. From Fig. 6(a), after 144 hours of UV exposure, the V - T curve of MLC-9200-000 in the SiO₂ cell remains nearly the same as that of fresh sample. This is not surprising because MLC-9200-000 is a low birefringence LC mixture; its absorption tail is shorter than $\lambda = 365$ nm. On the other hand, MLC-9200-000 in PI cells has a relatively short lifetime. The V - T curves of MLC-9200-000 in both PI cells start to change after 60 hours. The PI-B cell suffers an even more serious degradation. Once degradation occurs, the effective Δn is decreased and threshold behavior smeared because of the increased pretilt angle.¹¹

Comparing the lifetime of MLC-9200-000 in SiO₂ and PI cells, we found that the PI alignment layer is less UV resistant than MLC-9200-000. Thus, it is PI layers rather than LC that limits the device lifetime. Of course, some LCs may be less stable than PI alignment layers. We have to consider the lifetime of both alignment layers and LC mixtures when evaluating the UV stability of LC devices. Whichever has the least stability determines the overall device lifetime.

From the V - T curve, we calculated the LC birefringence after each UV illumination. Results are shown in Fig. 7. Here, the open squares, circles, and triangles represent the birefringence of MLC-9200-000 in SiO₂, PI-A, and PI-B

FIGURE 6 — The voltage-dependent transmittance of a (a) SiO_2 , (b) PI-A, and (c) PI-B alignment cell with MLC-9200-000 before (red line) and after (blue line) UV exposure. The UV intensity is 350 mW/cm^2 .

cells, respectively. The birefringence of MLC-9200-000 in the SiO_2 cell remains the same after 144 hours of UV exposure. On the other hand, the birefringence of MLC-9200-000 in PI-B after 60 hours of UV exposure is decreased to

FIGURE 7 — UV exposure-time-dependent birefringence of MLC-9200-000 and TL-216 in SiO_2 and PI cells. Open and filled symbols denote MLC-9200-000 and TL-216, respectively. Light source: $\lambda = 365 \text{ nm}$, $I = 350 \text{ mW/cm}^2$.

0.07. Compared to the fresh sample, this birefringence is reduced by 12.5%. PI-A cell has a similar result to PI-B cell.

We also investigated how UV-induced degradation affects the visco-elastic coefficient of the LC mixture. Results are plotted in Fig. 8. Here, the open squares, circles, and triangles represent the γ_1/K_{11} of MLC-9200-000 in SiO_2 , PI-A, and PI-B cells, respectively. The visco-elastic coefficient of MLC-9200-000 in the SiO_2 cell remains basically unchanged after 144 hours of UV illumination. On the contrary, in both PI cells, it begins to increase after 20 hours of UV illumination. The noticeable increase in the visco-

FIGURE 8 — The measured visco-elastic coefficient of MLC-9200-000 and TL-216 in SiO_2 and PI cells. Open and filled symbols represent data for MLC-9200-000 and TL-216, respectively. Light source: $\lambda = 365 \text{ nm}$, $I = 350 \text{ mW/cm}^2$.

FIGURE 9 — The voltage-dependent transmittance of a (a) SiO₂, (b) PI-A, and (c) PI-B alignment cell with TL-216 before (red line) and after (blue line) UV exposure. The UV intensity is 350 mW/cm².

elastic coefficient implies that the LC mixture has been seriously damaged by the UV light.

FIGURE 10 — Microscope photographs of PI-A cells filled with TL-216 after (a) 12 hours and (b) 16 hours of UV exposures. Photos (a) and (b) were taken when the cell rubbing direction was at 0° and 45° with respect to the polarizer, respectively. The polarizers are crossed.

3.3 UV stability of TL-216

Figures 9(a)–9(c) show the V - T curves of TL-216 in the SiO₂, PI-A, and PI-B cells, respectively. In all of the PI and SiO₂ cells, the V - T curves of illuminated samples were different from the fresh sample. Three common phenomena are observed as degradation gradually takes place: (1) the effective Δn is decreased, (2) the threshold voltage is smeared and decreased, and (3) the light scattering is gradually intensified. TL-216 has a longer lifetime in the SiO₂ cell than in the PI cells. The lifetime of TL-216 in the SiO₂ cell and PI cell are no longer than 96 and 18 hours, respectively. The shorter lifetime of TL-216 in the PI cell comes from the unstable PI alignment layer.

It is difficult to obtain accurate V - T curves of TL-216 in the SiO₂ and PI cells when the cells have been illuminated continually for more than 96 or 18 hours, respectively, because defects appear at the illuminated area and the cells become non-uniform. Figure 10 shows two microscope photos of the PI-A cell filled with TL-216. We heated the cell to above clearing temperature for few minutes and let it cool

FIGURE 11 — The measured birefringence of TL-216 in SiO₂ cell. Light source: He–Cd laser at $\lambda = 442$ nm and $I = 20$ W/cm².

down to room temperature on a polarizing optical microscope. This defected area has a non-uniform color, containing a bubble-like shape at the center of the cell. The bubble size shrinks very quickly when the temperature decreases. Meanwhile, the color inside the bubble changes continuously. From our previous studies,⁸ the clearing point and birefringence would decrease when the LC molecules were damaged by the UV light. Therefore, the TL-216 mixture at the center of the cell is damaged because it exhibits a different clearing temperature and birefringence from the unexposed area. From this phenomenon, we believed that the TL-216 LC mixture has a lower UV damage threshold than the PI alignment layers. Similar experiments using the inorganic SiO₂ alignment layers also confirm these observations.

The birefringence of TL-216 in the PI and SiO₂ cells were measured at $\lambda = 633$ nm and results are depicted in Fig. 7. The filled squares, circles, and triangles represent the birefringence of TL-216 in SiO₂, PI-A, and PI-B cells, respectively. The birefringence of TL-216 in SiO₂ cell after 96 hours of UV illumination is decreased by 0.01, as compared to the fresh sample. The LC degradation was more serious in PI cell than in SiO₂ cell. TL-216 in PI-A and PI-B has similar results. The birefringence after 18 hours of UV exposure drops by 0.05, which accounts for 75% of the fresh sample. In both PI cells, bubbles formed at the edge of the illumination area after 12 hours of UV exposure.

The LC degradation affects not only birefringence but also visco-elastic coefficient. The results of the visco-elastic coefficient (γ_1/K_{11}) of TL-216 in PI and SiO₂ cells after each UV exposure are also shown in Fig. 8. The filled squares, circles, and triangles represent the visco-elastic coefficient of TL-216 in SiO₂, PI-A, and PI-B cells, respectively. The visco-elastic coefficient of TL-216 in the SiO₂ cell starts to increase after 96 hours of UV illumination. Because of the degradation of the PI alignment layer, the visco-elastic coefficient of TL-216 in both PI cells increases dramatically after 18 hours of UV illumination.

4 Stability of TL-216 under blue light

One can argue that UV components of an arc lamp can be totally truncated by a proper filter. For a full-color LCD projector, red ($\lambda = 650$ nm), green (540 nm), and blue (440 nm) are the three primary colors. The low energy red and green photons are much less harmful than the high-energy blue photons. Thus, the ultimate photostability of a LC cell is determined by the blue light. We also studied the LC material stability at $\lambda = 442$ nm. We vacuum-filled TL-216 in SiO₂ cell and illuminated the test cell by using a He–Cd laser. After every 24 hours of illumination, we monitored the LC birefringence. Results are shown in Fig. 11. From Fig. 11, no sign of degradation of TL-216 in the SiO₂ cell is observed up to 2880 W-hour/cm² of laser irradiation.

5 Discussion

The lifetime of an LC material or alignment layer could be affected by several factors, *e.g.*, molecular structure, wavelength, and exposure intensity. For an LC material/alignment layer at a given wavelength, the degradation mechanism is not a linear function of the employed light intensity.¹⁴ The higher intensity is more harmful than the low intensity even though their total UV dosage (intensity multiplied by exposure time) remains the same. To obtain a realistic result, in principle, we should measure the lifetime at several intensities, fit the data, and extrapolate back to the intensity of the actual LCD projector. However, in our accelerated lifetime study we used a relatively high intensity ($I = 350$ mW/cm²) of UV light ($\lambda = 365$ nm) in order to observe degradation in a reasonable exposure time. Our main objective is to compare the lifetime of different LC materials and alignment layers under the same experimental conditions.

From our experiments, the SiO₂ alignment layer can withstand the longest UV exposure compared with other PI cells. We compared the lifetime of LC mixtures in SiO₂ cells by assuming the SiO₂ alignment layer was stable throughout the whole experiment. The birefringence of LC compounds is highly dependent on the conjugation length; the longer the conjugation length, the longer the absorption wavelength. Although the λ_2 absorption peak of MLC-9200-000 and TL-216 appears at the same wavelength and the absorption tails are far away from the cut-off UV wavelength (365 nm), the lifetime of TL-216 is relatively short. From our previous study,⁸ we learned that the electronic transition wavelength is not the sole factor affecting the material stability. Detailed molecular structure also plays an important role. From the study of UV stability of single LC compounds, we found that the carbon–carbon double bond, triple bond, and cyano terminal group are not very stable. By avoiding these structures, it is possible to create relatively UV stable and reasonably high-birefringence LC mixtures.

Although the inorganic SiO₂ alignment layer is very stable, the sputtering method is more costly because of the need of a vacuum chamber. From our experiment, MLC-

9200-000 is very stable in the SiO₂ cell up to 144 hours of UV exposure. The performance of the PI cells with MLC-9200-000, however, is deteriorated severely after 60 hours of UV exposure. The degradation of the MLC-9200-000 cell is determined by the PI alignment layers. For high-brightness projection displays, we have to choose UV stable LC materials and alignment layers. In the blue laser experiments, both LC materials and alignment layers are quite robust. No sign of degradation is observed within ~3000 W-hour/cm² of continuous irradiation. This implies if we can filter out any residual UV components from the arc lamp, the LCD projector will have a very long lifetime.

6 Conclusion

The UV and blue stability of PI and SiO₂ cells and LC mixtures (MLC-9200-000 and TL-216) were studied. Experimental results show the SiO₂ cells are much more stable than PI cells. The stability of the alignment layer is a critical factor affecting the stability of the entire device. Moreover, the UV stability of LC mixture depends not only on the electronic transition wavelength, but also on the molecular structures. From our study, although the high-birefringence LC mixture is less stable than the low-birefringence mixture under UV exposure, it is quite stable under blue laser ($\lambda = 442$ nm) irradiation. To ensure a long-lasting projection display, not only a longer cutoff-wavelength blue filter but also UV-resistant inorganic or organic alignment layers and LC mixtures should be carefully chosen.

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