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J. N. Jang [a], H. Xu [a], A. B. Davey [a], W. A. Crossland [a], F. Nishida [a], T. Clapp [b] & J. Hannington [b]

[a] Engineering Department, University of Cambridge, Cambridge, UK

[b] Dow Corning Co., Midland, Michigan, USA

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J. N. Jang
H. Xu
A. B. Davey
W. A. Crossland
F. Nishida
Engineering Department, University of Cambridge, Cambridge, UK

T. Clapp
J. Hannington
Dow Corning Co., Midland, Michigan, USA

Smectic layer rotations in ferroelectric liquid crystals (FLC) upon application of electric fields have been observed only in chiral smectic phases and believed to be related to the electroclinic effect. In this article, effects of electric field shape and frequency on smectic layer rotations in siloxane-based FLCs were investigated by applying various kinds of asymmetric ac waveforms for a range of frequencies and temperatures. For a given peak voltage, we have found that the asymmetry was one of the most important parameters and demonstrated that the modified step form showed the best efficiency for smectic layer rotations.

Keywords: asymmetric waveform; electroclinic; ferroelectric LC; layer rotation; smectic layer

INTRODUCTION

Twenty years ago the reorientation of smectic layers under asymmetric electric fields was demonstrated by Patel and Goodby [1,2]. They showed that the layer rotated away from the rubbing axis by an angle equal to the molecular tilt angle in the aligned sample prepared by unidirectional rubbing. In their case, the alignment treatment such

Address correspondence to J. N. Jang, Engineering Department, University of Cambridge, Trumpington St., Cambridge, CB2 1PZ, UK. E-mail: jnj21@eng.cam.ac.uk

as unidirectional rubbing of one substrate surface was required to achieve one way rotation, and the rotation angle was limited to the tilt angle. It was found that the growth rate at a given voltage and at a given frequency changed considerably with temperature and the rate of alignment also depended on the frequency of the applied voltage. At lower frequencies the rate of alignment was slow and there appears to be a cut-off frequency at a certain voltage above which the alignment again proceeded very slowly. Myojin *et al*. [3] reported alignment control of FLC in which these reorientations were irreversible.

Reversible smectic layer rotations with an angle much larger than the tilt angle (up to several hundreds of degrees) were reported in FLCs and antiferroelectric FLCs (AFLCs) by applying an asymmetric AC electric field [4,7∼10]. Ozaki *et al*. [4], showed smectic layer rotation in the antiferroelectric liquid crystal upon application of asymmetric pulses of electric field. Application of an electric field with a sawtooth waveform of more than 10^3 cycles (at 0.455 Hz) induced rotation of the direction of the smectic layer normal by more than 60° away from the initial alignment axis even in the sample without surface treatment for a unidirectional alignment. The layer rotation was found to be continuous and its direction was dependent on the asymmetry of the electric field and the sign of the spontaneous polarization. Nakayama *et al*. [7,8] tried several different shapes of electric fields to clarify the layer rotation and demonstrated that the sawtooth waveform and asymmetric triangular waveform consisting of two slopes with different gradients could cause layer rotation in both a rubbed cell and a nontreated cell. After applying the voltage for a certain time, the rotation rate drastically decreased. This might be attributed to the hindrance of the rotation due to the interaction between rubbing axis and molecules. Indeed, the cell with no surface treatment showed over 180° layer rotation [8]. The rotation angle was much larger than the tilt angle of 17° at the temperature 97°C. They showed that neither symmetric nor asymmetric rectangular waveforms could induce layer rotation. They claimed that the existence of some period of zero or low voltage was necessary for the layer rotation in the rectangular waveforms. In Ref. [9], similar results were shown in the SmC^*_A phase. Dierking *et al*. [10,11] demonstrated that asymmetric rectangular waveforms could induce the layer rotation in the SmC^* phase. Three different kinds of waveforms were: Biased square wave fields (amplitude asymmetry with a DC component); time asymmetric square wave fields (having a DC component); time asymmetric sawtooth fields with DC balance. In contrast to observations by Nakayama *et al*. [8], a smectic layer rotation was observed for both amplitude and time asymmetric square wave fields. They claimed [10]: The layer

rotation time decreases with increasing cell gap; The layer rotation time decreases with increasing amplitude of the AC field at constant bias or asymmetry; The frequency dependence of the layer rotation time is somewhat more complicated. The layer rotation time increases with increasing frequency until it reaches a maximum at approximately 100 Hz, after which the layer rotation time is found to decrease. For frequencies greater than about 2 kHz, the time needed for the layer rotation again strongly increases and diverges for high frequencies. Liquid crystal and surface interactions account for increasing rotation times as the cell gap is reduced. The molecular motion in a non-DC balanced waveform can be interpreted by the electroconvective effects due to ionic motion. For low frequencies, convection favours fast mass transport, leading to short reorientation times. At approximately 100 Hz frequency, ions can no longer follow the electric field and the expected frequency dependence due to the switching process alone is observed. The layer rotation of FLC in the SmC* phase by DC electric field was demonstrated by Nakayama *et al*. [12], but in this case, the FLC material was doped with a small amount of an ionic impurity (0.5 wt% of Tetracyanoquinodimethane). A pure sample without any ionic impurities did not show the layer rotation under DC voltage. In other words, the layer rotation by DC voltage is believed to occur only in the FLC sample in which the resistivity was reduced by doping with ionic impurities. This smectic layer rotation was interpreted as resulting from the electro-hydrodynamic flow due to the ionic impurity. Another type of electric field shape to rotate the layer of SmC* was a simple rectangular pulse wave with a positive or negative polarity [13]. The sample investigated was a FLC mixture consisting of two kinds of chiral dopants and five kinds of host liquid crystals. The pitch of the FLC is so short (about 100 nm) that the cell (2 μm thickness) is not a Surface Stabilized Ferroelectric Liquid Crystal (SSFLC). The layer rotated gradually by applying the simple rectangular pulse wave with a voltage of 20 V of positive polarity until it saturated at 40° (tilt angle 20°). As shown above, layer rotation by a DC biased or simple rectangular waveform occurred only at a very special case (ionic impurity doping and very short pitch FLC mixture) and was interpreted as electro-hydrodynamic in origin. In this article, the effects of electric field shape and frequency on smectic layer rotations in siloxane-based FLCs were investigated by applying various kinds of asymmetric ac waveforms (pulse, sawtooth, etc.) for a range of frequencies and temperatures. Only pure SmC* phase materials which are not from mixtures will be considered. For a given maximum peak voltage, the optimum waveform has been found with which smectic layers can be rotated most efficiently. We believe that

this study can be useful to improve the understanding of the layer rotation mechanisms involved and used to repair certain kinds of damage in liquid crystal devices.

EXPERIMENTS

The materials used in this investigation were siloxane-based ferroelectric liquid crystals from Dow Corning as shown in Figure 1. Phase sequences were Iso – 88.6°C – SmC* – 45°C – Crystal. FLC cells were prepared in our group with a cell gap varying between 1.5 μm and 3.5 μm. The FLC was sandwiched between indium-tin-oxide (ITO) coated glass plates whose surfaces were spin coated with polyimide or nylon 6. Both the spin coated glass surfaces were rubbed antiparallel to each other using a fiber cloth roller. The applied voltage was generated with Hewlett Packard 33120 A function generator and amplified by Hewlett Packard 6827 A Bipolar Power Supply/Amplifier. The layer reorientation process was observed using a Vickers Photoplan polarizing microscope equipped with an Instec HCS302 hot stage controlled by Instec STC200. Single domain bookshelf structures were formed on cooling from the isotropic phase to a temperature below melting point with a symmetric square wave voltage. The amplitude of the alignment field ranged from 5 V/μm to 8 V/μm with frequency 200 Hz–2 kHz depending on the temperature during the cooling process. The single domain was confirmed visually after the alignment process.

The rotation angle was defined as the difference between the smectic layer orientation of the initial state and that obtained after applying voltages. A clockwise direction of the layer rotation was defined as positive when a positive voltage was applied to the upper electrode. Figure 2 shows four different basic waveforms used to rotate the smectic layers. All waveforms were chosen to be DC balanced. The waveforms were: asymmetric sawtooth fields (Fig. 2(a)), extended sawtooth fields (Fig. 2(b)), half-sine fields (Fig. 2(c)), and step fields (Fig. 2(d)).

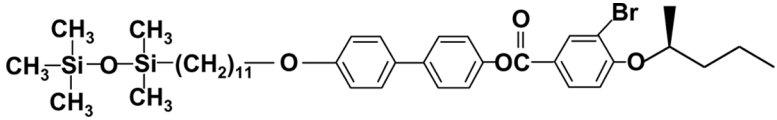

FIGURE 1 BrllSi2 siloxane material structure (Iso–88.6°C–SmC*–45°C–Cr, from Dow Corning).

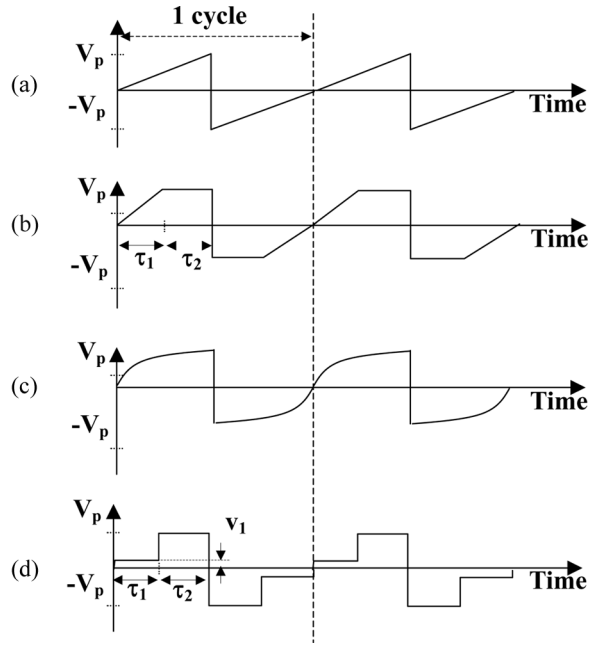

FIGURE 2 Aplied DC balanced electric waveforms: (a) asymmetric sawtooth, (b) extended sawtooth with different time ratio, (c) half sine, and (d) step with different time and voltage ratio.

In the cases of the extended sawtooth and step fields, several different time and field strength ratios of the DC balanced waveforms were investigated while the effects of the time asymmetry ratio in a DC unbalanced square waveform have been shown in Ref. [14]. Layer rotations were *in situ* monitored using the microscope. Field amplitudes up to 18 V/μm at several different frequencies were used. After each measurement, the layer was rotated back to the initial position because the rate of rotation was not linear through the region. Here, the initial position around 18° has no meaning except starting point of measuring layer rotation. The direction of layer normal was parallel to the rubbing direction when it was cooled from the isotropic phase to the chiral smectic C phase with a symmetric square wave voltage.

RESULTS AND DISCUSSIONS

As in Ref. [10], the rate of rotation was found to be dependent on the frequency of the applied voltage as shown in Figure 3. A 50 V peak

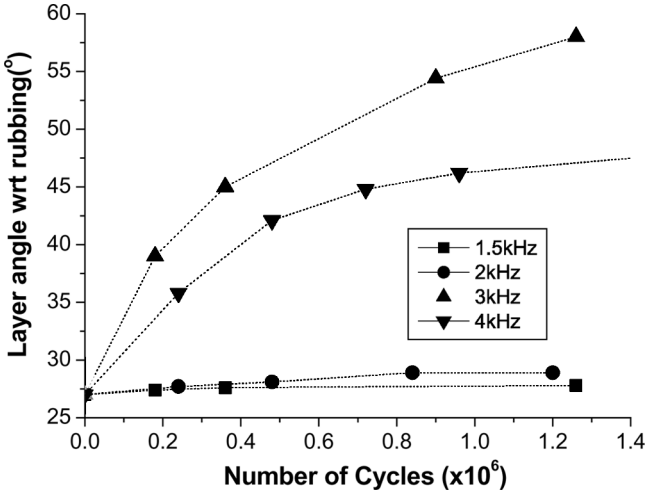

FIGURE 3 Frequency dependence on layer rotation rate at 70°C.

voltage of (1:1) extended sawtooth was applied to a 3.5 μm thickness cell. Among the frequencies, from 1.5 kHz to 4 kHz, 3 kHz was found to be optimum for layer rotation at 70°C. The frequency dependence may be due to the electrohydrodynamic effect [15]. For example, a commercially available compound (4-[(S,S)-2,3 epoxyhexyloxy] phenyl 4-decyloxy-benzoate) showed that the layer rotation time increased with increasing frequency until it reached a maximum at approximately 100 Hz, after which time was found to decrease with frequency and for frequencies greater than about 2 kHz, the time needed for the layer rotation again strongly increased and diverges for high frequencies [10]. In our experiments, for the frequencies less than 1 kHz, the rate of rotation at 70°C became very slow and around a few hundred Hz, it didn't show any measurable layer rotation. At lower temperature, the optimum frequency shifted to the lower value which is believed to be related to the viscosity. At 50°C, 3 kHz frequency didn't show the layer movement for quite a long time. Instead, 1 kHz is much better than 2 kHz and 3 kHz at 50°C. 3 kHz was chosen for all the rest of the experiments at 70°C.

In our experiments, the direction of the layer rotation depended on the asymmetry direction of the electric field, which means that it can be easily rotated back to the original layer position just by changing the electrode polarity of the cells. We also found that a simple symmetric square waveform moved the layers back to the original state quite quickly. It might be because the layer structure having a certain

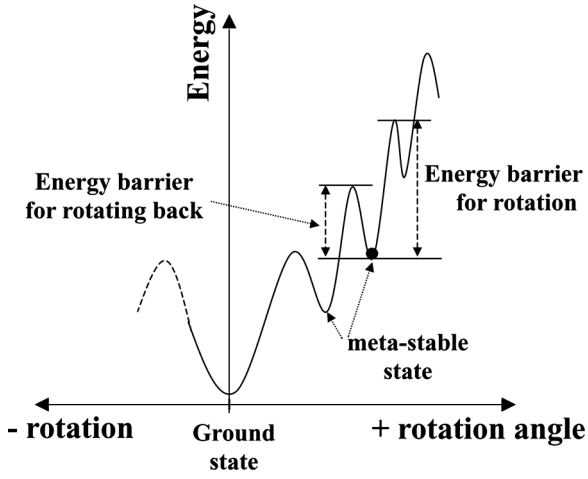

FIGURE 4 Energy level diagram of rotated layers.

angle with the original state is in an unstable or meta-stable energy state and therefore, some amount of energy perturbation makes it possible to overcome the energy barrier and return to the lower energy state more easily as shown in Figure 4.

To investigate the effects of the electric waveforms on the layer rotation, various (τ_1:τ_2) ratios of the extended sawtooth shape were investigated as shown in Figure 5. Peak voltages were set to 50 V for each waveform, which means root mean square (rms) voltage values are different from each other. (1:4) time ratio of extended sawtooth induced around 6 degrees after applying 1.8×10^6 pulses. The layer rotation rate was faster at the starting point and then slowly saturated as time went by. Also the degree of layer rotation was found to be dependent on the (τ_1:τ_2) ratio and it increased as the ratio increased (1:4) < (1:3) < (1:2) < (1:1), even though the rms voltage decreased. An interesting result is that the saturation angle of the layer rotation depends on the voltage shape. Of course, the saturation angle of the layer rotation is dependent on the peak voltage value if the voltage shape is the same [16]. This implies that the longer the voltage-constant-region (τ_2) compared to voltage-varying-region (τ_1), the less efficient the layer rotation. This is coincident with the fact that the symmetric square waveform tends to move the layer back to the original (low energy state) position. These two effects seemed to compensate each other.

As shown in Figure 5, a longer time for the voltage-varying-region (τ_1) is more efficient than the previous 4 cases, but in the order of

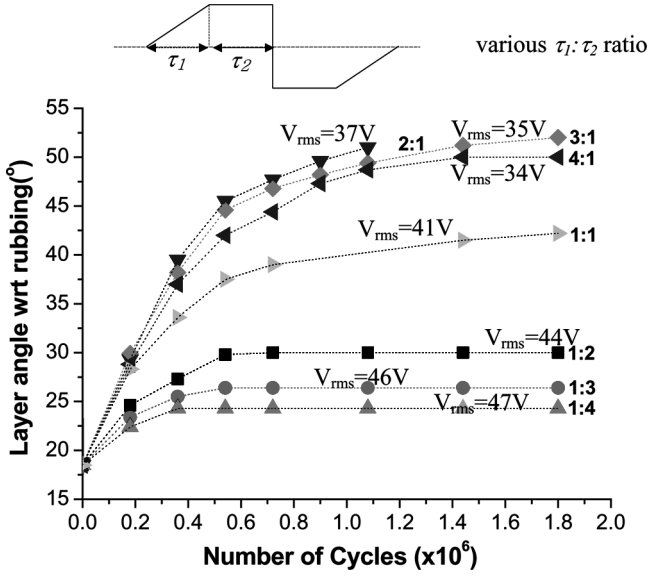

FIGURE 5 Layer rotation on various (τ_1:τ_2) ratios of extended sawtooth waveform.

(1:1) < (4:1) < (3:1) < (2:1) time ratios. The rms voltage may be one of the reasons in this case.

Carlsson *et al*. [17] proposed a theoretical model for layer rotation in the chiral smectic A phase using symmetry arguments and a generalized dynamical theory of the chiral smectic A phase. They applied the model in the specific case with an asymmetric sawtooth electric field. Up until now, the mechanism of the layer rotation in the chiral smectic C phase is not fully understood, but from the experimental results above, we think that the important parameters of the electric field for efficient layer rotation are the frequencies of the driving voltage, asymmetry of the electric waveform, and rms value of the voltage. Effect of the ionic concentration [18] is not covered in our work. It also depends on the sample thickness [10], because of the interaction between the alignment agent and liquid crystal materials. The rate of layer rotation will increase as the cell thickness increases. In a 1.55 μm thickness cell, the rotation angle was saturated to around 40° at 70°C but in a very thin cell (less than 1 μm thickness), it was very hard to rotate even at high temperatures.

From these experimental observations, we tried to find another efficient electric field form using the step voltage shape with different time (τ_1:τ_2) and different voltage (V_1:V_p) ratios as shown in Figure 6.

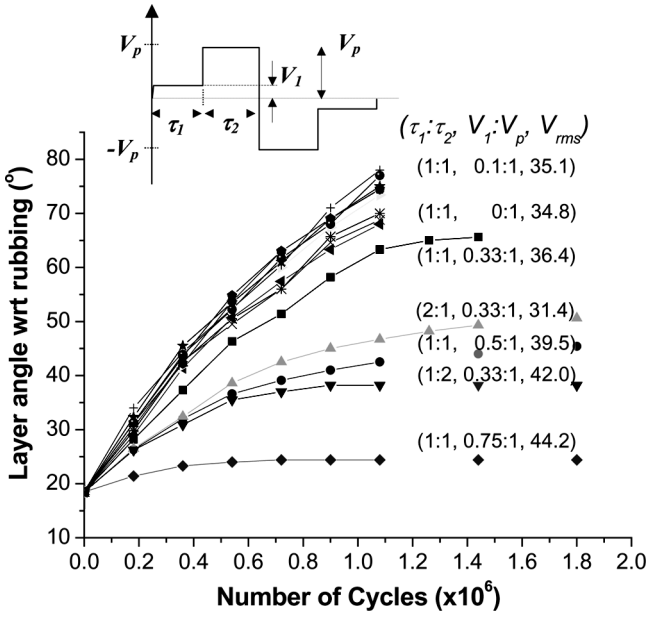

FIGURE 6 Layer rotation on various (τ_1:τ_2), (V_1:V_p) ratios of step voltage waveform.

For example, (0:1) for both time and voltage ratio means symmetric square waveform, and a pulse with (1:1) time and (0.5:1) for voltage ratio consists of 4 steps with the same height. For the same voltage ratio (0.33:1), a (1:1) time ratio shows $15^\circ \sim 25^\circ$ more rotation compared to (2:1) and (1:2) time ratio after applying 1.8×10^6 pulses. We fixed the time ratio as (1:1) and compared several different voltage ratios. (0.75:1) voltage ratio which is very close to a symmetric square wave shows only a few degree rotation. The most efficient group was around ($0.067 \sim 0.125$:1) voltage ratio and showed up to 77° layer rotation which is larger than the tilt angle, even though it is surface stabilized and thus the interaction between the liquid crystal material and the alignment agent is very strong.

The rotation angle measurements were stopped around 77° (Fig. 6), because domains with different layer orientation started to form around the angle, which relaxed the stresses accumulated by molecular rotations and translations. Layer rotation in the mono domain chiral smectic C phase which has no chevron domain structure might require some kind of molecular translations and rotations as in Figure 7. In case of the horizontal chevron domain structure [19],

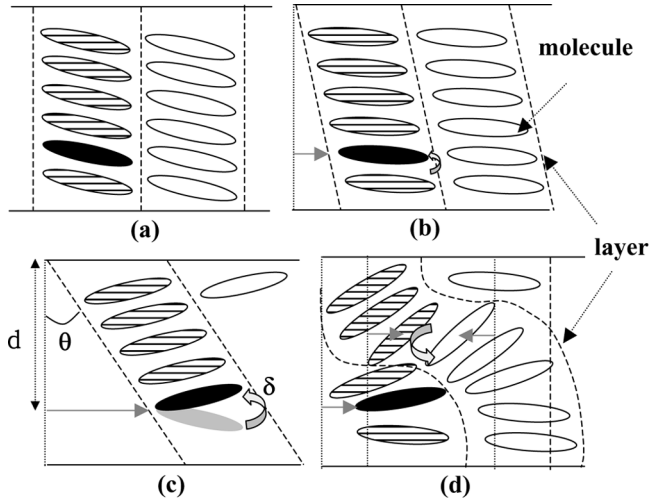

FIGURE 7 Two possible mechanisms of the layer rotation (a)–(b)–(c), and (a)–(d).

the favored domain type under application of a time asymmetric square wave field grows at the expense of the unfavored one until the whole electrode area exhibits a uniform layer inclination with respect to the rubbing direction. At this point the layer reorientation stops due to monostable planar anchoring conditions [11]. We assumed that the tilt angle was conserved during the layer rotation process. Process (a)–(b)–(c) in Figure 7 depicts the case that the molecules (black color) translate the distance of $d \cdot tan\theta$, and rotate an angle of δ, where d is the distance between the molecule and the upper plate and θ is the layer rotation angle. Figure 7(d) looks more complicated but the procedure (a)–(d) sounds more reasonable from the energy point of view of the system. Process (a)–(d) needs molecular rotation and only a small molecular traveling distance. As the layer rotates, the deformation energy by molecular translations and rotations is accumulated until other domains with different layer orientation are formed to release the stresses. It happened around 77° angle in the 3.5 μm cell. If the voltage is kept on for a longer time, domains recombine to a single domain.

Figure 8 shows a series of texture photographs of 3.5 μm cell with layer orientation of 0°, 45°, and 90° with respect to the rubbing direction. As shown in Figure 8(b), the angle of the layer close to the boundary is larger than that of the bulk area.

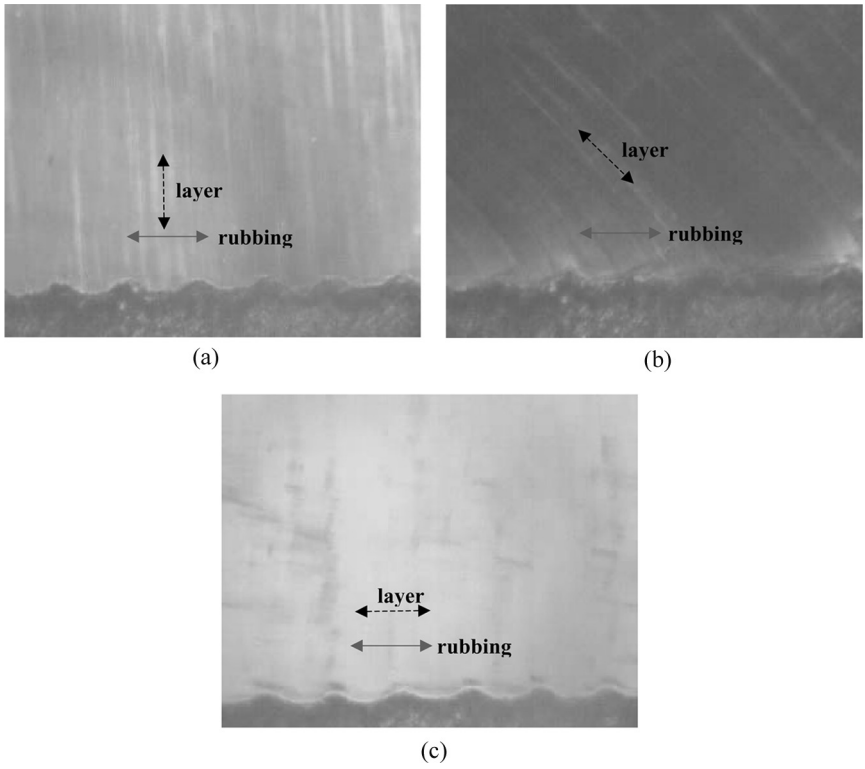

FIGURE 8 Texture of photographs of 3.5 μm cells. (a) layer makes 90° with respect to rubbing direction, (b) 45°, and (c) 0° layer is parallel to rubbing direction.

We compared the efficiency of various kinds of electric field shape in the same measurement conditions in Figure 9. A 1:1 time ratio and a 0.1:1 voltage ratio of the step form was found to be the most efficient way to rotate the layer in our experiments. From an 18° initial layer position, total rotated angle was 51° for the step (1:1, 0.1:1), 23° for the step (1:1, 0.5:1), and 13° for the basic sawtooth waveform after applying 0.9×10^6 pulses. As we mentioned above, one of the main reasons for this is that the rms voltage of the basic sawtooth is quite small compared to the others. But even for the same rms voltages, the rate from the basic sawtooth waveform is quite similar to that of the half sine waveform, which is very small compared to the most efficient group. We also believe that 'degree of asymmetry' does play

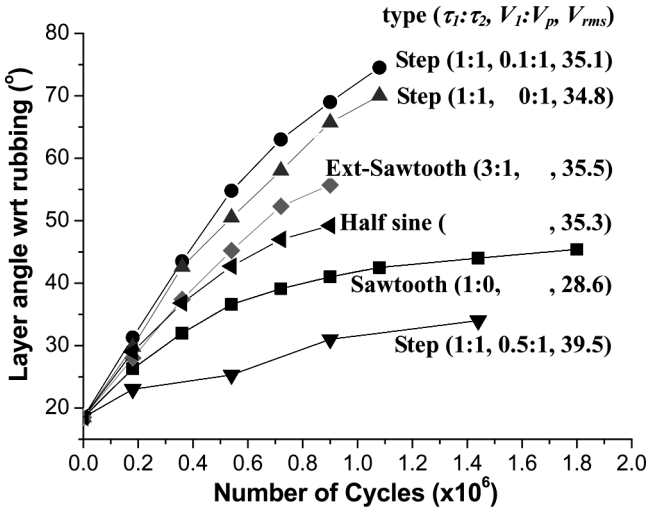

FIGURE 9 Comparison of the efficiency of various kinds of electric field shape in the same measurement conditions.

an important role in efficient layer rotation because of relatively poor rotation of the basic step (1:1, 0.5:1) with the largest rms voltage.

CONCLUSIONS

We have investigated the efficiency of the electric field frequencies and shapes on smectic layer rotation of a siloxane-based FLC material. The optimum frequency was found to be around 3 kHz, which shifted to the lower frequency as temperature decreased. We have demonstrated reversible smectic layer rotation with larger angle than the tilt angle even in very thin cells, which shows relatively strong interactions between the liquid crystal and the alignment layer. We could easily rotate the layers back to the initial position by applying an opposite polarity to the electrodes, or simply applying a symmetric square waveform. The direction of rotation was found to be dependent on the sign of P_s and the direction of asymmetry. For efficient layer rotation, we have shown that the asymmetry was one of the most important parameters and demonstrated that the modified step form showed the best results. The final angle of the layer can be controlled by the ratio of time and voltage of the electric field and thus these can be applied to control the layer angle to obtain bistability in FLC cells.

Layer rotation is a very interesting phenomenon and we hope this study can be useful in understanding the mechanism and for applications like efficient repair of damage in liquid crystal cells.

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