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Characteristics of Electrically Switchable Wettability Surfaces of Liquid Crystal and Polymer Composite Films

Ya-Ping Chiu*, Cheng-Yu Shen, and Yi-Hsin Lin¹

Department of Physics and Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Kaohsiung 804, Taiwan, R.O.C.

¹*Department of Photonics, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.*

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Experimentally, the electrically controllable surface wettability of liquid crystal and polymer composite film has been demonstrated. In the work, scanning probe microscopy has been used to investigate the surface characterization of liquid crystal molecular units at a polymer surface under external voltages applied. The surface morphologies as well as the sensitivity of measurement to surface adhesive force on the nanoscale are determined quantitatively for such unique nano-sized liquid crystals/polymer composite films. The surface wettability of the films deduced from the local adhesion properties demonstrated the electrical control of surface wettability properties, suggesting that the interfacial liquid-crystal molecular alignment of the films with external voltage applied should have significant influence on the modification of the surface characterization of liquid crystals. © 2010 The Japan Society of Applied Physics

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1. Introduction

The performance of modern optical devices, such as liquid crystal displays, electrically tunable privacy windows using polymer-dispersed liquid crystals (PDLC), and tunable focus LC lenses, relies heavily on alignment of LC materials deposited on the polymer surface.^{1–4} Manipulating highly controllable organic crystals can superb in mechanical, electrical, thermal, or optical properties. Therefore, understanding how orientations and alignment of LC materials play a pivotal role among many strategic optical devices requires knowledge of the material interfacial properties under more than one order parameters operating.^{5–8}

Recently, experimentally successfully developed LC and polymer composite films (LCPCF) not only has electrically surface-driven wettability, but also has capability of aligning LC directors.^{9–12} On the surface of LCPCFs, LC directors are anchored in nanometer- or sub micrometer-sized domains surrounded by polymer grains. Under an external in-plane electric field applied, in the orientation of LC molecules can be controlled and then subsequently modifying the interfacial wettability properties of LCPCFs. According to the previous studies, while the LC concentration of the composite film has a weight of 60%, the contact angle of a water droplet on the LC/polymer composite films at room temperature can be changed in the range between 65 and 80° by applying an in-plane electric field.⁶ In addition, since the increases at the transmission of the LCPCF when external voltages are applied to the film, the observed change of surface wettability may originate from the orientation change of the LCs anchored between polymer grains corresponding to different electric fields. Therefore, appropriately tailoring a spatial wetting property, such surfaces of LCPCFs can highly serve as a promising candidate for use in future microfluidic devices, liquid lenses, windshields, and polarizer-free displays. However, it is of considerable practical interest to realize the structurally driven changes of LC molecules at various external applied voltages. Specifically, what alteration of the interfacial wettability properties of LCPCFs under an in-plane electric field applied? Does this alteration from the orientation of the LC molecules correlate to the concentration of LCs?

Quantitatively characterize the voltage-dependent surface wettability of the composite film suggest the possible fundamental mechanism concerning the interaction of the polymer with the LC materials contributing from different LC concentrations or the structurally driven changes in surface adhesion properties, and further support the potential applications in future nanotechnology devices.

Adhesion force, i.e., a physical property arising from the attraction between two dissimilar molecules, is largely determined by the outermost monomolecular layer. In a typical system, adhesiveness can be quantified using the contact angle between two dissimilar molecules. Under these circumstances, a lower contact angle implies a larger adhesive. Generally, a strong adhesion force results in a high degree of wettability. To manipulate spatially changes in the surface properties of the outermost layers, various interesting surface phenomena can be induced, including wettability or a net mass transport of liquids.^{2,3,13} According to the previous studies, LCPCFs with different LC concentrations demonstrate different surface morphologies, depending on the phase separation process.^{11,12} Additionally, the contact angle of a water droplet on the LC/polymer composite films at room temperature can be significantly adjusted by an in-plane electric field, especially for higher LC concentrations, implying their intrinsically distinct surface adhesion properties. Therefore, of priority concern is how the surface properties vary with LC concentrations at various external voltages, as well as the physical mechanisms that govern their properties.

This work attempts to understand the inherent physico-chemical surface wettability properties of LCPCFs by elucidating the voltage-dependent geometrical configuration of the composite films by atomic force microscopy (AFM) at different LC concentrations of the film surfaces. With help of the AFM, we show conclusively that the orientation ability of LC molecules at the surface with various external voltages applied strongly determines the concentration of LC. Typically, electrically switchable wettability surface noticeably varies with increasing the external voltages for LC concentration larger than 60 wt %. Complementary measurements are taken of morphology and LC molecular alignment and correlated with the surface adhesion force of the composite films. Moreover, the dependence of the fundamental physical adhesion properties at various applied

*E-mail address: ypchiu@mail.nsysu.edu.tw

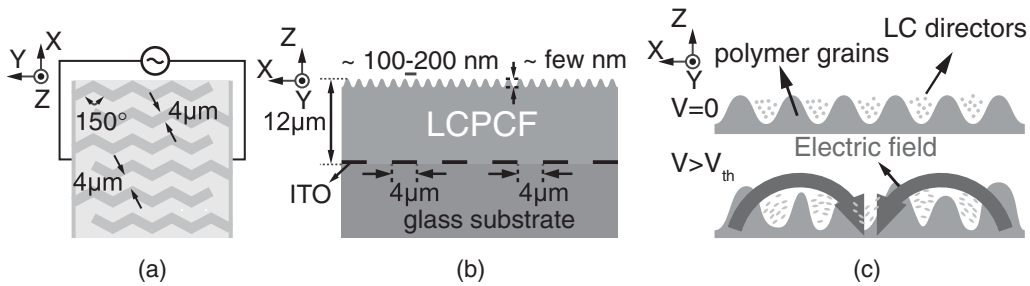


Fig. 1. Schematic illustration of (a) electrode design, surface of the LC/polymer composite film at (b) voltage-off, and (c) voltage-on states.

voltages is quantified, along with the adhesiveness derived to demonstrate the electrically switchable wettability of the LCPCFs.

2. Experimental Methods

The LCPCFs were prepared by mixing a nematic LC mixture E7 (Merck) and a liquid crystalline monomer [4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylene ester, Merck] at various weight ratios. The extent to which the concentration of LC (E7) affects the surface property of the LCPCF was then investigated by using E7–monomer blends with E7 : monomer weight ratios of 39, 49, 59, and 69 wt %. The LC/monomer mixture shows a nematic phase at room temperature. When the LC concentration exceeds 69%, the mixture of E7 and monomer at 70 °C is in the near phase transition state, thus limiting its applications.¹¹⁾

Figures 1(a)–1(c) shows the device structures and operating principles of the electrically switchable wettability system. An empty cell with a gap of 12 μm consists of an LC/polymer composite film on a glass substrate with a patterned indium tin oxide (ITO) electrode and a glass substrate without ITO on top. Furthermore, the bottom electrode stripes have a zigzag-like pattern along the y-axis, as shown in Fig. 1(a). In this work, the distance between working electrode and counter electrode was designed at 4.0 ± 0.5 μm. Additionally, the phase separation originating from the patterned electrodes on the bottom substrate was avoided by exposing only the top substrate of the LC/monomer mixtures to a unpolarized UV light with a homogeneous intensity $I = 10 \text{ mW/cm}^2$ for ~30 min. at 70 °C. Following phase separation and photo-polymerization, the top glass substrate was peeled off by a thermal release process, subsequently forming a solidified and uniaxial LC/polymer composite film with a thickness of 12 μm, as shown in Fig. 1(b). When the top glass substrate was peeled off, the LC molecules remained on the surface of the LC/polymer composite film, leaving the anisotropic topologies with valleys and polymer network structures.¹¹⁾

LCPCF surfaces were probed by AFM (Digital Instruments Dimension 3100) in a tapping mode at room temperature in air. Silicon nitride tips (Nanosensors) with a resonant frequency of 260 kHz were used. The cantilevers were excited just below its resonant frequency. Meanwhile, the apical radius of the tips is ~10 nm. Figure 2 shows the surface morphologies of LCPCFs with different LC concentrations at various voltages applied. Additionally, an attempt was made to study the dependence of liquid surface adhesion

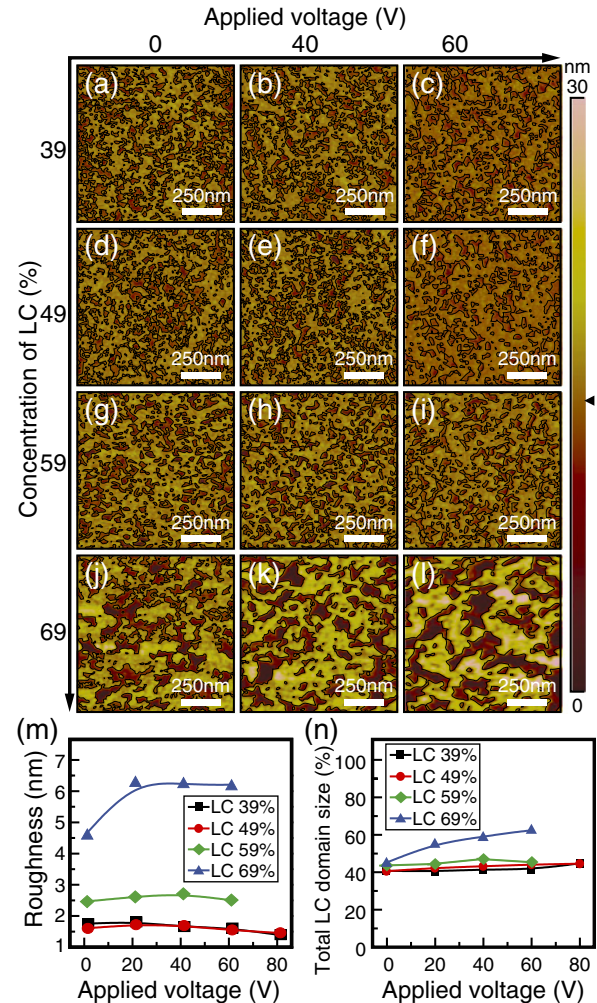


Fig. 2. (Color online) (a–l) AFM topography images of LC concentrations at different voltages applied. Statistical results concerning (m) roughness and (n) total LC domain size of the film surfaces at different LC concentrations.

on the external voltage, and to avoid LC molecules adhered on the tip, every force curve (F) as a function of the displacement of the cantilever (D) relationship was recorded by using a new constant-diameter AFM probe tip in a complete approaching and separating cycle. Meanwhile, to prevent electric fields from disturbing the piezo drive, we used external applied voltages of less than 80 V for higher LC concentrations. In the approaching step [black dotted curve of Fig. 3(a)], the tip approached the surface when it was extended to point a and, then, deflected to point b under the van der Waals force.

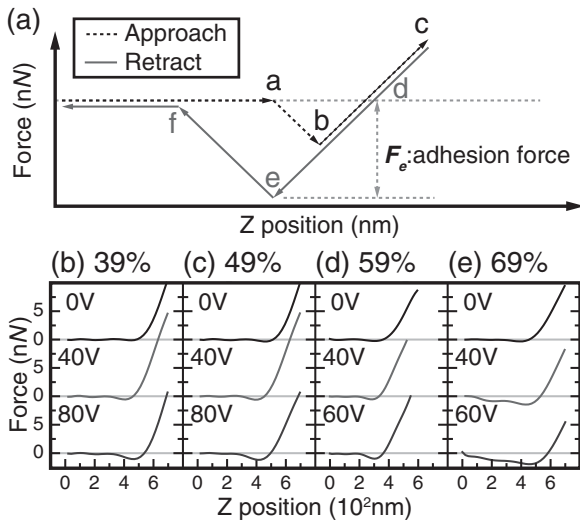


Fig. 3. (a) Idealized F - D curve of composite film. The approach is represented by the black dotted curve, while the departure is represented by the black solid curve. The corresponding F - D curves on the adhesion property measurements for (b) 39, (c) 49, (d) 59, and (e) 69 wt % of the LC concentration at various voltages applied.

Beyond point c , the tip departs from the surface of the composite film shown in the black solid curve in Fig. 3(a). While passing point d prior to removal from the liquid, the tip breaks free from the liquid with a maximum retractive force F_e . The force that corresponds to the position e of the maximum attractive force, which resists the retraction of the probe, is physically defined the value of adhesiveness. Upon further retraction, the tip completely departs from the liquid surface to a distance beyond point e , and the cantilever returns to zero force at point f .¹⁴⁾

3. Results and Discussion

Figure 2 shows the AFM topographical images of the experiments for LC concentrations- and external applied voltage-dependent investigations. The surface morphologies possessing topography nanometer-to-micrometer-scale were quantified at various voltages for different LC concentrations by simply analyzing the structural configurations of LCPCFs through the root-mean-square (RMS) roughness of the film surfaces and the variance of the total domain size of LC (%) at various applied voltages. Since the LC concentration has great influence on the phase separation morphology in the fabricating process for the LC/polymer film, the RMS roughness of the LCPCF surface depends on the concentrations without applying the external voltage.¹²⁾ The RMS roughness of the LCPCF surface is 1.8 nm at 39 wt % LC, 1.6 nm at 49 wt % LC, 2.4 nm at 59 wt % LC, and 4.5 nm at 69 wt % LC without any external voltages applied. Additionally, the different RMS roughness of the LCPCF surfaces may give rise to different anchoring forces on LC molecules. The LC molecules in the low LC concentration systems have to bear larger anchoring forces from polymer grids and thus need to apply a high external voltage on the films for LCs reorientations. Therefore, the RMS roughness and LC domain size of LCs are almost constant as increasing the applied voltage in the 39–59 wt % LC systems. However, the RMS roughness of the film surfaces varies when the

voltage turns on for 69 wt % LC [Fig. 2(m)]. Additionally, according to analysis of the topography images on the roughness of the film surfaces and the variance of the total domain size of LC (%) at different applied voltages [Fig. 2(n)], the accumulation behavior of the LC molecules was dramatically dependent of the applied voltages when the concentration of LC in the composite films is 69 wt %. Experimental results suggest that self-reorganization anchoring transitions of LC molecules significantly driven by electric fields reveal when the concentration of LC is 69 wt %. Higher voltages imply a larger domain size of the LC molecules. However, voltages on the lower concentrations of LC did not obviously differ with respect to the morphologies or the domain size of LCs. Experimental results indicate that electrically significant reorganization changes of the LCs anchored between polymer grains for the concentration of LCPCFs exceeds ~60%. Above observations suggest that control of the external voltage can crucially lead to orientation transitions in high concentrations of LCPCFs.

The attributes that the significant orientation change of the LCs anchored between polymer grains in high concentrations of LCPCFs at different electric fields might provide the fundamental mechanism responsible for the structurally driven changes in surface properties at various applied voltages. The features were also confirmed by the adhesion property measurements as a function of external applied voltages at different LC concentrations. Quantitative analyses of the F - D curve during a complete approach and separate cycle suggest schemes for determining the equilibrium state in the composite film at different LC concentrations with various external voltages, with the retractive force F_e reflecting the adhesion force in the departure process [Fig. 3(a)]. Figure 3 shows the quantitative measurements of the experimental F - D curves against LC concentrations with various external voltages applied. Since the retractive force F_e can be physically defined as the value of adhesiveness and the variance of the LCPCF surface can be observed at different LC concentrations with various voltages executed clearly, a portion of a complete cycle in the departure process is magnified in Figs. 3(b)–3(e).

In addition to analyzing the results of molecular rearrangement in the nanometer scale, this work also attempted to realize the functionally electrically surface-driven switchable wettability of the LC/polymer composite films. Owing to the chemical heterogeneity of the surface of the composite films, this work assessed several force curves at different locations and determined the surface adhesion property for the composite films at different voltages following the equation:

$$F_e(V) = f_{lc} \cdot F_{e,lc}(V) + f_p \cdot F_{e,p}(V), \quad (1)$$

where f_{lc} and f_p are the fractions of LC and polymer grains for the measured average adhesiveness $F_{e,lc}$ and $F_{e,p}$ in several locations at a specific external voltage applied, respectively. In principle, since the total summation of the fractions f_{lc} and f_p equals one, we thus can identify the f_{lc} and f_p of LC and polymer grains from the total LC domain size in Fig. 2(n). The average surface adhesion properties for different LC concentrations at various external voltages were

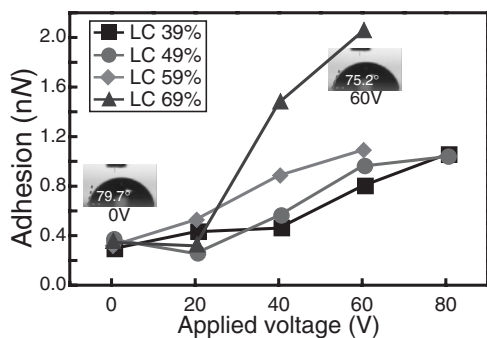


Fig. 4. Variation of measured adhesion force of a composite film as a function of the external voltages at different LC concentrations.

analyzed and summarized those results in Fig. 4. According to Fig. 4, the adhesion forces of the LCPCFs significantly depended on the external voltages at different LC concentrations. Typically, below 60 wt % of the LC concentration, the composite films did not significantly vary in the adhesion of the surface of the composite films. However, the adhesion force noticeably varies with the further increases in applied external voltages for LC concentration exceeding 60 wt %. The magnitude of the adhesion force reached 2.0 nN at 60 V for 69 wt % of the LC concentrations, i.e., about a quintuple value compared to the value of the adhesion force without an external voltage applied. The magnitude of the variance of adhesion force for different LC concentrations at various applied voltages reveals that different reorientations of LC molecular alignments at high and low concentrations of LCs in the composite film contribute to its value. Applied voltage on the composite films with high LC concentrations was accompanied by an obvious transition in the orientation of the LC molecules. According to the LC molecular structures (with CN⁻ and C_nH_{2n+1}- terminals groups), experimental results suggest that rotating the CN⁻ terminals groups of LCs under different applied voltages to point out of plane, subsequently yielding dramatic wettability properties of LCPCFs.

Accompanying the measurements of the surface adhesion force of the composite film, the switchable wettability of the LCPCFs under in-plane electric fields was also correlated by contact angle measurements using a ~3 μl drop of de-ionized water deposited on the film surfaces (Fig. 4). Notably, a larger adhesive implies a lower contact angle of a water drop on the LCPCFs surface.¹⁵⁾ Based on the previous work,¹¹⁾ experimentally, since there is no obvious variance of the water contact angle on the LC/polymer film for the LC/polymer composite films with 0 wt % LC, the surface wettability property was largely determined by molecular aggregation.

4. Conclusions

The work shows that the characterization of the surface properties of LCPCFs obtained by AFM can provide a picture of interfacial structure under external voltages applied. When an application of in-plane voltage on the films, LC molecular species demonstrating tunable wettability can be specifically realized. The CN⁻ terminal group of the LC molecule structure reorienting out of the surface results significantly wettability property, especially for high LC concentration of LCPCFs. These could be attributed from the various interactions of the polymer and LC materials with different LC concentrations, and could be elucidated in the future studies. Application to a tunable wettability surface enables us to have a detailed understanding of how the chemical structures of the outermost layers can be controlled to modify various interfacial behaviors of LCPCFs. The technique should also be exploited in future technologies, such as microfluidic devices, polarizer-free displays, and liquid lenses.

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