A Method for Estimating Interfacial Tension of Liquid Crystal Embedded in Polymer Matrix Forming PDLC

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ABSTRACT: A simple and convenient method based on sessile drop technique for measuring surface tensions of polymer and nematic liquid crystal (LC) is described. Contact angles formed by drops of probe liquids and a nematic LC on a photocurable polymer were measured. The surface energies were evaluated using the Fowkes method, Neumann's equation, and new equations developed based on Neumann's approach. The values of surface tensions were used to evaluate the interfacial interaction in term of work of adhesion between the LC and polymer. Further, the effect of dichroic dye on the extent of interaction and work of adhesion was examined by measuring contact angle in consequence of dye addition. A difference in work of adhesion between the lower and higher dye-doped LC droplets gave an indication of affinity relationship between polymer and LC molecules. A change in work of adhesion resulted in variability of nematic director configurations inside phase separated LC droplets embedded in polymer matrix; when viewed under polarizing optical microscope. Thus, our approach of estimating surface energy of polymer and LC has found to be useful in determining interaction at polymer–LC interface. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41137.

INTRODUCTION

There has been an increasing interest in the controlled preparation of micrometer and nanometer-sized materials by physical or chemical methods. One example is the heterogeneous thin films of polymer dispersed liquid crystal (PDLC), consisting of birefringent liquid crystal (LC) microdroplets embedded in a transparent polymer matrix. PDLCs have been extensively investigated for application in electro-optical control and display devices ranging from optical shutters to color displays due to their polarization independence.[1–6] The operational principle of a PDLC film is based on the refractive index matching or mismatching between the LC and polymer matrix. In the absence of electric field, surface anchoring causes an arbitrary orientation of LC droplets, and the film scatters light strongly due to the mismatching between the average refractive index (n_{avg}) of LC and the polymer refractive index (n_p). When a sufficient electric field is applied, LC directors align along the direction of the field, and for normal light incident, the film appears highly transparent if $n_o = n_p$.

Over the last few decades, intensive research is directed toward developing novel polymer–LC device concepts with the optimization of electro-optical performance as a corollary to the film preparation technique, type of constituents in addition to the use of various dopants.[7–13] It has been well established that a

number of factors viz., the sample composition, film architecture, dimensions of LC channels and/or domains, dielectric parameters, the work of adhesion on the interfaces, and the physical properties of both the components, such as refractive index, elasticity, and viscosity determine the PDLC device performance.[14–18] During the switching phenomenon, the electro-optical parameters like switching field, response time, and transmission of a PDLC film are greatly influenced by the interfacial interaction between its constituents.[18–21] In fact, the nematic configurations within the dispersed LC droplets depend on the elastic constants of LC which results from the microscopic interactions at the interfaces between the polymer and LC. This interaction at the interface referred to as anchoring is one of the key parameters that influences the morphology and also plays a major role for the alignment of LC molecules when PDLC is driven by an external electric field. The study of surface tension of LC and polymer and their interfacial energy is, therefore, of great interest. In general, the low interfacial interaction between the polymer and LC aligns the nematic directors easily, and hence, reduces the operating voltage.

It has been stated that a static method of measurement is best suited to estimate the surface tension of LCs.[22] Various methods like capillary rise technique, Wilhelmy plate, Du Nouy ring, pendant drop method, etc can be used to determine the surface

tension of liquids.[20,23] However, complicated experimental setup and measurements, long procedures, and calculations involved in these methods make them less preferable to implement.[23–26] In the capillary rise method, surface tension of a liquid is defined by the liquid elevation in a capillary where the angle of contact between the liquid meniscus with the solid surface of capillary walls is measured. The method requires essentially two prerequisite parameters; density value of the liquid to be investigated and the liquid–capillary walls interactions. Wilhelmy plate method employs a sensitive force meter of some sort to measure the force on a solid plate vertically dipped into the pool of a liquid and subsequently, translating the measured force into a value of contact angle. However, constraints like complicated measurement of equation parameters, large volumes of liquid, and sample preparation with a uniform cross-section in the submersion direction makes this technique less preferable to use. In addition, Wilhelmy plate technique requires that the solid sample has two identical surfaces; otherwise the measured data may be a result of two completely different interactions. Du Nouy ring method is based on the determination of the detachment force during the lifting of a ring from surface of a liquid. As the ring is moved during measurement, the time dependence of surface tension needs to be taken into account. A major trade-off in using Du Nouy ring method is the large volume of liquid needed for the analysis. Pendant drop method is one of the most widely used techniques to infer the surface tension of LCs. It is based on the profile measurement of a drop suspended from the end of a tube under the influence of surface and gravitational forces. However, the technique has certain issues to be addressed. For example, the syringe radius needs to be optimized for each kind of liquid to avoid capillary and necking effects during measurement.[26,27] Also, the value of surface tension obtained changes with a change in volume of liquid drop suspended from the tube end.[26,28] Additionally, the density of liquid under test should be known to determine the surface tension using pendant drop method. Hence, one requires a suitable methodology providing a convenient experimental approach for estimating surface tension and circumventing the time-consuming efforts involved in the measurements.

Consequently, in this work, we propose and demonstrate simple method based on contact angle measurements using sessile drop technique to evaluate the surface tensions of a nematic LC and a polymer. In this technique, the contact angle of a static sessile drop on a solid surface is measured shortly after its creation when a thermodynamic equilibrium is reached. Various methods exist in the literature to evaluate surface tension using contact angle measurement.[29–32] Recently, Deshmukh et al.[29] have developed simplified equations based on Neumann' approach to estimate free surface energy of solids using a single probe liquid. We have estimated surface energy using different models and equations based on contact angle measurement. One of the advantages of this technique is the minimal use of materials, thus providing a better solution in terms of cost effectiveness over the other techniques. Also, one does not require prerequisite knowledge of physical parameters like viscosity, density to evaluate surface energy through contact angle method. Further, an azo dichroic dye was added in LC and the interfacial interactions between the dye-doped LC and polymer were studied through contact angle measurements. It is believed that the nematic director configurations inside an LC droplet are strongly dictated by the surface anchoring conditions. The present work is possibly an effort to examine the variability of LC droplet configurations in the dichroic PDLC through surface energy measurements.

EXPERIMENTAL

The experiments were performed using an acrylate-based monomer SAM114 (Nematel GmbH & Co., Germany), a nematic LC BL038 (E. Merck, Japan), and an azo Disperse Red 1 (DR1) dichroic dye (Sigma Aldrich). BL038 is a eutectic mixture with nematic domain from $-20°C$ to $101.5°C$ and positive dielectric anisotropy, $\Delta\varepsilon = 14.4$. The dye has a strong absorption at $\lambda_{max} = 502$ nm. All the materials were used as received.

Measurement of surface tensions of SAM114 and BL038 were performed through sessile drop technique using a Kruss G-10 contact angle measurement system. The method involves measuring the angle of contact of a liquid drop placed on a solid surface. A transparent polymer film without LC was polymerized by UV light over a glass plate. Further, the contact angle on SAM114 surface was measured with LC BL038 and various liquids such as water, ethylene glycol, formamide, glycerol, and diiodomethane. All the measurements were done at room temperature and average of five readings were taken for calculations through various approaches of surface energy estimations discussed in the following section.

Dye DR1 was dissolved in LC BL038 in various concentrations (3%, 1%, 0.25%, 0.06%, and 0.015% wt/wt). Sessile drops of LC with different dye content were formed on the surfaces of the solid polymer and contact angle was measured. The PDLC samples were prepared by dispersing dye-doped LC into the UV-curable polymer matrix-SAM114 in 45/55% wt/wt ratio. The mixture was filled by capillary action in the cavity formed between two parallel indium tin oxide (ITO)—coated glass substrates separated by a poly(ethylene terephthalate) spacer of thickness 23 μm. The cavity was then sealed with an adhesive and the whole assembly was cured under UV light (intensity $\sim$2 mW/cm^2 and wavelength = 354 nm) for an hour at room temperature. Dispersion and director configurations of dichroic LC droplets in the polymer matrix were viewed under crossed polarizers through polarizing optical microscope (Olympus BX-53).

THEORY

Young's Equation

A drop of liquid resting on a solid surface forms an angle θ with the surface, called contact angle. In thermodynamical equilibrium conditions, Young[33] showed that

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \tag{1}$$

where γ_{lv} (or simply called γ_l) is the surface tension (or energy) of liquid, γ_{sv} (or simply called γ_s) is the solid surface energy and γ_{sl} is solid–liquid interfacial tension. Various methods have been proposed to calculate γ_s by measuring the contact angles formed by probe liquids with known surface tensions; these techniques are described below.
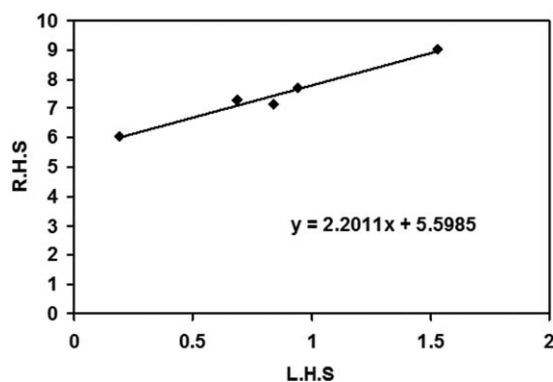
Figure 1. Determination of surface energy for SAM114 by Fowkes method.

Fowkes Approach Extended by Owens and Wendt

Fowkes assumed that the quantity γ_{sl} can be determined by various interfacial interactions depending upon the properties of both the measuring liquid and the solid. He postulated that the surface free energy is a sum of independent components, associated with specific interactions[34,35]:

$$\gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^h + \gamma_s^i + \gamma_s^{ab} + \gamma_s^o \qquad (2)$$

where γ_s^d, γ_s^p, γ_s^h, γ_s^i, γ_s^{ab} are the dispersion, polar, hydrogen (related to hydrogen bonds), induction, and acid–base components, respectively, while γ_s^o refers to all remaining interactions.

Owens and Wendt[36] significantly changed Fowkes approach while assuming that the surface free energy is primarily due to two types of molecular interactions: dispersion and polar. They assumed that the sum of all the components on the right-hand side of eq. (2), except γ_s^d, can be considered as associated with the polar interaction γ_s^p. Thus, the free energy γ resulting from these contributions is given as:

$$\gamma = \gamma^d + \gamma^p \qquad (3)$$

where the superscripts d and p represent the dispersion and polar contribution.

In order to determine the surface tension and its components of a solid using Owens and Wendt approximation, one needs to measure contact angle on a given surface with minimum two liquids of known polar and dispersion components. However, it is advisable to measure angle of contact with more than two liquids (at least one of them should be interacting through dispersion forces only, such as diiodomethane) to minimize the deviation from the actual surface energy value. The plot shown in Figure 1 is obtained using eq. (4) and it is clear from the plot that, for reliable values of surface free energy and its components, one should measure contact angle with various liquids starting from the highest value of surface tension such as water, ethylene glycol, formamide, glycerol, and diiodomethane. The equation to calculate surface energy by Owens and Wendt approximation is as follows[35–37]:

$$\left[\frac{1+\cos\theta}{2}\right] \times \left[\frac{\gamma_l}{\sqrt{\gamma_l^d}}\right] = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \qquad (4)$$

where γ_l is surface tension of liquid, γ_l^d dispersion component of liquid surface tension, γ_l^p is polar component of liquid sur-face tension, γ_s^p is polar component of solid surface tension, and γ_s^d is dispersion component of solid surface tension. The above equation is one of the most common methods for calculating the surface free energy of polymeric materials which involves the use of more than two liquids (it is also called as many-liquid approach).

The above equation is of the form

$$Y(\text{LHS}) = m \, x(\text{RHS}) + C \qquad (5)$$

The value of LHS can be obtained by measuring θ for the liquid used. RHS can be calculated using the polar and dispersion components of liquid used. Plot of LHS versus RHS gives straight line. Slope (m) and intercept (c) obtained on Y-axis are squared and added up to get total surface energy. Since, this approach is based on geometric mean; the results obtained are highly reliable.

Neumann Approach

Neumann approach for estimating surface energy is purely thermodynamic and results obtained from Neumann method are independent of the test liquid used. By measuring angle of contact with only one liquid, the value of solid surface tension can be estimated through the equation[38]

$$1 + \cos\theta = 2\left(\frac{\gamma_s}{\gamma_l}\right) e^{-\beta(\gamma_l - \gamma_s)^2} \qquad (6)$$

Empirically, it has been shown that,

$$\beta = 0.0001247 \qquad (7)$$

Neumann's eq (6) is not solvable by traditional methods. It requires mathematical programs and software to get the value of solid surface energy (SE). To calculate the surface energy of a solid by measuring the contact angle of five probe liquids, Deshmukh and Shetty[29] have developed very simple equations which are given as:

$$\text{SE using Water} = 2.9 \times 10^{-5}(\theta)^3 - 0.00652(\theta)^2 - 0.1326(\theta) + 72.8 \qquad (8)$$

$$\text{SE using Glycerol} = 2.9 \times 10^{-5}(\theta)^3 - 0.00648(\theta)^2 - 0.101(\theta) + 63.4 \qquad (9)$$

$$\text{SE using Formamide} = 2.9 \times 10^{-5}(\theta)^3 - 0.00631(\theta)^2 - 0.089(\theta) + 58.2 \qquad (10)$$

$$\text{SE using Ethylene Glycol} = 2.9 \times 10^{-5}(\theta)^3 - 0.00569(\theta)^2 - 0.072(\theta) + 48.0 \qquad (11)$$

$$\text{SE using Diiodomethane} = 2.9 \times 10^{-5}(\theta)^3 - 0.00585(\theta)^2 - 0.076(\theta) + 50.8 \qquad (12)$$

The general form of the above five equations is a third order polynomial and is given below.

$$\text{SE} = A(\theta)^3 - B(\theta)^2 - C(\theta) + \gamma_l \qquad (13)$$

where A, B, and C are constants for a given liquid.

The liquids mentioned above are used as probe liquids due to their high surface tension and comparatively less volatile nature.

Table I. Surface Tension Parameters for Various Liquids in mJ/m^2

Liquid	γ_l	γ_l^d	γ_l^p
Water	72.8	21.8	51
Glycerol	64	34	30
Formamide	58	39	19
Ethylene glycol	48	29	19
Diiodomethane	50.8	50.8	0

The surface tension parameters for these liquids are listed in Table I.[39]

Introducing the work of adhesion, W_a equal to the work necessary to separate the liquid from the solid in contact, we have[29]:

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \qquad (14)$$

Hence, the interfacial interaction between PDLC constituents in terms of adhesion work can be determined through the calculated surface energies of LC and polymer.

RESULTS AND DISCUSSION

Surface Energy of Polymer SAM114

The contact angles formed by drops of different liquids on the surface of fully cured polymer SAM114 are presented in Table II. Using Fowkes equation [eqs. (3) and (4)], the method of calculating polar and dispersion components of solid surface energy for polymer SAM114 using five different liquids is shown in Figure 1. The plot of LHS versus RHS gives a straight line with an intercept on Y-axis.

The values of slope and intercept are obtained as $m = 2.201$ and $c = 5.599$, respectively. The polar and dispersion components of SAM114 surface energy are calculated as

$$\gamma_s^p = m^2 = 4.84 \text{ mJ/m}^2, \qquad (15)$$

and

$$\gamma_s^d = c^2 = 31.34 \text{ mJ/m}^2 \qquad (16)$$

Hence, using eq. (3), the total surface energy of polymer SAM114 through Fowkes method is

$$\gamma_s = \gamma_s^p + \gamma_s^d = 36.19 \text{ mJ/m}^2 \qquad (17)$$

Similarly, the surface energy of SAM114 was determined for individual liquids using purely thermodynamic approach of Neumann by employing eqs. (8)–(12) developed by Deshmukh and Shetty,[29] and are given in Table III.

Table II. Contact Angles θ Made by Drops of Different Liquids on the Polymer Surface at 25°C

Liquid	Contact angle on SAM114 (θ)
Water	81
Glycerol	68
Formamide	55
Ethylene glycol	51
Diiodomethane	46

Table III. Surface Energies of Polymer SAM114 through Neumann's Method Using Various Liquids

Liquid	Contact angle on SAM114 (θ)	Surface energy of SAM114 (mJ/m^2)
Water	81	34.69
Glycerol	68	35.69
Formamide	55	39.04
Ethylene glycol	51	33.38
Diiodomethane	46	37.75

From Table III, the average value of SAM114 surface energy is found to be 36.11 mJ/m^2. This result was found in close proximity of the value obtained in eq. (17). Taking the average of the measured surface energy values using different methods, the SAM114 surface energy, γ_s, was found to be 36.15 mJ/m^2. This surface energy value of polymer was used as basis for calculating LC surface tension.

Surface Tension of LC BL038

The surface tension of LC BL038 was estimated using Neumann's equation [eq. (6)] by measuring the contact angle of BL038 on SAM114 surface (now sample of known surface energy). For the measured contact angle of 32°, the value of LC surface tension γ_l was 39.02 mJ/m^2.

Work of Adhesion

Considering the work of adhesion, i.e., the form of work necessary to separate two surfaces given by eq. (14):

$$W_a = \gamma_s + \gamma_l - \gamma_{sl}$$

Combining the above equation with the equilibrium between surface tensions given by the Young equation, we get the equation relating the measurable parameters γ_l and θ to the adhesion free energy, called as Young–Dupre equation[31]:

$$W_a = \gamma_l(1 + \cos\theta) \qquad (18)$$

Using above equation, the calculated work of adhesion between the polymer SAM114 and LC BL038 was 72.11 mJ/m^2.
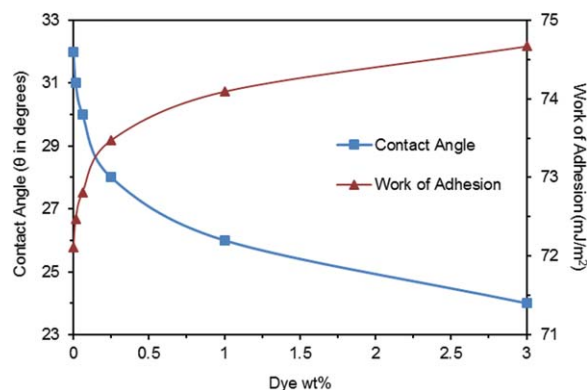

Figure 2. The variation in contact angle and work of adhesion of BL038 on SAM114 surface with the addition of Disperse Red 1 azo dye. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
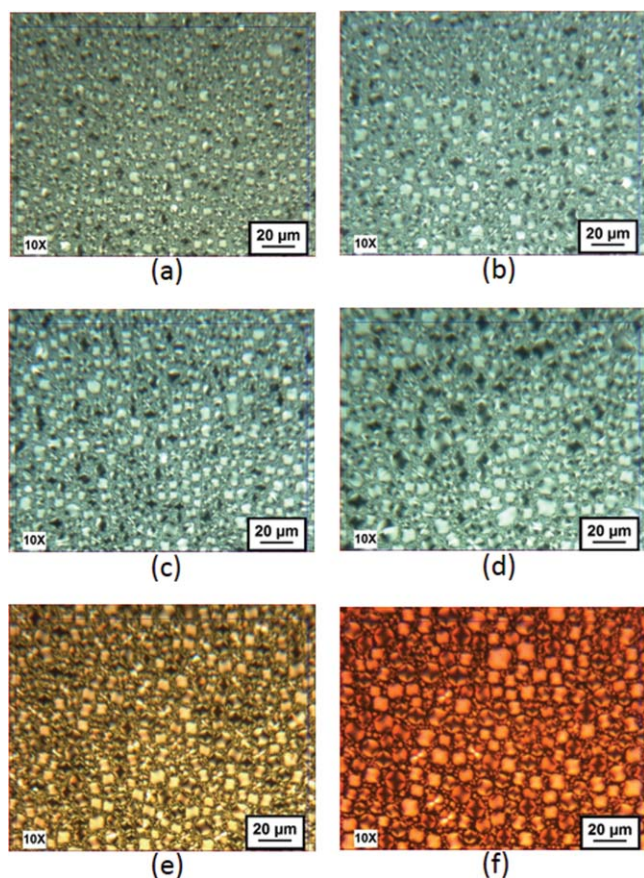
Figure 3. Droplet morphologies of dichroic PDLCs with different dye contents (a) 0% (b) 0.015% (c) 0.06% (d) 0.25% (e) 1%, and (f) 3%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Contact Angle and Work of Adhesion in Dye-doped PDLC

The measured contact angle and calculated work of adhesion of LC BL038 measured with different dye contents on SAM114 are shown in Figure 2. It is seen that as the dye content increased, the contact angle of LC dramatically decreased from 32° to 24°, giving an indication of affinity between dye-doped LC and polymer matrix. A strong affinity results in an increase of adhesion work between the polymer and LC with increasing dye content. The work of adhesion is known to have a substantial influence in determining the configuration of LC droplets embedded in a polymer matrix.[1] A variation in adhesion work enforces transformations of one type of nematic director arrangement into another, leading to variability of LC droplet configurations. Recent studies have shown that the morphology of LC domains inside the polymer matrix plays an important role in determining the electro-optical switching of dye-doped PDLC systems.[6,40] To examine the effect of surface anchoring conditions, we investigated the morphologies of phase separated dye-doped LC droplets embedded in polymer matrix and the results are shown in Figure 3.

It was seen that the droplets exhibit a combination of bipolar and radial configurations simultaneously, with a trend decrease in radial structures as dye content increased. It is known that bipolar droplets exist when the molecules are strongly anchored parallel to the surface with two point defects on the cylindrical symmetry axis.[1] A comparatively weak anchoring conditions result in the formation of radial structures with homeotropic anchoring of molecules at the surface. The high dye-doped films emerging with more number of bipolar droplets in Figure 3 can be interpreted as the higher dye-doped LC showed relatively high affinity for the polymer and thus facilitating strong anchoring conditions at the interface of polymer and LC molecules. It is clear from Figures 2 and 3 that work of adhesion plays an imperative role in determining director configuration in LC droplets and hence, the morphology of embedded LC domains in polymer matrix.

CONCLUSIONS

Interfacial tension between polymer and LC governs the morphology and electro-optical properties in PDLC systems. In the present investigation, our approach of estimating interfacial tension from the measurement of contact angle and using various approaches was found to be useful. Lowering of contact angle on addition of dichroic dye in LC increases the molecular affinity with the polymer and in turn, raises work of adhesion. Thus, our systematic and step by step approach of determining surface energy of polymer using various probe liquids followed by determining contact angle of LC on the polymer film and finally obtaining surface tension of LC opened up a method using Young–Dupre equation leading to the understanding of adhesion work. Hence, the method described in this article would be useful for estimating the free surface energies of PDLC constituents and in deriving the anchoring conditions at the polymer–LC interface.

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