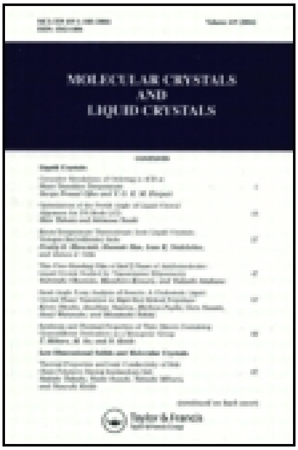

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Effect of Mechanical Rubbing on the Surface Free Energy of Poly(Vinyl) Alcohol Thin Films and the Contact Angle of a Liquid Crystal on the Rubbed Polymer Surfaces

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To cite this article: W. J. Zheng (2007): The Effect of Mechanical Rubbing on the Surface Free Energy of Poly(Vinyl) Alcohol Thin Films and the Contact Angle of a Liquid Crystal on the Rubbed Polymer Surfaces, Molecular Crystals and Liquid Crystals, 479:1, 3/[1041]-11/[1049]

To link to this article: http://dx.doi.org/10.1080/15421400701758816

Mol. Cryst. Liq. Cryst., Vol. 479, pp. 3/[1041]–11/[1049], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701758816

The Effect of Mechanical Rubbing on the Surface Free Energy of Poly(Vinyl) Alcohol Thin Films and the Contact Angle of a Liquid Crystal on the Rubbed Polymer Surfaces

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The surface free energy of rubbed polyvinyl alcohol was studied. A mechanical rubbing to the polymer causes change in chemicophysical characteristics in outermost layer of the polymer. The increase of rubbing strength causes the decrease in the surface free energy of the polymer. The rubbed polymer thin films show a significant anisotropy in wettability. It is found that in the anti-rubbing-direction the contact angle of a liquid crystal is smaller. The increase of the rubbing strength leads to the decrease in the contact angle.

Keywords: contact angle; rubbed polyvinyl alcohol; surface free energy; surface wettability

1. INTRODUCTION

A uniform orientation of the director of liquid crystals (LCs) on substrates is of primary importance for many electrooptic applications of LCs. Up to date, the most used technique for achieving a homogenous LC alignment is the rubbed polymer, in which a thin layer of polymer is spin-coated on to the inner surfaces of the substrates and subsequently rubbed unidirectionally [1]. It is widely believed that the alignment of LC molecules on the rubbed polymer surface is generated by the orientation of the polymer chains and the grooved surface due to the mechanical rubbing [2,3]. More fundamentally, the LC alignment on a solid surface is thought to be determined by

This work was supported by a Grant for 'Aim for the Top University Plan' from National Education Committee of ROC.

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the competition between the surface tensions of the LC and substrates which is based on the relation between surface energies of the substrates and the LC [1,4–6].

Recently, attention has been attracted on the controlling of surface energies to precisely tune interfacial and surface interactions of materials [7,8]. It has also been noticed that characteristics of wetting of the rubbed polymer surface provide a wide range of information on properties of the surface [9–11]. For example, contact angle, which is a measure of the wettability, of a liquid on an organic solid surface is sensitive to chemicophysical characteristics of the outermost surface of a few angstroms in thickness [12–14]. The values of contact angles obtained from similar systems with a variety of probe liquids can be used for elucidating characteristics of organic surfaces. In general, probing liquids used for the characterization of a solid surface are isotropic liquids, and wet the solid if surface tensions of the liquids are lower than that of the solid substrate. LCs are anisotropic liquids. The elastic stresses due to the deformation of the director field in the nematic phase play an important role. It has been reported that liquid crystals may not wet a solid with very high surface energy [15].

In the present studies, the surface free energy of rubbed polyvinyl alcohol (PVA) thin films and contact angles of a liquid crystal (LC) on the surfaces have been investigated. In this article, we report the initial results on the effect of rubbing strength (*RS*) on the surface free energy of the rubbed PVA. The variations of the contact angle of a liquid crystal on the rubbed PVA surface with the *RS* and the rubbing direction are also presented.

II. EXPERIMENTAL

A commercial PVA (BDH) was dissolved in deionzed water to make a 0.3 wt% solution, and spin-coated on ultrasonically cleaned glass substrates. The PVA coated substrates were then baked at 60°C for 60 minutes to remove residual water, subsequently rubbed unidirectionally using an in house made rubbing machine with a roller covered with velvet nylon. The *RS* is calculated using following equation [16].

$$RS = N \cdot \Lambda\left(\frac{2\pi R\omega}{\nu} - 1\right), \tag{1}$$

where N is the cumulative number of rubs, Λ is the pile impression of the velvet fibers, ω is the rotation speed of the roller, R is the radius of the roller, and v the translational speed of the substrate. In the present studies, the translational speed of the sample was fixed at

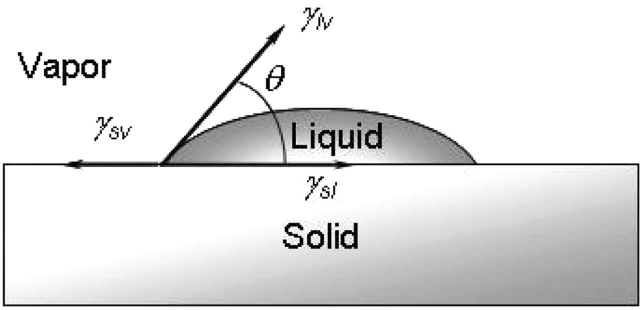

FIGURE 1 Schematic illustration of a liquid/solid system. γ_{lv}, γ_{sv} and γ_{sl} are refer to the interfacial tensions, or energies, of the liquid/vapor, solid/vapor and solid/liquid interfaces, respectively.

2.25 mm/s, and the rotation speed of the roller was fixed at 135 rpm. The rubbing strength was then controlled by varying the pile impression of the nylon velvet, and the number of rubbing cycle.

The surface free energy was determined using sessile drop measurement method and was performed using a surface tension meter (KRÜSS DSA100). In this method, the surface free energy is thought to consist of two components, the dispersive part and polar part, respectively. The surface free energy of a solid can be evaluated using following Owens-Wendt equation [17].

$$\frac{(1+\cos\theta)\gamma_{lv}}{2\sqrt{\gamma_{lv}^{d}}} = \sqrt{\gamma_{sv}^{p}} \cdot \sqrt{\frac{\gamma_{lv}^{p}}{\gamma_{lv}^{d}}} + \sqrt{\gamma_{sv}^{d}} \tag{2}$$

where θ is the contact angle, γ_{lv} and γ_{sv} are refer to the interfacial tensions, or energies, of the liquid/vapor and solid/vapor interfaces, respectively (c.f. Fig. 1), and d and p denote dispersive and polar components, respectively.

The contact angle θ is defined as the angle between the tangent to the liquid-vapor interface and the tangent to the solid interface at the contact line between the three phases (c.f. Fig. 1). The contact angle values for the PVA surfaces and a LC were measured by means of computer-aided analysis of shapes of liquid drops, as observed in an optical goniometer and recorded by a digital camera. The LC drops were applied by means of a micro-pipette on the surfaces of PVA or on the cleaned sonicated glass slides. The pictures taken of the drops were then analyzed using a PC and specialized software, and the contact angle values were obtained.

The LC used in the present studies was nematic K15 (E. Merck).

III. RESULTS AND DISCUSSION

Before rubbing, AFM images of PVA thin films on glass substrates, which are not shown here, show that the surfaces of PVA thin films are uniform and smooth. Mechanical rubbing a PVA thin film produces grooves on the polymer surface. Figure 2 shows an AFM image of a rubbed PVA surface. The parallel grooves on the surface clearly indicate that an isotropic PVA surface is broken and replaced by a surface with anisotropic topography. These grooves on the surface were thought to be responsible for the liquid crystal alignment [3]. The effect of LC alignment of the rubbed PVA was examined by sandwiching nematic K15 between substrates coated with rubbed PVA and observing the optical texture of the sample by means of optical microscopy. It has been confirmed that all samples show very good liquid crystal alignment.

The model used for the evaluation of the surface free energy is based on the assumption that the surface free energy of a solid or a liquid can be treated as consisting of two independent or partially independent components, the dispersion part and the polar part, each of them represents a distinctly different type of intermolecular interaction. In the present studies, we focused our attention on the general variation in the total surface free energy, but will not go further to analysis the details of the dispersion and the polar parts of the surface

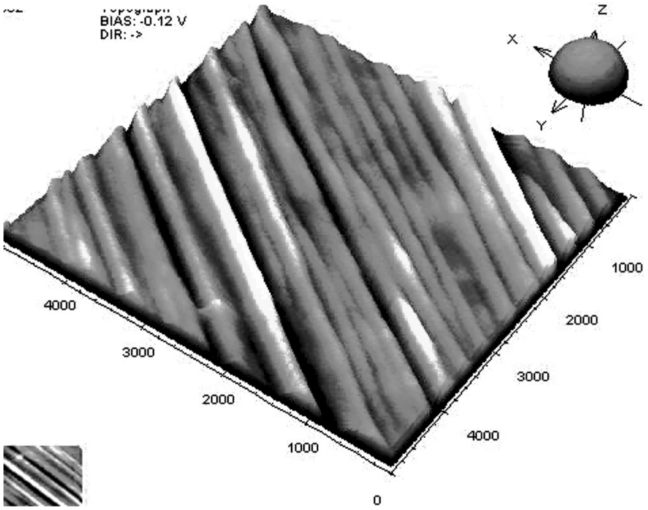

FIGURE 2 Showing AFM image of a rubbed PVA thin film. The unit for the scale in the picture is nm.

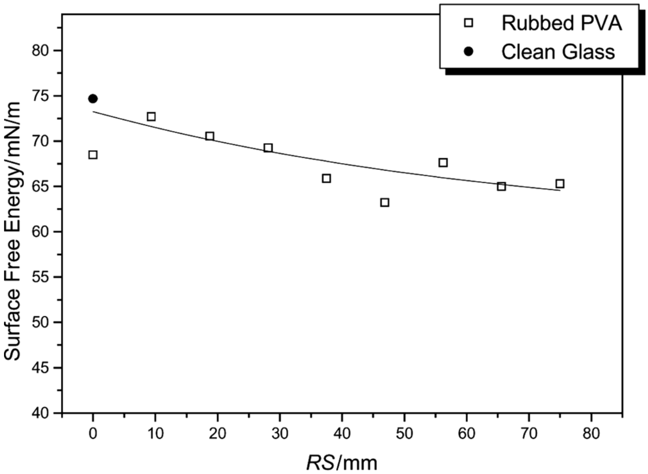

FIGURE 3 Surface energy of rubbed PVA vs. rubbing strength.

free energy. In the present studied, both the pile impression of the rubbing tissue and the speed of the sample holder have been used to determine the rubbing strength (c.f. Eq. (1)). In order to evaluate the influence of a mechanical rubbing on the surface free energy of a PVA thin film deposited on a glass plate, we first measure the surface free energy of the bare substrate. A piece of glass plate was ultrasonic cleaned and was measured to have a surface free energy of $74.68\,\text{mJ/m}^2$. The surface free energy of the PVA on the glass substrate, which was measured to have a value of $68.5\,\text{mJ/m}^2$, is smaller than that of the clean glass plate. Mechanical rubbing causes changes in the surface free energy of the PVA thin film. Figure 3 shows the variation of the surface free energy of the rubbed PVA with the rubbing strength. It was found that after the first cycle of rubbing, the surface free energy of the rubbed PVA increases, then the surface free energy decreases with *RS*.

When a small amount of nematic K15 was dropped on to the surface of a sample, the LC droplet spread out on the surface and the bare surface absorbs the vapor of the LC. Initially, the spreading of LC on the PVA surface was quite fast, and then slowed down after about one hour. An equilibrium state between the LC and the solid surface establishes gradually. Figure 4 shows the variation of contact angle of nematic K15 with time. As a comparison, the contact angle of K15 on clean glass was also measured. It has been reported [18] that due to the interactions between elastic distortion, molecular anchoring,

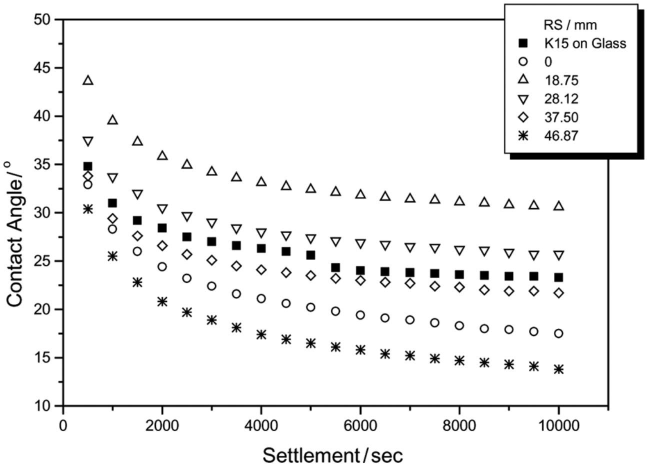

FIGURE 4 Variation of contact angle of K15 on glass plate and rubbed PVA with time for different rubbing strength.

and spreading forces, the nematic droplet exhibits a step-like profile when it spreads on a rough silicon monoxide film, and there is a thin layer of nematic film in front of the three phase contact line. The step-like drop profile is believed to result from different orientational structure of the nematic director at interface, and may affect the measurement of contact angle. In the present studies, the observation has been made with three hours, and such a step-like profile has not been observed on rubbed PVA surfaces. As can be seen, The contact angles of K15 on all, both rubbed and unrubbed, PVA surfaces are much smaller than 90°. It is also seen that the increase in *RS* results in decrease in the contact angle, indicating rubbing can improve affinity of PVA to the LC.

There are several phenomena that can contribute to contact angles. To evaluate the influence of the rubbing on the contact angle, we let the probing LC settle on the surfaces for about one hour, and then measured contact angles. Figure 5 shows the contact angles of the nematic K15 settled for 3500 seconds on the rubbed PVA surfaces. The contact angle of K15 on the unrubbed PVA is quite small, about 23°. When the PVA was rubbed with a low *RS*, the contact angle becomes significantly large, and then decreases as *RS* increases. The increase in the contact angle may result from the increase in the surface roughness, as having been shown in a previous study [19] that a weak rubbing will produce a polymer surface with large roughness. However, the decrease in contact angle may not be simply attributed

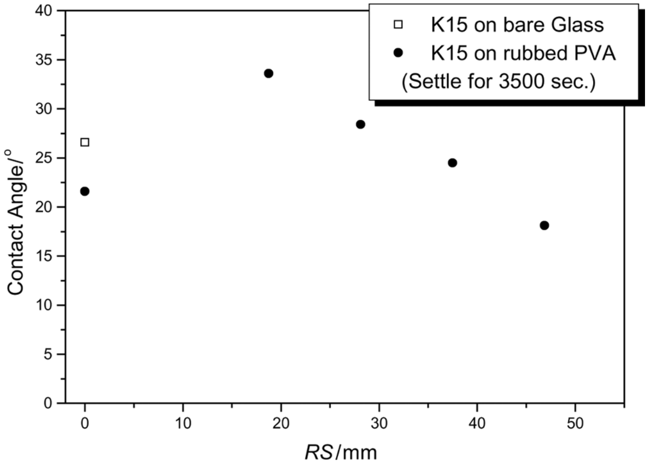

FIGURE 5 Contact angle of nematic K15 on the rubbed PVA when the LC has settled for 3500 seconds. The solid square mark represents the contact angle of the LC on the bare glass plate.

to the decrease in surface roughness due to further rubbing. We here consider the reorientation of the director in nematic phase at the surface of the polymer. It has been confirmed by many studies that rubbing can cause reorientation of molecular chains at rubbed polymer surface, and this can align the director of the nematic phase to the rubbing direction at the surface. According to Lin *et al.* [15], this alignment may reduce the potential barrier at contact line and make the LC act like a wetting liquid and as a result the contact angle becomes smaller.

Very little work has been reported on the anisotropic surface wettability of rubbed polymers. In the present studies, the wettability of the rubbed PVA thin films was evaluated by examining the contact angle of the probing LC on the surface. Figure 6 shows the variation of contact angle with the azimuthal angle against the rubbing direction. The contact angle was found to be larger when it was measured along the rubbing direction, and decreased when the azimuthal angle increases. In the direction antiparallel to the rubbing direction, i.e., azimuthal angle = 180°, the value of the contact angle becomes minimum. This indicates that along the rubbing direction the PVA surface will be more difficult to be wetted by the LC, whereas in the anti-rubbing-direction the surface has better wettability. The mechanisms for the anisotropy in the wettability of the rubbed PVA remain unclear. Here some possible explanations are given as follows.

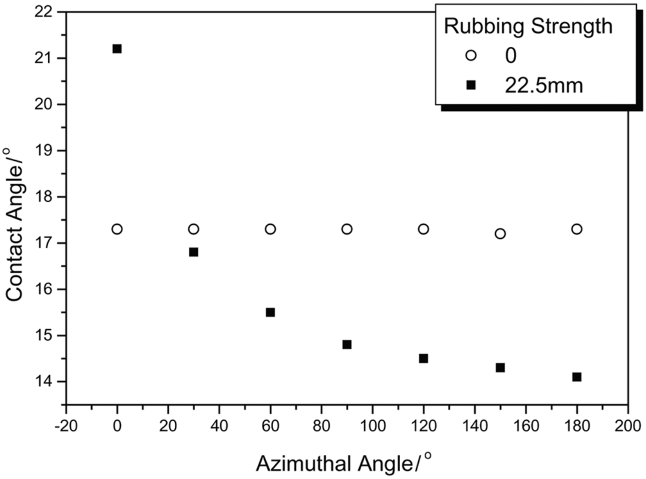

FIGURE 6 Contact angle against azimuthal angle for the nematic K15 on rubbed PVA. The PVA was rubbed with $RS = 22.5\,\text{mm}$.

Macroscopically, rubbing produces grooves on the surface and breaks isotropy in topographical structure of the PVA surface. How the changes in the topographical structure affect the wettability is still not clear. However, we believe that it must induce some interactions that contribute to cause the anisotropy in wettability. Microscopically, rubbing causes a reorientation of polymer chains at the surface. This may also cause a rearrangement of function groups at the surface. Surface wettability is sensitive to the polarity of the surface. In general, a more polar surface exhibits better wettability. The microscopic rearrangement of function groups might change surface polarity leading to changes in wettability of the surface.

IV. CONCLUSION

The influence of rubbing conditions on the surface free energy for rubbed PVA thin films on a glass substrate has been studied. The surface energy of the PVA decreases with the increase in the rubbing strength. The increase of rubbing strength results in the decrease in the contact angle of the liquid crystal on the rubbed PVA. On the unidirectionally rubbed PVA, the contact angle of the liquid crystal is varied with azimuthal angle against the rubbing direction. It has been found that the contact angle in the direction parallel to the rubbing direction is greater than that in anti-parallel to the rubbing direction. The experimental results indicate that the PVA cannot be total wetted by nematic K15. The wettability of the PVA is affected by the rubbing conditions. In the anti-parallel-direction to the rubbing direction the rubbed PVA exhibits better wettability. It is concluded that the surface wettability of the rubbed PVA is highly anisotropic.

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