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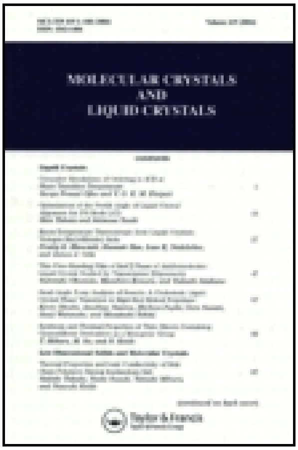

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Surface Wettability of Rubbed Polyimide Thin Films

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Surface Wettability of Rubbed Polyimide Thin Films

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The wetting characteristics of the rubbed polymer thin films is studied by both statically and dynamically examining contact angle of a droplet of deionized water on the polymer surface. The rubbed polyimide thin films exhibit anisotropic surface wettability. In rubbing direction the rubbed polyimide shows higher hydrophobicity, whereas in the anti-rubbing direction, the polymer surface is more hydrophilic. The asymmetric polarity of the polymer surfaces owing to rubbing is considered to be responsible for the appearance of anisotropy in the contact angle hysteresis.

Keywords: contact angle; contact angle hysteresis; rubbed polyimide; surface wettability

INTRODUCTION

Rubbed polyimide (PI) thin films have attracted a great deal of attention because of their usefulness in electro-photonic applications. By rubbing a PI thin film coated on a glass substrate using nylon velvet an alignment template can be created for the alignment of rod-like molecules in the liquid crystal (LC) phases [1,2]. Because of its simplicity, reliability, and repeatability, rubbed polymer becomes the most popular LC alignment technique, and has been widely used to align liquid crystal for applications in displays and other optoelectronic devices [3,4]. Although this technique has widely been used to achieve the desired LC alignment for both scientific research and the liquid crystal display (LCD) manufacture, the physical mechanisms behind the LC alignment of rubbed PI films are not yet well

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understood. One of the main reasons for this is the lack of knowledge on the interactions between LC molecules and the alignment polymer in the interfacial region.

Wetting characteristics of a polymer surface are remarkably sensitive to chemical compositions and morphology of the outmost surface, and can provide a wide range of information on physical properties of the surface. In general, the static wettability of a solid surface is evaluated using the contact angle (CA) of a probing liquid that is in contact with the surface of the solid. The CA is defined as the angle between the solid surface and the tangent of the probe liquid drop surface, through the liquid phase at the tri-phase contact point (TPP). In practical, however, it is often difficult to measure the static contact angle since an absolute equilibrium tri-phase state can rarely be realized in a lab, and the volume of the probe liquid is changing all the time. For a real solid surface, the CA measured while the volume of the probe liquid is increasing is known as the advancing CA θ_a, whereas the receding CA θ_r is defined as the CA measured while the volume of the probe liquid is decreasing. The contact angle hysteresis (CAH) h is then defined as

$$h = \Delta\theta = \theta_a - \theta_r. \tag{1}$$

In almost all investigations, the measurements of the CA reveal substantial hysteresis. The CAH is thought to consist of manifold information about the surface states of a material, and to describe the dynamic wettability of the surface. In rubbed PI thin films, a macroscopic effect, at a microscopic scale, of rubbing is the formation of a grooved surface indicating the break in original two-dimensional uniformity in topography of PI surface [5]. It has also been shown that rubbing causes polymer chains at PI surface to orient in the rubbing direction [6,7]. The changes in the surface topography and molecular restructure must cause changes in physical and chemical characteristics of the PI surface, and should be reflected by the wetting characteristics of the polymer surface.

In this paper, we demonstrate anisotropic behavior of CAH of PI thin films due to rubbing. As rubbing produces a preferential direction on the polymer surface, the azimuthal direction of the movement of the contact line (CL) of probing liquid against the rubbing direction is considered when measuring CAs. The behaviour of CAH is discussed based on the polarity of the rubbed PI surfaces. As the surface wettability is governed by surface free energy that describes the macroscopic states of the surface, the analysis of the surface wettability will provide useful information about the surface energetic characteristics of the alignment layer, and this may provide a new approach to the elucidation of the mechanism of the molecular alignment of LCs.

EXPERIMENTAL

In the present study, PI thin films were prepared by spin-coating a 5 wt% polyamide acid solution JASL-9800-R1 (JSR, Japan) onto ultrasonically cleaned Indium-Tin-Oxide (ITO) glass plates, and then thermally curing the samples to form a polymer film on the substrates. The surface morphology of the PI films was examined before and after rubbing by means of atomic force microscopy (AFM). For this purpose, an atomic force microscope (Dimension 3100, Veeco) was used. The PI films were unidirectionally rubbed using a custom-made rubbing machine which consists of a rotational drum rapping with a piece of velvet textile. The rubbing strength can be determined, in terms of the number of rubbing cycles and pile impression of the velvet fibers, using the following Eq. [8]

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

where ω is the rotation speed of the roller, R is the radius of the roller, and v the lateral speed of the substrate.

The CA was measured using a DSA100 surface tension meter (Krüss). The probing liquid used was deionized (DI) water. DI water was dispensed onto PI surfaces. The profiles of the water droplets were monitored using a charge coupled device (CCD) camera installed in the surface tension meter, and analyzed using the Drop Shape Analysis software (Krüss). In order to measure the azimuthal variation in the contact angels with respect to rubbing direction, the stage of the surface tension meter was modified to be rotatable. The experiments were carried out in a 10k class clean room.

RESULTS AND DISCUSSIONS

The PI films coated on ITO glass were flat and topographically uniform with a mean roughness of 0.334 nm. The PI thin films were then subject to unidirectional rubbing. In this study we fixed the rotation speed of the drum ω at 135 rpm and the translational speed of the sample v at 30 mm/min. Thus the RS, with a dimension of mm, was determined by pile impression Λ and the number of rubbing cycle N. AFM analysis of the rubbed PI surface was carried out. Figure 1 shows

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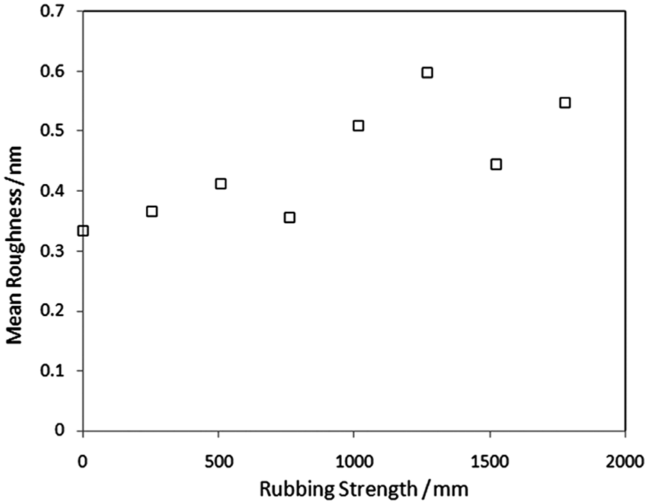

FIGURE 1 Effects of mechanical rubbing on surface roughness of rubbed polyimide thin film.

the effects of mechanical rubbing on surface roughness of the PI films. The average surface roughness of the PI surfaces, which were rubbed with a RS in a range up to 1600 mm, was below 1.0 nm indicating that the rubbed PI films were rather smooth. AFM images of the rubbed PI films, not being illustrated here, showed that mechanical rubbing produced grooves, which are parallel to the rubbing direction, on the PI surface. The formation of the grooved surface indicates that the uniformity in surface topography of the PI films is broken, and a preferential direction, which is parallel to the rubbing direction, has been created by rubbing. As the topographic uniformity of the surface is broken, the two dimensional uniformity in many physical properties at the surface may be lost or changed. Throughout this study, the rubbing direction has been taken as the reference direction when we examined surface characteristics of rubbed PI thin films.

Figure 2a shows azimuthal variation of the static contact angle of DI water on the rubbed PI surfaces. It is clearly seen that the surface wettablility of the rubbed PI films is not uniform, and varies azimuthally against the rubbing direction. The wetting characteristics measured in the rubbing direction is different from that measured against the rubbing direction. Figure 2b shows changes of contact angles with *RS*. The contact angle measured at the TPP on the side towards rubbing direction, i.e., with 0° azimuthal angle against rubbing direction, is larger than that on the side of the droplet against

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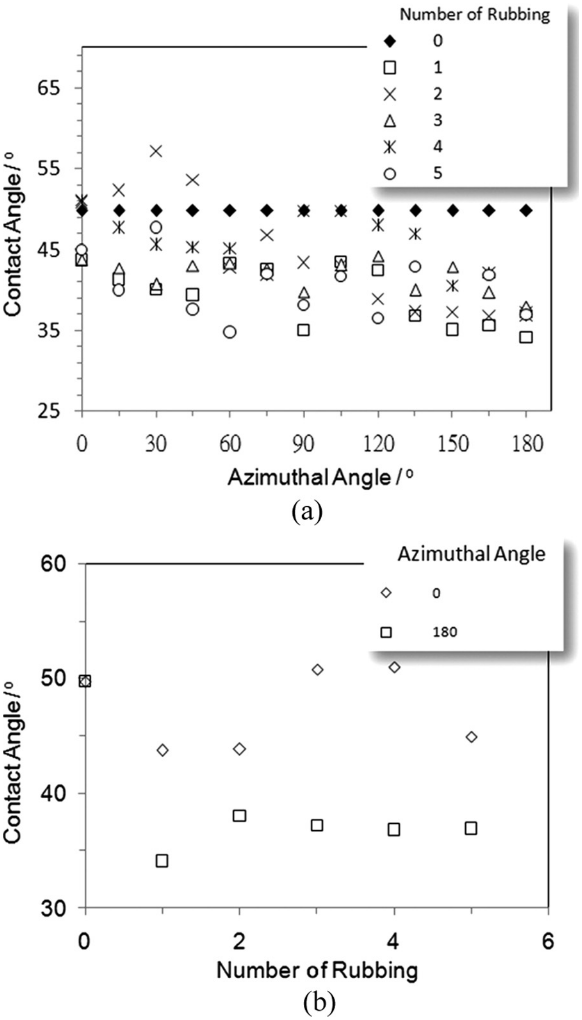

FIGURE 2 (a) Azimuthal variation of contact angles of deionized water for polyimide thin films rubbed with different rubbing strength. (b) Variation of contact angles of deionized water with rubbing strength. For each water droplet, the contact angles at tri-phase points towards and against rubbing directions, respectively, were measured.

the rubbing direction, i.e., with 180° azimuthal angle. So along the rubbing direction the surface of rubbed PI is more hydrophobic, whereas in the anti-rubbing direction the surface shows more hydrophilic. Both hydrophobicity and hydrophilicity in rubbing and against

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rubbing directions, respectively, are found to drop as *RS* increases. Such changes in the wetting characteristics of the rubbed PI can be attributed to a general increase in surface free energy of the PI surface due to the rubbing [9].

To examine dynamical wetting characteristics of the rubbed PI, a drop of 2 μl DI water was initially dispensed onto the PI surface, then extra DI water was added to the droplet at a rate of 1 μl/min and the advancing CA was measured during the CL of the DI water at the surface was moving outwards, whereas the receding CA was determined during the DI water was withdrawn from the droplet and the CL of the water moving inwards. The CAH of PI surface is 34.0°, with an advancing CA 86.8°. The experimental results also showed that there was no azimuthal difference in CAH indicating that the wettability of PI thin films was symmetric. This is expected as there is no preferential direction on the PI surface.

The profiles of the water droplet on the rubbed PI in both advancing and receding courses were found to be asymmetric. In the advancing course, as illuminated in Figure 3a, more water accumulated on the side of the droplet that the CL moves against rubbing direction, while in the receding course (c.f. Fig. 3b), on the side of the droplet the CL moved against the rubbing direction, the movement of the CL was hindered and the droplet was stretched and elongated to the side. This asymmetric profile of the water droplet indicates asymmetric surface characteristics of the rubbed PI thin films.

In the case of rubbed PI, in addition to the movement of the CL, the moving direction of the CL relative to the rubbing direction must also be taken into account when examining CAH. In this research, the CAH in the rubbing direction was determined by subtracting the receding CA measured at the TPP where the CL moved in the rubbing direction θ_r^p from the advancing CA measured at the TPP where the CL moving in the same direction θ_a^p, whereas CAH against rubbing direction is given as the difference of the advancing contact angle θ_a^{ap} and receding contact angle θ_r^{ap} measured at TPPs where the respective CLs move against rubbing direction (c.f. Fig. 3). Figure 4a shows the variation of CAH against *RS*. It can be seen that CAH decreases with an increase in RS, and, as illustrated in Figure 4b, varies azimuthally against the rubbing direction. The hysteresis against rubbing direction is found to be greater than that in rubbing direction. This clearly indicates that the CAH of water on the rubbed PI surface is anisotropy. In general, a more hydrophobic solid surface exhibits a smaller CAH. So what we have got here shows that rubbing causes an increase in the wettability of the PI thin films. The appearance of anisotropy in the CAH indicates anisotropic wetting

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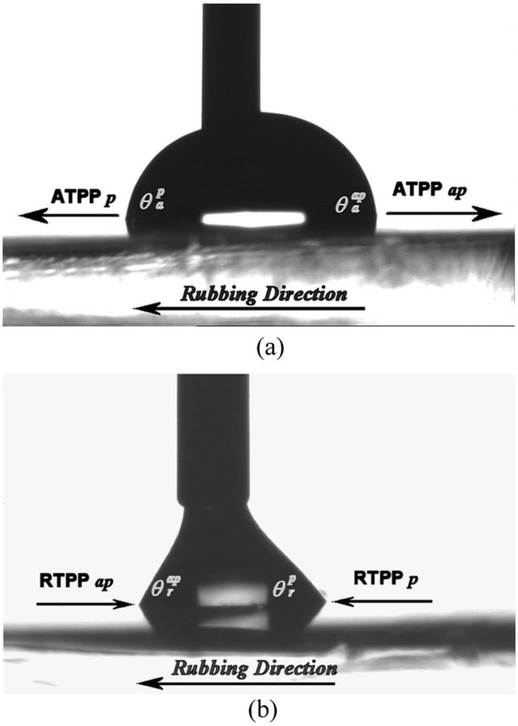

FIGURE 3 Images of profiles of a deionized water droplet (a) in advancing course, and (b) in receding course, respectively. θ_a^p and θ_r^p are advancing and receding contact angles measured when the tri-phase contact points ATPP_p and RTPP_p are moving in the rubbing direction in the advancing and the receding courses, respectively, whereas θ_a^{ap} and θ_r^{ap} are advancing and receding contact angles obtained when the tri-phase contact points ATPP_{ap} and RTPP_{ap} are moving against the rubbing direction in the advancing and the receding courses, respectively.

characteristics of the rubbed polymer surfaces. The hydrophobicity of rubbed PI in the rubbing direction is higher than that against the rubbing direction.

Roughness and chemical heterogeneity of the surface are usually considered as two major factors that determine the CAH. However, it has been shown that the effect of surface topography on the CAH is negligible when the surface roughness is not greater than 100 nm [9–11]. As the surface roughness of the rubbed PI films in the present study is very small, we omitted the effect of the roughness on the CAH. Besides, it was found that even on molecularly smooth surfaces CAH

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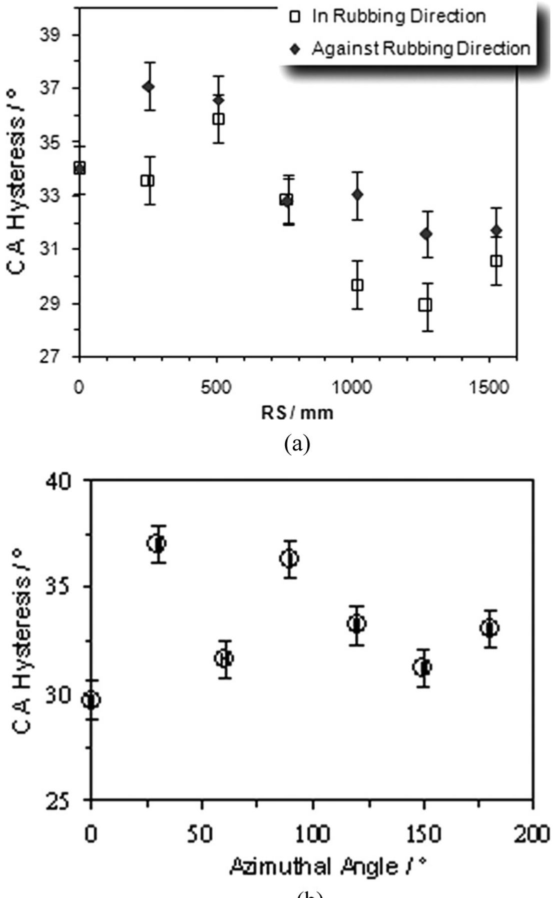

(a)

(b)

FIGURE 4 (a) Contact angle hysteresis of deionized water on rubbed polyimide thin films against rubbing strength. The hollow square spots represent hysteresis in the rubbing direction, whereas the solid diamond spots represent that against the rubbing direction. (b) Variation of contact angle hysteresis with azimuthal angle against the rubbing direction. The PI thin film was rubbed with a rubbing strength of 1016.67 mm.

can be quite significant [12,13]. So in many cases CAH cannot well be explained by surface roughness. Molecular level topography at outmost surface might be the key to elucidate CAH. The examination of the microscopic restructure of polymer at surface is outside of the scope of this study. Here we consider the effect of surface polarity on CAH.

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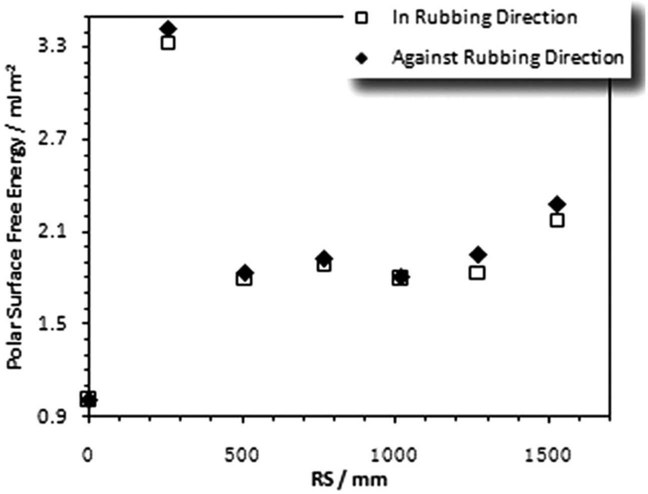

FIGURE 5 The variation of polar part surface free energy of polyimide thin films with rubbing strength. The hollow square spots are data for the polar surface free energy measured in rubbing direction, whereas the solid diamond spots are data for the polar surface free energy measured against rubbing direction.

We evaluated surface polarity of PI thin films using polar part of surface free energy. Figure 5 shows the variation in the polar part of surface free energies as a function of RS. The surface polarity of PI increases with RS. It can also be seen that the polarity in the rubbing direction is smaller than that against the rubbing direction. It is well known that the CA is very sensitive to the surface polarity, and a surface with a larger polarity exhibits lower hydrophobicity [14]. Comparing Figure 4a with Figure 5 one can find that the variation in the CAH of water on the rubbed PI corresponds with changes in the surface polarity. The increase in the surface polarity of rubbed PI was considered to result from a outwards reorientation of polar groups at the polymer surface [14,15]. It was also shown that rubbing caused polymer backbones to orient parallel to the rubbing direction [7,16]. A possible mechanism for the appearance of the anisotropy in the CAH is inferred as follows. The overall anisotropy in the CAH on the rubbed PI thin films may result from the anisotropic dispersion surface tension, which originates from a unidirectional orientation of the polymer backbonds, whereas the local orientation of the polar groups at outmost surface owing to the rubbing may be responsible for the difference in CAHs measured in and against the rubbing direction, respectively.

CONCLUSIONS

The CAH of DI water on the rubbed PI thin films has been investigated. Rubbing causes changes in the CAH. The CAH decreases with an increase in the RS. The CAH on the rubbed PI thin films is found to be anisotropic. In the rubbing direction PI surface exhibits a smaller CAH indicating a higher hydrophobicity. Rubbing causes restructure of functional chemical groups and reorientation of polymer chains at outmost surface leading to an asymmetry in surface polarity that may be responsible for the appearance of anisotropy in the wettability of rubbed PI thin films.

REFERENCES

[1] Cognard, J. (1982). *Mol. Cryst. Liq. Cryst.*, *78*(1), 1.

[2] Geary, J. M., Goodby, J. W., Kemtz, A. R., & Patel, J. S. (1987). *J. Appl. Phys.*, *62*, 4100.

[3] Becker, M. E., Kilian, R. A., Kosmowski, B. B., & Milynski, D. A. (1986). *Mol. Cryst. Liq. Cryst.*, *130*, 167.

[4] Filas, R. W. & Patel, J. W. (1987). *Appl. Phys. Lett.*, *50*, 1426.

[5] Zheng, W., Underwood, I., Macdonald, B. F., Cole, R. J., & Vass, D. G. (2004). *Mol. Cryst. Liq. Crys.*, *412*, 237.

[6] Ishihara, S., Wakemoto, H., Nakazima, K., & Matsuo, Y. (1989). *Liq. Cryst.*, *4*, 669.

[7] Arafune, R., Sakamoto, K., Ushioda, S., Tanioka, S., & Murata, S. (1998). *Phys. Rev. E*, *58*, 5914.

[8] Seo, D.-S. & Kobayashi, S. (1992). *Appl. Phys. Lett.*, *61*, 2392.

[9] Zheng, W., Lu, C.-H., & Ye, Y.-C. (2008). *Jap. J. Appl. Phys.*, *47*, 1651.

[10] Morra, M., Occhiello, E., & Garbassi, F. (1990). *Adv. Colloid Interface Sci.*, *32*, 79.

[11] Heng, J. Y. Y., Bismarck, A., Lee, A. F., Wilson, D., & Williams, D. R. (2006). *Langmuir*, *22*, 2760.

[12] Chibowski, E. (2003). *Adv Colloid Interface Sci.*, *103*, 149.

[13] Lam, C. N. C., Wu, R., Li, D., Hair, M. L., & Neumann, A. W. (2002). *Adv Colloid Interface Sci.*, *96*, 169.

[14] Lee, K.-W., Lien, A., Stathis, J. H., & Peak, S.-H. (1997). *Jpn. J. Appl. Phys.*, *36*, 3591.

[15] Lee, K.-W., Paek, S.-H., Lien, A., Durning, C. J., & Fukuro, H. (1996). *Macromolecules*, *29*, 8894.

[16] Arafune, R., Sakanoto, K., & Ushioda, S. (1997). *Appl. Phys. Lett.*, *71*, 2755.

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