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Surface Wetting Characteristics of Rubbed Polyimide Thin Films

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1. Introduction

Amide and imide based polymers are a catalogue of versatile materials that have a wide range of applications from scientific interests to commercial products because of their great thermal stability, excellent electric properties, highly mechanical strength, and superior chemical resistance (Sroog, 1976). In a thin film form, polyimides have been found to have many important uses in optoelectronic and photonic applications. One of the most successful examples in industrial applications is the use of polyimide thin films as molecular alignment layers in liquid crystal displays. By unidirectionally rubbing a thin layer of polyimide coated on a substrate a template with some form of anisotropy can be created. When a liquid crystal is put in contact with the rubbed polyimide film, the interactions between the surface and the liquid crystal molecules degenerate into actions with orientational features. As a result, liquid crystal molecules are driven to orient in a desired direction. Because of its outstanding ability and reliability in molecular alignment, the easiness in processing and cost effective, rubbing polyimide becomes the standard liquid crystal alignment technique, and rubbed polyimide thin films as efficient alignment layers are, up to date, still irreplaceable components in modern LCDs.

On the other hand, a surface process will cause changes in chemico-physical and physicochemical properties at outmost surface of a polymer, and these changes, in turn, will induce many interesting surface phenomena, and impose a number of interesting aspects for scientific research and may lead to engineering applications. In many circumstances, a comprehensive knowledge of surface properties of polyimide thin films is of prime importance for elucidating mechanisms behind surface phenomena. A number of experimental results have shown that rubbing causes polymer chains to become oriented unidirectionally along the rubbing direction (Sawa et al., 1994; Sakamoto et al., 1994; Hirose, 1996; Arafune, 1997), and the anisotropy in the distribution of the polymer chains is considered to be the main factor responsible for liquid crystal alignment. 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. The changes in surface characteristics of polyimide thin films due to mechanical rubbing must be reflected by surface wettability of the polymer

films. There are some reports on the influence of rubbing on the surface energy of the polyimide (Lee et al., 1996; Ban & Kim, 1999). However, very little work has been done on the anisotropic surface wettability of rubbed polymers.

In this chapter, attention has been concentrated on the influence of mechanical rubbing on the surface wettability of polyimide thin films. As unidirectional rubbing creates a preferential direction on polyimide surface, how a liquid wets the surface about this direction is an interesting aspect. An insight into the effects of mechanical rubbing on surface wetting characteristics of polyimide will allow us to reveal some key correlations between inter- and intra-molecular interactions at the interface.

2. Surface energetic characteristics of polymers

2.1 Surface energy and surface free energy of continua

For a continuum, in either a solid state or a liquid form, in thermal equilibrium state, all interactions that act upon each molecule in the bulk are balanced. When a surface is created, the molecules at the surface lose the balance, which they initially possessed in the bulk and extra forces are required to maintain the molecules at the surface in the stable state. The unbalance forces for the molecules at the surface lead to additional energy at the surface, and this additional energy at the surface is known as surface energy. Microscopically, surface energy of a solid state matter is the reversible work per unit area required for the creation of a new surface, and quantifies the disruption of intermolecular bonds that occurs when the surface is created. In nature, the surface energy originates from a break in the physicochemical uniformity in the bulk. The surface energy may therefore be referred to the excess energy at the surface of a material compared to that in the bulk.

A surface is a physical boundary that separates the two continua. The two continua can either be different materials or the same material in different phases. At the surface, molecules are in relatively stable state maintained by various intermolecular forces. When a flat membrane of a continuum is stretched, the force, F , involved in stretching the membrane is

$$F = \gamma L, \quad (1)$$

where γ is the surface tension. Surface tension is therefore a measure, in forces per unit length with a dimension of N/m, the extra force stored at surface to balance the difference between the interactions in the bulk and at the surface respectively.

The same issue can be approached based on the thermodynamic consideration. In order to increase the surface area of a continuum by an amount, dA , the amount of work, dW , is needed. This work can be thought to be the potential energy stored at the surface. When the surface is stretched by dx , the work, dW , involved in increasing the surface by the length is,

$$dW = F dx = \gamma L dx = \gamma dA = \sigma. \quad (2)$$

The surface free energy is then defined as

$$\sigma = \frac{dW}{dA}, \quad (3)$$

with a dimension of J/m².

Comparing Eq. 3 to Eq. 2, it can be found that surface free energy has the same value as surface tension does, but with different dimensions. The two physical quantities are interchangeable in terms of numerical value. However, the physical meanings behind the two quantities are different: one represents the energy stored at the surface, while another measures force stored in unit length at the surface.

Regarding surface energy of continua, one must distinguish between solids and liquids. For liquids, constituent atoms can move from the surface with the higher level of energy into the bulk of liquid with the lower energy, so that the area of the free surface can be significantly changed, and the surface free energy can be determined by connecting the energy with the area of contact between phases. In the case of solids, the geometry of the solid and the mechanical state of the solid may affect the apparent value of the surface energy. In particular, the surface energy inferred from the creation of a finite surface by peeling or cleavage is not necessarily equal to that of exposed surface when an infinite solid is cut along a plane and the resulting half-spaces are drawn apart to infinity, with their surfaces kept parallel at all times (Yudin & Hughes, 1994). For solids, usually surface tension does not equal to the surface free energy in value (Vanfleet & Mochel, 1995; Yu & Stroud, 1997).

2.2 Extra aspects in surface energy of polyimide

In general, polymers are the sort of uniform media in which those periodically spatial arrangements of molecules or molecular groups usually seen in an inorganic solid disappear. However, the physical origin of the surface energy remains the same: it arises from a break in the continuity at the surface.

The surface free energy of polyimides is related to chemistry of the surface, and significantly influenced by the nature of the functional group packing at the surface. For instance, Fluorination of polymers causes dramatic changes in their surface characteristics with respect to the corresponding fully hydrogenated materials. Perfluorinated polymers show low intra- and inter-molecular interactions and exhibit low surface free energy (Smart, 1994). While fluorine atoms lower the surface energy of polymer, oxygen raises the surface energy of most polymers. The technique most widely used to oxidization of polymer surface is to bombard polymer surface using oxygen plasma. The oxygen plasma bombardment of polyimide film can cause some atoms to be sputtered away and substituted by oxygen atoms. This substitution produces highly polar groups at the surface by breaking the imide and benzene rings and forming new polar species of carbon-oxygen and carbon-nitrogen-oxygen , and raises the surface energy (Naddaf et al., 2004).

The surface free energy of polyimides may be modified by polymerization of the precursors. For polyimide, the ratios of different functional groups vary with the degree of imidization (Zuo et al., 1998). Thus the degree of imidization can affect the surface energetic state of the resultant polyimide (Flitsch & Shih, 1990; Sacher, 1978; Inagaki et al., 1992). With the development of the imidization, more polar functional groups such as amide and acid become less polar imid groups, and this leads to a polyimide film with lower surface free energy. For thermal set polyimides, the degree of imidization is dependent on curing temperature and the duration the amide acid agent is kept at the temperature. Therefore, a proper curing temperature is crucial for imidization of amide acid. The curing temperature, depending upon the type of amic acid precursor, can be between 180 ~ 400°C, and the duration for thermal curing is normally one hour.

2.3 Wet a polymer surface

As long as surface wetting is concerned, at least one liquid and one solid surface are involved. Wetting a solid surface by a liquid is a surface phenomenon in which the liquid spreads on the surface and tends to cover it. Surface wetting has been thought to be a thermodynamic process which ends at equilibrium state of the system. According to their chemical activities, wetting of solid surfaces can be classified into two categories: non-reactive wetting, in which a liquid spreads on a substrate with no chemical reaction or absorption, and reactive wetting which is influenced by chemical reactions between spreading liquid and substrate material. Depending upon its basis – how the process is initiated and driven, wetting can be classified into two types: spontaneous spreading, which is defined as the spreading of a liquid on a solid by itself without any external interference; and driven spreading which is initiated and driven by some kind of external actions. Within the frame of this chapter, the discussions are focused on non-reactive spontaneous wetting.

2.3.1 Static contact angle

For thermal dynamic system, if the space is filled up with one continuum, the assembly of all co-contact points at which two thermal dynamic phases join together forms a surface; the assembly of all co-contact points at which three phases join together can form a line; the co-contact points for four phases joining together cannot contact each other in the real space. Therefore, topologically, the spatial boundary that separates two thermal dynamic phases is a two dimensional surface; when one more phase joins in, the boundary that separates the three phases degenerates to one dimensional line, and the boundary that separates four phases becomes isolated dimensionless points. There will be no real boundary that can connect more than four thermal dynamic phases in a real space.

When a small amount of a liquid is put in contact with a flat polymer surface, the tri-phase boundary that separates the three phases, i.e. solid state (*S*) of the substrate, liquid state (*L*) of the liquid droplet and vapour state (*V*), is known as the contact line (c.f. Fig. 1). If the substrate is chemical homogeneous and the surface is uniform, the contact line is a circle. The plane containing the normal of the solid surface and cutting through the apex of the liquid droplet is known as the meridian plane. The contact angle is defined as the angle between the solid surface and the tangent of the liquid at the tri-phase contact point in the meridian plane, through the liquid phase.

Fig. 1. a) A liquid droplet is put in contact with a solid surface, and b) the main features of the liquid droplet.

2.3.2 Contact angle hysteresis

Contact angle measurement must be carried out on an ideal solid surface, which is smooth, homogeneous, chemically and physically inert with respect to the probe liquid. Actually, no real surface exists that entirely satisfied to these exigencies. For dynamic liquid droplets on polymer surfaces, a range of contact angles appear along the contact line. Among all observed contact angles for a liquid droplet on a polymer surface, the largest one is advancing contact angle θ_a which is the contact angle measured while the volume of the liquid droplet is increasing and the contact line is moving outwards, whereas the smallest one is receding contact angle which is the one measured while the volume of the liquid droplet is decreasing and the contact line moving inwards (Fig. 2). The phenomenon of existence of multiple contact angles for the same probe liquid is known as hysteresis. The difference between advancing and receding contact angles is defined as contact angle hysteresis

$$h = \Delta\theta = \theta_a - \theta_r . \quad (4)$$

Fig. 2. Dynamical profiles of a liquid droplet on a JASL-9800 polyimide surface during (a) the advancing cause in which extra amount of liquid is added on, and (b) the receding cause in which liquid is withdrawn from the droplet, respectively. θ_a and θ_r are contact angles measured during the advancing and the receding causes, respectively.

The contact angle hysteresis could be due to substrate surface roughness and heterogeneity, impurities adsorbing on to the surface, rearrangement or attraction of the surface by the solvent, etc. It is generally observed that cleaner the surface, smaller the contact angle hysteresis. For a clean and chemically homogeneous surface, it is thought that roughness and chemical heterogeneity of the surface are major factors that cause the contact angle hysteresis (Li, 1996; Chibowski & Gonzalez-Caballero, 1993). Busscher et al. showed that surface roughening tends to increase the observed contact angle as far as the contact angle on the smooth is above 86° , whereas contact angle decreases if on a smooth surface the angle becomes 60° (Busscher et al., 1984). For polymer surfaces, the surface swelling may become an important factor that contributes to contact angle hysteresis.

In wetting a rough and chemically homogeneous solid, two different effects may be observed (Kamusewitz et al., 1999): (i) the barrier effect, in which the contact angle hysteresis increases with growing roughness, and (ii) the capillary attraction/depression. In

the case of a pure barrier effect, advancing contact angle increases by the same amount as receding contact angle decreases with growing roughness. Thus the equilibrium contact angle θ_e can be given by: $\theta_e = (\theta_a + \theta_r)/2$. Hence the relationship between static wetting and the dynamic one can be expressed as

$$\begin{cases} \theta_a = \theta_e + \frac{\Delta\theta}{2} \\ \theta_r = \theta_e - \frac{\Delta\theta}{2} \end{cases} \quad (5)$$

As a result of capillary attraction or depression of grooves in the surface, for $\theta_e < 90^\circ$, wettability will be worse on a rough surface than on a corresponding smooth surface. It is reported that, capillary effect causes an increase in both advancing and receding contact angles with growing roughness for $\theta_e < 90^\circ$ and an opposite effect is observed if $\theta_e > 90^\circ$. Only at $\theta_e = 90^\circ$, capillary has no effect.

2.3.3 Wettability

In wetting a polymer surface with a liquid, one of the following phenomena may take place: the liquid spread a little or may not spread at all, a case of non-wetting; the liquid spreads continuously and covers the entire substrate with a thin film of the liquid, the case is known as complete wetting; the liquid droplet spreads partially to some extent – a case generally referred as partial or incomplete spreading. Each of these phenomena depicts the degrees that a polymer surface may be wetted by a liquid. The degree that a polymer surface is wetted by a liquid is defined as the wettability of the surface wetted by the liquid. Wettability describes the tendency for a liquid to spread on a polymer surface, i.e. the degree of intimate contact between a liquid and the polymer surface.

There is no direct measure of wettability. In practice, the wettability of a polymer surface is evaluated by examining the profile of a probing liquid droplet which is put in contact with the polymer, and characterized by contact angle. For example, the two distinct extreme equilibrium regimes may be characterized by the value of contact angle as: complete wetting with the contact angle $\theta = 0$, or absolute non-wetting with the contact angle $\theta \rightarrow 180^\circ$. When the contact angle is measured with a finite value $0 < \theta < 180^\circ$, the surface is then partial wetted by the liquid.

In reality, a complete non-wetting is rarely seen, and most surfaces are partially wettable. In engineering, the wettability of a solid is classified as

$$\begin{cases} \theta > 90^\circ : \text{unwettable} \\ 0 < \theta < 90^\circ : \text{partially wettable} \\ \theta = 0 : \text{completely wettable} \end{cases} \quad (6)$$

Fig. 3. When wetting a solid surface, three cases of the spreading of a wetting liquid are normally seen: a) non-wetting ($\theta > \pi/2$), b) partial wetting ($\theta < \pi/2$), and c) complete wetting ($\theta = 0$).

If the probing liquid is water, a wettable surface is known as a hydrophilic (or lyophilic) surface; whereas an unwettable surface is referred to as a hydrophobic (or lyophobic) surface.

2.4 Evaluation of wetting characteristics of polymer surface

2.4.1 Measurement of surface free energy

The driving force for the spreading a wetting liquid on a solid surface can be written as:

$$F_d(t) = \gamma_s - \gamma_{SL} - \gamma_L \cos \theta(t), \quad (7)$$

where θ is contact angle, γ_s , γ_{SL} and γ_L are interfacial tensions in solid-vapour, solid-liquid and liquid-vapour interfaces, respectively. Eq. 7 is also known as the equation of state. γ_{SL} is a parameter that connects the properties of the solid and probing liquid. At thermodynamic equilibrium, the energy of the system must be stationary and the dynamic driving force is cancelled out, i.e. $F_d = 0$, due to a balance between all interactions at the surface, and as a result, the spreading of the liquid droplet comes to rest. These conditions lead to the famous Young's equation

$$\gamma_s - \gamma_{SL} = \gamma_{LV} \cos \theta. \quad (8)$$

Eq. 8 shows that contact angle θ is defined and is decided by the surface and interfacial energies. This indicates the importance of surface energetic states on determining the surface wetting characteristics. Therefore, the measurement of surface free energy forms an important part of the evaluation of surface wetting properties of a polymer surface.

Although it draws the basic principles for surface characterization, Young's equation cannot be solved straight away. Usually, $\gamma_{LV} \equiv \gamma$ can be obtained by separate measurements. Thus we are left with two unknown variables γ_{SL} and γ_s with only one datum θ .

A number of thermodynamic approaches have been proposed to determine γ_s and γ_{SL} . Detailed descriptions about these approaches can be found in literature (de Gennes P G, 1985; Gindl et al., 2001; Kumar & Prabhu, 2007). We adopt geometric mean approach for this study.

Zisman (Zisman, 1963) introduced the concept of critical surface free energy γ_c , which is defined as the surface tension of a probing liquid which fully wets the surface ($\cos \theta = 1$). The value of γ_c is determined from empirical investigations, and contact angles of the liquids of a homologous series of organic compounds on a solid are measured. The cosine of the contact angles is then plotted against the surface tension γ_L of the liquid, and this forms a straight line which can be described with a following relationship,

$$\cos \theta = 1 - b(\gamma_L - \gamma_c), \tag{9}$$

where b is the slope of the regression line. Extrapolation of this line to the point of $\cos \theta = 1$ yields the value of $\gamma_L = \gamma_c$ at the point. Combining Eq. 8 with Eq. 9, one can obtain

$$\gamma_s = \frac{(b\gamma_c + 1)^2}{4b}. \tag{10}$$

Zisman’s method is the geometric mean approach.

Fig. 4. A Zisman plot for estimating surface tension of a liquid.

Later an idea to partition of surface free energy into individual components includes the assumption that the quantity γ_{SL} is determined by various interfacial interactions that depend on the properties of both the measuring liquid and the solid-liquid of the studied solid. In his pioneer work, Fowkes assumed that the surface free energy of a surface is a sum of independent components, associated with specific interactions:

$$\gamma_s = \gamma_s^d + \gamma_s^p + \gamma_s^h + \gamma_s^i + \gamma_s^{ab} + \dots, \tag{11}$$

Where $\gamma_s^d, \gamma_s^p, \gamma_s^h, \gamma_s^i$, and γ_s^{ab} are the dispersion, polar, hydrogen bond, induction, and acid-base components, respectively. According to Fowkes, the dispersion component of the surface free energy is connected with the London interactions, arising from the electron dipole fluctuations. These interactions occur commonly in the matter and result from the attraction between adjacent atoms and molecules. The London forces depend on the kind of mutually attracting elements of the matter and are independent of other types of interactions. The remaining van der Waals interactions have been considered by Fowkes as a part of the induction interactions. This method is not widely accepted due to its complex.

With the consideration of the idea of the surface free energy partition, Owens and Wendt improved Zisman's fundamental work and developed a new method which has been widely accepted for measurement of contact angle for evaluation of surface free energy measurement (Owens & Wendt, 1969). In the Owens-Wendt method, it has been assumed that the sum of all the components occurring on the right-hand side of Eq. 6 except γ_s^d , can be considered as associated with the polar interaction (γ_s^p), and the equation of state can be written as

$$\gamma_{sl} = \gamma_s + \gamma_L - 2 \left(\sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^p \gamma_L^p} \right). \quad (12)$$

The combination of Eq. 8 and Eq. 12 leads to

$$\frac{(1 + \cos \theta) \gamma_L}{2 \sqrt{\gamma_L^d}} = \sqrt{\gamma_s^p} \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_s^d}, \quad (13)$$

The form of the Eq. 13 is of the type $y = bx + m$. For a certain solid, the surface free energy is assumed to be constant without varying with different probing liquids. One can graph $(\gamma_L^p)^{1/2} / (\gamma_L^d)^{1/2}$ vs $\gamma_L(1 + \cos \theta) / (\gamma_L^d)^{1/2}$. The slope will be $(\gamma_s^p)^{1/2}$ and the y-intercept will be $(\gamma_s^d)^{1/2}$. The total free surface energy is merely the sum of its two component forces.

2.4.2 Experimental determination of surface free energy

Young's equation explains theoretically the necessary conditions for a liquid drop to reside on a surface statically. The measurement of contact angle is then a practical way to obtain surface free energy. Depending upon how the probe liquid wets the surface to be tested, two different approaches are commonly used for the measurement of contact angles, goniometry and tensiometry. Tensiometry involves measuring the forces of interaction as a solid is contacted with a probe liquid whose surface tension is known. This technique is particularly suitable for the porous surfaces which may absorb the wetting liquid. Goniometry involves the observation of a sessile drop of test liquid on a solid substrate. Analysis of the shape of a drop of test liquid placed on a solid is the basis for goniometry, and this is particularly useful for evaluation of contact angle hysteresis. Goniometry is the technique we used to observe the wetting characteristics of rubbed polyimide films.

The equipment used for goniometrical measurement contact angles is a DSA100 which is commercially available from Krüss. During measurement, droplets of about $2 \mu\text{l}$ of test liquids are dispensed onto the polymer surface to be tested, and monitored with a charge-coupled device (CCD) camera. The images of test liquid captured are then analyzed with computer software which is written based on Owens-Wendt model (described by Eq. 13).

In order to detect unusual features created due to rubbing of polyimide films, the surface tension meter has been modified to have a stage, which can be rotated azimuthally, mounted.

3. Breaking down surface uniformity of polyimide thin films due to rubbing

3.1 Preparation of polyimide thin films

3.1.1 Coating a polymer precursor on to substrate

Several techniques are available for coating polyimide resin onto a surface. The most popular and reliable one is the spin-coating technique, which is also the one we used to prepare polyimide thin films for our studies. Spin coating provides uniform, pinhole free coating polymer layer on a substrate. Any standard photoresist spin coating technique can be used for the coating of polyimide. The factors which affect the thickness uniformity and overall quality of the final coating can be listed as following:

- substrate preparation (cleaning)
- Volume of solution dispensed
- Substrate acceleration
- Final spin speed
- Spin time
- environment conditions (e.g. Temperature, humidity, exhaust air flow rate, etc.)

Coating thickness for a solution with a particular concentration will vary as a function of spin speed and spin time. A spin speed of at least 1000 rpm and a spin time of at least 30sec are recommended for applications in which surface uniformity is of primary concern. If the packed resin is thinned, the diluted solution should be left still for de-bubbling. All dispensing should be as close as possible to avoid bubble formation. Tiny bubbles in the solution will cause comet-like defect in the coated film (cf. Fig. 5). The volume of solution dispensed should remain constant for each substrate to insure substrate to substrate uniformity.

Fig. 5. A 'comet' defect in polyimide coating film due to a micro-bubble in the resin solution, and a defect resulted from a solid particle on the substrate.

3.1.2 Imidization

Before thermal imidization, the amic acid solution coated on the substrate is soft bake to remove the residual solvent. The soft baking process also provides the precursor with sufficient chemical resistance and adhesion so that the coating will not be attacked.

The soft baking of precursor is carried out by putting the coated substrates on a hot plate at a temperature in a range of 60°C to 105°C for 30 – 60 min. The substrates should remain in a horizontal position during this process to avoid the reflow of the coated solution. An insufficient drying can result in the attack of the coating by some contaminants, such as residual thinner and some organic solvent, causing defects on the coating surface and/or the formation of pinholes. A too high temperature soft-baking can initiate partial crosslinking and /or imidization.

The minimum final cure temperature is dependent upon the type of amic acid resin used. For most polyimide precursors, imidization can occur when temperature exceeds 100°C, and the curing temperature for imidization can be within a wide range from 150°C to 300°C. To achieve a good imidization, amic acid is usually cured at 200°C for a period of 1 hour. The curing temperature can affect the surface free energy of the final polyimide film because of the correlation of the degree of imidization to the curing temperature. It has been shown that the degree of imidization increases with curing temperature (Lee et al., 1996; Zuo et al., 1998). The effect of the degree of imidization on the dispersed part of free energy, which relates to the long range molecular interactions, is small and can be ignored. However, the polar part of the surface free energy is strongly influenced by the degree of imidization. With the development of the imidization, more polar functional groups such as amic acid become less polar imid groups, and this causes a significant decrease in the strength of the polar part free energy. As a result, the surface free energy of the resultant polyimide film is reduced.

3.1.3. General features of polyimide thin films coated on Indium-Tin-Oxide glass substrates

During cure, a net weight loss up to 50% may occur to the coating film accompanied by a corresponding decrease in coating thickness. With this imidization induced film shrinkage being taken into account, the thickness of the final polyimide films is thought to be decided by the viscosity of the amic acid solution and the spin speed of the substrates. Figure 6 shows the thickness of polyimide films prepared from a commercial 5 wt% amide-acid solution JALS-9800 (JSR, Japan) against spin speed. The curing temperature for imidization was set at 240°C.

Fig. 6. Thickness of polyimide films vs spin speed of the substrate.

The atomic force microscopy (AFM) examination of polyimide films coated on the ITO glass substrates reveals that the surface of the polymer films are flat and smooth. As far as the surface characteristics of a thin polymer film coating on a solid surface is concerned, it is necessary to learn whether the measured results are distorted by the effects of the material beneath the polymer film. Experimental results reveal that surface free energy of the polyimide films is rather stable when the thickness of the polymer films is within the range from 80 – 150 nm (Fig. 7). These polyimide films were produced by coating the amic acid solution onto substrates which were spinning at speed ranged from 2000 to 4000 rpm (c.f. Fig. 6). We preferentially set the spin speed of the coater at 4000 rpm, and the polyimide thin films produced are 100 nm thick. The surface free energy of the films before further process is measured to be $45.532 (\pm 2.794) \text{ mJ/m}^2$.

Fig. 7. Surface free energy of polyimide films vs film thickness.

3.2 Rubbing process

The mechanical rubbing of polyimide films is carried out using a rubbing machine. An in house made rubbing machine is schematically illustrated in Fig. 8. The rubbing machine consists of a rotating drum which is wrapped with a piece of velvet textile. The sample holder is mounted on a translationally movable flat stage. The rubbing strength is the most important parameter for the rubbing process. It is a measure of the strength of the interaction between the rubbing textile and the polymer thin film, and depends on many factors such as the pressure of the rubbing textile applying to the surface, the hardness of the fibre of the velvet etc. A satisfactory method to determine mechanical rubbing strength is yet to be developed. In engineering, the rubbing strength is evaluated using following equation

$$RS = N \cdot \Lambda \left(\frac{2\pi R \omega}{v} \pm 1 \right), \quad (14)$$

where N is the number of rubbing cycles, Λ is the pile impression of the velvet fibres, ω is the rotation speed of the drum, R is the radius of the drum, and v is the translational speed of the sample holder. The sign before the factor of 1 indicating the relative moving direction between the sample and the rubbing velvet: “-” means the sample moving against rubbing velvet, whereas “+” means both the sample and the rubbing velvet moving in the same direction. The RS calculated using Eq. 14 is also known as specific rubbing length because it has a dimension of length.

Before rubbing the polyimide films are rather flat and smooth. The average roughness of the polyimide film, measured using AFM, is 0.33 nm. Mechanical rubbing is a crude process during which large quantities of polymer material in some regions may be excavated leading to considerable damage to a polymer surface. A macroscopic effect in a microscopic scale of the mechanical rubbing is the formation of microgrooves on the polymer surface.

Fig. 8. An in house made rubbing machine with following main features: the radius of the drum $R = 30$ mm, the rotation speed of the drum $\omega = 135$ rpm, the translational speed of the stage for the sample holder $v = 30$ mm/min, average length of fibre of velvet = 1.8 mm.

For a unidirection rubbing, the microgrooves, which can be clearly seen in an AFM image (Fig. 9), are parallel to the rubbing direction. The geometric dimension of the grooves and the density of the groove on the surface are determined by the physical characteristics, such as the length, the elasticity, the surface features etc., of the rubbing velvet, and the number of rubbings (Zheng et al., 2004). The surface roughness increases with rubbing strength.

Fig. 9. Atomic force microscopic image of a rubbed polyimide surface. The polymer film was rubbed 4 times by a velvet with a pile impression of 0.3 mm.

The changes in the surface roughness of the polyimide film due to rubbing may not be significant (Zheng et al., 2009). For JASL-9800, with the pile impression of rubbing velvet being set at 0.3 mm, the average surface roughness of the polymer films, which are rubbed up to seven times, is below 1.0 nm (Fig. 10). A reconstruction in surface topography has been observed. The surface roughness increases with the first two rubbing cycles, and drops when the film is rubbed three times; then increases as the rubbing continues and peaks at the completion of the fifth rubbing, then drops again when the polymer film is further rubbed. The surface roughness increases and decreases alternately with the rubbing cycle. The topographic reconstruction can be explained as follows. Rubbing causes the formation of grooves at the surface of the polyimide film. Although the grooved surface will lead to only a small variation in pile impression, and hence rubbing strength, across the surface, the peaks in the corrugated surface suffer higher abrasion rates than troughs leading to a reduction in surface roughness. Subsequent rubbings will cause more polyimide material to be excavated from the surface leading to a rougher surface. As rubbing continuing, a new course of flatness is started. It seems that with the polyimide (JALS-9800) used for the observation the repeating period in the variation of surface roughness with rubbing is three rubbing cycles.

Fig. 10. Surface roughness of rubbed polyimide films against rubbing strength.

The mechanical rubbing can force polar groups to reorient at the surface and thus leads to changes in polar strength of the polyimide surface (Lee et al., 1996). The way the polar strength changes depends on the chemical properties of the polyimide materials. For the polyimides whose surface polar strength can be enhanced by rubbing, the surface free energy will increase with rubbing strength (Ban & Kim, 1999). For polyimide thin films produced using JALS-9800, increasing rubbing strength, as illustrated in Fig. 11, results in a decrease in the surface free energy.

Fig. 11. The surface free energy of polyimide thin films against the number of rubbing cycles for different pile impression of the rubbing velvet.

3.3 Anisotropic wettability of rubbed polyimide films

The formation of the grooved surface clearly indicates that the topographical uniformity of the surfaces of the polyimide films has been broken, and anisotropy in surface topography

has been created. 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. The unidirectional rubbing produces grooves, which are parallel to the rubbing direction, on the polyimide surface. So the rubbing creates a preferential direction, which is parallel to the rubbing direction, on the surface. It is nature to take the rubbing direction as reference direction for the study of surface anisotropy.

For a solid state surface, several phenomena, such as the surface roughness, chemical heterogeneities, surface restructuring, material swelling and dissolution etc., can contribute to the contact angle. In many cases, the surface roughness and chemical heterogeneities are considered as major factors that affect the contact angle. However, for rubbed polyimide films, surface restructure may have significant effect on contact angle. The effect of the orientation of the polymer chains and rearrangement of polar groups at the surface due to rubbing should be reflected by wetting characteristics of the polymer films. The modified surface tension analyzer DSA100, equipped with a rotating state, enable us to carry out the observation. A static water droplet on the rubbed polyimide films exhibits a different contact angle in different viewing direction. Fig. 12a shows azimuthal variation in the contact angel of a deionized water droplet resided statically on the rubbed polyimide surfaces. The amplitude of the contact angles varies with rubbing strength. This indicates that wettability of the polyimide can be changed by mechanical rubbing. However, the profiles of the water droplet, evaluated by the curve of the contact angle, on polyimide films rubbed with different rubbing strength are similar. Therefore the anisotropy in wettability of rubbed polyimide about the rubbing direction is evident. The difference in contact angles measured respectively towards and against the rubbing direction is marked (cf. Fig. 12b).

Fig. 12. (a) Variation of contact angles of deionized water on rubbed polyimide thin films against azimuthal angle for different rubbing strength. (b) Variation of contact angle of deionized water with rubbing strength measured at tri-phase points towards and against rubbing direction respectively.

It was suggested that the effect of surface roughness on the contact angle can be omitted when the surface roughness is not greater than 100nm (Morra et al., 1990). Heng et al. (Heng et al., 2006) confirmed that the effect of surface roughness on contact angle hysteresis for

single crystalline paracetamol was negligible. For rubbed JASL-9800 films displayed here, the surface roughness is less than 1 nm. The effect of the surface roughness on the contact angle can be omitted. The evidence that support this argument can be found from the experimental results. For the parallel grooved surface, maximum surface roughness appears in the direction perpendicular to the grooves. The observed results, which show that the maximum contact angle, as illustrated in Fig. 12a, does not necessarily appear in the direction perpendicular to the rubbing direction, demonstrate that surface roughness of the rubbed PI under studying is not a decisive factor that determines the contact angle, and the anisotropic wettability of rubbed polyimide is resulted from other mechanisms rather than the geometrical surface topography.

3.3 Anisotropy in contact angle hysteresis

In principle, the measurement of static contact angle provides an effective means to evaluate wettability of a solid surface. In practical, however, it is often difficult to measure the static contact angle since the tri-phase system can hardly reach thermodynamic equilibrium in a laboratory environment, thus the volume of the probe liquid is changing all the time. In many cases, a dynamic analysis, in which the contact angle hysteresis is examined, can provide results which are more closed to the true wetting characteristics of a surface.

In order to examine dynamical wetting characteristics of the rubbed polyimide films, a drop of 2 μl deionized water was initially dispensed onto the polyimide surface, then extra deionized water is added to the droplet at a rate of 1 $\mu\text{l}/\text{min}$ and the advancing contact angle is measured during the contact line of the deionized water at the surface was moving outwards, whereas the receding contact angle was determined during the deionized water is withdrawn from the droplet and the contact line of the water moving inwards. For an unrubbed JSAL-9800 film, the contact angle hysteresis is measured to be 34.0° , with an advancing contact angle 86.8° . The contact angle hysteresis is independent of azimuthal angle indicating that the wettability of the polyimide film is symmetric. This is expected as there is no preferential direction on a uniform polyimide surface.

The profiles of a water droplet on a rubbed polyimide in both advancing and receding curves are asymmetric. In the advancing course, as illustrated in Fig. 13a, more water accumulated on the side of the droplet that the contact line move against rubbing direction, while in the receding course (cf. Fig. 13b), on the side of the droplet the contact line moves against the rubbing direction, the movement of the contact line is hindered and the droplet was stretched and elongated.

In the case of rubbed polyimide films, in addition to the movement of the contact line, the moving direction of the contact line to the rubbing direction must also be taken into account when evaluating contact angle hysteresis. The parallel contact angle hysteresis h_p is determined by subtracting the parallel receding contact angle θ_r^p measured at the tri-phase point, which is moving towards rubbing direction in the receding curve, from the parallel advancing contact angle θ_a^p measured at the tri-phase point which is moving towards the rubbing direction in the advancing curve, whereas the anti-parallel contact angle hysteresis h_{ap} is given as the difference between the anti-parallel advancing contact angle θ_a^{ap} measured at the tri-phase point which is moving against the rubbing direction and anti-parallel receding contact angle θ_r^{ap} measured at the tri-phase points which are moving against the rubbing direction during receding curve. Therefore, parallel contact angle hysteresis h_p and anti-parallel contact angle hysteresis h_{ap} are defined as

$$\begin{cases} h_p = \theta_a^p - \theta_r^p \\ h_{ap} = \theta_a^{ap} - \theta_r^{ap} \end{cases} \quad (14)$$

Notice that θ_a^p and θ_r^p (and also the θ_a^{ap} and θ_r^{ap} pair) are not at the same side of the droplet. This is due to the reversal of the moving direction of the tri-phase points with reference to the rubbing direction with the dynamic liquid droplet being switched over between the advancing and the receding courses.

Fig. 13. Images of profiles of deionized water droplet on the surface of a rubbed polyimide film in (a) advancing course and (b) receding course, respectively. θ_a^p and θ_r^p are advancing and receding contact angles measured when the trip-phase contact point $ATPP_p$ and $RTPP_p$ are moving in the rubbing direction in the advancing and receding courses, respectively, whereas θ_a^{ap} and θ_r^{ap} are advancing and receding contact angles obtained when the tri-phase points $ATPP_{ap}$ and $RTPP_{ap}$ are moving against the rubbing direction in the advancing and the receding courses, respectively.

The contact angle hysteresis varies with the rubbing strength. For JASL-9800, an increase in rubbing strength causes both parallel contact angle hysteresis and anti-parallel contact angle hysteresis to decrease. In general, a small contact angle hysteresis corresponds to a less polar surface, i.e. a more hydrophobic surface. The variation in wetting characteristics with rubbing strength is a well known phenomenon which has been observed by other researchers. What is interesting here is that the parallel contact angle hysteresis is different from the anti-parallel one indicating the anisotropy in wettability of rubbed polyimide films. This anisotropy in wettability can be clearly seen in Fig. 14.

A macroscopical effect of a mechanical rubbing in a microscopical scale is the formation of grooves on the surface of polyimide films. The surface with parallel grooves exhibits anisotropy in surface topography with a preferential direction that is parallel to the grooves. The anisotropy created due to a unidirectional geometrical structure is known as form anisotropy. The form anisotropy was once thought to be the main cause that was responsible for some interfacial phenomena such as a unidirectional alignment of liquid crystal molecules (Berreman, 1972). Roughness and chemical heterogeneity of the surface are usually considered as two major factors that determine the contact angle hysteresis. Chemical heterogeneity is a more complicated issue. It has been shown that the effect of surface topography on the contact angle hysteresis is negligible when the surface roughness

Fig. 14. (a) Contact angle hysteresis of deionized water on rubbed polyimide thin films against number of rubbing. (b) Variation of contact angle hysteresis with azimuthal angle against the rubbing direction. The polyimide films are rubbed with a rubbing strength of 1016.67 mm.

is not greater than 100 nm. As demonstrated in a previous section, the surface roughness can be controlled to be well below this amplitude with proper rubbing conditions. Furthermore, it has been revealed that even on molecularly smooth surfaces contact angle hysteresis can be quite significant (Chibowski, 2003; Lam et al., 2002). It seems that surface roughness becomes a less important factor when it is small enough (e.g. < 100 nm). This also suggests that the form anisotropy may not be the decisive factor for the anisotropic wettability of the rubbed polyimide films. Molecular scale topography at outmost surface might be the key to elucidate contact angle hysteresis.

3.4 Anisotropy in surface free energy

Rubbing does not always produce an observable geometrical structure on the surface, thus the surface anisotropy does not necessarily result from form anisotropy. Stöhr et al. (Stöhr et al., 1998) proposed a model to describe how rubbing pulls the polymer chains orienting them in one direction. According to Stöhr's model, at the rubbed polyimide surface, the polymer chains are pulled by the velvet fibres to align themselves with the rubbing direction, and there is a preferential out-of-plane tilt of phenyl rings. It has been shown by many researchers that rubbing can induce a reorientation of polymer chains (Arafune et al., 1997; 1998) and the rearrangement of functional groups in the polymer (Lee et al., 1997). The changes in surface energy, and consequently in surface wettability, have been attributed to the variation and rearrangement of polar and/or non-polar groups at the surface due to rubbing. However, how these changes in surface reconstruction act on a probe liquid has remained unknown. Surface free energy can be thought to be the total sum of the effects of all interactions at the surface. Owing to the close relation between surface free energy and contact angle, the anisotropy in contact angle hysteresis, in turn, indicates that the surface free energy may have an asymmetric pattern.

The surface free energy of the rubbed JASL-9800 polyimide thin films, as shown in Fig. 15, is anisotropic: for a rubbed polyimide film, the surface free energy towards the rubbing direction, e.g. for JASL-9800, is higher than that in the direction against rubbing direction.

Fig. 15. Azimuthal variation in surface free energy of rubbed JASL-9800 polymer films (a) within 180° range, and (b) for a full circle. The azimuthal angle is the angle the meridian plane of the water drop made against the rubbing direction.

The link between the orientation of the polymer chains and surface free energy is still missing. An impractical model based on the experimental observations is proposed as follows (Zheng et al., 2008). The overall anisotropy in the surface free energy of the rubbed polyimide films can be attributed to the macroscopic orientational order of the polymer chains at the surface, whereas the difference in the respective values measured parallel and antiparallel to the rubbing direction may be due to the microscopic orientation of functional groups in the polymer chains. The rubbing also has significant effects on the wettability of the rubbed polyimide.

It is widely accepted that the distribution of polar groups at the polyimide surface would determine the surface energetic state. We evaluated surface polarity of polyimide thin films using polar part of surface free energy. Fig. 16 shows the variation in the polar part of surface free energies as a function of rubbing strength. The surface polarity of polyimide increases with rubbing strength. The polarity in the rubbing direction is smaller than that against the rubbing direction. It is well known that the contact angle is very sensitive to the surface polarity, and a surface with a larger polarity exhibits lower hydrophobicity (Lee, K. W. Et al. 1997). The increase in the surface polarity of rubbed polyimide is considered to result from an outwards reorientation of polar groups at the polymer surface (Lee et al., 1996; 1997). Considering the orientation in polymer backbones induced by rubbing, a possible mechanism for the appearance of the anisotropy in the contact angle hysteresis is inferred as follows. The overall anisotropy in the contact angle hysteresis on the rubbed PI thin films may result from the anisotropic dispersion surface tension, which originates from a unidirectional orientation of the polymer backbones, whereas the local orientation of the polar groups at outmost surface owing to the rubbing may be responsible for the difference in contact angle hysteresis measured in and against the rubbing direction, respectively.

Fig. 16. The variation of polar part surface free energy of polyimide thin films with rubbing strength. The hollow squares are data for the polar surface free energy measured towards rubbing direction, whereas the solid diamond spots are data for the polar surface free energy measured against rubbing direction.

4. Conclusion

Mechanically rubbing polyimide thin film is a simple process. It, however, imposes some interesting surface phenomena. Mechanical rubbing breaks the two-dimensional topographical uniformity of the polyimide surface and causes changes in the surface energy of the polyimide thin films. The wettability of rubbed polyimide films is anisotropic. Water spreading on the rubbed polyimide thin films exhibits an asymmetric behaviour. For the rubbed polyimide thin films, the hydrophilicity of the surface towards the rubbing direction is different from that in the direction against the rubbing direction. The surface anisotropy in the rubbed polyimide surface is thought to be created due to an orientational arrangement of polymer chains at the surface. However, the evidence for this argument still remains unclear.

To find out links between thermodynamic phenomena and interactions in the interface at molecular level will be helpful for elucidating the mechanisms behind surface wetting phenomena.

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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