

Preparation and Characterization of Surface Energy of BPDA-BAPP Polyimide

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Received April 7, 2008; Revised January 16, 2009; Accepted January 16, 2009

Abstract: The surface properties (water sorption and repellency, adhesion) are closely related to the surface tension of polymer solids. The critical surface tension (γ_c) and surface tension (γ_s) of a polymer solid were estimated by the contact angle method by our quantitative imaging system. BPDA (3,3',4,4'-biphenyl tetracarboxylic dianhydride)-BAPP (1,3-Bis(4-aminophenoxy) propane) polyimide was successfully synthesized. The γ_c values were analyzed by a Zisman plot, a Young-Dupré-Good-Girifalco plot, and a $\log(1+\cos \theta)$ vs $\log \gamma_L$ plot. The γ_s value of BPDA-BAPP polyimide was evaluated using the geometric mean equation and our multiple regression analysis. The calculated values of γ_s^d (a dispersion component), γ_s^p (a polar component), γ_s^h (a hydrogen bonding component), and γ_s were 30.79, 9.32, 0.20, and 40.31 mN·m⁻¹, respectively. The γ_s of BPDA-BAPP polyimide containing both a methylene group and an ether group was larger than that of the polyimide containing only a methylene group.

Keywords: solid surface tension, critical surface tension, imaging method, contact angle, polyimide.

Introduction

Polyimides have been used in a wide variety of micro-electronic applications that include interlayer dielectrics in integrated circuits,¹ inter-metal insulators in high density interconnect packaging schemes,² and thermo-mechanical passivation buffer protection layers. They are thermally stable polymers that exhibit excellent chemical resistance, good mechanical properties, and superior dielectric properties.³⁻⁵ However, polyimide films are known to absorb water in some amounts,⁶⁻⁹ despite their relatively high chemical resistance characteristics.¹⁰⁻¹⁴ Water absorbed in polyimide films causes metal corrosion, package cracking, delaminating, failures of the adhesion to metal, and degradation of dielectric properties.¹⁵⁻¹⁸ To predict the behavior of polyimides and to optimize their fabrication, it is important to understand the relationship between polyimides structure and their surface properties.¹⁹⁻²⁸ The surface properties (water sorption and repellency, adhesion) are closely related to the surface tension of polymeric solid. Estimation of surface tension of polymer solid has generally been made by the contact angle method.

The existed experimental techniques for measuring a contact angle are as follows. Several investigators^{29,30} simply viewed a sessile drop through a comparator microscope fitted with a goniometer scale, thus measuring the angle directly. Ottewill made use of a captive bubble method³¹ wherein a bubble formed by manipulation of a micrometer syringe

was made to contact the solid surface. The contact angle might be measured from photographs of the bubble profile, or directly, by means of a goniometer telemicroscope.³² A reflected light method³³ was engaged in measuring the contact angle. The above-mentioned methods are inaccurate and irreproducible because a testing drop for contact angle measurement can be easily evaporated due to its tiny size and volatility. However, our lab-made quantitative imaging system could provide accurate and reproducible value of a contact angle since the computing system instantly grab the contact angle image and then store it to analyze.

BPDA-BAPP polyimide was newly synthesized to investigate the effect of the introduced both methylene group and ether group on the surface property. A contact angle was measured by a quantitative imaging system to investigate the relationship between a newly synthesized polyimide and its surface property. Three different groups of testing liquids,³⁴ e.g., dispersion, polar, hydrogen bonding liquids were used to measure the contact angle θ on a BPDA-BAPP polyimide film. Critical surface tensions γ_c were evaluated by a Zisman plot, a Young-Dupré-Good-Girifalco plot, and a $\log(1+\cos \theta)$ vs $\log(\gamma_L)$ plot.³⁵ The surface tension γ_s of BPDA-BAPP polyimide was determined by a geometric mean equation and the multiple regression analysis.

Theoretical Background

Young's Equation. The equilibrium contact angle (abbreviated θ here) for a liquid drop on a solid surface is usually discussed in terms of Young's equation;

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$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (1)$$

Critical Surface Tension.

Zisman Plot: The concept of critical surface tension was first proposed by Fox and Zisman.^{29,36,37} An empirical rectilinear relation was found between $\cos \theta$ and γ_L for a series of testing liquids on a given solid. When homologous liquids are used, a straight line is often obtained. When nonhomologous liquids are used, however, the data are often scattered within a rectilinear band or give a curved line. The intercept of the line at $\cos \theta = 1$ is the critical surface tension γ_c .³⁸ The $\cos \theta$ vs γ_L is known as the Zisman plot.

Young-Dupré-Good-Girifalco Plot: Fowkes,³⁹ Good,^{40,41} Good and Girifalco⁴² introduced an interaction parameter Φ_G , defined by.

$$\Phi_G = W_a / (W_{c1} W_{c2})^{0.5} \quad (2)$$

They presented the following equation

$$W_a = 2 \Phi_G (\gamma_S \gamma_L)^{0.5} \quad (3)$$

Using eq. (1) and Young-Dupré's equation

$$W_a = \gamma_L (1 + \cos \theta) \quad (4)$$

Eq. (5) can be derived and determine the magnitude of the interfacial tension, γ_{SL} .

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad (5)$$

W_a and γ_{SL} are very important parameters for wettability and adhesion.

Combining eq. (3) with eq. (4) leads to the equation of Young-Dupré-Good-Girifalco:

$$1 + \cos \theta = 2 \Phi_G (\gamma_S / \gamma_L)^{0.5} \quad (6)$$

The Young-Dupré-Good-Girifalco plot expressed by the $(1 + \cos \theta)$ vs $\gamma_L^{-0.5}$ gives rise to a good straight line with the experimental data obtained by the contact angle θ of homologous liquids on a polymer solid. However, in many cases the straight line greatly deviated from the origin with the polarity of liquids.⁴³ In such cases, the straight line can be expressed as:

$$1 + \cos \theta = \lambda \gamma_L^{-0.5} + \phi \quad (7)$$

where λ and ϕ are the slope and the intercept of $(1 + \cos \theta)$ at $\gamma_L^{-0.5} = 0$ in the $(1 + \cos \theta)$ vs $\gamma_L^{-0.5}$ plot known as the Young-Dupré-Good-Girifalco plot. These parameters are constant with homologous liquids. The critical surface tension γ_c can be obtained from the value of γ_L at $\theta \rightarrow 0$.

Using eq. (7), Young-Dupré's eq. (4) and Good-Giri-

falco's eq. (3), and neglecting equilibrium spreading pressure, the Good-Girifalco interaction parameter Φ_G is expressed as:

$$\Phi_G = (1/2 \gamma_S^{0.5}) [(2 - \phi) \gamma_C^{0.5} + \phi \gamma_L^{0.5}] \quad (8)$$

The parameter Φ_G^0 , defined as Φ_G at $\theta \rightarrow 0$, is expressed as follows.

$$\Phi_G^0 = (\gamma_C / \gamma_S)^{0.5} \quad (9)$$

The $\log(1 + \cos \theta)$ versus $\log(\gamma_L)$ Plot: As the interaction between liquid and solid is approximated by the use of the geometric mean law, Φ_0 is defined as the indication of polarity in Φ_G . Furthermore, we also took account of an adjustable parameter X_{LS} within Φ_G as a deviation from the interaction estimated by the geometric law.⁴³ Thus Φ_G is represented by:

$$\Phi_G = (X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5} + X_{LS} = \Phi_0 + X_{LS} \quad (10)$$

Wu⁴⁴ reported that the polarity X_j^p was estimated with the solubility parameter δ and the polarity component of the solubility parameter δ^p by the following equation:

$$X_S^p = (\delta^p / \delta)^2 \quad (11)$$

Also, the parameter a , determined with the polarity and X_{LS} , is introduced into Φ_G as follows:

$$\begin{aligned} \Phi_G &= \Phi_0 (\gamma_L / \gamma_S)^a \\ a &= \left[\log \left(1 + \frac{X_{LS}}{\Phi_0} \right) \right] / \log (\gamma_L / \gamma_S) \\ a &< 0.5 \text{ for } d \cos \theta / d \gamma_L < 0 \end{aligned} \quad (12)$$

The Φ_0 is equal to the bonding efficiency parameter of Kaelble and Uy.⁴⁵ Therefore, Φ_G^0 is expressed by:

$$\Phi_G^0 = [(X_C^d X_S^d)^{0.5} + (X_C^p X_S^p)^{0.5}] (\gamma_C / \gamma_S)^a \quad (13)$$

where X_C^d is the ratio of γ_C obtained with dispersion liquids and γ_C obtained with polar or hydrogen bonding liquids.⁴³ By solving eqs. (9) and (13), solid surface tension γ_S can be calculated from eq. (14):

$$\gamma_S = \gamma_C [(X_C^d X_S^d)^{0.5} + (X_C^p X_S^p)^{0.5}]^{2/(2a-1)} \quad (14)$$

Also, the reversible work of adhesion W_a is expressed by:

$$W_a = 2 \Phi_0 (\gamma_S^{0.5-a} \gamma_L^{0.5+a}) \quad (15)$$

Consequently, combining eq. (15) with Young-Dupré's eq. (4) leads to:

$$\log(1+\cos\theta) = -\Psi\log(\gamma_L) + \log(2\Phi_0\gamma_S^{0.5-a}) \quad (16)$$

Using eq. (16), the parameter a is determined with the slope $\Psi=(0.5-a)$ from $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot and γ_C can be found by extrapolating the linear function to $\log(1+\cos\theta)=\log 2$.

Surface Tension of Polymer Solid. Kitazaki and Hata³⁴ extended Fowkes' equation³⁹ to the following equation.

$$\gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h \quad (17a)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h \quad (17b)$$

They proposed that the surface tension of polymer film γ_S can be considered as a sum of a dispersion component γ_S^d , a polar component γ_S^p and a hydrogen bonding component γ_S^h . Liquid surface tension γ_L is also expressed as a sum of a dispersion component γ_L^d , a polar component γ_L^p , and a hydrogen bonding component γ_L^h . Using the work of adhesion W_a , the extended Fowkes' eq. (17) is expressed in the following equation.

$$W_a = 2[(\gamma_L^d\gamma_S^d)^{0.5} + (\gamma_L^p\gamma_S^p)^{0.5} + (\gamma_L^h\gamma_S^h)^{0.5}] \quad (18)$$

By solving the Young-Dupré eq. (4) and eq. (18), geometric mean eq. (19) is obtained.

$$\gamma_L(1 + \cos\theta) = 2[(\gamma_L^d\gamma_S^d)^{0.5} + (\gamma_L^p\gamma_S^p)^{0.5} + (\gamma_L^h\gamma_S^h)^{0.5}] \quad (19)$$

Eq. (19) can be transformed in eq. (20)

$$z = (\gamma_S^d)^{1/2} + (\gamma_S^p)^{1/2}x + (\gamma_S^h)^{1/2}y \quad (20)$$

$$\text{where } x = \sqrt{\frac{\gamma_L^p}{\gamma_L^d}}, \quad y = \sqrt{\frac{\gamma_L^h}{\gamma_L^d}}, \quad z = \frac{\gamma_L(1 + \cos\theta)}{2(\gamma_L^d)^{0.5}}$$

The surface tension of polymer solid γ_S and its fractional components (γ_S^d , γ_S^p , γ_S^h) can be determined by contact angles measured by three different group of test liquids³⁴ and eq. (20).

Experimental

Synthesis of BPDA-BAPP Polyimide. It was investigated how surface properties were affected by introducing both methylene group and ether group to the main chain of newly synthesized polyimide. Polyimide is an imide group-containing polymer synthesized by condensation polymerization of dianhydride with diamine. Depending on the structure of the chemical radicals attached to the imide group, polyimide can be aliphatic or aromatic, linear or branched.

This study polymerized BPDA (3,3',4,4'-biphenyltetracarboxylic dianhydride; Chriskev Co., Inc.) with lab-synthesized BAPP (1,3-bis(4-aminophenoxy) propane). The preparation process of polyamic acid and polyimide of

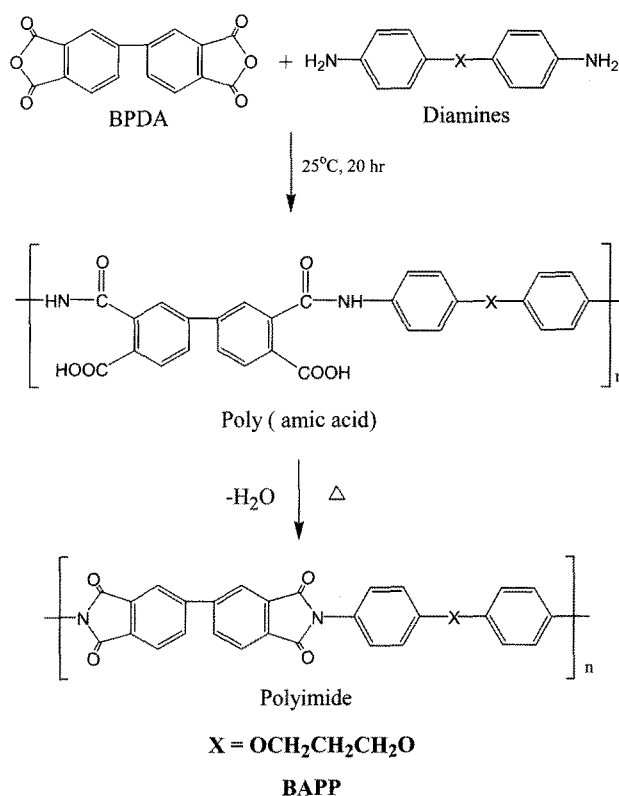


Figure 1. Synthetic process of BPDA-BAPP polyimide.

BPDA-BAPP demonstrated in Figure 1. A diamine of BAPP and a solvent of NMP (*N*-methyl-2-pyrrolidone, Aldrich Chem. Co., Inc.) were introduced into a four-necked flask (500 mL) equipped with a thermocouple, a stirrer, and a nitrogen inlet. The mixtures were stirred thoroughly in a nitrogen environment. After dissolving BAPP completely, BPDA was put into the flask at 1:1 stoichiometric ratio. A solvent soluble polyamic acid precursor was formed by the slow reaction of reaction mixtures for 20 h. The solid content of viscous reaction mixtures was about 15% (w/v) by NMP solvent.

A spin coater (Model 301 series, Able Co.) was used to make a thin film from the polyamic acid of BPDA-BAPP by coating on silicone wafer. After prebaking the coated film in an 80 °C vacuum oven for an hour, an additional process was performed by curing it in 150 °C for 30 min, 250 °C for 30 min, 350 °C for 1 h at 10 °C/min of heating rate under nitrogen. A distilled water bath was employed to separate the coated polyimide film from silicone wafer. The separated film was used for contact angle measurement after complete drying in the oven.

IR Spectroscopy. FTIR Spectrometer (Genesis II, Mattson Instrument) was used to confirm if a BPDA-BAPP polyimide was successfully synthesized. Examining the absorption bands of the carbonyl group (C=O) and the imide ring (C-N) could provide the right information of the imidization reaction.

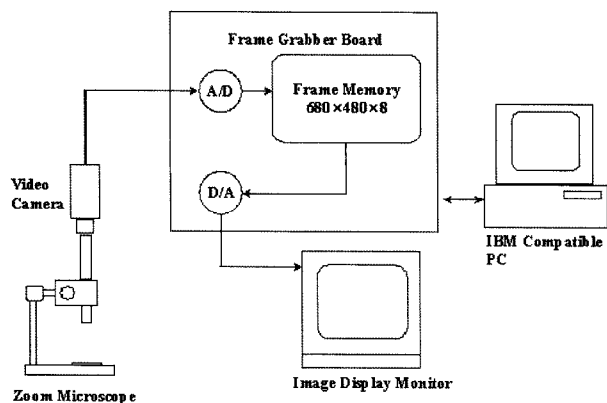


Figure 2. Schematic diagram of the image processing system.

Contact Angle Measurement by Quantitative Imaging System. A CCD camera (Model WV-BL 600, Panasonic) was connected to a zoom microscope (Model A52953, Edmund Scientific Ltd.) for acquiring contact angle images by a computer system. A personal computing system saved contact angle images captured by a Frame grabber (Model DT2867, Data Translation Inc.), the CCD camera, and the zoom microscope. The frame grabber possesses 256 gray scale photography and the resolution of 640×480 pixels. The captured contact angle image was quantitatively analyzed by an imaging software (Global Lab[®] Image, Data Translation Inc.) and a separate multisync monitor (Syncmaster 1000p, Samsung Co.).

Figure 2 indicates a schematic diagram of the quantitative

imaging system. The value of contact angle was determined by the following experimental procedure and imaging analysis method. A microsyringe injected an 1 mm size of a testing liquid to neglect the gravity effect. As soon as a testing liquid in Table I was equilibrated, a contact angle image was instantly grabbed. An 1-mm-diameter stainless ball was engaged to calibrate the actual dimension of the enlarged image of the contact angle. Image enhancement was performed to differentiate solid film from the sessile drop and the background from the sessile drop. After determining the radius r of the baseline formed by the solid film and the sessile drop, the height h of the sessile drop was calculated. Since direct reading of the contact angle provided a large experimental error, the contact angle was estimated by the $\theta/2$ method which gave accurate and reproducible results.^{46,47}

Results and Discussion

FTIR Spectra. It is confirmed from Figure 3 that the BPDA-BAPP polyimide is successfully synthesized.⁴⁸ The strongest absorption occurs at 1720 cm^{-1} (C=O symmetrical stretching). The more useful bands of imide groups are 1780 cm^{-1} (C=O asymmetrical stretching), 1380 cm^{-1} (C-N stretching), 725 cm^{-1} (C=O bending).

Contact Angles. Before measuring the contact angles formed by water on the BPDA-BAPP polyimide film, a PTFE (polytetrafluoroethylene) film was used to calibrate the quantitative imaging system and its analysis method. The contact angle on the PTFE film is 108 degree, which is

Table I. The Contact Angle θ on BPDA-BAPP Polyimide Film and Surface Tensions of All Testing Liquids at 20 °C [$\text{mN}\cdot\text{m}^{-1}$]

Species	Liquid	Contact Angle θ (°)	γ_L^d	γ_L^p	γ_L^h	γ_L	X_L^p
Dispersion Solution	Octane	spreading	21.8	0	0	21.8	0
	Nonane	spreading	22.9	0	0	22.9	0
	Decane	spreading	23.9	0	0	23.9	0
	Undecane	spreading	24.7	0	0	24.7	0
	Tetradecane	spreading	26.7	0	0	26.7	0
	Hexadecane	spreading	27.6	0	0	27.6	0
Polar Solution	Hexachlorobutadiene	21.9	35.8	0.2	0	36.0	0.006
	1,2-Dibromoethane	27.7	-	-	-	38.9	-
	α -Bromonaphthalene	36.3	44.4	0.2	0	44.6	0.004
	Tetrabromoethane	47.6	44.3	3.2	0	47.5	0.067
Hydrogen Solution	Dipropylene glycol	38.3	29.4	0	4.5	33.9	0.133
	1,3-Butanediol	56.1	-	-	-	37.8	-
	Polyethyleneglycol	61.5	29.9	0.1	13.5	43.5	0.313
	Diethyleneglycol	64.2	31.7	0	12.7	44.4	0.286
	Ethyleneglycol	67.2	30.1	0	17.8	47.7	0.373
	Water	88.1	29.1	1.3	42.4	72.8	0.600

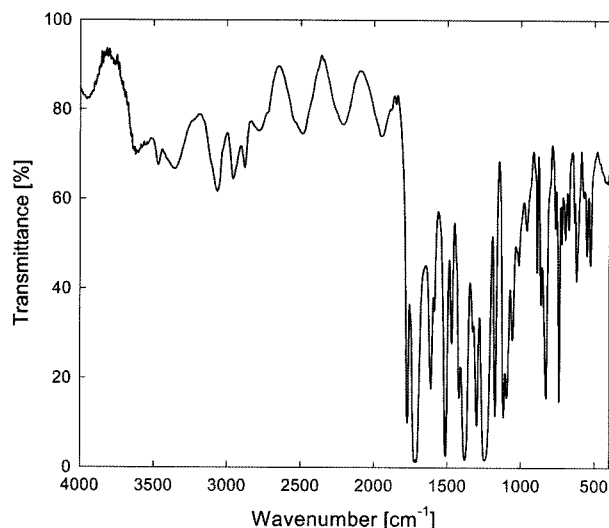


Figure 3. FTIR Spectrum of BPDA-BAPP polyimide film.

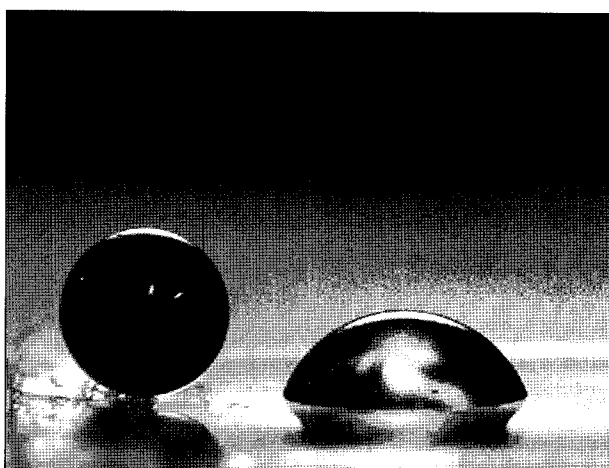


Figure 4. Typical contact angle image of a testing liquid drop of ethyleneglycol on BPDA-BAPP polyimide film.

corroborated the value in the literature.⁴⁹⁻⁵¹ It is verified that the quantitative imaging system and its analysis method can provide accurate and reproducible values of the contact angle. Contact angles were measured by dispersion, polar, and hydrogen bonding liquids in Table I. Figure 4 is a typical contact angle image of a liquid drop of ethyleneglycol equilibrated on the BPDA-BAPP polyimide film. It can be seen from Table I that the values of the contact angle increases with increasing of the surface tensions of the testing liquids used. The largest contact angle was measured by water whose surface tension is the largest among hydrogen bonding liquids. On the other hand, the smallest contact angle was observed by hexa-chlorobutadiene whose surface tension is the smallest among polar liquids. For a group of dispersion testing liquids, however, contact angles are not observed due to their complete spreading on polyimide film.

Critical Surface Tensions. The Zisman plots for the BPDA-BAPP polyimide film are shown in Figure 5. Table II

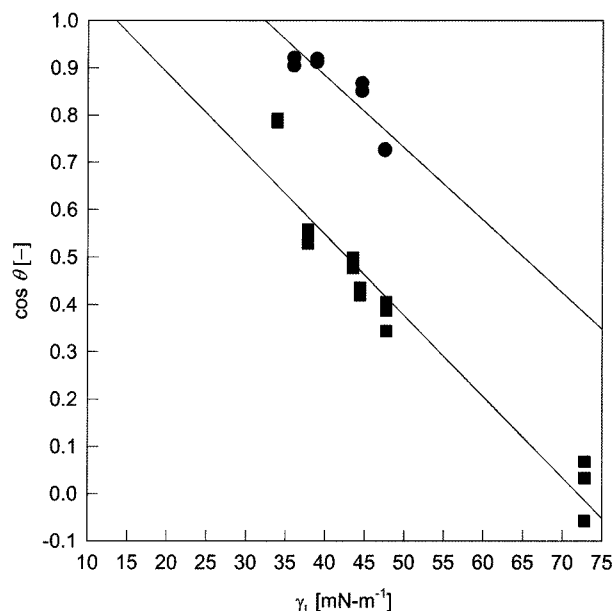


Figure 5. Zisman plots for BPDA-BAPP polyimide film: ●, Polar liquids; ■, Hydrogen bonding liquids.

Table II. The Critical Surface Tensions γ_c of BPDA-BAPP Polyimide Film and the Constants Determined from the $(1+\cos\theta)$ versus $\gamma_L^{-0.5}$ Plot

Polyimide	Plot	Testing Liquids	γ_c	ϕ
BPDA-BAPP	$\cos\theta$ vs γ_L	Polar	32.32	
		Hydrogen	13.53	
	$(1+\cos\theta)$ vs $\gamma_L^{-0.5}$	Polar	33.23	0.618
		Hydrogen	26.96	-0.527
	$\log(1+\cos\theta)$ vs $\log(\gamma_L)$	Polar	33.26	
		Hydrogen	27.7	

displays the critical surface tensions estimated by Figure 5. The values of the critical surface tensions by polar and hydrogen bonding liquids are 32.32 and 13.53 $\text{mN}\cdot\text{m}^{-1}$, respectively. The critical surface tensions by dispersion liquids can not be obtained because of their complete spreading on the polyimide film. The magnitude of critical surface tension, therefore, increases in the following order: hydrogen liquids < polar liquids. When plotting $\cos\theta$ as a function of the polarity of different liquids, different values of critical surface tensions γ_c are obtained. The γ_c for polar liquids is 2.39 times larger than γ_c for hydrogen bonding liquids. The larger variation is illustrated as follows.

On the Zisman plots, empirical relation between $\cos\theta$ and γ_L displays a reasonably straight line when the value of γ_L is in the vicinity of γ_c (in the case of polar liquids). On the other hand, data fitting displays a downwardly convex because a liquid with γ_L much greater than γ_c generally possesses hydrogen bonding.⁴⁴ The Zisman plots and the critical surface ten-

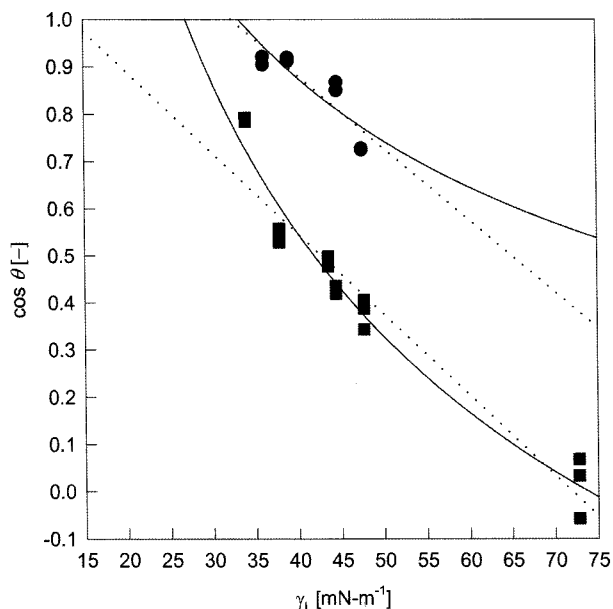


Figure 6. Theoretical curves of $\cos\theta$ vs γ_L based on eq. (21) for BPDA-BAPP polyimide film: ●, Polar liquids; ■, Hydrogen bonding liquids; ---- Straight line on the Zisman plots.

sions are corroborated by using the intercept ϕ of $(1+\cos\theta)$ at $\gamma_L^{-0.5}=0$ from the $(1+\cos\theta)$ vs $\gamma_L^{-0.5}$ plot. From eqs. (6) and (8), the relationship between $\cos\theta$ and γ_L can be rewritten by the following equation.

$$\cos\theta = (2 - \phi)(\gamma_c/\gamma_L)^{0.5} + (\phi - 1) \quad (21)$$

Therefore, eq. (21) indicates a downwardly convex curve. The γ_c values extrapolated by the Zisman plot and estimated by eq. (21) are provided as γ_c^E (experimental γ_c) and γ_c^T (theoretical γ_c), respectively. Combining eq. (21) with the ϕ and γ_c values in Table II becomes:

$$\text{for Polar liquid: } \cos\theta = 7.967(\gamma_L^{-0.5}) - 0.382$$

$$\text{for Hydrogen bonding liquid: } \cos\theta = 13.121(\gamma_L^{-0.5}) - 1.527$$

Both of the curves fitted by eq. (21) and the straight dashed line on the Zisman plot by using the least squares method are shown in Figure 6. Better consistency is observed between experimental data and the theoretical curve estimated by eq. (21). For the polar liquids, γ_c^E is nearly equal to γ_c^T . On the other hand, γ_c^E is obviously smaller than γ_c^T for the hydrogen bonding liquids. Consequently, it is concluded that the Zisman plot is essentially a downwardly convex curve with polar and hydrogen bonding liquids having $\gamma_c \ll \gamma_L$. This result is consistent with that of Gutowski.⁵²

Young-Dupré-Good-Girifalco plots represented by the $(1+\cos\theta)$ vs $\gamma_L^{-0.5}$ are shown in Figure 7. The straight lines on the $(1+\cos\theta)$ vs $\gamma_L^{-0.5}$ fitted by the least squares method greatly deviated from the origin. Table II indicates that the values of critical surface tensions by polar and hydrogen bonding liquids are 33.23 and 26.96 mN·m⁻¹, respectively.

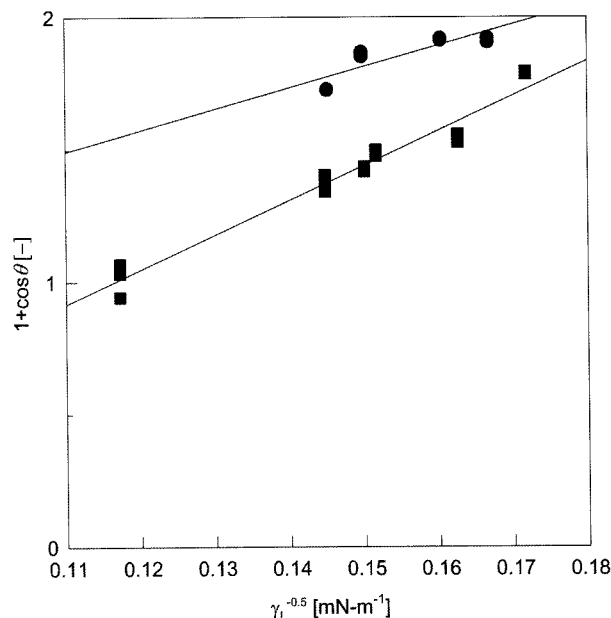


Figure 7. Young-Dupré-Good-Girifalco plots for BPDA-BAPP polyimide film: ●, Polar liquids; ■, Hydrogen bonding liquids.

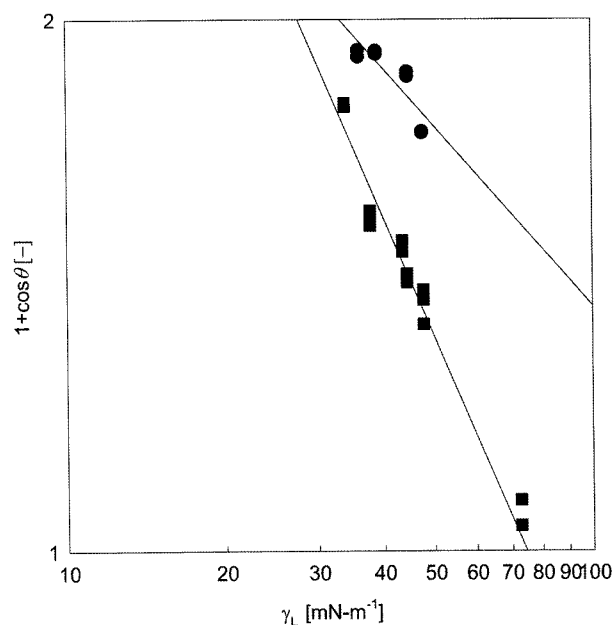


Figure 8. $\log(1+\cos\theta)$ vs $\log \gamma_L$ plots for BPDA-BAPP polyimide film: ●, Polar liquids; ■, Hydrogen bonding liquids.

From the $(1+\cos\theta)$ vs $\gamma_L^{-0.5}$ plot, γ_c by dispersion liquids also cannot be obtained due to their complete spreading. The magnitude of critical surface tension also increases in the same trend: hydrogen liquids < polar liquids. The values of γ_c estimated with the $(1+\cos\theta)$ vs $\gamma_L^{-0.5}$ plot also have different numbers with varying polarity of liquids used.

The $\log(1+\cos\theta)$ vs $\log \gamma_L$ plots are shown in Figure 8. Experimental data are fitted well with the straight lines fitted by the least squares method. Table II indicates that the

values of critical surface tensions by polar and hydrogen bonding liquids are 33.26 and 27.7 mN·m⁻¹, respectively. The order of the magnitude of γ_c evaluated with this plot is similar to those on other plots as mentioned before. The γ_c values calculated from the $\log(1+\cos\theta)$ vs $\log \gamma_L$ plot also have different numbers with varying polarity of liquids. The γ_c values by the Zisman plot are smaller than those estimated by either the Young-Dupré-Good-Girifalco plot or the $\log(1+\cos\theta)$ vs $\log \gamma_L$ plot.

The critical surface energies γ_c of BPDA-BAPP polyimide film obtained with the Zisman plot are smaller than those obtained with either the Young-Dupré-Good-Girifalco plot or $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot. It was found that the Zisman plot displays a favorable straight line when the value of γ_L is in the vicinity of γ_c . On the other hand, it displays a downwardly convex curve when γ_L has a value much larger than γ_c , because a liquid with much greater than γ_c generally possesses hydrogen bonding. Gutowski⁵² also pointed out that the Zisman plot essentially demonstrated a downwardly convex curve. Therefore, the Zisman plot are reanalyzed by the use of the Young-Dupré-Good-Girifalco plot (eq. (7)). The theoretical relationship between $\cos\theta$ and γ_L can be rewritten by eq. (21). The γ_c evaluated by $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot can be founded by extrapolating the linear function to $\log(1+\cos\theta) = \log 2$. The critical surface energy γ_c evaluated by the $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot and eq. (14) can estimate the surface energy γ_s unlike the Zisman plot and the Young-Dupré-Good-Girifalco plot.

Solid Surface Tension. Figure 9 represents the best correlation of experimental data using a multiple regression anal-

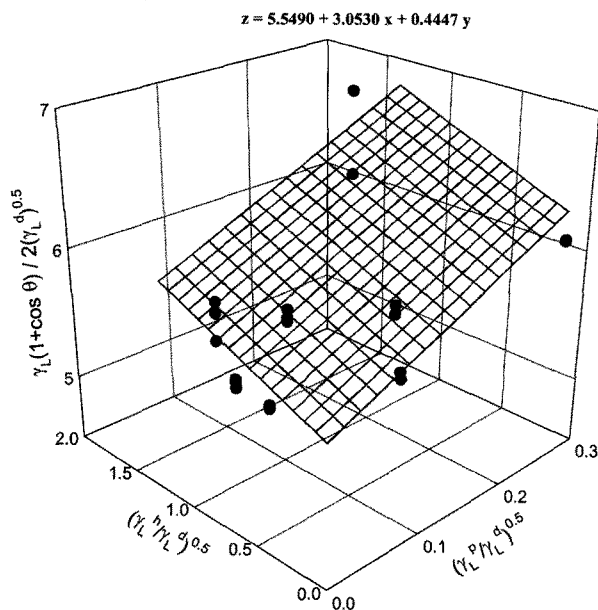


Figure 9. Determination of the dispersion (γ_s^d), the polar (γ_s^p), and the hydrogen bonding (γ_s^h) component of the surface tension of BPDA-BAPP polyimide by using geometric mean eq. (20).

ysis.^{53,54} The surface tension γ_s of the BPDA-BAPP polyimide can be determined by combining contact angles and three known components (γ_s^d , γ_s^p , γ_s^h) with geometric mean eq. (20). The calculated values of γ_s^d , γ_s^p , γ_s^h , and γ_s are 30.79, 9.32, 0.20, and 40.31 mN·m⁻¹, respectively. Two different Kapton[®] H films⁵⁵ are as follows. The first one is poly(1,3,5,7-tetraoxo-2,3,6,7-tetrahydro-1H,5H-benzo[1,2-c:4,5-c']dipyrrol-2,6-diyl-1,4-phenyleneoxy-1,4-phenylene) whose surface tension γ_s is 37.7 mN·m⁻¹ and the polarity is 0.223. The second one is poly(iminocarbonyl-(4,6-dicarboxy-1,3-phenylene)-carbonylimino-1,4-phenyleneoxy-1,4-phenylene) whose surface tension γ_s is 41.1 mN·m⁻¹ and polarity is 0.358. The γ_s of BPDA-BAPP polyimide is 40.31 mN·m⁻¹ which is 0.98 times smaller and 1.07 times higher than those of Kapton[®] H films, respectively. The polarity of BPDA-BAPP polyimide is 0.236 whose value was located between 0.66 and 1.06 magnitudes of Kapton[®] H films' polarity, respectively.

The value of γ_s^d is larger than γ_L^d of dispersion liquids (21.8-27.6 mN·m⁻¹). It can be seen from Table II that contact angles are not observed because dispersion liquids completely spread on the polyimide film. The reason of complete spreading is that γ_s^d is larger than γ_L^d . It is not because of both the relation of $\gamma_s > \gamma_L$ and polar properties. The γ_c values in Table II are generally smaller than γ_s . The two results are well corroborated with those reported by Kiatazaki and Hata.³¹ The γ_s of BPDA-BAPP polyimide containing both methylene group and ether group is larger than that of the polyimide containing methylene group only. The surface energy of BPDA-BAPE [1,2-di(4-aminophenoxy)ethane] polyimide⁵³ is 43.11 mN·m⁻¹. BPDA-BAPP polyimide has a lower surface energy than BPDA-BAPE polyimide which relates to the longer diamine structure, i.e. the longer repeating unit. It is the imide group that is the most polar part in the repeating units of BPDA-BAPP and BPDA-BAPE polyimide and thus contributes to increase in the surface energy most. All polyimides have two imides in the repeating unit. As the length of the repeating unit increases, the proportion of the polar imide moieties decreases, which results in the decrease of surface energy.

Conclusions

It is confirmed that the BPDA-BAPP polyimide is successfully synthesized. Contact angles on BPDA-BAPP polyimide film were measured by dispersion, polar, and hydrogen bonding liquids. It can be seen that the values of the contact angle increases with increasing of the surface tension of testing liquids used. For a group of dispersion testing liquids, however, contact angles are not observed due to their complete spreading on the polyimide film. The reason can be illustrated by the relation of $\gamma_s^d > \gamma_L^d$.

The γ_c values by the Zisman plot are smaller than those estimated by either the Young-Dupré-Good-Girifalco plot or the $\log(1+\cos\theta)$ vs $\log \gamma_L$ plot. The Zisman plot is essen-

tially a downwardly convex curve with the polar and hydrogen bonding liquids having $\gamma_c < \gamma_L$. Critical surface tensions γ_c calculated from all plots have different values with depending on polarity of liquids. The order of the magnitude of γ_c evaluated with all plots is as follows: hydrogen liquids < polar liquids. The calculated values of γ_s^d , γ_s^p , γ_s^h , and γ_s are 30.79, 9.32, 0.20 and 40.31 mN·m⁻¹, respectively. The γ_s of BPDA-BAPP polyimide is 40.31 mN·m⁻¹ which is 0.98 times smaller and 1.07 times larger than those of Kapton® H films, respectively. The polarity of BPDA-BAPP polyimide is 0.236 whose value was located between 0.66 and 1.06 magnitudes of Kapton® H films' polarity, respectively. The γ_s of BPDA-BAPP polyimide containing both methylene group and ether group is larger than that of the polyimide containing methylene group only. BPDA-BAPP polyimide has a lower surface energy than BPDA-BAPE polyimide which relates to the longer diamine structure, i.e. the longer repeating unit.

Nomenclature

a : parameter defined in Eq. (12) [-]
 h : height of the sessile drop [m]
 r : radius of the sessile drop [m]
 W_a : work of adhesion [J]
 W_c : work of cohesion [J]
 X_C^d : ratio of γ_c obtained with dispersion liquid [-]
 X_j^d : dispersion fraction of the j component [-]
 X_j^p : polar fraction of the j component [-]
 X_{LS} : adjustable parameter in Φ_G [-]
 X_S^p : the polarity of polymer solid [-]

Greek Letters

γ_c : critical surface tension [mN·m⁻¹]
 γ_c^E : experimental value of critical surface tension [mN·m⁻¹]
 γ_c^T : theoretical value of critical surface tension [mN·m⁻¹]
 γ_L : surface tension of liquid [mN·m⁻¹]
 γ_L^d : the dispersion component of liquid surface tension [mN·m⁻¹]
 γ_L^h : hydrogen bonding component of liquid surface tension [mN·m⁻¹]
 γ_L^p : the polar component of liquid surface tension [mN·m⁻¹]
 γ_s : surface tension of polymer solid [mN·m⁻¹]
 γ_s^d : the dispersion component of solid surface tension [mN·m⁻¹]
 γ_s^h : hydrogen bonding component of solid surface tension [mN·m⁻¹]
 γ_{SL} : the interfacial tension between the solid and the liquid [mN·m⁻¹]
 γ_s^p : the polar component of solid surface tension [mN·m⁻¹]
 δ : solubility parameter [-]
 δ^p : polarity component of solubility parameter [-]
 θ : contact angle [deg.]
 λ : the slope of the Young-Dupré-Good-Girifalco plot [-]

ϕ : the intercept of the Young-Dupré-Good-Girifalco plot [-]
 Φ_G : interaction parameter [-]
 Φ_G^o : parameter defined in Eq. (9) [-]
 Φ_b : indication of polarity in Φ_G [-]
 Ψ : slope of the log (1+cos θ) vs log γ_L plot [-]

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