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ORGINAL CONTRIBUTION

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Surface characterization of polyimide films

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Abstract Various kinds of poly(amide acid)s were prepared by the reaction of four kinds of acid dianhydride and three kinds of diamine in *N*,*N*-dimethylacetamide (DMAc). Polyimide films were prepared by casting the poly(amide acid) solution on soda glass substrates, followed by thermal imidization at various temperatures. Contact angles of polyimide films for the sides in contact both with air and with glass substrate (air side and glass side, respectively) were measured to evaluate the dispersive component (γ_S^D) and the nondispersive component (γ_S^P) of surface free energy (γ_S) of polyimide films. It was shown that, for the air side, γ_S^P value decreased greatly, and γ_S^D values increased slightly with the development of imidization. Values of γ_S^P for the glass side were much higher than those for the air side. Poly(amide acid) solution was also cast on quartz glass and silicone rubber, and was thermally imidized. The γ_S^P for the quartz glass side was almost the same as that for the soda glass side. But the γ_S^P for the silicone rubber side was as low as the γ_S^P for the air side. Attenuated total reflection infrared spectroscopy of polyimide films showed that the degree of imidization for the glass side surface was not as high as that for the air side surface, and that the amount of polar groups for the glass side surface was higher than that for the air side surface. Among the various kinds of polyimides, there is a slight but clear difference in the values of γ_S and its components, which can be rationalized from the difference in the chemical structure. It was also found that thermal degradation and oxidation can be easily detected from the change of surface free energy and its components for the polyimide films after being treated at high temperatures in both air and vacuo.

Key words Polyimide film – imidization – contact angle – surface free energy – dispersive component – nondispersive component

Introduction

Polyimide is one of the most promising thermally stable polymers with good mechanical properties [1, 2]. It has been applied as electrical insulators, substrates for flexible printed circuits, passivation layers, alignment films for liquid crystal displays, gas separation films, matrix resin for fiber reinforced plastics (FRP) and so on [2]. Polyimide is generally prepared by a two-step synthesis from diamine and dianhydride. Curing of polyimide, i.e. imidization of poly(amide acid), has been studied by various methods such as IR, NMR, TGA, DSC and density [1, 2]. Characterization of cured polyimide also has been extensively studied by mechanical analysis, dynamic mechanical analysis, DSC, TGA, X-ray, XPS, dielectric measurement, adhesion and photodegradation [2].

In many potential applications of polyimide, a knowledge of wetting and surface properties can provide valuable information relating to adhesion behavior. The surface behavior of polyimide has been studied using various methods, such as ion and electron microscopy, vibration spectroscopy, surface energy measurements and microscopic observation [3]. The surface of the cured polyimide film is found to be different from the bulk and sensitive to the interface against which it was created. For example, Toney et al. studied the surface structure of spin-coated films of PMDA/ODA polyimide using Grazing Incidence X-ray Scatter and found that the film was more ordered near the air surface than in the bulk [4, 5]. Hasegawa et al. studied degree of in-plane molecular orientation of various polyimides and their precursors, poly(amide acid)s, by measuring a visible dichroic absorption at an incident angle and found that cure of the poly(amide acid) film adhered on a substrate induced spontaneous orientation [6].

Almost all the information obtained as surface properties by the above measurements is as deep as ca. 500 nm in the film. Contact angle measurement is the method to give us the information as truly surface-sensitive measurement. Estimation of surface tension by contact angle measurements has been successfully performed to show the change of surface imported by various modification methods. Many papers described the surface free energy of PMDA/ODA polyimide films modified by various methods such as plasma [7], annealing [8], and tensile stress [9]. Very few studies, however, have been performed to characterize the imidization procedure from poly(amide acid) through heat treatment [10].

It was reported that the surface free energy by contact angle measurement is, at best, an estimate [11, 12]. Yet, contact angle measurement is important among surface sensitive techniques, because a simple apparatus allows us to probe the outer most surface of materials, which cannot be probed by other methods. In polyimide, information regarding the types of functional groups present at the surface can be obtained.

This study was undertaken to make clear the change of surface free energy of various kinds of polyimide films during imidization. Polyimide films are usually processed using poly(amide acid). Therefore, to get the information on the surface properties and their change during imidization is important from the point of using poly(amide acid). Poly(amide acid) was cast on glass substrates and imidized at various temperatures to give polyimide films with various degrees of imidization. The relationship between surface free energy and degree of imidization was discussed in accordance with the analysis of the surface structure of polyimide films. We also used surface free energy to investigate the degradation and oxidation of the surface, which cannot be measured by TGA.

Experimental

Materials

Pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane (6FDA), oxydianline (ODA) and 4,4′-phenylenediamine (PDA)) were purified by sublimation. 4,4′-Diaminodiphenylacetylene (*m*-intA) was prepared according to the reported method [13]. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure. Soda glass, quartz glass and the silicone plate were used as substrates for casting poly(amide acid) solutions. They were used after washing with acetone.

Preparation of polyimide

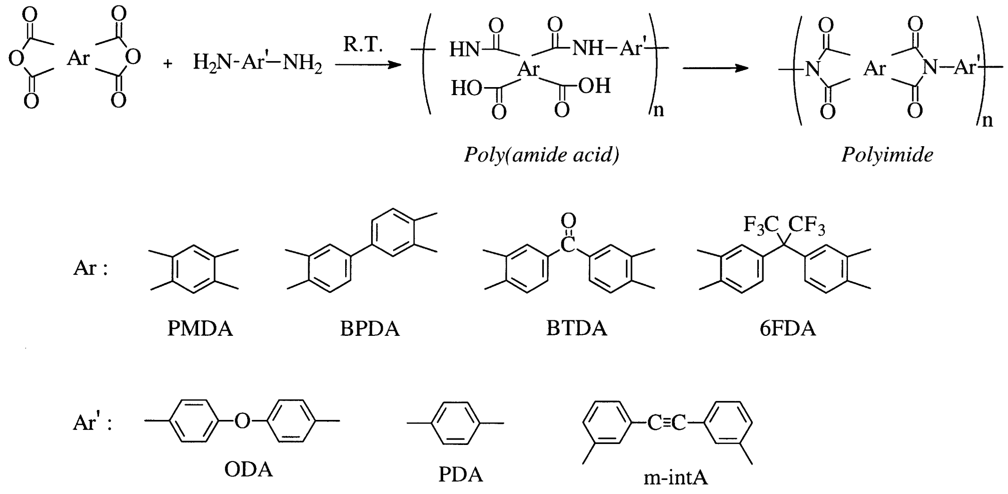
Various kinds of poly(amide acid)s were prepared by the reaction of dianhydride and diamine in DMAc at room temperature [14, 15] as shown in Scheme 1. Poly(amide acid) solutions were cast on substrates and dried at 50 °C for 16 h, followed by thermal treatment at 100 °C, 130 °C, 150 °C, 170 °C, 200 and 300 °C for 1 h each in vacuo to give polyimide films with various degrees of imidization. Two samples were prepared for each treatment, one for substrate side measurement and the other for air side measurement. Films were peeled off for contact angle measurement after each thermal treatment. Film thickness is 20–30 μm.

To examine the thermal stability of polyimide film surface, PMDA/ODA and BPDA/ODA polyimide films were cast on soda glass, and they were further treated, after the above-mentioned thermal treatment, at 300 °C, 350 °C and 400 °C for 1 h each both in vacuo and in the air as fixed on a glass plate.

Contact angle measurement

Contact angles were measured by one-liquid method [16]. The receding contact angles of the water and methyl iodide on the films were measured at 20 °C, using Kyowa contact angle meter with a goniometer. The contact angle was determined from an average of 10 drops. Surface free

Scheme 1 Preparation of polyimide



energy and its components were calculated based on the Kaeble's equation [17, 18].

Infrared spectroscopy

Transmission method for the determination of degree of imidization [19]

Degree of imidization of polyimide films was determined by means of infrared spectroscopoy using JEOL-7000 by comparing the absorption of imide groups at 1776 cm^{-1} with that of phenyl groups at 1500 cm^{-1} as a standard. More often, the degree of imidization was determined by normalizing the absorption of imide groups from the thickness of films. The sample treated at 300 °C was employed as a standard for 100% imidization. It was confirmed from the IR spectra of polyimide films treated at 300 °C that absorption due to amide acid has completely disappeared.

Reflection method for the surface analysis

Infrared spectra for the surface analysis of polyimide films were recorded on a Perkin–Elmer Model 1720 FT-IR, with the attenuated total reflection (ATR) technique using a ZnSe or a Ge prism. The incident angle of infrared light was 45°. The sampling depth in the range of 2000–400 cm^{-1} is estimated to be about 0.66–3.3 μm when a Ge prism was used. Difference spectra of polyimide were obtained by normalizing the absorption of 1500 cm^{-1} as a standard. The spectra resolution was 2 cm^{-1} and 32 scans were recorded on each sample.

Results and discussion

Surface free energy of PMDA/ODA polyimide films

First, PMDA/ODA polyimide films were prepared by casting the poly(amide acid) solution on a soda glass followed by thermal imidization. Contact angles of the polyimide films for the air side and the glass side were measured by one-liquid method and shown in Table 1. Contact angles, especially for water, increased with the increase of treatment temperatures, indicating that the surface of the polyimide films for both the air and the glass sides became less polar.

Change of surface free energy and its components with the degree of imidization for the air and the glass sides was calculated and shown in Fig. 1. Dispersive component of surface free energy slightly increased (32–37 $\mathrm{mJ\,m^{-2}}$) with the development of imidization. The values were very near to the reported value of ca. 30 $\mathrm{mJ\,m^{-2}}$ [7, 8, 20]. On the other hand, the nondispersive component decreased greatly from 18 to 4 $\mathrm{mJ\,m^{-2}}$ for the air side and from 32 to 18 $\mathrm{mJ\,m^{-2}}$ for the glass side with the development of imidization. The decrease of nondispersive component can be interpreted on the basis of the fact that polar functional groups of poly(amide acid) such as carboxylic acid and amide groups transformed to less polar imide groups with the development of imidization. The dispersive component can be considered in terms of the nature of the dispersive forces which, in general, depend on the electrical properties of the volume and the distance between elements, and can be expressed as follows [21]:

$$\gamma_S^D = -\frac{\pi N^2 \alpha^2 I^2}{8r^2}\,, \qquad (1)$$

Table 1 Contact angles (degree) of PMDA/ODA polyimide films prepared at various temperatures[a]

Side	Liquid	Treatment temperature [°C]						
		50	100	130	150	170	200	300
Air side	Water	54	57	66	74	77	82	82
Air side	M.I.[b]	33	34	37	38	40	41	37
Glass side	Water	35	30	40	56	56	54	63
Glass side	M.I.[b]	29	30	30	28	27	30	38

[a] Treated in vacuo.

[b] Methyl iodide.

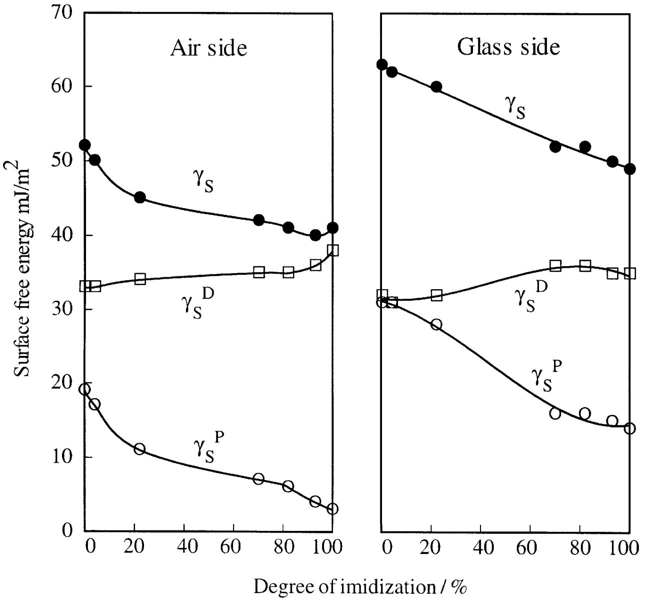
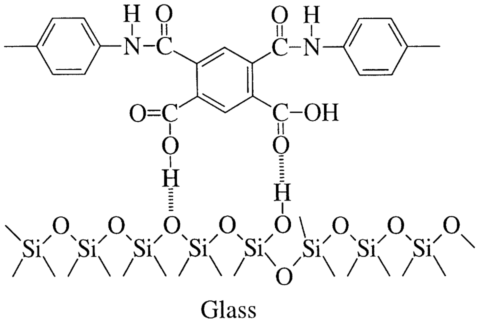


Fig. 1 Surface free energy of the PMDA/ODA film for the air and the glass sides

where N is the number of the volume elements per volume unit, α the polarizability, I the ionization potential, and r the distance between the volume elements. The value of α is considered to become small with the development of imidization, since polar functional groups such as amide and acid become less polar imide groups. The increase of the dispersive component suggests that the value of the distance between the volume elements (r) becomes small to compensate the smaller polarizability. In fact, an increase in the density of the films with the development of imidization has been reported [6].

As clearly shown in Fig. 1, nondispersive component for the glass side was much higher than that for the air side. Thus, it is suggested that there exist more polar groups on the film surface for the glass side than that for the air side. It is considered that polar solvent (DMAc) remained more



Scheme 2 Hydrogen bonding between silanol groups on the surface of glass and both carboxylic acid groups and amide groups on the surface of the polyimide film

on the the glass side surface than on the air side surface, but γ_S^P of DMAc is as low as 4.3 mJ m^{-2} [22]. Therefore, hydrogen bonding between silanol groups on the glass and both carboxylic acid and amide groups on the film surface is considered to be responsible as illustrated in Scheme 2, which would prevent the dehydration reaction of poly (amide acid) to polyimide at the glass side surface.

Surface free energy of polyimide film prepared on various substrates

The influence of substrates on the substrate-side surface free energy of polyimide films was investigated using PMDA/ODA as a representative of polyimide. Quartz glass and silicone rubber as well as soda glass were used as substrates. First of all, the surface free energy of the used substrates was determined from the contact angle measurement and shown in Table 2. The nondispersive component of soda glass is ca. 42 mJ m^{-2} and quartz glass ca. 18 mJ m^{-2}, whereas silicone rubber is almost nonpolar (1 mJ m^{-2}). Poly(amide acid) was cast on these three substrates, and thermally imidized at the temperatures between 50 °C and 200 °C. Contact angles of polyimide films for the substrate-side are shown in Table 3, and calculated surface free energy is shown in Fig. 2. We found that the nature of substrate strongly influences the surface free energy of polyimide films by comparing the surface free energy for the air side and for the substrate sides. That is, polar substrates had influences on the nondispersive component stronger than on the dispersive component, while that nonpolar substrate had influences on the dispersive component to some extent but not on the nondispersive component.

To explain these observations, effect of the interface free energy must be taken into account. The interface free energy between polyimide and substrates, γ_{SM}, can be expressed as follows [23]:

$$\gamma_{SM} = (\gamma_S + \gamma_M) - (2\sqrt{\gamma_S^P \gamma_M^P} + 2\sqrt{\gamma_S^D \gamma_M^D})$$
$$= (\sqrt{\gamma_S^D} - \sqrt{\gamma_M^D})^2 + (\sqrt{\gamma_S^P} - \sqrt{\gamma_M^P})^2 \,. \quad (2)$$

The value of γ_{SM} was calculated by taking the obtained free energy values under the supposition that the surface free energy of the substrate does not change before and after the film cast. As clearly shown in Table 4, calculated values of the interface free energy are small enough so as to constitute stable interface. In view of the above Eq. (2), the required condition to obtain the minimum γ_{SM} value is that dispersive as well as nondispersive components of the surface free energy should be identical or at least similar in both phases forming the interface. The cast poly(amide acid) must be oriented during imidization in such a way that the phase forming the interface should match with the substrate in both chemical and surface free energy.

Table 2 Contact angles and surface free energy of substrates

Substrates	Contact angles [°]		Surface free energy [mJ m^{-2}]		
	Water	M.I.[a]	γ_S^D	γ_S^P	γ_S
Soda glass	21	36	27	42	69
Quartz glass	60	46	28	18	46
Silicone rubber	98	60	28	1	29

[a] Methyl iodide.

Table 3 Contact angles (degree) for the substrate-side of PMDA/ODA films cast on different substrates

Substrates	Liquid	Treatment temperature [°C]			
		50	100	150	200
Soda glass	Water	35	30	56	54
	M.I.[a]	29	30	28	30
Quartz glass	Water	35	42	52	58
	M.I.[a]	27	25	18	18
Silicone rubber	Water	56	60	86	88
	M.I.[a]	36	43	63	55

[a] Methyl iodide.

ATR-IR analysis of polyimide film surface

Attenuated total reflection (ATR-IR) spectra were measured in order to obtain information on chemical changes at imidization on the film surface. A comparison of the ATR-IR spectra between the air side and the glass side of PMDA/ODA films treated at 200 °C is shown in Fig. 3 as a typical example. The air side of PMDA/ODA film

Table 4 The interface free energy between the polyimide film and substrate

	γ_{SM} [mJ m^{-2}]			
	50 °C	100 °C	150 °C	200 °C
Soda glass	1	1	6	7
Quartz glass	2	1	1	1
Silicone rubber	10	10	1	1

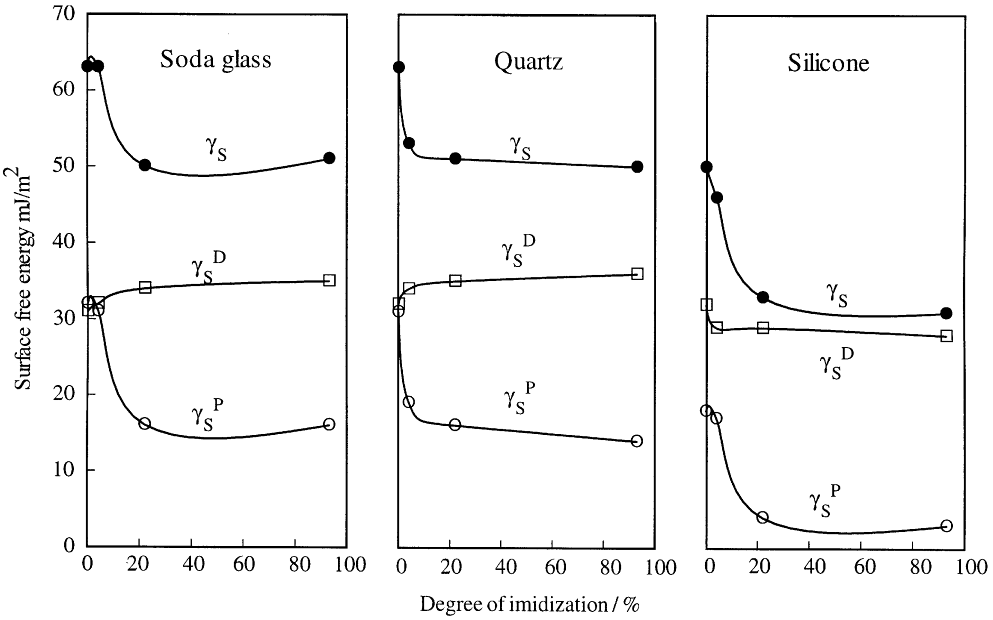


Fig. 2 Surface free energy of PMDA/ODA films for the substrate side

(Fig. 3a) shows strong characteristic absorption bands at 1776 ($\nu_{C=O}$ in phase), 1700 ($\nu_{C=O}$ out of phase), 1500 ($\nu_{C1,4-C6H4}$), 1378 (ν_{CN}), 1100 (imide), and 726 cm^{-1} (imide). The glass side (Fig. 3b) also gave a similar IR spectrum, but absorption intensity showed some difference which was shown in Fig. 3c (3b–3a). We detected positive absorption peaks at 1680 cm^{-1}, which is assigned to secondary amide of poly(amide acid) (–CO–NHR–), and negative absorption peaks of imide at 720 and 1776 cm^{-1}. The detected differences, though magnified in Fig. 3c, suggest that the degree of imidization of polyimide films for the glass side surface was not as high as that for the air side surface at the same treatment. Since the evanescent wave can sample to a depth on 0.7–3 μm into the curing film, it picks up the information mainly in the bulk. But, IR results were in accord with the above mentioned

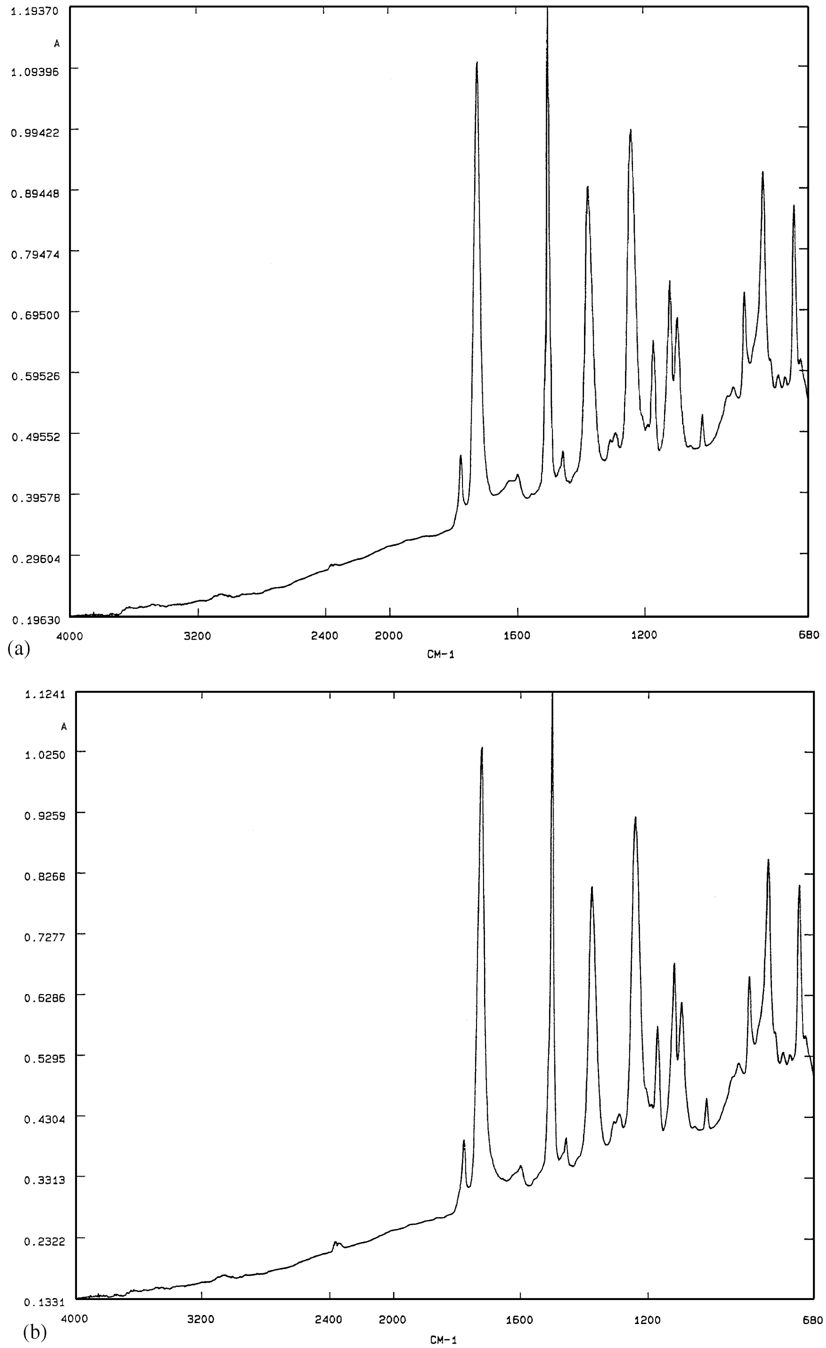


Fig. 3 IR spectra of PMDA/ODA polyimide films treated at 200 °C. (a) Air side, (b) Glass side, (c) Difference spectrum (b − a)

Fig. 3 (Continued)

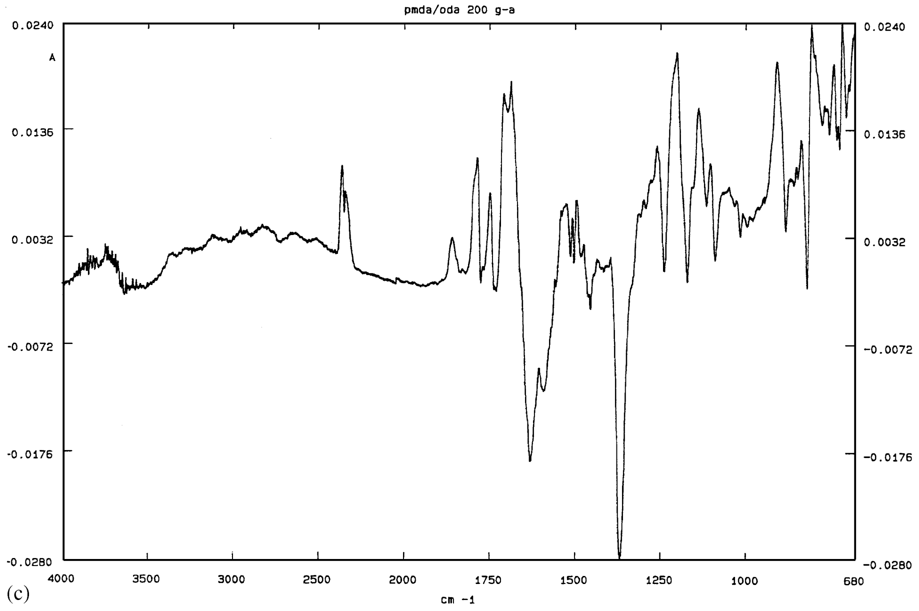


Table 5 Contact angles (degree) of various polyimide films prepared at various temperatures

Polyimide	Side	Liquid	Treatment temperature [°C]						
			50	100	130	150	170	200	300b)
BPDA/ODA	Air	Water	58.4	60.7	66.8	66.2	74.1	75.5	72.3
BPDA/ODA	Air	M.I.a)	34.2	34.3	34.5	35.9	31.5	36.3	35.0
BPDA/ODA	Glass	Water	34.7	30.1	40.3	56.1	56.1	54.0	47.4
BPDA/ODA	Glass	M.I.a)	29.4	29.8	29.7	27.7	27.3	30.2	37.2
BTDA/ODA	Air	Water	60.5	67.9	69.0	73.0	75.1	78.3	65.4
BTDA/ODA	Air	M.I.a)	35.5	34.4	37.7	36.7	36.2	35.0	15.0
BTDA/ODA	Glass	Water	49.6	51.4	58.4	58.8	60.2	58.3	33.1
BTDA/ODA	Glass	M.I.a)	32.2	28.9	31.5	25.6	28.0	26.8	34.5
6FDA/ODA	Air	Water	64.0	64.7	69.1	72.2	76.8	77.6	68.9
6FDA/ODA	Air	M.I.a)	40.4	41.1	41.4	41.0	40.8	39.6	39.5
6FDA/ODA	Glass	Water	56.3	58.1	62.8	65.1	67.5	67.5	61.6
6FDA/ODA	Glass	M.I.a)	39.1	39.3	38.6	36.4	36.2	36.6	36.4
BPDA/PDA	Air	Water	53.6	57.2	69.8	71.5	75.4	80.9	64.1
BPDA/PDA	Air	M.I.a)	35.5	37.1	37.9	36.6	35.6	36.5	19.2
BPDA/PDA	Glass	Water	46.4	46.5	47.1	52.9	60.2	60.9	57.5
BPDA/PDA	Glass	M.I.a)	28.9	27.3	25.2	23.4	20.2	16.6	14.0
PMDA/PDA	Air	Water	44.5	51.6	61.7	70.8	72.6	74.0	60.5
PMDA/PDA	Air	M.I.a)	31.5	33.2	34.0	32.6	33.1	33.3	24.4

a) Methyl iodide.
b) Treated in the air.

supposition that imidization is prevented on the glass side due to the hydrogen bonding between silanol groups on the glass and both carboxylic acid and amide groups on the film surface.

Surface free energy of various polyimide films

To examine the effect of chemical structure on the surface free energy, contact angles of various polyimide films for the air side and the glass side were measured and shown in Table 5. The surface free energies and its components with the degree of imidization were calculated and are shown in Fig. 4 for the air side and in Fig. 5 for the glass side. In these experiments, 300 °C treatment was performed in the air. This made the γ_S^p at 300 °C larger probably due to thermooxidative degradation. We will discuss this phenomena later. Here we discuss concerning the films treated in the temperature range of 50–200 °C. Compared with the film of PMDA/ODA, films of BPDA/ODA and

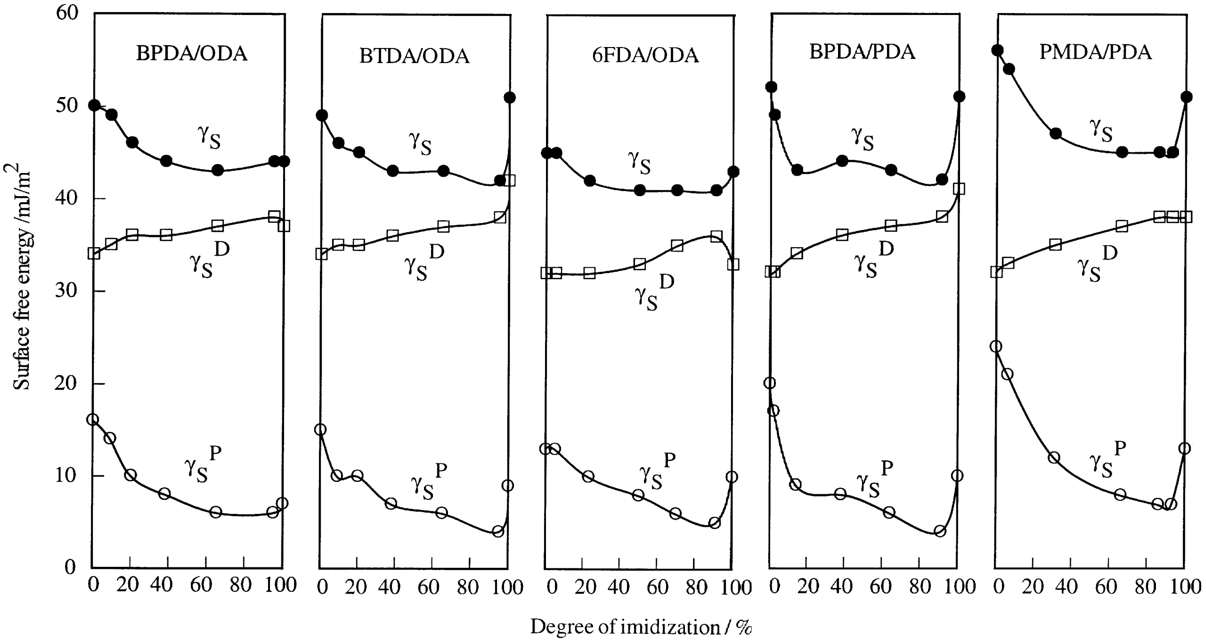
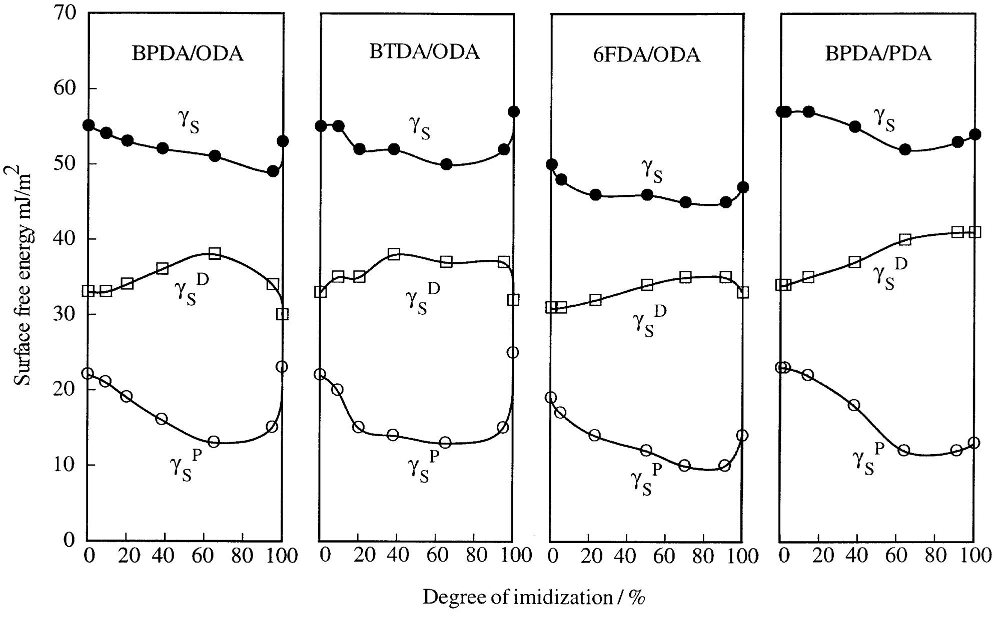


Fig. 4 Surface free energy of various polyimide films for the air side

Fig. 5 Surface free energy of various polyimide films for the glass side



BTDA/ODA have a slightly larger dispersive component and a slightly smaller nondispersive component, which became more pronounced at the glass side surface. The difference of each component can be explained from the difference in the chemical structure; both BPDA/ODA and BTDA/ODA have one more benzene ring in the repeated unit than PMDA/ODA, making them less polar. 6FDA/ODA that contains two trifluoromethyl groups in the repeated unit has the lowest dispersive component and the lowest nondispersive component. For rigid PMDA/PDA and BPDA/PDA polyimides, the increase of dispersive component and the decrease of nondispersive component were most pronounced with the progress of imidization.

Contact angles of polyimide films having internal acetylene groups (PMDA/m-intA) were also measured and surface free energy was calculated and shown in Table 6. Dispersive component of surface free energy was almost constant at 34–36 mJ m^{-2} for the films treated during 50–200 °C, and then increased to 40 mJ m^{-2} above 300 °C treatment. The increase of the dispersive component is considered to come from the crosslinking of acetylene groups, which occurs above 300 °C [14, 15, 24–27]. On the other hand, nondispersive component decreased from 11 to 5 mJ m^{-2} at treatment temperatures from 50 °C to 200 °C, and then increased above 300 °C treatment in the air. The increase is supposed to be due to the formation of oxygen-containing functional group by the thermo-oxidative degradation on the polyimide surface.

Analysis of thermal degradation of polyimide films from surface free energy

In order to investigate if thermal degradation can be followed by contact angle measurement, PMDA/ODA and BPDA/ODA films were treated at 300 °C, 350 °C, and 400 °C in both vacuo and air. From the contact angle measurements, surface free energy was calculated and shown in Table 7.

For PMDA/ODA films, nondispersive component of the films treated in vacuo increased after 400 °C treatment, suggesting that thermal degradation of the polyimide film took place in vacuo between 350 °C and 400 °C. Nondispersive component of the films treated in the air increased from 300 °C treatment, suggesting that the surface of the film was oxidized even below 300 °C in the air. At 400 °C in the air, both oxidation and thermal degradation should take place. The dispersive component for the films treated in the air is higher than that in vacuo, which may be ascribed to surface oxidation.

For BPDA/ODA films, we found that nondispersive component of the films treated in vacuo increased after 350 °C treatment, suggesting that thermal degradation for the polyimide film takes place between 300 °C and 350 °C. Nondispersive component of the films treated in the air increased above 300 °C treatment, suggesting that the surface of the film was oxidized at 300 °C treatment. Both oxidation and thermal degradation for the polyimide film take place at 350 °C in the air.

The thermal stability is most often analyzed by TGA. In these polyimides, temperature at 5% weight loss is above 500 °C and weight loss cannot be detected below 450 °C. Thus, from the change of surface free energy, we can easily detect the chemical changes in the surface due to thermal degradation, which cannot be analyzed by thermogravimetric analysis.

Table 6 Contact angles and surface free energy of PMDA/m-intA treated at various temperatures

Temperature [°C]	Contact angles [°]		Surface free energy [mJ m^{-2}]		
	Water	M.I.[a]	γ_S^D	γ_S^P	γ_S
50	65.9	36.1	34	11	45
100	65.6	36.5	34	11	45
150	73.4	36.3	36	7	43
200	79.9	42.0	35	5	40
300[b]	62.1	25.1	39	12	51
350[b]	59.9	20.0	40	13	53
400[b]	60.5	20.5	40	13	53

[a] Methyl iodide.
[b] Treated in the air.

Conclusions

1. The relationship between surface free energy and the change of surface functional groups can be determined through contact angles.
2. The polarity of the glass side of polyimide film is higher than that of the air side. Hydrogen bonding between the polar groups of polymer surface and silanol groups of glass is supposed to prevent imidization.
3. The substrates were found to influence surface free energy of polyimide films. Polar substrates have influences mainly on nondispersive component of the surface free energy, while nonpolar substrates have

Table 7 Surface free energy [mJ m^{-2}] of polyimide treated at higher temperatures

Treatment	Temperature [°C]	PMDA/ODA			BPDA/ODA		
		γ_S^D	γ_S^P	γ_S	γ_S^D	γ_S^P	γ_S
In vacuo	200	32	4	36	37	3	40
	300	33	4	37	41	3	44
	350	33	4	37	38	9	47
	400	32	9	41	41	9	50
In air	300	35	6	41	37	7	44
	350	37	6	43	43	9	52
	400	38	8	46	44	8	52

influences to some extent on the dispersive component but not on the nondispersive component. These influences must result in the formation of the interface with minimum free energy.

(4) Among various polyimide films, there is a slight but definite difference in the surface free energy and its components depending on the difference of chemical structure.

(5) The measurement of contact angles of polyimide films gave information on surface oxidation and thermal degradation at the very initial stage, which could not be analyzed by thermogravimetric analysis.

References

1. Sroog CE (1976) J Polym Sci Macromol Rev 11:161
2. Ghosh MK, Mittal KL (1996) Polyimide: Fundamentals and Applications. Marcel Dekker, New York
3. Garbassi F, Occhiello E, Morra M (1996) Polyimide: Fundamentals and Applications In: Ghosh MK, Mittal KL (eds) Ch 14, p 367. Marcel Dekker, New York
4. Factor BJ, Russell TP, Toney MF (1993) Macromolecules 26:2847
5. Saraf RF, Dimitrakopoulos C, Toney MF, Kowalczyk SP (1996) Langmuir 12:2802
6. Hasegawa M, Matano T, Shindo Y, Sugimura T (1996) Macromolecules 29:7897
7. Flitsch R, Shih DY (1990) J Vac Sci Technol A 8(3):2376
8. Sacher E (1978) J Appl Polym Sci 22:2137
9. Sacher E (1982) J Colloid Interface Sci 88:309
10. Buchwalter LP (1989) J Vac Sci Technol A7:1772
11. Jonson Jr RE, Dettre RH (1993) In: Berg JC (ed) Wettablity, Ch 1, p 1. Marcel Dekker, New York
12. Fowkes FM, Riddle Jr FL, Pastore WE, Weber AA (1990) Colloid Surf 43:367
13. Takeichi T, Stille JK (1986) Macromolecules 19:2103
14. Takeichi T, Takahashi N, Yokota R (1994) J Polym Sci Part A, Polym Chem 32:167
15. Takeichi T, Nakajima K (1996) React Func Polym 30:3745
16. Yamada K, Yamada M, Kimura T, Izumi T, Hirata M (1989) Nippon Kagaku Kaishi 1:105
17. Kaelble DH (1970) Physical Chemistry of Adhesion, Ch 5. Wiley/Interscience, New York
18. Tsutsumi K, Ishida S, Shibata K (1990) Colloid Polym Sci 269:31
19. Sroog CEA, Endrey L, Abramo SV, Berr CE, Edwards WM, Olivier KL (1965) J Polym Sci Part A, Polym Chem 3:1373
20. Inagaki N, Tasaka S, Hibi K (1992) J Polym Sci Part A, Polym Chem 30:1425
21. Fowkes MF, Riddle Jr LF, Pastore WE, Weber AA (1990) Colloid Surf 43:367
22. London F (1937) Trans Faraday Soc 33:8
23. Mori K, Oishi Y, Hirahara H, Kanae K, Iwabuchi A, Tutumi A, Yamabe H (1993) Kobunshi Ronbunshu 50:629
24. Takeichi T, Date H, Takayama Y (1990) J Polym Sci Part A, Polym Chem 28:1989
25. Takeichi T, Kobayashi A, Takayama Y (1992) J Polym Sci Part A, Polym Chem 30:2645
26. Takeichi T, Ogura S, Takayama Y (1994) J Polym Sci Part A, Polym Chem 32:579
27. Takeichi T, Tanikawa M, Zuo M (1997) J Polym Sci Part A, Polym Chem 35:2395