Studies on PI/PI Adhesion Strength

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SYNOPSIS

The adhesion of polyimide to polyimide was studied by measuring the peel strength of
various polyimide–polyimide composites. Different factors such as diffusion of polyamic
acid to polyimide substrate, contact angle, wettability, and the thermal expansion coefficient
of polyimide films and the presence of siloxane can affect this adhesion and are discussed
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INTRODUCTION

Polyimide (PI) has the characteristic of high thermal stability, low dielectric constant, high chemical resistance, and ease of processing. It is widely used in the production of electronic packaging materials, such as multichip modules, flexible printed circuit boards, and tape automated bonding. For example, polyimide can improve the signal propagation and reduce the crosstalk of the resulting product when it is bonded to metal foil. For successful applications, reliable adhesion between the polyimide and the substrate is crucial. A number of studies on polyimide adhesion have been performed with metal evaporated onto the cured PI surface in an ultrahigh vacuum system.[1-4] The polymer-on-metal-type interfaces have also been widely studied recently.[5-7] The adhesion of polymers to themselves is a subject of echnical importance in that there are some reports concerned with self-adhesion of the polyimide or interfacial interactions between polyimide layers.[8-11]

The fundamental adhesion as defined by Mittal[12] is the summation of all interatomic or intermolecular interactions at the interface of the adherend and the adherate. The thermodynamic work of adhesion is the change in free energy when the materials to be adhered are brought together. The measured adhe-

sion, which is called practical adhesion, is a function of basic adhesion and several other factors such as intrinsic or local stresses, presence of easy fracture sites, and techniques of measurement.

The generally accepted mechanism of polymer-polymer adhesion[11] include the (1) mechanical interlocking theory, (2) theories based on surface energies, wetting, and adsorption, (3) diffusion theory, (4) electronic or electrostatic theory, (5) chemical bonding, and (6) weak boundary layers. The diffusion of polymer molecules across the interface that allows chains to entangle seems to be generally accepted as the major role in polymer–polymer adhesion.[8,9]

In the process of manufacturing polyimide/metal multilayer devices, polyamic acid is first spin-coated on the polyimide substrate with copper conductors and is then converted to the polyimide by curing at elevated temperature. The interfacial strength of polyimide to polyimide is dependent on the interdiffusion of the two layers according to diffusion theory. However, the importance of wettability of the polyimide substrate by the top layer polyamic acid, and the thermal expansion coefficient of both polyimide layers after imidization, should not be neglected.

To obtain a better understanding on polyimide-polyimide adhesion, the peel strengths of various polyimide–polyimide interfaces have been studied. The contact angles for various polyimides wetted by polyamic acid were measured. By using the equation of state of Neumann et al.[13-16] together with Young's equation, the solid surface tension γ_{SV} and solid/
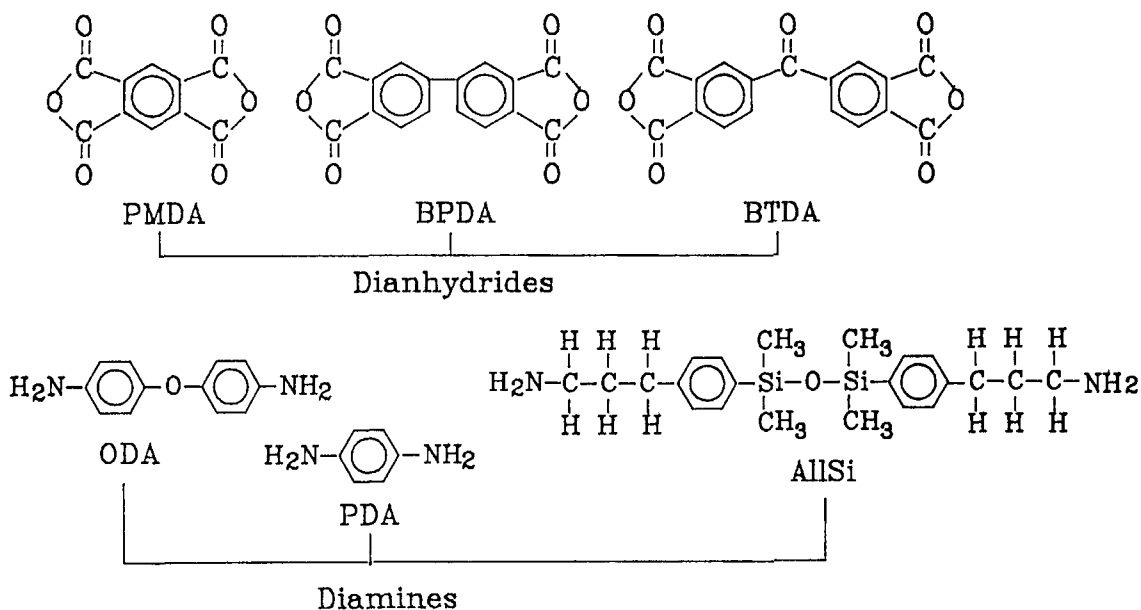
Figure 1 The structures of dianhydride and diamine of polyamic acid.

liquid interfacial tension γ_{SL} have been calculated through the data of the contact angle and the liquid surface tension. The thermal expansion coefficient of polyimide films were also investigated. A correlation among contact angle, thermal expansion coefficient, and peel strength has been conducted.

EXPERIMENTAL

The polyimide substrates were prepared by spread-coating separately three series of polyamic acid on clean Al foil. These series are PMDA/ODA, PMDA/ODA/PDA, PMDA/ODA/AllSi; BPDA/ODA, BPDA/ODA/PDA, BPDA/ODA/AllSi; and BTDA/ODA, BTDA/ODA/PDA, BTDA/ODA/AllSi. (Their molecular structures are shown in Fig. 1.) Next, they were cured at high temperature by increasing the temperature from room temperature to 350°C in 90 min and then kept at 350°C for 30 min under ambient condition. The film thickness was about 7 μm. The thermal expansion coefficient of each film was measured by a TMA 2940 thermomechanical analyzer from DuPont. On each polyimide substrate film, nine kinds of polyamic acid varnish were separately spread-coated on top. These specimens were then put in an oven and cured as before. The top polyimide film was then incised into $\frac{1}{2}$ in.-wide strips. The adhesion strength between two layers was studied by a 90° peel test machine from Shimadzu, Model AG-5000A. The peeling speed was kept constant at 25 mm/min. The contact angle of

each polyimide/polyamic acid varnish interface was measured by contact anglemeter CA-A from Kyowa Kaimenkagaku Co.

The surface tension of each polyamic acid varnish was measured by a C2000 electrobalance from CAHN. The surface tension of the polyimide film, γ_S, was calculated using the equation of state of Neumann et al.:

$$\gamma_{SL} = \frac{\gamma_{SL} + \gamma_{LV} - 2\beta \sqrt{\gamma_{SL} \cdot \gamma_{LV}}}{1 - 2\alpha \sqrt{\gamma_{SV} \cdot \gamma_{LV}}} \quad (1)$$

and the Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_e \quad (2)$$

where $\alpha = 0.0075$; $\beta = 1.00$; γ_{SV} is the solid/vapor interfacial tension; γ_{LV}, the liquid/vapor interfacial tension; γ_{SL}, solid/liquid interfacial tension; and θ_e, the equilibrium contact angle. Substitution of γ_{SL} in Eq. (2) into Eq. (1) and rearranging the terms, the following equation was obtained:

$$\gamma_{SV}^3 - \frac{2}{\alpha} (\alpha \cdot \gamma_{LV} \cos \theta_e + \beta) \gamma_{SV}^2$$

$$+ \frac{1}{\alpha^2} (\alpha \cdot \gamma_{LV} \cos \theta_e + \beta^2) \gamma_{SV}$$

$$- \frac{1}{4\alpha^2} (1 + \cos \theta_e)^2 \gamma_{LV} = 0 \quad (3)$$

Table I   Surface Tension of Polyamic Acid Varnishes and Solvent NMP, γ_L

Surface Tension		Polyamic Acid									
	PMDA/ ODA	PMDA/ ODA/ AllSi	PMDA/ ODA/ PDA	BPDA/ ODA	BPDA/ ODA/ AllSi	BPDA/ ODA/ PDA	BTDA/ ODA	BTDA/ ODA/ AllSi	BTDA/ ODA/ PDA	NMP
γ_L (erg/cm^2)	41.76	42.23	36.19	41.76	42.23	42.69	44.55	39.91	42.69	40.37

The contact angle θ_e for each polyamic acid/ polyimide interface and liquid surface tension γ_{LV} for each polyamic acid were measured and substituted into the above equation. Therefore, the only unknown in Eq. (3) is γ_{SV}, which was calculated by solving the above equation using a computer program reported by Neumann et al.[13] Only one real root was obtained; the other two were imaginary and had no physical significance. The liquid/solid interface tension γ_{SL} was calculated by substition of the real root into Eq. (2).

RESULTS

The surface tensions of different types of polyamic acid varnishes are very close to that of pure solvent NMP ($\sim$ 40.37 erg/cm) as shown in Table I.

The contact angles for polyamic acid varnish/ polyimide substrate interfaces were measured (Table II). The siloxane-containing polyimide substrates showed a larger contact angle than that of the other two homologous substrates without sil-

oxane. On the other hand, siloxane-containing varnish has smaller contact angles than those without siloxane.

The polyimide/polyamic acid varnish interface energies, γ_{SL}, and the polyimide solid surface tensions, γ_{SV}, were calculated and are shown in Tables III and IV, respectively. With the same polyamic acid top coating, the polyimide substrates containing siloxane show larger interface energies, γ_{SL}, and smaller solid surface tension, γ_{SV}, than those of the other two homologous substrates. According to Eq. (3), it is found that with the same γ_{LV} value, i.e., with the same top polyamic acid coating, substrates with larger contact angles show smaller γ_{SV} values but larger γ_{SL} values, i.e., a solid surface with higher surface free energy but smaller interfacial energy is more readily wetted by the liquid phase.

The binding forces between polyimide layers studied by the peel strength measurement are shown in Table V. Generally, the top-layer polyimide films are more fragile when the underlayer film (i.e., the substrate) contained siloxane, especially for those whose top films also contained siloxane. In the ho-

Table II   Contact Angles of the Polyamic Acid Varnish/Polyimide Interface

Polyimide	Polyamic Acid								
	PMDA/ ODA	PMDA/ ODA/ AllSi	PMDA/ ODA/ PDA	BPDA/ ODA	BPDA/ ODA/ AllSi	BPDA/ ODA/ PDA	BTDA/ ODA	BTDA/ ODA/ AllSi	BTDA/ ODA/ PDA
	Contact Angle								
PMDA/ODA	28°	28°	28°	38°	15°	24°	25°	28°	42°
PMDA/ODA/AllSi	36°	36°	44°	42°	28°	45°	36°	38°	33°
PMDA/ODA/PDA	22°	24°	33°	32°	14°	22°	20°	20°	23°
BPDA/ODA	20°	30°	30°	40°	15°	25°	25°	19°	25°
BPDA/ODA/AllSi	47°	42°	53°	56°	48°	51°	48°	50°	49°
BPDA/ODA/PDA	23°	30°	30°	42°	27°	28°	24°	24°	23°
BTDA/ODA	26°	29°	25°	37°	26°	26°	22°	20°	29°
BTDA/ODA/AllSi	44°	47°	46°	51°	37°	43°	38°	41°	38°
BTDA/ODA/PDA	20°	20°	19°	25°	15°	18°	17°	16°	24°

Table III   Polyimide/Polyamic Acid Varnish Interface Energies, γ_{SL} (erg/cm^2)

| | Polyamic Acid | | | | | | | | |
Polyimide	PMDA/ ODA	PMDA/ ODA/ AllSi	PMDA/ ODA/ PDA	BPDA/ ODA	BPDA/ ODA/ AllSi	BPDA/ ODA/ PDA	BTDA/ ODA	BTDA/ ODA/ AllSi	BTDA/ ODA/ PDA
	Interface Energy								
PMDA/ODA	0.27	0.28	0.22	0.84	0.03	0.16	0.20	0.25	1.24
PMDA/ODA/AllSi	0.69	0.71	1.12	1.20	0.28	1.14	0.78	0.78	0.52
PMDA/ODA/PDA	0.11	0.16	0.40	0.45	0.02	0.11	0.09	0.07	0.14
BPDA/ODA	0.08	0.36	0.28	1.01	0.03	0.19	0.20	0.06	0.19
BPDA/PDA/AllSi	1.77	1.22	2.13	3.16	1.93	2.41	2.11	2.03	2.11
BPDA/ODA/PDA	0.13	0.36	0.28	1.20	0.24	0.29	0.17	0.14	0.14
BTDA/ODA	0.21	0.32	0.14	0.76	0.21	0.22	0.12	0.07	0.33
BTDA/ODA/AllSi	1.41	1.80	1.31	2.33	0.78	1.35	0.94	1.02	0.87
BTDA/ODA/PDA	0.08	0.08	0.05	0.18	0.03	0.05	0.05	0.03	0.16

mologous series with the same top polyamic acid coating, substrates containing only ODA diamine showed stronger peel strength than did those containing both ODA and PDA diamines. In general, BTDA-based polyimide substrates had stronger peel strength than that of BPDA-based polyimide substrates, with PMDA-based polyimide substrates being the weakest.

The molecular structure of the three series of polyamic acid studied are shown in Figure 1. The thermal expansion coefficients of the polyimide films are shown in Table VI. From these two sets of data, we found that there is a strong correlation between the molecular structure and the thermal expansion coefficient. If the molecule contains a more rigid segment or longer rigid segment, it shows a smaller thermal expansion coefficient. On the other hand, if the molecule contains a more flexible segment or a longer flexible segment, it exhibits a larger thermal expansion coefficient. In all three series studied, within the homologous series, the films containing siloxane show the largest thermal expansion coefficient and the films containing PDA have the smallest thermal expansion coefficient. Another obvious trend is that the thermal expansion coefficient of the BTDA series is larger than that of the BPDA series, with the PMDA series being the smallest provided that they contain the same diamine.

Table IV   Polyimide Solid Surface Tensions, γ_S (erg/cm^2)

| | Polyamic Acid | | | | | | | | | |
Polyimide	PMDA/ ODA	PMDA/ ODA/ AllSi	PMDA/ ODA/ PDA	BPDA/ ODA	BPDA/ ODA/ AllSi	BPDA/ ODA/ PDA	BTDA/ ODA	BTDA/ ODA/ AllSi	BTDA/ ODA/ PDA	Average
	Solid Surface Tension									
PMDA/ODA	37.15	37.57	32.17	33.75	40.82	39.16	40.58	35.49	32.97	36.63
PMDA/ODA/AllSi	34.49	34.87	27.16	32.23	37.57	33.36	36.82	32.23	36.33	33.89
PMDA/ODA/PDA	38.83	38.74	30.75	35.87	41.20	39.70	41.95	37.57	39.43	38.20
BPDA/ODA	39.32	36.93	31.62	33.00	40.82	38.88	40.58	37.79	38.38	37.53
BPDA/ODA/AllSi	30.25	32.69	23.91	26.51	30.19	29.27	31.92	27.68	30.11	29.17
BPDA/ODA/PDA	38.57	36.93	31.62	32.23	37.87	37.98	40.87	36.60	39.43	36.90
BTDA/ODA	37.74	37.25	32.94	34.12	38.17	38.59	41.43	37.57	37.66	37.27
BTDA/ODA/AllSi	31.45	30.60	26.45	28.61	34.51	32.17	36.05	31.14	34.51	31.76
BTDA/ODA/PDA	39.32	39.76	34.26	38.03	40.82	40.65	42.65	38.39	39.16	39.23

Table V   Peel Strength^a of Polyimide/Polyimide

Polyimide	Polyamic Acid								
	PMDA/ODA	PMDA/ODA/AllSi	PMDA/ODA/PDA	BPDA/ODA	BPDA/ODA/AllSi	BPDA/ODA/PDA	BTDA/ODA	BTDA/ODA/AllSi	BTDA/ODA/PDA
				Peel Strength					
PMDA/ODA	Strong	0.141	1.162	0.884	0.211	1.408	Strong	1.232	1.566
PMDA/ODA/AllSi	0.194	0.123	0.106	Weak fragile	0.070	Strong fragile	0.106	Strong fragile	Strong
PMDA/ODA/PDA	0.563	0.088	0.422	0.211	0.141	0.007	0.211	1.162	1.338
BPDA/ODA	Strong	0.229	2.640	3.391	0.422	2.816	Strong	Strong	3.872
BPDA/ODA/AllSi	Strong	Weak fragile	Weak fragile	Strong	Strong fragile	Strong	0.135	Strong fragile	Strong
BPDA/ODA/PDA	Strong	0.176	Strong	3.344	1.144	9.328	Strong	Strong	4.576
BTDA/ODA	Strong	Strong	Strong	Strong	Strong	Strong	Strong	Strong	Strong
BTDA/ODA/AllSi	Strong	Weak fragile	Strong	Strong fragile	Strong fragile	Strong fragile	Strong	Strong fragile	Weak fragile
BTDA/ODA/PDA	Strong	0.141	Strong	2.112	0.141	3.520	Strong	Strong	1.549

^a The unit of peel strength is pounds/inch. "Strong" means that the composite is very difficult to delaminate, and "weak," that the composite is easy to delaminate.

Table VI   Thermal Expansion Coefficient of Polyimide Films

Thermal Expansion Coefficient (μm/m °C)	Polyamic Acid								
	PMDA/ ODA	PMDA/ ODA/ AllSi	PMDA/ ODA/ PDA	BPDA/ ODA	BPDA/ ODA/ AllSi	BPDA/ ODA/ PDA	BTDA/ ODA	BTDA/ ODA/ AllSi	BTDA/ ODA/ PDA
α	18.1	46.4	16.3	30.8	52.0	23.4	31.6	59.6	29.8
Rigid/flexible	Rigid flexible	Rigid flexible flexible	Rigid flexible rigid	Rigid flexible	Rigid flexible flexible	Rigid flexible rigid	Flexible flexible	Flexible flexible flexible	Flexible flexible rigid

DISCUSSION

The factors that influence the adhesion of polyimide film to polyimide film are

1. the diffusion of polyamic acid across the interface;
2. the curing schedule of both layers; and
3. the molecular structure at the interface after imidization.

In this study, both the substrate polyimide and the top layer were cured under a fully imidized schedule[17]; therefore, the influence of curing schedule on adhesion is negligible here.

The Effect of Polyamic Acid Diffusion on Adhesion

After the polyamic acid is spin-coated on the substrate polyimide, the latter might be swelled by the NMP solvent, allowing polyamic acid small molecules to penetrate into the polyimide substrate. If this penetration really took place, upon curing, acid–base interaction or chemical-bond formation between the substrate polyimide and the polyamic acid might occur. It is a common fact that the lower the packing density of the substrate polyimide the higher the possibility for polyamic acid penetration. Based on the molecular structures of the three dianhydrides, the PMDA series has the highest packing density, and the BTDA series, the lowest. The sequence of these substrates showing easy susceptibility to polyamic acid penetration is the following: substrate of PMDA series < substrate of BPDA series < substrate of BTDA series.

There is also a correlation between polyamic acid penetration and adhesion strength. As shown in Table V, BPDA-based polyimide substrates show stronger peel strength than that of PMDA-based

polyimide substrates and the peel strength of BTDA-based polyimide substrates was comparable with that of BPDA-based substrates.

The structure of diamines can also affect polyamic acid penetration, which, in turn, affects the adhesion strength. As ODA diamine contains a more flexible molecular structure than that of PDA, polyimide substrate containing ODA alone is less compact than those containing both ODA and PDA; therefore, it is easier for the polyamic acid to penetrate into it. As a result, those ODA-containing substrates have higher adhesion strength than that of those containing both ODA and PDA diamines (Table V).

In this study, the contact angle was measured right after a small drop of polyamic acid was in contact with the substrate, i.e., the contact period is short. Also, the penetration of polyamic acid was mainly during the curing process; therefore, polyamic acid penetration did not affect the contact angle. The result of the solid surface energy study indicates also that there is no direct relationship between contact angle and adhesion strength.

The Effect of Wettability and Thermal Expansion Coefficient of Polyimide Films on Peel Strength

The wetting of polyamic acid on polyimide film depends on short-range molecular forces. When there is a strong intermolecular force, the contact angle is small. After imidization, the molecular structure at the interface will influence the binding force of the composite films. Experimental results indicate that there is a strong correlation between molecular structure and the thermal expansion coefficient (Table VI). When the contact angle is small (θ_e < 30°), even spreading occurs, and after imidization, if the difference of the thermal expansion coefficient between the top and the substrate layers of polyimide films is small ($\Delta\alpha$ < 5), a strong adhesion between these two layers may result. This is well

Table VII   Contact Angle θ_e and the Difference of Thermal Expansion Coefficient $\Delta\alpha$ of Those Without Siloxane: A: $\theta_e \leq 30°$; B: $\theta_e > 30°$; C: $\Delta\alpha \leq 5$; D: $\Delta\alpha > 5$

	Polyamic Acid					
Polyimide	PMDA ODA	PMDA ODA PDA	BPDA ODA	BPDA ODA PDA	BTDA ODA	BTDA ODA PDA
PMDA/ODA	AC	AC	BD	AD	AD	BD
PMDA/ODA/PDA	AC	BC	BD	AD	AD	AD
BPDA/ODA	AD	AD	BC	AD	AC	AC
BPDA/ODA/PDA	AD	AD	BD	AC	AD	AD
BTDA/ODA	AD	AD	BC	AD	AC	AC
BTDA/ODA/PDA	AD	AD	AC	AD	AC	AC

demonstrated by most of the AC samples (A: $\theta_e \leq 30°$; C: $\Delta\alpha \leq 5$) in Table VII. (Their peel strengths are shown in Table III.) On the other hand, when the contact angle is large ($\theta_e > 30°$), noneven spreading may result; after imidization, if the difference of the thermal expansion coefficient between the top and the substrate layers of polyimide films is large ($\Delta\alpha > 5$), poor adhesion between these two layers may result. This may be the reason for the low peel strength (Table III) shown by the BD samples in Table VII (B: $\theta_e > 30°$; D: $\Delta\alpha > 5$). For the case of a small contact angle ($\theta_e < 30°$) and a large difference in the thermal expansion coefficient ($\Delta\alpha > 5$), the wettability between the layers is good, but the stress is large. If one of the molecular structures at the interface is very flexible, it is still possible that an interaction between two layers may occur and result in moderate or high peel strength as shown by most AD samples (A: $\theta_e \leq 30°$; D: $\Delta\alpha > 5$) in Table VII (Their peel strengths are shown in Table III.) In the case of a large contact angle ($\theta_e > 30°$) and a small difference in the thermal expansion coefficient ($\Delta\alpha < 5$), the one with flexible structure will result in high peel strength, as shown by the composite of the BPDA/ODA interface with the BPDA/ODA film. Also, the composite with a rigid structure will result in low peel strength, as demonstrated by the composite of the PMDA/ODA/PDA interface with the PMDA/ODA/PDA film.

The Impact of Siloxane on Adhesion

The viscosity of polyamic acid containing siloxane decreases with time even below 5°C because a reaction similar to hydrolysis occurs and the molecule becomes smaller.[18] As a result, the contact angle is smaller when the top-layer polyamic acid contained siloxane (BPDA series is a typical example) but

larger when the polyimide substrates contained siloxane. Also, the top-layer polyimide is fragile when the substrate polyimide contained siloxane. The hydrophobic character of siloxane groups that was found in higher concentration near the surface for siloxane-containing polyimide films is responsible for the occurrence of a large contact angle, and the appearance of siloxane domains results in the fragility of the top-layer polyimide films.[19]

The inclusion of siloxane in the substrate film will greatly increase the thermal expansion coefficient and the contact angle when interfaced with any polyamic acid top coating. As a result, there is no siloxane-containing composite with a small contact angle ($\theta_e < 30°$) and a small difference in the thermal expansion coefficient ($\Delta\alpha < 5$). In this study, only two of the composites show a large contact angle ($\theta_e > 30°$) and a small difference in the thermal expansion coefficient ($\Delta\alpha < 5$), one of which has a flexible structure (BPDA/ODA/AllSi interface with PMDA/ODA/AllSi film), which results in high peel strength. The other one has a rigid structure (PMDA/ODA/AllSi interface with PMDA/ODA/AllSi film), which results in low peel strength. Most of the polyimide/polyimide composites studied in this paper have a large difference in the thermal expansion coefficient. However, if the molecular structure of the diamine and dianhydride of either layer is flexible, a high peel strength composite can be obtained.

CONCLUSION

Experimental results of this study indicated that the structure of the substrate polyimide has a great influence on adhesion by interfering with the diffusion of polyamic acid. It is a common fact that if the

packing density of the substrate polyimide is high the peel strength of the composite is low; if the packing density of the substrate polyimide is low, the peel strength is high. Our experimental results found that, in general, the peel strength is lower for the PMDA series substrate polyimide than for the BPDA or BTDA series, and in the homologous series, with the same polyamic acid top coating, the peel strength is stronger for the substrate film containing ODA as the only diamine than for those containing both ODA and PDA diamines.

Also, the wettability and thermal expansion coefficient of polyimide films can affect adhesion. If the contact angle is small ($\theta_e < 30°$) and the difference of thermal expansion coefficient between the top and the substrate layers of polyimide films is also small ($\Delta\alpha < 5$), a strong adhesion will result; however, when the difference of the thermal expansion coefficient is large, the molecular structure at the interface should be flexible to obtain a high peel strength composite.

The hydrophobic character of siloxane and the appearance of the siloxane domain at the film surface can greatly increase the contact angle, which, in turn, affects the adhesion; however, if a flexible molecular structure is present at the interface, a high peel strength composite can also be obtained.

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