

# Adhesion of Polyimide to Silicon and Polyimide

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## SYNOPSIS

The characteristics of the adhesions of polyimide to silicon and to polyimide and the autohesion of a polyimide blend have been investigated. As found, the peel strength of pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA) on silicon can be greatly improved by blending with 20 or 40% benzophenone tetracarboxylic dianhydride-*p*-phenylene diamine (BPDA-PDA). Exposing in air for a 2 day period resulted in a serious deterioration in adhesion for the pure PMDA-ODA system, while in no deterioration for the blend systems. Regardless of adhesion or autohesion, the resulting peel strength decreased markedly with the increase of the curing temperature. It was also found that based on the same curing temperature the diffusion of NMP is much faster in the film of PMDA-ODA than in the blend containing 20% BPDA-PDA. Beside curing temperature, imide-to-imide compatibility seems to play an important role in affecting the adhesion characteristics. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polyimides are promising materials for a wide range of applications, such as microelectronic packaging, because of their excellent mechanical properties, low dielectric constant, high glass transition temperature, and high planarization characteristics.<sup>1-7</sup> In multichip packaging, for example, the adhesion of polyimide to other materials or to itself is one of the major concerns to processing feasibility or device reliability. Generally speaking, the adhesion of polyimides on silicon or quartz substrates is relatively poor. To avoid any possible adhesion failure, an appropriate adhesion promoter is usually applied. This would somehow make the corresponding processing at least more costly. However, the adhesion strength of polyimide with silicon may vary with different imide structures. Therefore, it would be very beneficial to search for any polyimide or polyimide blend capable of adhering strongly with silicon and other substrates.

Furthermore, the adhesion strength of a given polyimide on a substrate may be affected by water

or solvent. This may, respectively, result from uptaking moisture when exposing the polyimide-cast structure in air or uptaking solvent during fabrication. Hence, the effects of uptake moisture and a solvent, *n*-methylpyrrolidone (NMP), on the adhesion strength of polyimide on silicon are investigated. The effects may, in turn, be controlled by their diffusion processes if the exposure time is finite. Especially for NMP, its diffusion in most polyimides is relatively slow,<sup>8,9</sup> compared to the diffusion of water.<sup>10</sup> The diffusion rate of NMP may vary in polyimides with different imide structures and curing temperatures. Therefore, also investigated is the effect of curing temperature on the diffusion of NMP in two different polyimide films. They are semiflexible polyimide, pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA), and its blend with a rigid rodlike polyimide, benzophenone tetracarboxylic dianhydride-*p*-phenylene diamine (BPDA-PDA). The solvent diffusion experiments were performed using a bending beam technique.<sup>9</sup>

Beside the typical polyimide-on-silicon structure, structures with polyimide-on-polyimide are often encountered in most recently developed multichip modules, wherein multiple polyimide layers are cast and cured alternately successively for a multilevel interconnection purpose.<sup>2,11,12</sup> Unlike that between

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a polyimide film and an unpenetratable substrate like silicon, the autohesion or adhesion of a given polyimide film on a prior cast polyimide film having the same or different imide structure has its own uniqueness. That is that a later-cast polyimide film could penetrate into the prior-cast film and the strength of adhesion would then strongly depend on the depth of penetration.<sup>13</sup>

However, varying with the extent of curing, polyimide films would become insoluble and difficult to swell once cured. This would, in turn, make the penetration or diffusion of the polymeric chains of the later-applied film into the prior film very difficult, if not at all impossible. It is believed that penetration of the polymeric chains would become possible or much more effective only after the prior film is swollen. This swelling process is actually governed by the diffusion of solvent. Therefore, in this report, the resulting solvent diffusion data have been correlated to the peel test results regarding the strengths of the adhesion of 6FDA-PDA on PMDA-ODA and the autohesion of an imide blend.

## EXPERIMENTAL

### Materials

The starting materials used in this study were dianhydrides: pyromellitic dianhydride (PMDA),

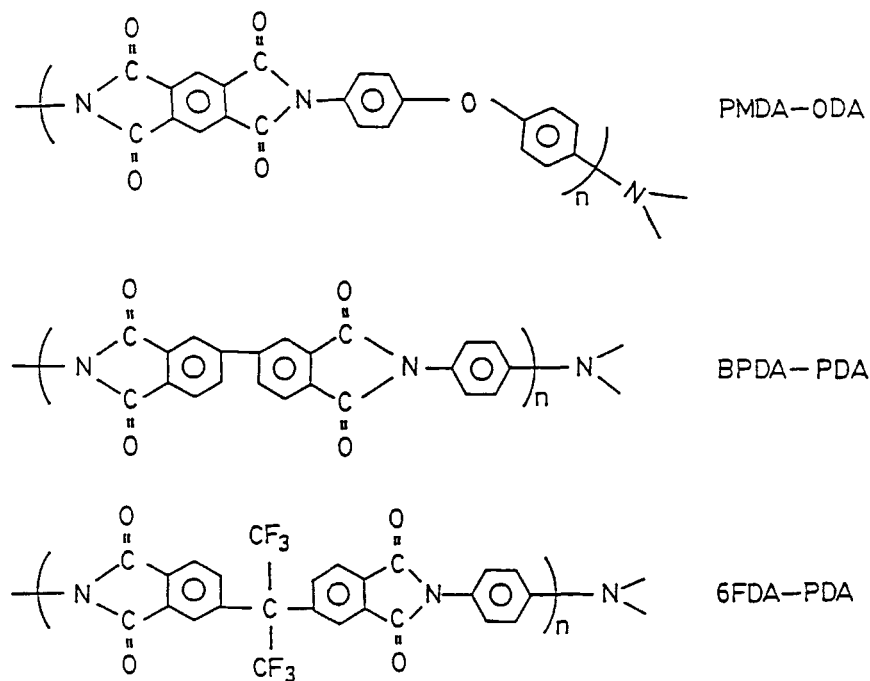
3,3',4,4'-benzophenone tetracarboxylic dianhydride (BPDA), and 6F-dianhydride (6FDA); and diamines: *p*-phenylene diamine (PDA) and 4,4'-oxydianiline (ODA). The solvent was *N*-methylpyrrolidone (NMP). These materials were used as received.

### Preparation of Polyimide Precursors-Polyamic Acids

PMDA-ODA, BPDA-PDA, and 6FDA-PDA polyamic acids were prepared as follows: In a four-neck round-bottle flask, diamine (PDA or ODA) was dissolved in the NMP solvent. When the diamine had been completely dissolved, equal molar dianhydride (6FDA, BPDA, or PMDA) was added gradually. The reaction proceeded for 5 h with stirring. The entire process was done under nitrogen atmosphere. The resulting solution had a solid content of 14 wt %. The molecular structures of the resultant polyamic acids (after cured to solid imides) are shown in Figure 1.

### Polyimide Blend

Blends of PMDA-ODA and BPDA-PDA with four different compositions were obtained by mixing the resulting polyamic acids. The mixing was done under nitrogen atmosphere for 20 min and then kept frozen before use.



**Figure 1** Molecular structures of the studied polyimides.

### Peel Test Specimen Preparation

Polyimide-on-silicon peel test specimens were prepared by spin-casting the resulting polyamic acids on silicon wafers. These silicon wafers had been pretreated by washing with soap water, rinsing with deionized water and isopropyl alcohol, and hot-air drying. The resulting samples were prebaked at 80°C for 30 min and then heated up, with a 2°C/min ramp rate, to 400°C for curing for another 30 min. The resulting polyimide films were about 30 μm. To investigate the effect of moisture absorption, one batch of the samples was kept in vacuum until testing and another batch was exposed to the ambience with a 55% RH. A 90° peel test was employed to determine the strengths of adhesion of these polyimide-on-silicon samples, as illustrated in Figure 2(a). The test was performed at a pull rate of 39 μm/s.

Polyimide-on-polyimide peel test specimens were prepared as follows: The first layer of polyimide film was prepared according to the procedures mentioned above, but on a glass substrate. After the first layer was cured at a chosen temperature, ranging from 200 to 400°C, a desired second polyimide layer was cast thereon and cured at 400°C for 30 min. A T-type peel test was employed to determine the strengths of adhesion of these polyimide-on-poly-

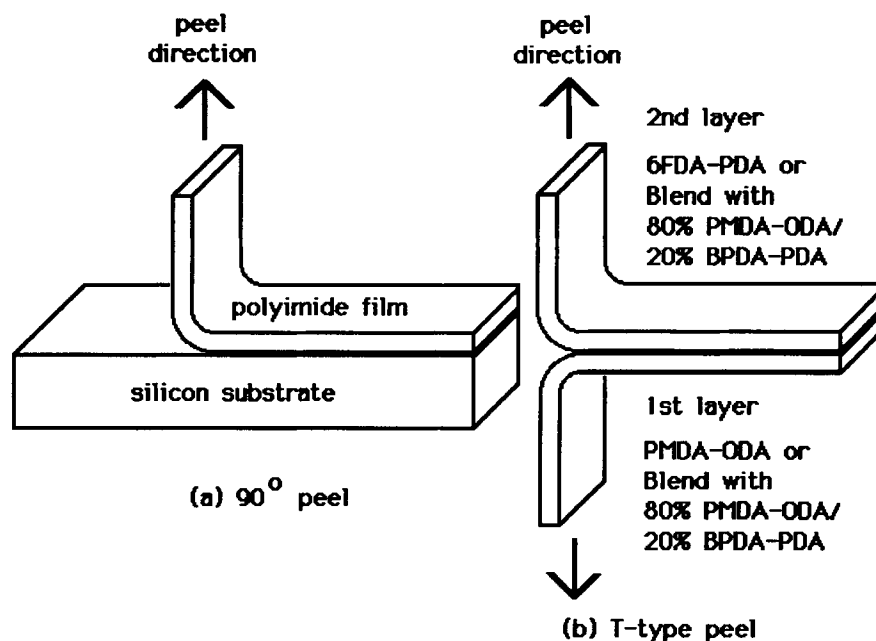
imide samples, as illustrated in Figure 2(b). The test was also performed at a pull rate of 39 μm/s.

### Fracture Surface Replica Preparation

The fracture surfaces of the samples with 6FDA-PDA cast on PMDA-ODA after peeling were investigated using a transmission electron microscope (TEM). The corresponding replicas were prepared as follows: On the fracture surface of the 6FDA-PDA film, a 20 nm-thick carbon film was deposited. On the carbon film, a 5 nm-thick platinum film was deposited. The resulting sample was then soaked in a *N,N'*-dimethyl acetamide solvent to remove the polyimide film. The surface of the resulting carbon film was then investigated.

### Bending Beam-Diffusion Specimen Preparation

The substrates used for the solvent diffusion-in-polyimide experiments are (100) silicon strips with 7.5 cm in length, 0.5 cm in width, and 390 μm in thickness. Polyimide films were prepared by spin-casting their polyamic acid solutions on the silicon strips. This was followed by prebaking at 80°C for 30 min and then curing to the desired temperature. The diffusions of NMP in the resulting polyimide films were determined according to the bending cur-



**Figure 2** Schematic illustration of the experiment setups for peel strength measurements: (a) a 90° peel test of the polyimide-on-silicon specimens; (b) a T-type test for the polyimide-on-polyimide specimens.

vature variation ratios of the specimens with respect to time recorded by a bending beam apparatus. For convenience, the bending curvature variation ratio is defined as follows. " $\Omega(t)$ " =  $[1/R(t) - 1/R(0)] / [1/R(\text{infinity}) - 1/R(0)]$ , where  $R(0)$ ,  $R(t)$ , and  $R(\text{infinity})$  are the bending curvatures of the polyimide-silicon bilayer structure prior to diffusion, at any diffusion time,  $t$ , and at equilibrium, respectively. In the event of case I diffusion, the resulting  $\Omega(t)$  vs.  $t^{1/2}$  should be linear for  $\Omega(t) < 0.8$ ,<sup>14</sup> and a diffusion coefficient can be calculated therefrom. For a case II diffusion,  $\Omega(t)$  vs.  $t$  should be linear,<sup>9</sup> and a constant diffusion front velocity can be obtained. Experimental and theoretical details about the bending beam technique employed in the measurement of solvent diffusion in polymer film can be referred to in Refs. 9, 10, and 14.

## RESULTS AND DISCUSSION

### Adhesion of Polyimide to Silicon

The peel strengths of several different polyimide films cast on silicon substrates, measured by using a 90° peel test, are listed in Table I. These films were made of pure PMDA-ODA, BPDA-PDA, and their blends. The peel strengths of the films of 100% PMDA-ODA, 80% PMDA-ODA with 20% BPDA-PDA, and 60% PMDA-ODA with 40% BPDA-PDA are relatively high when comparing with those of the films containing 60% BPDA-PDA or more. When carefully examining the data, it can be obviously seen that the peel strength increased markedly with the increase of the addition of BPDA-PDA up to 40%. When the composition of BPDA-PDA was increased to 60% or above, there was a

catastrophic change in the resulting peel strength, i.e., the peel strength dropped sharply and became too weak to be detected.

By examining the molecular structures of the two polyimides, it can be realized that BPDA-PDA is more planar than is PMDA-ODA. Furthermore, as investigated in several studies,<sup>15-17</sup> polyimide films cast on substrates all exhibit an in-plane orientation, i.e., the imide chains in the films are preferentially aligned in the film direction. These polyimide films should adhere on the silicon substrates by themselves since no adhesion promoter has been used, which could provide strong chemical bonds firmly interconnecting a given film to its substrate. It is very likely that the strength of these films adhering on the silicon substrates resulted mainly from the forces of physical interaction between the film and substrate. The resulting strength should, therefore, strongly depend on how intimately the two surfaces could be brought into contact. Since BPDA-PDA has a more planar structure that could provide a better contact against the substrate, it should then give a much better adhesion strength. This postulation may be used to explain why the peel strength shown above first increases with the increase of the addition of BPDA-PDA.

However, by examining the changes in the molecular structures of the two polyimides upon curing, it can be seen that PMDA-ODA would change from a flexible amic acid to a semirigid imide chain structure, and BPDA-PDA, from a flexible amic acid to a rigid imide chain structure. The structure variation that occurred on BPDA-PDA is relatively drastic. Furthermore, all the different polyimide films would become solidified and adhere on their substrates upon prebaking. When subjected to subsequent curing, any solvent residing in the given film would be driven off and the film would therefore be brought

**Table I** The Measured Peel Strengths of the Polyimide-on-Silicon Specimens with Different Compositions

	Composition of Polyimide					
	100P	80 P/20 B	60 P/40 B	40 P/60 B	20 P/80 B	100 B
	Thickness ( $\mu\text{m}$ )					
	(35)	(30)	(30)	(25)	(18)	(21)
Peel strength (g/mm)	20.2	54.4	71.2	—	—	—

All the specimens were cured at 400°C for 30 min. "P" denotes PMDA-ODA, and "B", BPDA-PDA. "—": not detectable within machine resolution.

in contact with the substrate more intimately. In the meanwhile, all the chains in the film, including those adhering on the substrate, would tend to shrink. This is due to both deswelling of the amic acid chains uncured and imide chains, if any, upon solvent evaporation and imidization upon curing. Especially, the shrinkage of the polymeric chains that adhered on the substrate would be greatly inhibited by the substrate due to a direct contact and would then give rise to an intrinsic stress.

Besides, upon imidization, the chain conformation of BPDA-PDA would tend to change from random coil- to rigid rodlike. The latter conformation is considered to be the most stable structure, thermodynamically, for the imide chain of BPDA-PDA. The variation in dimension for changing from a random coil- to rigid rodlike conformation for BPDA-PDA is very marked compared with that for PMDA-ODA. In PMDA-ODA, due to the presence of the easily rotating ether linkage, —O—, the stress could be somewhat released via self-adjusting the chain conformation to a less distorted state. Coupled with the effect from the dimensional variation due to deswelling and chemical structure change from amic acid to imide, a relatively high intrinsic stress exhibiting at the polyimide-substrate interface could result, especially for the films containing a higher content of BPDA-PDA.

In reality, the magnitude of the stress as well as the adhesion may vary from site to site from a microscopic point of view. If the stress surmounts the limit of adhesion globally, the entire piece of the polyimide film could delaminate from the substrate. If this would happen at some sites, blisters could result. Both these two phenomena actually have been seen frequently in preparing BPDA-PDA films on silicon or glass substrates for this study. These observations may be used to support the above pos-

tulate concerning the cause of the catastrophic change of adhesion in the systems containing 60% or more BPDA-PDA.

### Moisture Effect on the Adhesion of Polyimide to Silicon

To investigate the effect of moisture, a duplicate batch of the above peel test specimens were exposed to air for 2 days prior to peel-testing. As shown in Table II, the peel strength of the (PMDA-ODA)-on-silicon specimen dropped significantly. It changed from 20.2 to 6.5 g/mm. Deterioration of the peel strength can be attributed to the absorption of moisture of the polyimide film from the air. As known, water is commonly used in stripping polyimide films from many different substrate materials that they adhere on, especially when no adhesion promoter is applied. This clearly indicates that water molecules could penetrate to the film-substrate interface and alter the bonding status, and, eventually, destroy the corresponding adhesion. If the specimen is immersed in water, it would just be a matter of time to completely strip the polyimide film from its substrate.

However, the situation would be different when exposing the specimen to the ambient moisture. Under a certain humidity, the content of uptake moisture in a given film at equilibrium is limited and may vary significantly from one polyimide to another. It then may or may not be sufficient to cause a significant change in the corresponding adhesion status and strength. This may depend on the type of polyimide investigated. Therefore, it is thought that the adhesion for a given polyimide film having a higher water absorption tendency and poorer adhesion characteristics would be affected more markedly when exposed the ambient moisture.

**Table II The Effect of Moisture on the Peel Strengths of the Polyimide-on-Silicon Specimens with Different Compositions**

	Composition of Polyimide					
	100 P	80 P/20 B	60 P/40 B	40 P/60 B	20 P/80 B	100 B
	Thickness ( $\mu\text{m}$ )					
	(37)	(32)	(28)	(25)	(18)	(23)
Peel strength (g/mm)	6.5	58.2	84.0	—	—	—

All the specimens were cured at 400°C for 30 min and exposed to a 55% RH for 2 days prior to peeling.

As shown in Ref. 18, at 75% RH, PMDA-ODA film would absorb 2.50 wt % water, while BPDA-PDA, 1.37 wt %. Though the absorbed moisture contents would be different at 55% RH, wherein the above experiments were performed, BPDA-PDA undoubtedly has a much lower moisture uptake tendency than does PMDA-ODA. Besides, the diffusion coefficients of water in the films of PMDA-ODA and BPDA-PDA are  $5.5$  and  $0.3 \times 10^{-9}$  cm<sup>2</sup>/s, respectively.<sup>10</sup> In these peel tests, the thicknesses of the films of PMDA-ODA and BPDA-PDA are 37 and 32  $\mu$ m, respectively. A 2 day period was sufficient for the diffusions of moisture in the two different films to reach their film-substrate interfaces and reach equilibrium. Therefore, the peel strength, for the film containing 20% or 40% BPDA-PDA, that was unaffected by the absorbed moisture may be attributed to its inherently strong adhesion characteristics with silicon and low-moisture uptake characteristics.

#### Solvent Effect on the Adhesion of Polyimide to Silicon

In the above experiments, regarding the effect of moisture on the adhesion of polyimide-on-silicon, a 2 day period was chosen to ensure an equilibrium absorption of moisture. It is because some devices that compose such a polyimide/silicon structure or the like may unceasingly be exposed to moisture in the ambience during processing and/or in use and the resulting moisture absorption may eventually become equilibrium with the ambient humidity. However, it would be very unusual for such devices or structure components to immerse in a solvent like NMP for more than a 1 or 2 h period in processing. Therefore, a 2 h period of soaking in solvent has been chosen.

After soaking in NMP solvent for 2 h, the peel strength of the (PMDA-ODA)-on-silicon specimen changed from 20.2 to 14.2 g/mm, as listed in Table III. Comparing to the above moisture effect, the effect of soaking in NMP is apparently much weaker. According to the experiments of NMP diffusion in polyimides, 2 h seem to be far too short for the solvent to penetrate through the film of PMDA-ODA with a thickness of 26  $\mu$ m and reach the film-substrate interface and then cause any deterioration in the adhesion. The slight decrease in the above peel strength may be attributed to the fact that the NMP solvent could penetrate directly into the film-substrate interface from the cut edges of the sample.

Similar to the results concerning the effect of moisture, soaking in NMP did not degrade the peel strength of the system containing 20% or 40% BPDA-PDA. As mentioned above, the film containing 20% or 40% BPDA-PDA has exhibited a much better adhesion, indicating a much stronger interaction force between the film and the substrate. This could also greatly inhibit the diffusion of NMP along the interface from the cut edges. As a result, soaking in NMP caused no deterioration in the peel strengths of these blend systems.

#### Adhesion of Polyimide on Polyimide

In this part, two different sets of polyimide-on-polyimide peel test specimens have been prepared. The first set is to determine the peel strength of a 6FDA-PDA film cast on a PMDA-ODA film, and the second is reversed. The peel strength results of the first set are listed in Table IV. As seen, the second polyimide layer, 6FDA-PDA, could hardly adhere on the first polyimide layer, PMDA-ODA, if the PMDA-ODA layer was cured at 300°C or higher, since there was no detectable peel strength within

**Table III** The Effect of NMP on the Peel Strengths of the Polyimide-on-Silicon Specimens with Different Compositions

	Composition of Polyimide					
	100 P	80 P/20 B	60 P/40 B	40 P/60 B	20 P/80 B	100 B
	Thickness ( $\mu$ m)					
	(26)	(21)	(16)	(20)	(20)	(21)
Peel strength (g/mm)	14.6	63.0	76.6	—	—	—

All the specimens were cured at 400°C for 30 min and soaked in NMP solvent for 2 h prior to peeling.

**Table IV The Peel Strengths of the Specimens with 6FDA-PDA Cast on PMDA-ODA**

	Curing Temperature of the First Layer (°C)				
	200	250	300	350	400
Peel strength (g/mm)	6.6	< 0.1	—	—	—

After the deposition of the second layer, 6FDA-PDA, all the specimens were cured at 400°C for 30 min.

machine resolution under these curing conditions. This (6FDA-PDA)-on-(PMDA-ODA) system started to exhibit some peel strength when the film of PMDA-ODA was cured at a lower temperature, 250°C. The peel strength rose significantly when the first layer was cured at 200°C.

These results seem to be reasonable since the film of PMDA-ODA would be cured nearly completely at 300°C or higher.<sup>17</sup> Once the first polyimide film is fully cured, diffusion or penetration of the precursor molecules of the second polyimide layer into the first layer would become very difficult. It is because by curing from flexible amic acid chains to semirigid imide chains, the film structure of PMDA-ODA would become more ordered according to a Fourier transform infrared study.<sup>17</sup> As indicated in Ref. 15, the film density of PMDA-ODA increases as the curing temperature increases. Furthermore, as understood, the diffusion or penetration of these polyamic acid chains of the second layer into the first layer must be led by the diffusion of the solvent presented in the second layer prior to solidifying. Upon uptaking solvent, the film of PMDA-ODA would swell and more space would be created to make the diffusion of a given polymeric chain possible or faster. Generally speaking, the diffusion of a given solvent would be slower in a polymer film with a more ordered structure. Therefore, upon curing at an elevated temperature, a more ordered film would result and the diffusion of solvent would, consequently, be hindered. This would, in turn, result to a poor polymeric chain diffusion and a poor polyimide-to-polyimide adhesion, as observed.

At 250 and 200°C, the degrees of imidization of PMDA-ODA are about 80 and 50%, respectively.<sup>17</sup> In other words, the film of PMDA-ODA at these two stages still contained significantly large fractions of soluble amic acid chains or segments and could then be swollen and penetrated much more easily by the NMP solvent in the second layer. This would then be followed by a much more effective and/or

deeper penetration of the amic acid chains of 6FDA-PDA into the first layer. These results are in accordance with those revealed in Ref. 13, wherein the autohesion of PMDA-ODA to PMDA-ODA is relatively high if the first layer is cured at 200°C. From these studies, it can be seen clearly that the strength of the adhesion of one polyimide to another polyimide with a different imide structure or the autohesion of polyimide strongly depends on the curing temperature, or, more specifically, the degree of imidization of the prior cast polyimide film.

### Fracture Surface

In the above peeling experiments, it has been postulated that the specimen with a near-zero peel strength could be attributed to the lack of the polymeric chains from the film of 6FDA-PDA penetrating into the film of PMDA-ODA. If this was the case, there would be no mechanical interlocking between the two polyimide films. The two films could then be easily separated, as observed, and leave a relatively smooth fracture surface. Actually, this has been evidenced by the TEM experiments.

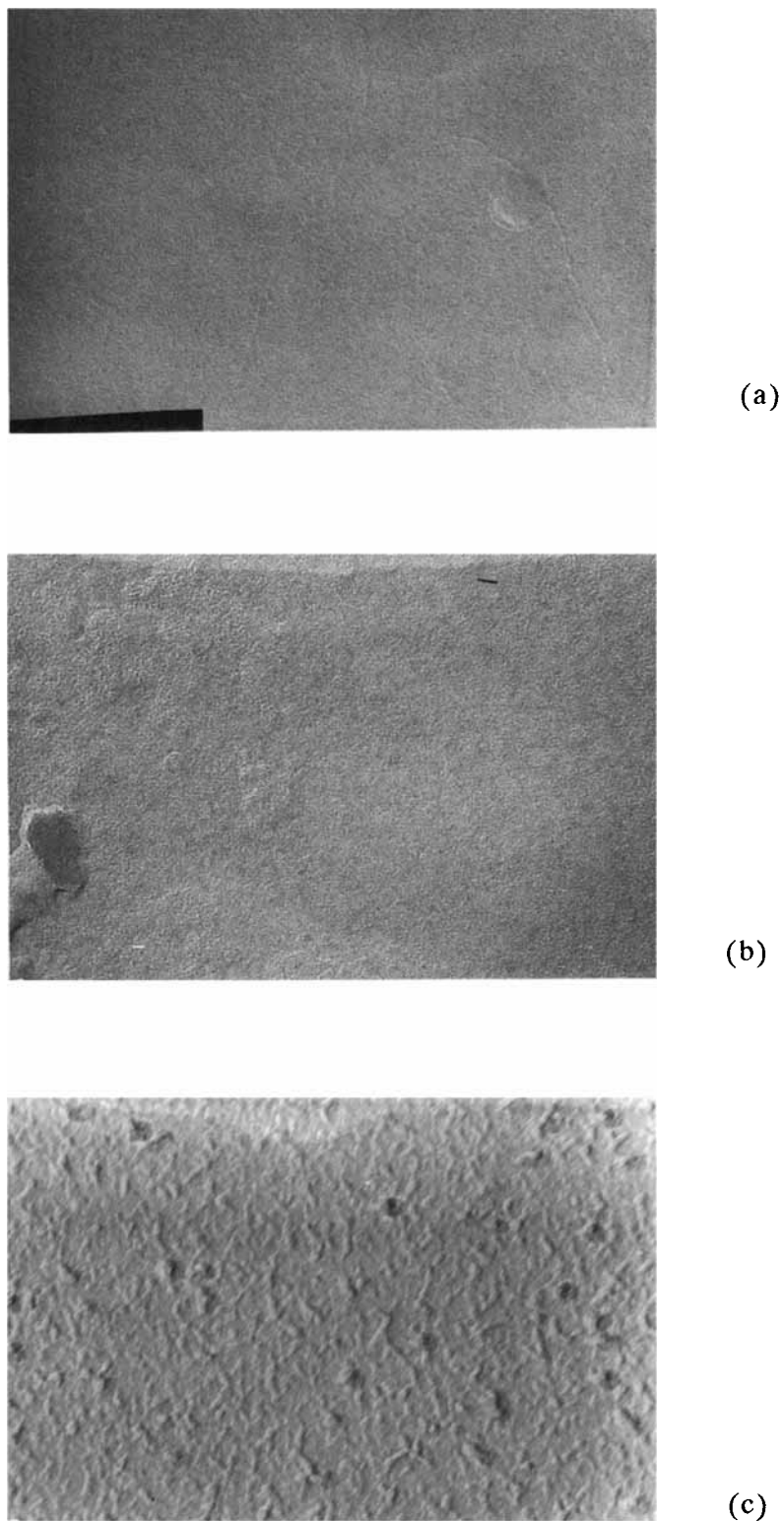
Figure 3 shows the fracture surface of the film of 6FDA-PDA after peeling. The fracture surface of the film was relatively smooth if the first PMDA-ODA layer was cured at 350°C or higher. The smoothness of these fracture surfaces is similar to that of the free surface of any other 6FDA-PDA film as cast, by comparing micrographs (a) and (b) with (f). At these stages, no 6FDA-PDA molecules have diffused into the film of PMDA-ODA. Therefore, the two different polyimide layers could be easily peeled off from each other and exhibited no peel strength.

When the first layer was cured at 300°C, the fracture surface started to show some degrees of roughness. It seems that, at this stage, some 6FDA-PDA chains or segments must have penetrated into the

**Table V The Peel Strengths Concerning Autohesion of the Blends Containing 80% PMDA-ODA and 20% BPDA-PDA**

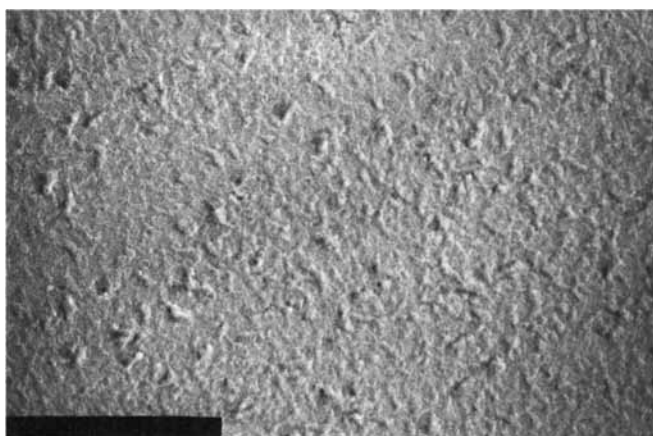
	Curing Temperature of the First Layer (°C)			
	250	300	350	400
Peel strength (g/mm)	23.2	18.7	2.3	1.8

After the deposition of the second layer, all the specimens were cured at 400°C for 30 min.

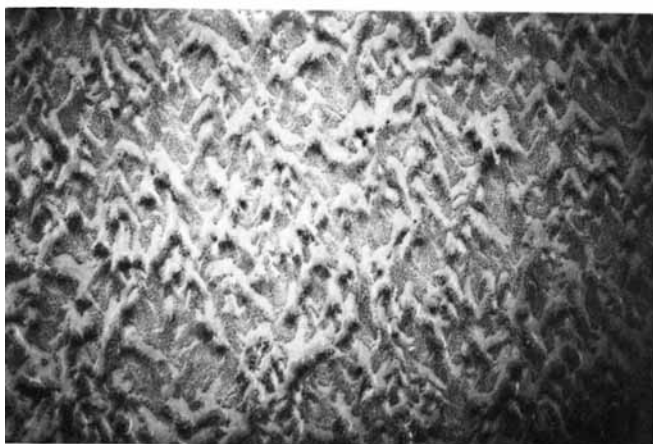


**Figure 3** Fracture surfaces of the specimens with 6FDA-PDA cast on PMDA-ODA after peeling investigated by using a transmission electron microscope with the first (PMDA-ODA) layer cured at (a) 400°C, (b) 350°C, (c) 300°C, (d) 250°C, and (e) 200°C. Micrograph (f) corresponds to the free surface of a separately prepared 6FDA-PDA film as cast and is used for reference.

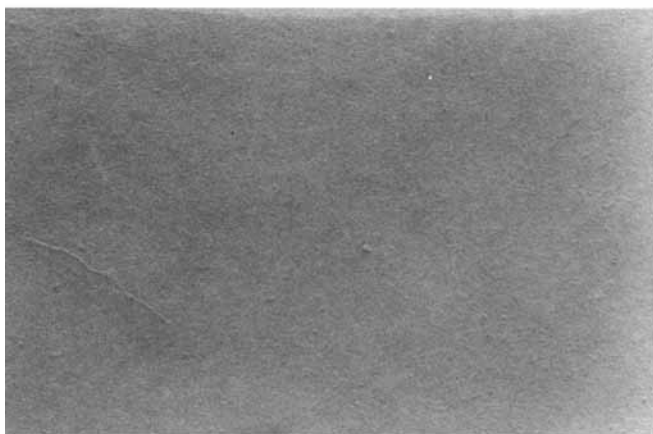




(d)

0.1  $\mu\text{m}$ 

(e)

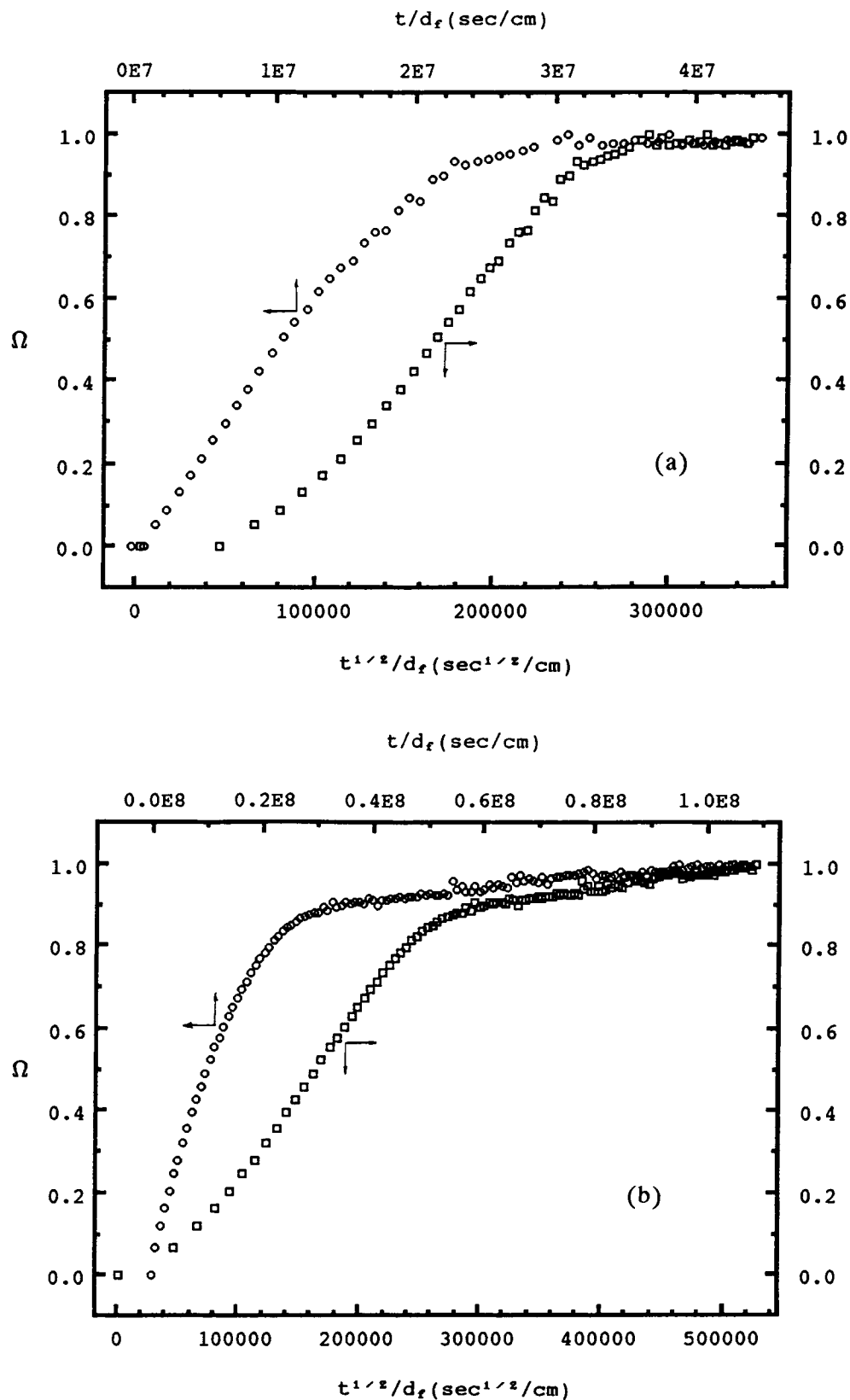


(f)

**Figure 3** (continued from the previous page)

film of PMDA-ODA. These chains or segments would be tightly embedded in the first layer when deswelling took place due to the desorption of the uptaken solvent when subjected to a subsequent

curing. A rough fracture surface would then result upon peeling. However, the corresponding penetration density must have been relatively low and/or the penetration depth, on average, must have been



**Figure 4** The resulting bending curvature variation ratio vs. time for the diffusion of NMP solvent in the imide film of PMDA-ODA measured at room temperature. Plots (a)–(d) correspond to curing temperatures of 250, 300, 350, and 400°C, respectively.

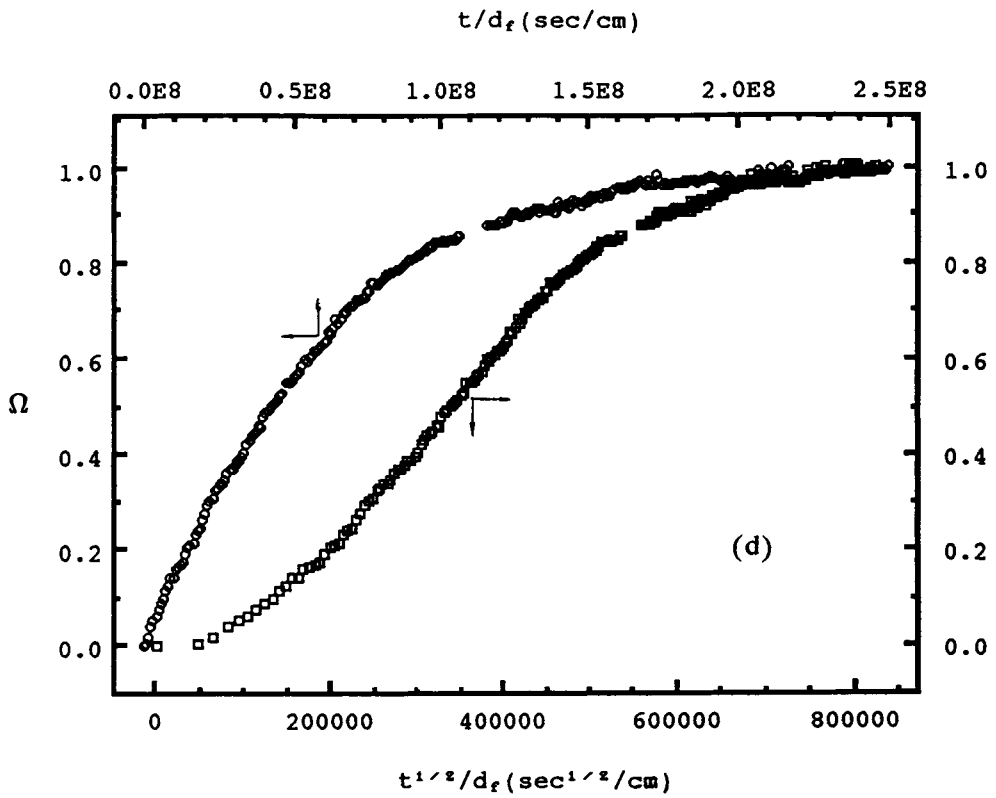
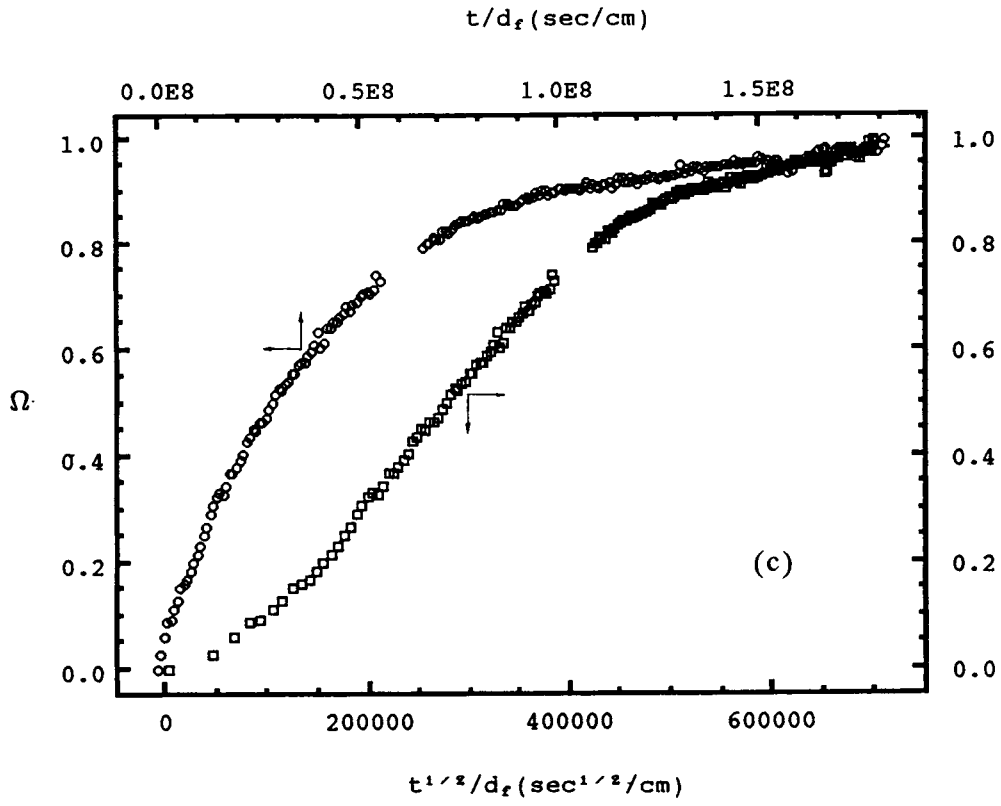


Figure 4 (continued from the previous page)

relatively short; otherwise, its peel strength would not be undetectable within machine resolution. Actually, this fracture surface showed only a scattering of plastic deformation tracks as seen in micrograph (c).

The degree of roughness of the fracture surface was higher when the first layer was cured at 250°C and even higher at 200°C, as shown in micrographs (d) and (e). These match what has been observed in the peel tests. Apparently, the amic acid chains of 6FDA-PDA could more effectively diffuse into the PMDA-ODA layer that was not fully cured. Since the first PMDA-ODA layer would become solidified when cured at 200°C or above, it would be difficult for the amic acid chains of 6FDA-PDA, even prior to curing, to diffuse into the solid film of PMDA-ODA without the aid of solvent. From a different point of view, the diffusion of the amic acid chains of 6FDA-PDA into the first PMDA-ODA layer should fall behind the diffusion of the solvent presented in the as-cast 6FDA-PDA film. Therefore, the above results indicate that the diffusion of NMP solvent into the film of PMDA-ODA, which cured partially at 200 or 250°C, should be much faster than that cured more completely at 300°C or higher.

In the second set of experiments, PMDA-ODA films were cast on the films of 6FDA-ODA cured at various temperatures. However, due to the easiness of dissolution of the films of 6FDA-PDA, cured at temperatures below 350°C, in NMP solvent, no ideal specimen could be made. As a result, no similar peel tests could be performed for comparison.

### Autohesion of Polyimide Blend

Peel test results regarding the autohesions of the films made of a blend with 80% PMDA-ODA and 20% BPDA-PDA are listed in Table V. Compared with the system with 6FDA-PDA casting on PMDA-ODA, this autohesion system exhibited a relatively high peel strength, especially when the first layer was cured at 250 or 300°C. Even when the first layer was cured at 350 or 400°C, this system still exhibited nonnegligible peel strength, though weak. The two different systems, though, have shown a similar trend that the peel strength decreased when the curing temperature of the first layer increased, regardless of adhesion or autohesion.

Nevertheless, the adhesion of the film of 6FDA-PDA to the film of PMDA-ODA is apparently much more unfavored than is the autohesion of the blend to itself. As also shown previously,<sup>13</sup> the peel strength, regarding the autohesion of the films of PMDA-ODA, is fairly high, though the curing temperature of the first layer is 300 or 400°C. Comparing

these three different systems, i.e., 6FDA-PDA to PMDA-ODA, PMDA-ODA to itself, and the blend with 80% PMDA-ODA and 20% BPDA-PDA to itself, it can be seen that beside curing temperature the chemical structures of the polyimides studied seem to play an important role in affecting the adhesion of polyimide to polyimide. This point will be discussed further in the next section.

### NMP Diffusion in Polyimide Films

The diffusion of NMP solvent in the film of PMDA-ODA at room temperature is shown in Figure 4. To avoid problems that may result from a nonideal sample-to-sample reproducibility, the same film was used repeatedly for a series of diffusion experiments to investigate the effect of curing temperature. This was done by successively measuring the diffusion of NMP each time after the film was cured at a chosen temperature varied in an ascending order from 250 to 400°C. Since PMDA-ODA film could be cured only partially at 200°C and might dissolve more or less in NMP during diffusion, the diffusion experiment was performed after the film was cured at 250°C in lieu of 200°C. As seen, the diffusion process became slower with the increase of the curing temperature.

When the film was first cured at 250°C, the diffusion of NMP seems to be anomalous, but very close to case I according to an analysis method presented elsewhere.<sup>9</sup> After the film was cured at 300°C, the diffusion of NMP obviously followed a case I mechanism. Such a case I diffusion behavior was retained for the film cured up to 400°C. To compare quantitatively, all the above diffusion processes were treated as case I. The diffusion coefficients as calculated are 2.4, 1.4, 0.39, and  $0.35 \times 10^{-11}$  cm<sup>2</sup>/s in the film of PMDA-ODA after curing at 250, 300, 350, and 400°C, respectively.

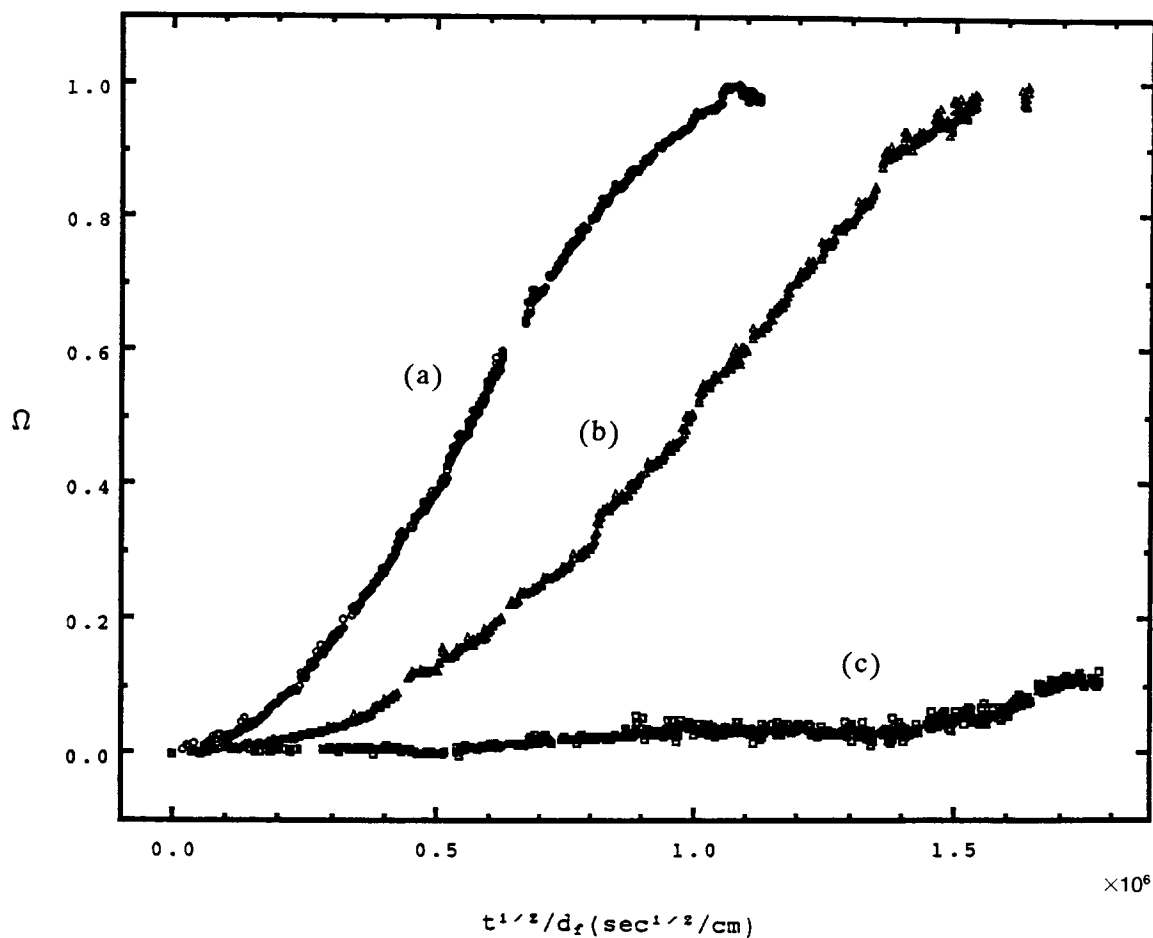
Different from the diffusion behavior in the film of PMDA-ODA, the NMP solvent would dissolve the film of 6FDA-PDA if it was cured at a temperature lower than 350°C. When the film of 6FDA-PDA was cured at 250°C, it dissolved readily once being immersed in the NMP solvent. Even cured at 300°C, it took less than 10 min for the 6FDA-PDA film with a thickness of 4.6 μm to be partially dissolved but completely stripped from the silicon substrate. It is noteworthy that it would take the NMP solvent more than 1 day to diffuse and reach equilibrium in a 4 μm-thick PMDA-ODA film cured at 250°C. The dissolution of the film of 6FDA-PDA in NMP explains why no ideal peel test specimens could be made for the systems with PMDA-ODA casting on 6FDA-PDA, especially when the first

layer, 6FDA-PDA, was cured at temperatures below 350°C. The ease of dissolution of the film of 6FDA-PDA in NMP can be attributed to its inherently amorphous film structure and relatively weak interchain interaction, as indicated by its relatively weak and diffused pattern and long interchain spacing, respectively, revealed by X-ray diffraction.<sup>19</sup>

Figure 5 shows the diffusion of NMP in the film of the blend containing 80% PMDA-ODA and 20% BPDA-PDA. The diffusion mechanism of NMP in the blend cured at 250 or 300°C seems to be anomalous but close to case I. The corresponding diffusion coefficients as estimated are  $1.5$  and  $0.66 \times 10^{-12}$   $\text{cm}^2/\text{s}$ , respectively. If the film was cured at 350°C or above, no diffusion progress could be observed in a 1-week period.

Overall, the diffusion of NMP in the blend was very much slower than in the film of PMDA-ODA under the same curing conditions. This can be attributed to the addition of BPDA-PDA, whose imide

film structure is highly crystalline and has a relatively small interchain spacing, as revealed in a previous investigation.<sup>19</sup> Even in the blend cured at 250°C, the diffusion of NMP was slower than in the film of PMDA-ODA cured at 400°C. However, the peel strength of the blend to itself is unanimously much higher than that of the film of 6FDA-PDA to PMDA-ODA based at least, on the same curing conditions. Apparently, the adhesion of polyimide-to-polyimide is not only governed by the solvent diffusion that, in turn, is governed by the curing temperature. It is thought that right after the occurrence of swelling in the first layer upon uptaking the solvent presented in the second layer the diffusion or penetration of the polymeric chains of the second layer for the blend system must have been very effective and/or fast relative to that for the (6FDA-PDA)-on-(PMDA-ODA) system. On the contrary, the diffusion of the polymeric chains of 6FDA-PDA into the swollen first PMDA-ODA layer must have



**Figure 5** The resulting bending curvature variation ratio vs. time for the diffusion of NMP solvent in the blend with 80% PMDA-ODA and 20% BPDA-PDA measured at room temperature. Plots (a)–(c) correspond to curing temperatures of 250, 300, and 350°C, respectively.

been greatly inhibited. This may presumably be due to the inherently incompatible characteristics of the two different polyimides, 6FDA-PDA and PMDA-ODA.

Actually, it has been found that 6FDA-PDA is, in nature, incompatible with several different polyimides, such as PMDA-PDA and PMDA-benzidine (-B), even in the soluble precursor state.<sup>19</sup> However, PMDA-PDA is compatible with PMDA-ODA.<sup>16</sup> It is therefore very plausible that 6FDA-PDA is incompatible with PMDA-ODA. Such an inherent incompatibility would make the diffusion of one polymer into its incompatible counterpart extremely difficult, though the solvent diffusion is highly favorable. This would then result to a relatively poor adhesion between the films of 6FDA-PDA with PMDA-ODA as observed.

## CONCLUSION

From this study, it has been found that the peel strength of (PMDA-ODA)-on-silicon can be greatly improved by blending with 20 or 40% BPDA-PDA. The enhancement can be attributed to the planar imide structure of BPDA-PDA, which can provide the film a better intimate contact against the surface of the silicon substrate and then a better adhesion. Upon exposing in a 55% RH surrounding for a 2 day period, there was a serious deterioration in adhesion for the PMDA-ODA system, while no deterioration for the blend systems containing 20 and 40% BPDA-PDA. No deterioration in the latter cases may be attributed to inherently high adhesion strength and low-moisture uptake characteristics that originated from the addition of BPDA-PDA. Soaking in NMP for a 2 h period resulted in a somewhat weaker adhesion strength for the PMDA-ODA system, whereas it showed no effect on the blend systems.

In the adhesion system of 6FDA-PDA to PMDA-ODA or the autohesion system of a blend comprising 80% PMDA-ODA and 20% BPDA-PDA to itself, the corresponding peel strength decreased markedly with the increase of the curing temperature or, more specifically, the degree of imidization of the first polyimide layer. From the solvent diffusion experiments, it is learned that the diffusion of NMP is much faster in the film of PMDA-ODA than in the blend, having been cured at the same temperature. Though the diffusion results seem to be overwhelmingly favorable to the diffusion of 6FDA-PDA into PMDA-ODA, this system has exhibited a comparatively weak peel strength. This should presumably

be due to the inherently incompatible characteristics of the two polyimides, 6FDA-PDA and PMDA-ODA.

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