

Relationship between structure and adhesion properties of aromatic polyimides

Takao Miwa*, Rie Tawata and Shunichi Numata

Hitachi Research Laboratory, Hitachi Ltd, 7-1-1 Omika-Cho, Hitachi-shi, Ibaraki-ken 319-12, Japan

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The adhesion properties of aromatic polyimide films on SiO₂ and on various polyimides without any adhesion promoter were studied. Flexibility of the polyimide chains was found to be necessary for good adhesion. Polyimides with a flexible structure gave higher adhesion than those with a rigid structure for both substrate types. On SiO₂, delamination occurred within 100 h on exposure to steam at 120°C. On polyimides, the adhesion depended on both the substrate and the coating, and the peel strength increased in the following order of coating/substrate combinations: rigid/rigid < flexible/rigid < rigid/flexible < flexible/flexible. For the case of a rigid polyimide substrate, the adhesive property was greatly improved when coatings were spun on partially imidized substrate. This suggests that the dominant factors affecting adhesion are the degree of freedom of the molecular chain, which will affect the interaction between polyimide and SiO₂, and the diffusibility of the molecular chain at the polyimide/polyimide interface. The existence of a diffusion layer was observed at the polyimide/polyimide interface with energy-dispersive X-ray analysis/transmission electron microscopy.

(Keywords: structure; polyimides; SiO₂; adhesion; flexibility; mutual diffusion; films)

INTRODUCTION

In electronics applications, demand is high for thin-film multi-level fine wiring boards using polyimides, such as very fine wiring for very-large-scale integrated circuits and Cu-polyimide wiring boards for large-scale mainframes. For these applications, stable adhesion at various interfaces, as well as reduction of thermal stress and insulation resistance, good mechanical properties and easy processing become more important. As for the thermal stress arising from differences in thermal expansion coefficients between various materials, low-thermal-expansion-coefficient polyimides developed by Hitachi¹ have overcome this problem. However, problems with adhesion between polyimides or between polyimide and another material have not yet been resolved, even though investigations have been carried out²⁻⁹. In particular, low-thermal-expansion-coefficient polyimides with rigid and linear polymer chains have a significant problem with adhesion. To understand adhesion phenomena of polyimide interfaces, relationships between structure and adhesion properties at the interfaces of polyimide on SiO₂ and polyimide on polyimide were examined.

Factors determining adhesion at the interface of the polymer substrate and coating were: (1) intermolecular interactions, (2) chemical bonding and (3) entanglement of polymer chains. For polyimide coated on SiO₂, the intermolecular interactions seem to be the dominant factor because there is no entanglement of polymer chains and very little chemical bonding between them. Intermolecular interactions, such as dispersion force and electrostatic interaction between polar groups, should be affected by flexibility of the molecular chain, since a rigid

molecular chain cannot change its conformation to maximize intermolecular interactions. For a polyimide/polyimide interface, the entanglement of molecular chains at the interface between polymers of the substrate and coating as well as intermolecular interactions seem to be important. This entanglement of the polymer molecules is caused by diffusion of the molecular chain. Its extent should be affected by the flexibility of the polymer chains of the substrate and coating.

Owing to the importance of flexibility, its relationships to adhesive properties were studied in detail and the findings are given here.

EXPERIMENTAL

Materials

A poly(amic acid) varnish was prepared by reacting an aromatic diamine with a stoichiometric amount of aromatic dianhydride in *N*-methyl-2-pyrrolidone at room temperature. As the parameter indicating flexibility of the molecular chain, Kuhn's segment length (*KS* value) proposed by Birshtein's group¹⁰⁻¹² was adopted. The polyimides that were used and their *KS* values are listed in Table 1.

Adhesion strength by peeling test

Adhesion strength was measured by a peeling test using the samples shown in Figure 1. These samples were fabricated as follows:

Sample 1 for polyimide coated on SiO₂. Poly(amic acid) varnish, spin-coated on the thermally oxidized Si wafer, was converted to polyimide at 400°C for A2 and at 350°C for the others for 30 min (Figure 1a).

* To whom correspondence should be addressed

Table 1 Details of polyimides used in experiments

Ref. no.	Diamine	Dianhydride	Kuhn's segment (KS) value (Å)
A2	PDA	BPDA	118
A3		BTDA	34
B1		PMDA	72
B2	ODA	BPDA	58
B3		BTDA	34
C1		PMDA	39
C2	BAPP	BPDA	39
C3		BTDA	32

PDA = *p*-Phenylene diamine

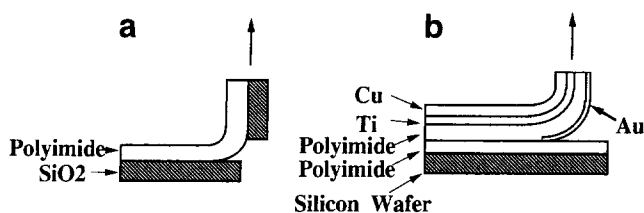
ODA = Oxydianiline

BAPP = Bis(aminophenoxyphenyl)propane

PMDA = Pyromellitic dianhydride

BPDA = Biphenyl tetracarboxylic dianhydride

BTDA = Benzophenone tetracarboxylic dianhydride

**Figure 1** Measurement of peel strength: (a) polyimide on SiO₂; (b) polyimide on polyimide

Sample II for polyimide/polyimide interface on fully cured polyimides. Aluminium chelate solution as an adhesion promoter was used on the substrate before spin-coating of poly(amic acid) to form the first layer. A gold thin film was deposited on part of the first layer as a delamination layer. The second layer was fabricated by spin-coating and thermal imidization on the first layer. The curing conditions for both layers were the same as for sample I. A Ti and Cu layer was deposited as the reinforcement layer for the peeling test⁵ (Figure 1b).

Sample III for polyimide/polyimide interface on semi-cured polyimides. The polyimide first layer was fabricated by spin-coating on a substrate that had had aluminium chelate solution applied. Thermal imidization was done at temperatures between 150 and 300°C for 30 min. Other steps were the same as for sample II.

Conversion of the imidization reaction

Conversion of the imidization reaction was calculated from the weight loss during high-temperature heating of dried poly(amic acid) measured using thermogravimetric analysis (t.g.a.)¹³.

RESULTS AND DISCUSSION

Adhesiveness of polyimides to the SiO₂ substrate

Peel strengths of polyimide films on SiO₂ are shown in Figure 2. Polyimides B2, B3, C2 and C3 gave substantial peel strengths (250–650 g cm⁻¹) before exposure to saturated H₂O vapour at 120°C. But after the exposure no polyimide adhered. At polyimide/SiO₂ interfaces mutual diffusion and creation of new chemical bonds between polyimide and SiO₂ can be neglected. Inter-

molecular interactions such as dispersion force and dipole–dipole attraction dominate peel strength.

If functional groups of polyimides have specific interactions with SiO₂, these groups should be in close proximity to the SiO₂. Therefore, although it is difficult to find a clear relationship between the KS value and the peeling strength, poor adhesion of polyimides with a large KS value is understandable. The H₂O molecules at the interface should weaken dipole–dipole interactions between SiO₂ and polyimides because of its large ϵ value ($\epsilon = 84.5$), leading to detachment of polyimide molecules from SiO₂. The delamination of all the polyimide films after exposure is reasonable if there is no interdiffusion layer and no chemical bonds at the interfaces.

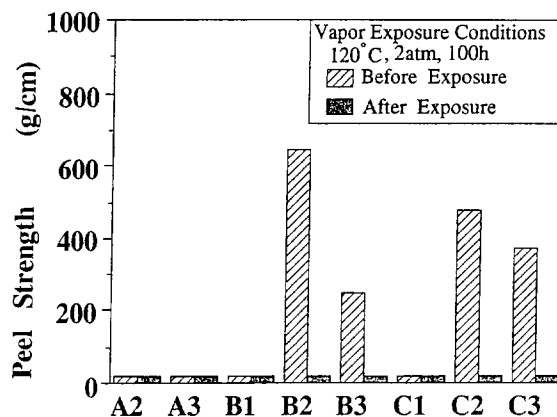
Adhesiveness between polyimide and polyimide

The peel strengths of polyimide films coated on fully cured A2 (KS=118) and B2 (KS=58) are shown in Figure 3. No polyimides adhered on A2 even before exposure (Figure 3a). For B2, all the polyimides except A2 gave substantial peel strengths (400–750 g cm⁻¹) and the values were retained even after exposure (Figure 3b).

The results show the importance of rigidity of substrate molecules. Polyimides that have large KS values tend to have an ordered structure compared to other polyimides; e.g. the liquid-crystalline nature of a rod-like polyimide has been reported¹⁴. Once substrate polyimides assume ordered structures, it might be difficult to cause mutual diffusion at the interfaces.

The change in peel strength on B2 after exposure is quite different from that on SiO₂. At the polyimide/polyimide interface, a certain amount of mutual diffusion of the polymer chain should take place and entanglement of the chain causes the peel strength to be less affected by exposure. Although no reason for decreasing peel strength after exposure can be given easily, it might correspond to intermolecular interactions as discussed with regard to adhesion on SiO₂.

The less adhesive nature of A2 on B2 can be explained by considering the curing process of A2 and the glass transition temperature of semi-cured B2. Both polymers should have enough mobility to diffuse into each other. The poly(amic acid) solution serving as a precursor of A2 that was coated on B2 had a high mobility, but it should completely undergo the imidization reaction and have no mobility at the glass transition temperature of B2 (300°C). The above discussion means a good adhesive

**Figure 2** Peel strength at polyimide/SiO₂ interfaces

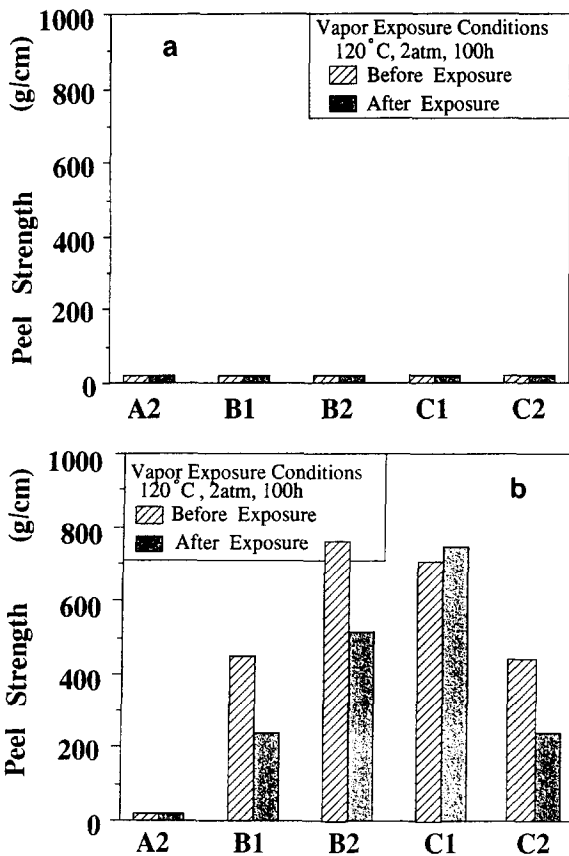


Figure 3 Peel strength at (a) polyimide/A2 interfaces and (b) polyimide/B2 interfaces

property is possible for the polyimide/polyimide interface fabricated on semi-cured polyimide.

Peel strengths of polyimide films coated on semi-cured (200°C, 1 h) A2 ($KS=118$) and B2 ($KS=58$) are shown in Figure 4. As expected, the peel strengths (ca. 800 g cm^{-1}) are higher than on polyimide and almost identical for all combinations. Furthermore, the value does not decrease after exposure. The high value of the peel strength before and after the exposure may be caused by entanglement of polyimide chains at the interface.

Relation between adhesiveness and curing temperature of lower layer

The peel strength of polyimide/polyimide interface fabricated on a semi-cured polyimide first layer was investigated for the combination of A2 ($KS=118$) and B2 ($KS=58$). The results are shown in Figure 5. For all combinations, peel strengths are large and almost identical (ca. 800 g cm^{-1}) when the semi-cure temperature is below 200°C. On semi-cured A2 that was cured above 250°C, the values decrease sharply to almost zero, regardless of which material formed the second layer.

On the other hand, on semi-cured B2, B2 adheres well regardless of semi-cure temperature of the first layer. Then, when A2 was used as the second layer, on B2 the strength decreases when the semi-cure temperature of B2 was above 250°C; the value is 480 g cm^{-1} at 300°C.

The results indicate that all polyimides have enough mobility to diffuse at the interfaces when semi-cure temperature is below 200°C. Figure 6 shows the curing temperature dependence for the conversion of imidization reaction of A2. The temperature range for imidization to progress the most, 200 to 300°C, corresponds to the temperature at which the peel strength on semi-cured A2

decreased rapidly. This means that the loss of mobility of the A2 chain as imidization proceeds is the main cause for the decreasing peel strength on A2.

A combination of flexible polymers is preferred to form a diffusion layer at the interface. And it is easy to understand that the interface B2 on B2 gives high adhesion for all semi-cure temperatures. Since A2 loses its mobility above 250°C, interdiffusion of the polymer chain at the interface A2 on B2 should take place below that temperature. The remaining value of the peel strength at 300°C implies that B2 semi-cured at 250°C has some mobility below 250°C. These results indicate that entanglement of the polymer chains at the interface

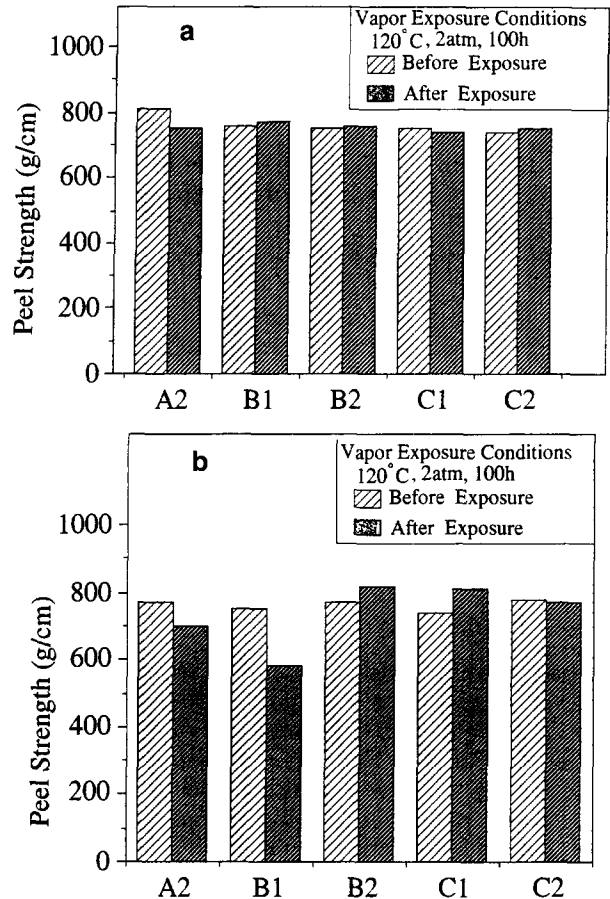


Figure 4 Peel strength at (a) polyimide/A2 interfaces and (b) polyimide/B2 interfaces

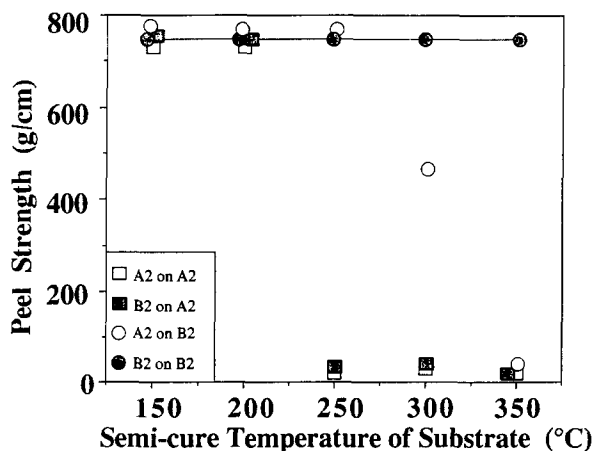


Figure 5 Peel strength of polyimide coated on semi-cured polyimide

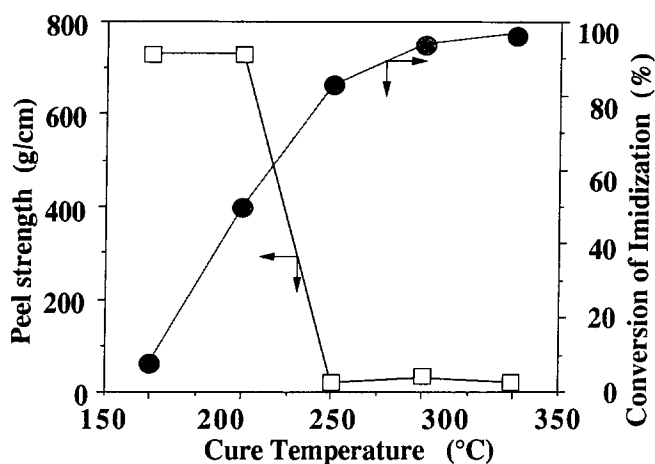


Figure 6 Cure temperature dependences of peel strength and conversion of imidization

due to diffusion of polymer molecules is the dominant factor for adhesion between polyimide and polyimide.

Observation of the diffusion layer between polyimide and polyimide

The diffusion layer at the interface of Si-containing polyimide (KS=35) on A2 (curing at 200°C, 30 min) was measured by energy-dispersive X-ray analysis/transmission electron microscopy. The results are shown in Figure 7. The Si content decreases gradually with increasing distance in the region of 1450–3100 Å, indicating diffusion. The same diffusion layer is expected to form for other polyimide/polyimide interfaces that give good adhesion.

CONCLUSIONS

The relationships between chemical structure of polyimides and adhesiveness of polyimide coatings, which were coated and thermally imidized on SiO₂ or polyimides, were studied. For polyimides on SiO₂ substrate, those having a flexible molecular chain had higher adhesiveness than those having a rigid structure. The latter had delamination within 100 h on exposure to steam at 120°C. For polyimide on polyimide, the highest peel strengths were obtained for combinations of flexible polyimides. Combinations of rigid polyimides did not adhere. By contrast, even though the coating and/or substrate had a rigid and linear molecular chain after imidization, good adhesiveness was obtained in the case

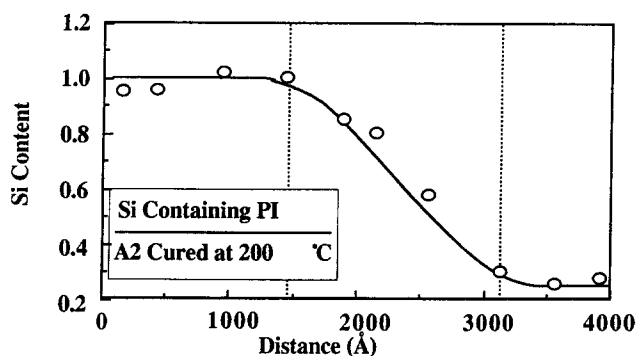


Figure 7 Changing in Si concentration at the polyimide/polyimide interface

of polyimide fabricated on a partially imidized one. These results indicated that adhesiveness was strongly affected by the flexibility of the molecular chain of polyimides. This suggested that the dominant factors for adhesion were the degree of freedom of the molecular chain, which accelerated the interaction between polyimide and SiO₂, and the diffusibility of the molecular chain at the polyimide/polyimide interface.

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