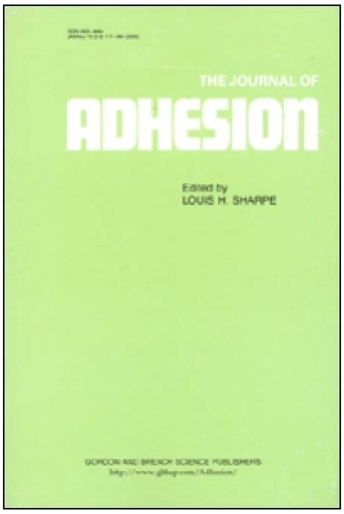

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Adhesive Properties of Siloxane Modified Polyimides and Application for Multi-Layer Printed Circuit Boards*

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(In final form March 25, 1996)

The adhesive properties of various siloxane modified polyimides were studied for the development of suitable adhesive materials with good thermal stability. Their adhesive properties were influenced by siloxane content in the polymer backbone and the structure of the aromatic component. Among them, the copolyimides with small amounts of the siloxane unit showed the better lap shear strength compared with the corresponding all-aromatic polyimides. They had excellent adhesive strength to various substrates. Their adhesive durability under the highly humid condition (25°C, 90%RH) was also improved mainly due to their lower moisture sorption and lower moisture permeability. However, further siloxane modification lowered their adhesive strength and durability. On the other hand, thee T-peel strength of copolyimides was lowered according to the increase of siloxane content. Based on this study, a new type of adhesive film which was composed of a copolyimide as a major component, SPB-505A, was developed and reported. This is useful for multi-layered printed circuit boards due to the excellent adhesive properties, good electrical properties and distinguished reliability under the hot / wet condition (121°C, 2 atm, 85%RH).

KEY WORDS: siloxane; polyimide; siloxane modified polyimide; adhesive; adhesive film; adhesive durability; printed circuit; printed circuit board; multi-layer.

1. INTRODUCTION

Polyimides have been widely used in advanced microelectronics, aerospace and printed circuit industries mainly due to their high thermal stability and good mechanical properties[1,2]. In the last decade, several copolyimides with polydimethylsiloxane in their polymer backbones, which have a number of additional benefits such as enhanced solubility, lower water sorption, good thermo-oxidative stability and lower dielectric constant, have also been reported[3–5]. These advantages render siloxane modified polyimides (SPI) more attractive as good candidates for high performance adhesives and specialty coatings[3–8].

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In this work, the adhesive properties of various SPI films and their applications for multi-layered printed circuit boards are discussed. The effects of siloxane content and structure of aromatic component on adhesive properties are studied in two series of polyimides. These copolymers were prepared from 3,3′4,4′-Benzophenonetetracarboxylic dianhydride (BTDA)/bis[4-(3-aminophenoxy)phenyl]sulfone (BAPSM) (Series A) and 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA)/2,2-bis[4-(4aminophenoxy)phenyl]propane (BAPP) (Series B). Both were amorphous and soluble in several organic solvents. In a previous study, it was proved that adhesive properties of all-aromatic polyimides were dependent on their aromatic component^9. Adhesive strength of polyimide from BTDA/BAPSM was superior to that of polyimide from DSDA/BAPP. Effects of incorporation of siloxane into both system on their adhesive properties are an interesting theme. The adhesive properties of copolyimides were dependent on siloxane content and siloxane molecular weight. It was found that the copolyimides with small amounts of siloxane showed better adhesive properties compared with the corresponding all-aromatic polyimides. Their adhesive durability under a highly humid condition was also improved.

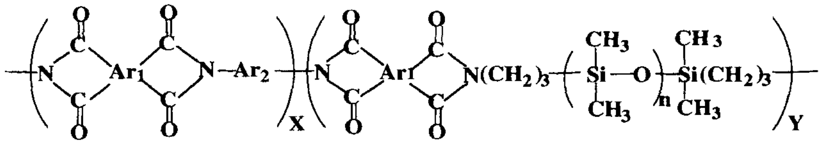
Based on this study, an adhesive film which was made from a siloxane modified polyimide was developed and commercialized. The newly-developed adhesive film is useful for multi-layered printed circuit boards due to its excellent adhesive properties, high stability to a molten solder bath, good processability and distinguished reliability under hot/wet conditions.

2. EXPERIMENTAL

2.1. Preparation of Polyimide and Adhesive Film

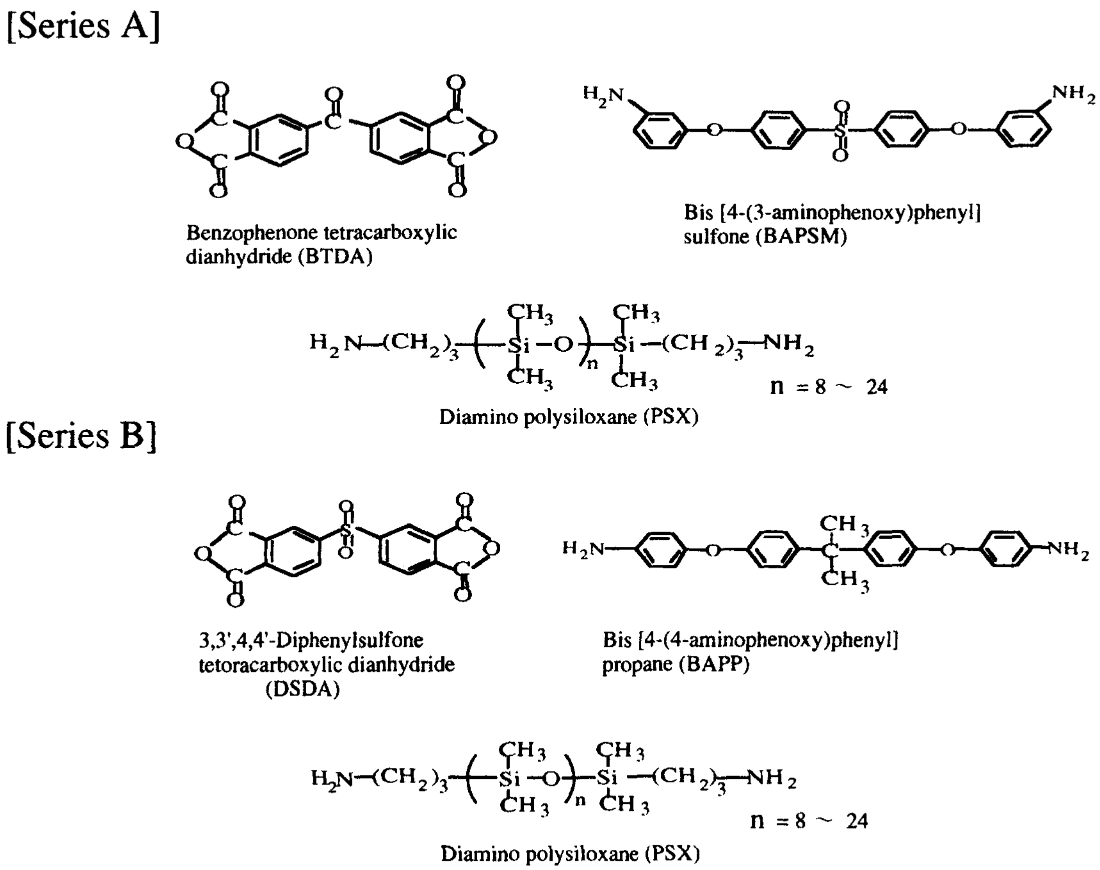
Two series of siloxane modified polyimides were prepared from BTDA (Daisel Chem. Co., Ltd., Tokyo, Japan) / BAPSM (Wakayama Seika Co., Ltd., Wakayama, Japan) (Series A), DSDA (New Japan Chem. Co., Ltd., Kyoto, Japan) / BAPP (Wakayama Seika Co., Ltd., Wakayama, Japan) (Series B), and bis(γ-aminopropyl)polydimethylsiloxane (PSX) in N-methylpyrrolidinone (NMP). Typical structure of siloxane modified polyimide is shown in Scheme 1.

Three kinds of bis(γ-aminopropyl)polydimethylsiloxane, PSX750 ($\overline{Mw} = 750$), PSX1200 ($\overline{Mw} = 1200$) and PSX2300 ($\overline{Mw} = 2300$) (Dow Corning Toray Silicone Co., Ltd., Tokyo, Japan), were used as siloxane components. All reagents were commercially obtained and used without further purification. Monomers for the preparation of siloxane modified polyimides are shown in Scheme 2. Fully imidized copolyimides with variable amount and molecular weight of siloxane unit were



Ar : Aromatic component

SCHEME 1 Typical structure of siloxane modified polyimide (SPI).



SCHEME 2 Structure of momomer components for siloxane modified polyimides.

synthesized by the solution imidization technique with azeotropic reagents such as diethyleneglycol dimethylether (methyldiglyme). Two series of polyimides with inherent viscosity 0.5 ~ 0.6 were obtained by this method (Scheme 3).

The viodless transparent films were prepared by casting method from polyimide solutions followed by heating at 100, 250°C for 30 minutes at each temperature. Thickness of the adhesive film was controlled at the level of 25 ± 1μm.

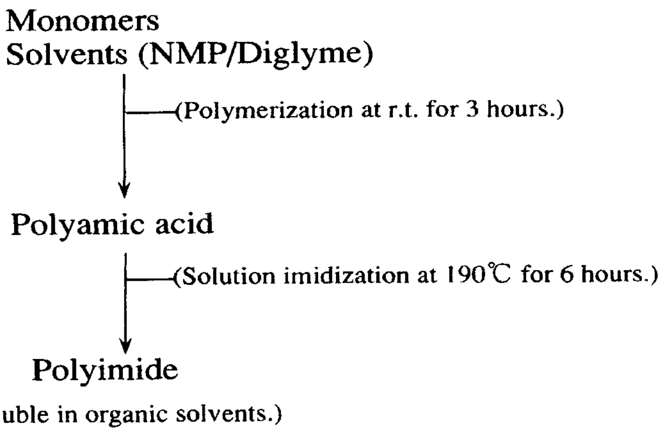
2.2. Polymer Characterization

Dynamic mechanical analysis (DMA) was used to confirm the compatibility and to determine the glass transition temperature (Tg1, Tg2) with a REOBIVRON DDV-II EP (ORIENTECH CO., LTD.). Thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) were performed with a SSC5200 Thermal Analysis System and SSC 5670 Thermomechanical Analysis System (Seiko Electric Co., Ltd.). Adhesive strength and mechanical properties were measured with an Autograph AG-500A (Shimadzu Co.) at a drawing rate of 5mm/min. XPS analysis was conducted with an Electron Spectrometer ESCA 750 (Shimazu Co.).

Moisture permeation was measured with a Water Vapor Permeation Tester (Lyssy Co., Ltd.) based on the JIS K 7129 method. Moisture sorption was determined by measurement of the weight increase of the polyimide films after treatment at 23°C, 78%RH, for 24 hours.

2.3. Adhesive Specimen

Single lap shear strength and T-peel strength was measured by using the cast film of polyimide. Steel was used as an adherend according to JIS G 3141. Lap shear strength was determined according to JIS K 6850. The adhesive specimen was cured at (Tg2 + 50)°C for a constant holding time of ten minutes and under a pressure of



SCHEME 3 Typical synthetic method of siloxane modified polyimides by solution imidization.

1.96 GPa. T-peel strength was determined according to JIS K 6848. The adhesive strength was determined from the average value of three test samples.

3. RESULTS AND DISCUSSION

3.1. Polymer Characterization

(1) Thermal and Mechanical Properties The polyimide from DSDA/BAPP (Series B) has a relatively rigid structure since it has a higher Tg than that of polyimides from BTDA/BAPSM (Series A). Both polyimides possessed two different glass transition temperatures. One was attributed to the siloxane phase in the lower temperature range (Tgl) and the other was for the aromatic component in the higher temperature range (Tg2). It is suggestd that the shift of Tgl and Tg2 is dependent on the compatibility between the siloxane and aromatic components (Tab. I, Tab. II). The glass transition temperature was gradually lowered with increasing siloxane content and decreasing molecular weight of siloxane component in the polymer backbone (Fig. 1). The tensile modulus of polyimides were also lowered with increasing the siloxane content as indicated in Figure 2.

(2) Surface Properties The contact angles of the polyimide films were measured at 25°C and the results are shown in Figure 3. The 10wt% of incorporation of siloxane

TABLE I
Glass transition temperature of SPI. Effect of siloxane content on Tgl and Tg2

Siloxane content (PSX 750)	Glass transition temperature (°C)[1]			
	Series A		Series B	
	Tgl	Tg2	Tgl	Tg2
0Wt%	—	240	—	288
10wt%	−103	227	−103	253
30wt%	−133	187	−108	215

[1] Tg 1 and Tg 2 were determined by dynamic mechanical analysis.

TABLE II
Glass transition temperature of SPI. Effect of siloxane molecular weight on Tgl and Tg2 (Series A)

Siloxane momomer (wt%)	Tg 1 (°C)[1]	Tg 2 (°C)[1]
0wt%	—	240
PSX 750 (10wt%)	−103	227
PSX1200 (10wt%)	−119	231
PSX2300 (10wt%)	−127	237

[1] Tg 1 and Tg 2 were determined by dynamic mechanical analysis.

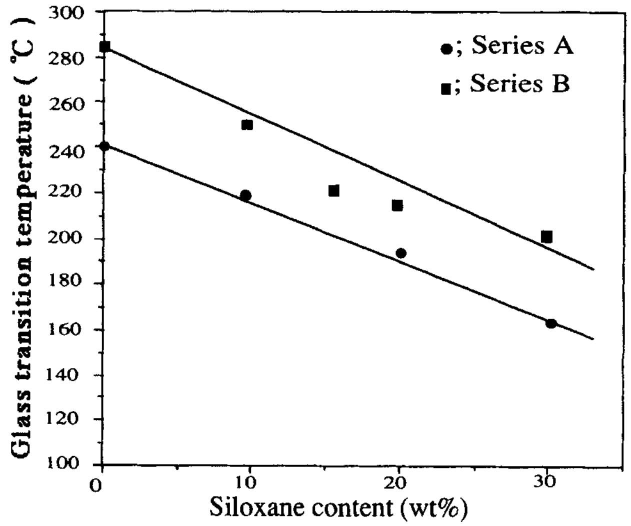


FIGURE 1 Relationship between siloxane content (PSX 750) and glass transition temperature of polyimides.

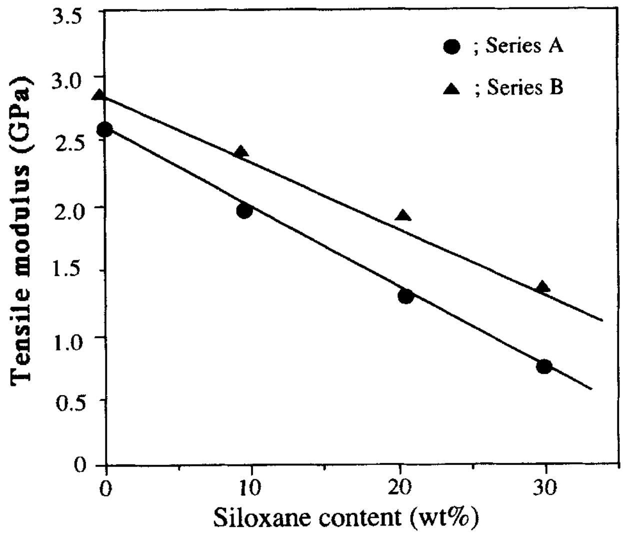


FIGURE 2 Relationship between siloxane content (PSX 750) and tensile modulus.

increased the water contact angle. The water contact angles of SPIs were comparable with those of hydrophobic silicone film. Further incorporations of siloxane into the polyimide backbone did not contribute to an increase in water contact angle.

Additionally, the concentration of silicon atoms in the surface of the polyimide films was revealed by XPS studies. The results of XPS analysis of the copolyimide

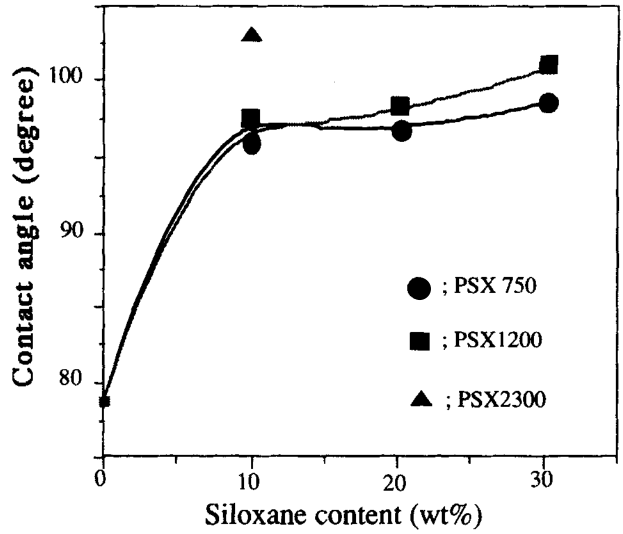


FIGURE 3 Water contact angle of SPI at 25°C.

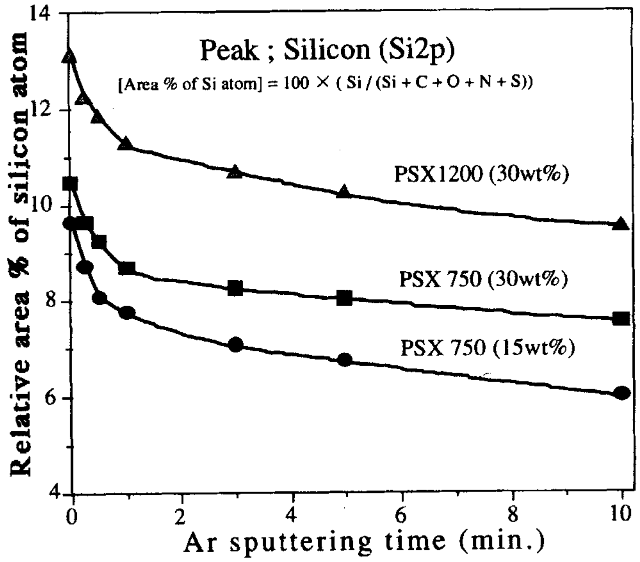


FIGURE 4 Results of XPS analysis of SPI films (Series A). Dependence of area % of silicon atom on argon sputtering time.

are shown in Figure 4. The relative area% of silicon atoms was obtained by calibrating peak areas with the intensity factors of $C_{1s} = 1.00$, $N_{1s} = 1.77$, $Si_{2p} = 0.86$, $O_{1s} \times 2.90$ $S_{2p} = 1.79$. It was proved that the siloxane density at the surface was higher than that in the bulk. The surface enrichment of siloxane was dependent on

TABLE III
Relationship between retention of adhesive strength and moisture sorption and water vapor permeability (Series A)

Siloxane monomer	Siloxane content (wt%)	Moisture[1] sorption (wt%)	WVPC [2]	Strength[3] retention (%)
–	0	0.6	0.4	66
	10	<0.1	0.6	99
PSX750	20	<0.1	0.9	74
	30	<0.1	2.2	55
	10	<0.1	0.7	93
PSX1200	20	<0.1	1.3	32
	30	<0.1	2.6	18

[1] Under the test condition at 25°C, 90%RH for 72 hrs.
[2] Water vapor permeability coefficient (g/cm/cm^2.sec.cmHg).
[3] Strength retention (%) = 100 × (SLLS after the treatment)/(SLSS of control).

both the molecular weight of siloxane and the content of siloxane. The introduction of higher molecular weight siloxane is effective for siloxane enrichment at surface.

(3) Moisture Sorption and Permeability The introduction of siloxane into polyimide leads to lower moisture sorption ($\leqslant$0.1wt%) due to hydrophobicity of the polydimethyl siloxane. On the other hand, moisture permeability was gradually increased with increase of the siloxane content. The results of moisture sorption and permeability are summarized in Table III.

3.2. Adhesive Properties

(1) Lap Shear Strength The single lap shear strength (SLSS) and fracture mode of the polyimide adhesive joints is summarizeed in Figure 5 and Table IV. The joints of all-aromatic polyimide from BTDA/BAPSM exhibited higher lap shear strength than those from DSDA/BAPP. Both polyimides with 10wt% of siloxane had better lap shear strength than the corresponding all-aromatic polyimides. 10wt% of incorporation of siloxane into aromatic polyimide from DSDA/BAPP was extremely effective for increasing the lap shear strength at room temperature, probably because the lower tensile modulus enhanced stress relaxation and the lower glass transition temperature increased fluidity. The polyimide with 10wt% of siloxane (Series B) had excellent lap shear strength to various substrates (Tab. V). However, further modification of siloxane lowered the bond strength in both series. 30wt% of incorporation of siloxane drastically lowered the bond strength due to the increase in elastomeric nature. The SLSS of SPI was lowered with the increase in siloxane content and siloxane molecular weight. The change of fracture mode suggests that the interface between the adhesive and the adherend plays some important roles. The results of surface analysis and fracture mode analysis indicate that the further incorporation of siloxane leads to the formation of a weak boundary layer, which is composed of the siloxane phae. The lap shear strength of polyimide at 200°C was lowered, since the tensile strength of polyimide was decreased as previously reported[4].

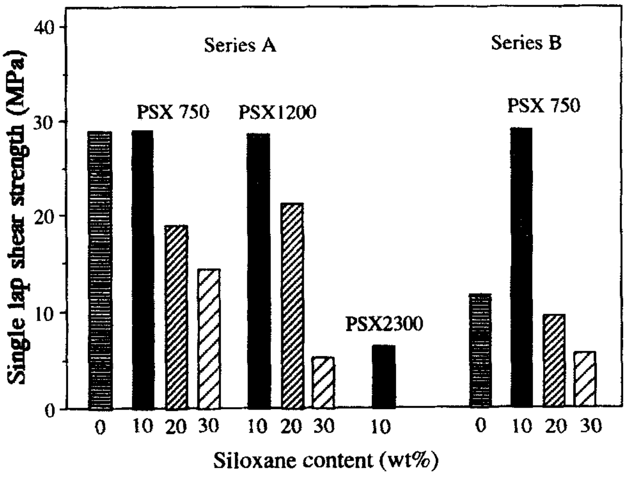


FIGURE 5 Single lap shear strength of SPI at room temperature.

TABLE IV
Fracture mode of adhesive specimens (Series A)

Siloxane content (wt%)	—	PSX750			PSX1200			PSX2300
	0	10	20	30	10	20	30	10
Fracture mode1)	Co	Co	Co/Ad	Co/Ad	Co	Co/Ad	Ad	Ad

1)Fracture mode of SPI films. (Ad = Adhesive, Co = Cohesive, Co/Ad = Combined)

TABLE V
Single lap shear strength of SPI adhesive film on various substrates (Series B)

Substrate	Lap shear strength (Mpa) 1)
Steel	29.0
Aluminum	23.9
Ceramics (Alumina)	24.0

1)Adhesive film of siloxane modified polyimide with 10wt% of PSX750.

(2) Adhesive Durability A series of polyimides from BTDA/BAPSM was used for the study of adhesive durability under a highly humid condition (25°C, 90%RH, 72 hours). The polyimides with 10wt% of siloxane (PSX750, PSX1200) have excellent adhesive durability comapred with the corresponding all-aromatic polyimides as shown in Figure 6. The results of fracture mode analysis are summarized in Table VI. The polyimides with 10wt% of siloxane (PSX750, PSX1200) exhibit

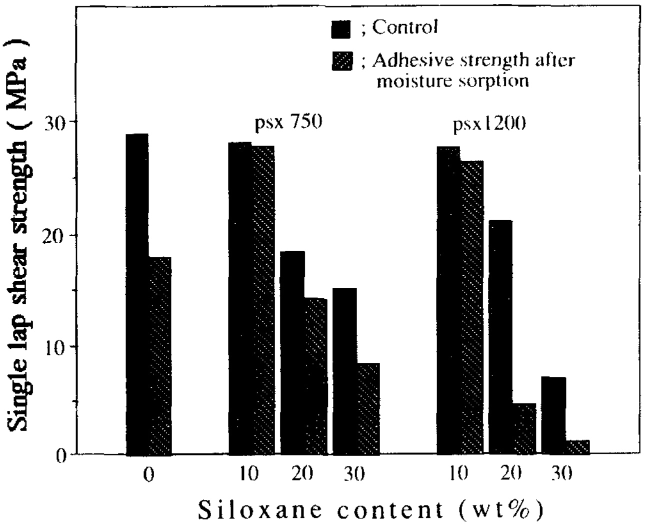


FIGURE 6 Single lap shear strength of SPI (Series A) after the treatment under the test conditions (25°C, 90%RH, for 72 hrs (JIS K 6857)).

TABLE VI
Fracture mode of adhesive specimens after treatment under the hot/wet condition (Series A)

Siloxane content (wt%)	—	PSX750			PSX1200		
	0	10	20	30	10	20	30
Fracture mode[1]	Co	Co/Ad	Co/Ad	Ad	Co/Ad	Ad	Ad

[1] Fracture mode of SPI films. (Ad = Adhesive, Co = Cohesive, Co/Ad = Combined)

favorable properties such as low moisture sorption and low moisture permeability as shown in Table III[9]. The 20wt% and 30wt% of siloxane incorporation lowered the adhesive durability of SPIs, in spite of their lower moisture sorption. These results show that polyimides with small amounts of siloxane component have specific interactions with water vapor[10]. The interface between adhesive and adherend is probably stabilized by incorporation of a small amount of siloxane, since low moisture uptake and moisture permeability is achieved.

(3) T-Peel Strength The T-peel strength of polyimides at room temperature is summarized in Table VII. Both polyimides with 10wt% of siloxane possessed the same T-peel strength as the corresponding all-aromatic polyimides. The T-peel strength of SPIs was lowered with increasing siloxane content, in spite of their enhanced ductility. It is presumed that the T-peel strength of SPIs is lowered by the surface enrichment of siloxane component since the ductile siloxane phase leads to a poor adhesive strength at room temperature.

TABLE VII
T-peel strength of SPI adhesive films at room temperature

	T-peel strength (kN·m^{-1})		
	Series A		Series B
Content of PSX (wt%)	PSX750	PSX1200	PSX750
0	0.47 (Co/Ad1))	—	0.30 (Co/Ad)
10	0.45 (Co/Ad)	0.45 (Co/Ad)	0.14 (Ad)
20	0.10 (Ad)	0.06 (Ad)	0.06 (Ad)
30	0.09 (Ad)	0.02 (Ad)	0.05 (Ad)

1) Failure mode; Ad = Adhesive, Co = Cohesive.

TABLE VIII
Typical properties of adhesive films for printed circuit boards

			Conventional type	
Properties	Test conditions	SPB-050A1)	Epoxy type	Acrilic type
Adhesion (T-peel strength) (kN·m^{-1})	Copper2)	1.0	1.0	1.0
	KAPTON™3)	2.0	2.0	2.0
Resistance to molten solder bath (°C)	105 °C, 1hrs	350	320	280
	23 °C, 50%RH, 15hrs	280	260	240
Electrical properties Line-to-line insulation resistance	23 °C, 50%RH, 15hrs (DC 50V, 23 °C, 50%RH)	1.2×10^{13}	1.0×10^{13}	9.7×10^{12}
	121 °C, 85%RH, 300 hrs (DC 50V, 23 °C, 50%RH)	8.9×10^{12}	No detect	No detect
Dielectric constant	1MHz	3.2	4.5	5.5

1) Adhesive film developed for printed wiring board by NSCC.
2) peel strength was measured after treatment by 5% H_2SO_4 for 30 min at 40°C.
3) Commercial Polyimide film (DuPont).

Based on these results, a new type of adhesive film for printed circuit construction was developed and characterized. The newly-developed adhesive film, SPB-050A, is composed of the siloxane modified polyimide as a major component and a small amount of thermosetting resin for an improvement in peel strength[11,12]. The general properties of adhesive films are summarized in Table VIII. The properties of SPB-050A were improved compared with those of conventional adhesive films. SPB-050A exhibited good adhesive strength to substrates such as copper foil and the conventional polyimide film (KAPTON™). The excellent stability of printed circuit boards constructed with SPB-050A in a molten solder bath without blistering or delaminating was also confirmed. After thermal exposure at 150°C for several days, the change in peel strength at 20°C with exposure time for conventional adhesives and SPB-050A was measured. The results are shown in Figure 7.

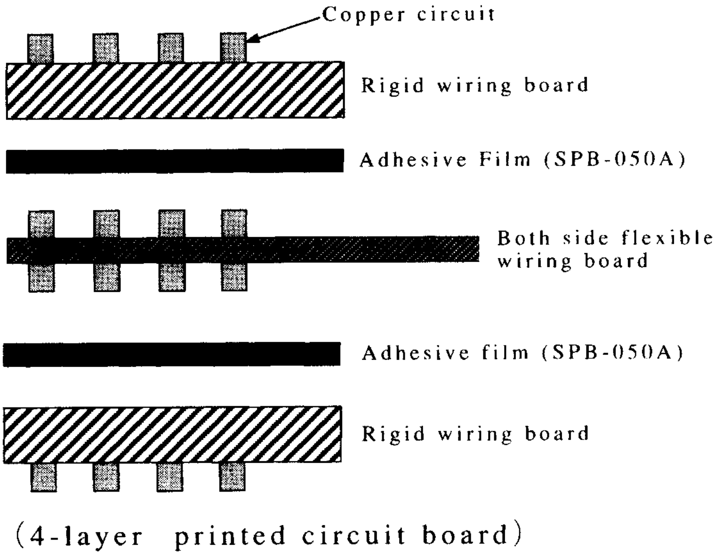


FIGURE 7 Application of new type of ahesive film for multi-layer printed circuit board.

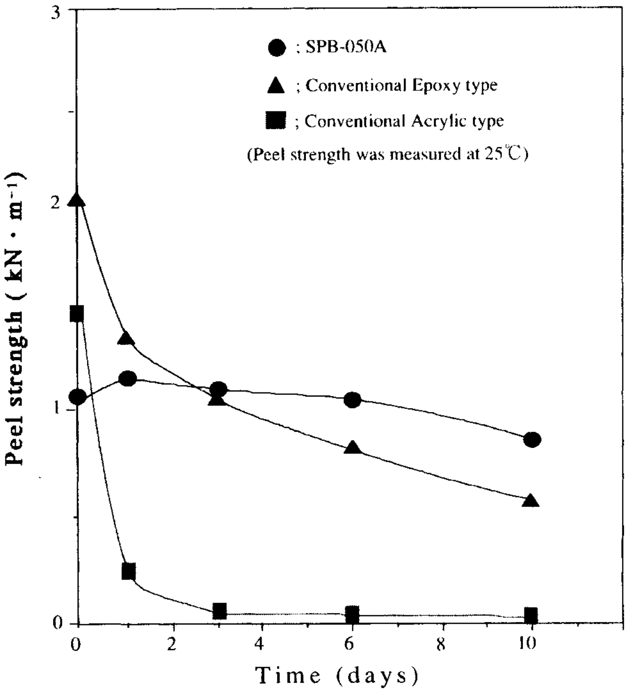


FIGURE 8 Peel strength for three kinds of adhesive films after thermal exposure at 150°C for 10 days.

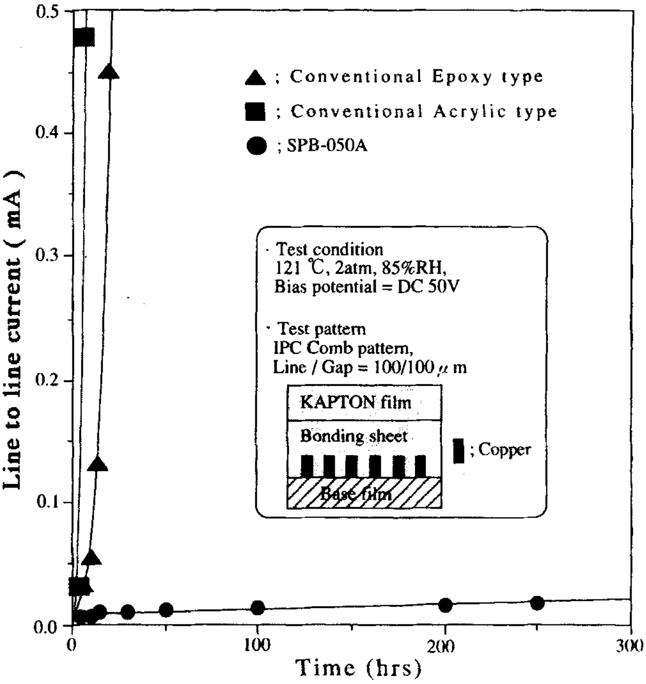


FIGURE 9 Leakage current properties of three kinds of adhesive films, under the hot/wet condition.

3.3. Electrical Properties and Reliability

Siloxane modified polyimides are excellent candidates for the adhesive film in printed circuit industries because of their excellent adhesive and electrical properties. The several properties such as low dielectric constant ($\leqslant 3.2$), good electric insulation, high stability to molten solder bath and improved reliability in hot / wet environments, have been well-known to be required to this application. A typical schematic of a multi-layer printed circuit board is shown in Figure 8. The electrical properties of the newly-developed adhesive film are reported in Table VIII.

Measurements of electric leakage currents on interdigitated-comb circuits are used for estimating fracture rates of the inter-layer dielectrics of multi-layer printed circuit boards. The printed circuit boards were exposed to a hot / wet environment for promoting deterioration of the interface between the developed adhesive and the copper circuit. The holding time dependence of leak current under the hot / wet condition (121°C, 2 atm, 85%RH) is shown in Figure 9. The measured values of leakage currents were extremely low. Furthermore, the newly-developed adhesive film had excellent adhesive strength as mentioned above.

4. CONCLUSIONS

Incorporation of siloxane into the backbones of polyimides increases their chain flexibility due to suppression of their upper glass transition temperatures. These copolymers are soluble in several organic solvents and show good processability at low temperature (⩽ 250°C). The new series of siloxane modified polyimides showed good adhesive strength at room temperature and excellent durability under a highly humid condition. A new type of adhesive film for multi-layered printed circuit board was also successfully developed.

The several important conclusions are summarized as follows:

(1) A small amount of siloxane incorporation (10wt%) enhances not only initial adhesive strength but also adhesive durability.
(2) Further siloxane incorporation into the aromatic polyimides is not effective for adhesive strength and durability.
(3) Incorporation of PSX750 as a siloxane component is more effective for enhancing adhesive properties comapared with PSX1200.
(4) Lower moisture uptake and permeability contributes to overall adhesive durability under highly humid conditions (25°C, 90%RH, 72 hours).
(5) The adhesive film prepared from a specific siloxane modified polyimide is useful for multi-layer printed circuit boards due to its superior reliability.

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