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Adhesion improvement of epoxy resin/ polyimide joints by amine treatment of polyimide surface

H. K. Yun, K. Cho, J. K. Kim and C. E. Park*
Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

and S. M. Sim, S. Y. Oh and J. M. Park
Packaging Development Team, Semiconductor R & D Center, Samsung Electronics, PO Box 37, Suwon, 449–900, Korea

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Polyimide (PI) surfaces were modified to improve the adhesion strength of epoxy resin/PI joints by immersing in amine solutions. Adhesion strength of epoxy resin/amine-treated PI joints were measured depending on structure, molecular weight, concentration, treatment time and drying temperatures of amines. There was an optimum drying temperature for maximum adhesion strength after amine-treatment of PI surface. The optimum drying temperature and the maximum adhesion strength increased with increasing the molecular weight of diamines or polyamines. Poly(amic amide) was formed by the reaction of primary amine of diamines and imide group of PI, and the other primary amine of poly(amic amide) reacted with the imide groups of adjacent PI chains to form cross-linked structure. In this way, adhesion strength of epoxy resin/PI joints was improved by reinforcing the weak PI surface layer. Another additional adhesion mechanism could be the chemical reaction of epoxide in the epoxy resin and unreacted amine of poly(amic amide). Adhesion strength decreased at above the optimum drying temperature since poly(amic amide) was imidized. The adhesion mechanisms and existence of optimum drying temperature were investigated using *FT*i.r., contact angle goniometer, X-ray photoelectron spectroscopy and rheometric dynamic spectroscopy.

(Keywords: adhesion strength; amine treatment; polyimide)

INTRODUCTION

Polyimides have been widely used as protective overcoats and dielectric layers for semiconductor devices because of their good properties, e.g. low dielectric constant, excellent thermal and mechanical properties, and good planarizability[1]. Since polyimides are applied as an interlayer between substrates such as metals, ceramics, and other polymers, the adhesion between the polyimide and these materials is particularly important for the performance of semiconductor devices[2].

Polyimides have been coated onto semiconductor chips to block the alpha-particle from the silica in the epoxy moulding compound (EMC) for minimization of soft error. Since surface mounting is used as a packaging method instead of through-hole mounting, 225°C of high solder reflow temperature is required. Therefore, the adhesion strength between EMC and polyimide is more important than ever. The water absorbed in the EMC can be accumulated in the interface of EMC and polyimide[3], and the water cluster can vaporize at 225°C of solder reflow temperature to induce the delamination at the interface and fracture in the EMC[4].

The imide groups of polyimide and polyetherimide surfaces were converted to amic acid by treating the surfaces with KOH or NaOH aqueous solutions to improve the adhesion of polyimide to polyimide[5] and epoxy resin to polyetherimide[6]. Although surface treatment by alkaline solutions increased the adhesion strength, the practical application into semiconductor device was limited because of the metal corrosion by KOH or NaOH solutions.

In this study, the adhesion strength between epoxy resin and polyimide was improved by treating the polyimide surface with amines. The improvement of adhesion strength was investigated as a function of the concentration of amine solution, the treatment time of polyimide, drying temperature after amine treatment and the structure of amine. Adhesion mechanisms were also studied.

EXPERIMENTAL

Materials

Polyimides (PI) used were pyromellitic dianhydride-4,4′-oxydianiline (PMDA-ODA; Pyralin PI 2545, Du Pont) and hexafluoro isopropylidene bisphthalic anhydride-4,4′-oxydianiline (6FDA-ODA). 6FDA-ODA poly(amic acid) was synthesized from 6FDA (Hoechst, Germany) and ODA (Wakayama, Japan) according to the literature[7]. Polyetherimide (PEI; Ultem 1000) from

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* To whom correspondence should be addressed

Table 1 The amines used for surface treatment of polyimide and polyetherimide

Group	Chemical structure	Chemical name	Abbrev.	Maker
I	$C_4N_9NH_2$	Butyl amine	BA	Aldrich
II	$CH_3NH(CH_2)_3NH_2$	N-methyl-1,3-propane diamine	MPDA	Aldrich
III	NH_2NH_2	Hydrazine	HA	Aldrich
	$NH_2(CH_2)_2NH_2$	Ethylene diamine	EDA	Junsei
	$NH_2(CH_2)_3NH_2$	1,3-Propane diamine	PDA	Janssen
	$NH_2(CH_2)_4NH_2$	1,4-Butane diamine	BDA	Janssen
	$NH_2(CH_2)_6NH_2$	1,6-Hexane diamine	HDA	Junsei
IV	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Diethylenetriamine	DETA	Aldrich
	$NH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$	Triethylenetetramine	TETA	Kukdo
	$NH_2CH_2CH_2(NHCH_2CH_2)_3NH_2$	Tetraethylenepentamine	TEPA	Aldrich
	$NH_2CH_2CH_2(NHCH_2CH_2)_4NH_2$	Pentaethylenehexamine	PEHA	Aldrich

General Electric was also used. The amines used for the surface treatment of PI and PEI were listed in *Table 1*.

O-cresol novolac epoxy resin (LER N-673, epoxy equivalent weight = 200–230 g eq^{-1}) manufactured by Lucky Epoxy (Korea) and brominated epoxy resin (YDB-400, epoxy equivalent weight = 380–420 g eq^{-1}) manufactured by Kukdo Chemicals (Korea) were used. Nadic methyl anhydride (NMA) and benzyldimethylamine (BDMA), both from Kukdo Chemicals (Korea), were used as a cross-linking agent and a catalyst, respectively.

Preparation of epoxy resin/polyimide joints

Poly(amic acid) solution was cast onto 18 μm thick aluminium foil using a doctor blade and imidized in a forced-air convection oven under the following imidization schedule, 100°C for 1 h, 200°C for 1 h and 300°C for 1 h. The thickness of PI film after final imidization was about 20 μm. Methylene chloride (Samchun Chemicals, Korea) solution of PEI (15 w/v%) was cast onto the aluminium foil by a doctor blade and dried at 150°C for 1 h. The thickness of PEI film was about 20 μm.

Unless other conditions are specified, the surfaces of PI and PEI films were modified by immersion in 0.5 w/v% amine solution at room temperature for 5 min. The solvents used were double-distilled water and isopropyl alcohol (Samchun Chemicals, Korea). Then, amine-treated PI films were dried in a convection oven at the various temperatures for 1 h.

One-hundred parts of novolac epoxy resin and 83 parts of NMA were mixed at 90°C for 30 min, and then two parts of BDMA were added at room temperature. One-hundred parts of brominated epoxy resin and 45 parts of NMA were mixed at 80°C for 30 min, and then 2 parts of BDMA were added at room temperature. The mixture was poured onto the PI films in a silicone rubber mould, and then cured at 90°C for 2 h and 150°C for 4 h in a forced-air convection oven. The thickness of cured epoxy resin was about 3 mm.

Peel tests

Adhesion strength of epoxy resin/PI joints was measured by a 90° peel test at a peel rate of 5 mm min^{-1} using Instron Model 4206. The aluminium foil layer of the joints was backed up with 140 μm thick duct tape to prevent the tearing of PI film during peel test. 5 mm wide PI layer strips cut with a razor blade were peeled from the epoxy resin.

Surface energies

The surface energies of amine-treated PI were determined by measuring the contact angles with a contact angle goniometer (CA-A, Kyowa Surface Science, Tokyo, Japan). The following simultaneous equations[8] were solved to obtain the dispersive (γ_s^d) and polar (γ_s^p) components of the surface energies of PI from the contact angles using two test liquids, water (1) and methylene iodide (2):

$$(1+\cos\theta_1)\gamma_1 = 2[(\gamma_1^d\gamma_s^d)^{0.5} + (\gamma_1^p\gamma_s^p)^{0.5}]$$

$$(1+\cos\theta_2)\gamma_2 = 2[(\gamma_2^d\gamma_s^d)^{0.5} + (\gamma_2^p\gamma_s^p)^{0.5}]$$

The surface energy γ, the dispersive component γ^d, and the polar component γ^p values used in these calculations were 72.2, 22.0 and 50.2 mJ m^{-2} for water and 50.8, 48.5 and 2.3 mJ m^{-2} for methylene iodide, respectively, as reported in the literature[9].

Fourier transform infrared spectroscopy (FTi.r.)

ATR (attenuated total reflection) *FT*i.r. spectra of amine-treated PI films were obtained using a Perkin–Elmer 1800 *FT*i.r. spectrophotometer with a KRS-5 (45°, trapezoid) crystal and an ATR accessory. Transmission *FT*i.r. spectra of amine-modified PEI were also obtained: The mixture of 0.25 g amine and 2.5 g PEI in 100 ml methylene chloride was cast onto a slide glass and analysed after drying the free film at various temperatures. The thickness of PEI film was about 15 μm.

X-ray photoelectron spectroscopy (X.p.s.)

The surface atomic compositions of the amine-treated PI and peeled surfaces of epoxy resin/amine-treated PI joints were analysed with a Perkin–Elmer Phi-5400 X-ray photoelectron spectrometer using a MgK_α X-ray source (1253.6 eV, 350 W). The take-off angles between an analyzer and sample surface were varied from 15° to 75° to examine the variation in the atomic compositions as a function of depth from the surface.

Rheometric dynamic spectroscopy (RDS)

The complex viscosity (η^*) of amine-modified PEI in 1-methyl-2-pyrrolidinone (NMP; Aldrich) was measured by RDS (RDS II, Rheometrics, USA) at room temperature. η^* of the mixture of 0.1 g amine and 0.5 g PEI in 15 ml NMP was measured between parallel plates with the gap of 1.2 mm. The strain was 15% and the frequency was swept in 10^{-2}–100 rad s^{-1} range.

RESULTS AND DISCUSSION

Adhesion strength of epoxy resin/amine-treated polyimide joints

Amine concentration. The effects of triethylenetetramine (TETA) concentration in aqueous and isopropyl

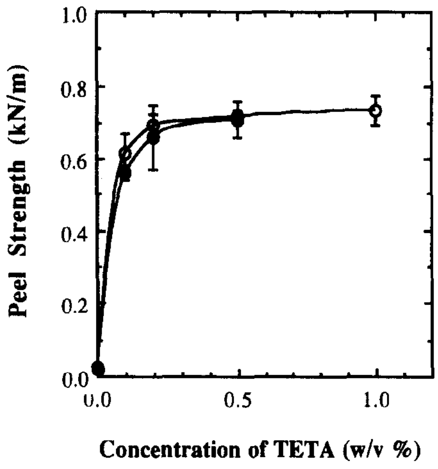


Figure 1 Effects of the concentration of TETA solutions for PMDA-ODA treatment on the adhesion strength of novolac epoxy resin/PMDA-ODA joints: (●) aqueous solution and (○) isopropyl alcohol solution

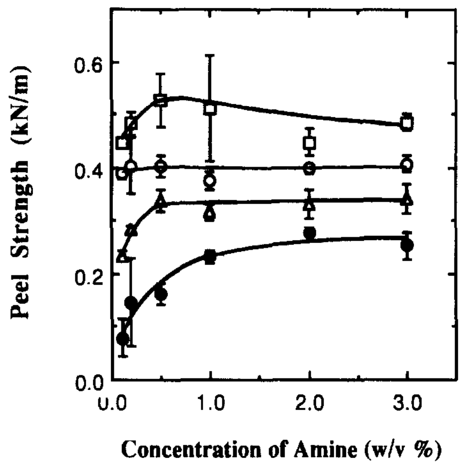


Figure 2 Effects of the concentration of diamines in aqueous solution for PMDA-ODA treatment on the adhesion strength of novolac epoxy resin/PMDA-ODA joints: (●) HA, (△) EDA, (○) PDA and (□) HDA

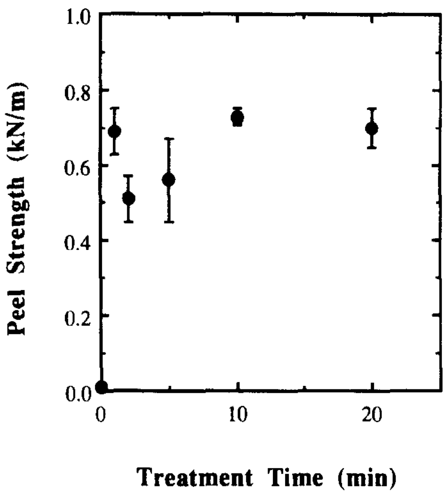


Figure 3 The adhesion strength of novolac epoxy resin/PMDA-ODA joints as a function of treatment time of PMDA-ODA in 0.5 w/v% TETA aqueous solution

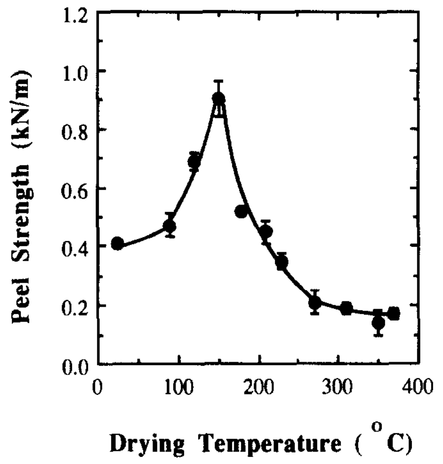


Figure 4 Effects of drying temperature after TETA treatment of PMDA-ODA on the adhesion strength of novolac epoxy resin/PMDA-ODA joints

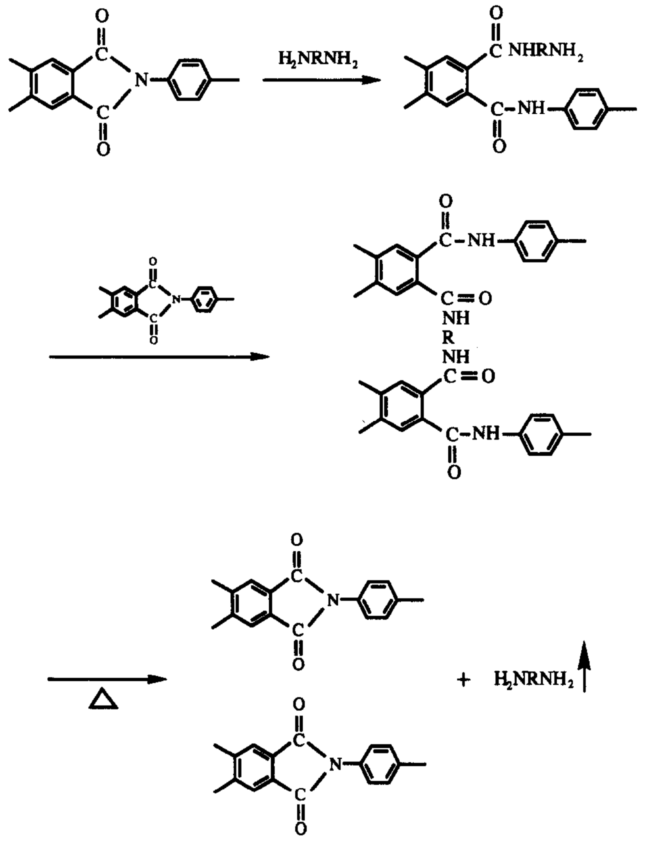
alcohol solutions for surface treatment of PMDA-ODA on the adhesion strength of novolac epoxy resin/amine-treated PMDA-ODA joints were shown in *Figure 1*. The adhesion strength reached to a plateau at about 0.5 w/v% of TETA concentration. The similar adhesion strengths were obtained with above two different solvents.

Figure 2 shows the concentration effects of primary diamines listed in group III of *Table 1* on the adhesion strength of novolac epoxy resin/amine-treated PMDA-ODA joints. The adhesion strength also reached to a plateau at about 0.5 w/v% of diamine concentration except hydrazine (a plateau at about 2.0 w/v%). As the molecular weight of diamine increased, the adhesion strength increased.

Treatment time. The adhesion strength of novolac epoxy resin/PMDA-ODA joints reached to the maximum with surface treatment of PMDA-ODA by immersing in the 0.5 w/v% TETA aqueous solution for about 1 min as shown in *Figure 3*. Since the diffusion depth of amine into PI surface increases with treatment time, it seems that modification of very thin surface layer of PI is enough to improve the adhesion strength of epoxy resin/PI joints.

Drying temperature. Figure 4 shows the adhesion strength of novolac epoxy resin/TETA-treated PMDA-ODA as a function of drying temperature after TETA treatment of PMDA-ODA. The adhesion strength shows a maximum at 150°C of drying temperature. The increase of adhesion strength from room temperature to 150°C of drying temperature comes from the more reaction between TETA and PMDA-ODA with the higher drying temperature. The decrease of adhesion strength above 150°C of drying temperature comes from the imidization of poly(amic amide) formed by amine-treatment of PI.

As shown in *Scheme 1*, by increasing the drying temperature up to 150°C, poly(amic amide) is formed by the reaction of primary amine and imide group of PI and untreated primary amine of poly(amic amide) can react with imide group of other PI to form the cross-linked structure, which can reinforce the surface layer of PI and improve the adhesion strength of epoxy resin/PI joints. The cross-linked structure is broken by the imidization of poly(amic amide) and diamine is released above 150°C of drying temperature as shown in *Scheme 1*. Formation of poly(amic amide) and cross-linked structure, and imidization of poly(amic amide) were investigated and



Scheme 1 The formation of poly(amic amide) and cross-linked structure, and imidization of poly(amic amide) into polyimide

experimentally observed as explained later. The chemical reaction of epoxide in the epoxy resin and primary or secondary amine of poly(amic amide) could be considered as another adhesion mechanism.

Structure of amine. Treatment of PI with monoamine such as *n*-butyl amine (BA) could not improve the adhesion strength of epoxy resin/PI joints. Since poly(amic amide) formed by reaction of monoamine with imide group of PI cannot react with imide group of other PI molecule, cross-linked structure cannot be formed.

Optimum drying temperature and adhesion strength of novolac epoxy resin/PMDA-ODA joints increased with increasing the molecular weight of diamine as shown in *Figure 5*. The optimum drying temperature was 80°C for hydrazine (HA) and ethylene diamine (EDA), and 120°C for 1,3-propane diamine (PDA) and 1,6-hexane diamine (HDA) treatments. The more cross-linked structure appears to be formed in the PI surface layer with increasing the molecular weight of diamine at higher drying temperature since the longer chain length of the higher molecular weight diamines is advantageous to connecting two neighbouring PI chains. And imidization of poly(amic amide) and releasing of diamine also begin at higher drying temperature with increasing the molecular weight of diamine. As shown in *Figure 6*, the adhesion strength of novolac epoxy resin/amine-treated PMDA-ODA joints increased with increasing the number of methylene units in diamines used for surface treatment of PI. Drying temperature after amine treatment was fixed at 80°C for every primary diamine. Similar results were also obtained with novolac epoxy resin/PEI joints.

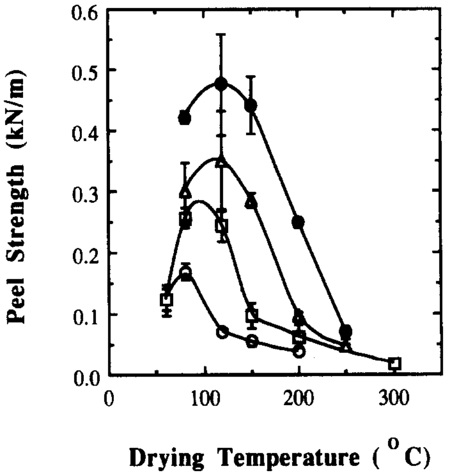


Figure 5 Effects of drying temperature after diamine treatments of PMDA-ODA on the adhesion strength of novolac epoxy resin/PMDA-ODA joints: (○) HA, (□) EDA, (△) PDA and (●) HDA

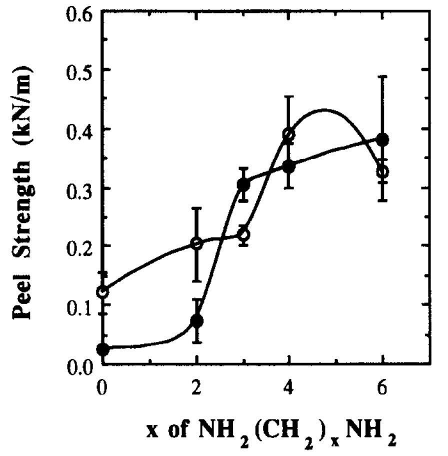


Figure 6 Effects of the number of methylene units in diamines for surface treatment on the adhesion strength of novolac epoxy resin to (○) PMDA-ODA and (●) PEI

Table 2 The peel strength of novolac epoxy resin/PMDA-ODA joints depending on drying temperature and polyamines used for surface treatment (unit: kN m^{-1})

	Drying temperature		
Polyamine	80°C	150°C	300°C
TETA	0.73 ± 0.04	0.90 ± 0.06	0.35 ± 0.02
TEPA	0.69 ± 0.04	NM[a]	0.44 ± 0.05
PEHA	0.61 ± 0.08	NM	0.63 ± 0.05

[a] Cannot be measured due to tearing of polyimide

Table 2 shows the adhesion strength of novolac epoxy resin/polyamine-treated PMDA-ODA joints with three different drying temperatures of 80°C, 150°C and 300°C. The adhesion strength decreased with increasing the molecular weight of polyamines at 80°C of drying temperature, where higher molecular weight polyamines seem to be less diffused into PI than lower molecular weight of polyamines. However, the adhesion strength increased with increasing the molecular weight of polyamines at 150°C of drying temperature. For tetraethylene pentamine (TEPA) and pentaethylene hexamine (PEHA) treated systems, peel strengths were too strong to measure owing to tearing of PI films. Adhesion strengths of polyamine-treated systems were much higher than those of diamine-treated systems. Polyamines have primary diamines at the end and secondary amines in the middle. When PI was treated with polyamines, most of the diamines reacted with PI to form poly(amic amide) and then cross-linked structure in the PI surface, but secondary amines could not react with PI due to steric hindrance. Therefore, when epoxy resin was applied on PI surface, secondary amines of polyamine could react with epoxide to form a chemical bond between epoxy resin and PI during the curing process of epoxy resin, which could be another additional reinforcing mechanism of epoxy resin/PI joints. At 300°C of drying temperature, the adhesion strengths were larger with higher molecular weight polyamine. For PEHA treated system, high adhesion strength of 0.63 kN m^{-1} was obtained with 300°C of drying temperature, which indicates that adhesion strength of epoxy resin/PI joints can be maintained even with 300°C of processing temperature.

Adhesion strength 0.6 kN m^{-1} was obtained for *N*-methyl-1,3-propane diamine (MPDA) treated system with 120°C of drying temperature as shown in *Figure 7*. As will be discussed later, the PI chains cannot form cross-linked structure with MPDA probably owing to the steric hindrance of secondary amine, although poly(amic amide) formation is possible by primary amine of MPDA. Therefore, the adhesion mechanism in the case of MPDA treatment seems that the primary amine reacts with imide group and the secondary amine reacts with epoxide in the epoxy resin.

Characterization of epoxy resin/amine-treated polyimide joints

FT*i.r.* The ATR *FT*i.r. analysis was performed on the TETA-treated PMDA-ODA. However, the poly(amic amide) could not be detected because ATR *FT*i.r. analysis has a much deeper analytical depth than TETA-modified depth.

Figure 8 shows *FT*i.r. spectra of TETA-modified PEI after drying at room temperture, 100°C and 210°C. The amide I peak of 1660 cm^{-1} (C=O stretching) and amide II peak of 1540 cm^{-1} (N–H bending) were observed with TETA modified PEI dried at room temperature, and increased by increasing drying temperature to 100°C. Then, these amide peaks disappeared at 210°C of drying temperature. As discussed earlier, formation of poly(amic amide) by the reaction of PEI with TETA increased with increasing drying temperature and then poly(amic amide) was imidized at higher drying temperature.

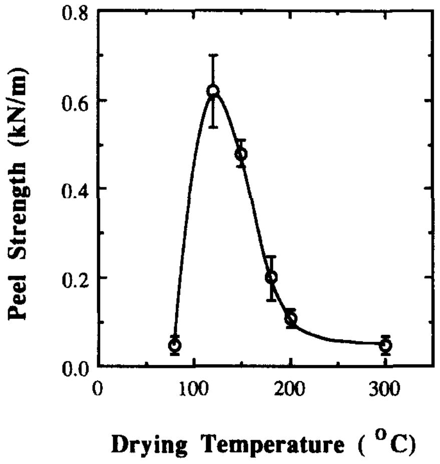


Figure 7 Effects of drying temperature after MPDA treatment of PMDA-ODA on the adhesion strength of novolac epoxy resin/PMDA-ODA joints

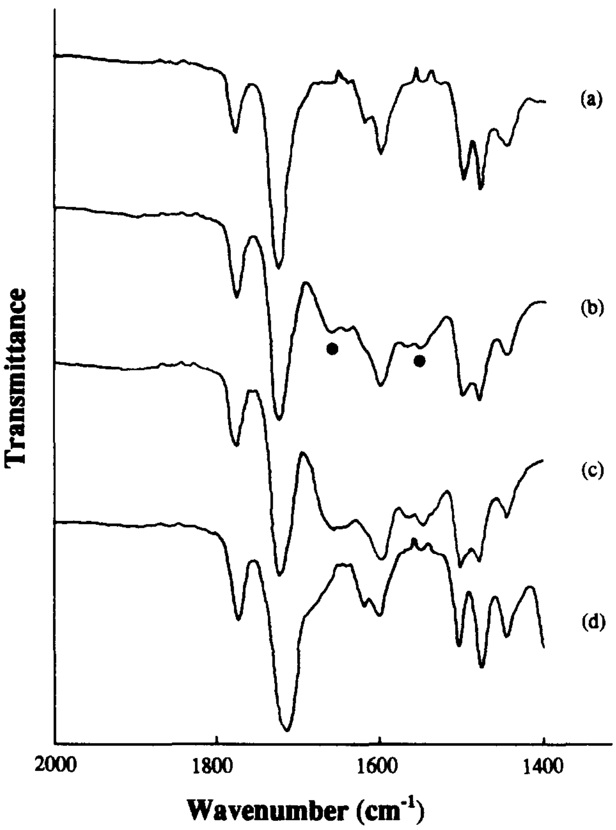


Figure 8 *FT*i.r. spectra of (a) PEI; TETA-modified PEI dried at (b) room temperature, (c) 100°C and (d) 210°C

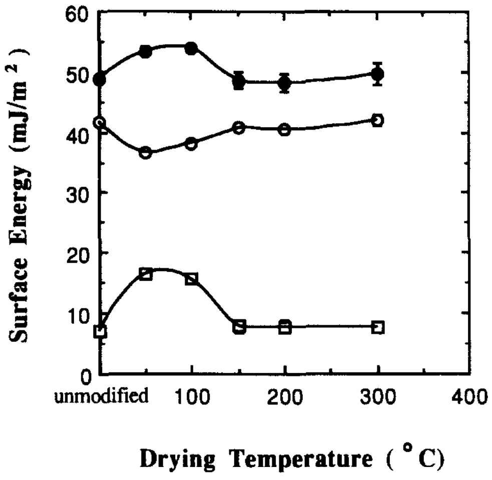


Figure 9 The surface energies of TETA-treated PMDA-ODA depending on drying temperature: (○) dispersive component, (□) polar component of surface energy and (●) total surface energy

Surface energies. *Figure 9* shows the surface energies of 0.5 w/v% aqueous TETA solution treated PMDA-ODA for 5 min depending on drying temperature. The total surface energies and polar surface energies were higher, and the dispersive surface energies were lower than those of unmodified PMDA-ODA up to 100°C of

Table 3 Atomic compositions of PMDA-ODA, novolac epoxy resin and peeled surfaces of novolac epoxy resin/PMDA-ODA joints by X.p.s. analysis

		C 1s	N 1s	O 1s
Theoretical PMDA-ODA		75.9	6.9	17.2
theoretical epoxy resin		81.6	0.1	18.3
PMDA-ODA	15°	78.5	6.7	14.8
	45°	77.3	7.7	15.0
	75°	77.0	7.7	15.3
Epoxy resin	15°	84.0	0.0	16.0
	45°	83.7	0.0	16.3
	75°	83.1	0.0	16.9
Peeled PI after 1st adhesion	15°	79.2	5.7	15.1
	45°	77.3	8.9	13.8
	75°	77.6	8.0	14.4
Peeled epoxy after 1st adhesion	15°	77.5	4.8	17.7
	45°	82.6	1.3	16.1
	75°	82.8	1.2	16.0
Peeled PI after 2nd adhesion	15°	78.6	6.7	14.7
	45°	78.7	6.9	14.4
	75°	78.9	6.7	14.4
Peeled epoxy after 2nd adhesion	15°	81.2	3.2	15.6
	45°	81.9	2.0	16.1
	75°	82.7	1.3	16.0
Peeled epoxy after 3rd adhesion	45°	82.2	1.1	16.7

drying temperature. And all the surface energies were the same as those of unmodified PMDA-ODA above 150°C of drying temperature. The surface energy changes coincide with the poly(amic amide) formation and subsequent imidization at higher drying temperature.

X.p.s. *Table 3* shows atomic compositions measured by angle-resolved X.p.s. on the surfaces of PMDA-ODA and novolac epoxy resin, and the peeled surfaces of novolac epoxy resin/PMDA-ODA joints. The sampling depth was varied from 1.5 to 5.5 nm by changing the take-off angle from 15° to 75°[10]. The atomic compositions of PMDA-ODA and novolac epoxy resin surfaces agree with the theoretical compositions. 0.1% theoretical nitrogen of novolac epoxy resin could not be detected since the sensitivity of X.p.s. is about 0.3%[11]. Significant amounts of nitrogen were measured from all of the epoxy resin surfaces peeled from PMDA-ODA as shown in *Table 3*. The results suggest that the locus of failure of the joint was 1 nm on the inner side of PMDA-ODA layer from interface, which was estimated by matching the atomic composition of peeled novolac epoxy resin surface with the atomic compositions of PMDA-ODA and novolac epoxy resin. Although the adhesion strength of novolac epoxy resin/unmodified PMDA-ODA joints was $0.02\,\mathrm{kN\,m^{-1}}$, the adhesion strength increased to $0.29\,\mathrm{kN\,m^{-1}}$ when the epoxy resin was cured on the peeled PMDA-ODA after peel tests. And the adhesion strength was $0.30\,\mathrm{kN\,m^{-1}}$ when the epoxy resin was cured on the twice peeled PMDA-ODA. This indicates that the weak boundary layer was removed from the first peel test, and then the adhesion strengths increased for the second and third peel tests. Judging from the atomic compositions of the three different peeled novolac epoxy resins as shown in *Table 3*, the loci of failure were similar to each other. The cohesive failure in PMDA-ODA surface layer for the second and third peel tests represents that the cohesive strength of PMDA-ODA surface layer is still weaker than the interfacial strength of epoxy resin/PMDA-ODA joints even after eliminating the weak boundary layer from the first peel test.

Table 4 shows atomic compositions of 6FDA-ODA, brominated epoxy resin and peeled surfaces of brominated epoxy resin/6FDA-ODA joints. The adhesion strength of brominated epoxy resin/6FDA-ODA joints, $0.02\,\mathrm{kN\,m^{-1}}$, was very poor. Nitrogen and fluorine on the peeled brominated epoxy resin indicate cohesive failure in the 6FDA-ODA layer. Bromine on the peeled 6FDA-ODA surface indicates cohesive failure in the epoxy resin, the diffusion of brominated epoxy resin into 6FDA-ODA layer or interfacial failure. The locus of failure of brominated epoxy resin/6FDA-ODA joints is not a perfect cohesive failure in the PI layer. It suggests that adhesion improvement of epoxy resin/PI joints can be obtained by two different ways: one is cohesive strengthening of the PI layer by cross-linking reactions with diamines, and the other is chemical reaction of epoxy resin and PI.

Table 5 shows the atomic composition of TETA treated PMDA-ODA. The nitrogen composition of TETA-treated PMDA-ODA dried at 150°C for 1 h increased compared with that of untreated PMDA-ODA, and the atomic compositions of TETA-treated PMDA-ODA dried at 300°C for 1 h approached to those of untreated PMDA-ODA. Since TETA and PMDA-ODA form poly(amic amide) at 150°C of drying temperature and then the poly(amic amide) was imidized at 300°C of drying temperature, the nitrogen

Table 4 Atomic compositions of 6FDA-ODA, brominated epoxy resin and peeled surfaces of brominated epoxy resin/6FDA-ODA joints by X.p.s. analysis

		C 1s	N 1s	O 1s	F 1s	Br $3d_{5/2}$
6FDA-ODA	Theoretical	70.5	4.5	11.4	13.6	–
	15°	71.7	5.1	7.8	15.4	–
	45°	73.4	5.1	7.8	13.7	–
	75°	73.4	4.6	8.1	13.9	–
Br epoxy resin	15°	75.0	0.0	18.3	–	6.7
	45°	74.3	0.0	17.1	–	8.6
	75°	74.8	0.0	15.9	–	9.3
Peeled 6FDA-ODA	15°	73.4	3.1	8.2	15.0	0.3
	45°	74.3	4.0	8.5	13.1	0.1
	75°	73.9	4.3	8.6	13.1	0.1
Peeled Br epoxy resin	15°	74.9	0.9	14.2	3.4	6.6
	45°	75.8	0.6	14.6	1.4	7.5
	75°	75.8	0.4	15.3	1.1	7.4

Table 5 Atomic compositions of TETA-treated PMDA-ODA and peeled surfaces of novolac epoxy resin/TETA-treated PMDA-ODA joints by X.p.s. analysis

		C 1s	N 1s	O 1s
Theoretical PMDA-ODA		75.9	6.9	17.2
Theoretical epoxy resin		81.6	0.1	18.3
PMDA-ODA	15°	78.5	6.7	14.8
	45°	77.3	7.7	15.0
	75°	77.0	7.7	15.3
TETA, 150°C drying[a]	15°	76.6	10.8	12.6
	45°	76.8	10.6	12.6
	75°	76.3	10.8	12.9
TETA, 300°C drying	15°	78.2	8.1	13.7
	45°	76.9	8.7	14.4
	75°	77.8	8.5	13.7
Peeled PI[a]	15°	78.4	8.6	13.1
	45°	78.3	8.0	13.8
	75°	78.1	8.2	13.7
Peeled epoxy resin	15°	74.0	6.3	19.7
	45°	79.4	5.3	15.3
	75°	79.8	5.2	15.0

[a] Drying temperture of 150°C after treatment

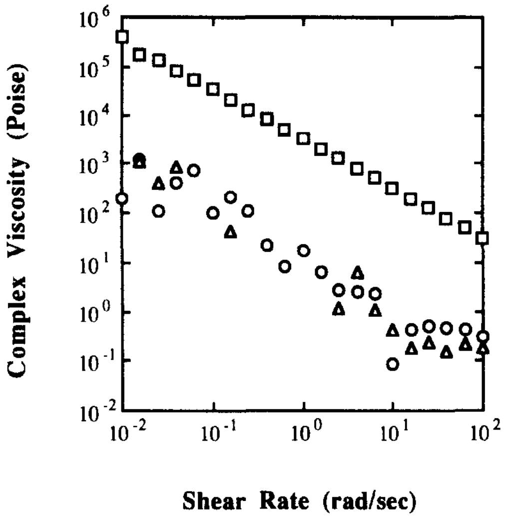


Figure 10 Complex viscosity measured by RDS: (○) PEI + NMP, (□) TETA + PEI + NMP and (△) BA + PEI + NMP

composition increased up to 150°C of drying temperature and then decreased to that of untreated PMDA-ODA.

The atomic compositions of the peeled surfaces of joint where TETA-treated PMDA-ODA was dried at 150°C for 1 h are shown in *Table 5*. The locus of failure was also 1 nm on the inner side of PMDA-ODA layer from interface, which was estimated by matching the atomic compositions of the peeled surface with the atomic compositions of novolac epoxy resin and TETA-treated PMDA-ODA. That also proves the adhesion mechanism of epoxy resin/amine-treated PI joints is the reinforcement of the PI surface layer through cross-linking of PI chains by diamines or polyamines.

RDS. The complex viscosities measured by RDS decreased with increasing shear rate as shown in *Figure 10*. The mixture of PEI, BA, and NMP (0.5 g: 0.1 g: 15 ml) showed the similar viscosities to that of the mixture of PEI and NMP (0.5 g: 15 ml). But the mixture of PEI, TETA and NMP (0.5 g: 0.1 g: 15 ml) showed three orders of magnitude higher viscosities than those of above mixtures. That represents PEI chains were cross-linked by the reaction with TETA, which was visualized by the formation of gel. All the mixtures of PEI with primary diamines or polyamines were gelled. However, the mixture of PEI with MPDA having a primary amine and a secondary amine was not gelled.

CONCLUSIONS

Adhesion strengths of epoxy resin/PI joints were improved by surface treatment of PI with amine solutions. The suitable amine concentration and treatment time were 0.5 w/v% and 1 min, respectively. Poly(amic amide) was formed by the reaction of primary amine of diamines and imide group of PI, and the other primary amine of poly(amic amide) reacted with the imide group of adjacent PI chains to form cross-linked structure.

From the study of X.p.s., the locus of failure of epoxy resin/PI joints was estimated to be 1 nm on the inner side PI layer from the interface. Therefore, the adhesion mechanism was the reinforcement of the weak PI surface layer by forming the cross-linked structure. The adhesion strength increased with increasing the molecular weight of diamines or polyamines. And the higher drying temperatures were needed with the higher molecular weights. That means longer chain length of amines is advantageous to the cross-linking reaction of adjacent PI chains and needs more energy to diffuse into the PI layer. However, there was an optimum drying temperature for maximum adhesion strength since poly(amic amide) was imidized at above an optimum drying temperature.

Adhesion strengths of polyamine-treated systems were much higher than those of diamine-treated systems. In the polyamine-treated systems, secondary amines could react with epoxide to form a chemical bond between epoxy resin and PI, which could be another additional adhesion mechanism. High molecular weight polyamines such as pentaethylenehexamine (PEHA) treated systems showed the best adhesion strengths, and the good adhesion strengths were maintained even with 300°C of processing temperature.

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