

Effect of Imidization Temperature on the Adhesion of Polyimide on Aluminum

JYONGSIK JANG* and JEUNG HOON LEE

Department of Chemical Technology, College of Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul, 151-742, South Korea

SYNOPSIS

Peel strength and lap shear strength between aluminum and polyimide were measured at different imidization temperatures. Polyimide was synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-diaminophenylether (ODA). The interfacial adhesion between polyimide and aluminum shows a maximum value at the imidization temperature of 320°C. To relate the interfacial adhesion strength with chemical interaction between polyimide and aluminum, the Fourier transform infrared spectroscopy (FTIR) ATR technique was used. In addition, morphological studies on the peeled surfaces were also carried out. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides are a class of polymers which have excellent mechanical, dielectric, and thermal properties. In addition, adhesion of polyimide to metal is a very crucial factor in applications such as microelectronics and aerospace industries. Therefore, much research on the adhesion between polyimide and metal has been performed.¹⁻⁸

In copper-polyimide adhesion, it has been known that there exists chemical bonding between copper and polyimide and that copper inhibits imidization forming copper carboxylate.⁹⁻¹¹ Contrary to copper, aluminum has been known to be inert, so that an adhesion promotor such as γ -aminopropyltriethoxysilane (γ -APS) is applied onto an aluminum surface.¹² In the presence of γ -APS, it has been reported that the reaction between polyimide and the adhesion promotor is accompanied by chain scission, which is detrimental to adhesion due to reduction of the bulk strength.¹³ Flament et al. studied the PMDA-ODA polyimide/aluminum interface by XPS and suggested that a direct chemical bond between the polyimide and aluminum is formed.¹²

This work was performed to elucidate the chemical interaction between polyimide and aluminum

with relation to interfacial adhesion strength. The adhesion strength between polyimide and aluminum was measured by the 180° peel test and lap shear test with different imidization conditions. The interfacial chemistry was investigated by Fourier transform infrared spectroscopy (FTIR), and the morphology of the peeled surfaces, by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co.) was dehydrated with phosphorus pentoxide and distilled under reduced pressure. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, Aldrich) and 4,4'-diaminophenylether (ODA, Aldrich) were recrystallized in acetic anhydride and ethanol, respectively. Aluminum foil (0.05 mm thick, Aldrich) was used as received.

Synthesis of Polyamic Acid

ODA was first dissolved in NMP, and then BTDA was added portionwise to the solution. Total solid content was kept to 15%. Stirring continued for 6 h in an ice-water bath. The resulting viscous polyamic acid solution was sealed and refrigerated until use.

* To whom correspondence should be addressed.

The polymerization scheme is represented in Figure 1.

Peel Test

Polyamic acid solution was applied to aluminum foil. The solvent was evaporated for 1 h at 100°C. Heating was continued for 30 min at 150°C and another 30 min at 175°C. The composite films were further imidized at 290, 320, and 350°C, respectively. The composite films were sliced into 5 mm pieces, the polymeric sides of which were glued to substrates with epoxy adhesive. Aluminum foil of the composite film was 180° peeled with a 5 mm/min peel rate. The Instron 4201 universal testing machine (UTM) was used. Figure 2 shows a schematic representation of the peel test.

Lap Shear Test

Adhesive tape was prepared to fabricate the lap shear test specimen. The polyamic acid solution was brush-coated onto E-glass fabric with a γ -APS finish. After each coat, the coated fabric was heated to drive off solvent and other volatiles. The heating proceeded as follows: 1 h at 100°C, 30 min at 150°C, and 30 min at 175°C. The coating was repeated until the thickness of the adhesive tape reached about 0.25 mm.

Aluminum plates (1.5 mm thick) were mechanically polished with No. 5 chrome oxide, ultrasonically cleaned in methanol, and coated with diluted polyamic acid solution. Specimens for the lap shear test were fabricated by hot pressing the adhesive tape between the aluminum plates. The temperature was increased from room temperature to the bonding temperature with a 5°C/min heating rate and held

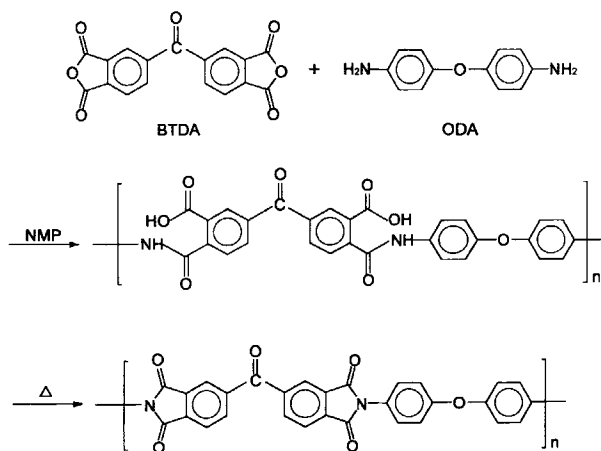


Figure 1 Synthesis of BTDA-ODA polyimide.

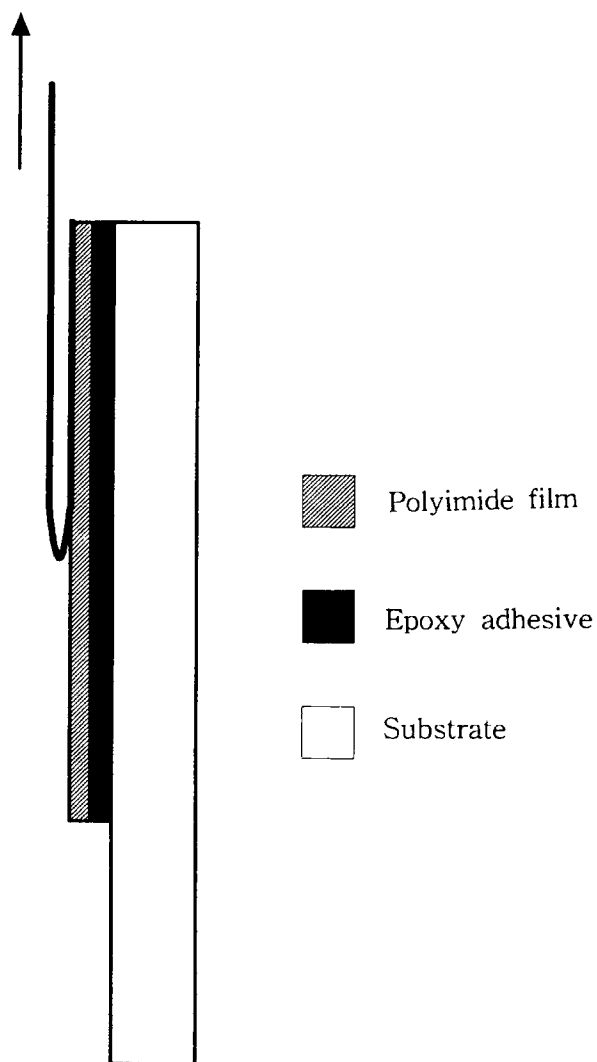


Figure 2 Schematic representation of peel test.

for 1 h at the bonding temperature. The bonding temperatures were 290, 320, and 350°C, respectively. Pressure of 500 psi was applied throughout the process. Lap shear strengths were determined according to ASTM D1002 with at least four specimens¹⁴ using the Instron 4201.

Instrumental Analysis

A Bomem MB-100 FTIR spectrophotometer was used to investigate the interface between polyimide and aluminum. Spectra of the peeled surfaces of polyimide films were obtained by the ATR technique. One hundred coadded scans were collected with a spectral resolution of 4 cm^{-1} . The absorption difference between the maximum and minimum absorbance is designated as ΔA .

Table I Peel Strengths between Polyimide and Aluminum with Different Imidization Temperatures

Imidization Temperature (°C)	Peel Strength (N/m)
175	484
290	953
320	1040
350	811

A DuPont 2100 thermogravimetric analyzer was used to observe the thermal stability of the polyimide film under air atmosphere. A JEOL scanning electron microscope (JSM-35) was used to examine the peeled surface of the polyimide.

RESULTS AND DISCUSSION

The peel strengths between aluminum and BTDA-ODA polyimide with different imidization conditions are summarized in Table I. The peel strengths increase drastically when polyamic acid-coated aluminum was further imidized over 290°C, and the maximum peel strength was shown in the sample imidized at 320°C.

Figure 3 shows the FTIR ATR spectra of polyimide imidized on aluminum. Band assignments for some important peaks are summarized in Table II. More extensive assignments are reported elsewhere.^{15,16} Compared with spectrum (a), a new peak at 1710 cm⁻¹ begins to appear as a shoulder in spectrum (b). Spectra (c) and (d) show new peaks at 1710 and 1740 cm⁻¹. New peaks at 1710 and 1740 cm⁻¹ are assigned to carboxylic acid and ester, respectively. Moreover, a peak assigned to C=O stretching in the BTDA moiety shifted from 1670 to 1660 cm⁻¹. A peak at 1778 cm⁻¹ assigned to C=O stretching of the imide group becomes weaker.

The drastic increase of the peel strength can be related to these spectral changes mentioned above. The existence of an ester functional group implies that chemical interactions occur between the imide ring and hydroxyl groups on the aluminum surface. The carboxylic acid band, which usually appears around 1725 cm⁻¹ in the spectrum of polyamic acid, appears at 1710 cm⁻¹ due to chemical interaction with the aluminum surface hydroxyl groups. Weakening of the imide stretching band at 1778 cm⁻¹ indicates that the chemical reaction occurred at the expense of the imide ring. The peaks related to the

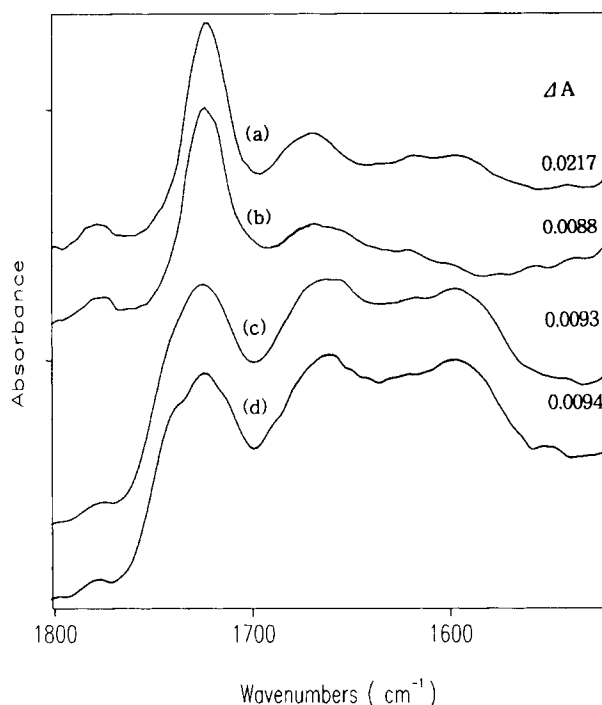


Figure 3 FTIR ATR spectra of polyimide imidized on aluminum with different imidization temperatures: (a) 175°C; (b) 290°C; (c) 320°C; (d) 350°C.

chemical interaction become stronger as the imidization temperature increases.

Additionally, the peak shift from 1670 to 1660 cm⁻¹ indicates that the carbonyl group in the BTDA moiety interacted with a hydroxyl group at the aluminum surface. When a carbonyl group has a chemical interaction with a hydroxyl group, the electron density of the carbonyl group decreases; thus, its absorption peak shifts to lower frequency. This can also be responsible for the increase of the adhesion strength. Figure 4 shows the proposed chemical interaction mechanism between polyimide and aluminum.

Figure 5 shows the spectra of BTDA-ODA films cast onto glass plates. The spectra show little difference with different imidization temperature and

Table II IR Band Assignments for BTDA-ODA Polyimide

Peak Position (cm ⁻¹)	Probable Assignments
1778	ν (C=O) imide [in-phase]
1740	ν (C=O) ester
1724	ν (C=O) imide [out-of-phase]
1710	ν (C=O) acid
1670	ν (C=O) phenyl

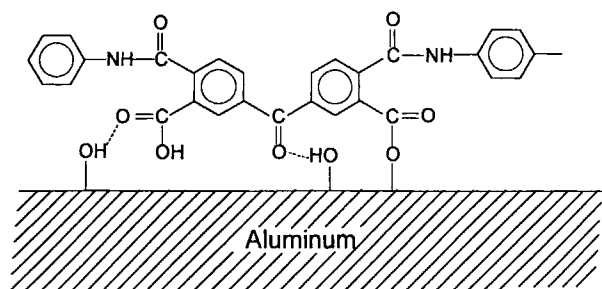


Figure 4 Proposed chemical interaction between polyimide and aluminum.

they resemble Figure 3(a). This means that there is no interaction between the polyimide and aluminum when imidized up to 175°C and the interaction is established when imidized at higher temperature. When no aluminum is present, there is no chemical interaction so that spectra show little difference with different imidization temperatures.

When polyimide was cured at 175°C, the solvent (NMP) is not completely removed. Complete removal of the solvent can be achieved when cured over 250°C.¹⁷ The residual solvent is thought to interfere with the chemical interaction between polyimide and aluminum forming the complex with the polyimide chain.¹⁸ When imidized over 290°C, the solvent molecules are removed almost completely and the chemical interaction between polyimide and aluminum can be established. Figures 6 and 7 show the TGA thermogram of the polyimide film imidized at 175 and 250°C, respectively. In contrast to the film imidized at 250°C, the film imidized at 175°C shows the weight loss around 250°C. The weight loss is due to the removal of the solvent which is forming complex with the polyimide chain. As a conclusion, imidization should take place over 290°C to maximize the chemical interaction between polyimide and aluminum.

As shown in Figure 3, band heights at 1710 and 1740 cm^{-1} increase as imidization temperature increases. The extent of chemical interaction between polyimide and aluminum is greater when the imidization temperature is higher, as evident from the spectral changes. The increase in peel strength with increasing imidization temperature from 290 to 320°C can be attributed to this increase in chemical interaction between polyimide and aluminum. However, when imidization was carried out at 350°C, the peel strength between polyimide and aluminum decreased although more chemical interaction was observed.

As the temperature increases, thermal mismatch between polyimide and aluminum becomes greater

due to the difference in thermal expansion coefficient of polyimide and aluminum. By this thermal mismatch, internal stress at the interface develops. If the internal stress is σ_i , the actual adhesion strength is then

$$\sigma = \sigma_0 - \sigma_i$$

where σ_0 is the adhesion strength for the internal stress free adhesive bond.¹⁹

Another factor that influences the adhesion strength is the mechanical strength of the polyimide near the interface. The interaction between polyimide and aluminum accompanies imide ring breakage. When the imide rings break to react with aluminum surface hydroxyl groups, the cohesive strength of the polyimide decreases, acting as a weak boundary.

As the imidization temperature increases, more chemical interaction occurs between polyimide and aluminum at the interface. The reduced cohesive strength through breakage of the imide ring can affect adhesion strength when the polyimide layer acts as a weak boundary. Greenblatt et al. reported that when using the adhesion promoter γ -APS the chain scission of the polyimide was detrimental to adhesion due to the reduced cohesive strength of polyimide near the interface.¹³ The greater internal stress

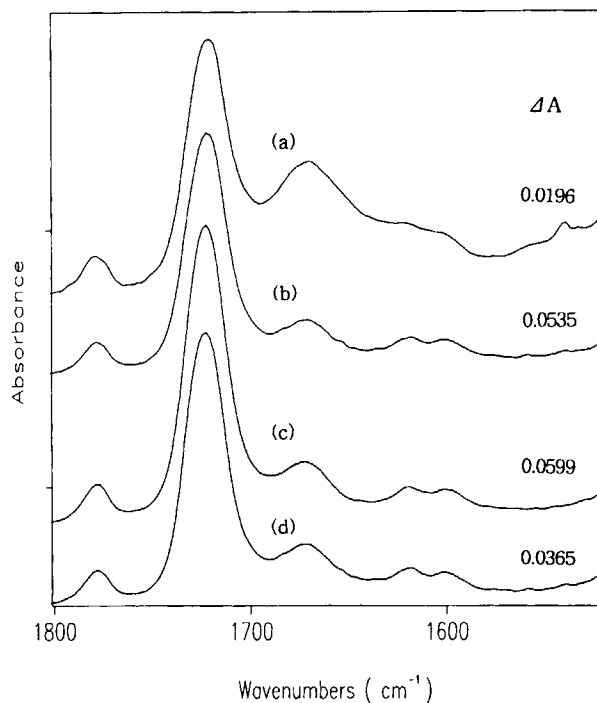


Figure 5 FTIR ATR spectra of polyimide film with different imidization temperatures: (a) 175°C; (b) 290°C; (c) 320°C; (d) 350°C.

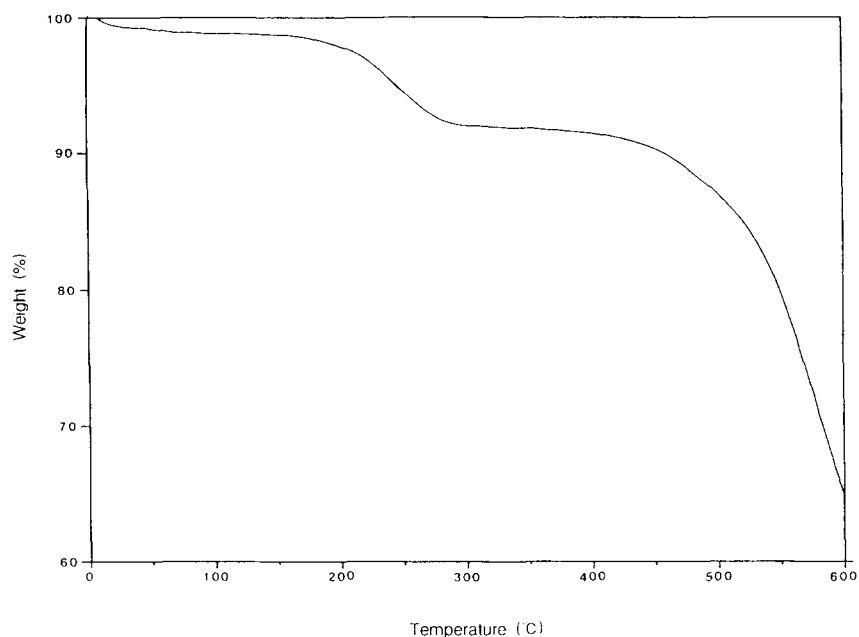


Figure 6 TGA thermogram of BTDA-ODA film imidized at 175°C.

and reduction of polyimide bulk strength are thought to decrease the peel strength when imidization temperature is increased from 320°C to 350°C.

Figure 8 shows SEM photographs of peeled polyimide surfaces. In Figure 8(b-d), stripe patterns are observed on the peeled polyimide surfaces. These imply that the peel crack propagates by a discontinuous process which occurs when

there is strong bond across the interface between two materials.²⁰ In Figure 8(a), the stripe pattern cannot be observed, which means that a strong bond is not formed at the interface. In addition, when the peeled surface is rougher, the peel strength value is higher. These morphological appearances are in good accord with the results of peel strength values.

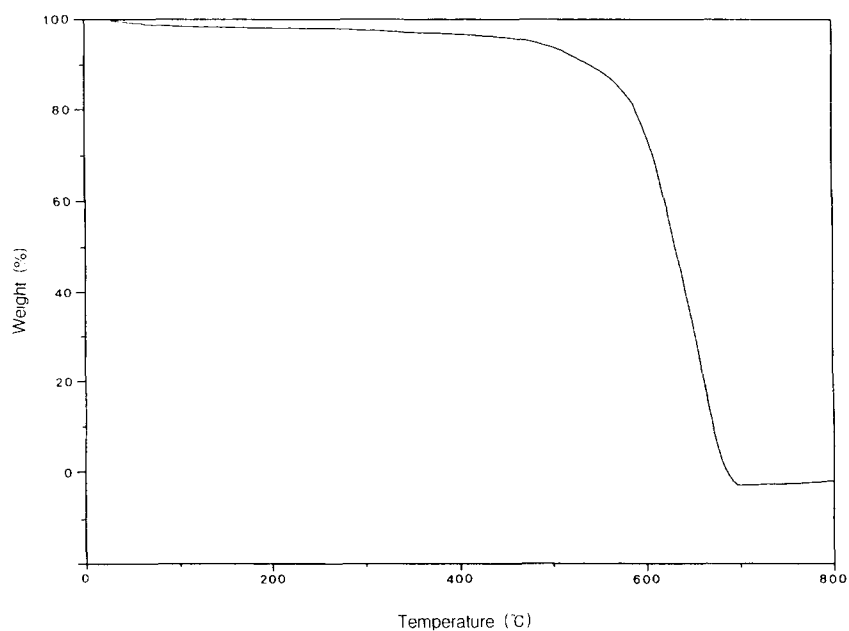


Figure 7 TGA thermogram of BTDA-ODA film imidized at 250°C.

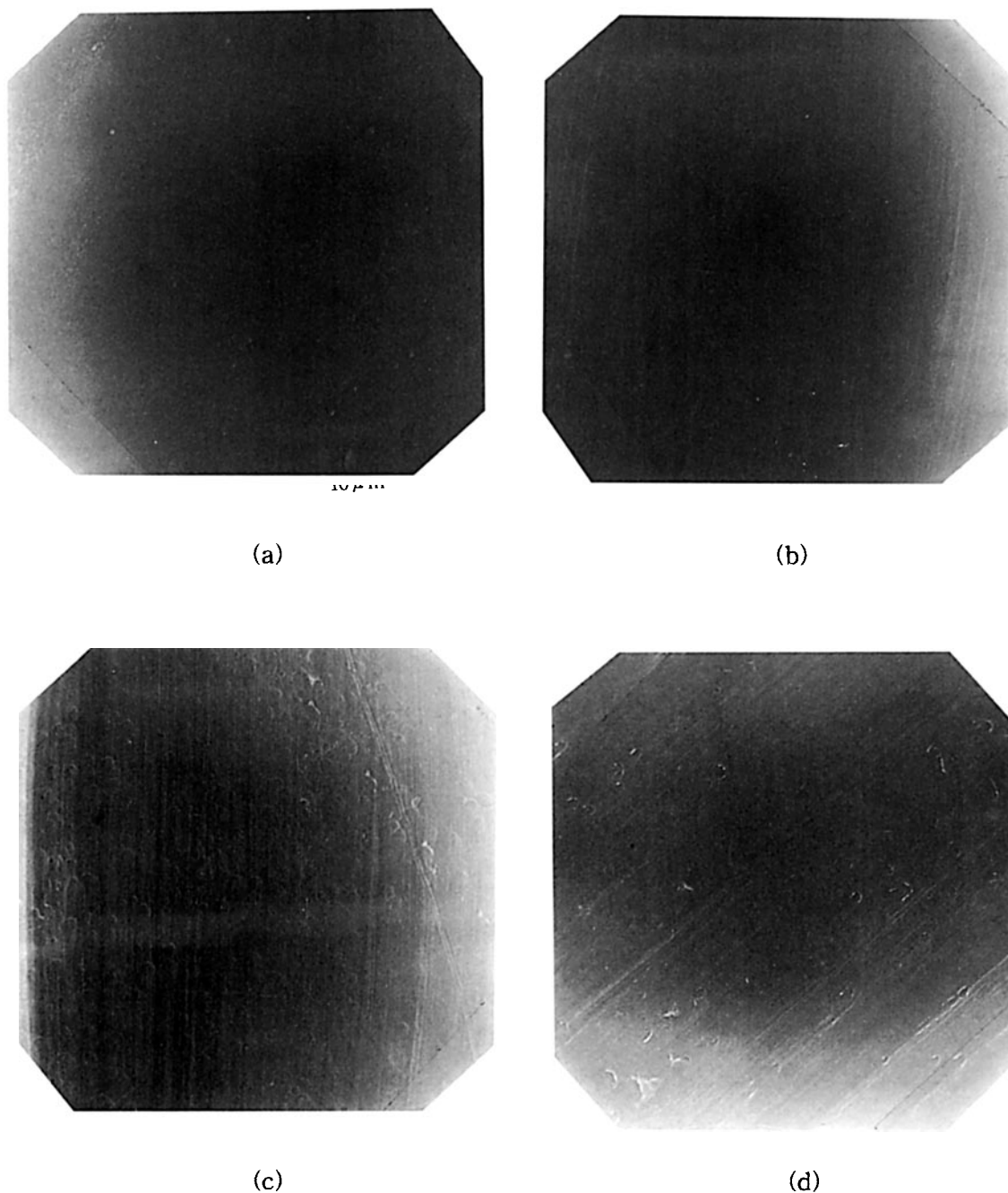


Figure 8 SEM photographs of peeled polyimide surface imidized with different imidization temperatures: (a) 175°C; (b) 290°C; (c) 320°C; (d) 350°C.

Table III shows the lap shear strengths with different bonding temperatures. The change of lap shear strength with different bonding temperatures shows a similar trend to the change of peel strength with different imidization temperatures.

All specimens showed interfacial failure in the lap shear test. Therefore, it is predictable that peel strength and lap shear strength show a similar trend with the same variable. However, lap shear strength values indicate that they are less sensitive to imidization temperature since they are less governed

Table III Lap Shear Strengths with Different Bonding Temperatures

Imidization Temperature (°C)	Lap Shear Strength (MPa)
290	4.70
320	5.16
350	3.65

by interfacial adhesion strength compared with peel strength.

CONCLUSION

BTDA-ODA polyimide was synthesized by solution polymerization. Peel strength and lap shear strength between the polyimide and aluminum were measured with different imidization temperatures. Peel strength increased largely when imidized at 290°C and above. The maximum peel strength between the polyimide and aluminum was achieved when the polyimide was imidized at 320°C. The evidence of chemical interaction between BTDA-ODA polyimide and aluminum, the formation of ester and carboxylic acid groups, was observed by FTIR. The chemical interaction started to evolve when imidization took place over 290°C. An SEM photograph confirmed these observations and the lap shear strengths showed a similar trend to the peel strength.

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