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Interfacial study of polyimide/copper system using silane-modified polyvinylimidazoles as adhesion promoters

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Abstract

Polyvinylimidazoles(PVIs) modified with vinyltrimethoxysilane (VTS) in different mole ratios were applied as adhesion promoters for polyimide (PI)/copper interface. The effects of the composition of VTS-modified PVI copolymers on lap shear strengths between PI and copper were investigated at different bonding temperatures. Fourier transform infrared spectroscopy was applied to examine the thermo-oxidative degradation of PI and oxidation of copper. In addition, scanning electron microscope and contact angle measurement analysis were performed to investigate the compatibility of VTS-modified PVIs with PI. An improvement in interfacial adhesion strength was obtained using the adhesion promoters. Especially at higher bonding temperatures, a significant increment in lap shear strength was seen when the mole ratio (VI:VTS) was 3:7, due to the high thermal stability of the silane unit. However, at lower bonding temperatures, lap shear strength does not increase as above, owing to the poor compatibility between the VTS-modified PVI with PI. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide-on-copper; Silane-modified polyvinylimidazole; Adhesion promotion

1. Introduction

Polyimides are widely used as adhesives, dielectrics, in microelectronics and composite applications, because they offer high thermal stability, low dielectric constant and chemical resistance [1,2]. Good adhesion properties of polyimide to metal are essential for applications in microelectronics and other circumstances. Numerous works have been performed to improve the adhesion of PI to metal [3–9]. Especially, polyimide-on-copper interfaces can be formed by spin-coating polyamic acid (PAA) onto a copper surface from a solution and then curing to obtain the polyimide; related works have been intensively performed [10–12]. It is well known that the thermal degradation of a polyimide layer is accelerated in the presence of copper and deteriorates material properties such as mechanical properties and adhesion to copper surfaces [13–15]. It was found that acid groups of the PAA react with copper and diffuse the copper ions into the polyimide layer. During thermal curing, diffused cuprous and/or cupric ions may cause the decomposition of hydroperoxides formed when the polyimide layer on copper began to oxidize at elevated temperatures. The radical produced during these reactions then lead to the accelerated oxidation of the polymer [11,16]. Transmission electron microscopy verified the existence of spherical copper particles in the polyimide layer [17].

To prevent the diffusion of copper into the polyimide layer and to reduce the thermal degradation of polyimide to maintain the adhesion strength of the polyimide/copper interface at elevated temperatures and its mechanical properties, a barrier film should be inserted between the polyimide and copper. Many inorganic metals such as Cr, Ni and Ta were layered onto copper as a thin passivation/adhesion-promoting agents [1]. However, this method is not simple and cost effective because it contains a metal capping step by depositing the metal onto copper. To simplify the manufacturing process, a new process using the polymer as a layer was proposed [18].

Imidazole and its derivatives have been reported to be the effective corrosion inhibitors for copper at elevated temperature [19–21]. In particular, the copolymers of 1-vinylimidazole and silane coupling agents have been used as good anticorrosion agents for copper [22–26]. The N–H bond in the imidazole ring reacts with copper to form a stable complex to protect the copper surface from corrosion, and silane-coupling agents were introduced to promote the thermal stability of the polymer films. In the previous study,

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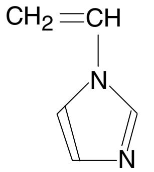
Table 1
The chemical structures of 1-vinylimidazole and vinyltrimethoxysilane

Monomers	Chemical structures
1-Vinylimidazole (VI)	
Vinyltrimethoxysilane (VTS)	$CH_2{=}CHSi(OCH_3)_3$

copolymers of 1-vinylimidazole and various silane-coupling agents were applied as a degradation inhibitor and an adhesion promoter for polyimide on copper [27]. Especially, vinyltrimethoxysilane (VTS)-modified polyvinylimidazole (PVI) showed the best performance as a barrier film due to its high thermal stability according to its highest siloxane bond number per weight.

In this study, PVI and VTS-modified PVIs were synthesized as the primers and their mole ratios were changed. VI was homopolymerized and copolymerized with VTS at different mole ratios. The effects of the copolymer composition on the lap shear strengths were investigated at different bonding temperatures of PMDA-ODA polyimide. In addition, Fourier transform infrared reflection and absorption spectroscopy (FTIR-RAS), scanning electron microscopy (SEM) and contact angle measurements were used to characterize the interfacial phenomena in the polyimide/PVI or VTS-modified PVI/copper systems.

2. Experimental

2.1. Materials

N-methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co.) was dehydrated with phosphorous pentoxide and distilled under reduced pressure. Pyromellitic dianhydride (PMDA, Aldrich Chemical Co.) and 4,4-oxydianiline (ODA, Tokyo Chemical Industry Co.) were recrystallized in 1,4-dioxane and ethanol, respectively. VI (Aldrich Chemical Co.) and VTS (Aldrich Chemical Co.) were distilled in vacuo to yield pure and colorless liquids. Azobisisobutyronitrile (AIBN, Wako Pure Chemical Industries, Ltd.) was recrystallized in methanol.

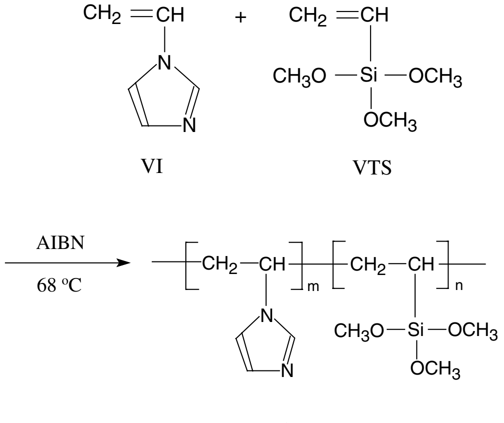


Fig. 1. The synthetic scheme of VTS-modified PVI.

Copper plates (1 mm thick, Poongsan Co., South Korea) were mechanically polished with No. 5 chromic oxide, washed with *n*-hexane and ethanol in an ultrasonic bath, rinsed with a 1% HCl/distilled water solution, distilled water and ethanol, then dried with a stream of nitrogen gas [21,22].

2.2. Synthesis

ODA was dissolved in NMP and PMDA was added within several times at room temperature to obtain a clear yellow viscous PAA solution. The total solid content was 14 wt%.

PVI and VTS-modified PVIs (primers) were synthesized by free radical polymerization using AIBN as an initiator. VI was homopolymerized and copolymerized with VTS. The mole ratios of VI to VTS in the feed were 7:3 and 3:7. The chemical structures of VI and VTS are represented in Table 1, and the synthetic scheme of VTS-modified PVI is shown in Fig. 1.

2.3. Lap shear test

PVI and VTS-modified PVI solution was cast onto copper plates, followed by coating of diluted PAA solution (7 wt%) on the copper plates. The primer film thickness was calculated based on the concentration of the copolymer solution, the copolymer density and the area of the copper surface. The coating thickness of the primers used in this study was 2 μm.

Pre-imidization was performed at 100°C for 1 h, at 150°C for 30 min in NMP-saturated condition. After heat treatment, the overall coating thickness was approximately 15 μm.

An adhesive tape was prepared for the lap shear test specimen. E-glass fabric with a γ-aminopropyltriethoxysilane (γ-APS) finish was coated with PAA solution. After coating, E-glass fabrics were heat-treated to drive off the solvent and other volatiles. The heat treatment process was performed for 1 h at 100°C, 30 min at 150°C and 30 min at 175°C. The coating thickness of an adhesive tape was approximately 0.25 mm.

Specimens for lap shear test were fabricated by hot pressing. The adhesive tape was placed between the two copper plates and coated with pre-imidized PAA. The cure temperature was raised from room temperature to the bonding temperature at a heating rate of 5°C/min and held for 1 h at the bonding temperature in NMP-saturated condition. The bonding temperatures were 290, 320, 350 and 380°C.

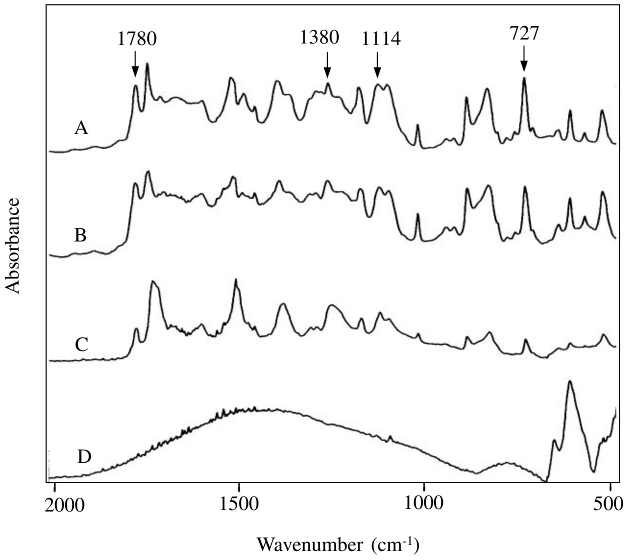


Fig. 2. R–A spectra of PI on copper with the different bonding temperatures: (A) 290; (B) 320; (C) 350; and (D) 380°C.

1.72 MPa of pressure was applied during the cure process. The lap shear test was performed with an universal testing machine (MTS 10/GL) according to ASTM D1002.

2.4. Instrumental analysis

A Bomem MB 100 FT-IR spectrometer was used to characterize the PI/PVI or VTS-modified PVI/copper systems. PAA solution was cast onto bare copper surfaces or copper plates coated with primers. The copper plates were then heat-treated by the same conditions used in the fabrication of the lap shear test specimens. IR spectra were obtained by the reflection–absorption (R–A) technique. 64 scans were collected with a spectral resolution of 4 cm^{-1}.

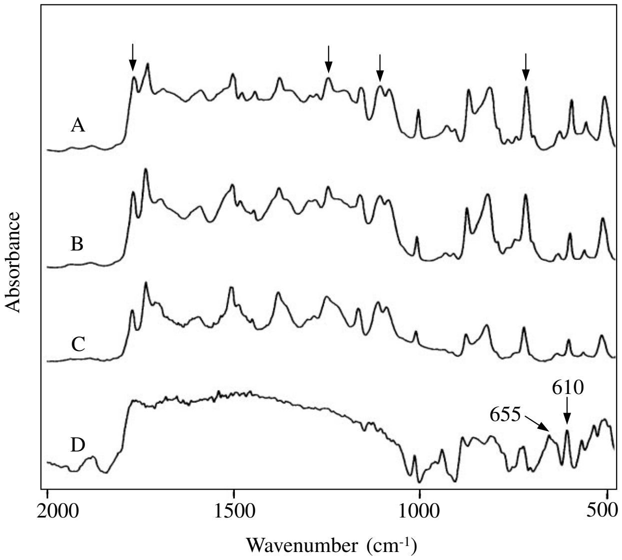


Fig. 3. R–A spectra of PI on PVI-treated copper with the different bonding temperatures: (A) 290; (B) 320; (C) 350; and (D) 380°C.

Contact angles of diluted PAA solution (7 wt%) on the primer-coated copper surface were measured to investigate the initial wettabilities of PAA solution on each case. The measurements were carried out using a Ramé-Hart NRL contact angle goniometer.

The fractured surfaces of PI/PVI and PI/VTS-modified PVI systems were examined with a scanning electron microscope (Jeol JSM T-200). The PI and primer were solution blended and imidized at 250°C. The imidized samples were fractured in liquid N_2 to observe the fractured surface. The specimens were coated with a thin layer of gold to eliminate charging effects.

3. Results and discussion

FT-IR reflection and absorption (R–A) spectra of the PMDA-ODA PI on bare copper and PI on PVI-treated copper are demonstrated in Figs. 2 and 3, respectively. The spectral changes of the PI film are shown at different bonding temperatures. Samples were heated at 100°C for 1 h, at 150°C for 30 min in NMP-saturated condition and isothermally for 1 h at each bonding temperature. The characteristic peaks of PI appear at 1780 cm^{-1} (the asymmetric C=O stretching), 1380 cm^{-1} (C–N stretching), 1114 cm^{-1} (aromatic C–H in-plane bending) and 727 cm^{-1} (C=O bending) [28]. The distinct decrease of peak intensities are observed in Fig. 2, but there is less decrease in Fig. 3. In Fig. 2(D) PI films were severely degraded, and the cuprous oxide appears as a strong doublet at 655 and 610 cm^{-1}, but not strong in Fig. 3(D). The peak at 655 cm^{-1} corresponds to the longitudinal optical mode and the peak at 610 cm^{-1} is attributed to the transverse optical mode of the high-frequency phonon [29]. The differences of the cuprous oxide peak intensity between Figs. 2(C) and 3(C) indicate that PVI primer layer on copper suppresses both PI degradation and copper corrosion. Also, comparing Fig. 2(D) with 3(D), the extent of the peak decrease is more remarkable in the PI/Cu system than in the PI/PVI/Cu system.

Fig. 4 shows the lap shear strengths of PI/Cu and PI/primer/Cu systems. In all the cases, the lap shear strengths increase up to 350°C and then decrease. The PI/PVI/Cu system showed a lower value than the PI/Cu system at lower bonding temperatures (290 and 320°C). This is due to the weak bond formation between Cu and PI [5,13]. At higher bonding temperatures (350 and 380°C), the PI/PVI/Cu system showed higher lap strength value than the PI/Cu system. In the case of the PI/VTS-modified PVI/Cu system, higher lap strength was seen at all bonding temperatures. Especially at higher bonding temperatures, the PI/VTS-modified PVI/Cu systems showed large increase of adhesion strengths than the PI/PVI/Cu systems.

In order to study the effect of VTS-modified PVI on copper, R–A IR spectra were taken. Figs. 5 and 6 represent PI/VTS-modified PVI/Cu with a different mole ratio at 350 and 380°C, respectively. In Fig. 5 at 350°C, the characteristic

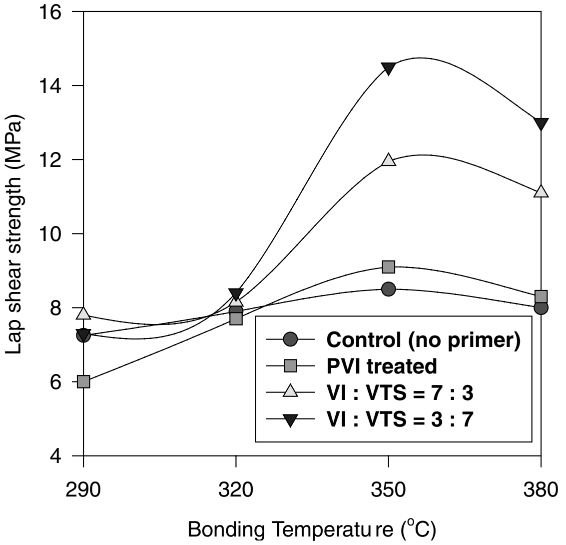


Fig. 4. The lap shear strength of PI/primers/Cu with different mole ratios as a function of the bonding temperature.

peaks of PI are observed in both spectra and the differences between the spectra at different primer composition are not very certain. However, in Fig. 6 at 380°C, the differences between the spectra were clearly appeared. A decrement of the PI peak intensities appeared more vividly in the spectrum of VTS-modified PVI, where the VI to VTS mole ratio was 7:3, rather than 3:7. Therefore, it can be concluded that VTS-modified PVIs with a higher VTS content are more efficient in suppressing both the PI degradation and the copper corrosion. This is due to the high thermal stability of the silane unit. Furthermore, VTS can form the polymeric film through the Si–O–Si bond formation which makes the silane unit thermally more stable [25]. In all spectra, the copper oxide peaks were not observed.

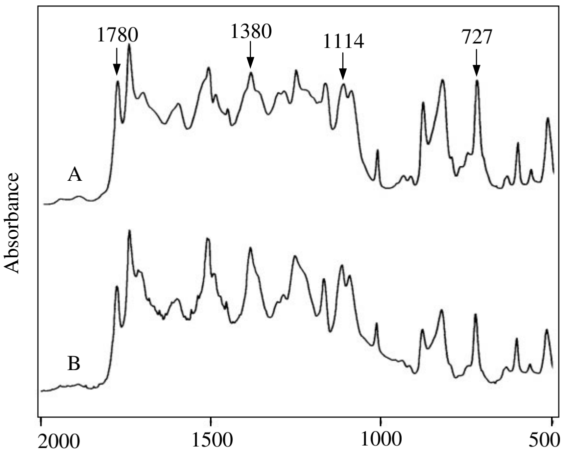


Fig. 5. R–A spectra of PI/VTS-modified PVI/Cu with different mole ratios heated at 350°C: (A) VI:VTS = 3:7; and (B) VI:VTS = 7:3.

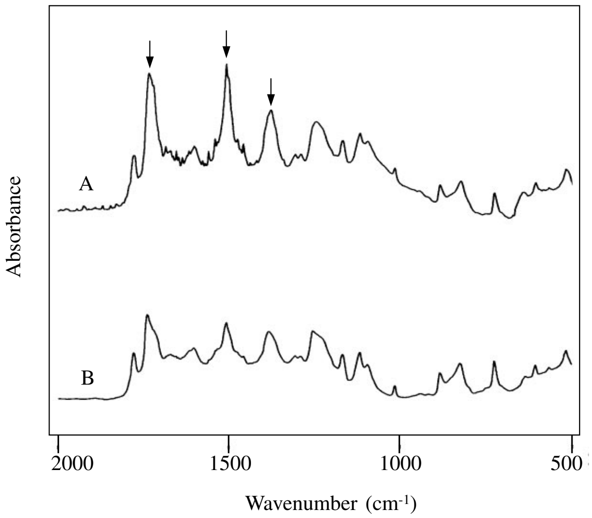


Fig. 6. R–A spectra of PI/VTS-modified PVI/Cu with different mole ratios heated at 380°C: (A) VI:VTS = 3:7; and (B) VI:VTS = 7:3.

Although VTS-modified PVI is effective for the suppression of both PI degradation and copper corrosion to promote the adhesion properties at higher bonding temperatures, very little increment was seen in the lap shear strength at lower bonding temperatures. Thus other factors influencing the lap shear strengths of the PI/primer/Cu could be considered. First it can be thought that it resulted from the mechanical properties of PI films caused by different isothermal bonding temperatures. Chen et al. [30] proposed that the cure schedule with 350°C may be the optimum choice in order to obtain a high thermomechanical PI film with high packing density and strong interchain interaction or crystal formation. Another factor is the compatibility between the primer with PI. To investigate the miscibility between the primers and PI, fractured surfaces of PI/primer blend films were observed by SEM. The fractured surfaces of PI and PI blended with primers are shown in Fig. 7. Pure PI shows a smooth fractured surface, and also there are no separated particles seen in the PI/PVI blend film. This indicates the phase separation between PVI and PI has not occurred. However, it appeared somehow different in the PI/VTS-modified PVI film. In Fig. 7(C), many small fibrils are seen at the mole ratio (VI/VTS) of 7:3. These fibrils are considered to be formed due to the improved mutual interaction between VTS-modified PVI and PI. When the VI to VTS mole ratio was 3:7, many small spheres are seen at the fractured surfaces of the blend system. This sphere could be formed by phase separation between the VTS-modified PVI and PI. Therefore, it can be concluded that the VI unit is more compatible than the VTS unit. Accordingly, it can be inferred that the interdiffusion of polymer chains between the primer and PI can be facilitated at bonding temperatures when increasing the VI content in the primer. It could form a stronger interface with PI. On the other hand, the compatibility of the primer with PI decreases with increasing VTS content in the primer and weakened the interfacial adhesion strength between PI on copper.

In order to determine the initial wettabilities of the PAA

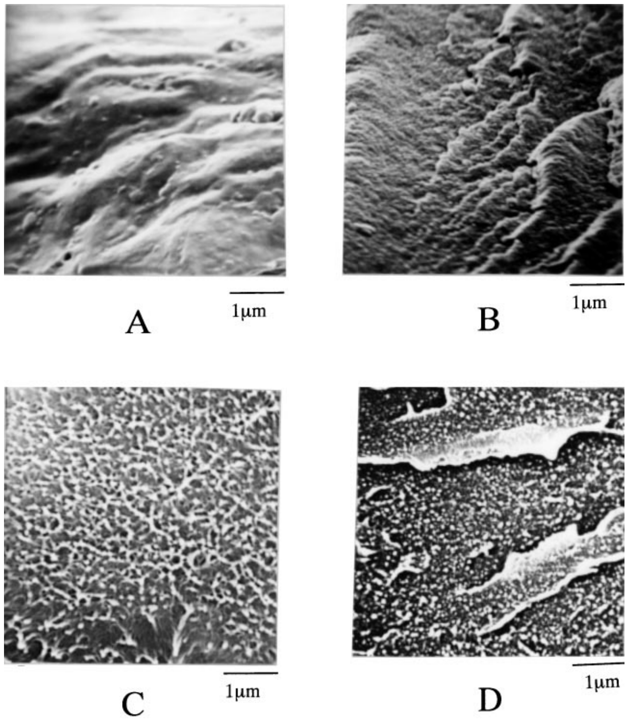


Fig. 7. SEMs of the fractured surfaces of pure PI and PI blended with the primers: (A) pure PI; (B) PVI; (C) VI:VTS = 7:3; and (D) VI:VTS = 3:7.

solution on various primers, the contact angle was measured by dropping the diluted PAA solutions onto copper surfaces coated with PVI or VTS-modified PVIs. The observed contact angles are represented in Table 2. As shown in the table, the contact angle of the PAA solution on PVI is very small. When the VTS content in the primer grows, the contact angle becomes larger in comparison with that on PVI. This implies that the PVI can form a good interface with the PAA solution easily at the initial stage of coating, whereas introduction of the VTS into the PVI has a negative effect on the formation of good interfaces between the primer and the PAA solution. This is in agreement with the above SEM results. As the VTS content in the primer increases, the compatibility of the primer with PI decreases. This could be the reason why the VTS-modified PVI-coated copper did not showed large adhesion promotion at lower bonding temperatures compared with the treated copper at higher bonding temperatures. At 290°C in Fig. 4, the lap shear strength was lower when the VI to VTS mole ratio was 3:7, rather than 7:3. This denotes that the poor compatibility of the primer with PI reduced the interfacial adhesion strength. However, the high thermal stability of the silane unit in the primer had a major effect on suppressing both the PI degradation and the copper corrosion, disregarding the poor compatibility of the primer with PI at higher bonding temperatures.

Table 2
The contact angles of PAA solution on primer-treated copper

Primer	Contact angle (°)
PVI	16
Poly(VI-*co*-VTS) (7:3)	35
Poly(VI-*co*-VTS) (3:7)	58

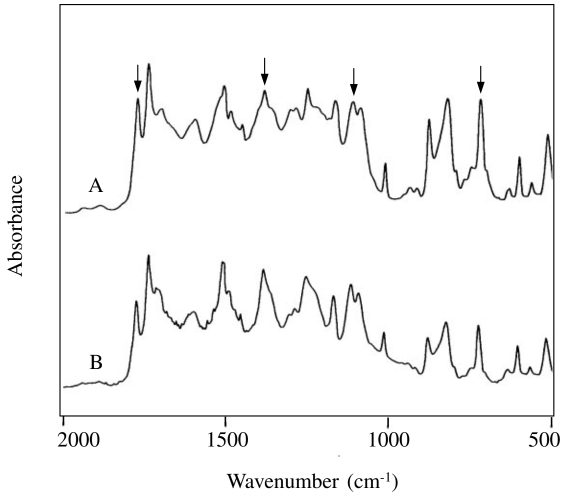


Fig. 8. R–A spectra of the lap sheared copper surfaces of the samples prepared at 350°C: (A) VI:VTS = 3:7; and (B) VI:VTS = 7:3.

Fig. 8 represents the R–A IR spectra of copper surfaces in PI/VTS-modified PVI/Cu systems at 350°C after the lap shear test. In both the cases of a different VI to VTS mole ratio, characteristic peaks of PI are seen. This indicates a cohesive failure in the PI layer, and it means that after the lap shear test a locus of failure exists in the PI layer (Fig. 9). This is as a result of good adhesion between the primers and PI.

From the above FT-IR, SEM analyses and contact angle measurements, it can be concluded that the adhesion promotion of PI on copper is attributed to the improved thermal property of the primer layer itself and the suppression of degradation of PI by the insertion of the primer layer. The adhesion promotion of PI/primers/Cu systems was significant at higher bonding temperatures, but not so large at lower bonding temperatures. These differences are attributed to the thermal stability of the primer and the compatibility of the primers with PI. PVI is compatible with PI but sensitive to thermal degradation. In the case of the PI/PVI/Cu system, the physical property of PVI is deteriorated during heat treatment due to its thermal degradation, and there is very little improvement in the lap shear strength. On the other hand, the introduction of VTS into the primer layer improves the thermal stability on the copper of the primer, but it decreases the compatibility of the primer with PI. However, the thermal stability of the VTS had a major effect on the adhesion promotion in spite of the poor compatibility of the primer with PI at higher bonding temperatures. Especially, the silane unit of the copolymer forms a thermally and mechanically stable siloxane network structure after heat treatment. Copper oxide formation and the migration of copper oxide into the PI layer was inhibited by the silane unit of the primer. The suppression of copper diffusion

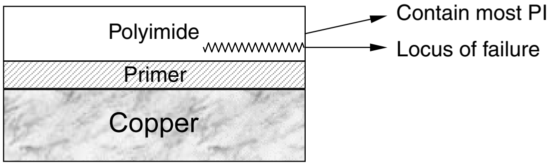


Fig. 9. Schematic diagram of the locus of failure in PI/primer/copper system.

prevented the PI from thermal degradation and improved the adhesion strength between the PI on copper.

4. Conclusions

To investigate the effects of different primer compositions of PI/PVI or VTS-modified PVI/Cu systems, the lap shear strengths of PI/PVI or VTS-modified PVI/Cu systems were measured at different bonding temperatures. FT-IR analysis, SEM and contact angle measurements were performed to study the interaction between the primers and PI. From these results, the following conclusions can be derived.

The primers between PI and copper improved the lap shear strengths of PI/PVI or VTS-modified PVI/Cu systems. The adhesion promotion of the PI on copper is attributed to the thermal property of the primers itself, as well as its efficiency in suppressing the degradation of PI. Especially at higher bonding temperatures, the primer with higher VTS content was very effective in the improvement of lap shear strengths due to its thermal stability. However, the lap shear strengths were not increased significantly owing to the poor compatibility between the primers with PI at lower bonding temperatures.

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