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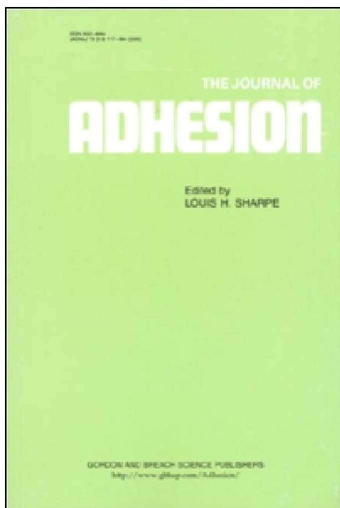

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Modified Imidazoles: Degradation Inhibitors and Adhesion Promoters for Polyimide Films on Copper Substrates

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Polyimide films on copper substrates that are exposed to elevated temperatures and an oxidizing environment will be subject to degradation. In order to halt this degradation without changing the properties of the system, a polymeric agent could be placed between the polyimide and the copper. This paper will investigate three such materials that will not only slow down the degradation of the polyimide and the oxidation of the copper, but will also improve adhesion within the system. Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS) will be used to investigate the polyimide/polymeric agent/copper system.

KEY WORDS silane modified polyvinylimidazole; silane modified polybenzimidazole; humidity resistance; Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS); chromium; oxidation.

1 INTRODUCTION

The interaction of polyamic acid (PAA) and polyimide with copper at elevated temperatures has been documented.[1] The result of this interaction is degradation of the polymer film and the oxidation of the copper substrate.[1] When polyimide is used as an insulator in a microchip, the degradation of the polymer will result in changes in characteristics of the film which will alter its insulating properties.[2,3] In order to maintain the integrity of the polyimide film, even at high temperatures above 200°C and in an oxidizing environment, a polymer agent that is placed between the polymer and the copper could be used.

The polymeric agents that are used in this study are silane-modified polyvinylimidazole (PVI) and polybenzimidazole (PBI). It was hoped that these polymeric agents would not only protect the polyimide from degradation and the copper from oxidation, but also improve the adhesion properties of the polyimide/copper interface. Anti-corrosion agents for copper, such as benzotriazole, benzium, indazole and imidazole have been reported.[4–22] These corrosion inhibitors can be classified as contact inhibitors, which means that they are applied beforehand to the substrate

surface.[23] The anti-corrosion mechanisms of these substances for copper substrates are, however, very poorly understood. It is believed that the complex formation between the copper and nitrogen on the imidazole ring will inhibit oxygen adsorption onto the copper surface.[24–27] The above molecules are quite small, and the inhibition properties at elevated temperatures are unsatisfactory due to the evaporation of ligands. Therefore, recent research has been focused on the use of polymers for corrosion inhibitors. Very little research, however, has been done involving polymeric inhibitors for copper, especially for use at high temperatures.

Eng and Ishida have introduced poly(N-vinylimidazole) and poly(4-vinylimidazole) as new polymeric anti-corrosion agents for copper at elevated temperatures.[4] PVI's were chosen for this use for the following reasons. PVI's have the imidazole ring as their pendent group which would lead to complex formation with the copper. Also, the polymers can easily form thin films of relatively higher ductility than small molecules on the copper surface. Finally, Eng and Ishida have found that oxidation of copper with a PVI film on it was suppressed even at 400°C due to the low volatility of the film.[4]

Jang and Ishida have improved on the aforementioned chemical system by incorporating a coupling agent, γ-methacryloxypropyltrimethoxysilane (γ-MPS), with the PVI to make a copolymer.[44] A weakness of PVI, and other imidazoles similar to it, is that they are sensitive to humidity.[45] The addition of a silane coupling agent will reduce the polymer's sensitivity to water. The γ-MPS will also improve the adhesion between the polymer and the copper, as will be seen from the present study.

In this paper, modified PVI and PBI will be used to protect the polyimide from degradation and the copper from oxidation. These films will be studied at elevated temperatures with Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS). Adhesion of the polymer films with the copper substrate will also be studied with a simple adhesion tape test, ASTM D 3359-83.

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2 EXPERIMENTAL

The synthesis procedure of the silane-modified PVI will be reported elsewhere, but the product was believed to be a complex mixture of the copolymer and some silane homopolymer. The mole ratio between vinylimidazole (VI) and γ-MPS was 2:1. Hydrolysis of the alkoxy groups of the silane was complete after one hour in a mixture of more than the stoichiometric amount of water at a pH of 3.5 and tetrahydrofuran (THF). The chemical structure of this copolymer is shown in Figure 1.

The PBI was mixed with (aminoethylaminomethyl)phenethyltrimethoxysilane (AAPS) and was used as a 1% solution in dimethylacetamide (DMAc). The mole ratio of the PBI and AAPS was 3:1. It should be noted that the PBI/AAPS system is a physical mixture of these two components rather than a copolymer. Hydrolysis of this solution was done as above with excess water. The chemical structures for the PBI and the AAPS are shown in Figure 2.

Copper plates were $2.5 \times 5.0 \times 0.2$ cm and were ASTM B 152, type ETP. The copper mirrors were mechanically polished with No. 5 chrome oxide and then ultra-

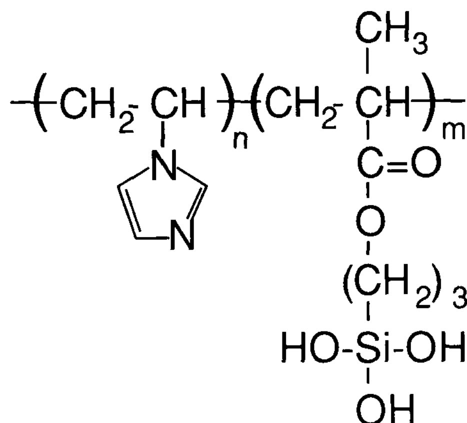

FIGURE 1 Molecular diagram of copolymer of vinylimidazole and γ-MPS.

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sonically cleaned with a bath of acetone, one bath of a 1% solution of HCl in distilled water, three baths of distilled water, and a final bath of acetone. The plates were then dried in a stream of nitrogen gas.

The modified PVI and PBI were solution cast on the copper mirrors with a microsyringe and dried in a solvent saturated environment. The film thickness was calculated based on the concentration of the solution, the quantity used, the density of the polymer and the area of the substrate. The thickness of the film was calculated to be 50 nm.

After drying, the films were further dried under a vacuum for 24 hours. The PBI was then exposed, under pure nitrogen gas, to a 400°C thermal treatment for 2 hours. The PVI was similarly treated in air for 30 minutes at 110°C. The thermal treatment was done to promote chelation of the imidazole groups in the polymer with the copper.

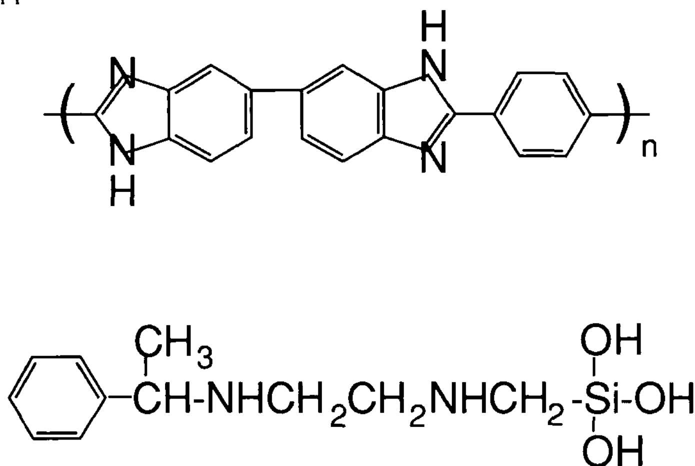

FIGURE 2 Molecular diagram of polybenzimidazole and the hydrolyzate of (aminoethylaminomethyl)-phenethyltrimethoxysilane.

Polyamic acid films were cast on top of the PVI or PBI films again using a microsyringe. The thickness of the polyamic acid was calculated to be 100 nm. After drying, the polyamic acid/imidazole films were exposed to various thermal treatments.

Polymer films were analyzed with Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS). The reflection-absorption attachment (Harrick-Scientific), along with a gold wire grid polarizer (Perkin-Elmer) were mounted in a Digilab FTS-14 Fourier transform infrared spectrometer. The spectrometer was equipped with a triglycine sulfate detector and was purged with dry air. The spectra were collected as the average of 200 scans at 4 cm^{-1} resolution and an angle of incidence of 75°. The spectra of the samples with the polymer films were subtracted from a reference spectrum of bare copper.

Adhesion studies were done according to ASTM D 3359-83. This test is used to assess the adhesion of a coating on a metallic substrate by applying and removing pressure sensitive tape over cuts made in the film. Although this procedure is sufficient for establishing an adequate level of adhesion of a coating to a substrate, it does not distinguish between higher levels of adhesion.

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3 RESULTS AND DISCUSSION

3.1 Modified PVI/Polyimide on Copper

A transmission spectrum of an unhydrolyzed, silane-modified PVI(I) is shown in Figure 3. The band at 3412 cm^{-1} is assigned to the O—H stretching mode from residual water in the molecule. The C—H stretching mode of the imidazole ring is observed at 3137 cm^{-1}. The bands in the 2970-2850 cm^{-1} region are due to the CH stretching of the polymer backbone. The free carbonyl band of γ-MPS appears at 1723 cm^{-1} and the band at 1300 cm^{-1} is associated with the ester functionality. The 845 cm^{-1} symmetric Si-OCH_3 stretching band is drastically reduced after hydrolysis of the γ-MPS. The hydrolysis will yield silanol groups (SiOH) which will absorb near 900 cm^{-1}. The appearance of this band ensures that hydrolysis has occurred and that the silanol groups are available for chemical reaction with the surface of the metal. As siloxane linkages are formed with the surface, the 900 cm^{-1} band will disappear and the splitting of the 1040 and 1115 cm^{-1} bands due to the siloxane group will become prominent.[48] When the modified PVI(I) is covered by a film of polyamic acid, the spectrum in Figure 4 is seen. The overriding features of the spectrum are that of a PAA as seen by the small imide bands at 1778, 1722 and 1168 cm^{-1}. The other imide bands are not yet resolvable, indicating that curing is slight.

Figure 5 shows the spectrum of heat treated modified PVI(I)/polyimide on copper after 2 hours at 250°C. A small amount of degradation is seen as evidenced by the appearance of the band at 2197 cm^{-1}, which has been assigned to a nitrile and is the first degradation product of the polyamic acid or of PVI(I).[1,4] There are also signs of oxidation of the copper as seen by the cuprous oxide band at 640 cm^{-1}. However, curing of the polyimide has continued as indicated by the increase in absorption of the 1778, 1726, 1375, 1169 and 727 cm^{-1} bands. At this point, the

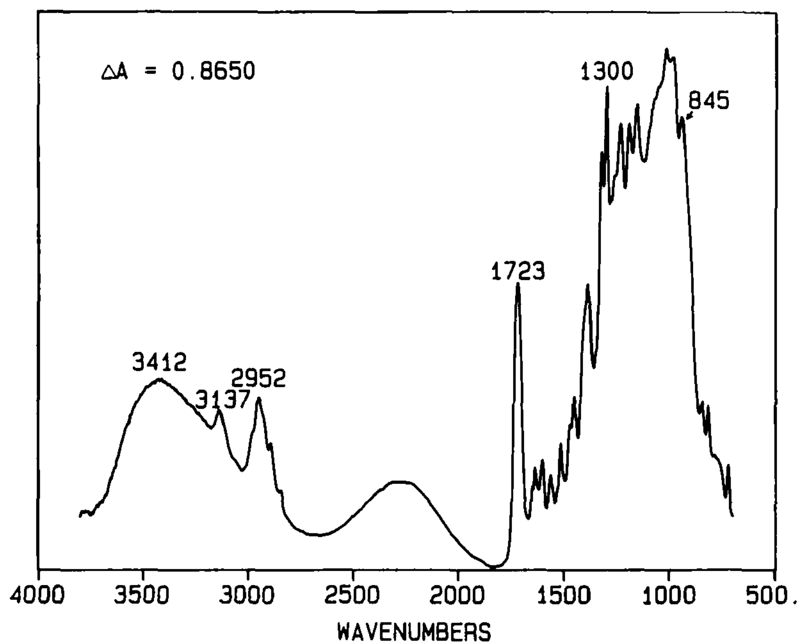

FIGURE 3 Transmission spectrum of the silane-modified PVI.

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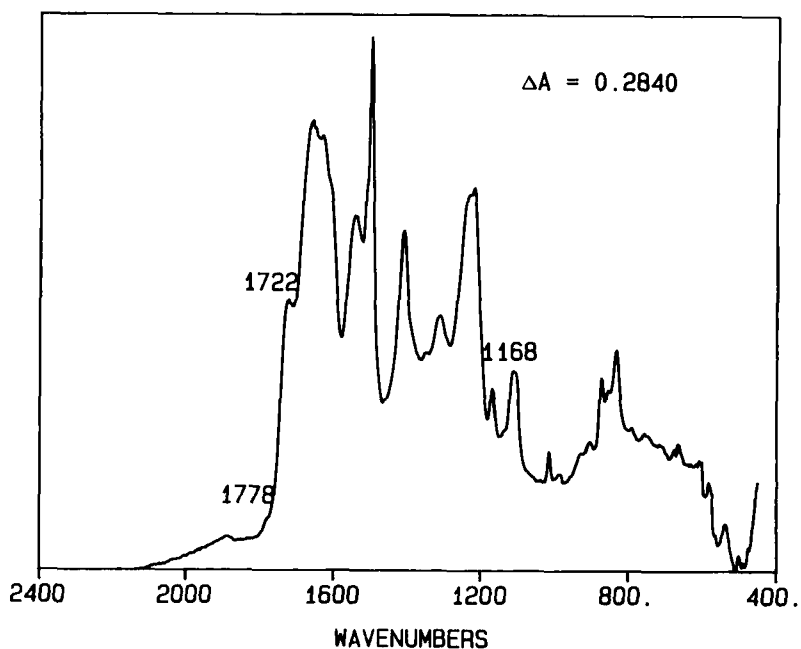

FIGURE 4 RAS spectrum of uncured, silane-modified PVI/polyimide coating on copper.

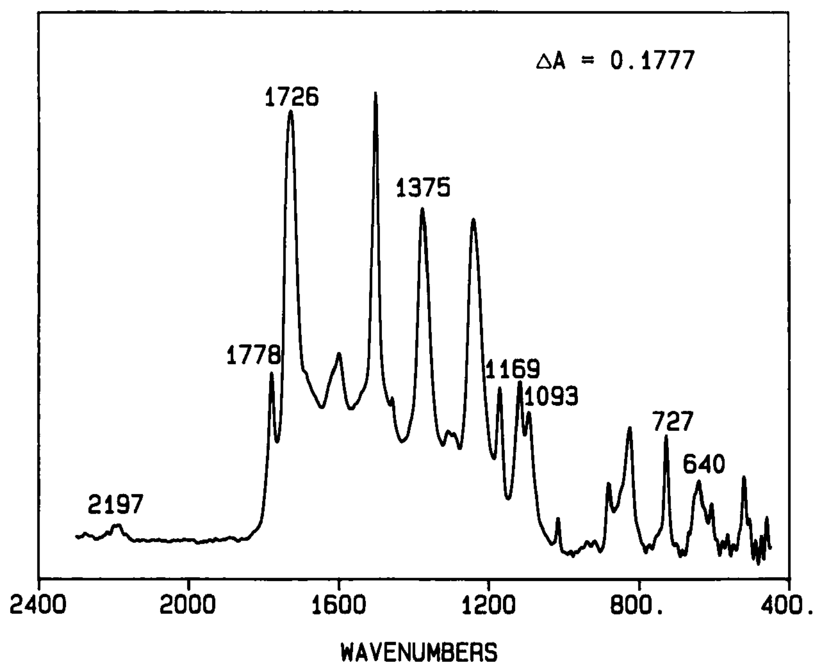

FIGURE 5 RAS spectrum of silane-modified PVI/polyimide coating on copper substrate, which is heat treated for 2 h at 250°C.

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modified PVI(I) is beginning to degrade; any degradation of the polyimide is slight.[49,53]

Jang and Ishida have found that modified PVI(I) will maintain its anticorrosion action above 350°C, even though the polymer will undergo structural rearrangement at lower temperatures.[44] This study also indicates local oxidation of the copper at temperatures as low as 250°C. It is felt that this is not due to the quality of the copolymer but, rather, to the quality of the film such as the existence of pinholes. The thinness of the films that are used in this study will allow defects in the film that will make it possible for the copper surface to oxidize locally. Another problem was the evaporation of water which left holes in the PVI(I) as the film dried. It was thought that if less water was used in the copolymer that perhaps the quality of the film would improve. The silane-modified PVI(I) was, therefore, used as partially hydrolyzed or unhydrolyzed. This did improve the quality of the film, but at the expense of the protection of the polyimide and the copper system (Figure 6).

As the degree of hydrolysis decreased, the degree of degradation increased. This occurred most likely because the silane moiety contained methoxy groups instead of silanol groups. Silanol groups are necessary for the reaction of the silane with the substrate surface. Their absence would prevent the silane from binding with the copper substrate, and therefore adhesion with the substrate would decrease. When the adhesion of the polymer with the substrate is poor, oxygen can enter the copper/polyimide interface and initiate the degradation reaction.

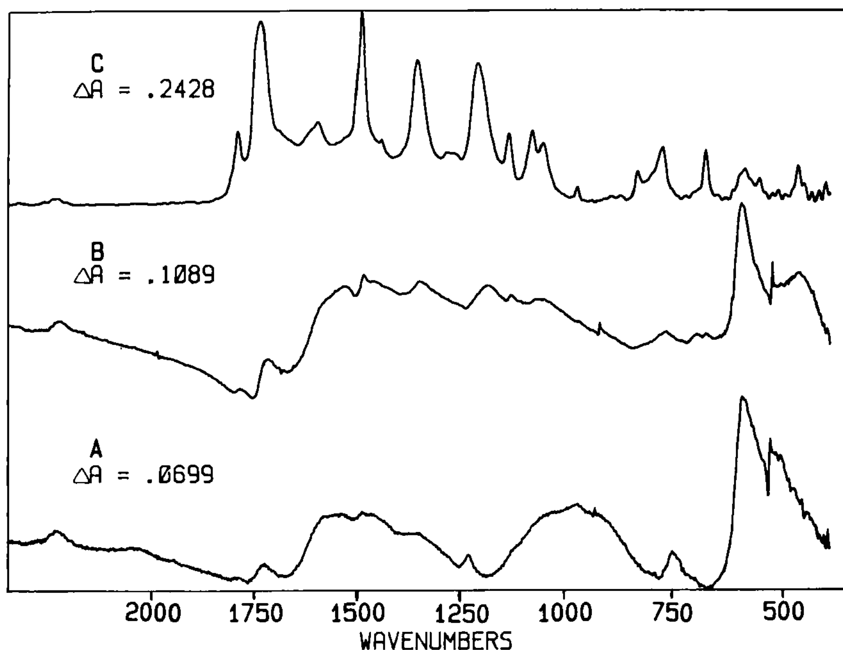

FIGURE 6 RAS spectra of silane-modified PVI/polyimide coating on copper substrate, which is heat treated for 2 h at 250°C: (A) unhydrolyzed, silane-modified PVI; (B) partially hydrolyzed, silane-modified PVI; and (C) completely hydrolyzed, silane-modified PVI.

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3.2 PBI/Polyimide on Copper

The spectrum of PBI is shown in Figure 7 A. This polymer will remain unchanged when heat treated below a temperature of 400°C. Therefore, in order to induce chelation of the PBI to the copper, high temperatures above 400°C were necessary.[54] When the polyamic acid was cast over the PBI, the spectrum in Figure 7 B was obtained. Contributions from both polymers make up this complex spectrum, as seen by the appearance of weak imide bands at 1718 and 1167 cm^{-1} and benzimidazole bands at 1541 and 1436 cm^{-1}. The benzimidazole bands, however, are quite weak, while the main features of the spectra are due to the slightly cured polyamic acid.

When the PBI/polyamic acid on copper system was exposed to 250°C for up to 34 hours, the spectra in Figure 8 were obtained. The results were similar to that seen with PVI(I) after being exposed to an elevated temperature for two hours (Figure 8 A). The band at 2222 cm^{-1}, which has been assigned to an α, β-unsaturated nitrile is the first degradation product to be seen.[4] Other changes in this spectrum indicate that curing of the polyamic acid is occurring (note imide bands at 1777, 1724, 1377, 1169 and 726 cm^{-1}). Feairheller *et al.* have studied the degradation of PBI at elevated temperatures.[54] They have cited the band near 700 cm^{-1}, which is due to a vibration of the 2-substituted benzimidazole, as a band that will indicate

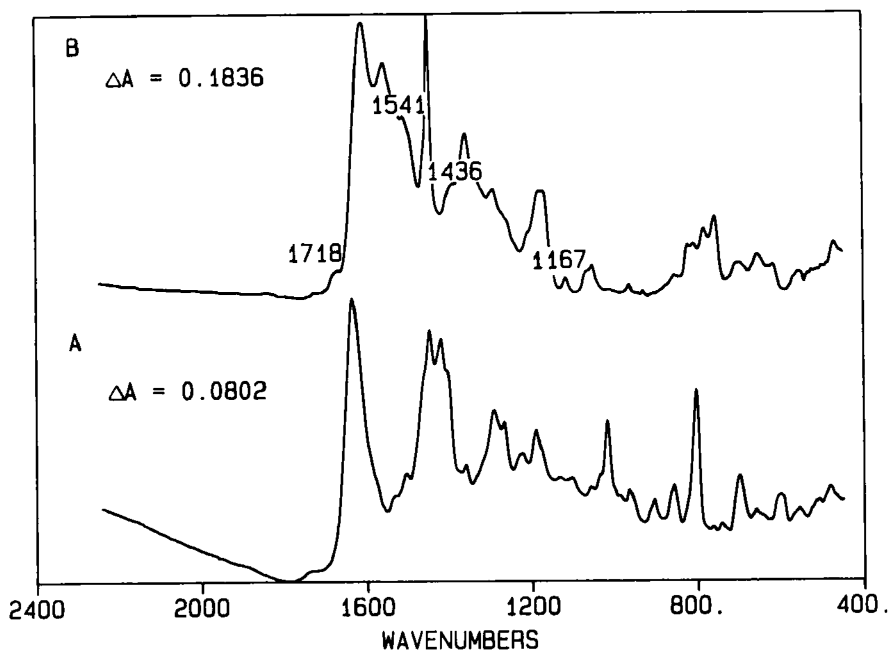

FIGURE 7 RAS spectra of: (A) PBI on copper; and (B) PBI/polyamic acid on copper.

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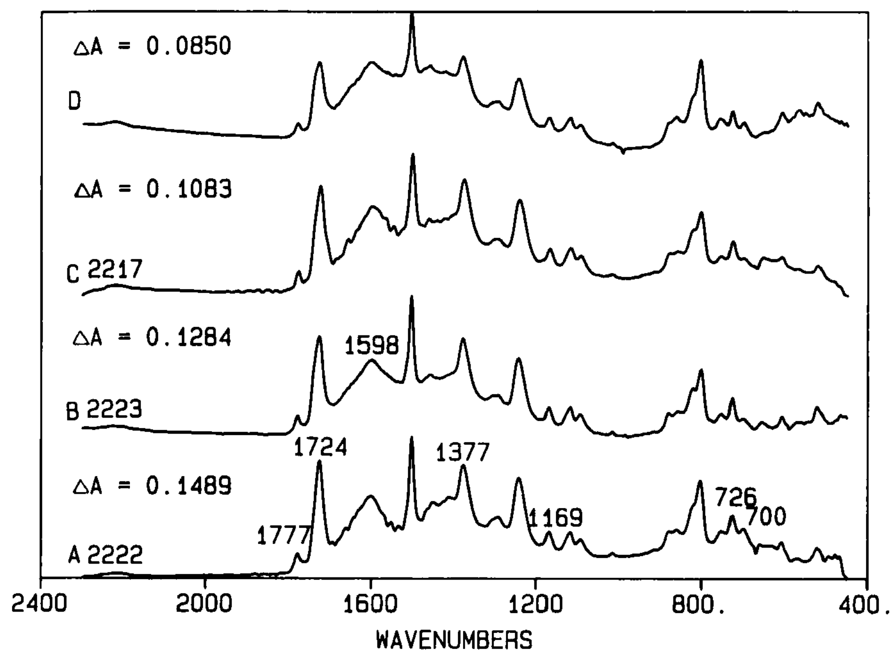

FIGURE 8 RAS spectra of PBI/polyimide coating on copper: heat treated at 250°C for (A) 2 h; (B) 4 h; (C) 8 h; and (D) 34 h.

the decomposition of the five-membered ring in the PBI. This band will, therefore, decrease in intensity with degradation; however, in this study, no decrease after 2 hours is seen. Also, no copper oxides were observed.

After 4 hours at 250°C, the nitrile band increases in intensity and further curing of the polyimide is seen by the increased imide bands described above (Figure 8 B). The band at 700 cm^{-1} does decrease, indicating that the benzimidazole ring is beginning to degrade. Along with this change is a general weakening of all the bands associated with PBI. It is questionable at this point if degradation of the polyimide is occurring. The band at 1598 cm^{-1} has been assigned to an aromatic ring structure indicative of degradation of the polyimide, but this band is associated with decreasing absorbance of the C=O bands which is not seen in this case. No cuprous oxide is seen up to this point.

The absorbance of the carbonyl bands and the other imide bands begin to decrease after 8 hours at 250°C, as seen in Figure 8 C. This is accompanied by a further decrease in the 700 cm^{-1} band and an increase in the band at 1598 cm^{-1}. A very interesting point to note is the nitrile band. This band also increases in intensity, which further illustrates the degradation of PBI and/or polyimide. However, this band has shifted from 2223 cm^{-1} to 2217 cm^{-1}, a shift of 6 wavenumbers. Eng *et al.* have found that this type of shift occurs when a π-coordination complex is formed between an α, β-unsaturated nitrile ligand and copper.[4] There is no indication of copper oxides being formed.

The above trend continues after 34 hours of heat treatment (Figure 8 D). Although slight degradation of the polyimide is noted as seen by the decreasing imide bands, the low degree of degradation is surprising. The polyimide is barely touched, and no sign of cuprous oxide is seen.

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3.3 Modified PBI/Polyimide on Copper

In order to improve humidity effects and adhesion, the PBI, like the PVI, was mixed with a silane coupling agent. Unlike copolymers of VI and γ-MPS, PBI was used as a physical mixture with AAPS. A spectrum of the PBI/AAPS system is shown in Figure 9. Although the molar ratio of PBI to AAPS was 3:1, the spectral differences between plain PBI and the PBI/AAPS system are quite evident. Most notable is the strong band at 1133 cm^{-1} which is known to be the stretching mode of the SiOC group in $R\text{-}Si(OR')_3$. Upon deconvolution, it can also be seen that this band contains the 1103, 1040 and 1014 cm^{-1} bands (Figure 10), the first two of which are typical of the siloxane group. Once again, it was hoped that a silane coupling agent would improve adhesion with the substrate and, therefore, also improve the protection of both the polyimide and the copper substrate.

Figure 11 shows the spectrum of the PBI/AAPS/polyimide system when it is uncured. The bands at 1134, 1103 and 1014 cm^{-1} can be seen here, although they are weaker in this spectrum than in Figure 9. The bands previously attributed to the PBI, 1541 and 1434 cm^{-1}, are also seen in this spectrum. Several other PBI features can also be seen. These are 949, 700 (benzene ring vibrations) and 756 cm^{-1} (hetrocyclic ring vibration). The other spectral features belong to polyamic acid that has partially cyclized into polyimide.

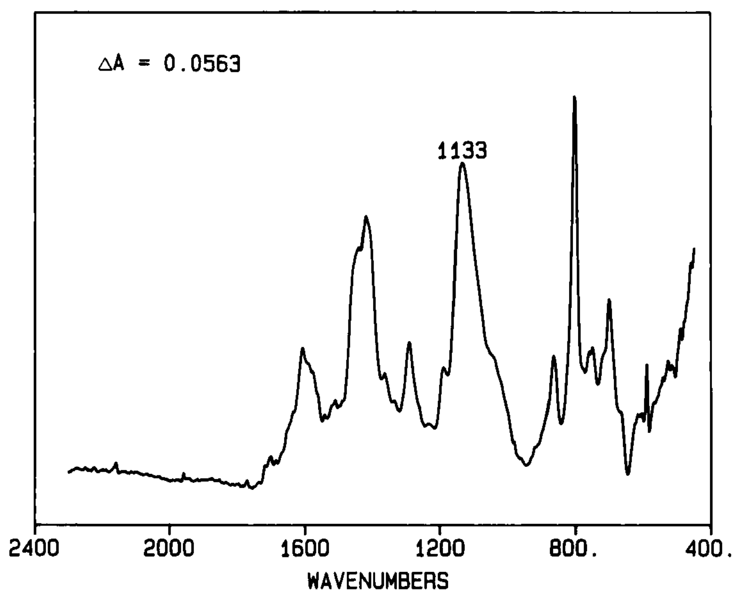

FIGURE 9 RAS spectrum of PBI/AAPS mixture on copper which is heat treated for 2 h at 400°C in nitrogen.

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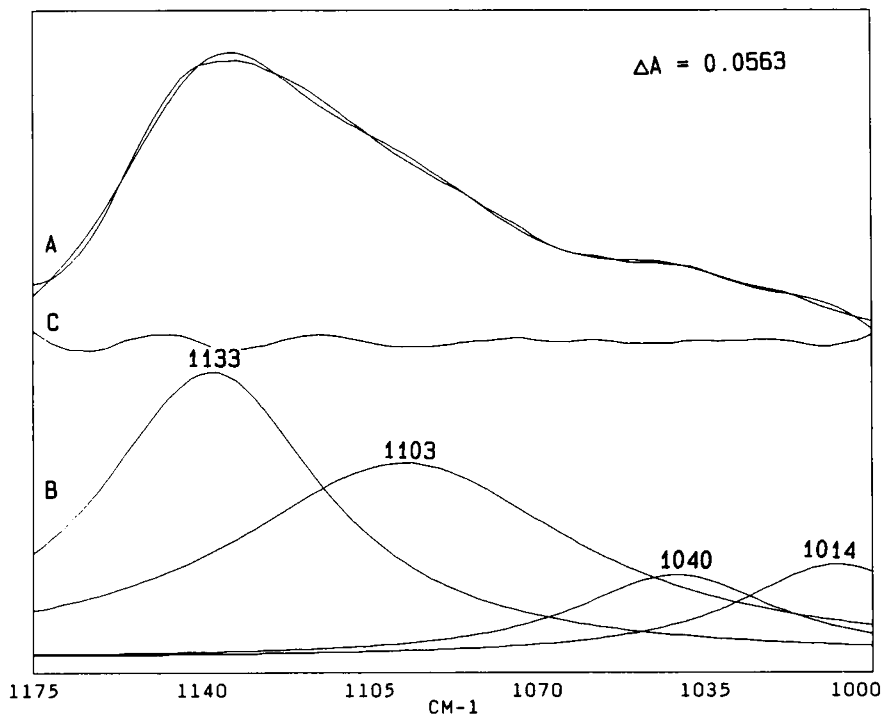

FIGURE 10 Deconvolution result of the 1175–989 cm^{-1} region: (A) original spectrum; (B) synthesized spectrum after deconvolution; and (C) difference spectrum (C=A—B).

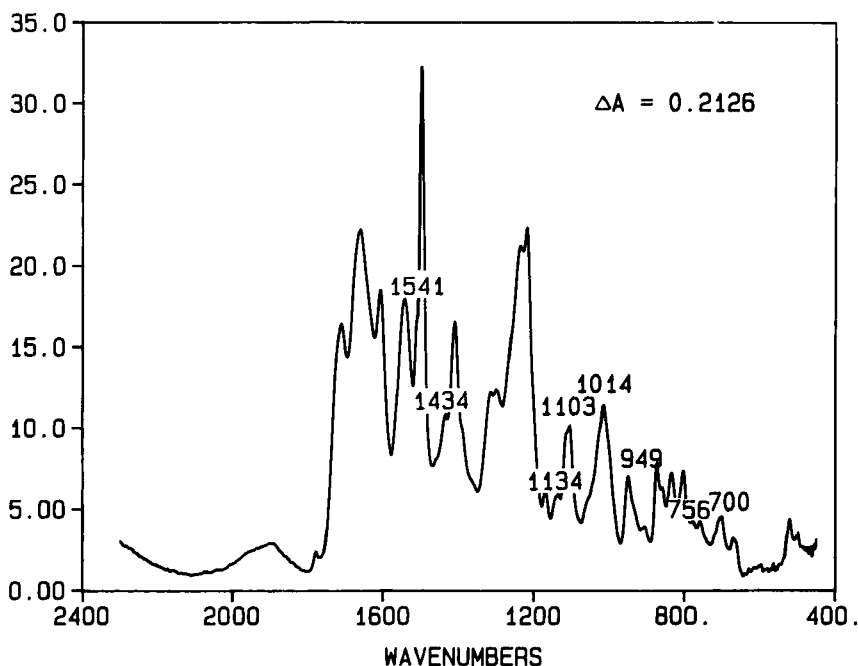

FIGURE 11 RAS spectrum of PBI/AAPS/polyamic acid on copper.

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The spectra in Figure 12 show a thermally treated PBI/AAPS/polyimide system on copper from 2 to 34 hours at 250°C. Both spectra 12 A and B, 2 and 4 hour-treatment, respectively, show a polyimide that is almost fully cured. The band at 2212 cm^{-1} is an α, β-unsaturated nitrile which, unlike the nitrile band seen with the PBI, does not undergo any shifts toward lower wavenumbers. There is a decrease in absorbance of the 700 cm^{-1} band, which as shown previously indicates cleavage of the benzimidazole ring. This is accompanied by a decrease in other PBI structures such as the bands at 1438, 949 and 756 cm^{-1}.

Degradation of the silane group is not seen until a thermal treatment of 34 hours at 250°C is done, as seen in Figure 12 C. The broad band around 1169 cm^{-1} is most likely due to the degraded silane, although at this time this is speculative. Other features of the spectra indicate degradation of the polyimide: a decrease in all imide bands and the appearance of the fused aromatic ring at 1594 cm^{-1}. There is also a broad band centered at 620 cm^{-1} that, when deconvolved, shows a band at 650 cm^{-1} that can be assigned to cuprous oxide.

On the whole, degradation after 34 hours is more severe with the AAPS mixed with the PBI that with just the PBI alone. This is most likely due to the loss of adhesion caused by the degradation of the silane, which was also seen with the PVI(I). Prior to 34 hours, the PBI/AAPS system allowed a further degree of curing than the PBI alone. There is, therefore, a trade off with these systems. PBI/AAPS is better for the short term curing treatment of polyimide since the silane does not undergo severe degradation during this period, while the PBI alone is better for the long term thermal treatment of the system.

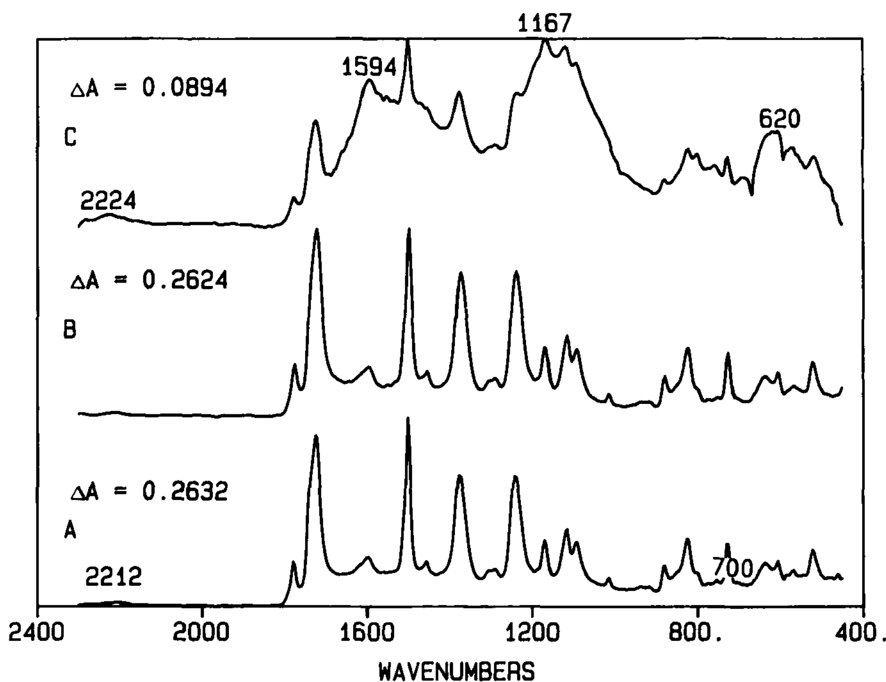

FIGURE 12 RAS spectrum of PBI/AAPS/polyimide which is heat treated at 250°C for: (A) 2 h; (B) 4 h; and (C) 34 h.

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3.4 ASTM Adhesion Tests

Discussion up to this point has focused on the degradation of polyamic acid and polyimide and on the improvement of the thermal stability of polyimide on copper. From a mechanophysical point of view, the adhesion of the polymer insulator to the substrate is of utmost importance. If multilevel coatings are to maintain their integrity through not only processing, but also through their useful lifetime, adhesion between the layers must remain intact.[2,3] To this end, adhesion tests were performed on all the systems that have been studied in this paper: polyamic acid and polyimide on copper and chromium, modified PVI(I)/polyimide on copper, and PBI/polyimide and PBI/AAPS/polyimide on copper. Chromium was used as reference.

When polyamic acid is cast on copper and exposed to a thermal treatment of 250°C for 2 hours and then to a humidity treatment for more than 96 hours at 80°C at a relative humidity of 100%, the results of the adhesion test can be graphed as percent film removed *versus* treatment conditions, as seen in Figure 13 for three samples at each data point. Adhesion increased drastically after the first thermal treatment. Hahn *et al.* have shown that polyimide easily absorbs and desorbs water.[55] When the polymer absorbs water, the reduction of adhesion results as seen in the figure.

The same trend is seen with polyamic acid cast on chromium which is evaporated on copper (see Table I), but to a lesser degree. When the polyamic acid is cured,

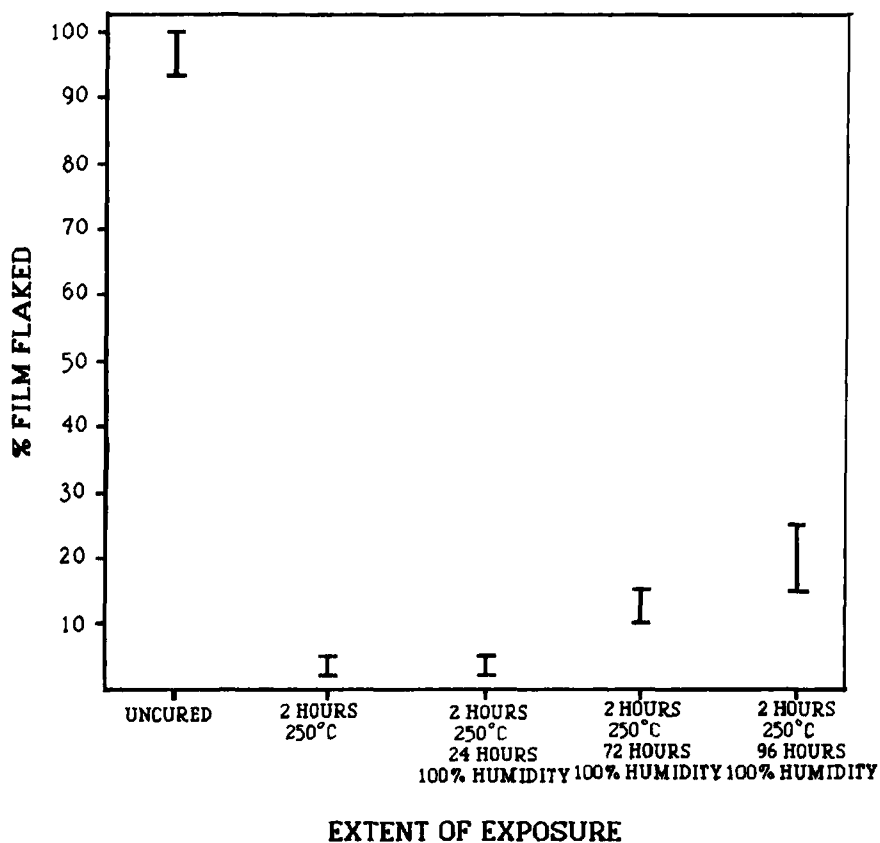

FIGURE 13 Change in percent film flaked *versus* extent of exposure to humid environment for ASTM tape test.

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TABLE I
ASTM adhesion test results (percent of coating removed in ASTM tape test) for polyimide films cured on various surface treatments on copper substrate

Surface treatment on Cu	Control (PI coating on treated surface)	Tested at 80°C at 100% relative humidity				
Chromium	Cured for 2 h at 250°C	24 h	48 h	72 h	96 h	—
	0%	<5%	<5%	<5%	5%	—
Modified PVI	Cured for 2 h at 250°C	24 h	48 h	—	—	144 h
	0%	0%	0%	—	—	0%
PBI	Cured for 2 h at 400°C in N_2	24 h	48 h	72 h	—	—
	0%	14%	25%	25%	—	—
PBI/AAPS	Cured for 2 h at 400°C in N_2	24 h	48 h	72 h	—	144 h
	0%	<5%	<5%	5%	—	5%

none of the polymer can be removed, and after the humidity treatment for 96 hours, only 5% of the film is flaked from the chromium. This is as expected, since all previous studies have indicated that adhesion of polyimide to chromium is approximately 6 times better than for polyimide to copper.[56]

The polymeric agents used to protect the polyimide from degradation, PVI(I) and PBI, were also used in adhesion tests. The modified PVI(I) showed especially good results. After 2 hours at 250°C, 0% of the film was flaked. Even after 144 hours at 100% humidity at 80°C, none of the film was lost.

The results with the PBI and PBI/AAPS mixture were not as quite as favorable. When the PBI was used alone, up to 25% of the film was lost after 48 hours in a 100% humidity environment, with no further loss being seen up to 96 hours. When the silane was added, adhesion improved substantially, as expected, but still approximately 5% of the film was flaked after 72 hours at 80°C and 100% humidity. These results tend to agree with the findings seen using infrared analysis: the PBI/AAPS performs very well in the short term, but in the long term, modified PVI(I) is more useful for improvement of both degradation and adhesion.

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4 CONCLUSIONS

Previous tests have indicated that polyimide cannot be used alone on copper at elevated temperatures in an oxidizing environment. If the elimination of the chromium layer is desired, something must be used to protect the polyimide from degradation and the copper from oxidation. This study has suggested two viable options for the replacement of the chromium layer.

Silane-modified PVI(I) has shown itself to be a good polymeric agent for protection of the polyimide from oxidation at elevated temperatures and for adhesion promotion. PVI(I) also has the distinct advantage of requiring a common solvent such as THF. Since THF is also volatile, films can be made quickly and easily.

PBI, on the other hand, requires the use of a solvent like DMAc, which is known to be dangerous to human health and therefore demands that stringent health measures be followed. A very high boiling point solvent will also require longer periods of time for film casting.

Comparison of PBI alone and the PBI/AAPS mixture shows that PBI is better for the long term protection of the polyimide, while the PBI/AAPS mixture is better for the short term curing of the polymer. Adhesion is greatly improved by the addition of the silane coupling agent.

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