

Interaction of Polyamic Acids and Polyamic Esters with Copper and Substituted Polysilsesquioxane Copolymers

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SYNOPSIS

The interactions of biphenyldianhydride-*p*-phenylenediamine (BPDA-PDA) polyamic acid and ester polymers with copper and copper-treated surfaces containing polysilsesquioxanes formed from 3-aminopropyltriethoxysilane (APS) (or copolymers of APS and phenyltriethoxysilane) were compared by grazing-incidence infrared spectroscopy. This investigation of a flexible dianhydride-stiff diamine copolymer compliments earlier work using the stiff dianhydride-flexible diamine polyamic acid and ester of pyromellitic dianhydride-oxydianiline (PMDA-ODA). Results support earlier findings that amic acids form thermally labile salts on copper but esters do not. Further, while APS forms a copper-interactive film that insulates amic acid/metal interaction, APS-phenylsilsesquioxane copolymers create an interfacial region interactive with both copper and overlying polyamic acid.

INTRODUCTION

The interactions of polyamic acids and esters with metals and aminopropylsilane adhesion promoter interfaces play a significant role in the reliability of laminate composites encountered in some VLSIC devices. The chemistry of these interfaces has been studied to better address concerns of polymer-substrate bonding and thermal stability of near-surface regions.¹⁻³

Recently, it was reported that pyromellitic dianhydride-oxydianiline (PMDA-ODA)-derived polyamic acids reacted directly with copper or its oxide to form an amic acid salt and that this salt decomposed under conditions typical of thermal imidization ($> 300^{\circ}\text{C}$), destroying the polymer.^{4,5} It was further observed that the amino group of 3-aminopropyltriethoxysilane (APS) adhesion promoter solutions appeared to coordinate on the copper surface, forming a protective silsesquioxane polymeric layer. This layer was found to inhibit the interaction of amic acid with copper and permit imidization during the normal thermal-cure sequence.⁶ Amic

ethyl esters (PAEE) did not appear to attack copper below 400°C .

The present study determines the interaction of a second polyamic acid (and ethyl ester) with copper, and the silsesquioxane polymers formed on copper by APS and a copolymer mixture of APS and phenyltriethoxysilane (1 : 1).

The polyimide precursor used in this study is a biphenyldianhydride - *p* - phenylenediamine (BPDA-PDA) polyamic acid (or ester) that differs significantly from the earlier PMDA-ODA system in that the new polyamic acid contains a more flexible dianhydride and a stiff diamine, whereas PMDA-ODA contains a stiff dianhydride and a flexible diamine.⁷ Further, where previous studies were run on only APS sesquioxanes, the current study adds a noninteracting phenyl group as part of the adhesion promoter. This group inhibits direct surface interaction by substituting insulating units between surface-active amines in a copolymer of mixed functionality.

EXPERIMENTAL

The method, using grazing-incidence Fourier transform infrared spectroscopy on copper layers vapor-deposited on silicon wafers, has been described.^{5,6}

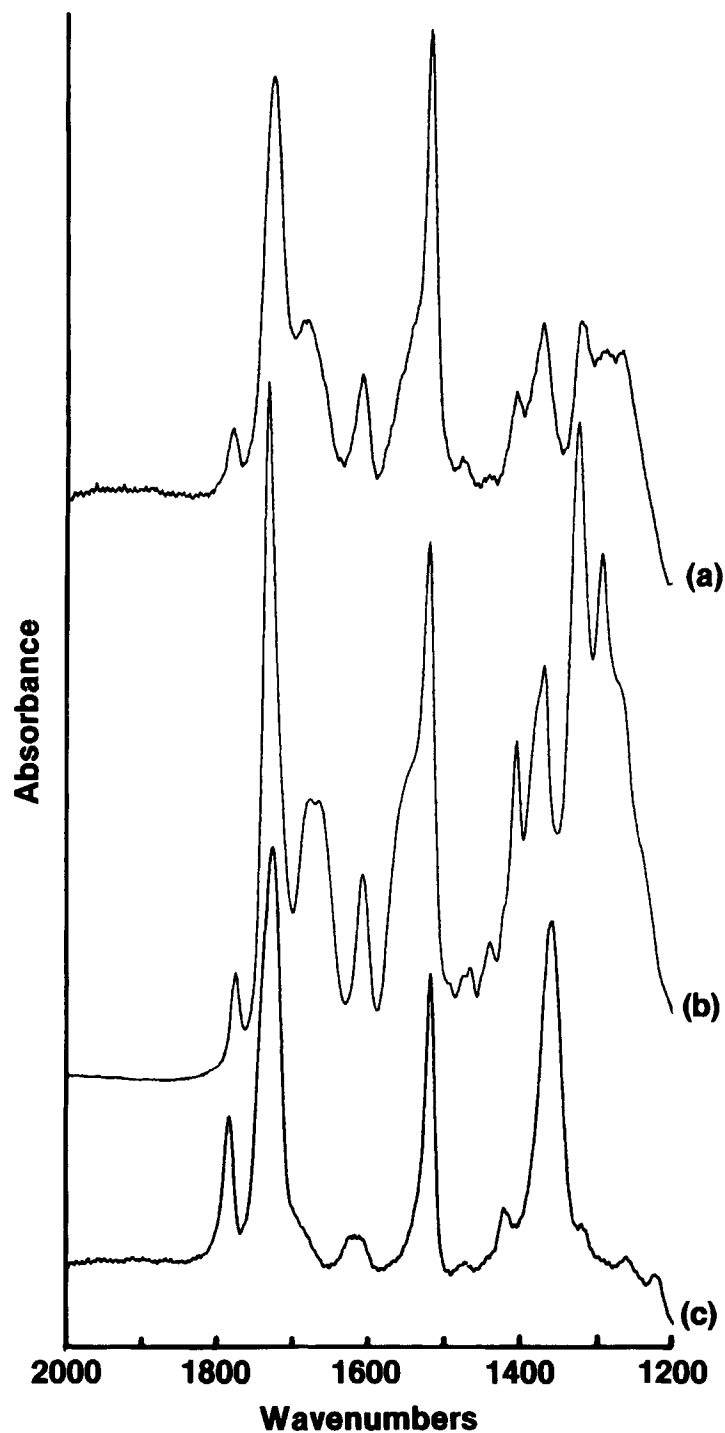


Figure 1 Infrared spectrum of BPDA-PDA ester (a) on silicon (transmission) and (b) on copper (grazing-angle reflection); thick film ($\sim 1000 \text{ \AA}$). (c) Infrared spectrum of BPDA-PDA ester on silicon, heated to 300°C .

Polymers were spin-applied from solutions of about 2% solids in NMP using speeds of about 4000 rpm. In some cases, the films were dipped in DI water to remove NMP from the film. (This procedure seemed to rapidly produce amic acid copper salt.)

RESULTS AND DISCUSSION

Reference infrared spectra of thick, water-washed BPDA-PDA ester films on silicon (transmittance) and on copper (reflectance) appear in Figure 1 (a)

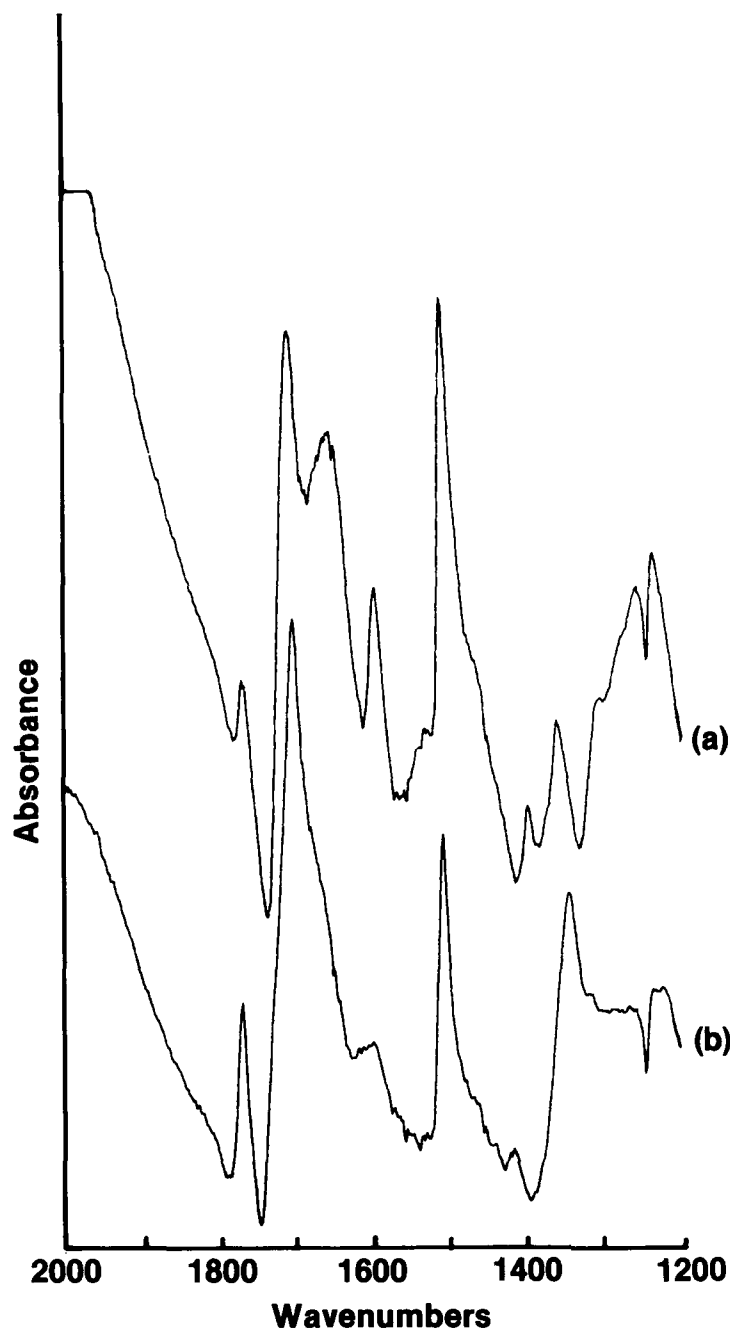


Figure 2 Infrared spectrum (GI) of BPDA-PDA ester on copper (a) 200°C and (b) 300°C.

and (b). Amic ester is apparent at 1725 cm^{-1} , as well as amide carbonyl at 1680 cm^{-1} ; aromatic ring absorptions appear at 1605 and 1515 cm^{-1} .

When sequentially heated on silicon, a thin film of the ester is unreactive to 200°C , but imidizes when heated to 300°C [Fig. 1(c)]. Similar results occur with thicker films on copper (Fig. 2).

Surface orientation of a thin film on copper is such that the BPDA-PDA ester does not display a

1515 cm^{-1} absorption but reveals only strong ester and amide carbonyl (Fig. 3). This observation is consistent with ordering of the BPDA segment so that ester and amide carbonyl groups are largely perpendicular to the copper surface and that the PDA segment is more or less parallel to the surface (Fig. 4).⁸⁻¹⁰

The imidized film displays a significant imide carbonyl at 1725 and 1780 cm^{-1} ; however, the related

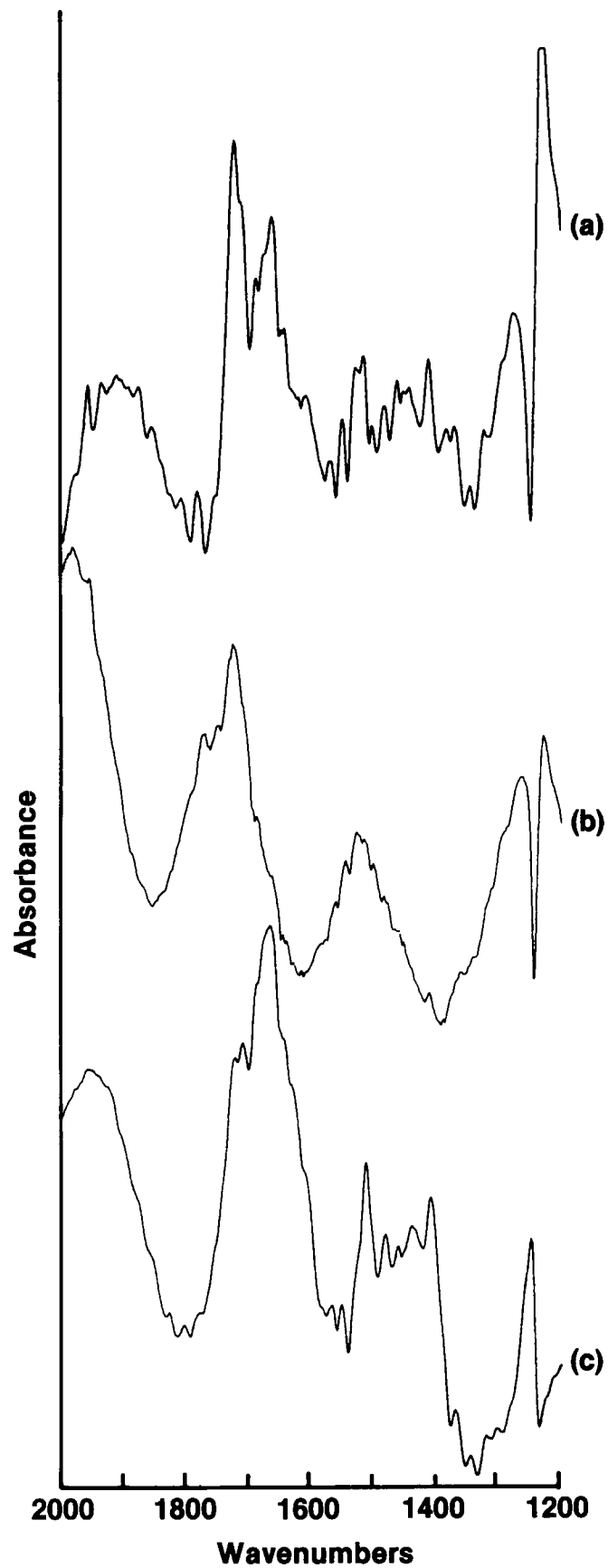


Figure 3 Thin BPDA-PDA ester on copper (a) unheated and (b) heated to 250°C. (c) BPDA-PDA amic acid on copper.

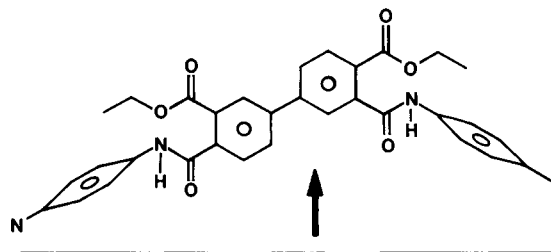


Figure 4 Probable ordering of polymer groups on copper.

N-C-O absorption at 1365 cm^{-1} is relatively weaker than in transmitted films. Orientation of the imide carbonyl in the surface region necessarily fixes the N-C-O orientation so that the dipole vector of both groups cannot be in the same (perpendicular) plane. The formation of an imidized film reveals that interactions between polymer and the copper surface are nondestructive, so that salt formation and related polymer degradation are minimal.

On copper, the BPDA-PDA acid is similar to PMDA-ODA (Fig. 6).⁵ Here, acid salt formation predominates; however, a significant acid carbonyl is displayed above 1700 cm^{-1} , probably arising from the acid groups on the second biphenyl ring (that

are unattached to the surface) (Fig. 5). While the amic acid thermally imidizes on silicon (Fig. 6), metal interactions alter the surface chemistry. Here, orientation of the acid species seems academic, since heating to approximately 200°C alters the polymer to such a significant extent that spectral identification of functional groups is lost as the polymer degrades.

Washing the thin amic acid film with water (to remove residual *N*-methylpyrrolidinone solvent from the film) renders the polymer more susceptible to thermal degradation, presumably by oxidation and ionization of surface copper by water. This washing and alteration changes the preferred conformation of amide and diamine aromatic rings, enhancing the 1605 and 1515 cm^{-1} absorptions [Fig. 6(c)]. The resulting configuration appears to order the carboxylates in the surface plane, with amine rings more perpendicular to the metal plane.

Application of a 2.0% APS solution, formulated in methanol/water, alters the chemistry of the copper surface.⁶ When heated to 200°C in nitrogen, a spun film creates a polysilsesquioxane coating that may coordinate to the copper through the amino-propyl group. In a similar fashion, a polymer composition formulated with a 1 : 1 ratio of APS and

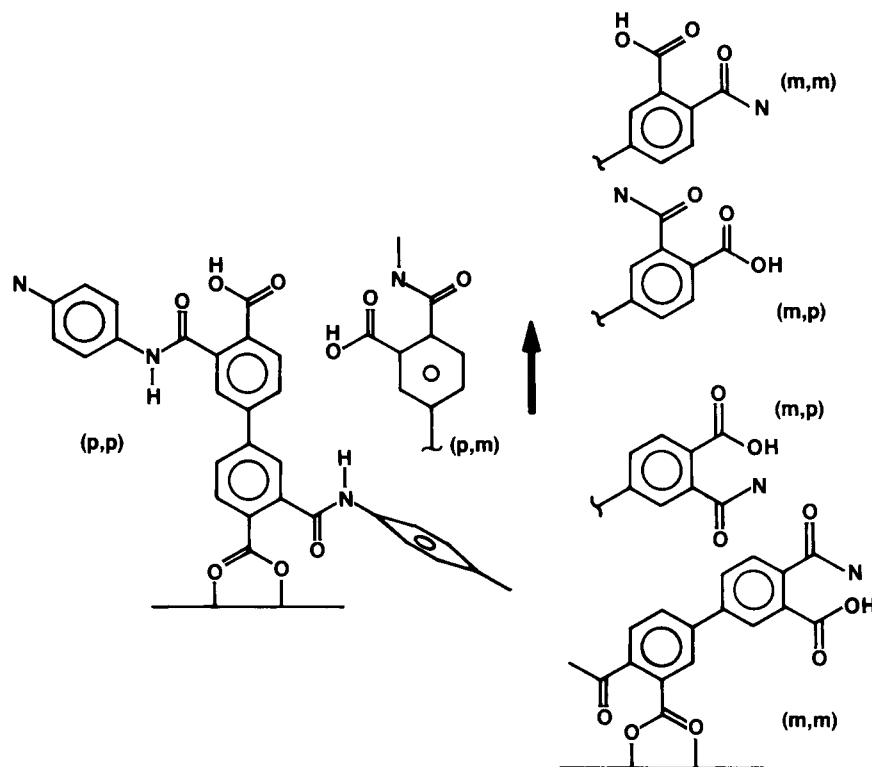


Figure 5 Probable ordering of polyamic acid on copper.

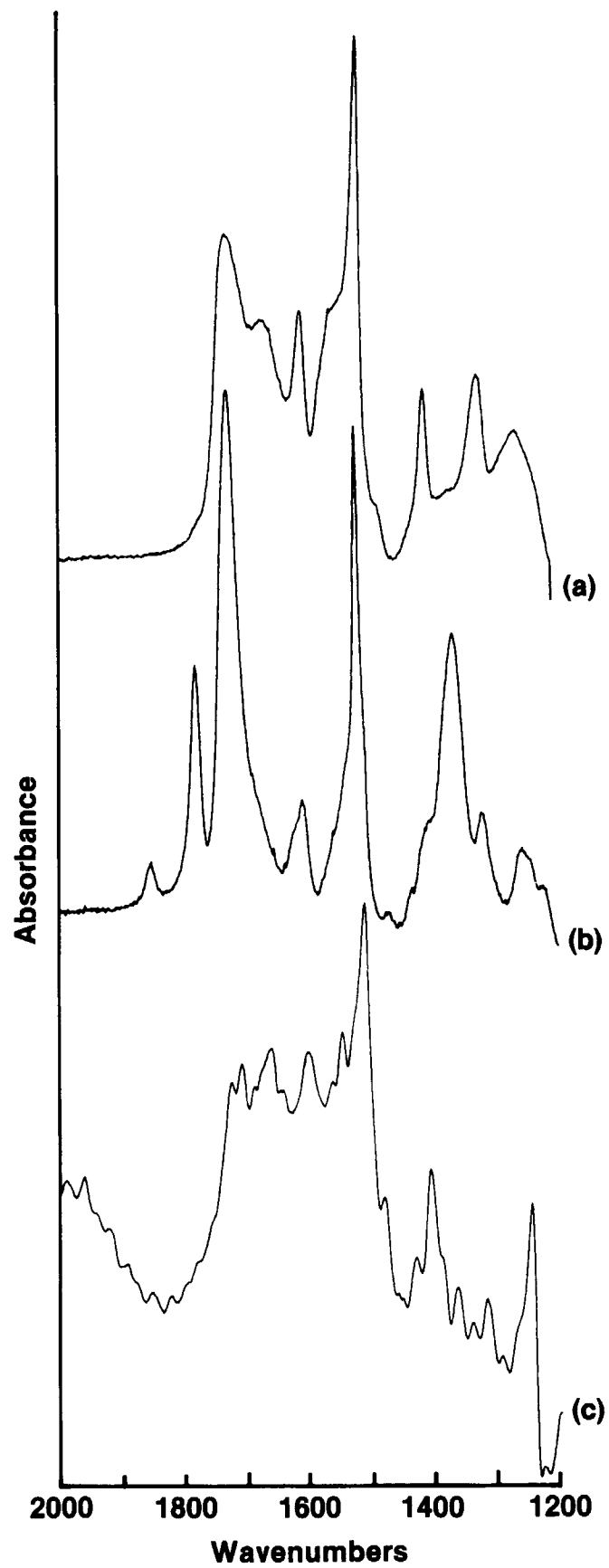


Figure 6 Thick BPDA-PDA amic acid on silicon (transmission) (a) unheated and (b) heated to 200°C. (c) Water-washed BPDA-PDA amic acid thin film on copper.

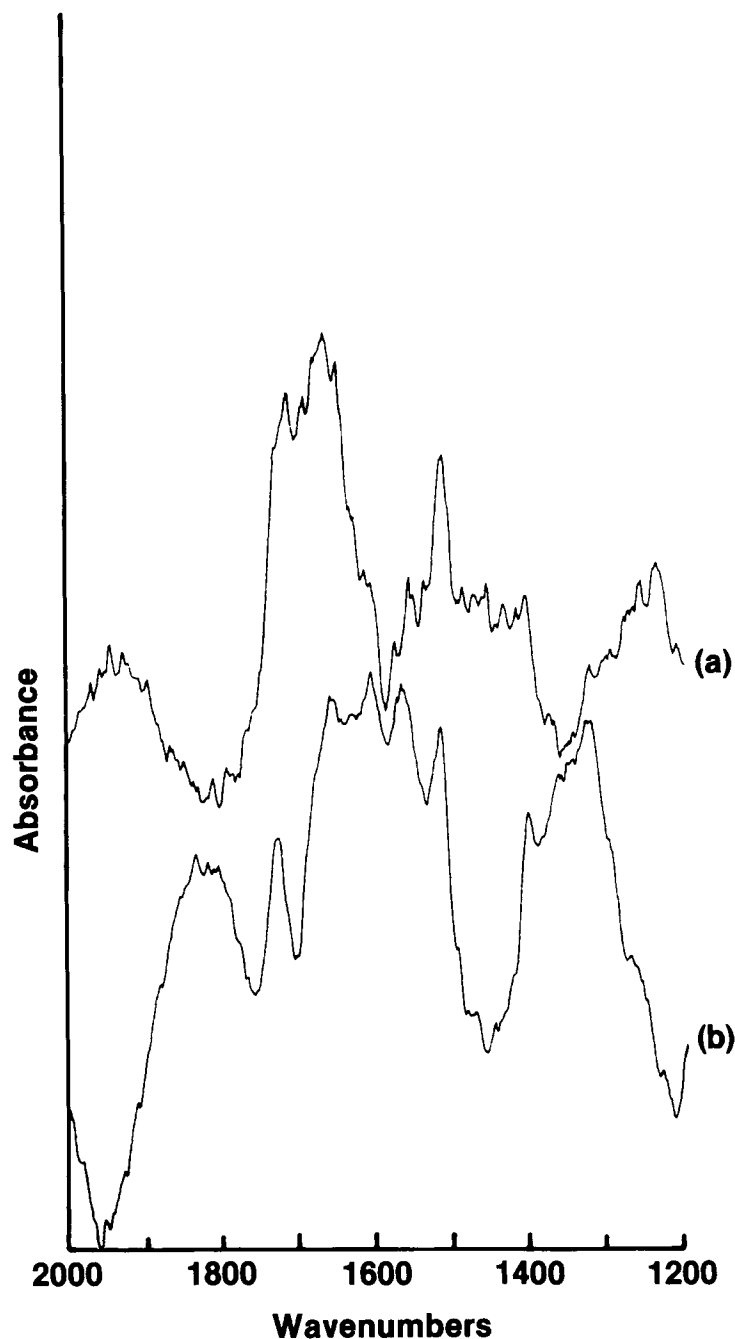


Figure 7 (a) BPDA-PDA amic acid on baked APS film over copper; (b) BPDA-PDA amic acid on phenyl-APS copolymer over copper.

phenyltriethoxysilane produces a copper-interactive polysilsesquioxane coating that seems to passivate the copper surface.

Application of BPDA-PDA (amic acid) over copper surfaces that had been treated with 2% solutions of APS or phenyl-APS mixtures (baked at 200°C) resulted in dramatically different interactions.

Whereas films on APS [Fig. 7(a)] revealed acid (1710 cm^{-1}), amide (1665 cm^{-1}), and aromatic ring (1510 cm^{-1}), material deposited on the phenyl-APS copolymer (PH-APS) revealed acid (1725 cm^{-1}), amide (1655 cm^{-1}), amine/aromatic ring (1600 cm^{-1}), carboxylate salt (1560 cm^{-1}), and aromatic ring (1515 cm^{-1}) absorptions [Fig. 7(b)]. These observations are evidence for an amine-inhibited

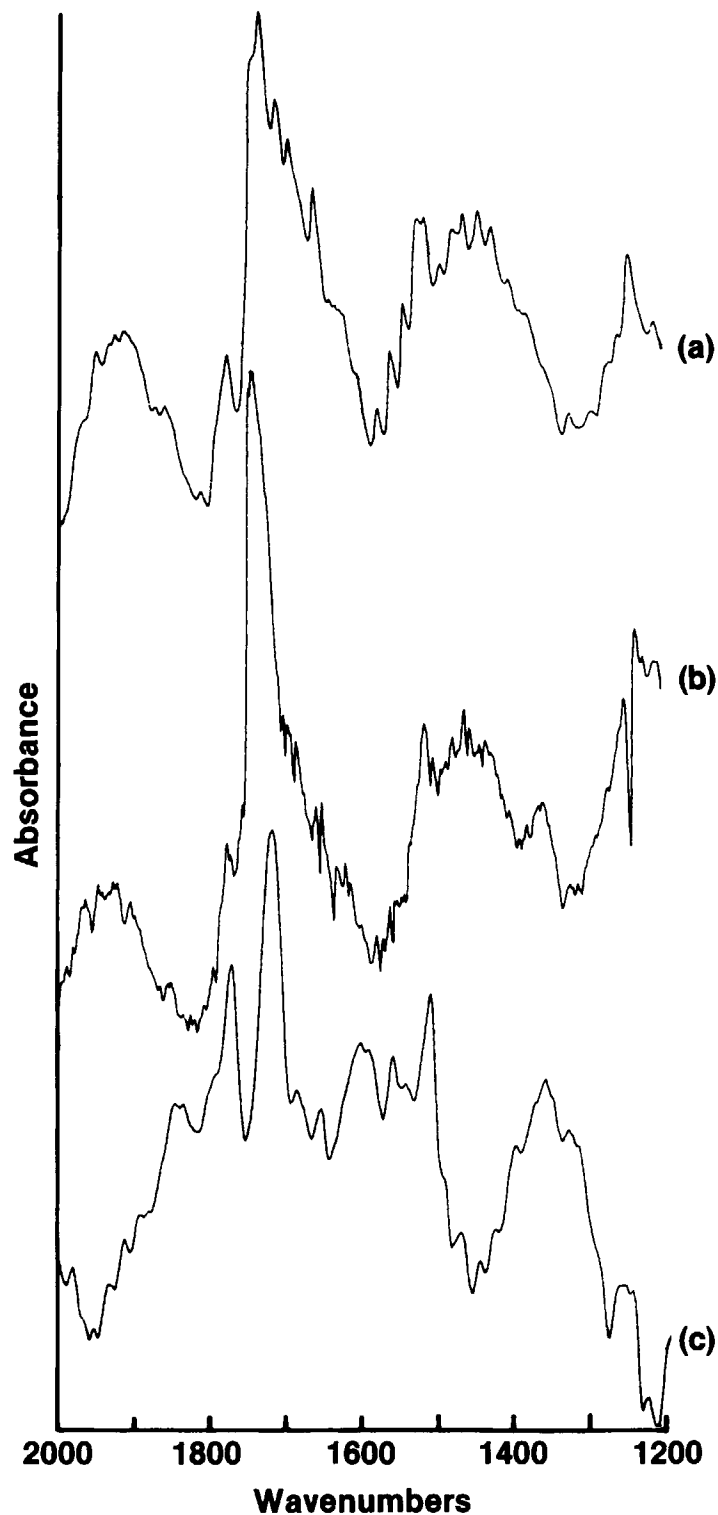


Figure 8 Thermal imidization of amic acid on APS film (over Cu) at (a) 200°C and (b) 300°C. (c) Thermal imidization of amic acid on phenyl-APS copolymer over copper.

APS siloxane layer on copper and for a free amine-containing surface layer, capable of further polyamic acid interaction, with the PH-APS mixture. The

amine/carboxylic acid interaction and salt formation with the PH-APS copolymer is the same as that observed when APS is used as an adhesion pro-

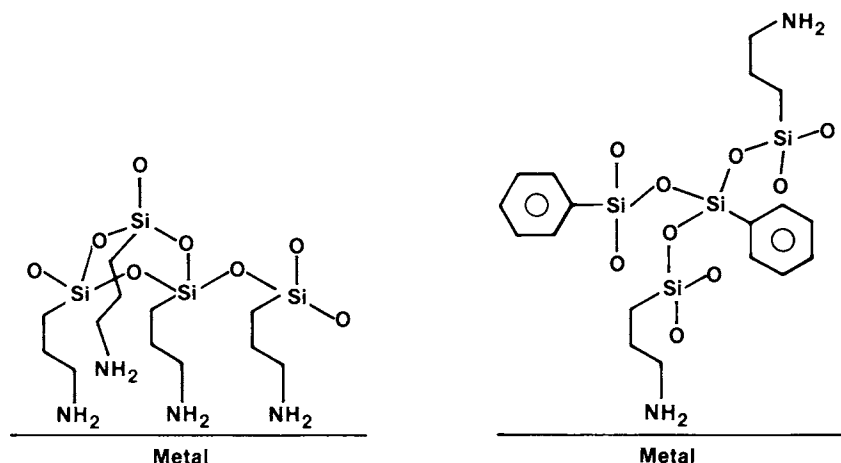


Figure 9 Probable interfacial difference between APS and phenyl-APS copolymer on copper.

moter on silicon dioxide.¹ Further, both APS films appear to halt the amic acid/copper surface interaction.

Heating of the BPDA-PDA amic acid on both APS/Cu and PH-APS/Cu yielded the imide [Fig. 8(a), (b), and (c)]; however, the phenyl surface coating is probably covalently attached to the polyimide by a substrate-linking aminopropyl group.

The ramifications of these differences are important since it appears that the PH-APS copolymer coordinates only a portion of the aminopropyl functionality to copper, has an insulating phenyl core, and allows other aminopropyl groups exposure to the air/polymer surface (Fig. 9). Thus, the polyimide/phenyl copolymer interface seems covalently attached while the APS system does not. Apparently, both adhesion strength and temperature/humidity reliability can be enhanced using the phenyl-containing system.

CONCLUSIONS

BPDA-PDA amic acid reacts directly with Cu/CuO surfaces to form a thermally labile salt at the interface, but ethyl esters do not. Curing of the acid salt destroys the polymer; however, the ester appears to imidize in the normal fashion, with ordering on the metal surface. These reactions mimic those of PMDA-ODA (amic acid and ester) systems, indicating backbone flexibility is not a major factor in these interactions.

A polymeric layer of APS silsesquioxane interacts with the copper surface to passivate amic acid salt formation. Presumably, this is through amine-copper coordination and formation of a protective sil-

sesquioxane interface. Amic acids do not appear to interact with this interface but thermally imidize in the normal fashion.

Polymeric phenyl-APS silsesquioxane copolymers also passivate the copper surface, but further react directly with the amic acid to form the alkyl amine salt. Presumably, this salt imidizes in the usual fashion (as PMDA-ODA-APS interfaces), forming a covalent surface bond through the aminopropyl groups. This covalent attachment should provide enhanced adhesion in both acids and esters.³

REFERENCES

1. H. Linde, *J. Polym. Sci. Chem.*, **20**, 1031-1041 (1982).
2. H. Linde and R. Gleason, *J. Polym. Sci. Chem.*, **22**, 3043-3062 (1984).
3. H. Linde, *J. Polym. Sci. B*, **26**, 1149-1158 (1988).
4. H. Linde and R. Gleason, *J. Polym. Sci. B*, **26**, 485-497 (1989).
5. H. Linde, *J. Appl. Polym. Sci.*, **40**, 2049-2063 (1990).
6. H. Linde, *J. Appl. Polym. Sci.*, **40**, 613-622 (1990).
7. M. M. Koton, *Polyimides—A New Class of Thermally Stable Polymers*, Progress in Material Science Series, Vol. VII, Technomic, Stamford, CT, 1970.
8. J. F. Rabolt, F. C. Burns, N. E. Schlotter, and J. D. Swalen, *J. Chem. Phys.*, **78**, 946-952 (1983).
9. F. J. Boerio and R. G. Dillingham, in *Adhesive Joints: Formation, Characteristics and Testing*, K. L. Mittal, Ed., Plenum, New York, 1984.
10. F. J. Boerio, L. Armogon, and S. Y. Cheng, *J. Colloid Interface Sci.*, **73**, 416 (1980).

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