Adhesion Promotion at High Temperature for Epoxy Resin or Polyimide onto Metal by a Two-Component Coupling System of Polybenzimidazole and 4-Aminophenyl Disulfide

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SYNOPSIS

A two-component coupling agent layer consisting of polybenzimidazole and 4-aminophenyl disulfide showed better anticorrosive performance and higher adhesive strength for copper and resins than did each single component even at high temperature. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The adsorption of organic sulfur compounds on gold, silver, and copper metals represents a chemisorption system with unique and important properties. A general description of the chemisorption of organic disulfides from solution on noble metals was presented.[1,2] Given the inertness of gold toward the chemisorption of most polar organic functionality, it was found that all the disulfides under investigation formed very strong chemisorption bonds and that it was possible to prepare structurally and chemically complex organic surfaces with well-defined microscopic characteristics when an adsorbate molecule with appropriate molecular structure was used.[1,2]

There is considerable interest in the mechanism by which organic disulfides, thiols, and sulfides adsorbed to metal surfaces. Recently, they have become popular as anchors for constructing self-assembled organic layers on metals.[3] These kinds of molecules are particularly useful in building up supermolecular structures on metals. Since much of the work has been on noble-metal surfaces and the symmetric disulfide stretches are IR inactive, many of the surface studies have used surface-enhanced Raman scattering (SERS) as a spectroscopic tool.[4-7]

The adhesion of epoxy resins and polyimides to copper metal at elevated temperatures is important both from scientific and technological points of view. Since copper metal easily oxidizes at elevated temperatures, the interfacial corrosion results in a reduction in adhesion strength. Some of the sulfur- or nitrogen-containing heterocyclic compounds have found widespread use not only as corrosion inhibitors[8-11] for copper and other transition metals but also as curing agents for epoxy resins.[12-14] By the use of SERS, we recently found that polybenzimidazole (PBIM) can react with silver, copper, and other transition metals to form metal azolate "inner" complexes, which cover the surface in the form of a thin polymeric layer.[15,16] After doping the polybenzimidazole/metal surface with a 4-aminophenyl disulfide solution, a two-component anticorrosive system is formed, which shows better anticorrosive properties at elevated temperature and provides active sites for coordinating or covalent bonding by which strong adhesion of epoxy resin to the metal can be achieved. By a suitable combination of the chemical reactivities of polybenzimidazole toward epoxy resin and metal, it was thought that a new coupling agent could be designed showing both an anticorrosion effect for metals and an adhesion-promotion effect for epoxy coating and polyimides to the metals.

EXPERIMENTAL

SERS Study of Chemisorption on Copper

Commercial copper foils (99.999%) provided by Aldrich, 0.05 mm thick, were immersed in a stirred $2M$ HNO_3 solution at room temperature for 2–3 min. This procedure removes surface oxides and creates a spongelike surface with features on the 10–100 nm size scale.[17,18] After etching, the copper foil was thoroughly rinsed with water, dried under nitrogen, and dip-coated with polybenzimidazole–dimethyl-formamide (DMF) solution (0.06 wt %) at 50°C for 5 min. After withdrawal, the physisorbed layers were washed away with DMF. The copper plate covered with polybenzimidazole was then immersed in a 4-aminophenyl disulfide solution in ethanol (0.1 wt %) for 5 min at room temperature. After withdrawing, the specimens were then rinsed with ethanol and dried under air. Raman spectra of these samples were recorded with a Spex 1403 Raman spectrometer. The incident laser excitation was the 632.8 nm line from a He—Ne laser, and the incident power was about 100 mW. A back-scattering geometry in air was used for all samples. The foils were mounted onto a heating cell for the *in situ* Raman measurement at elevated temperature.

Adhesion Test

The coupling effect of chemisorbed polybenzimidazole and 4-aminophenyl disulfide for epoxy resin and polyimide on copper was studied by a mechanical test. Copper plates (80 × 20 × 3 mm) were mechanically polished and washed with dilute HCl. The plates were then immersed in polybenzimidazole–DMF solution at room temperature for 5 min and then treated with 4-aminophenyl disulfide solution for another 5 min. The copper specimens treated with the two-component coupling system were ready for adhesion studies. Test specimens were prepared by coating a layer (20 × 10 mm) of epoxy resin–triethyltetramine (100 : 6) to the end of one metal plate, placing the other plate on it, lightly clamping the assembly (ca. 1.5 kg force), and curing at 150°C for 1 h. The cured thickness was 0.1–0.2 mm. The excess of cured resin was carefully trimmed from the test specimens with a scalpel before testing. An Instron instrument was used to pull the specimens in tension according to ASTM D 1002-72. Five sets of specimens were used for each study, and their average data were calculated as the lap shear strength. The adhesion for the untreated and the two-component-treated copper plates was studied before and after heating at 250°C for 30 min. For comparison, γ-GPS silane (γ-glycidoxypropyltri-methoxy silane) coupling agent-treated copper plates and polybenzimidazole or 4-aminophenyl disulfide single-component-treated copper plates were also prepared for the adhesion test under the same conditions described above.

Differential Scanning Calorimeter Studies

The thermal behavior of polyamic acid on copper, glass, and the polybenzimidazole-treated copper was investigated by using a differential scanning calorimeter (Perkin-Elmer Model DSC-2C) with a heating rate of 10°C min^{-1}. Polyamic acid solution in DMF was prepared from pyromellitic dianhydryde and oxydianiline by the known method as described in the literature.[19] The polyamic acid was converted to polyimide in the following manner: Polyamic acid films deposited on a glass slide or on copper are dried near 100°C for 15 min to remove the solvent. The films were thermally cured by gradual heating from 130 to 250°C, then at 300°C for 1 h in an inert atmosphere to complete the imidation.

RESULTS AND DISCUSSION

The adsorption geometry of 4-aminophenyl disulfide on metals was studied by the use of SERS spectroscopy. Figure 1 shows a normal Raman spectrum of 4-aminophenyl disulfide in the solid state [Fig. 1(A)] and the SERS spectra of this compound adsorbed on copper plates before [Fig. 1(B)] and after heating [Fig. 1(C)], respectively. Based on the reported infrared spectrum and comparison of the Raman spectrum with its diselenide counterpart, the line at 461 cm^{-1} in Figure 1(A), may be assigned as the S—S stretching mode,[20] which exists in the normal Raman spectrum but disappears in the SERS spectra. By comparing the SERS spectra of 4-aminophenyl disulfide with its normal Raman spectrum, we proposed that the S—S linkage was readily cleaved to form mercaptide species on the copper surface. The enhancement of the 386 cm^{-1} line in Figure 1(B) also implies chemisorption via the S atom since this line is due to a ring in-plane bending mode sensitive to the S atom. The appearance of the new Raman line at 263 cm^{-1} in Figure 1(B) can be attributed to the Cu—S bond. The very broad bands ranging from 400 to 630 cm^{-1} shown in the spectrum of Figure 1(C) are attributed
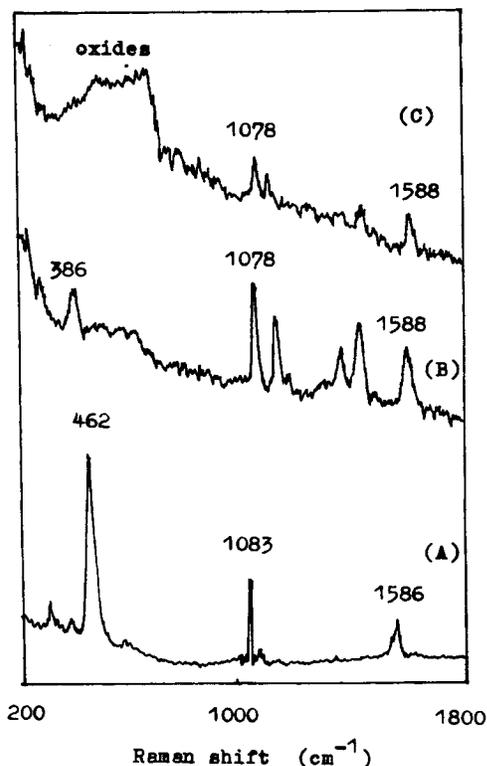
Figure 1 (A) A normal Raman spectrum of 4-amino-phenyl disulfide in the solid state; (B) SERS spectrum of 4-aminophenyl disulfide adsorbed on copper foil; (C) SERS spectrum of the specimen in (B) after heating at 250°C for 1 h.

to metal surface oxides. The appearance of oxide bands in the copper SERS spectrum implies that a 4-aminophenyl disulfide-covered surface does not protect the metal from heat corrosion.

Figure 2(A) shows the room-temperature SERS spectrum of polybenzimidazole on a copper surface. We postulated that polybenzimidazole can react with the copper surface in the presence of oxygen, yielding cuprous polybenzimidazolate covering the surface.[17] The appearance of oxide bands in the copper SERS spectrum of Figure 2(A) indicates that a polybenzimidazole-covered surface does not possess substantial resistance to oxygen permeation. Even though the surface film of polybenzimidazole is in multilayers, it cannot suppress oxidation even at room temperature. This may be due to the fact that there are pinholes under the coatings that are not covered by the rigid polymer chains. The surface oxidation was accelerated upon heating, resulting in a prominent intensity of the oxide bands in Figure 2(B). To see the influence of the thickness of polybenzimidazole coating, an additional 10 μL solu-

tion was spread onto a 1 cm² polybenzimidazole/copper surface and the solvent was evaporated. The SERS spectrum was taken after the specimen was heated at 250°C for 1 h and is shown in Figure 2(C). It is clear that the additional overlayer of polybenzimidazole did not retard oxidation at the interface.

Figure 3(A) shows a room-temperature SERS spectrum of polybenzimidazole and 4-aminophenyl disulfide coadsorbed on the copper surface, in which there are very weak bands for oxides. Here, a HNO₃-etched copper foil was first pretreated with a 0.06 wt % DMF solution of polybenzimidazole for 5 min at room temperature, then in a ethanol solution of 4-aminophenyl disulfide (0.1 wt %) for 5 min at room temperature. No oxide bands were detected on the copper surface. Figure 3(C) was the SERS spectrum of polybenzimidazole and 4-aminophenyl disulfide coadsorbed from a solution of their mixture. The oxide film formation did not occur even when the treated copper had been heated to 250°C. The distinction between Figure 3(A) and Figure 2(A) is the appearance of 368 and 1078 cm⁻¹ bands due
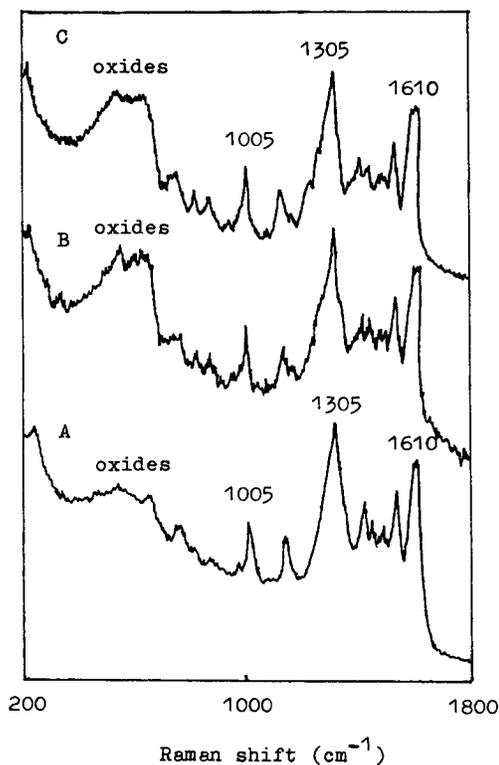

Figure 2 (A) SERS spectrum of polybenzimidazole on copper foil; (B) SERS spectrum of the specimen in (A) after heating at 250°C for 1 h; (C) SERS spectrum of the specimen in (A) over a coated additional layer of polybenzimidazole and then heated at 250°C for 1 h.
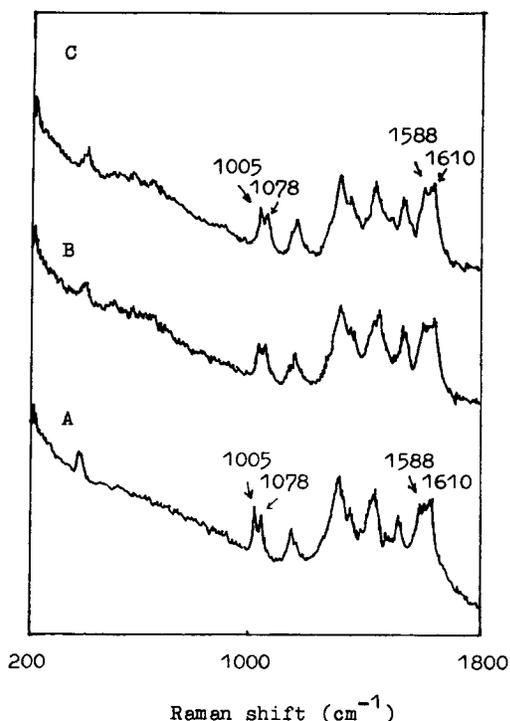
Figure 3 (A) SERS spectrum of a copper foil pretreated with a two-component coupling system containing polybenzimidazole and 4-aminophenyl disulfide by a two-step procedure; (B) SERS spectrum of the specimen in (A) after heating at 250°C for 10 h. (C) SERS spectrum of a specimen coadsorbed polybenzimidazole and 4-aminophenyl disulfide from a solution of their mixture after heating at 250°C for 10 h.

to the adsorption of 4-aminophenyl disulfide. Other bands, e.g., the 1305 and 1610 bands in Figure 3 (A), may be attributed to those from polybenzimidazole. As illustrated in Figure 2, oxidation cannot be suppressed by polybenzimidazole. We therefore conclude that the surface pinholes on the metal left by polybenzimidazole have been filled with chemisorbed 4-aminophenyl disulfide.

The SERS spectra of Figure 3(B) and (C) show that oxide film formation did not occur even when the treated copper had been heated to 250°C for 10 h. This property is very important, because a copper surface treated with either polybenzimidazole or 4-aminodiphenyl disulfide alone oxidizes in 1 h at 250°C. This corrosion inhibition is synergetic and may be explained by the physicochemical mechanism of corrosion protection by organic coatings.[21] This physicochemical mechanism consists of blocking the diffusion of corrosive agents, like water and oxygen, and of corrosion stimulants. This barrier action of organic coatings may be enhanced signif-

icantly by fillers, pigments, or extenders which greatly increase the length of diffusional pathways through the cross section of the coating film. Since 4-aminophenyl disulfide could be easily adsorbed on metal, as it makes contact with the metal surface, a stable Cu — S bond is formed, filling up the pinholes left by polybenzimidazole. The excellent anticorrosion effect of the two-component system containing polybenzimidazole and 4-aminophenyl disulfide was ascertained by a prolonged heating test in which oxide bands were ultimately observable after heating at 250°C for 60 h.

An electrochemical study, complementary to SERS spectroscopy, was carried out using cyclic voltammetry. Cyclic voltammetry of copper electrodes pretreated with only 4-aminophenyl disulfide is shown in Figure 4(A). On the second and successive sweeps after immersion treatment, the currents of the first oxidation peak ($Cu^0 \rightarrow Cu^+$) increase relative to the second oxidation peak ($Cu^+ \rightarrow Cu^{2+}$), and the peak currents observed on the reverse sweep increase in magnitude. In the initial sweep, the reaction $Cu^0 \rightarrow Cu^+$ is inhibited. The anodic current was observed above 0.70 V. This
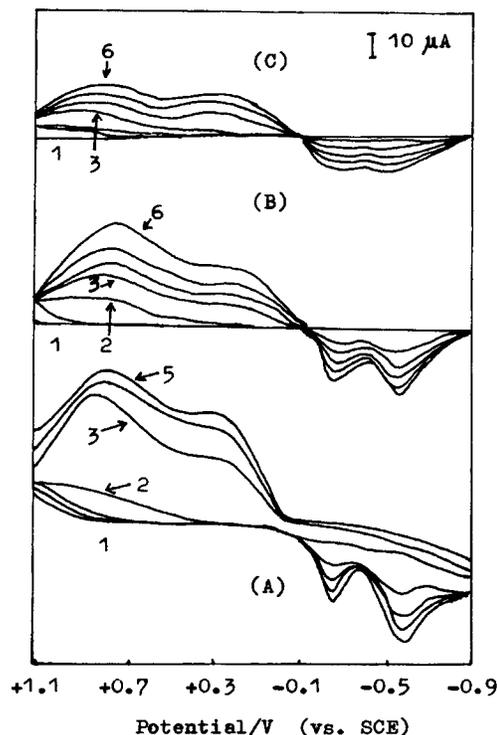

Figure 4 Cyclic voltammetry of copper pretreated with (A) 4-aminophenyl disulfide, (B) polybenzimidazole, and (C) a two-component system containing polybenzimidazole and 4-aminophenyl disulfide.

suggests that CuO is the predominant oxidation product on the forward scan. On the reverse scan, the oxide film is at least partially reduced, first to Cu_2O and then to Cu^0. By comparison, the cyclic voltammogram obtained from the polybenzimidazole-pretreated copper electrode is given in Figure 4(B), where it can be seen that the oxide peak obtained in the sixth cycle has nearly the same intensity as that obtained in the third cycle shown in Figure 4(A).

The copper electrode pretreated with a two-component system containing polybenzimidazole and 4-aminophenyl disulfide displays the cyclic voltammogram shown in Figure 4(C). The anodic oxidation reaction of copper was inhibited in the first two scans, and the behavior is more pronounced than that in Figure 4(B). Subsequent cycling resulted in a gradual increase in the anodic and cathodic peaks. However, comparing Figure 4(C) with Figure 4(B), one finds that the peak currents are much less for copper electrode coadsorbed with polybenzimidazole and 4-aminophenyl disulfide than those for polybenzimidazole-modified electrode in their corresponding cycles. This means that the protective two-component coating fully covered the electrode surface as illustrated by the high-temperature SERS results.

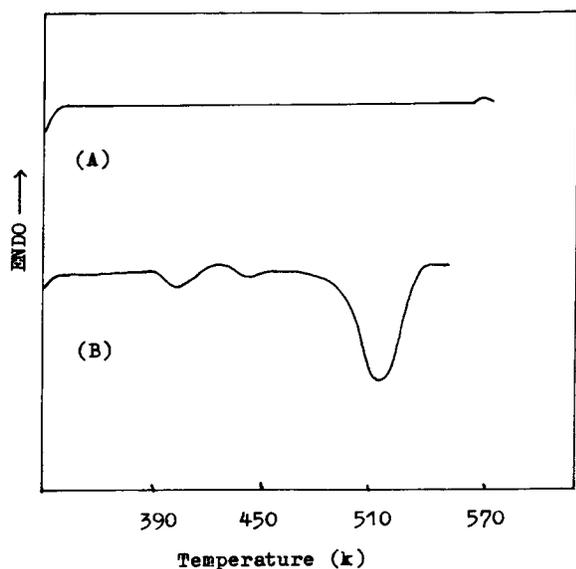Since each component of the surface species on copper pretreated with polybenzimidazole and 4-

Table I   Lap Shear Strength for Copper Plates Bonded with Epoxy Resin Before and After Heating at 250°C for 30 Min

Samples	Lap Shear Strength (kg/cm^2)		
	Before Heating	After Heating	Retention Ratio
Untreated plates	163	45	28%
With γ-GPS silane	183	44	24%
With 4-aminophenyl disulfide	107	78	72%
With polybenzimidazole	135	95	70%
With a two-component system[a]	173	128	74%

[a] The two-component system consists of polybenzimidazole and 4-aminophenyl disulfide.

aminophenyl disulfide consists of NH groups, it is thought that an epoxy resin could chemically react with the surface film. By a suitable combination of the chemical reactivity of polybenzimidazole and 4-aminophenyl disulfide toward metal and epoxy resins, a new type of coupling agent system for bonding epoxy resin to metals can be designed. Figure 5 illustrates dynamic curing curves for an epoxy resin (Epon 828, Nanjing Chemical Co.) on the surface of treated and untreated metallic copper studied by DSC. The curve for the untreated copper sample is almost a straight line, while the curve for the copper powder treated with polybenzimidazole and 4-aminophenyl disulfide shows exothermic peaks, which may be assigned probably to initiation and propagation stages of the curing process, respectively.

The two-component system consisting of polybenzimidazole and 4-aminophenyl disulfide shows an excellent anticorrosion effect at elevated temperature, as illustrated in Figures 3 and 4. It is thought that by suitable combination of the chemical reactivities of polybenzimidazole and 4-aminophenyl disulfide toward metal and epoxy resins a new type of coupling agent for bonding epoxy resin to metals can be designed. The epoxy/metal adhesive test specimens were of the single lap joint configuration. The lap shear strength for copper plates treated by polybenzimidazole, 4-aminophenyl disulfide, and their combination was measured and is shown in Table I. Experimental values indicated that treatment with the two-component coupling system of polybenzimidazole and 4-aminophenyl disulfide im-

Figure 5   DSC curves of an epoxy resin with (A) copper powder and (B) copper powder pretreated with a two-component system containing polybenzimidazole and 4-aminophenyl disulfide.

Table II Adhesion of Polyimide to Cu Measured by a Tape Peel Test

Samples	PI Film Removed
Untreated Cu	50%
With 4-aminophenyl disulfide	20%
With polybenzimidazole	25%
With polybenzimidazole and 4-aminophenyl disulfide	12%

Table III Lap Shear Strengths of Copper Plates Bonded with Polyimide

Samples	Lap Shear Strengths (kg/cm^2)
Untreated copper plates	48
Pretreated with 4-aminophenyl disulfide	47
Pretreated with polybenzimidazole	44
Pretreated with polybenzimidazole and 4-aminophenyl disulfide	63

proved significantly the adhesion for epoxy resin to copper under heating. γ-GPS could improve the initial adhesion, but the strength reduced quickly after heating at 250°C.

Polyimides are a class of high-temperature polymers used in a number of technologies such as microelectronic device fabrication, corrosion inhibition, α-particle barriers, aerospace, and wire insulation. The polyimide coatings are usually applied to the inorganic substrates from polyamic acid solutions followed by thermal imidization. The imidization reaction will be retarded in the presence of Cu. This reaction is incomplete below 300°C. But decomposition will take place above 300°C. Pretreating the Cu surface with a thin layer consisting of polybenzimidazole and 4-aminophenyl disulfide can make the imidization proceed without retardation and avoid decomposition above 300°C, resulting in an improvement of adhesion between polyimide film and Cu substrate. Table II lists the results of the tape peel test for polyimide on Cu. Table III shows the lap shear strength for copper plates bonded with polyimide. The tape peel test was used by applying and removing pressure-sensitive tape over cuts made in the polyimide film on a Cu plate. The data listed in Tables II and III clearly indicate that adhesion improvement between polyimide and copper may be achieved by pretreating Cu with the two-component system consisting of polybenzimidazole and 4-aminophenyl disulfide.

Figure 6 illustrates the thermal behavior of polyamic acid on a glass slide, Cu foil, and pretreated Cu. In the DSC curve of neat polyamic acid film [Fig. 6(C)] cast from a DMF solution, the endothermic peak below 400 K is due mainly to the evaporation of DMF solvent associated with polymeric acid macromolecules. Heating to 450 K exhibits an endothermic peak due mainly to the imidization process which ends at about 500 K. Further heating to about 590 K will exhibit a weak endothermic peak, which is commonly regarded as the intercrosslinking

of polyimide chains, necessary to the mechanical and electrical properties of the film. The DSC curve of Figure 6(A) is recorded from a polyamic acid film cast on a copper substrate. One can see that the imidization peak occurs at 480 K and ends at 530 K, temperatures which are 30 K higher than those in the absence of copper, indicating the retardation of imidization. Further heating will result in the decomposition of the polyimide as can be inferred from the steep rise of the DSC curve in Figure 6(A) after 610 K. Since the loss of the thermal stability in polyimide, which is unfavorable to many applications, is induced by carboxylate salt formation between the Cu and polyimide, we propose an improved ap-
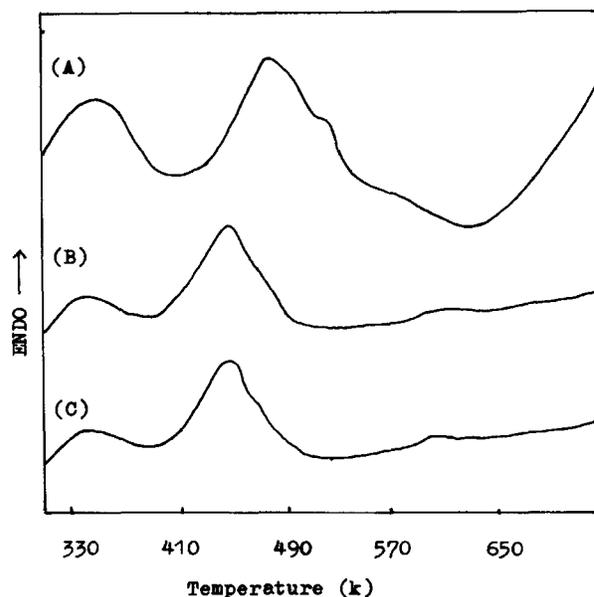

Figure 6 DSC curves of polyimide films casted on (A) a copper plate, (B) a copper plate pretreated with a two-component system containing polybenzimidazole and 4-aminophenyl disulfide, and (C) a glass slide.

proach to overcome the shortcomings of direct contact of polyamic acid with Cu by introducing a thin layer of thermally stable polybenzimidazole and 4-aminophenyl disulfide at the interface. The DSC curve of polyamic acid film prepared on copper pretreated with polybenzimidazole and 4-aminophenyl disulfide is shown in Figure 6(B). The imidization reaction proceeds smoothly without any retardation, resulting in a very stable polyimide film, comparable to the neat polyimide, as shown in Figure 6(C).

SUMMARY

We have demonstrated that the two-component system containing polybenzimidazole and 4-aminophenyl disulfide is an effective coupling agent for an epoxy resin and a polyimide to copper. By pretreating the copper surface with polybenzimidazole and 4-aminophenyl disulfide solutions, improved thermal stability of adhesion for these resins to copper could be achieved.

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