

Low-Temperature Thermal Graft Copolymerization of 1-Vinyl Imidazole on Fluorinated Polyimide Films with Simultaneous Lamination of Copper Foils

A. K. S. ANG,¹ B. Y. LIAW,² D. J. LIAW,² E. T. KANG,¹ AND K. G. NEOH¹

¹ Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

² Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, ROC

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ABSTRACT: A simple technique of thermal graft copolymerization of 1-vinyl imidazole (VIDZ) on pristine and argon plasma pretreated fluorinated polyimide (FPI) films with simultaneous lamination of copper foils was demonstrated. The simultaneous thermal grafting and lamination process was carried out in the temperature range of 80–140°C under atmospheric conditions and in the complete absence of a polymerization initiator. Three different FPI samples of different chemical structures were employed in the present study. An optimum T-peel strength about 15 N/cm was achieved for the copper/FPI laminate. The adhesion strength, however, decreased with increasing fluorine content in the FPI film. The onset of cohesive failure occurred in the FPI film for assemblies with T-peel strength greater than 6 N/cm. The T-peel strengths are reported as a function of the argon plasma pretreatment time of the FPI films and thermal lamination temperature. The adhesion strengths were compared to that of the similarly prepared copper/polyimide (Kapton HN) laminate. Time-dependent water contact angle (θ) measurements indicated that the surfaces of FPI films are significantly more hydrophobic and more resistant to water diffusion or hydration than the Kapton HN films. The surface compositions of the pristine FPI films, as well as the delaminated FPI films and copper foils were studied by X-ray photoelectron spectroscopy. The thickness of the graft VIDZ polymer layer was in the order of 200 nm, as derived from the cross-sectional view of the scanning electron micrograph. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1478–1489, 1999

Key words: graft copolymerization; lamination, fluorinated polyimides; copper; T-peel strength; X-ray photoelectron spectroscopy

INTRODUCTION

Polyimides are used extensively as dielectric layers in the microelectronics industry due to their superior mechanical stability, high temperature resistance, solvent resistance, and low dielectric constants.^{1–5} In the development of flexible

printed circuit and multichip module components packaging, material with low dielectric constant and metal with high electrical conductivity are essential for faster signal speed and lower signal cross-talk. Fluoropolymers, such as poly(tetrafluoroethylene) (PTFE), have excellent dielectric properties and chemical inertness, which can serve as an ideal dielectric material. However, one major disadvantage of PTFE is its lack of dimensional stability under mechanical stress or impact. Therefore, up to the present date, pristine

Correspondence to: E. T. Kang (e-mail: cheket@nus.edu.sg).

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PTFE is deemed unsuitable to be employed in the rigorous processing environment of the microelectronics manufacturing industry. Recently, fluorinated polyimides (FPIs) have received much attention with great research interest. FPIs, in addition to possessing most of the desirable properties of the conventional polyimides, also exhibit lower dielectric constants and higher moisture repellency than the latter. These attractive features of FPIs make them useful as the future generation dielectric materials required in the microelectronic applications.^{6,7}

A great deal of effort has been devoted to the surface modification of polyimides for adhesion improvement to metals.^{8–15} Our previous work has demonstrated that strong adhesion of copper to polyimide (Du Pont's Kapton HN) film can be achieved via the one-step thermal graft copolymerization of 1-vinyl imidazole (VIDZ) on PI film surface with simultaneous lamination of copper foil.^{13,14} In the present work, we demonstrate that strong adhesion of copper to fluorinated polyimides can also be achieved using the simple one-step simultaneous surface modification and lamination process.

Xue et al.¹⁶ reported that the imino groups of benzimidazole interacted with copper metal at the zero oxidation state to form a complex. Inagaki et al.^{17,18} have carried out extensive experiments to show that the adhesion of copper to polyimides can be achieved and enhanced by first carrying out plasma graft copolymerization of VIDZ onto polyimides, followed by the evaporation of copper on the graft modified polyimide surface and thermal treatment at 80°C. The imino groups of the grafted VIDZ polymer form charge transfer complexes with copper metal, thus enhancing the adhesion strength. In a parallel development, Rånby et al.^{19–21} demonstrated that initiator-promoted surface graft copolymerization, when carried out at the interface between two contacting polymer films, was accompanied by the simultaneous lamination of the polymer films. The lamination phenomenon arose from the entanglement and interaction, at the lapped interface, of the grafted chains from the two polymer film surfaces. More recently, we had demonstrated that simultaneous surface graft copolymerization and lamination of polymer films could be achieved in the complete absence of an added polymerization initiator when the surfaces of polymer substrates were pretreated or preactivated by gas plasma or ozone to generate the peroxide or hydroxyl peroxide species.^{13–15} By

combining the above techniques, it is demonstrated in the present work that relatively strong adhesion between FPI and Cu foil can be readily achieved through thermal graft copolymerization of VIDZ on the surface of pristine and plasma-pretreated FPI films in contact with a Cu foil. It is further demonstrated that this low-temperature, one-step grafting/lamination process can be carried out under atmospheric conditions and in the complete absence of an added polymerization initiator. The surfaces of the FPI film and copper foil after delamination by T-peel were characterized by X-ray photoelectron spectroscopy (XPS). The thickness of the graft layer was determined from cross-sectional scanning electron micrographs (SEM). The surface wettability of the FPI films, on the other hand, was characterized by the static contact angle of water.

EXPERIMENTAL

Materials

The precursor, 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA), was supplied by Chriskev, Inc., while 1,4-bis(4-aminophenoxy)benzene (BAB) and 4,4'-bis(4-aminophenoxy)biphenyl (BABP) were obtained from Wakayama Seika Co. Ltd., Japan. The above chemicals were used as received. The other precursor, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BAPHF), was synthesized according to the method reported earlier.²² The three types of FPI films used in the present study included BAB-6FDA (Type 1), BABP-6FDA (Type 2), and BAPHF-6FDA (Type 3). The chemical structures of the FPIs are shown in Figures 1(a) to 1(c), respectively. Type 1 FPI film is prepared by gradually adding 6FDA (0.444 g, 1.0 mmol) to a solution of BAB (0.292 g, 1.0 mmol) in dimethylacetamide (5 mL) with constant stirring. The mixture was stirred at room temperature for 3 h under an Ar atmosphere to form the poly(amic acid) solution. The poly(amic acid) solution was cast into the FPI film on a glass plate by heating under vacuum according to the following steps: 8 h at 80°C, 2 h at 150°C, 2 h at 200°C, 3 h at 250°C, and 1 h at 300°C.²² The resulting BAP-6FDA film was a tough, flexible film of about 100 μm in thickness. Using similar procedures, the Type 2 FPI film was prepared from BABP and 6FDA, and the Type 3 FPI was prepared from BAPHF and 6FDA. The surface of the film was cleaned with

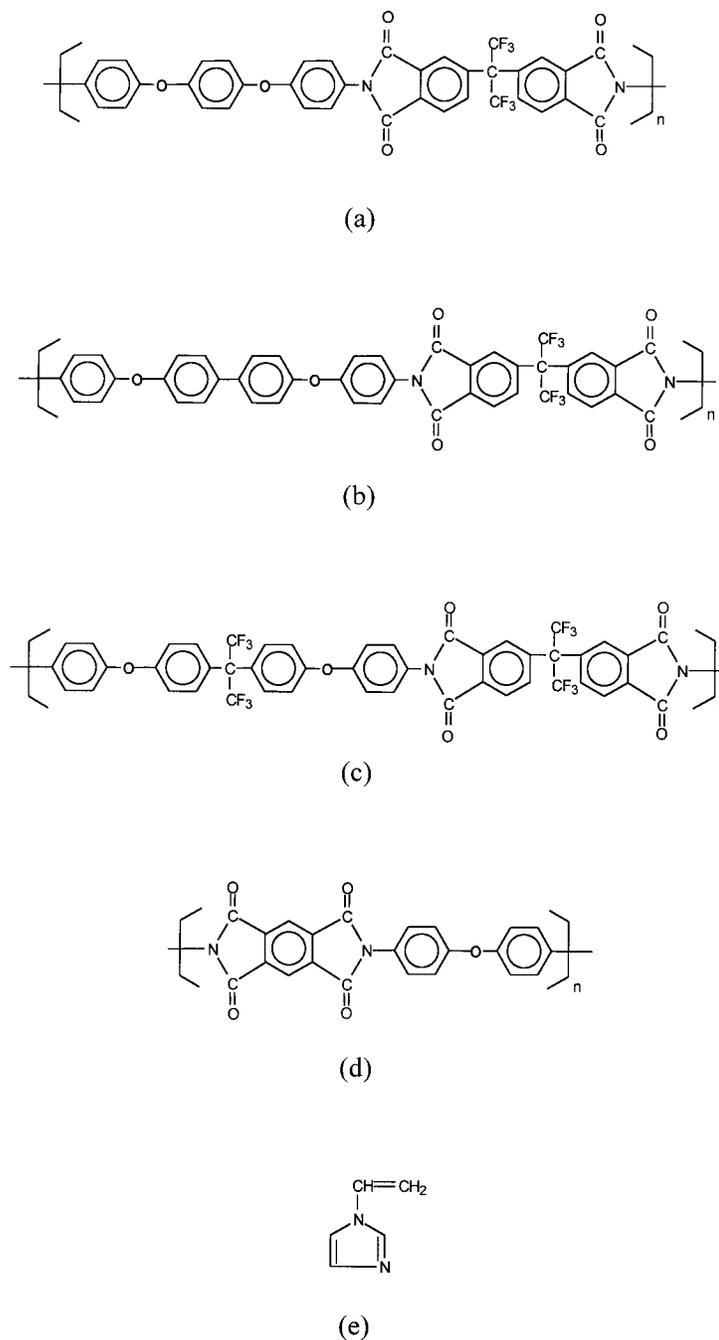


Figure 1 Chemical structures of (a) BAB-6FDA or Type 1 FPI, (b) BABP-6FDA or Type 2 FPI, (c) BAPHF or Type 3 FPI, (d) poly[*N,N'*-(oxydiphenylene) pyromellitimide] (Kapton HN), and (e) VIDZ.

doubly distilled water and methanol in an ultrasonic water bath before use. The conventional polyimide (PI) films used were the commercial products, Kapton HN, of the Du Pont Chemical Company. The structure of Kapton HN is shown in Figure 1(d). Copper foils of 100 × 100 mm in

area and 0.1 mm in thickness were purchased from Goodfellow, Inc., of Cambridge, UK. The surface of the copper foil was cleaned with a mixture of aqueous 0.01M HCl/0.01M HNO₃/0.01M H₂SO₄ in the volume proportion of 6:1:1, respectively, before use. The monomer, VIDZ, with chemical

structure shown in Figure 1(e), was purchased from Aldrich Chemical Co. of Milwaukee, USA, and was purified by vacuum distillation before used.

Simultaneous Graft Copolymerization and Lamination

The FPI film strips of about 0.4×0.8 cm in area were pretreated with argon plasma before the thermal graft copolymerization with concurrent lamination experiment. The Ar plasma pretreatment was carried out in an Anatech SP100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at a plasma power of 35 W, an applied oscillator frequency of 40 kHz, and an argon pressure of 0.6 Torr. The duration of the glow discharge pretreatment for the present study was between 5 and 30 s. The plasma pretreated films were subsequently exposed to the atmosphere for about 5 min to allow the surface activated species to react with oxygen to generate the peroxide or hydroxyl peroxide species²³ for the subsequent thermal grafting and lamination experiment. Each FPI film strip was further diced into two strips of 0.2×0.8 cm in area before proceeding to the next step. In the simultaneous grafting and lamination experiment, a small quantity of pure VIDZ monomer was introduced between the FPI film and the copper foil. Thermal graft copolymerization with concurrent lamination to Cu was achieved by heating the Cu/VIDZ/FPI assembly in a hot press set at a constant load of about 20 kg/cm². The samples were introduced into the hot press only after the set temperature was reached and maintained at a steady state. After the grafting and lamination experiment, the samples were returned to room temperature by cooling slowly under the constant load in the hot press to minimize the thermal stress at the metal/polymer interface.¹³ In this case, the average cooling rate was only in the order of only 9–10°C/h.

Adhesion Strength Measurements and Surface Characterization

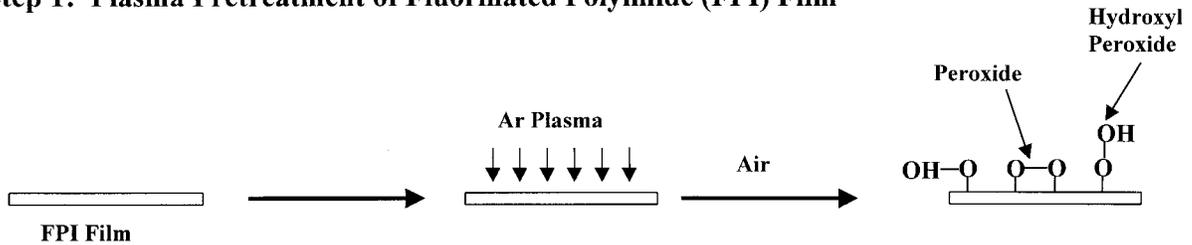
The adhesion strengths were determined by measuring the T-peel strength with an Instron Model 5540 tensile strength tester. All measurements were performed at a crosshead speed of 1.0 cm/min. Each adhesion strength value reported is the average of three sample measurements. The lapping area of each sample was 0.2×0.8 cm.

XPS measurements were carried out on a VG ESCALAB MKII spectrometer with a nonmonochromatized Mg *K* X-ray source (1253.6 eV photon) at a constant retard ratio of 40. The polyimide films and copper foils were mounted on the standard sample studs by means of double-sided adhesive tape. The X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA). The operating pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during the measurements. The core-level spectra were obtained at a photoelectron take-off angle (α , measured with respect to the sample surface) of 75°. All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV, to compensate for the effects of charging. In the peak synthesis, the line width (full width at half maximum, FWHM) for the Gaussian peaks was maintained constant for all components in the spectrum of a particular sample. Cross-sectional SEM micrographs were obtained using the Hitachi Scanning Electron Microscope, Model S-2150, at a magnification of 11,580 \times . The samples were attached to the sample studs by means of epoxy glue and double sided adhesive tape. Atomic force microscopic (AFM) images were obtained from the Nanoscope III scanning force microscope. All images were collected under atmospheric conditions using a constant force mode at a set point of 3.34 V, a scan rate of 0.5 Hz, and a scan size of $2.0 \mu\text{m} \times 2.0 \mu\text{m}$. Static water contact angle was measured on a Ramé-Hart Model 100-230 goniometer. Each contact angle reported is the average of five measurements at different locations on the film surface. The volume of water used for each measurement was about 3 μL . All measurements were carried out at room temperature (25°C) and a relative humidity of 60%.

RESULTS AND DISCUSSION

The application of plasma generated from various gases and under various glow discharge conditions in the surface modification of polymers has been widely reported.^{24–31} The simultaneous graft copolymerization and lamination process used in the present work is shown schematically in Figure 2. The T-peel adhesion strength of the Cu/FPI interface as a function of the Ar plasma pretreatment time of the FPI film for thermal graft copolymerization and lamination carried out at 120°C for 4 h in the presence of VIDZ is shown in Figure 3. Four adhesion strength curves are

Step 1: Plasma Pretreatment of Fluorinated Polyimide (FPI) Film



Step 2: Simultaneous Thermal Graft Copolymerization and Lamination

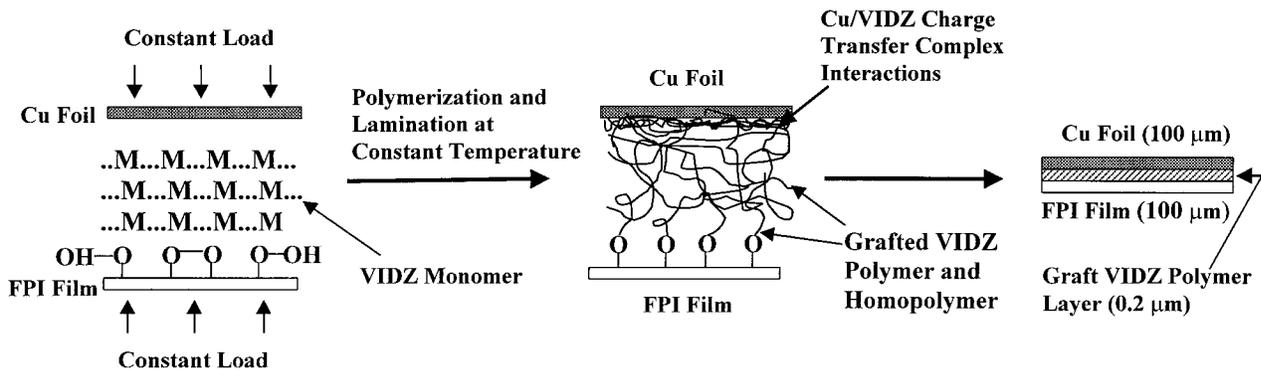


Figure 2 Schematic diagram showing the procedure and mechanism for thermal graft copolymerization with simultaneous lamination process.

presented: three for the FPI films and one for the Kapton HN PI film. Significant peel strengths were obtained for assemblies involving FPI films with no Ar plasma pretreatment. A maximum adhesion strength approaching 15 N/cm was obtained for assemblies with 5–10 s of Ar plasma pretreatment time for Type 1 FPI film, while Type 2 and Type 3 FPIs films showed maximum adhesion strengths at 10–20 s of plasma pretreatment. Increase in the Ar plasma pretreatment time does not seem to result in the further increase in adhesion strength. It has been observed that the onset of cohesive failure, which involves fracture of the FPI film and incomplete delamination of the polymer film from the copper surface, occurs at and above the peel strength of 6 N/cm. The fracture of the FPI film is clearly indicated by the presence of a substantial amount of the scattered polymer debris, which still adheres to the copper surface and that is readily visible to the naked eyes, after the delamination process. A control experiment was also performed to ascertain the effect of VIDZ graft copolymerization. When a 20-s Ar plasma pretreated Type 1 FPI film was

laminated with the Cu foil at 120°C for 4 h in the absence of VIDZ, the Cu/FPI interface exhibited negligible T-peel adhesion strength. For the evaluation of surface graft copolymerization of VIDZ on FPI, a poly(tetrafluoroethylene)/VIDZ/FPI assembly was employed under the same grafting/lamination condition, followed by the removal of the PTFE film. The presence of grafted VIDZ polymer on the FPI surface pretreated with Ar plasma was confirmed by the persistence of distinct XPS N 1s components at the binding energies of 398.5 and 399.7 eV, associated with the imine and amine nitrogen of the VIDZ polymer, respectively,¹³ even after the FPI film had been subjected to exhaustive washing and extraction. The thickness of the grafted VIDZ polymer layer was in the order of 200 nm, as derived from the cross-sectional view of the scanning electron micrograph. The susceptibility of the plasma and ozone pretreated Kapton HN PI film surface to graft copolymerization with vinyl monomers has also been demonstrated in the earlier studies.¹⁵

In the earlier work of Inagaki et al.,¹⁸ the VIDZ graft-copolymerized polyimide film surface was

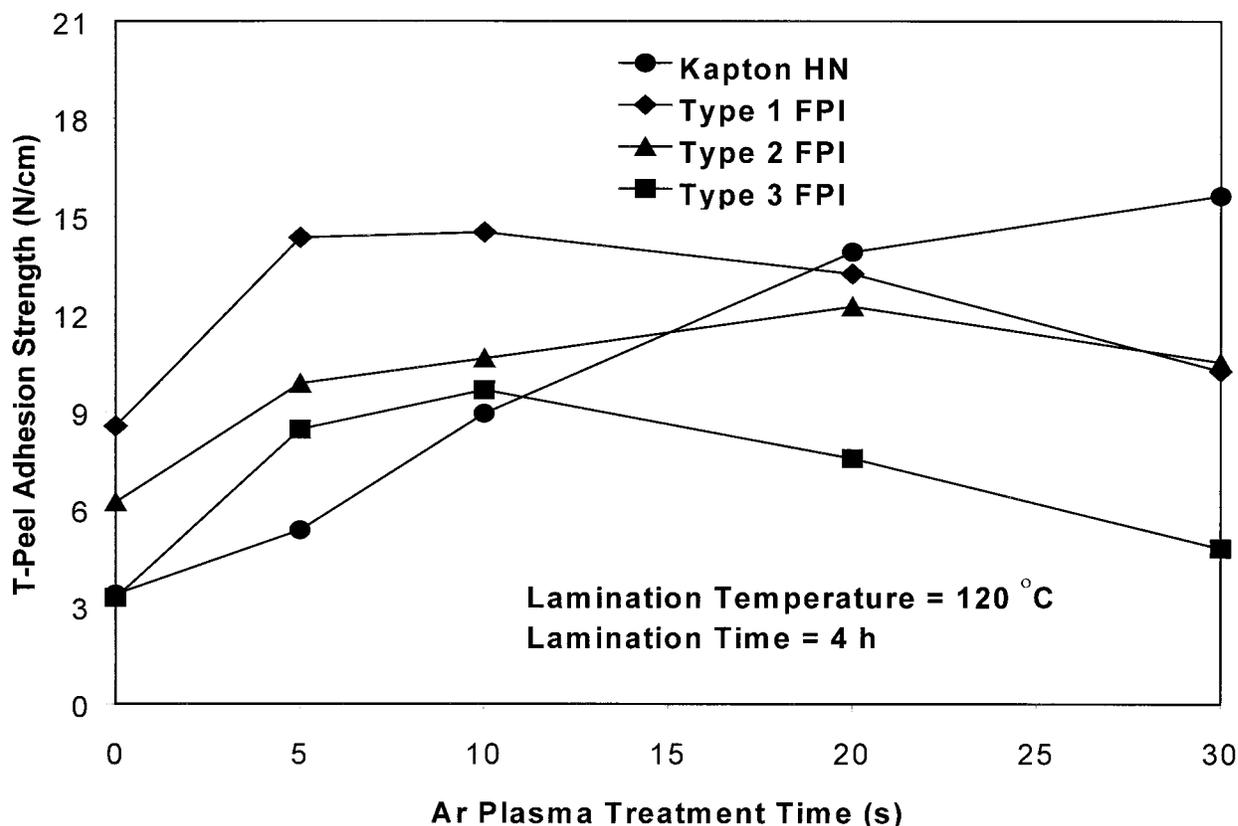


Figure 3 Variation in adhesion strengths of the Cu/FPI and Cu/PI laminates with Ar plasma pretreatment time of polyimide films. All samples were subjected to thermal grafting/lamination at a temperature of 120°C for 4 h.

metallized by vacuum deposition of copper metal in a separate step. The maximum T-peel strength of the resulting metal/polymer interface was on the order of 6.4 N/cm. This adhesion strength is lower than half of that of the present Cu/FPI joint formed from the thermal graft copolymerization with concurrent lamination technique. Nevertheless, both techniques involve the imidazole groups, which are capable of forming strong charge transfer complexes with copper.³² Earlier work of Xue et al.¹⁶ has also reported on the interaction of benzimidazole with copper metal at zero oxidation state. In fact, new polyimide containing imidazole units in the main chain to improve copper adhesion has been reported.³³ This polymer exhibits good adhesion with copper but is too brittle for microelectronics packaging applications.

Figure 4 summarizes the dependence of T-peel adhesion strength of the Cu/VIDZ/FPI assemblies on the temperature of thermal graft copolymerization/lamination for FPI films with 10 s of Ar

plasma pretreatment and 4 h of thermal grafting/lamination time. An optimum thermal lamination temperature of 100°C is observed for assemblies involving Type 1, and 120°C for assemblies involving Type 2 FPI, Type 3 FPI, and PI films. A decrease in peel strength is observed for grafting/lamination carried out at temperatures above 120°C. Prolonged exposure of the assemblies to temperatures above 120°C may have resulted in the gradual thermal degradation of the VIDZ polymer at the Cu/FPI interface.

Figure 5 shows the XPS wide scan spectra, obtained at the photoelectron take-off angle α , of 75°, for the pristine FPI and PI film surfaces. The spectra typically display four major peaks at binding energies of about 685, 532, 400, and 285 eV, corresponding to the F 1s, O 1s, N 1s, and C 1s core-level signals, respectively. The F 1s core-level spectra for all the three FPIs exhibit a small FWHM of about 1.5 eV, consistent with the presence of a single fluorine species dictated by the chemical structures of the polymers. The surface

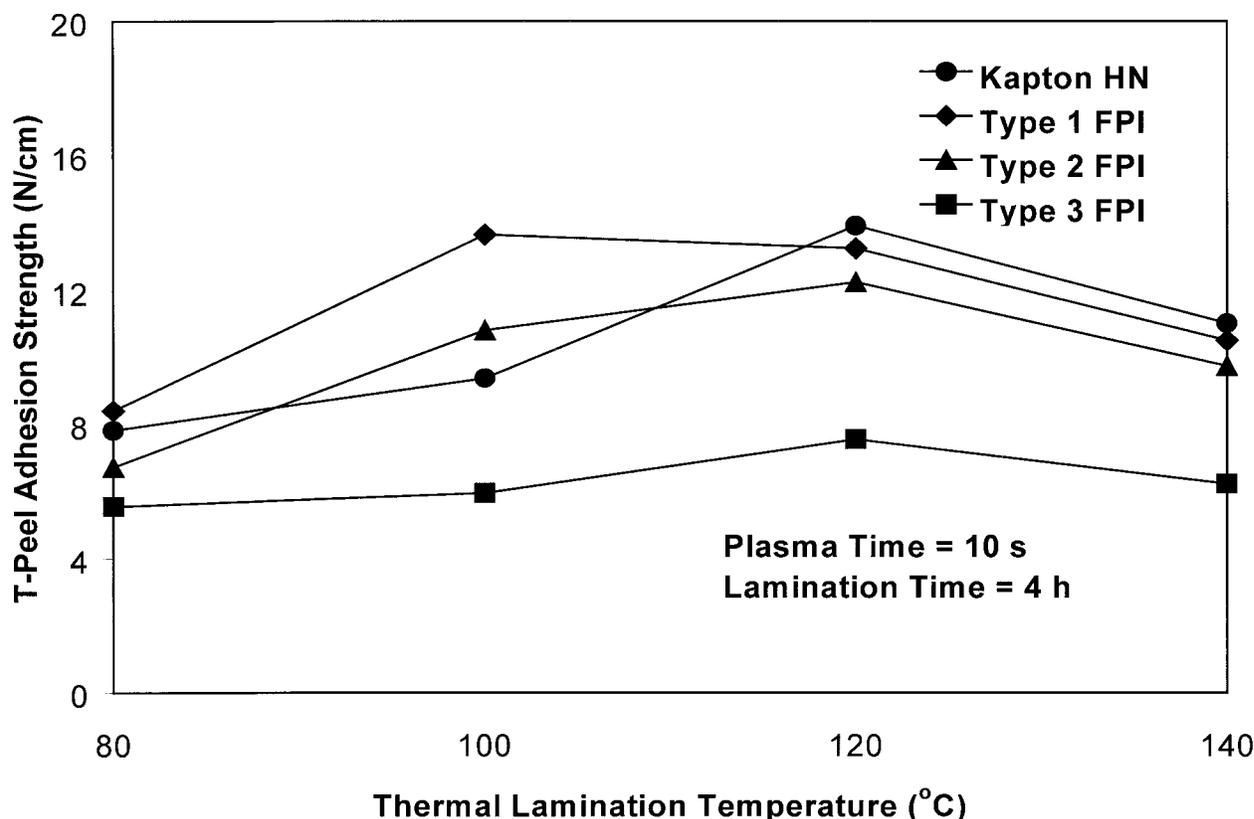


Figure 4 Variation in adhesion strengths of the Cu/FPI and Cu/PI laminates with thermal grafting/lamination temperature. All samples were subjected to 4 h of thermal grafting/lamination and 10 s of Ar plasma pretreatment time for the polyimide films.

elemental compositions of the FPI and Kapton HN films before and after 20 s of Ar plasma treatment are shown in Table I. The static water contact angles and surface roughness values (as evaluated from AFM images) of the respective film surfaces are also shown in the same table. For all the pristine FPI films, the proportions of fluorine and nitrogen at the surface agree fairly well with the theoretical values dictated by the chemical structures of the respective polymers. The unusually high deviation in oxygen content from the theoretical value for each pristine FPI film may have resulted from the surface oxidation of the polymers during curing. Ar plasma results in an increase in the [O]/[C] ratio, albeit not to the same extent, for all four types of films. The effects of Ar plasma treatment on the surface [O]/[C] ratios of the FPI and PI films are also summarized in Figure 6. The decrease in surface [O]/[C] ratio at plasma treatment time above 20 s for the FPI films may have resulted from the onset of surface etching effect of the plasma treatment, which removes the plasma-activated species at the surface

and thus also causes a decrease in the extent of surface graft copolymerization. These effects can then help to account for the fact that the T-peel adhesion strengths of the assemblies involving the three FPI films decrease at plasma times above 20 s (Fig. 3). The largest increase in the surface [O]/[C] ratio (and thus the peroxide concentration and extent of graft copolymerization) for the Type 1 FPI film is also consistent with the highest adhesion strength observed for the assembly involving this type of film.

The static water contact angles (θ 's) for each film were made within 5 s and after 60 s of the water droplet contact. The hydrophobic nature of the FPI films is indicated by their significantly larger water contact angles, in comparison with that of the Kapton HN film, and by their relative insensitivity to the wetting water droplets as a function of time. The relatively larger water contact angles of the FPI film surfaces, as compared to that of the Kapton HN, is also indicative of the inherently lower surface energy of the FPI films. Thus, one would also

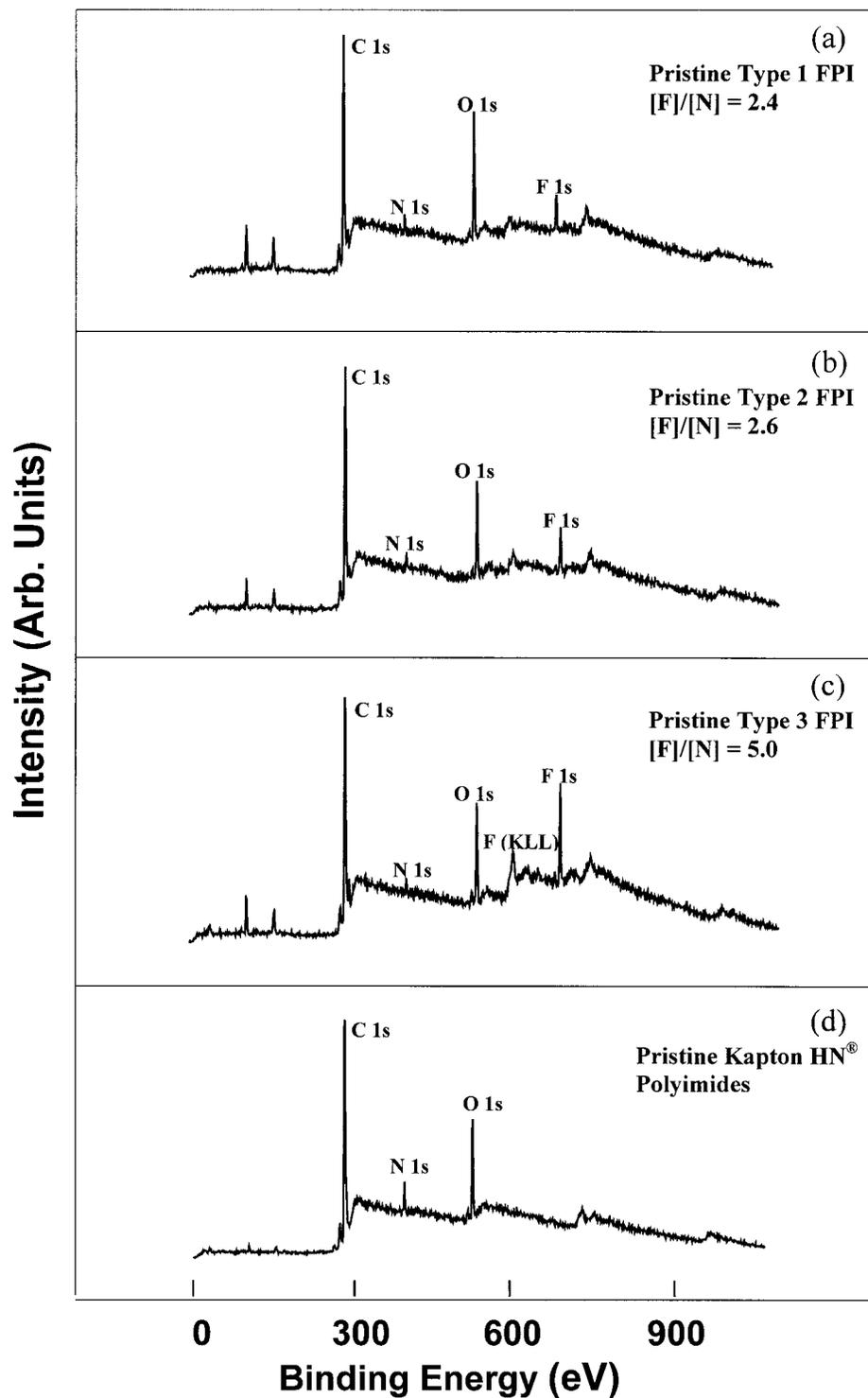


Figure 5 XPS wide scan spectra, obtained at the photoelectron take-off angle of 75° for pristine (a) Type 1 FPI, (b) Type 2 FPI, (c) Type 3 FPI, and (d) Kapton HN polyimide films.

expect a significantly reduced extent of moisture absorption by the FPI films. Ar plasma treatment not only causes a substantial in-

crease in the surface [O]/[C] ratio of each FPI film, but also results in a significant extent of surface defluorination. As a result, the water

Table I Elemental Composition, Water Contact Angle (θ), and Surface Roughness (Ra) of Pristine and Ar Plasma Treated Polyimide Films

Polyimide	Source	Elemental Composition (%)				θ ($^\circ$)	Ra (nm)
		C	N	O	F		
FPI (Type 1)	Obsd ^a	53.4	3.2	39.5	4.0	10, ^d 8 ^e	3.4
	Obsd ^b	65.8	4.4	19.2	10.7	94, ^d 91 ^e	5.9
	Calcd ^c	72.5	3.9	11.8	11.8		
FPI (Type 2)	Obsd	66.8	5.5	22.2	5.6	10, 9	1.1
	Obsd	67.2	4.0	18.6	10.2	93, 91	2.6
	Calcd	75.4	3.5	10.5	10.5		
FPI (Type 3)	Obsd	54.6	5.4	29.1	11.0	10, 9	1.2
	Obsd	64.6	3.6	14.5	17.3	98, 95	2.2
	Calcd	69.7	3.0	9.1	18.2		
Kapton HN	Obsd	66.1	8.7	25.2	0.0	7, 5	5.4
	Obsd	75.1	7.1	17.8	0.0	55, 48	1.4
	Calcd	75.9	6.9	17.2	0.0		

^a Based on the areas of the XPS spectra taken at $\alpha = 75^\circ$ after 20 s Ar plasma treatment.

^b Based on the areas of the XPS spectra taken at $\alpha = 75^\circ$ for the pristine polyimide film.

^c Calculation based on the stoichiometry of each repeating unit of the pristine polyimide film.

^d Water contact angle measured after 5 s.

^e Water contact angle measured after 60 s.

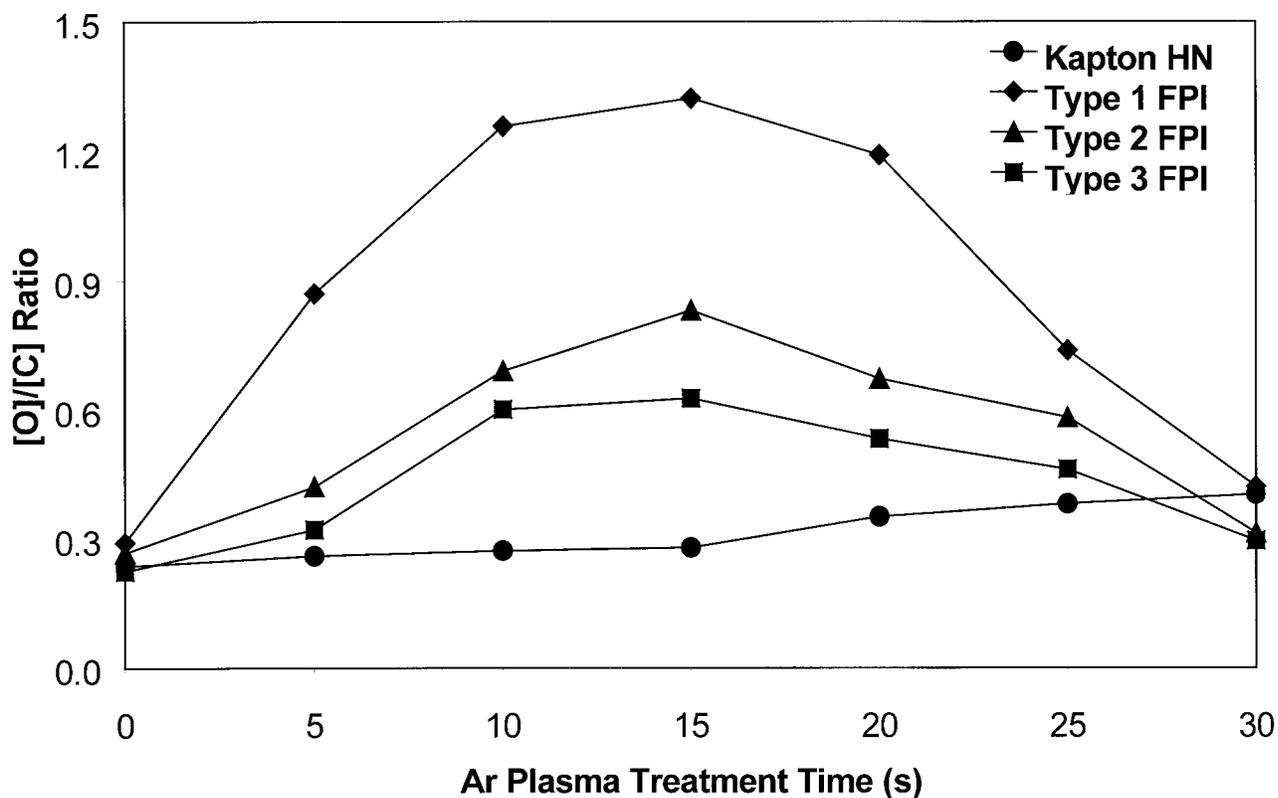


Figure 6 Effect of Ar plasma treatment on the surface [O]/[C] ratios of the various PI films.

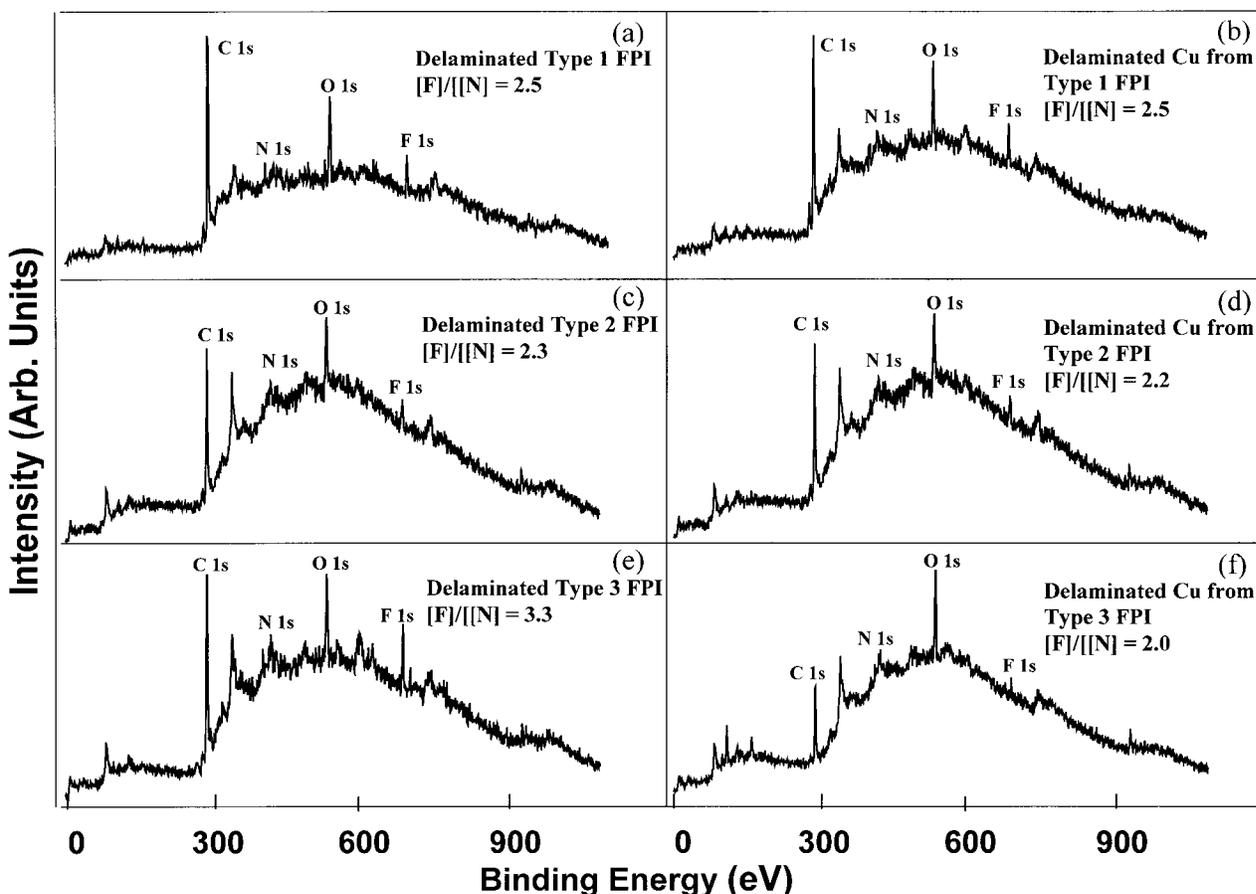


Figure 7 XPS wide scan spectra, obtained at the photoelectron take-off angle of 75° for the FPI and Cu surfaces after delamination from assemblies involving the three types of the FPI substrates.

contact angles of the FPI films decrease sharply after the plasma treatment (Table I).

For the characterization of the Cu/FPI interface, XPS wide scan spectra of the FPI and Cu surfaces, from mechanical delamination of the various Cu/VIDZ/FPI assemblies, are shown in Figure 7. All spectra show the presence of F 1s signals, albeit not of the same intensity. The baselines of these spectra are affected by the presence of a trace amount of Cu, which is represented by the core-level signal of Cu 2p at the BE range of about 925–950 eV. The relatively small amount of Cu gives rise to a relative weak signal, which is indistinguishable with the noise level of the spectra. The diffusion of the copper/VIDZ charged-transfer complex into the FPI films is believed to account for the presence of Cu on the delaminated FPI film surfaces. Despite the effect of Cu on the lineshapes of all the spectral in Figure 7, the spectra of the delaminated Type 1 FPI and Cu

surfaces from an assembly having a peel strength of 14 N/cm [Figs. 7(a) and 7(b)] are similar and comparable to that of the corresponding pristine FPI surface. The spectra of the delaminated Type 2 FPI and Cu surfaces from an assembly having a peel strength of 12 N/cm [Figs. 7(c) and 7(d)] are also similar to that of the corresponding pristine FPI surface. However, the spectra from the delaminated Type 3 FPI and Cu surfaces with a peel strength of 6 N/cm [Figs. 7(e) and 7(f)] show varied peak heights of C 1s, N 1s, and F 1s. In particular, the relative intensities of the N 1s peaks for both surfaces are higher than the pristine FPI films, and must be due to the contribution of the nitrogen from the VIDZ polymer. It is obvious that after the delamination, the failure mode is cohesive in nature for the Cu/FPI assemblies involving Type 1 and Type 2 FPI films, and is a combination of cohesive and adhesional failures for assemblies involving Type 3 FPI. The

failure from the last assembly is partially in the grafted VIDZ polymer layer and partially in the bulk of the FPI film. It is also apparent from Figures 2 and 3 that the adhesion strength using Type 3 FPI always shows lower values than those using the other two FPIs. The adhesion strength decreases in the order of increasing relative amount of fluorine content in the FPI, as indicated by the [F]/[N] ratio. It is reasonable to suggest that increasing fluorine content also contributes to the chemical inertness of the polymer surface. In the case of Type 3 FPI, which has the highest fluorine content among the three FPIs, the chemical inertness of the polymer surface has thus resulted in a reduced extent of graft copolymerization, even after the FPI has been subjected to Ar plasma pretreatment. It should be noted that regardless of the adhesion strength, the failure for assemblies using Types 1 and 2 FPIs is always within the bulk FPI, and that using Type 3 FPI is both within the VIDZ polymer layer and from the bulk FPI. This conclusion is also consistent with the fact that a substantially lower [F]/[N] ratio than that of the pristine Type 3 FPI is observed in the wide scan spectrum of the delaminated copper surface from assembly involving Type 3 FPI [compare Fig. 7(f) and Fig. 5(c)]. Nevertheless, the chemical structures of the Type 1 and Type 2 FPIs, which differ by the phenyl group in the ether linkages, can also affect the interactions with VIDZ during the thermal graft copolymerization process. Type 1 FPI consists of the phenyl-O-phenyl-O-phenyl linkage, whereas Type 2 FPI consists of the phenyl-O-phenyl-phenyl-O-phenyl linkage. The formal linkage is expected to be more flexible than the latter due to the lower steric hindrance to rotation of the -phenyl-O-bonds than the -phenyl-phenyl-O-bonds present in the latter. It is also expected that the more flexible linkage with higher free rotational energy around the oxygen bond of the ether linkage can give rise to better interactions with VIDZ during graft copolymerization.

CONCLUSION

The surface characteristics and metal adhesion properties of three types of FPI films were evaluated. The hydrophobic nature of the FPI films are indicated by their significantly larger water contact angles than that of the Kapton HN film, as well as by their relative insensitivity to the wetting water droplets as a function of time. Strong

adhesion between a FPI film and a copper foil can be achieved by direct thermal graft copolymerization of 1-vinyl imidazole onto FPI film with simultaneous lamination to the Cu foil under atmospheric conditions and in the absence of an added polymerization initiator. The adhesion strengths are substantially enhanced by a mere 10 s of Ar plasma pretreatment of the FPI films prior to the simultaneous grafting and lamination process. An optimum adhesion strength of 15 N/cm was achieved when the simultaneous grafting and lamination was carried out at 120°C for 4 h with the 5 s Ar plasma pretreated BAB-6FDA (Type 1) film. Strong adhesion between FPI and Cu arises from the charge transfer interactions between the VIDZ polymer and Cu, and the fact that the VIDZ polymer chains are tethered on the FPI film as a result of the graft copolymerization process.

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