Surface Modification of Poly(tetrafluoroethylene) Films by Graft Copolymerization for Adhesion Improvement with Evaporated Copper

Shaoyu Wu, E. T. Kang,* and K. G. Neoh

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

H. S. Han and K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

Received February 27, 1998; Revised Manuscript Received October 19, 1998

ABSTRACT: Surface modifications of Ar plasma-pretreated poly(tetrafluoroethylene) (PTFE) film via UV light-induced graft copolymerization with 1-vinylimidazole (VIDz) and glycidyl methacrylate (GMA) were carried out to improve the adhesion with evaporated copper. The surface compositions of the graft-copolymerized PTFE films were studied by X-ray photoelectron spectroscopy (XPS). The graft yield increases with the monomer concentration. The adhesion strength of the graft-copolymerized PTFE film and the evaporated copper is affected by the type of monomer used for graft copolymerization, the graft concentration, the plasma posttreatment time after graft copolymerization, and the extent of heat posttreatment after evaporation of copper. A double graft copolymerization process, which involved first the graft copolymerization with VIDz, followed by graft copolymerization with GMA, was also employed to enhance the adhesion of evaporated Cu to PTFE. The T-type peel strength of the PTFE/Cu interface so obtained is about 15 N/cm, which represents a 10-fold increase over that obtained when the PTFE film was treated by plasma only. The mechanism of the peel strength enhancement and the cohesive failure of the polymer−metal interface were also investigated.

Introduction

Poly(tetrafluoroethylene) (PTFE) has many desirable properties such as thermal stability, low dielectric constant, and surface inertness which make it ideal for microelecronic application.[1−3] Many studies on metallization of PTFE have been carried out.[4−6] But because of the surface inertness of PTFE, the adhesion between the polymer and various metals does not satisfy many of the industry requirements.[7] In many occasions, activation of polymer surfaces prior to metal deposition has been shown to enhance metal adhesion. The most widely used method for activating the PTFE surface is the treatment with a reducing etchant,[8,9] such as sodium naphthelene[10] and potassium *tert*-butoxide/benzoin/dimethy sulfoxide.[11] The etchant can affect not only the surface aspects of the polymer but also its bulk properties.[12] Apart from the wet chemical treatment, ion bombardment, X-ray irradiation, and cold plasma treatment have also been employed to activate the surface of PTFE.[13]

Gas plasma treatment, under various glow discharge conditions, has been used extensively in the surface modification of fluoropolymers. Recently, Shi et al.[14] reported on the improvement of adhesion between evaporated Cu and PTFE modified by N_2, O_2, H_2, and mixed-gas plasmas and proposed that Cu reacted with both oxygen and nitrogen to form respectively Cu−O and Cu−N moieties at the interface. Modification of polymer surface by graft copolymerization with specific functional monomers will also improve the adhesion properties.[15] Wang et al.[16] reported that the adhesion between two PTFE films could be substantially improved by graft copolymerization with certain functional monomers.

Vargo et al.,[17] on the other hand, reported that the metal ion-chelating organosilane was chemisorbed onto a plasma-hydroxylated fluoropolymer surface, and it exhibited excellent adhesion to some metals.

In the present work, surface modification of Ar plasma pretreated PTFE film was carried out via UV light-induced graft copolymerization with 1-vinylimidazole (VIDz) and glycidyl methacrylate (GMA) to enhance the adhesion of PTFE surface with evaporated copper metal. Physicochemical parameters affecting the adhesion between surface graft-copolymerized PTFE and evaporated copper, such as monomer concentrations, Ar plasma pretreatment time, and heat posttreatment temperature were studied. In addition, plasma posttreatment of the graft copolymerized surfaces to improve adhesion between PTFE and copper was also investigated. A novel surface modification method involving a double graft copolymerization process was also shown to be an effective means for enhancing the adhesion of metals to fluoropolymer surfaces. The chemical compositions of surface-modified PTFE film were characterized by X-ray photoelectron spectroscopy (XPS).

Experimental Section

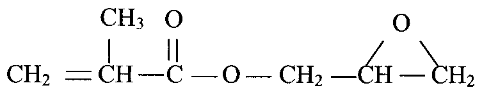
Materials. PTFE film having a thickness of about 0.01 cm and a density of 2.18 g/cm^3 was used in this study and was obtained from Goodfellow Inc. of Cambridge, U.K. The surface of the film was cleaned by Soxhlet extraction with acetone for 6 h before use. The monomers 1-vinylimidazole (VIDz) and glycidyl methacrylate (GMA) and the solvent 1,4-dioxane used for surface graft copolymerization were obtained from Aldrich

---

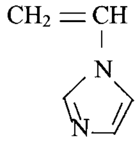
* To whom correspondence should be addressed. Fax (65) 779−1936, e-mail cheket@nus.edu.sg.

10.1021/ma9803133 CCC: $18.00

Chemical Co. of Milwaukee, WI. The chemical structures of GMA and VIDz monomers are shown below:



GMA



VIDz

Graft Copolymerization and Plasma Posttreatment. The PTFE films were cut into strips of about 2 cm × 3 cm in size. They were pretreated with Ar plasma before graft copolymerization. A cylindrical type glow discharge cell, model SP100, manufactured by Anatech Ltd. of USA was used for plasma treatment. The plasma power applied was kept at 30 W at a radio frequency of 40 kHz. The film was placed between the two electrodes and subjected to glow discharge for a predetermined period of time at an Ar pressure of 0.5 Torr. The Ar plasma-pretreated polymer films were then exposed to the atmosphere to affect the surface peroxide formation[18] before graft copolymerization. The pretreated PTFE films were immersed in 30 mL of 1,4-dioxane monomer solutions in a Pyrex tube. The concentrations of each monomer were varied from 5 to 70 vol %. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. It was then subjected to UV irradiation for 30−60 min in a Riko Rotary mode, RH 400-10W photochemical reactor, manufactured by Riko Denki Kogyo of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV light-induced graft copolymerizations were carried out at a constant temperature of 28 °C. After each grafting experiment, the PTFE film was washed with copious amounts of acetone to remove the residual monomer and adsorbed homopolymer.

In the double graft copolymerization process, the graft modified film was subjected to a second round of Ar plasma treatment and then subjected to the UV light-induced graft copolymerization with the second monomer. Plasma posttreatment after grafting was carried out under the same glow discharge conditions as mentioned above with purified Ar and O_2.

XPS Measurement. XPS measurement was made on a VG ESCALAB MKII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron takeoff angle of 75° (with respect to the sample surface). The X-ray source was run at a reduced power of 120 W. The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. In the peak synthesis, the line width (full width at half-maximum, fwhm) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. Each XPS data point was the average of at least three sample measurements.

Water Contact Angle Measurement. The static water contact angles were measured at 25 °C and 50% relative humidity using a telescopic goniometer (Rame-Hart model 100-00(230)). The telescope with a magnification power of 23× is equipped with a protractor of 1° graduation. For each angle reported, at least five readings were averaged.

T-Type Peel Strength Measurement. A copper layer of 1000 Å in thickness was thermally evaporated onto the surface of the PTFE film in a model LEE-400 vacuum evaporator (JEOL, Japan). The deposition was carried out at a pressure of 10^{-6} Torr or less and at a deposition rate of about 5 Å/s. The metallized sample was posttreated in a vacuum oven at different temperatures. The metallized surface was adhered to a copper sheet (0.1 mm in thickness) using an epoxy adhesive. The assembly was cured at 100 °C for 2 h or at room temperature for 24 h. The assembly was then subjected to T-peel test in an Instron model 5544 materials tester. All measurements were carried out a crosshead speed of 1.0 cm/min. For each T-type peel strength reported, at least three sample measurements were averaged.

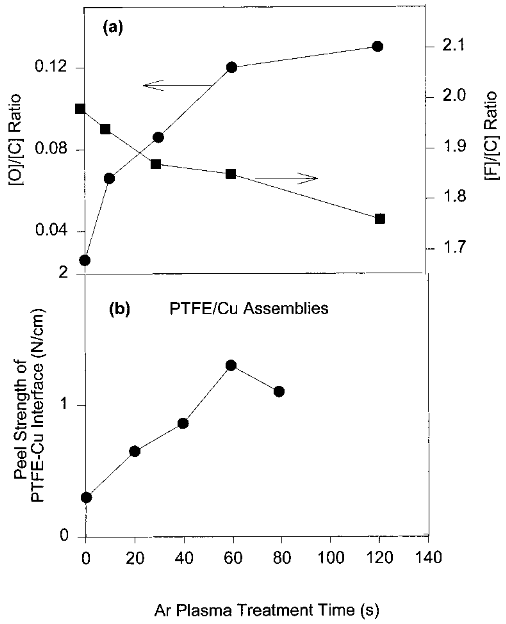


Figure 1. Effect of Ar plasma treatment time on (a) the [O]/[C] and [F]/[C] ratios of the PTFE surface and (b) the peel strength of PTFE and copper interface.

Results and Discussion

Surface Modification of PTFE Films via Ar Plasma Treatment: The PTFE/Cu Assemblies. The changes in the [F]/[C] and [O]/[C] atomic ratios, as determined from the corrected C 1s, O 1s, and F 1s core-level spectral peak-area ratios at the photoelectron takeoff angle (α) of 75°, as a function of the Ar plasma treatment time are shown in Figure 1a. An increase in the [O]/[C] ratio and a decrease in the [F]/[C] ratio were observed upon increasing the Ar plasma treatment time, in agreement with the results generally reported in the literature.[16] The Ar plasma treatment causes the breakage of some C−F bonds, resulting in the defluorination of the film surface. The subsequent exposure of the activated surface to air causes oxygen to be incorporated on the PTFE surfaces, leading to surface oxidation and the formation of peroxide and hydroxyl peroxide species.[18] The peroxide species can be utilized to initiate the surface free-radical polymerization in a mechanism generally proposed for the UV light-induced graft copolymerization. Figure 1b shows the effect of Ar plasma treatment time of the PTFE film on the T-peel adhesion strength of evaporated Cu. It was found that the simple plasma treatment of the PTFE surface could enhance the peel strength of the PTFE−Cu interface to about 1.3 N/cm from the value of about 0.3 N/cm for evaporated Cu on pristine PTFE film.

Surface Modification of PTFE Films via Graft Copolymerization with 1-Vinylimidazole: The PT-

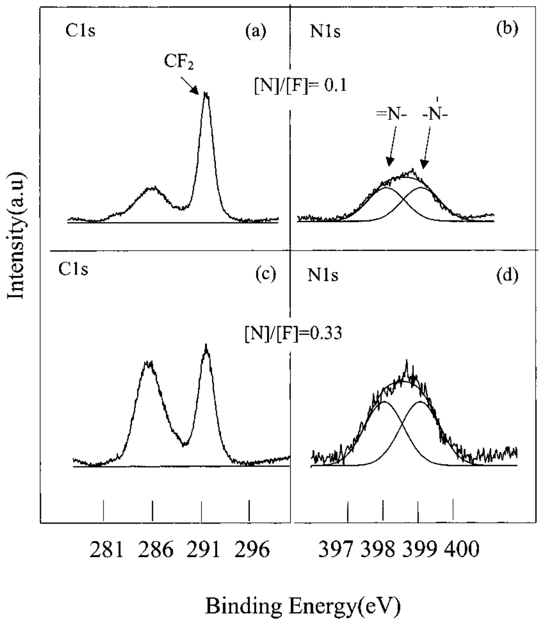


Figure 2. C 1s and N 1s core-level spectra of the VIDz graft-polymerized PTFE surfaces from graft copolymerization of the 60 s Ar plasma-pretreated PTFE films in (a, b) 5 vol % and (c, d) 20 vol % VIDz monomer solutions.

FE/VIDz/Cu Assemblies. It has been reported[19,20] that the benzimidazole interacted with copper metal at zero oxidation state to form a complex. Inagaki et al.[21] reported that the adhesion between Kapton film and evaporated copper was increased by 2.9 times after the Kapton film surface had been modified by graft copolymerization with 1-vinylimidazole (VIDz). Figure 2 shows the C 1s and N 1s core-level spectra, obtained at α of 75°, for a 60 s Ar plasma-pretreated PTFE film after having been subjected to UV light-induced graft copolymerization in different concentrations (5 and 20 vol %) of VIDz solution for 30 min. The presence of surface-grafted VIDz polymer can be deduced from the appearance of a low binding energy (BE) C 1s core-level spectrum centered at about 284.6 eV and the N 1s core-level signal. The N 1s core-level spectra can be curve-fitted with two peaks components of about equal sizes at BEs of 398.2 and 399.5 eV, arising from the =N– and –N– species, respectively, of the VIDz polymer.[22] The C 1s peaks component at the BE of 291.2 eV, on the other hand, can be attributed to the CF_2 species of the PTFE substrate. The graft concentration, defined as the number of repeating units of VIDz polymer per repeating CF_2 unit of the PTFE substrate, can be determined simply from the [N]/[F] ratio, as each VIDz unit also contains two nitrogen atoms.

The graft concentration as a function of monomer concentration used for graft copolymerization is summarized in Figure 3. The [N]/[F] ratio increases with the monomer concentration up to a monomer concentration of about 20 vol %, after which the graft yield tends to decrease gradually, probably as a result of excess homopolymerization in the concentrated reaction mixture which attenuates the intensity of the UV light reaching the PTFE surface. The water contact angle of the graft copolymerized surface as a function of VIDz monomer concentration used for graft copolymerization is shown in Table 1. The changes in surface hydrophilicity are in general agreement with the changes in graft concentration in Figure 3. Figure 3 also shows the effect of graft concentration, expressed in terms of the VIDz monomer concentration, on the T-type peel strength of the PTFE–Cu interface at different curing temperatures. The optimum peel strengths, especially for sample cured at elevated temperature after the metal evaporation, coincide with the maximum in graft concentration at a monomer concentration of about 20 vol %. This result testifies to the effective contribution of the grafted VIDz polymer in improving the adhesion strength of copper metal to the modified surface. The peel strength is substantially enhanced for an interface cured at elevated temperature after the metal evaporation. Thus, the charge-transfer interaction between the evaporated Cu and the grafted VIDz units is promoted by exposure to high temperature.

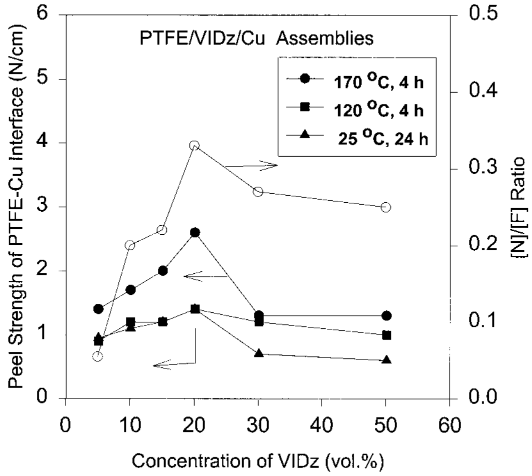


Figure 3. Effect of monomer concentration on the graft concentration and the peel strength of VIDz graft-polymerized PTFE–copper interface (Ar plasma pretreatment time = 60 s, UV time = 30 min).

Table 1. Water Contact Angles of the VIDz and GMA Graft-Copolymerized PTFE Film Surfaces[a]

concn of VIDz (vol %)	contact angle (deg)	concn of GMA (vol %)	contact angle (deg)
5	71	10	82
10	61	20	63
20	40	30	54
30	64	50	52
50	70	70	51

[a] Water contact angle of the pristine PTFE film surface is 118°.

The effect of plasma posttreatment of the VIDz graft copolymerized PTFE surface before Cu evaporation on the peel strength of the resulting PTFE/VIDz/Cu assemblies was also studied in this work. The results are shown in Table 2 for assemblies prepared from the 60 s Ar plasma-pretreated PTFE substrates with 30 min of UV-induced graft copolymerization in 20 vol % VIDz solution. The peel strength of the PTFE–Cu interface increases with increasing Ar or oxygen plasma posttreatment time to about 4.5 N/cm, which is almost twice that of the sample without the plasma posttreatment after graft copolymerization (Figure 3) or 3 times that of the PTFE substrate with plasma pretreatment alone (Figure 1b). Thus, the peel strength between VIDz graft-copolymerized PTFE and copper is readily affected by the graft yield, as well as the extents of plasma posttreatment after graft copolymerization and heat posttreatment after metal evaporation.

Surface Modification of PTFE Films via Graft Copolymerization with Glycidyl Methacrylate: The PTFE/GMA/Cu Assemblies. Figure 4 shows the C 1s

Table 2. Effect of Plasma Posttreatment on the Peel Strength of PTFE/VIDz/Cu, PTFE/GMA/Cu, and PTFE/VIDz-GMA/Cu Assemblies (with 4 h of Curing at 170 °C) and on the Ratios of the Oxidized Carbon Species on the GMA Polymer Grafted PTFE Film Surface

plasma posttreatment time (s)	{[C=O] + [O−C−O]}/[C][d]	peel strength (N/cm)				
		PTFE/VIDz/Cu[a]		PTFE/GMA/Cu[b]		PTFE/VIDz−GMA/Cu[c]
		Ar	O_2	Ar	O_2	O_2
0	0	2.4	2.4	4.3	4.3	9.7
10	0.05	2.7	2.6	12.2	7.8	11.5
20	0.07	3.4	3.1	11.8	11.2	12.6
40	0.12	3.5	4.5	8.3	15.4	15.3
60	0.14	3.2	3.4	6.4	12.1	10.2

[a] For VIDz graft copolymerization: Ar plasma pretreatment time = 60 s, UV time = 30 min, and VIDz monomer concentration = 20 vol %. [b] For GMA graft copolymerization: Ar plasma pretreatment time = 60 s, UV time = 1 h, and GMA monomer concentration = 50 vol %. [c] For VIDz−GMA double graft copolymerization: combining the graft copolymerization conditions of VIDz and GMA. [d] Ratio of GMA graft polymerized PTFE surface after O_2 plasma posttreatment.

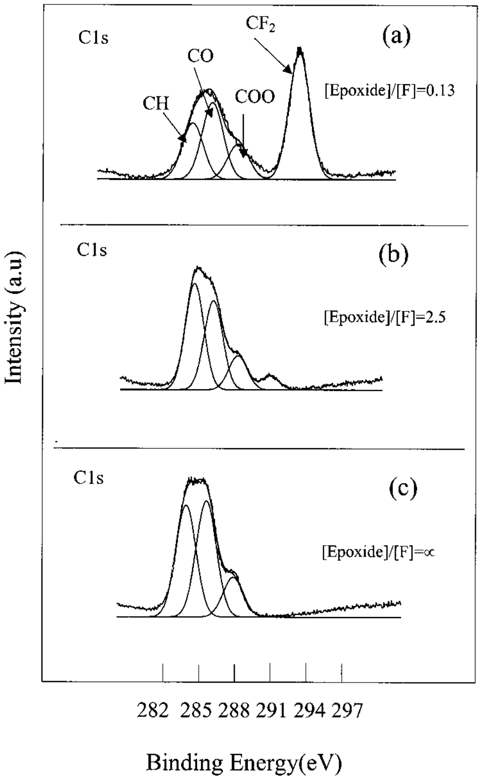


Figure 4. C 1s core-level spectra of GMA graft-polymerized PTFE surface: (a) [epoxide]/[F] = 0.13; (b) [epoxide]/[F] = 2.5; (c) [epoxide]/[F] = ∝.

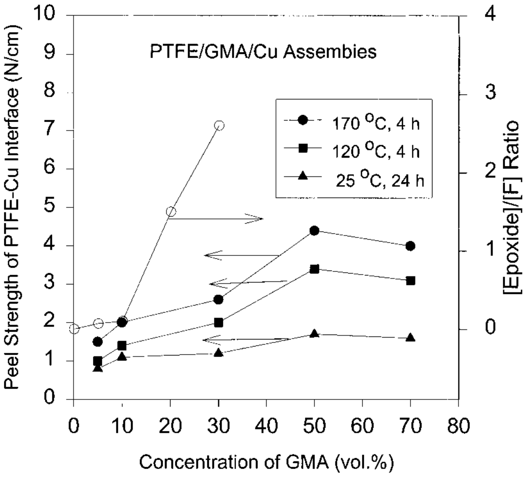


Figure 5. Effect of monomer concentration on the graft concentration of GMA copolymer on the PTFE surface and on the peel strength of GMA graft-polymerized PTFE−copper interface (Ar plasma pretreatment time = 60 s, UV time = 1 h).

core-level spectra for a 60 s Ar plasma-pretreated PTFE film after having been subjected to UV light-induced graft copolymerization in different concentrations (10, 30, and 50 vol %) of GMA solution for 1 h. The presence of surface-grafted GMA polymer can be deduced from the three C 1s peak components with BEs similar to those of the GMA homopolymer:[16] 284.6 eV for the C−H species, 286.2 eV for the CO species, and 288.5 eV for the COO species, in an area ratio of about 3:3:1. The graft concentrations, defined in this case as the [epoxide]/[F] ratios and derived from the *C*OO to F 1s spectral component area ratios (as each GMA molecule has one *C*OO species and one epoxide unit), of the corresponding samples as a function of the concentration of GMA monomer used during graft copolymerization are also shown in Figure 5. The [epoxide]/[F] ratio increases with increasing concentration of the GMA monomer. The water contact angle of the GMA graft copolymerized surface as a function of GMA monomer concentration is shown in Table 1. The changes in hydrophilicity are in agreement with the changes in graft concentration shown in Figure 5.

The effect of graft concentration, expressed in terms of the GMA monomer concentration, on the peel strength of the surface graft-copolymerized PTFE and evaporated Cu is shown in Figure 5. The peel strength increases with increasing concentration of the GMA monomer or the concentration of the grafted GMA polymer. Thus, the effective contribution of the grafted GMA polymer in improving the adhesion with copper metal is again ascertained. The heat posttreatment after evaporation of copper was also studied, and the results are also summarized in Figure 5. The peel strength, again, is enhanced by the heat posttreatment of the polymer−metal interface. A maximum peel strength of about 4.3 N/cm was obtained after 4 h of curing at 170 °C. The enhanced adhesion may have resulted from the increased extent of charge-transfer interaction between the epoxide group and Cu at elevated temperature. The peel strength can be further enhanced if the GMA graft-copolymerized PTFE surfaces are treated with Ar or oxygen plasma before the metal evaporation. Relevant results were also shown in Table 2. The peel strength increases from 4.3 N/cm for the nonplasma-posttreated sample to 15.4 N/cm for the sample with 40 s of oxygen plasma posttreatment before metallization. Two mechanisms are probably operative to account for the enhanced peel strength. The plasma posttreatment introduces additional polar groups, such as the carbonyl and

Table 3. Effect of Ethylenediamine Treatment on the [N]/[C] Ratios of the GMA Graft Copolymerized PTFE Film Surfaces before and after Plasma /Heat Treatment

sample	[N]/[C]
PTFE film graft copolymerized with GMA	0.052
after heat treatment at 170 °C for 4 h	0.056
after 60 s O_2 plasma treatment, then heating at 170 °C for 4 h	0.055

hydroxyl groups (see below); the latter not only promotes the interaction with the evaporated metal but also can participate in the curing or cross-linking reaction of the epoxy groups.

The effects of heat and plasma posttreatments on the epoxide functional groups of the grafted GMA polymer are evaluated as follows. The various PTFE films with surface-grafted GMA polymer were immersed in 10 vol % dioxane solution of ethylenediamine overnight and then transferred into an excess volume of acetone for 48 h, followed by washing with copious amounts of acetone to remove the residue amine. The data in Table 3 indicate that the [N]/[C] ratios for the heat-treated and post-plasma-treated samples differ only slightly from that of the original, as-grafted surface. The data in Table 3 thus suggest that the epoxide rings of the grafted GMA polymer remain intact, even after heat and plasma treatment as they remain active toward the diamine curing agent. Furthermore, for the ethylenediamine-treated samples, the adhesion strengths with evaporated Cu decreased readily by more than 1 order of magnitude. All of these results indicate that the enhanced peel strengths are attributable predominantly to the increased extent of interaction between the epoxide groups of the GMA polymer and copper metal after the heat or plasma posttreatment. Figure 6 shows the C 1s core-level spectra of a GMA graft-copolymerized PTFE film before and after 20 and 60 s of oxygen plasma posttreatments. The new C 1s peak component at the BE of 287.7 eV, which appears after the plasma posttreatment, may be assigned to the O−C−O or C=O species.[23] The proportion of this new component increases with increasing plasma posttreatment time, as shown in Table 2. As the appearance of this new species is also accompanied by the partial reduction in the proportion of the C−O species, some of the latter species must have been further oxidized by the plasma posttreatment. Now as the epoxide group concentration is not significantly affected by the plasma posttreatment, as suggested by the results of ethylenediamine reaction (Table 3), the CO species which undergoes further oxidation must have involved predominantly the CO unit outside the epoxide ring (see chemical structure of GMA in the Experimental Section). The postulation is also consistent with the observation that the proportion of the oxidized species approaches an asymptotic value of about 0.14 (or 1 out of every 7 carbon atoms) in Table 2. Furthermore, the C 1s line shapes of the oxygen plasma-posttreated samples in Figure 6 do not suggest the production of any significant amount of carboxylic acid groups under the present glow discharge conditions.

Generally, for the improvement of adhesion with Cu, GMA is a better choice for surface graft copolymerization with PTFE than VIDz. In both cases, the peel strengths are dependent on the graft concentrations, heat posttreatment, and Ar or oxygen plasma posttreatment. The maximum peel strength between the GMA graft-copolymerized PTFE and copper can reach up to about 15 N/cm, which represents a 10-fold increase over that achievable with PTFE subjected to Ar plasma pretreatment alone or an over 3-fold increase over that achievable with the VIDz graft-copolymerized PTFE−Cu interface. Our recent in situ XPS studies on the metallization of GMA graft-copolymerized PTFE films have revealed strong interactions between the evaporated metal atoms and the epoxide functional groups of the graft chains. The C−O peak intensity of the C 1s core-level spectrum decreased steadily with increasing metal coverage, while the COO group concentration only showed a slight decrease. The interfacial reactions between the evaporated metal atoms and the various types of graft-modified PTFE surfaces will be reported shortly in a separate communication.

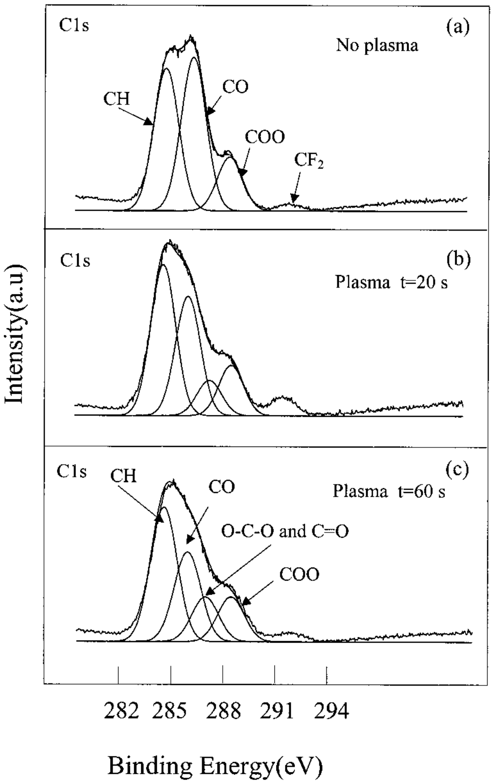


Figure 6. C 1s core-level spectra of the GMA graft-polymerized PTFE surface (GMA concentration = 50 vol %, Ar plasma pretreatment time = 60 s, UV time = 1 h) before and after O_2 plasma posttreatment.

Surface Modification of PTFE Films via Double Graft Copolymerization: The PTFE/VIDz−GMA/Cu Assemblies. In the present work, double graft copolymerization or double grafting is taken to mean that a second monomer is graft-copolymerized onto the surface of a PTFE film that has been previously modified also by graft copolymerization.

Figure 7a shows the C 1s core-level spectrum of the PTFE film after modification via graft copolymerization in 20 vol % VIDz solution. The corresponding C 1s core-level spectra of the VIDz polymer-modified PTFE surface after further graft copolymerization in 5 and 50 vol % GMA solutions are shown in Figure 7, b and c, respectively. The C 1s core-level spectra suggest the presence of both types of grafted polymer at moderate extent of grafting (Figure 7b). On the other hand, the use of a high monomer concentration during the second grafting process has resulted in the complete coverage of the PTFE−VIDz surface by GMA (Figure 7c). The peel strengths of the PTFE/Cu interface as a function of the grafted VIDz polymer concentration (expressed

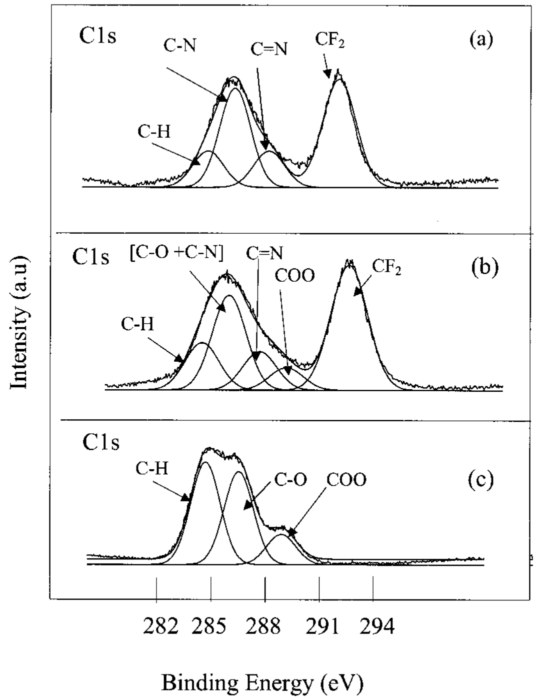


Figure 7. C 1s core-level spectra of the PTFE film surface after (a) graft copolymerization in 20 vol % VIDz solution, followed by graft copolymerization in (b) 5 vol % and (c) 50 vol % GMA solution.

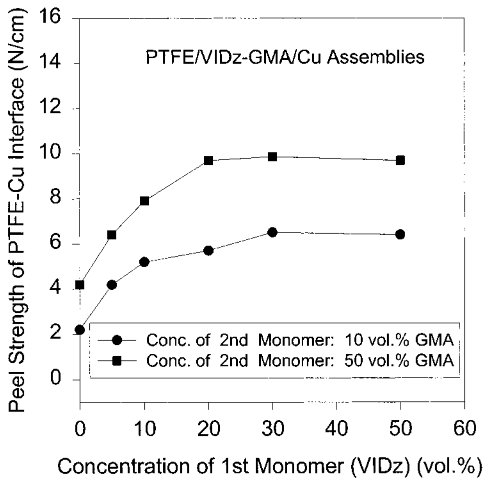


Figure 8. Effect of concentration of the first monomer (VIDz) on the peel strength of the doubly graft-copolymerized PTFE−copper interface.

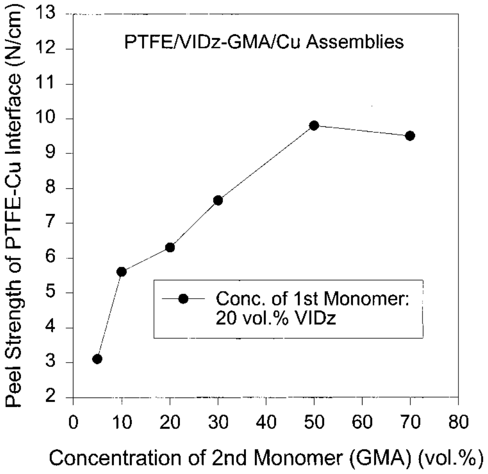


Figure 9. Effect of concentration of the second monomer (GMA) on the peel strength of the doubly graft-copolymerized PTFE−copper interface.

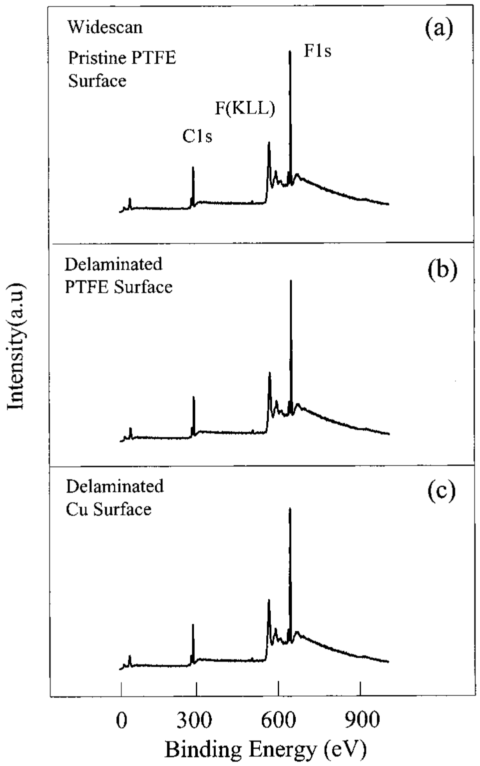


Figure 10. XPS wide-scan spectra of (a) the pristine PTFE and (b, c) the delaminated PTFE and Cu surfaces from a PTFE/GMA/Cu assembly having a peel strength of about 7 N/cm.

as the VIDz monomer concentration used for grafted copolymerization) after further modification by 60 s of Ar plasma treatment, followed by 1 h of UV graft copolymerization in 10 and 50 vol % GMA solutions, are shown in Figure 8. The peel strengths reported are obtained after the PTFE/VIDz−GMA/Cu assemblies have been cured at 170 °C for 4 h. In comparison with the similarly cured PTFE/VIDz/Cu assemblies (Figure 3) and the PTFE/GMA/Cu assemblies (Figure 5), the adhesion strength of the doubly graft-copolymerized PTFE−Cu interfaces have been enhanced to beyond the linear combination of the effects of the individual polymer graft, particularly at high concentrations of the VIDz monomer. The effect of concentration of the second monomer (GMA) used for graft copolymerization on the peel strength of a 20 vol % VIDz graft copolymerized PTFE surface is shown in Figure 9. Again, the synergetic effect from the simultaneous presence of both grafts on the resulting peel strength is discernible. The synergetic effect from double grafting must have resulted from the fact that the nitrogen moieties of the VIDz ring (tertiary amine structure) can promote the curing or cross-linking reactions of the epoxide groups of GMA polymer. The effect of O_2 plasma posttreatment prior to metal evaporation on the peel strength of the doubly grafted PTFE/VIDz−GMA/Cu assembly is also shown in Table 2. Thus, the peel strength of the doubly grafted PTFE and copper interface can be further enhanced from 10 N/cm to a maximum value of over 15 N/cm by O_2 plasma posttreatment of the graft-modified PTFE surface prior to Cu evaporation.

The effect of the graft microstructure on the peel strength of the PTFE−Cu interface is illustrated by the

Table 4. Effect of GMA and VIDz Concentration in the 50 vol % Dioxane Solution of Mixture on the Peel Strength (N/cm) of PTFE−Cu Interface

GMA:VIDz	peel strength	GMA:VIDz	peel strength
0:50	1.3	40:10	2.4
10:40	1.1	50:0	4.3
30:20	1.6		

Table 5. Comparison of the Peel Strength of the PTFE/GMA−VIDZ/Cu Assembly with that of the Other Assemblies

	peel strength (N/cm)	
assembly	no plasma posttreatment	O_2 plasma posttreatment for 40 s
PTFE/GMA−VIDz/Cu[a]	3.5	8.2
PTFE/VIDz−GMA/Cu[b]	9.7	15.3
PTFE/GMA/Cu[c]	4.3	15.4
PTFE/VIDz/Cu[c]	2.4	4.5

[a] GMA was graft copolymerized first, followed by VIDz. [b] VIDz was graft copolymerized first, followed by GMA (data fromTable 2). [c] Data from Table 2.

result of Table 4. When the 60 s Ar plasma-pretreated PTFE films were subject to 60 min of UV-induced graft copolymerization in 50 vol % dioxane solutions of GMA and VIDz monomer mixtures, no synergetic effect as in the previous case of double grafting were observed. In the double-grafting process, the sequence of graft copolymerization of the monomers also has a profound effect on the subsequent peel strength of the PTFE−Cu interface, at least for the VIDz−GMA pair studied in this work. The peel strength of the PTFE/GMA−VIDz/Cu assembly, obtained from 60 min of UV induced graft copolymerization of a 60 s Ar plasma-pretreated PTFE film, first in 50 vol % GMA solution and then in 20 vol % VIDz solution after the second 60 s of Ar plasma pretreatment, is compared to that of the PTFE/VIDz−GMA/Cu assembly, prepared under the same conditions but with the first graft copolymerization carried out in 20 vol % VIDz solution in Table 5. Two other relevant assemblies, viz., the PTFE/GMA/Cu and PTFE/VIDz/Cu assemblies prepared with graft copolymerization carried out in 50 vol % GMA solution and 20 vol % VIDz solution, respectively, are also included in Table 5. The fact that the peel strength of the PTFE/GMA−VIDz/Cu assembly is lower than those of the PTFE/VIDz−GMA/Cu and the PTFE/GMA/Cu assemblies suggests that the interfacial cross-linking is less effective when GMA is graft copolymerized before VIDz. Some of the epoxide groups of GMA probably have been deactivated or consumed during the second grafting process.

The Failure Mode of Graft-Polymerized PTFE and Copper Interface. The failure mode of the PTFE−Cu interfaces obtained from the evaporation of the copper metal onto the graft-modified PTFE surfaces was briefly investigated. Figure 10a−c shows the respective wide-scan spectra of the pristine PTFE surface and the delaminated surfaces of a PTFE/GMA/Cu assembly having a peel strength of about 7 N/cm. The XPS-derived elemental compositions for the three surfaces are summarized in Table 6. The XPS wide-scan spectra of the delaminated PTFE and Cu surfaces are grossly similar to that of the pristine PTFE surface. For the delaminated PTFE surface, the surface [F]/[C] ratio is also almost identical to that of the pristine PTFE. On the other hand, however, the [F]/[C] ratio for the delaminated Cu surface is slightly below 2, probably due to contributions of carbon signal from the grafted GMA polymer in the subsurface region which is within the probing depth of the XPS technique. The fact that the wide-scan spectrum of the delaminated Cu surface resembles that of the pristine PTFE surface, together with the fact that virtually no Cu signal was detected on the delaminated Cu surface, readily suggests that the polymer−metal interface delaminated by cohesive failure inside the PTFE substrate. In fact, for all the PTFE−Cu assemblies studied in the present work, clean cohesive failure of the polymer−metal interface is always observed when the peel strength of the assembly exceeds 5 N/cm.

Table 6. Comparison of the Surface Atomic Ratios among the Pristine PTFE Film and the Delaminated Surface of a PTFE/GMA/Cu Assembly

sample	[F]/[C]	[O]/[C]	[Cu]/[C]
pristine PTFE surface	1.98	0.010	0
delaminated PTFE surface	1.98	0.040	0
delaminated Cu surface	1.76	0.043	0

Conclusion

Ar plasma-pretreated PTFE films are subjected to further surface modification via UV light-induced graft copolymerization with VIDz, GMA, or both monomers. The microstructure and composition of the graft-copolymerized PTFE surface were analyzed by XPS. In general, the graft yield increases with the concentration of monomer used during graft copolymerization. The peel adhesion strength between the graft-modified PTFE film and evaporated copper is enhanced by plasma posttreatment prior to metal evaporation and by thermal treatment or curing after the evaporation of the metal. Heat curing promotes the interactions between the grafted functional groups and metal, while plasma posttreatment introduces additional functional groups that provide additional sites for interaction with the evaporated Cu and may have also promoted cross-linking reactions in the graft layer. A novel approach that involves the consecutive surface graft copolymerizations of VIDz and GMA has been shown to be very effective in enhancing the adhesion between PTFE and Cu. A T-type peel strength in excess of 15 N/cm was achieved between evaporated Cu and the doubly graft-copolymerized PTFE surface. This adhesion strength represents a 10-fold increase over that of the PTFE surface treated by plasma alone. The failure mode of the present graft-modified PTFE and copper laminates is cohesive in nature when the peel strength of the polymer−metal interface exceeds 5 N/cm.

References and Notes

(1) Park, J. M.; Matienzo, L. J.; Spencer, D. F. *J. Adhes. Sci. Technol.* **1991**, *5*, 153.
(2) Granneman, E. H. A. *Thin Solid Films* **1993**, *228*, 1.
(3) Silvain, J. F.; Ehrhardt, J. J.; Picco, A.; Lutgen, P. *ACS Symp. Ser.* **1990**, *440*, 453.
(4) Vopel, S. L.; Schowhom, H. *J. Appl. Polym. Sci.* **1979**, *23*, 495.
(5) Chang, C. A.; Kim, Y. K.; Schrott, A. G. *J. Vac. Sci. Technol.* **1990**, *A8*, 3304.
(6) Shi, M. K.; Lamentagne, B.; Selmani, A.; Martinu, L.; Sacher, E.; Wertheimer, M. R.; Yelon, A. *J. Vac. Sci. Technol.* **1994**, *A12*, 29.
(7) Sacher, E. *Prog. Surf. Sci.*. **1994**, *47*, 273.
(8) Celerier, A.; Machet, J. *Thin Solid Films* **1987**, *148*, 323.
(9) Mathieson, I.; Brewis, D. M.; Sutherland, I.; Cayless,R. A. *J. Adhes.* **1994**, *46*, 49.
(10) Costello, C. A.; MacCarthy, T. J. *Macromolecules* **1984**, *17*, 2940.

(11) Huang, M.; Burch, R. R. *J. Appl. Polym. Sci.* **1995**, *55*, 549.
(12) Badey, J. P.; Espuche, E. U.; Jugnet, Y.; Sage, Tran Minn Due, D.; Chabent, B. *Polymer* **1994**, *35*, 2472.
(13) Liston, E. M.; Martinn, L.; Wertheiner, M. R. *J. Adhes. Sci. Technol.* **1993**, *7*, 1091.
(14) Shi, M. K.; Selmani, A.; Martinu, L.; Sacher, E.; Wertheimer, M. R.; Yelon, A. In *Polymer Surface Modifications: Relevance to Adhesion*; Mittal, K. L., Eds.; VSP: The Netherlands, 1995; p 73.
(15) Kang, E. T.; Tan, K. L.; Kato, K.; Uyama, Y.; Ikada, Y. *Macromolecules* **1996**, *29*, 6872.
(16) Wang, T.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Cui, C. Q; Lim, T. B. *J. Adhes. Sci. Technol.* **1997**, *11*, 679.
(17) Vargo, T. G.; Gardellar, J. A., Jr.; Calvert, J. M.; Chen, M. *Science* **1993**, *262*, 1711.
(18) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.
(19) Xue, G.; Dai Q.; Jiang, S. *J. Am. Chem. Soc.* **1988**, *110*, 2393.
(20) Xue, G.; Shi, G.; Ding, J.; Chang, W.; Chen, R. *J. Adhes. Sci. Technol.* **1992**, *4*, 723.
(21) Inagaki, N.; Tasaka, S.; Masumoto, M. *Macromolecules* **1996**, *29*, 1642.
(22) Ang, A. K. S.; Kang, E. T.; Noeh, K. G.; Tan, K. L. *J. Adhes. Sci. Technol.* **1998**, *12*, 889.
(23) Jama, C. J.; Dessaux, O.; Goudmand, P.; Gengembre, L.; Grimblot, *J. Surf. Interface Anal.* **1992**, *18*, 751.

MA9803133