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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### **SURFACE MODIFICATION OF POLY(VINYLIDENE FLUORIDE) FILMS BY GRAFT COPOLYMERIZATION FOR ADHESION IMPROVEMENT WITH EVAPORATED METALS**

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Online publication date: 26 September 2000

**To cite this Article** Liu, Y. X. , Kang, E. T. , Neoh, K. G. and Tan, K. L.(2000) 'SURFACE MODIFICATION OF POLY(VINYLIDENE FLUORIDE) FILMS BY GRAFT COPOLYMERIZATION FOR ADHESION IMPROVEMENT WITH EVAPORATED METALS', *Journal of Macromolecular Science, Part A*, 37: 10, 1121 – 1139

**To link to this Article:** DOI: 10.1081/MA-100101144

**URL:** <http://dx.doi.org/10.1081/MA-100101144>

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## **SURFACE MODIFICATION OF POLY(VINYLIDENE FLUORIDE) FILMS BY GRAFT COPOLYMERIZATION FOR ADHESION IMPROVEMENT WITH EVAPORATED METALS**

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Key Words: PVDF, Surface Graft Copolymerization, Plasma, Peel Strength, Aluminum, Copper

### **ABSTRACT**

Surface modification of Ar plasma pretreated poly(vinylidene fluoride) (PVDF) films via UV-induced graft copolymerization with glycidyl methacrylate (GMA) and 1-vinyl imidazole (VIDz) was carried out to improve the adhesion with evaporated metals, such as aluminum and copper. The surface compositions of the graft copolymerized PVDF films were determined by X-ray photoelectron spectroscopy (XPS). The adhesion strengths

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were affected by the type of monomer used for graft copolymerization, the plasma pretreatment time of the PVDF film, the UV graft copolymerization time, and the interaction between the metal and the grafted polymer. T-peel adhesion strengths in excess of 8 and 10 N/cm were obtained, respectively, for the Cu/graft-modified PVDF and Al/graft-modified PVDF laminates. The failure mode for the laminates was found to be strongly dependent on the adhesion strength. The strong adhesion between the metal (Cu or Al) and the surface modified PVDF film arises from the strong interaction between the functional moiety of the grafted chain and the evaporated metal atom, as well as the fact that the graft chains are covalently tethered on the PVDF film surface as a result of the surface graft copolymerization process.

## INTRODUCTION

As a fluoropolymer, poly(vinylidene fluoride) (PVDF) has many desirable properties, such as thermal stability and low dielectric constant, which are useful in microelectronic applications [1-3]. However, because of its surface inertness, the adhesion between PVDF and various metals does not satisfy many of the industry requirements [4-7]. A number of methods for activating polymer surfaces prior to metal deposition have been shown to be effective in enhancing metal adhesion. Among these methods, chemical etching, high energy ion implantation, X-ray irradiation, electron beam bombardment, plasma treatment and surface graft copolymerization are often used with various degrees of success [8-14].

Gas plasma treatment, under various glow discharge conditions, has been used extensively in the surface modification of fluoropolymers [14]. Treatment of Teflon<sup>®</sup> PFA (polytetrafluoroethylene-co-perfluoroalkoxy vinyl ether) in N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, or mixed gas plasma, was found to improve its hydrophilicity and its adhesion with evaporated Cu [15]. Using similar plasma treatments, Shi *et al.* [15] also reported the improvement of adhesion between evaporated Cu and polytetrafluoroethylene (PTFE).

Surface modification of PVDF films has been investigated extensively in recent years. For example, Boutevin *et al.* [16, 17] had modified PVDF surfaces under the optimum conditions of ozonolysis. The subsequent graft copolymer from the ozonized PVDF was used as an emulsifier. Similarly, Crowe and Badyal [18] reported on the treatment of PVDF films with aqueous lithium

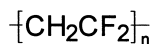
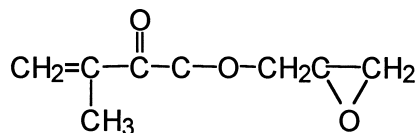
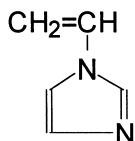
hydroxide to improve their lamination and adhesion properties. Duca *et al.* [19] had studied the surface modification of PVDF films by radio frequency (rf) Ar plasma treatment and found that Ar plasma treatment of the PVDF surface caused the dehydrofluorination of PVDF chains and the toughening of the polymer surface. The extent of modification depended on both the exposure time and the rf power. Chen and Mukhopadhyay [3] had investigated the interaction of three different polymers, PVDF PTFE and polyethylene, with a medium resistivity metal, such as Ni. They concluded that the  $-\text{CF}_2-$  species was attacked by Ni whereas the  $-\text{CH}_2-$  species was unaffected. The Ni atoms react with the  $-\text{CF}_2-$  species to form nickel fluoride and other carbon containing species, including a graphite or carbide-like phase.

In the present work, surface modification of Ar plasma pretreated PVDF film was carried out via UV-induced graft copolymerization with 1-vinyl imidazole (VIDz) and glycidyl methacrylate (GMA) to enhance the adhesion of PVDF film with evaporated metals, such as copper and aluminum. Physicochemical parameters associated with surface graft copolymerization, such as Ar plasma pretreatment time of the PVDF substrate, UV graft copolymerization time, and the nature of the monomers, were studied. The chemical compositions of surface modified PVDF films and the delaminated surfaces from the various metal/polymer laminates were characterized by X-ray photoelectron spectroscopy (XPS).

## EXPERIMENTAL

### Materials

Poly(vinylidene fluoride) (PVDF) films having a thickness of 0.08 mm and a density of  $1.76 \text{ g/cm}^3$ , and copper and aluminum wires with a purity of 99.999% (for thermal evaporation) were purchased from Goodfellow Inc. of Cambridge, UK. The polymer films were cleaned with methanol in an ultrasonic water bath and then dried under reduced pressure at room temperature. Glycidyl methacrylate (GMA) of 97% purity, 1-vinyl imidazole (VIDz) of 99% purity, 1,4-dioxane of 99.8% purity and acetone of 99.7% purity were purchased from Aldrich Chemical Co. of Milwaukee, WI. The GMA monomer was used as received, while VIDz monomer was distilled under reduced pressure to remove the oligomers before the graft copolymerization experiment. The chemical structures of PVDF, GMA and VIDz are shown below:

**PVDF film****GMA monomer****VIDz monomer**

### Plasma Pretreatment and UV-induced Graft Copolymerization

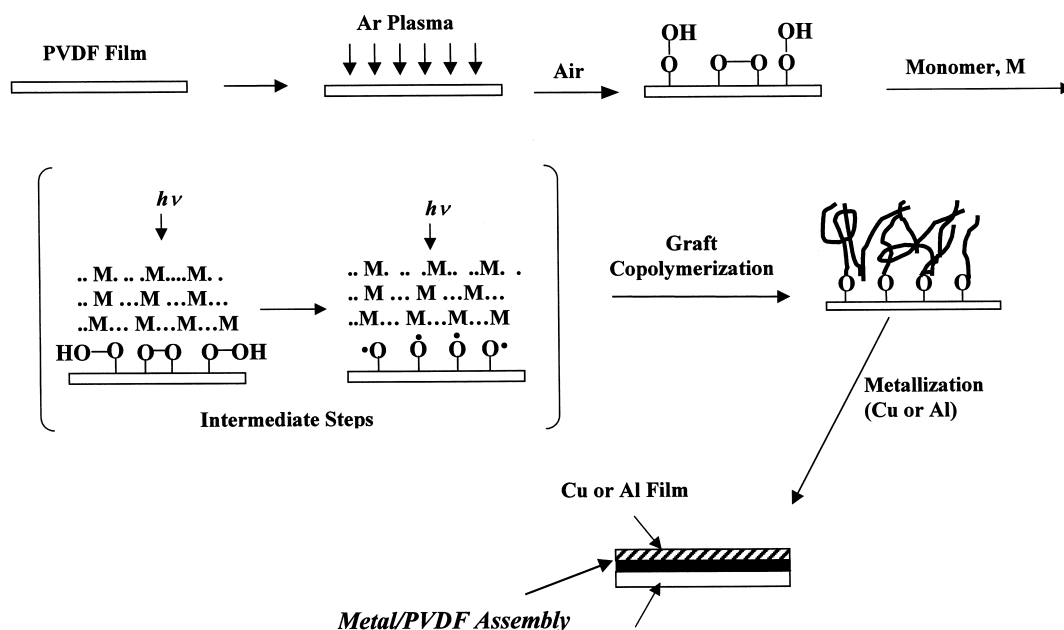
PVDF film strips of about 2.0 cm × 0.5 cm were pretreated with Ar plasma before the UV-induced graft copolymerization. Ar plasma treatment was carried out in an Anatech SP 100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at an applied frequency of 40 kHz, a plasma power of 35 W, and an Ar pressure of about 0.60 Torr. After the plasma treatment, the PVDF films were exposed to the atmosphere for about 30 minutes to allow the formation of surface peroxide and hydroxyl peroxide species which were used to initiate the subsequent graft copolymerization [20]. The plasma pretreated PVDF film was immersed in about 20 ml of 1,4-dioxane (for GMA) or aqueous (for VIDz) monomer solution in a Pyrex<sup>®</sup> tube. The dissolved air in the reaction mixture was removed by purging with purified nitrogen for about 30 minutes before the tube was sealed off with a silicone stopper. The reaction mixture was then exposed to UV illumination in a Riko rotary (Model 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 the UV-induced graft copolymerization experiments were carried out at a constant temperature of 28°C. After the graft copolymerization experiment, the PVDF film was washed thoroughly with copious amounts of 1,4-dioxane (for GMA graft copolymerization) or doubly-distilled water (for VIDz graft copolymerization) to remove the residual monomer and adsorbed homopolymer before being dried under reduced pressure.

### Thermal Evaporation of Aluminum and Copper

An aluminum or copper layer of about 1500 Å in thickness was thermally evaporated onto the surface-modified PVDF films in a JEOL Model LEE-400 vacuum evaporator. The deposition was carried out at a pressure of  $10^{-6}$  Torr or less and at a rate of about 10 Å/s. The processes of plasma pretreatment, UV-induced surface graft copolymerization and metal evaporation leading to the formation of the Al/PVDF or Cu/PVDF laminate are shown schematically in Figure 1.

### Adhesion Strength Measurements

The metallized sample surface was adhered to an aluminum sheet (0.1 mm in thickness) using an epoxy adhesive. The assembly was subsequently cured at 120°C for 4 hours. The adhesion strengths of the metal/polymer interfaces were determined by measuring the T-peel adhesion strength [21] on an Instron Model 5544 single column tensile tester from the Instron Corp. of USA. All measurements were performed at a cross-head speed of 10 mm/min. For each



**Figure 1.** Schematic representation of the process of plasma treatment, UV-induced graft copolymerization and metallization.

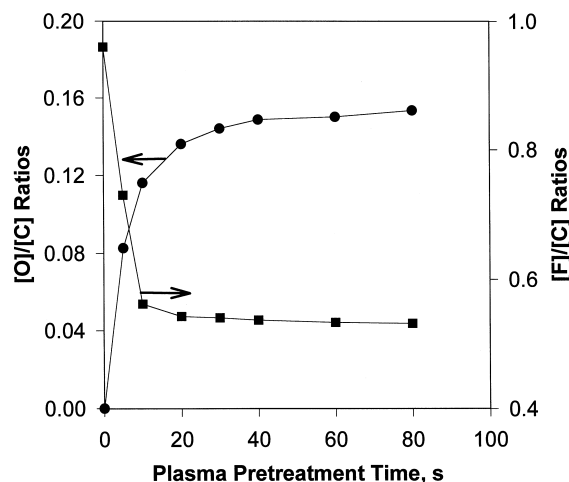
value of adhesion strength reported, at least six sample measurements were averaged.

### Surface Characterization

XPS measurements were made on a VG ESCALAB MKII spectrometer with a Mg K $\alpha$  X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The graft-modified PVDF films and the delaminated PVDF films and Cu foils were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle ( $\alpha$ , measure with respect to the sample surface) of 75°. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at  $7.5 \times 10^{-9}$  Torr or lower during each measurement. All binding energies (BE's) were referenced to the  $\text{CF}_2$  peak at 291.2 eV. In peak synthesis, the line width (full width at half maximum or FWHM) of 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  $\pm 10\%$ . The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

## RESULTS AND DISCUSSION

The changes in O/C and F/C atomic ratios of the PVDF films, as determined from the C1s, O1s and F1s core-level spectral peak area ratios, as a function of Ar plasma treatment time are shown in Figure 2. An increase in the O/C ratio, together with a decrease in the F/C ratios were observed upon increasing the Ar plasma treatment time, in agreement with the result generally reported in the literature for the plasma treated fluoropolymer films [22, 23]. The O/C ratio approaches an asymptotic values of about 0.14 at plasma treatment time greater than 20 s under the glow discharge conditions used in the present work. Prolonged plasma treatment does not result in the further introduction of oxygen atoms or peroxides species onto the PVDF surface, probably due to the establishment of an equilibrium between the surface etching effect of plasma treatment and the generation of the surface active species for the incorporation of oxygen species.

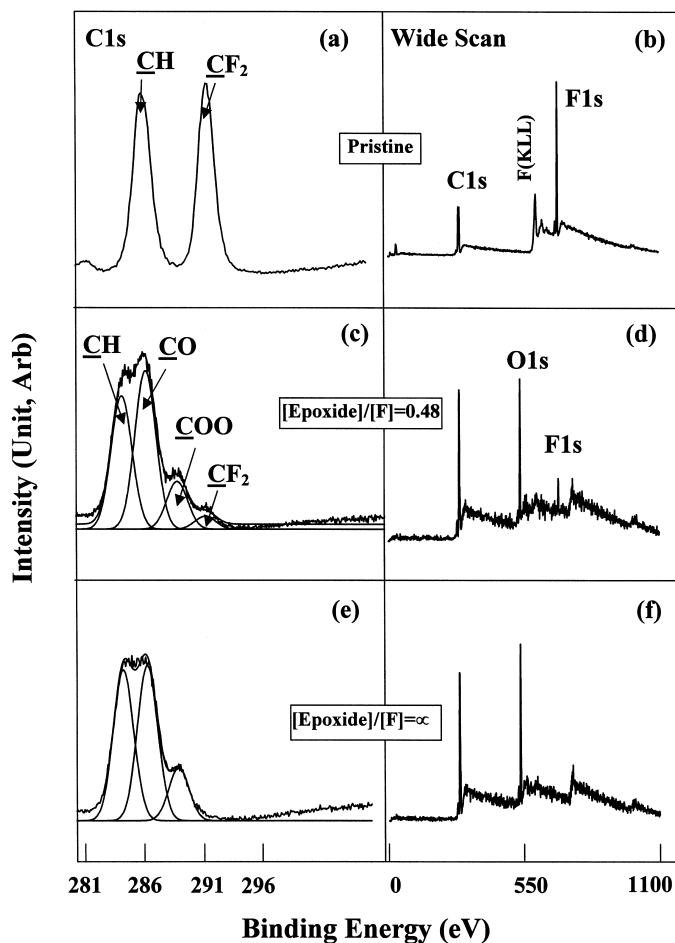


**Figure 2.** O/C ratio and F/C ratio of the PVDF film surface as a function of plasma pretreatment time.

The increase in O/C ratio on the PVDF surface can be attributed to the Ar plasma treatment and the subsequent exposure to the atmosphere. The Ar plasma treatment causes the breakage of C-F and C-H bonds of PVDF substrates, resulting in the abstraction of fluorine and hydrogen atoms from the PVDF main chains, and the formation of radicals. Upon exposure to the atmosphere, these radicals can react with oxygen to form peroxide and hydroxyl peroxide species, which are used to initiate the subsequent surface graft copolymerization [20]. The relationship between defluorination and surface oxidation is further suggested by the anti-symmetric nature of the O/C and F/C curves in Figure 2.

Figure 3 shows the respective C1s core-level spectra and the wide scan spectra, obtained at the photoelectron take-off angle ( $\alpha$ ) of  $75^\circ$ , of the pristine PVDF film (3(a) and 3(b)), and the 5 s (3(c) and 3(d)), and 20 s (3(e) and 3(f)) Ar plasma pretreated PVDF films after UV-induced graft copolymerization in 20 vol% 1,4-dioxane solution of GMA for 60 minutes. The pristine PVDF surface exhibits two main C1s components of about equal sizes at the binding energies (BE's) of 291.2 and 286.8 eV, which are attributed to the  $\underline{\text{C}}\text{F}_2$  and  $\underline{\text{C}}\text{H}_2$  species, respectively [24]. The BE for the  $\underline{\text{C}}\text{H}_2$  species of PVDF is shifted by about 2 eV towards the higher energy side of that (284.6 eV) of the neutral  $\underline{\text{C}}\text{H}_2$  species. This phenomenon is caused by the electron withdrawing effect of the fluorine atoms of  $\text{CF}_2$  units on the adjacent carbon atoms. The low BE tail below 284 eV in the





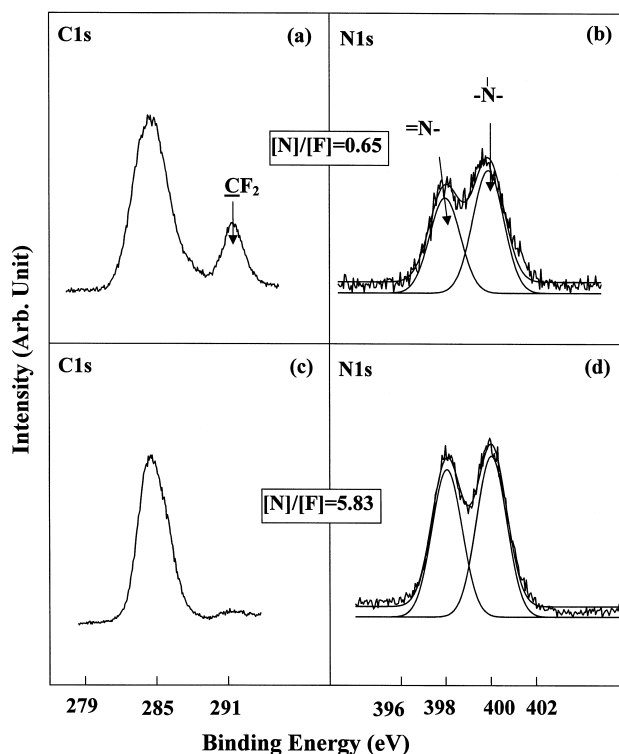
**Figure 3.** C1s and wide scan spectra for (a, b) a pristine PVDF film, (c, d) a 5 s, and (e, f) a 20 s plasma pretreated PVDF film after UV-induced graft copolymerization in 20 vol%GMA monomer solution for 60 minutes.

C1s spectrum is mainly due to the contribution of  $MgK\alpha_{3,4}$  satellite lines of the  $\underline{CF}_2$  species. The slight broadening in the line width of the  $\underline{CH}_2$  peak component probably arises from the presence of a small fraction of the head-to-head addition in the PVDF chains.

The presence of surface grafted GMA polymer can be deduced from the C1s peak components with BE's similar to those of the GMA homopolymer, *viz.*, 284.6 eV for the  $\underline{CH}$  species, 286.2 eV for the  $\underline{CO}$  species and 288.5 eV for the  $\underline{COO}$  species. The C1s component at the highest BE of 291.2 eV, on the other hand, is associated with the  $\underline{CF}_2$  species of PVDF substrate. In the case of the 20

s plasma pretreated PVDF film, complete coverage (to beyond the probing depth of the XPS technique) of the PVDF surface by GMA polymer occurs, as indicated by the complete disappearance of the  $\text{CF}_2$  signal. The high surface graft copolymerization efficiency is consistent with the high O/C atomic ratio (and thus the high peroxides concentration) shown in Figure 2. The relative peak-area ratio for the  $\text{CH}$ ,  $\text{CO}$  and  $\text{COO}$  species of this PVDF surface is very close to the theoretical ratio of 3:3:1 dictated by the chemical structure of GMA. This observation is also confirmed by the presence of only two main elemental components (C1s and O1s) in the wide scan spectrum.

Figures 4 (a) to (d) show that the respective C1s and N1s core-level spectra, obtained at  $\alpha$  of  $75^\circ$ , of the 20 s Ar plasma pretreated PVDF films after having been subjected to UV-induced graft copolymerization in 10 vol% VIDz aqueous solution for 30 minutes and 90 minutes. The presence of surface grafted

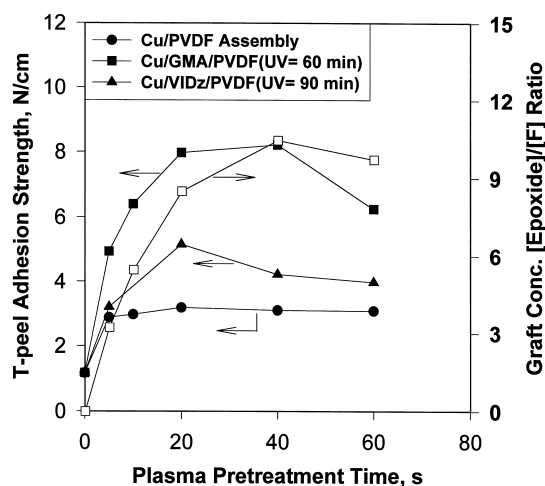


**Figure 4.** C1s and N1s core-level spectra for the 20s plasma pretreated PVDF films after UV-induced graft copolymerization in 10 vol%VIDz aqueous solution for (a, b) 30 minutes and (c, d) 90 minutes.

VIDz polymers can be deduced from the diminished  $\text{CF}_2$  component at the BE of about 291.2 eV, and the appearance of the N1s core-level signal. The N1s core-level spectra can be curve-fitted with two peak components of about equal sizes at the BE's of 398.2 and 400.1 eV, arising from the =N- and -N- species, respectively, of the VIDz ring [25, 26]. The lower BE C1s component, on the other hand, is attributable to the presence of the  $\text{CH}$ ,  $\text{CN}$ , and  $\text{CO}$  species. Upon prolonging the UV graft copolymerization time, the intensity of the  $\text{CF}_2$  component decreases while the intensity of the N1s core-level spectrum increases due to the increasing coverage of the grafted VIDz polymer on the surface of the PVDF film. Almost no  $\text{CF}_2$  signal was discernible above 90 min of UV graft copolymerization time, suggesting the near-complete coverage of the PVDF surface by the VIDz polymer. The graft concentration, defined as the number of repeat units of VIDz polymer per repeat unit of PVDF substrate, can be determined simply from the  $[\text{N}]/[\text{F}]$  ratio, as each VIDz unit contains two nitrogen atoms.

The adhesion strengths of the metals to the fluoropolymer films are evaluated in the T-peel adhesion tests. The effect of Ar plasma pretreatment time of the PVDF film on the T-peel adhesion strength of the Cu/GMA/PVDF assembly, prepared by metallization of the PVDF film from 60 minutes of UV graft copolymerization in 20 vol% of 1,4-dioxane solution, and that of the Cu/VIDz/PVDF assembly from 90 minutes of UV graft copolymerization time in 10 vol% of VIDz aqueous solution are shown in Figure 5. For comparison purpose, the adhesion strengths of the Cu/PVDF assemblies prepared from the metallization of the PVDF films with plasma treatment alone, i.e., no surface graft copolymerization, are also shown in Figure 5. For the Cu/PVDF assembly, the adhesion strength increases with increasing plasma pretreatment time and approaches an asymptotic value of about 3 N/cm at 20 s of plasma treatment. The enhanced adhesion strength for this assembly is mainly attributable to the incorporation of oxygen and polar species on the polymer surface arising from the plasma treatment and subsequent atmospheric exposure. The result is also consistent with the observation that the O/C atomic ratio of the PVDF film surface approaches an asymptotic value after 20 s of plasma treatment (Figure 2).

The dependence of the adhesion strengths of both the Cu/GMA/PVDF and Cu/VIDz/PVDF assemblies on the plasma pretreatment time of the PVDF films is similar to that of the Cu/PVDF assembly. The peel strengths for both of these assemblies increase initially upon increasing plasma pretreatment time and then tend to decrease slightly at higher plasma pretreatment time. The phenomenon is probably due to the increasing extent of etching of the PVDF substrate



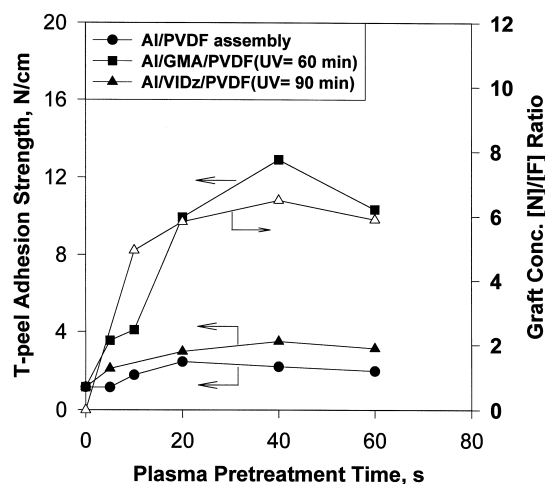
**Figure 5.** Effect of the plasma pretreatment time on the T-peel adhesion strength of the Cu/PVDF, Cu/GMA/PVDF (UV time = 60 minutes) and Cu/VIDz/PVDF (UV time = 90 minutes) assemblies, and the concentration of the grafted GMA polymer and the PVDF film (UV time = 30 minutes).

upon increasing the plasma pretreatment time, as is also indicated by the leveling-off in graft concentration (see below). However, the obtainable adhesion strengths for both types of the assemblies involving the graft-modified PVDF films are significantly higher than those of the Cu/PVDF assemblies. This improvement in adhesion strength arises from the effect of graft copolymerization of the functional monomers on the PVDF films. Also shown in Figure 5 is the graft concentration of the GMA polymer, expressed in terms of the [Epoxide]/[F] ratio, which is also equivalent to the [COO]/[F] ratio (obtained from the COO component and F1s core-level spectral peak area ratio), as a function of plasma pretreatment time of the PVDF film. To avoid excess coverage of the PVDF surface by the GMA polymer, the graft concentration curve in Figure 5 was obtained at a proportionally reduced graft copolymerization time of 30 minutes. The graft yield increases initially with the plasma pretreatment time and then decreases slightly at large plasma pretreatment time. This decrease in graft concentration at large plasma pretreatment time is attributable to the etching effect of the plasma treatment on the PVDF surface as mentioned earlier. In general, the dependence of the graft concentration on the plasma pretreatment time coincides approximately with that of the adhesion strength on the plasma pre-

treatment time. Thus, the effect of graft chains on the observed adhesion strengths of the present assemblies is ascertained.

It is generally known that the imidazole ring of VIDz can interact with copper metal at zero oxidation state to form a complex [25-27]. This interaction accounts for the high adhesion strength of the Cu/VIDz/PVDF assembly. The enhanced adhesion strength for the Cu/GMA/PVDF assembly, on the other hand, may have resulted from the strong interaction between the epoxide groups of the graft GMA chains and the evaporated Cu atoms (see also below). The data in Figure 5 suggest that, for the improvement of adhesion strength with Cu, GMA is a better choice for surface graft copolymerization with the PVDF substrate than VIDz. The peel strengths of the Cu/GMA/PVDF assemblies are about twice of those of the corresponding Cu/VIDz/PVDF assemblies prepared under similar experimental conditions. The optimum peel strength for the Cu/GMA/PVDF assembly is about 8.4 N/cm and that for the Cu/VIDz/PVDF assembly is only about 5.2 N/cm.

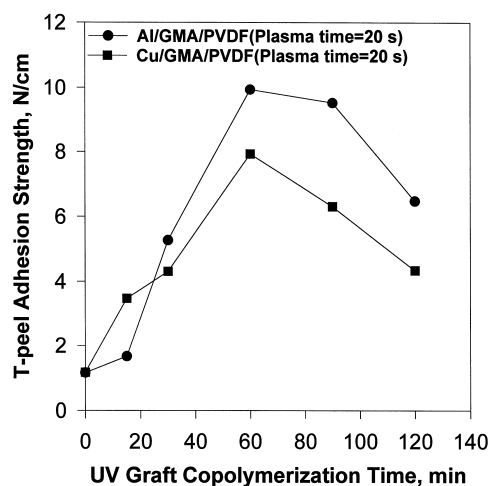
Similarly, Figure 6 shows the effect of plasma pretreatment time of the PVDF films on the adhesion strengths of the Al/PVDF, Al/GMA/PVDF and Al/VIDz/PVDF assemblies prepared under similar experimental conditions as those of Figure 5. The corresponding effect on the graft concentration of the VIDz polymer (in terms of [N]/[F] ratio) on the PVDF surface is also shown. The graft concentration of the VIDz polymer increases with the plasma pretreatment time in a manner similar to that of the GMA graft copolymerization surface. Nevertheless, the optimum T-peel strength for the Al/VIDz/PVDF assembly is only in the order of 3 N/cm and is only marginally higher than that of the Al/PVDF assembly involving PVDF film with plasma treatment alone. In comparison, the T-peel adhesion strength of the Al/GMA/PVDF assembly is substantially higher. A maximum T-peel adhesion strength of about 13.0 N/cm is achieved for the Al/GMA/PVDF assembly from a 40 s plasma pretreated PVDF substrate. These results suggest that the GMA polymer interacts much more effectively with the Al atoms than the VIDz polymer. Our recent *in situ* XPS studies on the Al metallization of GMA graft copolymerized PTFE surface has also revealed strong interactions between the evaporated Al atoms and the epoxide functional groups of the graft chains, as well as the formation of an Al-oxygen-carbon complex. Both of these factors account for the strong adhesion strength between Al and PVDF in the Al/GMA/PVDF assembly. The interaction between Al atom and VIDz, however, is relatively weak, even although there exists strong interaction between the evaporated Cu atoms and the graft VIDz chains, as suggested by the adhesion data in Figure 5. Copper atoms form com-



**Figure 6.** Effect of the plasma pretreatment time on the T-peel adhesion strength of the Al/PVDF, Al/GMA/PVDF (UV time = 60 minutes) and Al/VIDz/PVDF assemblies (UV time = 90 minutes).

plexes readily with the imidazole group of VIDz, probably due to the presence of electrons in the d orbital of Cu atoms [27]. The Al atoms, on the other hand, react more readily with the epoxide groups than with the N atoms of the imidazole rings. In summary, the epoxide groups are capable of interacting strongly with both the evaporated Cu and Al atoms. However, the imidazole rings interact strongly only with the Cu atoms and not with the Al atoms. This conclusion is further ascertained by the following experiments.

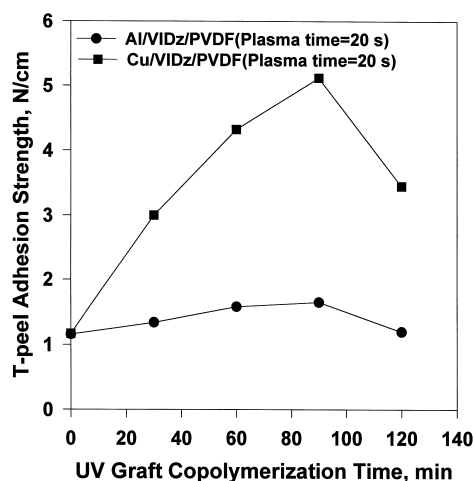
The T-peel adhesion strengths of the Al/GMA/PVDF and Cu/GMA/PVDF assemblies involving the 20 s plasma pretreated PVDF film as a function of UV graft copolymerization time are shown in Figure 7. It is observed that the T-peel adhesion strength increases steadily with UV illumination time and reaches about 10 N/cm in the case of Al/GMA/PVDF assembly and about 8.0 N/cm in the case of Cu/GMA/PVDF assembly at the UV graft copolymerization time of 60 minutes. This observation is consistent with the result shown in Figure 3 that complete coverage of the GMA polymer on the PVDF surface is achieved after the 20 s plasma pretreated PVDF film has been subjected to 60 minutes of UV-induced graft copolymerization. Both of these adhesion values are much higher than those obtained for the laminates involving evaporated Cu on PVDF films with the plasma treatment alone. Thus, the effective contribution of the grafted GMA polymer in improving the adhesion strength between evaporated



**Figure 7.** Effect of UV-induced graft copolymerization time on the T-peel adhesion strength of the Al/GMA/PVDF and Cu/GMA/PVDF assemblies (Plasma pretreatment time = 20 s, GMA Conc. = 20 vol%).

Cu and PVDF is again ascertained. The fact that the adhesion strength of the Al/GMA/PVDF assembly is higher than that of the corresponding Cu/GMA/PVDF assembly prepared under the same experimental conditions, suggests the presence of a stronger interaction between the Al atoms and the epoxide groups of the grafted GMA polymer.

Figure 8 shows the dependence of T-peel adhesion strengths of the Al/VIDz/PVDF and Cu/VIDz/PVDF assemblies involving the 20 s plasma pretreated PVDF films on the UV graft copolymerization time. The T-peel adhesion strength of the Cu/VIDz/PVDF assembly increases with UV illumination time up to 90 min and then decreases slightly. The optimum peel strength for the Cu/VIDz/PVDF assembly is about 5.2 N/cm. This adhesion strength is lower than that of the corresponding Cu/GMA/PVDF assembly. In comparison with the adhesion data in Figure 7, this result further demonstrates that the grafted GMA polymer is more effective in improving the adhesion strength between Cu and PVDF. Furthermore, for the Al/VIDz/PVDF assembly, the adhesion strength is low and appears to be independent of the UV graft copolymerization time. This result again suggests that a much weaker interaction exists between evaporated Al and the grafted VIDz polymer.

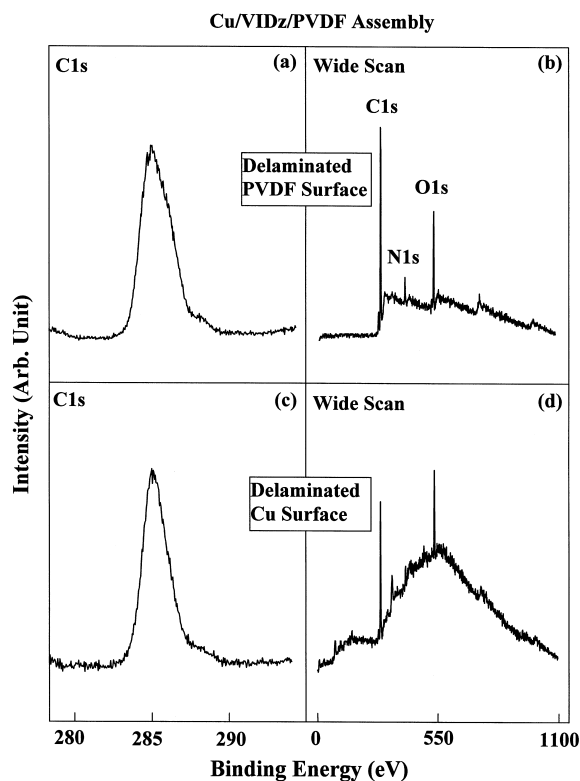


**Figure 8.** Effect of UV-induced graft copolymerization time on the T-peel adhesion strength of the Al/VIDz/PVDF and Cu/VIDz/PVDF assemblies (Plasma pretreatment time = 20 s, VIDz Conc. = 10 vol%).

It is essential to determine the locus of the strength loss for the metal/fluoropolymer assembly. In our present work, the failure mode of various assemblies was investigated also by the XPS technique. Figures 9(a) to 9(d) show the respective C1s core-level and wide scan spectra of the delaminated PVDF film surface and copper surface from a Cu/VIDz/PVDF assembly having a peel strength of about 4.8 N/cm. The C1s core-level spectra of the delaminated PVDF and Cu surfaces are almost identical to that of the VIDz graft copolymerized PVDF surface shown in Figure 4(c). The wide scan spectra of both delaminated surfaces also reveal the presence of the nitrogen signal arising from the grafted VIDz polymer. These results, together with the fact that no fluorine signal is detected on the delaminated surfaces and the fact that fairly strong copper signals are detected on the delaminated copper surface, readily suggest that adhesion failure occurs within the interfacial graft layer near to the copper surface.

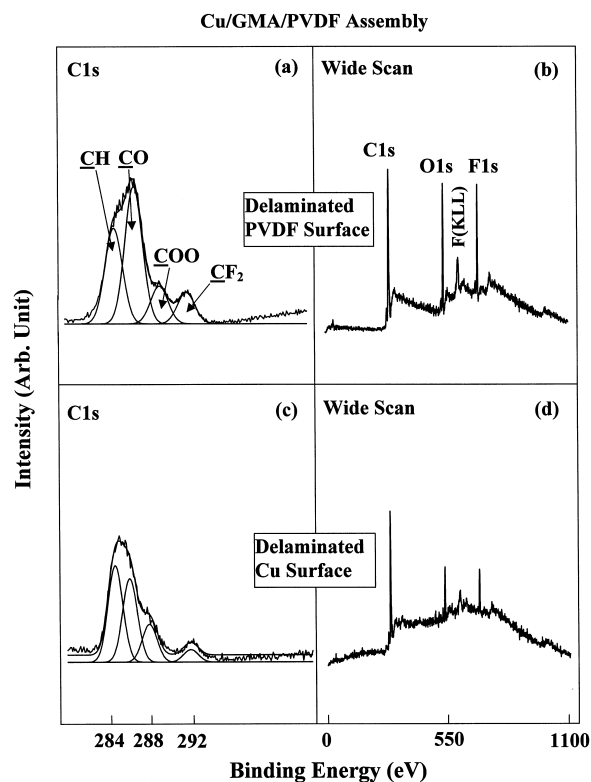
Similarly, Figures 10(a-d) show the respective C1s core-level and wide scan spectra of the delaminated PVDF surface and copper surface from a Cu/GMA/PVDF assembly having a peel strength of about 8.3 N/cm. The C1s core-level spectrum of the graft-modified PVDF surface used in this assembly before metallization is shown in Figure 3 (e), and thus suggests the complete coverage of the PVDF surface by the GMA polymer. Nevertheless, the C1s core-





**Figure 9.** C1s core-level and wide scan spectra of (a, b) the delaminated PVDF surface and (c, d) the delaminated copper surface from a Cu/VIDz/PVDF assembly having a T-peel adhesion strength of about 4.8 N/cm.

level spectra of both delaminated surfaces show the presence of the  $\text{CF}_2$  component arising from the PVDF substrate. This result is also confirmed by the presence of strong fluorine signals in the respective wide scan spectra. Furthermore, only faint Cu signals are observed on the delaminated surfaces. These XPS results, together with the fact that the C1s core-level spectra show features which are characteristic of the grafted GMA polymer, suggest that the assembly fails by a mixed cohesive and adhesional mode, with the locus of failure near or inside the PVDF substrate. In comparison with result shown the Figure 9, it can be concluded that the failure locus will shift from within the interfacial graft layer towards the sub-surface layer of the PVDF substrate with increasing adhesion strength.



**Figure 10.** C1s core-level and wide scan spectra of (a, b) the delaminated PVDF surface and (c, d) the delaminated copper surface from a Cu/GMA/PVDF assembly having a T-peel adhesion strength of about 8.3 N/cm.

## CONCLUSION

The surfaces of Ar plasma pretreated PVDF films were modified by UV-induced graft copolymerization with glycidyl methacrylate (GMA) and 1-vinyl imidazole (VIDz) to improve their adhesion with evaporated metals, such as aluminum and copper. The T-peel adhesion strengths of the various assemblies depended on the nature of the metal, the nature of the monomer used for graft copolymerization, the plasma pretreatment time of the PVDF substrate, and the UV graft copolymerization time. A maximum T-peel adhesion strength of about 13.0 N/cm was achieved for laminates involving GMA graft copolymerized PVDF film and evaporated aluminum metal. The aluminum atoms appeared to interact more effectively with the graft GMA polymer than the copper atoms.

However, the reverse is true for the interaction with the grafted VIDz polymer. Furthermore, for the enhancement of adhesion strength with either metal, GMA is a better choice for surface graft copolymerization with PVDF substrate than VIDz. The failure mode of the laminates involving GMA graft copolymerized PVDF films is a combined adhesional and cohesive failure, and those involving VIDz grafted copolymerized PVDF films is adhesional in nature.

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Received July 10, 1999