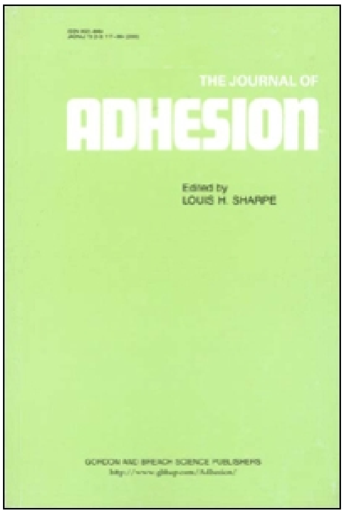

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Liu, Y. X. , Kang, E. T. E. , Neoh, K. G. , Tan, K. L. , Huan, C. C. and Liaw, D. J.(1999) 'Surface Graft Copolymerization of Poly(vinylidene fluoride) Film with Simultaneous Lamination to Copper Foil', The Journal of Adhesion, 71: 1, 35 — 54

To link to this Article: DOI: 10.1080/00218469908009565

URL: http://dx.doi.org/10.1080/00218469908009565

J. Adhesion, 1999, Vol. 71, pp. 35–54
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Surface Graft Copolymerization of Poly(vinylidene fluoride) Film with Simultaneous Lamination to Copper Foil

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(Received 9 January 1999; In final form 16 March 1999)

Surface thermal graft copolymerization with concurrent lamination was carried out between an Ar plasma pretreated poly(vinylidene fluoride) (PVDF) film and a copper foil in the presence of a small quantity of a *N*-containing monomer, such as 4-vinyl pyridine (4-VPN) and acryloyl morpholine (ACMO), under atmospheric conditions and in the complete absence of an added polymerization initiator and system degassing. The adhesion strength, as reported by *T*-peel strength, was dependent on the argon plasma pretreatment time of the PVDF film, the thermal lamination temperature and the type of monomer. An optimum *T*-peel adhesion of about 10 N/cm was readily achieved in the Cu/PVDF laminate for grafting and lamination carried out in the presence of 4-VPN. A lower adhesion strength was obtained using ACMO and other *N*-containing monomers. The chemical compositions of the graft copolymerized and delaminated sample surfaces were studied by X-ray photoelectron spectroscopy (XPS). The failure mode of the Cu/4-VPN/PVDF assembly was a combined adhesional and cohesive failure. The strong adhesion between the Cu foil and the PVDF film arises from the strong charge transfer interaction between Cu and the pyridine ring, as well as the fact that the graft chains are covalently tethered on the PVDF films surfaces as a result of surface graft copolymerization.

Keywords: Poly(vinylidene fluoride); copper; plasma; graft copolymerization; lamination; 4-vinyl pyridine; XPS

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1. INTRODUCTION

Surface modification of fluoropolymers has been of particular interest as fluoropolymers belong to one of the most important families of engineering polymers well known for their high thermal stability, excellent chemical inertness, low friction coefficient and low dielectric constant [1, 2]. However, they also have very low surface energy and, thus, exhibit negligible adhesion to other materials, especially metals [3]. As a result, many studies have been devoted to the improvement of metal adhesion to fluoropolymers [3–9]. For adhesion improvement, different treatments have been used: chemical etching, high-energy ion irradiation, X-ray and electron beam irradiation, plasma treatment and surface graft copolymerization [10–19]. Plasma surface modification has been considered to be one of the most efficient techniques for surface activation of polymers [20–23]. It has been reported that the adhesion of poly(tetrafluoroethylene) (PTFE) with Cu metal can be considerably enhanced when the polymer surface is modified first by plasma pretreatment and subsequently by graft copolymerization [21, 22]. Treatment of Teflon® PFA (polytetrafluoroethylene-co-perfluoroalkoxy vinyl ether) in different gas plasmas, such as the N_2, O_2, H_2 and mixed gas plasmas, was found to improve its hydrophilicity and its adhesion with evaporated Cu [8]. In most cases, the observed adhesion improvement is a consequence of the chemical surface modification of the fluoropolymer rather than the metal itself. It is well known that the plasma environment contains neutral species, energetic ions, electrons and photons [23]. The interaction of plasma with the polymer surfaces can cause chemical and physical modifications and produce more reactive surfaces, while leaving the bulk properties relatively unchanged.

The mechanical properties of PVDF are superior to those of many other fluoropolymers. Its surface modification has been extensively investigated in recent years. For example, Boutevin *et al.* [24, 25] modified the PVDF surface under the optimum conditions of ozonolysis. The subsequent graft copolymer from the ozonized PVDF was used as an emulsifier. Similarly, Crowe and Badyal [26] reported on the treatment of PVDF films with aqueous lithium hydroxide to improve the lamination and adhesion properties. Duca *et al.* [27] studied the surface modification of PVDF 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 [28] investigated the interaction of three different polymers, PVDF, PTFE and PE, with a medium-resistivity metal, such as Ni. They concluded that the (—CF_2—) species was attacked by Ni whereas the (—CH_2—) species is unaffected. The Ni atoms react with the (—CF_2—) species to form nickel fluoride and other carbon-containing species, including a graphite or carbide-like phase.

Surface modification of polymers *via* grafting and graft copolymerization has also been reviewed [29–31]. Ikada *et al.* [31–33], for instance, successfully incorporated a large number of functional groups onto polymer surfaces *via* graft copolymerization, usually in the absence of a polymerization initiator. In our earlier studies [10–13], we reported on the surface modification of PTFE films *via* UV-induced graft copolymerization. The technique resulted in covalently-tethered polymer chains on the fluoropolymer surfaces. Thus, by selecting the graft chains with appropriate functional groups which can interact strongly with the metal, enhanced adhesion of the metal to fluoropolymer surface can be expected. In view of the fact that copper/polymer laminates have been used extensively in the electronic industry in the production of cards and boards [3], we demonstrate in this work that improved adhesion between the Ar-plasma-pretreated PVDF film and copper foil can be obtained through a simple, one-step, simultaneous surface graft copolymerization and lamination process. The effects of plasma pretreatment time of the PVDF film and the lamination temperature on the *T*-peel adhesion strength of the Cu/PVDF laminates were investigated. Surface characterization was accomplished using X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

2.1. Materials

Poly(vinylidene fluoride) (PVDF) films, having a thickness of 0.08 mm and a density of 1.76 g/cm^3, were purchased from Goodfellow Inc. of

Cambridge, UK. The films were cleaned with methanol and doubly-distilled water in an ultrasonic water bath and then dried under reduced pressure at room temperature. Copper foil with a thickness of 0.05 mm and a purity of 99.9% was also purchased from Goodfellow Inc. The copper foil was first immersed in acetone for 10 min to remove organic deposits, washed with distilled water, and then immersed in dilute hydrochloric acid for 5 min to eliminate the natural copper oxide. The 4-vinyl pyridine (4-VPN) monomer was obtained from Aldrich Chemical Co. of Milwaukee, Wisconsin, USA, and was used after purification by distillation under reduced pressure. The monomer, acryloyl morpholine (ACMO) was obtained from Kohjin Chem. Co. of Tokyo, Japan and was used as received. Other chemicals were used as received from Aldrich Chem. Co.

2.2. Thermal Graft Copolymerization with Concurrent Lamination

PVDF film strips of about 2.0 cm × 0.5 cm were pretreated with Ar plasma before the grafting and lamination processes. Ar plasma treatment was carried out in an Anatech SP 100 plasma system, equipped with a cylindrical quartz reaction 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. The plasma-treated PVDF films were exposed to the atmosphere for about 30 min to allow the formation of surface peroxide and hydroxyl peroxide species [33] before the grafting and lamination experiments. The plasma-pretreated PVDF film was lapped with a Cu foil in the presence of a small quantity of the monomer. The Cu/monomer/PVDF assembly was then sandwiched between two glass plates by means of mechanical clips, providing an equivalent pressure of about 10 N/cm^2. The lamination temperature and time used in the present work are summarized in the follow Table:

Assembly	*Lamination temperature (°C)*	*Lamination time (h)*
Cu/4-VPN/PVDF	120	4
Ca/ACMO/PVDF	140	4

After the grafting and lamination processes, the assembly was cooled to room temperature slowly in the well-insulated oven over a period of no less than 6 h to minimize the thermal stress at the lapped metal-polymer interface.

2.3. Adhesion Strength and Contact Angle Measurements

The lamination strengths were determined by measuring the *T*-peel adhesion strengths [34] of the various assemblies, after the thermal grafting and lamination, in an Instron Model 5544 single column tensile tester. All measurements were performed at a cross-head speed of 10 mm/min. The lapped area was held at 0.5 cm × 0.5 cm. At least six sample measurements were used in determining the average adhesion strength at each condition.

The static water contact angles were measured at 25°C and 50% relative humidity by the sessile drop method in a telescopic goniometer (Ramé-Hart Model 100-00(230)). The telescope with a magnification power of 23x is equipped with a protractor of 1° graduation. The measurements for the plasma-treated PVDF films were performed 30 min after the exposure to the glow discharge. For each angle reported, at least 10 readings on different surface locations were averaged and is reliable to ± 2°.

2.4. Surface Characterization

The graft-modified PVDF films for surface composition measurements were obtained from self-delamination in an appropriate solvent of the PVDF/monomer/PVDF assemblies, in which only one PVDF film was pretreated with Ar plasma, after the thermally-induced graft copolymerization with concurrent lamination experiment under atmospheric conditions. The PVDF films from the self-delaminated PVDF/PVDF joints, as well as the PVDF films and Cu foils from the mechanically-delaminated Cu/PVDF joints, were characterized by X-ray photoelectron spectroscopy (XPS).

XPS measurements were 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 PVDF films and Cu foils were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron take-off angle (α, measured with respect to the sample surface) of 75°. The X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained below 7.5×10^{-9} Torr during each measurement. All binding energies (BE's) were referenced to the $\underline{C}F_2$ peak at 291.4 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 factor, and were reliable to ±10%. The elemental sensitivity factors were calibrated using stable binary compounds of well-established stoichiometries. The surface elemental stoichiometries obtained by using only sensitivity factors is expected to be independent of the materials matrix for all homogeneous materials. The minor effect arising from the photoelectron mean free paths of the elements was accounted for in the stated ± 10% reliability of the data.

3. RESULTS AND DISCUSSION

Argon plasma pretreatment, followed by atmospheric exposure, causes an increase in the surface concentration of oxygen on the PVDF film surface. The XPS survey spectra, obtained at the photoelectron take-off angle (α) of 75°, of the pristine, 5 s and 20 s argon plasma pretreated PVDF films are shown in Figure 1. The pristine PVDF film shows two main core-level components, C1s and F1s. In addition to the prominent $F(KL_{23}L_{23})$ line at the binding energy (BE) of 598.7 eV, the $F(KL_1L_{23})$ and $F(KL_1L_1)$ lines at the BE's of 624.8 eV and 643.8 eV, respectively, are also discernible. The low BE peak at about 30 eV, on the other hand, is attributable to the F2s component. The appearance of the O1s component in the XPS wide scan spectra of the 5 s and 20 s plasma-pretreated PVDF films suggests the oxidation of the polymer film surfaces arising from the argon plasma treatment and subsequent atmospheric exposure. Furthermore, the intensity of the oxygen component for the 20 s plasma-pretreated PVDF film is higher than that for the 5 s plasma-pretreated PVDF film. The changes

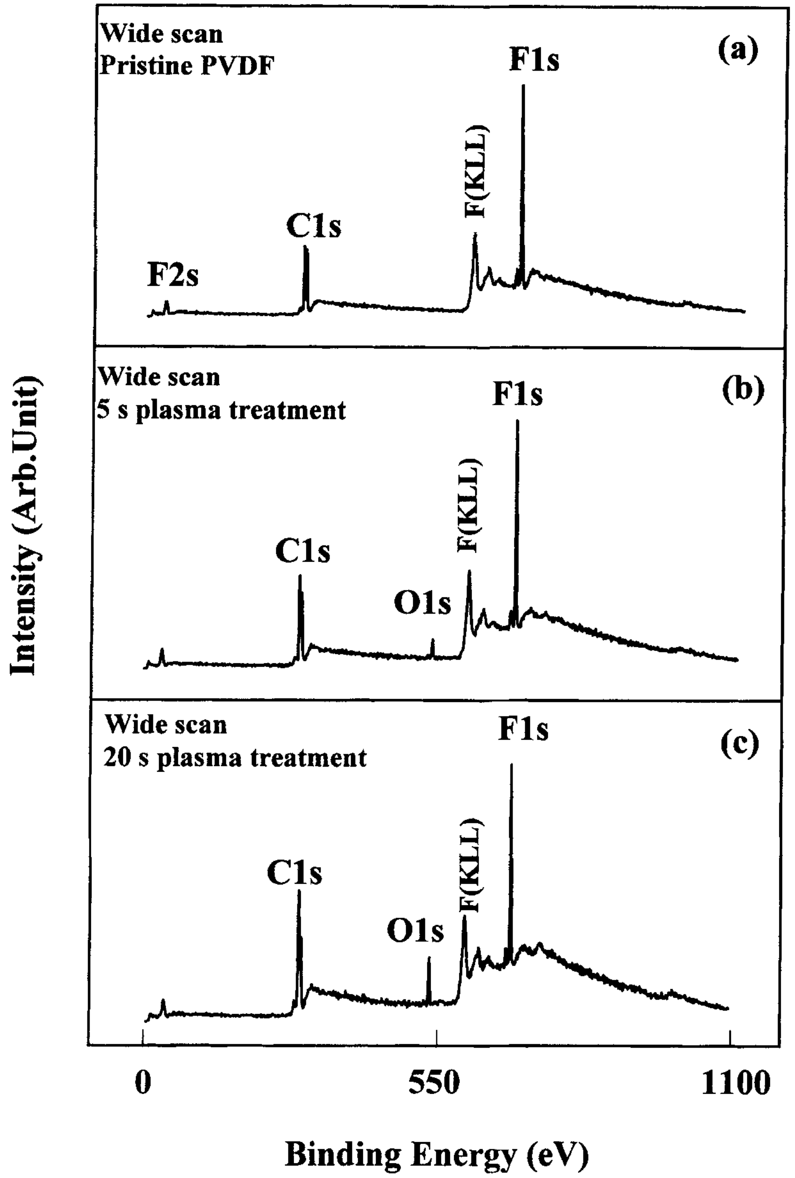

FIGURE 1 XPS wide scan spectra of (a) the pristine PVDF surface, (b) the 5 s argon-plasma-pretreated PVDF surface and (c) the 20 s argon-plasma-pretreated PVDF surface.

in the O/C and F/C atomic ratios of the PVDF film, as determined from the C1s, O1s and F1s core-level spectral peak area ratios, as a function of the Ar plasma treatment time are shown in Figure 2. An increase in the O/C ratio, together with a decrease in the F/C ratio, were observed upon increasing the Ar plasma treatment time, in general agreement with the results reported in the literature for plasma-treated fluoropolymer films [35, 36]. The O/C ratio approaches an asymptotic value of about 0.14 at plasma treatment time greater than 20 s. Prolonged plasma treatment does not result in more oxygen atoms or peroxides on the PVDF surface, probably due to the onset of the surface etching effect of the plasma. These results agree with those reported previously for the plasma-treated polyethylene (PE) or polypropylene (PP) surfaces [33, 37].

The increase in O/C ratio is attributed to the argon plasma treatment and subsequent exposure to the atmosphere. The Ar plasma

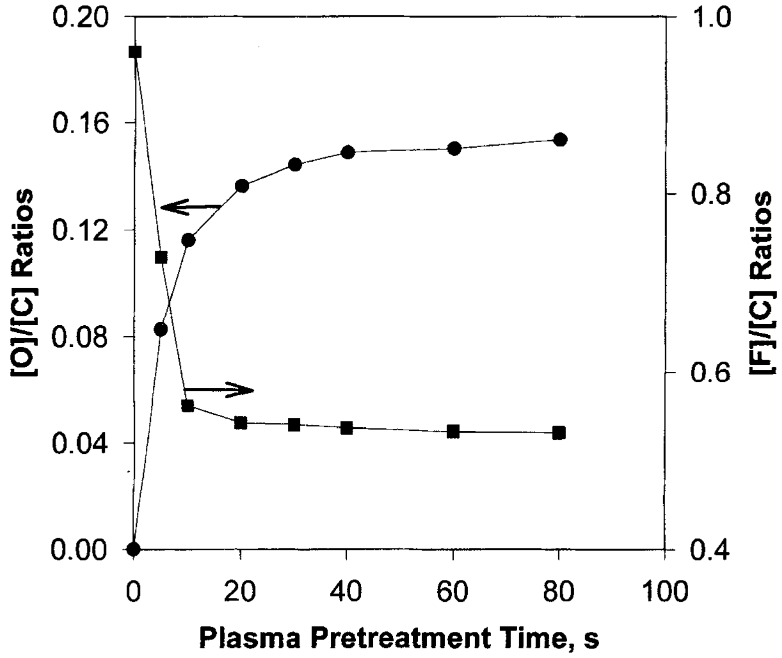

FIGURE 2 O/C ratio and F/C ratio of the PVDF film surface as a function of plasma-pretreatment time.

treatment, under the present glow discharge condition, also breaks C—F and C—H bonds, resulting in the abstraction of fluorine and hydrogen atoms from the PVDF surface and the subsequent formation of radicals. Upon exposure to the atmosphere, the radicals on the surface can react with oxygen to form peroxide or hydroxyl peroxide species which are used to initiate the subsequent surface graft copolymerization [32]. 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.

The wettablity of the PVDF surface was substantially improved by the introduction of the oxygen species. Contact angles of water droplets, expressed in terms of the $\cos\theta_0$ values of the PVDF film surfaces, as a function of plasma treatment time is shown in Figure 3. It is observed that upon increasing the plasma treatment time, $\cos\theta_0$ increases from 0.28 for the pristine PVDF film to 0.73 for the 40 s plasma-treated PVDF film. The latter value remains nearly constant

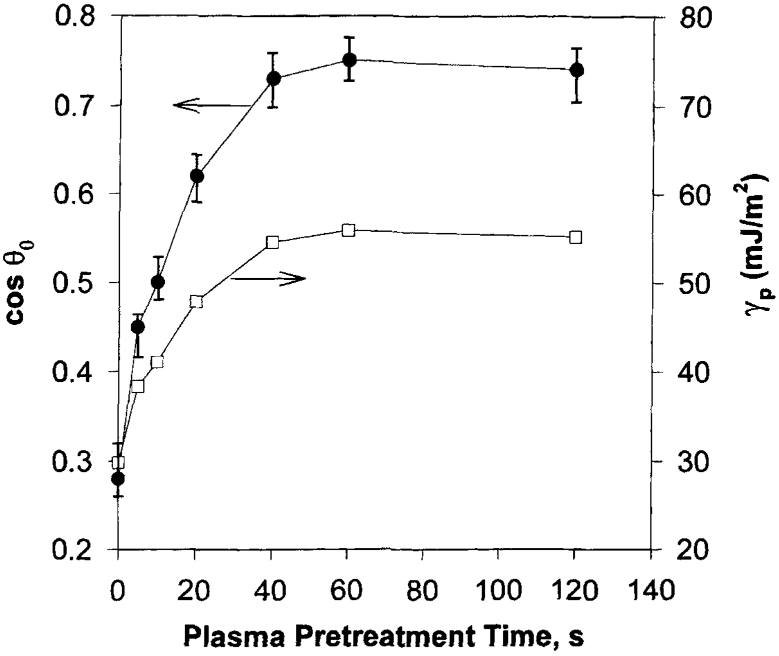

FIGURE 3 Water contact angle and surface free energy of the PVDF surface as a function of plasma-pretreatment time.

with further increase in plasma exposure time and is in general agreement with the stability of surface oxygen content at this extent of plasma treatment.

Measurement of the water contact angle of the surface allows a rapid and quantitative evaluation of the polymer surface free energy according to the Young-Dupre equation [38]:

$$\gamma_w(1+\cos\theta_0) = W_{pw} \tag{1}$$

where θ_0 is the contact angle at equilibrium, and γ_w is the surface free energy of water ($73\,\mathrm{mJ/m^2}$). W_{pw} is the adhesion energy of the water to the PVDF surface and is given roughly by [39]:

$$W_{pw} = 2(\gamma_w\gamma_p)^{1/2} \tag{2}$$

where γ_p denotes the surface free energy of PVDF.

Combining Eq. (1) with Eq. (2) gives

$$\gamma_p = (\gamma_w/4)(1+\cos\theta_0)^2 \tag{3}$$

Using Eq. (3), the surface free energy of PVDF, γ_p, can be calculated and the results are shown in Figure 3. Thus, a higher value of $\cos\theta_0$ corresponds to a higher γ_p. The decrease in the water contact angle and the increase in the surface free energy are related to the extent of oxygen incorporation resulting from the plasma treatment.

Figures 4(a) and 4(b) show, respectively, the C1s core-level spectra of the pristine PVDF film and a 20 s Ar plasma pretreatment PVDF film after 4 h of simultaneous thermal graft copolymerization and lamination in the presence of a small quantity of 4-VPN monomer. The corresponding N1s core-level spectrum and wide scan spectrum for the 4-VPN graft copolymerized surface are also shown in Figures 4(c) and 4(d). The pristine PVDF surface exhibits two main C1s components of about equal size at the binding energies (BE's) of 291.4 eV and 286.8 eV, which are attributable to the $—\underline{C}F_2—$ and the $—\underline{C}H_2—$ species, respectively. The BE for the $—\underline{C}H_2—$ species of the PVDF film is about 2 eV higher than that of the neutral $—\underline{C}F_2—$ species and is consistent with that reported by Golub *et al.* [40]. The positive BE shift is due to the presence of the electron-withdrawing effect of the fluorine atoms of the CF_2 units on the adjacent carbon

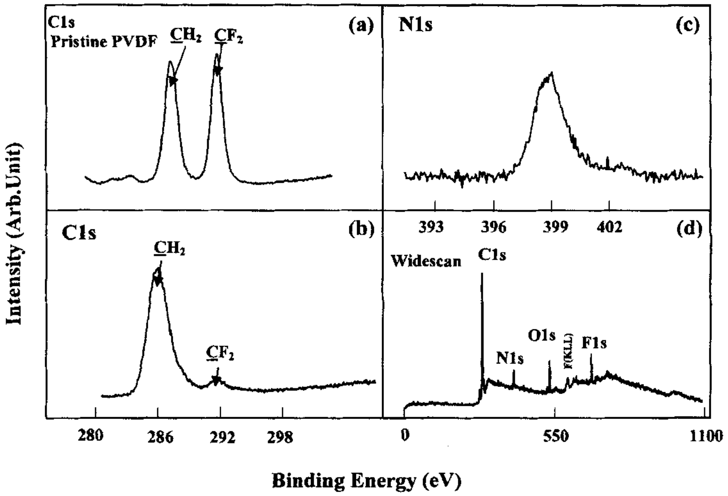

FIGURE 4 (a) Cls core-level spectrum of a pristine PVDF film, and (b) Cls, (c) Nls core-level and (d) wide scan spectra of 20 s Ar pretreated PVDF film after the simultaneous thermal copolymerization and lamination with VPN monomer at 120°C for 4 h.

atoms [41]. The slightly reduced peak intensity and broadened line width for the $\underline{C}H_2$ peak component, in comparison with those of the $\underline{C}F_2$ component, in Figure 4(a) is probably attributable to the fact that the head-to-head : head-to-tail polymerization ratio of PVDF can be as high as 0.1 : 0.9. The low BE components in the region of 283–285 eV is mainly due to the contribution of Mg $K\alpha_{3,4}$ satellite lines of the $\underline{C}F_2$ species. Upon grafting of the 4-VPN polymer, the Cls spectrum exhibits a drastic change in line shape and intensity in comparison with that of the pristine PVDF surface. The $\underline{C}H_2$ component is considerably broadened with its peak BE shifted to the lower BE of 286.0 eV. These changes are due to the grafting of the 4-VPN polymers and the introduction of C—N groups of the 4-PVD rings on the PVDF surface, as well as the reduced withdrawing effect of the fluorine atoms due to the diminished $\underline{C}F_2$ component. The intensity of the $\underline{C}F_2$ component diminishes substantially, as a result of the coverage of 4-VPN polymer on the PVDF surface. The presence of surface-grafted 4-VPN polymer is further confirmed by the appearance of the Nls signal, as shown in Figures 4(c) and 4(d). The Nls core-level spectrum consists of predominantly a peak component at the BE of about 398.5 eV, which is characteristic of the nitrogen atom in the pyridine ring of the 4-VPN polymer [42].

The concentration of surface-grafted polymer can be determined directly from the relative intensities of the N1s and F1s components, based on the sensitivity-factor-corrected N1s and F1s spectral area ratios. Thus, the concentration of the surface-grafted 4-VPN polymer, defined as the number of repeating units of the graft chain per repeating unit of the PVDF chain, can be calculated from the following expression:

$$\text{Graft Conc.} = \frac{[\text{N1s area}] \times 0.79/1}{[\text{F1s area}] \times 0.52/2}$$

where the two numbers, 0.79 and 0.52, are the sensitivity factors of the N1s and F1s signals, and the factors 2 and 1 are introduced to account, respectively, for the fact that there are two fluorine atoms per repeating unit of PVDF and there is only one nitrogen atom per repeating unit of the grafted 4-VPN polymer. The graft concentration of the 4-VPN polymer as a function of the plasma pretreatment time of the PVDF film is shown in Figure 5.

The metal/fluoropolymer adhesion strength has been evaluated by *T*-peel adhesion tests. The effect of Ar plasma pretreatment time of the PVDF films on the *T*-peel adhesion strength of the Cu/4-VPN/PVDF assembly is shown in Figure 5. This process was carried out in the absence of an added initiator at a constant temperature of 120°C for 4 h. As shown in the figure, the *T*-peel adhesion strength increases initially with plasma pretreatment time up to 20 s, but exhibits a slight decrease at plasma pretreatment time greater than 20 s under the glow discharge conditions used in the present study. A maximum *T*-peel adhesion strength of about 9.0 N/cm was obtained. This adhesion strength is about 20 times higher than that involving the pristine PVDF substrate. The observation that both the graft concentration and the *T*-peel adhesion strength exhibit a similar dependence on the plasma pretreatment time is consistent with a peroxide-initiated surface graft copolymerization mechanism [29, 31, 33]. Furthermore, the increase in adhesion strength coincides approximately with the increase in surface graft concentration, suggesting that a graft chain-induced adhesion mechanism is operative. The observed optimum

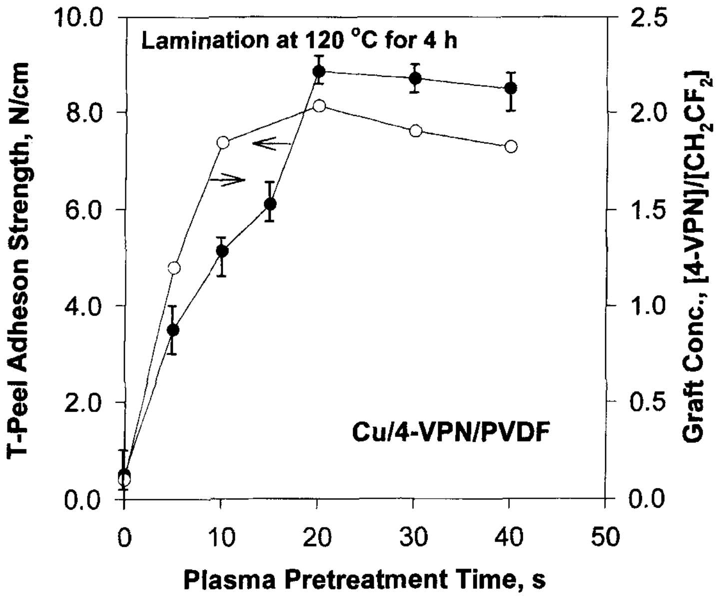

FIGURE 5 *T*-peel adhesion strength for the Cu/VPN/PVDF assembly and the graft concentration of the 4-VPN polymer, as a function of plasma-pretreatment time. (Lamination temperature = 120°C, Lamination time = 4 h).

adhesion strength and graft concentration are also consistent with the fact that the surface O/C ratio of PVDF film approaches an asymptotic value at 20 s of plasma pretreatment time. A proposed mechanism for adhesive strength evolution of the Cu/PVDF interface arising from the simultaneous thermal graft copolymerization and lamination is shown schematically in Figure 6.

Cu/PVDF laminates of respectable adhesion strength are also obtained from the present simultaneous graft copolymerization and lamination, carried out in the presence of other *N*-containing vinyl monomers, such as acryloyl morpholine (ACMO). Figure 7 shows the *T*-peel adhesion strength of the Cu/AMCO/PVDF assembly as a function of the Ar plasma pretreatment time of the PVDF film for graft copolymerization and lamination carried out at 140°C and for 4 h. The dependence of peel strength on the plasma pretreatment time for this assembly is similar to that of the Cu/4-VPN/PVDF assembly, although a lower peel strength is observed for the present Cu/ACMO/PVDF assembly. Our previous study [43] has shown that the presence

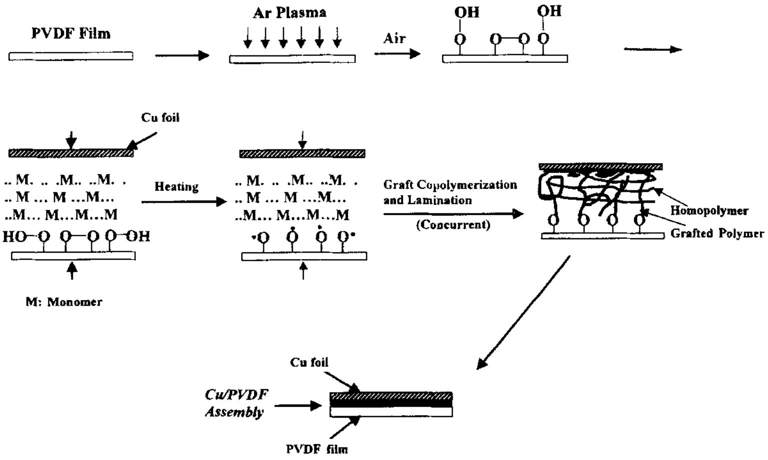

FIGURE 6 Plausible mechanism of adhesion at the Cu/PVDF interface arising from the present simultaneous graft copolymerization and lamination process.

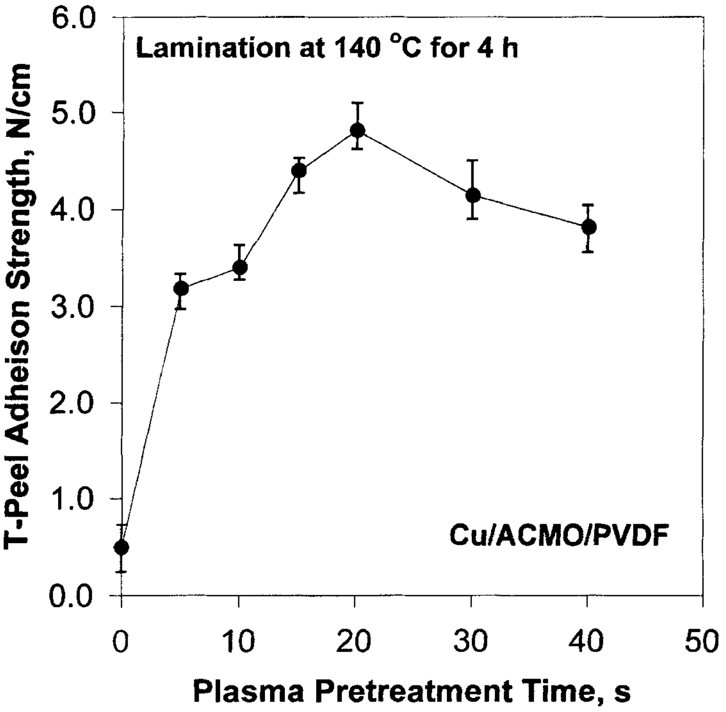

FIGURE 7 *T*-peel adhesion strength for the Cu/ACMO/PVDF assembly as a function of plasma-pretreatment time. (Lamination temperature = 140°C and time = 4 h).

of solvent has a pronounced effect on the adhesion strength. Thus, pure 4-VPN and ACMO liquid monomer are used in all the present simultaneous graft copolymerization and lamination experiments. Studies on the use of other monomers, such as 2-vinyl pyridine (2-VPN) and 1-vinyl imidazole (VIDz), reveal even lower peel strengths. The optimum attainable peel strengths were only in the order of 1 to 2 N/cm for the Cu/VIDz/PVDF and Cu/2-VPN/PVDF assemblies obtained from the simultaneous grafting and lamination process.

The graft chain induced adhesion at the Cu/PVDF interface can be described in terms of the microscopic interaction at the interface and is related to the sum of all the intermolecular interactions [44,45]. For the Cu/4-VPN/PVDF assembly, the nitrogen atoms in the pyridine rings of the growing 4-VPN graft interact directly with the copper atoms of the contacting Cu foil. The strong charge transfer interaction between Cu and the pyridine ring [46] accounts for the strong metal/polymer adhesion. The extent of charge transfer interaction is reduced in the case of the grafted ACMO polymer as the nitrogen atoms in this polymer are more sterically hindered than those in the 4-VPN polymer due to the presence of the neighboring carboxyl groups. Steric hindrance has also accounted for the reduced charge transfer interaction and adhesion strength [46,47] between Cu and poly(2-vinyl pyridine). Although strong interaction between the imidazole ring of the VIDz polymer and Cu atoms has been reported earlier [48], a much lower adhesion strength is achieved for the Cu/VIDz/PVDF assembly in the present work. The phenomenon is probably due to the low thermal graft copolymerization efficiency of VIDz on the PVDF surfaces under the present experimental conditions.

The effect of lamination temperature on the *T*-peel adhesion strength of the Cu/4-VPN/PVDF and Cu/ACMO/PVDF assemblies from the simultaneous graft copolymerization and lamination process carried out for 4 h with 5 s and 20 s Ar plasma pretreated PVDF films is shown in Figure 8. For the Cu/4-VPN/PVDF assembly, the peel adhesion strength increases monotonically up to a lamination temperature of 140°C, but decreases at 160°C. At temperature above 140°C, the changes in phase structure of the PVDF substrate may also have to be taken into account in interpreting the temperature effect on the lamination strength, as PVDF has been known to be a prolific polymorphic polymer. For the assembly involving 20 s Ar plasma pretreated

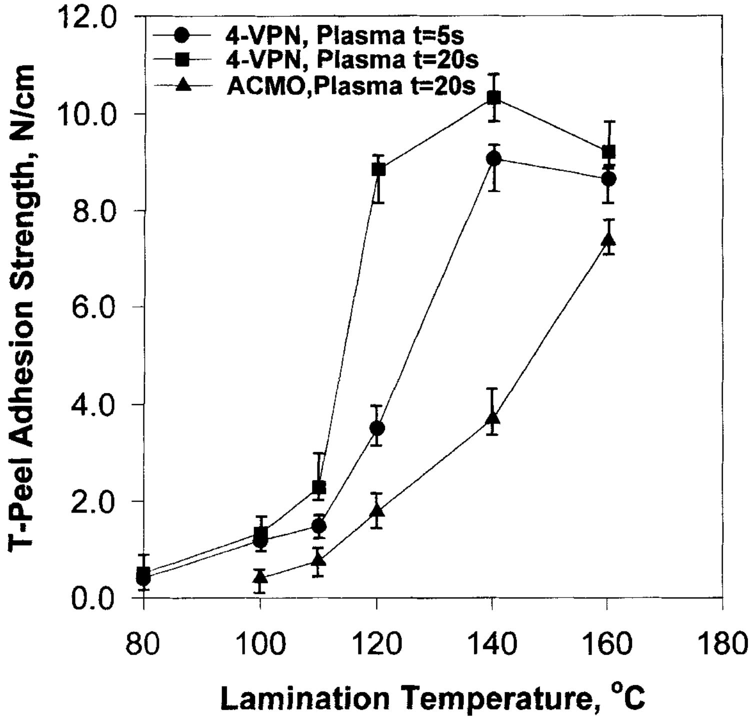

FIGURE 8 *T*-peel adhesion strength for the Cu/VPN/PVDF and Cu/ACMO/PVDF assemblies as a function of the lamination temperature. (Lamination time = 4 h).

PVDF film, the largest increase in adhesion strength is achieved at temperatures between 100 and 120°C. These temperatures are increased to between 120 to 140°C for the assembly involving 5 s Ar plasma pretreated PVDF film. For the Cu/ACMO/PVDF assembly involving the 20 s plasma pretreated PVDF film, the adhesion strength increases abruptly with the lamination temperature, but is everywhere lower than that obtained at comparable lamination temperature for the Cu/4-VPN/PVDF assembly involving PVDF film with only 5 s of Ar plasma pretreatment.

Generally, the free radical on the substrate surface originating from the Ar plasma pretreatment, and the macromolecular free radical tethered on the polymer substrate after the initiation of the graft copolymerization process, will be more sterically hindered and of low mobilities. Therefore, elevating the reaction temperature not only is beneficial to the increase in reactivity of the above radicals, but will also increase the polymerization rate. Furthermore, for the present polymerization mechanism, the decomposition of the peroxides species would also be favored by the higher reaction temperature. All of the above factors associated with the increase in lamination temperature would account for the increase in the graft efficiency on the PVDF surface and, thus, the enhanced adhesion. At an even higher temperature, thermal degradation of the functional groups introduced by the plasma pretreatment and the grafted polymer will commence owing to their limited thermal stability. In addition, the increased thermal stress at the metal/polymer interface during cooling from higher temperatures will also cause a decrease in the adhesion strength [49].

The failure mode of the Cu/PVDF laminates from the present technique of simultaneous thermal graft copolymerization and lamination was also investigated. The wide scan spectrum and C1s core-level spectrum of the PVDF and Cu surfaces delaminated from a Cu/4-VPN/PVDF assembly, having a peel strength of about 9.0 N/cm and prepared from the simultaneous grafting and lamination process at 120°C for 4 h using a 20 s Ar plasma pretreated PVDF film, are shown in Figure 9. The wide scan spectra of the delaminated PVDF and Cu surfaces show great resemblance to each other and to that of the 4-VPN graft-copolymerized PVDF film surface shown in Figure 4(d). All of the wide scan spectra show the presence of the F1s and N1s components, which are attributable to the presence of the PVDF substrate and the grafted 4-VPN polymer on the surfaces, respectively. The corresponding C1s core-level spectra of both of the delaminated surfaces, which are dominated by the $\underline{C}H_2$ peak component, resemble one another. They are also similar to that of the 4-VPN graft copolymerized PVDF film surface shown in Figure 4(b), except for the enhanced intensities of the $\underline{C}F_2$ component of the PVDF substrate at 291.4 eV. The XPS results readily suggest that the present Cu/4-VPN/PVDF assembly from thermal grafting and lamination fails by the combined adhesional and cohesive mode, with the cohesive failure occurring in the PVDF substrate near enough to the metal to reveal some copper signals in the survey scan in Figure 9(c). The presence of the Cu signal in the wide scan spectrum of the delaminated Cu surface further suggests that a certain portion of the polymer-metal interface is within the probing depth of the XPS technique. Earlier study [22] has

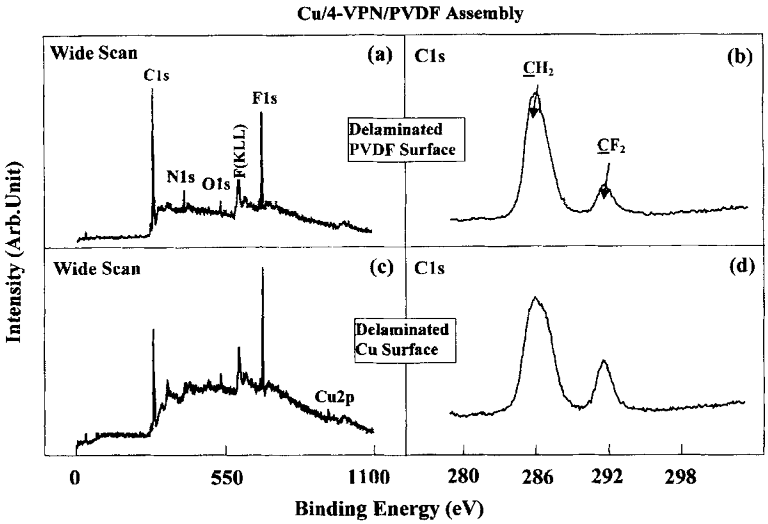

FIGURE 9 XPS wide scan and C1s core-level spectra of (a), (b) the delaminated PVDF surface, and (c), (d) the delaminated Cu surface from the Cu/VPN/PVDF assembly having a peel strength of about 9 N/cm.

shown that cohesive failure is always observed for the similarly-prepared Cu/VIDz/PTFE laminates with peel strength above 4.0 N/cm. This disparity between the PVDF and PTFE substrates must be due to the fact that PTFE has a lower mechanical strength than PVDF (about 25 MPa for PTFE film *vs*. 43 MPa for PVDF film in tensile strength for the films used in the present work). The lower mechanical strength of the PTFE substrate makes it more susceptible to peel and rupture.

4. CONCLUSION

Thermal graft copolymerization of *N*-containing functional monomers, such as 4-vinyl pyridine (4-VPN) and acryloyl morpholine (ACMO), on Ar-plasma-pretreated PVDF films with simultaneous lamination with copper foil was carried out under atmospheric conditions and in the complete absence of an added polymerization initiator. The adhesion strengths of the Cu/PVDF laminates were measured as a function of the plasma pretreatment time of the PVDF film, the graft concentration and the thermal lamination temperature. For the

Cu/4-VPN/PVDF assembly, a *T*-peel adhesion strength of about 10 N/cm was readily achieved when the simultaneous grafting and lamination was carried out at 140°C for 4 h with the 20 s plasma-pretreated PVDF film. For the Cu/ACMO/PVDF assembly, *T*-peel adhesion strength in excess of 7 N/cm was also achieved under similar conditions, except a higher lamination temperature of 160°C was used. XPS characterization of the delaminated interfaces reveal that the failure mode is a combined adhesional and cohesive failure, differing from that involving the PTFE substrate.

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