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Surface modification of poly(tetrafluoroethylene) films by double graft copolymerization for adhesion improvement with evaporated copper

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Abstract

Surface modifications of Ar plasma-pretreated poly(tetrafluoroethylene) (PTFE) film via UV-induced double graft copolymerization were carried out to improve the adhesion with evaporated copper. The PTFE film surface was first modified by graft copolymerization with a monomer, such as hydroxylethylacrylate and acrylamide, which contained functional moities for curing the epoxide groups. The so-modified PTFE surface was subsequently re-exposed to Ar plasma and subjected to UV-induced graft copolymerization with glycidyl methacrylate. The surface compositions of the PTFE films from single and double graft copolymerization were studied by X-ray photoelectron spectroscopy. The adhesion strength of the evaporated copper on the double graft copolymerized PTFE film was affected by the type of monomer used during the first graft copolymerization, the concentration of the first and second graft, the extent of O_2 plasma post-treatment after the second graft copolymerization, and the extent of heat treatment after metallization. The T-type peel strength of the Cu–PTFE laminate obtained under optimum conditions was about 19 N/cm, which represented a more than ten-fold increase over that obtained when the PTFE film was treated by plasma alone. The mechanism of the peel strength enhancement and the cohesive failure of the metal–polymer laminate were also investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: PTFE; Surface modification; Double graft copolymerization

1. Introduction

Because of its excellent thermal and dielectric properties, polytetrafluoroethylene (PTFE) is potentially an ideal material for microelecronic application [1–3]. Many studies on the metallization of PTFE have been carried out [4–6]. Because of the chemical inertness of PTFE, the adhesion between the polymer and various metals fails to satisfy many of the industry requirements [7]. Activation of polymer surfaces prior to metal deposition has been shown to enhance metal adhesion. One of the most widely used methods for activating the PTFE surface is the treatment with a reducing etchant [8–11], such as sodium naphthalene and potassium *t*-butoxide/benzoin/dimethy sulfoxide. 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 films modified by N_2, O_2, H_2, and mixed-gas plasmas. It was proposed that Cu reacted with both oxygen and nitrogen to form, respectively, Cu–O and Cu–N moieties at the interfaces. Modification of polymer surfaces by graft copolymerization with specific functional monomers will also improve their adhesion properties [15]. It has also been reported [16] that the adhesion between two PTFE films can be substantially improved by graft copolymerization with certain functional monomers. Vargo et al. [17], in contrast, reported that the metal-ion-chelating organosilane could be chemisorbed onto a plasma hydroxylated fluoropolymer surface, resulting in excellent adhesion to some metals.

In the present work, surface modification of Ar plasma pretreated PTFE film was carried out via UV-induced double graft copolymerization, firstly with hydroxylethylacrylate (HEA), or acrylamide (AAm), and subsequently with glycidyl methacrylate (GMA) to enhance the adhesion of PTFE surface with evaporated copper metal. Physicochemical parameters affecting the adhesion between the

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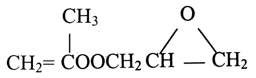
surface-graft copolymerized PTFE films and evaporated copper, such as the monomer concentrations, the first and second graft concentrations, the extent of O_2 plasma post-treatment after double graft-copolymerization and the extent of heat treatment after metallization, were investigated. The results show that modification of PTFE surface by double graft copolymerization is an effective means for enhancing the adhesion of copper to fluoropolymer surfaces. The chemical compositions of the surface modified PTFE films, as well as the delaminated Cu and PTFE surfaces, were characterized by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. 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. (Cambridge, UK). The surface of the film was cleaned by Soxhlet extraction with acetone for 6 h before use. The monomers HEA, AAm and GMA, and the solvent 1,4-dioxane used for surface graft copolymerization were obtained from Aldrich Chemical Company (Milwaukee, USA). The chemical structures of GMA, HEA and AAm monomers are shown below:



GMA

$CH_2{=}CHCOOCH_2CH_2OH$ **HEA**

$CH_2{=}CHCOONH_2$ **AAm**

2.2. Surface graft copolymerization

The PTFE films were cut into strips of about 2 × 3 cm^2 in size. They were pretreated with Ar plasma before graft copolymerization. A cylindrical type glow discharge cell, Model SP100, manufactured by Anatech Ltd. (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 pre-determined 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 formation of surface peroxides and hydroxyl peroxides [18] before graft copolymerization. The surface activated PTFE films were immersed in 30 ml of 1,4-dioxane (for GMA) or aqueous (for HEA and AAm) monomer solutions in a Pyrex® tube. The concentrations of each monomer were varied from 5 to 50 wt.%. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. It was then subjected to UV irradiation for 10–60 min in a Riko RH 400-10W rotary photochemical reactor, manufactured by Riko Denki Kogyo (Chiba, Japan). The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerizations were carried out at a constant temperature of 28°C. After each grafting experiment, the PTFE film was washed thoroughly with copious amounts of acetone (for GMA graft copolymerization) or double distilled water (for HEA and AAm graft copolymerization) 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, followed by the UV-induced graft copolymerization with the second monomer. Plasma post-treatment after graft copolymerization was carried out under the same glow discharge conditions as mentioned above with purified oxygen.

2.3. 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 take-off 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 C1s neutral carbon peak at 284.6 eV. In 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.

2.4. T-type peel strength measurement

A copper layer of about 1000 Å in thickness was thermally evaporated onto the surface of the PTFE film in a Joel Model LEE-400 vacuum evaporator. 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 heat-cured in a vacuum oven at different temperatures. The metallized surface was then 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 adhesion test in an Instron Model 5544 materials tester. All measurements were carried out at a crosshead speed of 1.0 cm/min.

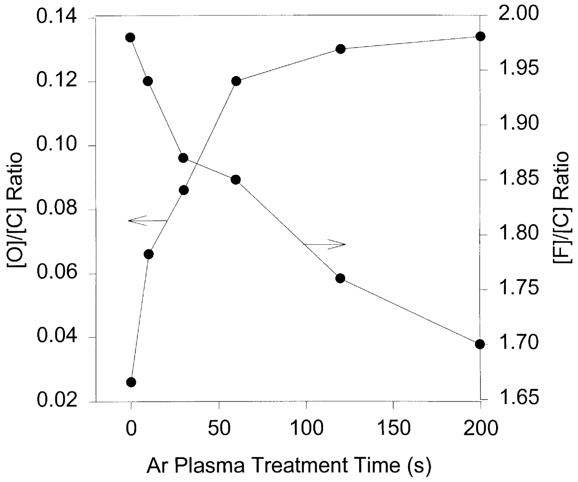


Fig. 1. Effect of Ar plasma treatment time on the [O]/[C] and[F]/[C] ratios of the PTFE surface.

For each T-type peel strength reported, at least three sample measurements were averaged.

3. Results and discussion

3.1. Surface modification of PTFE films via Ar plasma treatment and graft copolymerization with GMA: the Cu/PTFE assembly and the Cu/GMA/PTFE assembly

The changes in the [F]/[C] and [O]/[C] atomic ratios, as determined from the corrected C1s, O1s and F1s XPS core-level spectral area ratios at the photoelectron take-off angle (α) of 75°, as a function of the Ar plasma treatment time under the present glow discharge conditions are shown in Fig. 1. 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-induced graft copolymerization.

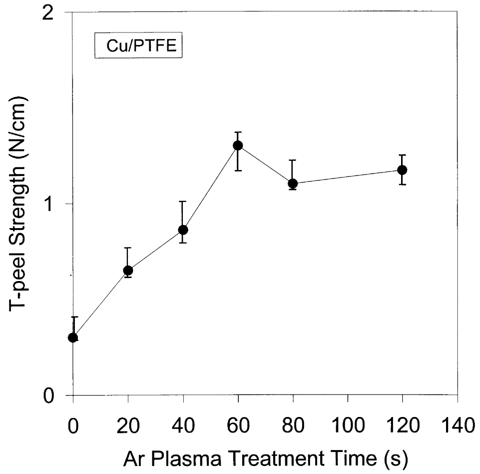


Fig. 2. Effect of Ar plasma treatment time on the adhesion strength between PTFE film and evaporated copper.

Fig. 2 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 for about 60 s under the present glow discharge conditions could enhance the peel strength of the Cu–PTFE laminate to about 1.3 N/cm, from the value of about 0.3 N/cm for evaporated Cu on pristine PTFE film. The [O]/[C] ratio increases from 0.024 to 0.12 (see Fig. 1) at the corresponding extent of plasma treatment, caused by the oxidation of PTFE surface. The increased extent of surface oxidation contributes to the enhancement of adhesion between the polymer and the metal. After reaching the maximum peel strength at 60 s of Ar plasma treatment, the peel adhesion strength changes only slightly with further increase in plasma treatment time. The result is consistent with the fact that the surface [O]/[C] ratio of the PTFE film approaches an asymptotic value after 60 s of Ar plasma treatment, as shown in Fig. 1.

Fig. 3(a)–(d) shows the respective C1s core-level spectra for a pristine PTFE film and the 60 s Ar plasma-pretreated PTFE films after having been subjected to UV-induced graft copolymerization in three different concentrations (10, 30 and 50 wt.%) of GMA solutions for 1 h. The C1s core-level spectrum of the pristine PTFE surface consists of a main component at the binding energy (BE) of about 291.4 eV, attributable to the CF_2 species [16], and a broad minor component which is about 8 eV lower in BE. The area of this minor component is about 13% of that of the C1s core-level component at 291.4 eV. This low BE component is attributable to the combined contribution of the X-ray satellite peaks of the CF_2 species arising from the Mg K$\alpha_{3,4}$ radiation (about 9% of the main X-ray component) and the adventitious hydrocarbon CH species present on the film surface [19]. The presence of surface-grafted GMA polymer can be deduced from the appearance of the three C1s peak components with BEs similar to those of the GMA homopolymer [16], i.e. the component at 284.6 eV for the *C*H species, 286.2 eV for the *C*O species, and 288.5 eV for the *C*OO species. The theoretical peak area ratio of the CH:CO:COO species for GMA polymer is 3:3:1. For the PTFE surface with low graft concentration (Fig. 3(b)), this ratio deviated from the theoretical value due to the contribution of the CF_2 satellite peaks. In contrast, the CH:CO:COO ratios of the surfaces with higher graft concentrations (Fig. 3(c) and (d)) are in good agreement with the theoretical ratio of 3:3:1. The graft concentration, defined in this case as the [Epoxide]/[F] ratio and derived from the ratio of the *C*OO component area in the C1s core-level spectrum and

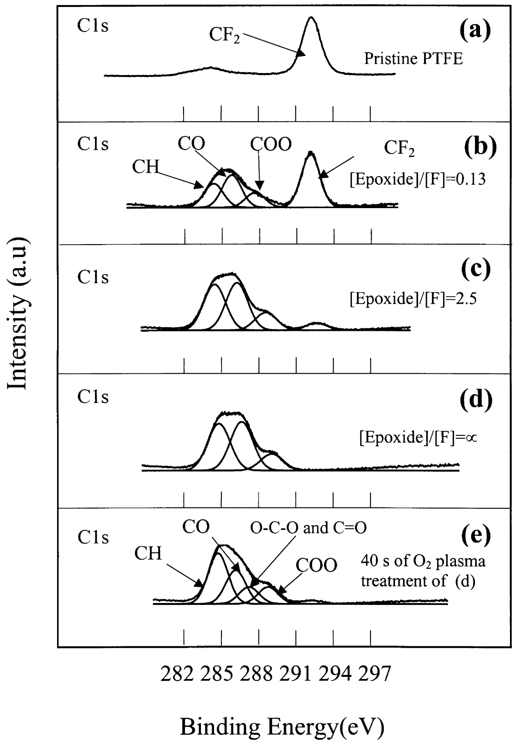


Fig. 3. C1s core-level spectra of pristine and GMA graft copolymerized PTFE surface: (a) Pristine PTFE film; (b) [Epoxide]/[F] = 0.13; (c) [Epoxide]/[F] = 2.5; (d) [Epoxide]/[F] = ∝; (e) 40 s of O_2 plasma post-treatment of the sample in (d).

the F1s core-level spectral area (as each GMA molecule has one *C*OO and one epoxide group), as a function of the concentration of the GMA monomer used for graft copolymerization is shown in Fig. 4. The corresponding [F]/[C] atomic ratios of the graft-modified surfaces are also shown. The [Epoxide]/[F] ratio increases with increasing concentration of the GMA monomer solution. The [F]/[C] ratio, in contrast, decreases sharply to almost zero at high GMA monomer concentration, suggesting the complete coverage of the PTFE surface by the grafted GMA polymer.

The effect of the graft concentration of the GMA polymer, expressed in terms of the GMA monomer concentration used during graft copolymerization for a 60 s Ar plasma pretreated PTFE film with 1 h of UV graft copolymerization time, on the T-peel adhesion strength with evaporated Cu is shown in Fig. 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 strength with copper metal is ascertained. The effect of

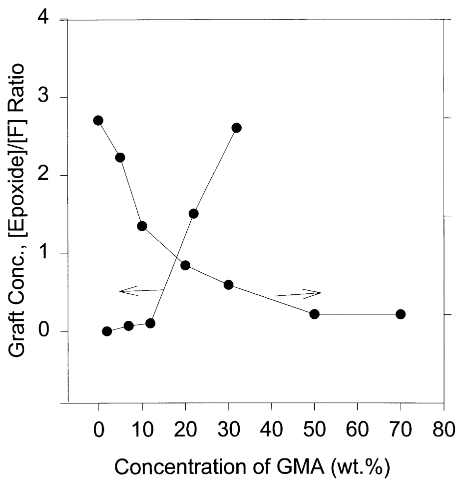


Fig. 4. Effect of monomer concentration on the graft concentration of the GMA polymer on the PTFE surface (Ar plasma pretreatment time = 60 s, UV time = 1 h).

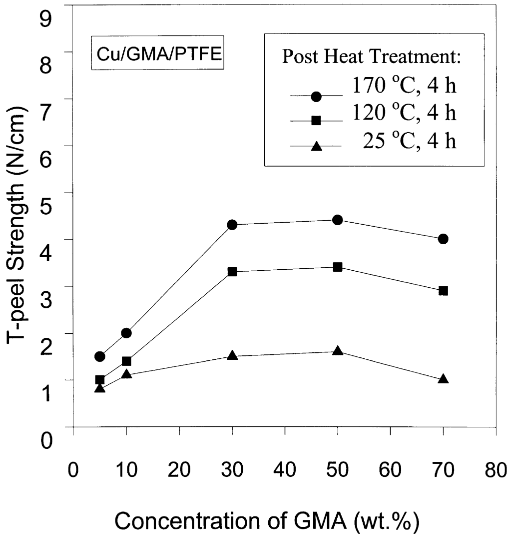


Fig. 5. Effect of graft concentration, expressed in terms of the monomer concentration used for graft copolymerization and of the curing temperature after metallization, on the peel strength of the Cu/GMA/PTFE assembly (Ar plasma pretreatment time = 60 s, UV time = 1 h).

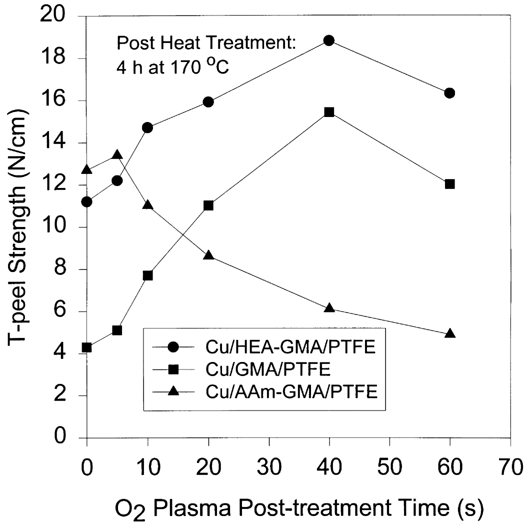


Fig. 6. Effect of O_2 plasma post-treatment time on the peel strength of the Cu/GMA/PTFE, Cu/HEA–GMA/PTFE and Cu/AAm–GMA/PTFE assemblies.

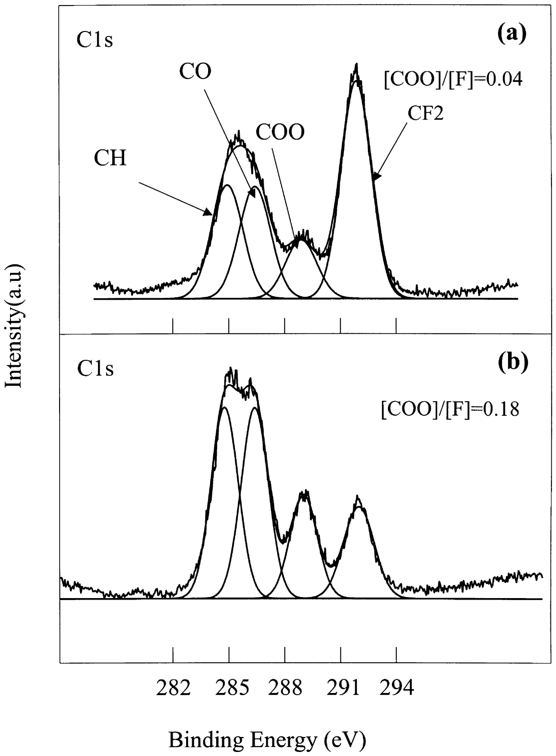


Fig. 7. C1s core-level spectra of the HEA graft copolymerized PTFE surface from graft copolymerization of the 60 s Ar plasma pretreated PTFE films in: (a) 5 wt.%; and (b) 10 wt.% HEA monomer solutions (UV time = 20 min).

post-heat-treatment after metallization on the metal–polymer adhesion strength was also studied, and the results are summarised in Fig. 5. The peel strength is enhanced by the post-heat-treatment of the metal–polymer laminate. A maximum peel strength of about 4.3 N/cm was obtained after 4 h of curing at 170°C. The improved adhesion may have resulted from the enhanced charge transfer interaction between the epoxide group and Cu at elevated temperatures, in a manner similar to the thermally induced curing reaction of the epoxide group with, for example, an amine curing agent.

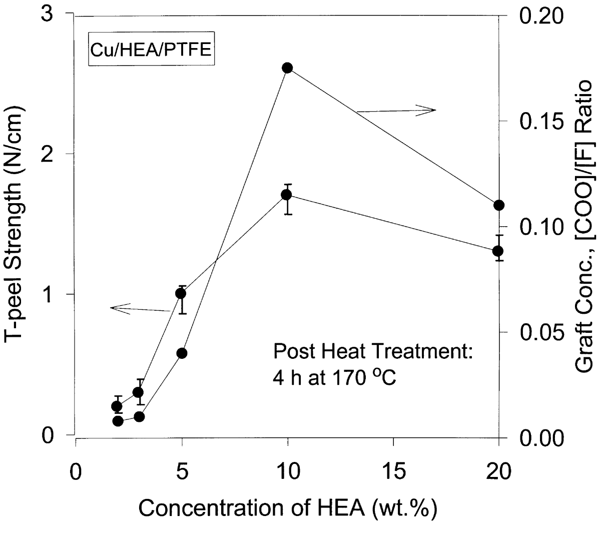


Fig. 8. Effect of monomer concentration on the graft concentration of HEA polymer on the PTFE surface and the peel strength of the resulting Cu/HEA/PTFE assembly (Ar plasma pretreatment time = 60 s, UV time = 20 min).

The effect of O_2 plasma post-treatment of the GMA graft polymerized PTFE surface prior to metallization on the adhesion strength of the Cu/GMA/PTFE assembly is shown in Fig. 6. The peel strength increases from 4.3 N/cm for the non-plasma post-treated assembly to 15.4 N/cm for the assembly with 40 s of oxygen plasma post-treatment before metallization. Fig. 3(e) shows the C1s core-level spectrum of the sample in Fig. 3(d) after 40 s of O_2 plasma post-treatment. A new C1s peak component with the BE at 287.7 eV, attributable to the O–C–O or C=O species [20], appears after the plasma post-treatment and must have contributed in part to the enhancement of the peel strength. After reaching the maximum, the peel strength decreases with further increase in the O_2 plasma treatment time. The phenomenon may be attributable to the ‘etching’ effect [7] of the O_2 plasma on the grafted GMA polymers upon increasing the plasma treatment time. The etching effect can cause the partial degradation or removal of the grafted GMA chains and the activated surface species. Alternatively, prolonged O_2 plasma treatment may result in the over-oxidation or degradation of the epoxide species prior to metallization.

3.2. Surface modification of PTFE films via double graft copolymerization: the Cu/HEA–GMA/PTFE assembly

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 PTFE film which has been previously modified also by graft copolymerization.

Fig. 7 shows the C1s core-level spectra, obtained at α of 75°, for a 60 s Ar plasma pretreated PTFE film after having been subjected to UV-induced graft copolymerization in two different concentrations (5 and 10 wt.%) of hydroxylethylacrylate (HEA) solutions for 20 min. The presence of surface-grafted HEA polymer can be deduced from the three C1s peak components with BEs at 284.6 eV for the *C*H species, 286.2 eV for the *C*O species, and 288.5 eV for the *C*OO species. The theoretical area ratio for the three species in HEA polymer is 2:2:1. The component ratios for surfaces with low graft concentration (Fig. 7(a)) and high graft concentration (Fig. 7(b)) are both in agreement with the theoretical ratio. The graft concentration, defined in this case as the [COO]/[F] ratio, was derived from the area of the *C*OO component in the C1s core-level spectrum and the F1s core-level spectral area.

The graft concentration of the HEA polymer as a function of the monomer concentration used for graft copolymerization is shown in Fig. 8. The [COO]/[F] ratio increases with

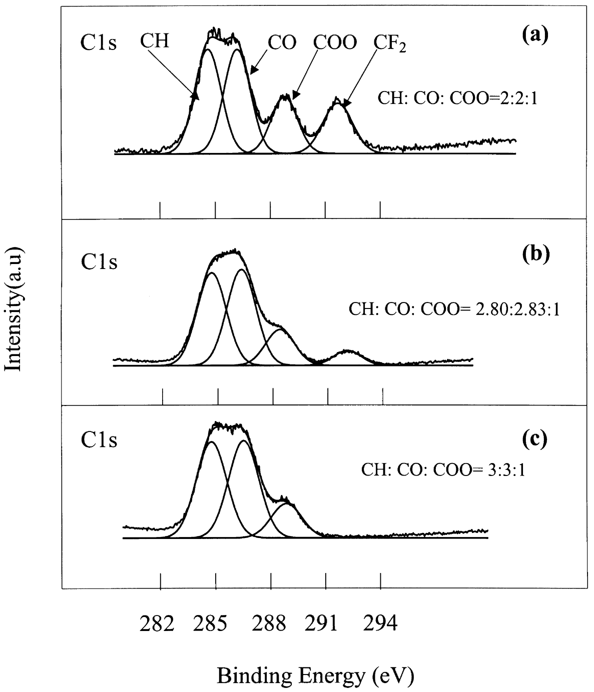


Fig. 9. C1s core-level spectra of the PTFE film surface after (a) graft copolymerization in 10 wt.% HEA solution, followed by an additional 60 s of Ar plasma treatment and graft copolymerization in (b) 5 wt.%, and (c) 30 wt.% GMA solution.

the monomer concentration up to a monomer concentration of about 10 wt.%, 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 source reaching the PTFE surface. More efficient homopolymerization was observed for the HEA monomer solution than for the GMA solution, as indicated by the much more rapid rise in solution viscosity of the former during the UV-induced graft copolymerization process. Fig. 8 also shows the effect of graft concentration, expressed in terms of the HEA monomer concentration, on the T- peel adhesion strength of the metal–polymer laminate after the Cu/HEA/PTFE assembly has been cured at 170°C for 4 h. The optimum peel strength of about 1.7 N/cm coincides with the maximum in graft concentration at a monomer concentration of about 10 wt.%.

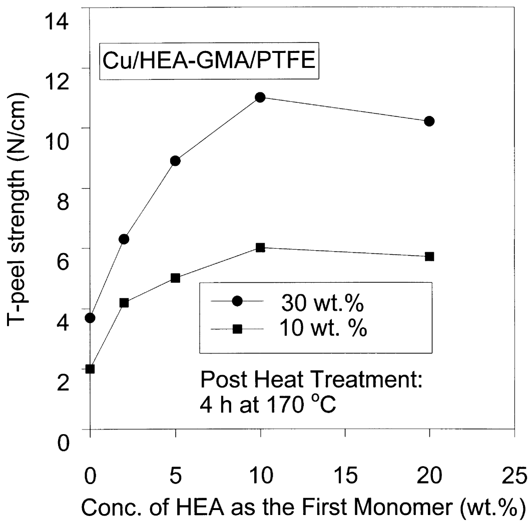


Fig. 10. Effect of concentration of the first monomer (HEA) on the peel strength of the Cu/HEA–GMA/PTFE assembly.

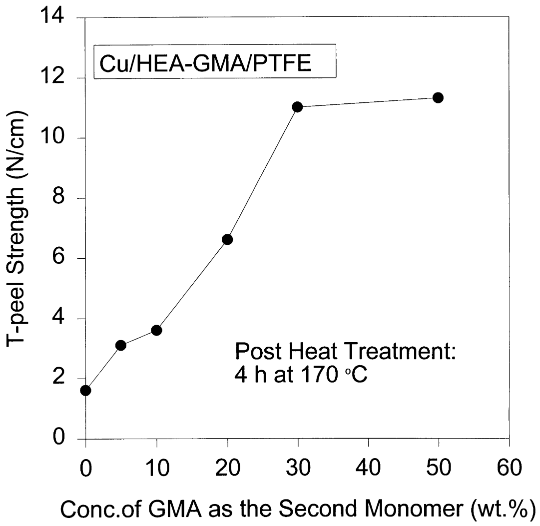


Fig. 11. Effect of concentration of the second monomer (GMA) on the peel strength of the Cu/HEA–GMA/PTFE assembly.

Fig. 9(a) shows the C1s core-level spectrum of a 60 s Ar plasma pretreated PTFE film after modification via UV-induced graft copolymerization in 10 wt.% HEA solution for 20 min. The corresponding C1s core-level spectra of the HEA polymer modified PTFE surface after further modification by 60 s of Ar plasma treatment and 1 h of UV-induced graft copolymerization in 5 and 30 wt.% GMA solutions are shown in Fig. 9(b) and (c), respectively. The C1s core-level line shape and a peak area ratio of 2.80:2.83:1 for the CH:CO:COO species suggest the presence of both types of the grafted polymers at moderate extent of grafting (Fig. 9(b)). In contrast, the peak area ratio of 3:3:1 indicates that the use of a high GMA monomer concentration during the second graft copolymerization process has resulted in the complete coverage of the HEA polymer modified PTFE surface by the GMA polymer (Fig. 9(c)). The peel strength of the Cu–PTFE laminate as a function of the grafted HEA polymer concentration after further modification by 60 s of Ar plasma treatment, followed by 1 h of UV graft copolymerization in 10 and 30 wt.% of GMA solutions are shown in Fig. 10. The peel strengths reported are obtained after the Cu/HEA–GMA/PTFE assemblies have been cured at 170°C for 4 h. In comparison with the similarly cured Cu/HEA/PTFE assemblies (Fig. 8) and the Cu/GMA/PTFE assemblies (Fig. 5), the adhesion strengths of the doubly graft copolymerized Cu/HEA–GMA/PTFE assemblies have been enhanced to beyond the linear combination of the effects of the individual polymer

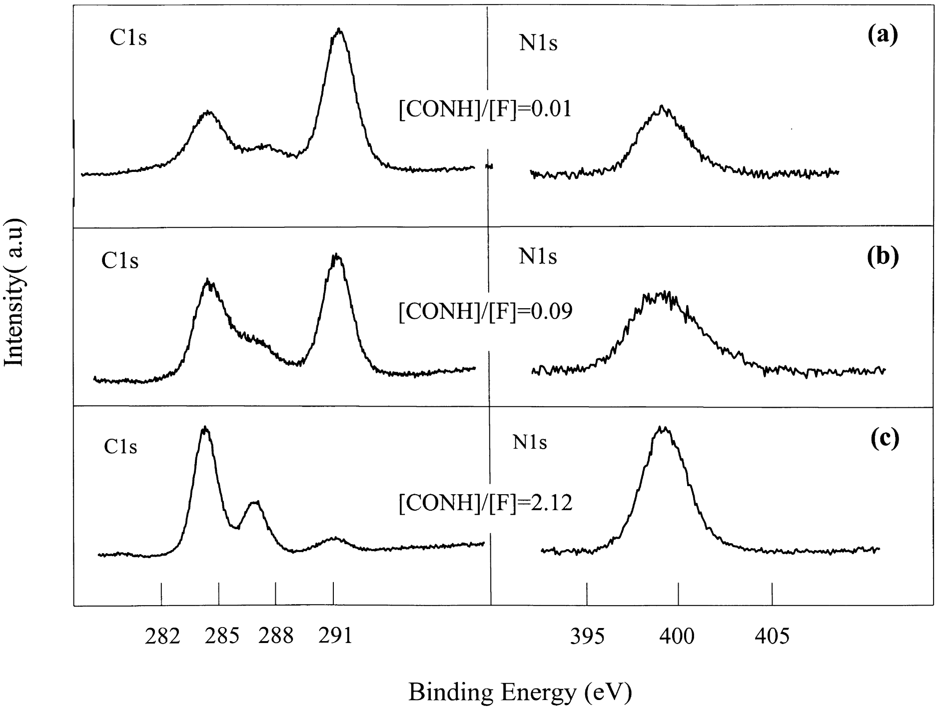


Fig. 12. C1s and N1s core-level spectra of the modified PTFE surfaces from graft copolymerization of the 60 s Ar plasma pretreated PTFE films in: (a) 3 wt.%; (b) 5 wt.%; and (c) 10 wt.% AAm monomer solutions.

graft, particularly for surfaces graft copolymerized at high concentrations of the HEA monomer. The effect of concentration of the second monomer (GMA) used for graft copolymerization on the peel strength of a 10 wt.% HEA graft copolymerized PTFE surface is shown in Fig. 11. Thus, the synergetic effect on the peel strength resulting from the simultaneous presence of both types of grafts is discernible. The synergetic effect from the double grafting must have resulted from the fact that the hydroxy moieties of the HEA polymer can promote the curing or the cross-linking reactions of the epoxide groups of the GMA polymer.

The effect of O_2 plasma post-treatment on the peel strength of the Cu/HEA–GMA/PTFE assembly is shown in Fig. 6. The peel strength increases from 11.4 N/cm for the non-plasma post-treated assembly to 18.8 N/cm for the O_2 plasma post-treated assembly, for the same effect discussed in the case of the O_2 plasma post-treated Cu/GMA/PTFE assembly (Fig. 3(e)).

3.3. *Surface modification of PTFE films via double graft copolymerization: the Cu/AAm–GMA/PTFE assembly*

Fig. 12 shows the C1s core-level spectra, obtained at α of 75°, for a 60 s Ar plasma pretreated PTFE film after having been subjected to UV-induced graft copolymerization in different concentrations (3, 5 and 10 wt.%) of AAm solution for 10 min. The presence of surface-grafted AAm polymer can be deduced from the appearance of a low BE C1s core-level spectrum with a peak component centered at about 284.6 eV for the *C*H species and 287.7 eV for the *C*ONH species, as well as the N1s core-level signal centered at about 399.0 eV for the amide species. The graft concentrations, defined in this case as the [CONH]/[F] ratios, were derived from the area of the *C*ONH component in the C1s core-level spectrum and the F1s core-level spectral area.

The graft concentration as a function of monomer concentration used for graft copolymerization is shown in Fig. 13. The [CONH]/[F] ratio increases with the monomer

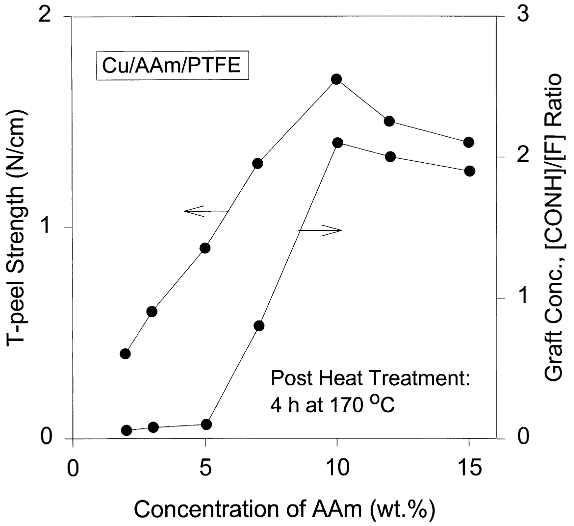


Fig. 13. Effect of monomer concentration on the graft concentration of AAm polymer on the PTFE surface and the peel strength of resulting the Cu/AAm/PTFE assembly (Ar plasma pretreatment time = 60 s, UV time = 10 min).

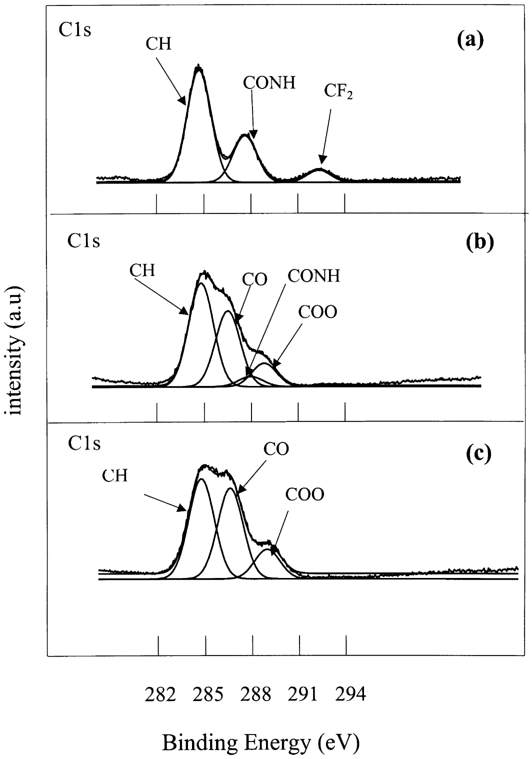


Fig. 14. C1s core-level spectra of the PTFE film surface after (a) graft copolymerization in 10 wt.% AAm solution, followed by 60 s Ar plasma treatment and graft copolymerization in (b) 5 wt.%, and (c) 30 wt.% GMA solution.

concentration up to a monomer concentration of about 10 wt.%, 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 source reaching the PTFE surface. Efficient AAm homopolymerization is again indicated by the rapid rise in solution viscosity of the reaction mixture during the UV-induced graft copolymerization process. Fig. 13 also shows the effect of graft concentration, expressed in terms of the AAm monomer concentration used for graft copolymerization, on the T-peel adhesion strength of the Cu–PTFE laminate after curing at 170°C for 4 h. The optimum peel strength of about 1.7 N/cm again coincides approximately with the maximum in graft concentration at a monomer concentration of about 10 wt.%.

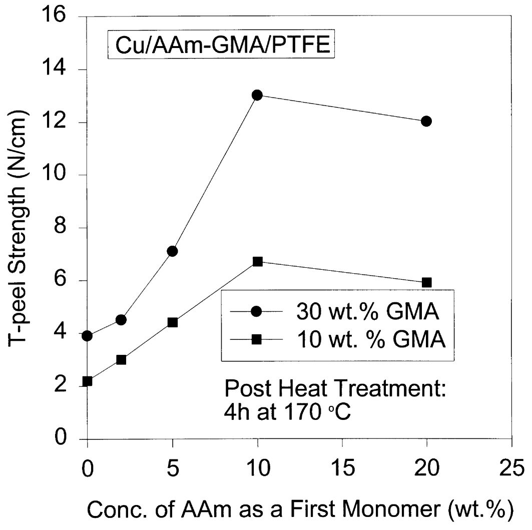


Fig. 15. Effect of concentration of the first monomer (AAm) on the peel strength of the Cu/AAm–GMA/PTFE assembly.

Fig. 14(a) shows the C1s core-level spectrum of the PTFE film after modification via UV-induced graft copolymerization of a 60 s Ar plasma pretreated PTFE in 10 wt.% AAm solution for 10 min. The corresponding C1s core-level spectra of the AAm polymer modified PTFE surface after 60 s of Ar plasma treatment and further graft copolymerization in 5 and 30 wt.% GMA solutions are shown in Fig. 14(b) and (c), respectively. The C1s core-level spectra suggest the presence of both types of the graft polymers at moderate extent of grafting (Fig. 14(b)). In contrast, the use of a high GMA monomer concentration during the second grafting process has resulted in the complete coverage of the AAm polymer-modified PTFE surface by the GMA polymer (Fig. 14(c)), as indicated by the formation of a C1s line shape not unlike that of the GMA homopolymer. The T-peel strength of the Cu–PTFE laminate as a function of the grafted AAm polymer concentration after further modification by 60 s of Ar plasma treatment, followed by 1 h of UV-induced graft copolymerization in 10 and 30 wt.% GMA solutions are shown in Fig. 15. The peel strengths reported are obtained after the Cu/AAm–GMA/PTFE assemblies have been cured at 170°C for 4 h. In comparison with the similarly cured Cu/AAm/PTFE assemblies (Fig. 13) and the Cu/GMA/PTFE assemblies (Fig. 5), the adhesion strengths of the doubly graft copolymerized Cu–PTFE laminates have been again enhanced to beyond the linear combination of the effects of the individual polymer graft, particularly at high concentrations of the AAm monomer. Thus, the synergetic effect from the simultaneous presence of both types of grafts on the resulting peel strength is again discernible. The synergetic effect from double grafting must have resulted from the fact that the nitrogen moiety of the AAm, similar to the hydroxyl moiety of HEA, can promote the curing or crosslinking reactions of the epoxide groups of the GMA polymer.

The effect of O_2 plasma post-treatment on the peel strength of the Cu/AAm–GMA/PTFE assembly is shown in Fig. 6. The peel strength increases marginally with O_2 plasma post-treatment and then decreases rapidly from 13 to about 4 N/cm at 60 s of O_2 plasma post-treatment time prior to metallization. In addition to the etching effects of the O_2 plasma, other factors may also have contributed to this decrease. Various PTFE films with surface grafted GMA, HEA–GMA and AAm–GMA polymers before and after O_2 plasma post-treatment were immersed in 10 wt.% 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 ethylenediamine is known to

Table 1
Effect of ethylenediamine treatment on the [N]/[C] ratios of the GMA, HEA–GMA and AAm–GMA graft copolymerized PTFE film surfaces before and after O_2 plasma post-treatment

Sample	Post-treatment	[N]/[C]
PTFE film graft copolymerized with GMA	Before treatment	0.052
	After 40 s of O_2 plasma treatment	0.055
PTFE film graft copolymerized with HEA and GMA	Before treatment	0.056
	After 40 s of O_2 plasma treatment	0.054
PTFE film graft copolymerized with AAm and GMA	Before treatment	0.086
	After 40 s of O_2 plasma treatment	0.063

react effectively with the epoxide group and become covalently bonded [16]. The data in Table 1 indicate that the [N]/[C] ratios of the GMA and HEA–GMA graft copolymerized surfaces before and after O_2 plasma post-treatment differ only slightly. The [N]/[C] ratio after the O_2 plasma post-treatment, however, decreases significantly for the AAm–GMA graft copolymerized surface. The data in Table 1 thus suggest that the epoxide rings of the grafted GMA and HEA–GMA polymers remain intact after the O_2 plasma post-treatment, as they remain active towards the diamine curing agent. However, the epoxide rings of the grafted AAm–GMA polymer remain only partially intact. The latter result indicates that the epoxide rings in the AAm–GMA graft copolymer are active towards the O_2 plasma. After 40 s of O_2 plasma post-treatment of the AAm–GMA graft copolymerized surface, nearly half of the epoxide rings lose their reactivities towards the diamine. This result helps to account for the rapid decrease in peel strength of the Cu/AAm–GMA/PTFE assembly upon increasing the O_2 plasma post-treatment time.

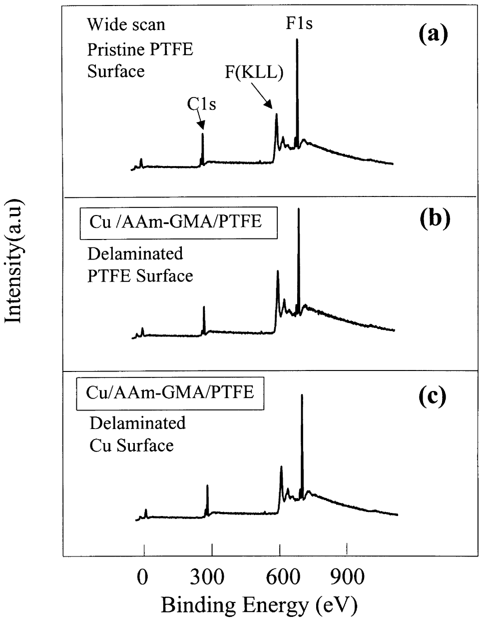


Fig. 16. XPS wide scan spectra of: (a) the pristine PTFE film, (b) the delaminated PTFE, and (c) Cu surfaces from a Cu/AAm–GMA/PTFE assembly having a peel strength of about 10 N/cm.

3.4. The failure mode of doubly graft-polymerized PTFE and copper interface

The failure mode of the Cu–PTFE laminate obtained from the evaporation of the copper metal onto the graft-modified PTFE surfaces was briefly investigated. Fig. 16(a)–(c) shows the respective wide scan spectra of a pristine PTFE surface, and the delaminated PTFE and Cu surfaces of a Cu/AAm–GMA/PTFE assembly having a peel strength of about 10 N/cm. The XPS-derived elemental compositions for the three surfaces are summarised in Table 2. 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 surface. In contrast, however, the [F]/[C] ratio for the delaminated Cu surface is somewhat below 2, probably due to the contribution of carbon signal from the grafted AAm–GMA polymer in the subsurface region which is still 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 suggest that the metal–polymer assembly is delaminated by cohesive failure inside the PTFE substrate. In fact, for all the Cu–PTFE assemblies studied in the present work, clean cohesive failure in the PTFE below the metal–polymer interface is always observed when the peel strength of the assembly exceeds about 5 N/cm.

4. Conclusion

Argon plasma pretreated PTFE films were subjected to further surface modification via UV-induced double graft copolymerization initially with HEA or AAm, and subsequently with GMA. The microstructure and composition of the singly and doubly graft copolymerized PTFE surfaces were characterized by XPS. In general, the graft yield increased with the concentration of monomer used during graft copolymerization. Double surface graft copolymerization was shown to be very effective in enhancing the adhesion of PTFE with evaporated Cu. An optimum T-type peel strength of about 19 N/cm was achieved between evaporated Cu and the HEA–GMA doubly graft copolymerized PTFE surface in the present of O_2 plasma post-treatment before metallization and proper thermal curing

Table 2
Comparison of the surface atomic ratios among the pristine PTFE film and the delaminated surface of a Cu/AAm–GMA/PTFE assembly having a peel strength of 10 N/cm

Sample	[F]/[C]	[O]/[C]	[Cu]/[C]
Pristine PTFE surface	1.98	0.01	0
Delaminated PTFE surface	1.97	0.031	0
Delaminated Cu surface	1.74	0.037	0

of the interface after metallization. This adhesion strength represents a more than ten-fold increase over that of the PTFE surface treated by plasma alone. The synergetic effect on adhesion strength arising from the interfacial crosslinking reactions between the two types of graft chains contributed to such an enhancement. The failure mode of the graft-modified PTFE and copper laminates was cohesive in nature when the peel strength of the metal–polymer laminate exceeds about 5 N/cm.

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