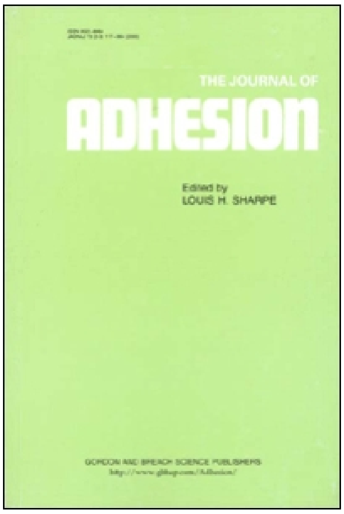

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Surface Modification of Poly(Tetrafluoroethylene) Films by Graft Copolymerization for Adhesion Improvement with Sputtered In-Sn Oxides

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Surface modification of Ar plasma-pretreated poly(tetrafluoroethylene) (PTFE) films was carried out *via* UV-induced graft copolymerization with glycidyl methacrylate (GMA), acrylamide (AAm) and hydroxylethylacrylate (HEA) to improve the adhesion strength with sputtered indium-tin-oxide (ITO). The surface compositions of the graft-copolymerized PTFE films were studied by X-ray photoelectron spectroscopy (XPS). The graft yield increases with increasing monomer concentration and Ar plasma pretreatment time of the PTFE films. The T-peel adhesion strength was affected by the type of monomer used for graft copolymerization, the graft concentration, and the thermal post-treatment after ITO deposition. A double graft-copolymerization process, which involved initially the graft copolymerization with AAm or HEA, followed by graft copolymerization with GMA, was also employed to enhance the adhesion of sputtered ITO to PTFE. T-peel adhesion strengths in excess of 8 N/cm were achieved in the ITO/graft-modified PTFE laminates. The adhesion failure of the ITO/PTFE laminates in T-peel tests was found to occur inside the PTFE films. The electrical resistance of ITO on all graft-modified PTFE surfaces before and after thermal post-treatment remained constant at about 30 Ω/square, suggesting that the graft layer did not have any significant effect on the electrical properties of the deposited ITO.

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Keywords: PTFE; surface modification; graft copolymerization; plasma; T-peel adhesion strength; ITO

1. INTRODUCTION

Fluoropolymers, such as polytetrafluoroethylene (PTFE), belong to one of the most important families of engineering polymers well known for their physical and chemical inertness [1]. The PTFE, for example, has found many applications where these properties are essential and desirable [2]. However, the surface of PTFE is extremely hydrophobic and is not well suited for a number of applications, especially those requiring adhesion to the surface of other materials. Due to their low surface free energy, surface modification of fluoropolymers has to be carried out prior to any application that requires a good bondability to other materials [3–9].

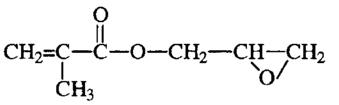
Many different methods for polymers surface modification have evolved over the past fifty years [10–14]. Among these methods, radio frequency glow discharge treatments (RFGD) have been used increasingly to modify polymer surfaces. The plasma gas of RFGD contains vacuum-UV radiation plus many reactive species, such as free radicals and energetic electrons and ions, which can cause a number of different reactions on the polymer surface [14–18]. When the PTFE surface is exposed to Ar plasma, different types of radicals and reactive species are formed on it. Some of these active species are transformed rapidly into the corresponding peroxides and hydroxyl peroxides during the subsequent exposure to air. These peroxides or hydroxyl peroxides are stable at room temperature over a period of time. They are capable of initiating radical polymerization of vinyl monomers, resulting in surface-grafted polymer chains [19–22]. Surface graft copolymerization appears to be one of the most versatile methods for introducing new surface functionalities and microstructures into the existing polymer substrates [11, 20–22]. Surface modification of PTFE films by graft copolymerization with certain functional monomers, for example, has been employed recently to improve the adhesion of metals to the fluoropolymer films [23–25].

Thin films of transparent conducting oxides (TCO's) have found important applications in selective heat mirrors, anti-reflection coatings, solar cells, gas sensors, and flat panel-displays [26]. One of such TCO's is indium-tin-oxide (ITO). In the present work, surface modification of Ar-plasma-pretreated PTFE films was carried out *via* UV-induced graft copolymerization with GMA, AAm, and HEA to enhance their adhesion with sputtered ITO. A double graft copolymerization process, which involves initially the graft copolymerization with an acrylate monomer containing functional groups for curing the epoxides (HEA or AAm), followed by graft copolymerization with the epoxide-containing methacrylate monomer (GMA), has also been employed. Thermal curing and crosslinking of the grafted GMA polymer by the grafted HEA or AAm polymer at the ITO/PTFE interface is expected to enhance further the adhesion of ITO to PTFE. The surface compositions of the graft-modified PTFE films, as well as those of the delaminated ITO and PTFE surfaces, were characterized by X-ray photoelectron spectroscopy (XPS).

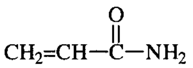
2. EXPERIMENTAL

2.1. Materials

The PTFE films having a thickness of about 10 μm and a density of 2.18 g/cm^3 were used in this study and were obtained from Goodfellow, Inc., of Cambridge, UK. To eliminate the surface contaminants, the polymer films were cleaned with reagent grade methanol and acetone in an ultrasonic water bath. The monomers used for graft copolymerization included glycidyl methacrylate (GMA), acrylamide (AAm), and hydroxylethylacrylate (HEA). They were obtained from Aldrich Chemical Company of Milwaukee, USA. The chemical structures of GMA, AAm and HEA monomers are shown below:

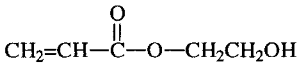


GMA



$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2$$

AAm



$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_2OH$$

HEA

2.2. Plasma Pretreatment

Argon plasma pretreatment of the PTFE film strips of 2 cm × 3 cm in area was performed between two parallel-plate electrodes in a glow discharge quartz reactor (Model SP 100 Plasma System), manufactured by Anatech Co. Ltd. of USA. The plasma power applied was 35 W, at a radio frequency of 40 kHz. The film was exposed to the glow discharge at an argon pressure of about 0.58 Torr for a predetermined period of time. The plasma-pretreated PTFE films were subsequently exposed to the atmosphere for about 10 min to effect the formation of surface peroxide and hydroperoxide species for the initiation of the subsequent surface graft copolymerization process [20, 22].

2.3. UV-induced Surface Graft Copolymerization

The Ar-plasma-pretreated PTFE film was immersed in 30 ml of 1,4-dioxane (for GMA) or aqueous (for AAm and HEA) monomer solution in a Pyrex® tube. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. It was then subjected to UV irradiation for a predetermined period of time in a Riko RH 400-10 W rotary photochemical reactor, manufactured by Rilo-Kogaku Sangyo Co. Ltd. of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerization 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 doubly-distilled water (for AAm and HEA graft copolymerization) to remove the residual monomer and adsorbed homopolymer. In the double graft-copolymerization process, the graft-modified PTFE film was subjected to a second round of Ar plasma treatment, followed by the UV-induced graft copolymerization with the second monomer.

2.4. Sputtering of Indium-Tin-Oxide (ITO) Thin Film and Surface Conductivity Measurements

The pristine and surface-modified PTFE films were metallized with ITO. The ITO films of about 1000 Å in thickness were deposited in a RF magnetron sputtering system (Model D-18 Deposition System), manufactured in Denton Vacuum of USA. An alloy target of In_2O_3 and SnO_2 in a weight proportion of 9:1 was used. The sputtering power input to the target was 50 Watts. The base pressure in the system was about 5.0×10^{-7} Torr. The total pressure of the sputtering gas mixture was adjusted to 3.0×10^{-3} Torr during the ITO film deposition. The surface conductivities of the ITO-metallized PTFE surfaces were measured by means of the two-probe method using an HP 4140B electrometer.

2.5. Surface Characterization

The graft-copolymerization PTFE surfaces and the delaminated ITO/PTFE interfaces were characterized by X-ray photoelectron spectroscopy (XPS). XPS measurements were made on a VG ESCALAB MKII spectrometer with a non-monochromatic Mg K_α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The core-level signals were obtained at a photoelectron take-off angle (α, measured with respect to the sample surface), of 75°, which was the maximum (optimum) take-off angle dictated by the configuration of the XPS apparatus used. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The operating pressure in the analysis chamber was kept below 5×10^{-10} Torr. To compensate for surface charging effects, all binding energies (BE's) were referenced either to the C1s neutral carbon peak at 284.6 eV or the $\underline{C}F_2$ carbon peak at 291.2 eV. In peak synthesis, the linewidth of the Gaussion peaks was maintained constant for all components in a particular spectrum. Surface elemental stochiometries were determined from peak area ratios, after correcting with the experimentally-determined sensitivity factors, and were accurate to within ± 5%. The sensitivity factors were determined using stable binary compounds of well-defined stochiometries.

The graft concentration, expressed as the number of repeat units of the grafted polymer per repeat CF_2 unit of the substrate PTFE, was determined from the XPS-derived surface stochiometries. Thus, the graft concentrations were determined from the C1s peak component area ratios according to the following formulae:

$$[\text{Graft Concentration of the GMA Polymer}] = [\underline{C}OO]/[\underline{C}F_2]$$
$$[\text{Graft Concentration of the HEA Polymer}] = [\underline{C}OO]/[\underline{C}F_2]$$
$$[\text{Graft Concentration of the AAm Polymer}] = [\underline{C}ONH]/[\underline{C}F_2]$$

as each GMA and HEA unit contains one $\underline{C}$OO functional group and each AAm unit contains one $\underline{C}$ONH functional group.

2.6. T-peel Adhesion Strength Measurements

The ITO-metallized surface was adhered to a copper sheet (0.1 mm in thickness and 99.9% in purity from Goodfellow Inc.) using a commercial epoxy adhesive (Araldite®, manufactured by Ciba-Geigy AG of Switzerland). The assembly was either cured at 170°C for 4 h or at room temperature for 24 h. The assembly was then subjected to the T-peel adhesion test in an Instron Model 5544 materials tester. All measurements were carried out at a crosshead speed of 5 mm/min. For each T-peel adhesion strength reported, at least three sample measurements were averaged.

3. RESULTS AND DISCUSSION

3.1. Surface Modification of PTFE Films *via* Ar Plasma Treatment: The ITO/PTFE Assemblies

The changes in the [F]/[C] and [O]/[C] atomic ratios, as determined from the sensitivity-factor-corrected C1s, O1s and F1s core-level spectral area ratios at the photoelectron take-off angle (α) of 75°, as a function of Ar plasma treatment time under the glow discharge conditions of the present work, are shown in Figure 1. A decrease in the [F]/[C] ratio and an increase in the [O]/[C] ratio are observed upon increasing the Ar-plasma treatment time, in agreement with the results generally reported in the literature [23, 27, 28]. The first step in the surface activation by plasma probably involves the breakage of some C—F bonds by the ionizing species, resulting in the abstraction of fluorine atoms from the surface. Some of the generated backbone $-\dot{C}F-$ radicals are attacked by oxygen and oxygen-containing species when they come into contact with the atmosphere, leading to surface oxidation and the formation of the peroxide and hydroperoxide species [20, 29]. The peroxide species can be utilized to initiate the surface free-radical polymerization in a mechanism generally proposed for the UV-induced surface graft copolymerization [20, 22].

The insert in Figure 1 shows the effect of Ar plasma treatment time of the PTFE film on the resulting T-peel adhesion strength of the

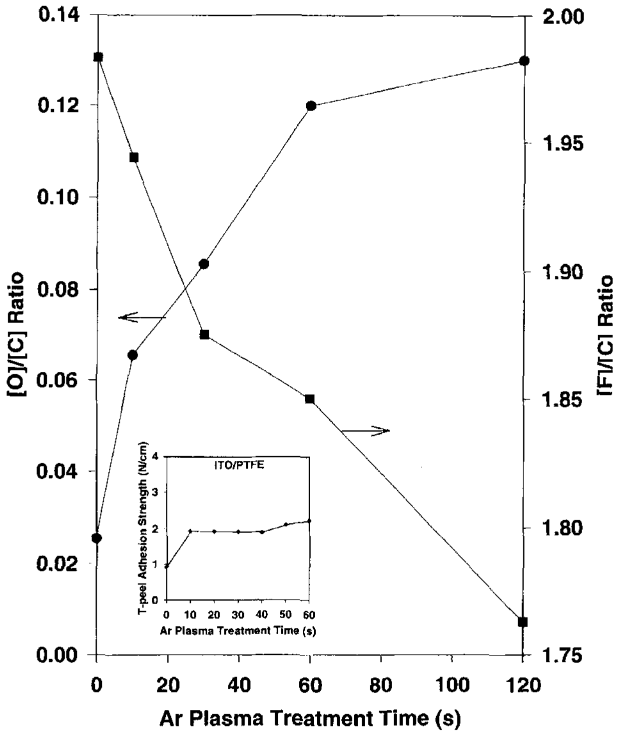


FIGURE 1 Effect of Ar-plasma-treatment time on the [O]/[C] and [F]/[C] ratios and the T-peel adhesion strength of the ITO/PTFE laminate.

sputtered ITO. The T-peel adhesion strength increases from 0.9 N/cm for the pristine PTFE surface to about 2.0 N/cm for the 10 s Ar plasma-treated PTFE film. This value increases only marginally upon further increase in the plasma treatment time, suggesting that plasma treatment alone is not an effective means for enhancing the adhesion of ITO to the PTFE surface.

3.2. Surface Modification of PTFE Films *via* Graft Copolymerization with Functional Monomers: The ITO/GMA/PTFE, the ITO/AAm/PTFE, and the ITO/HEA/PTFE Assemblies

Figures 2(a) to 2(d) show the respective C1s core-level spectra, obtained at an α of 75°, for a pristine PTFE film and for three 60 s Ar-plasma-

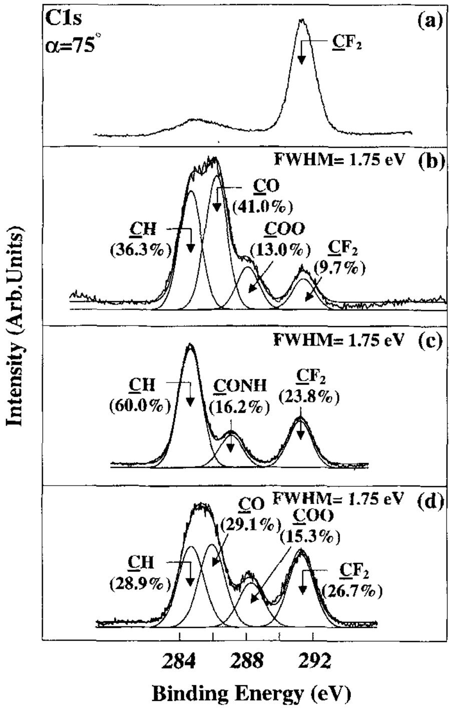


FIGURE 2 C1s core-level spectra of a pristine PTFE film (a), and three 60 s Ar-plasma-pretreated PTFE films after having been subjected to the UV-induced graft copolymerization in (b) 20 vol.% 1,4-dioxane solution of GMA for 1 h, (c) 6 wt.% aqueous solution of AAm for 10 min, and (d) 15 vol.% aqueous solution of HEA for 20 min.

pretreated PTFE films after having been subjected to UV-induced graft copolymerization in 20 vol.% 1,4-dioxane solution of GMA for 1 h, in 6 wt.% aqueous solution of AAm for 10 min, and in 15 vol.% aqueous solution of HEA for 20 min. For the pristine PTFE surface, the C1s core-level spectrum consists of a main peak component at the binding energy (BE) of about 291.2 eV, attributed to the $\underline{C}F_2$ species [22], and a broad minor component at about 8 eV below this main peak. The low BE component is associated predominantly with the contribution of the X-ray satellites of the $\underline{C}F_2$ species arising from the Mg $K_{\alpha 3,4}$ radiation, as well as the minor contribution from a trace amount of surface contaminants. Successful surface graft copolymerization, in each case, is indicated by the appearance of the various functional groups of the grafted polymer on the PTFE surface, as revealed by the XPS core-level spectrum. In Figure 2(b), the C1s core-level spectrum of the GMA-graft-copolymerized PTFE surface is curve-fitted with peak components at BE's of 284.6 eV for the $\underline{C}$-H species, 286.2 eV for the $\underline{C}$-O species, and 288.5eV for the $\underline{C}OO$ species [23], in addition to that at 291.2 eV for the $\underline{C}F_2$ species of the PTFE substrate. The relative peak-area ratio for the first three species is about 3 : 3 : 1, in excellent agreement with the theoretical ratio of 3 : 3 : 1 dictated by the chemical structure of GMA. The presence of surface-grafted AAm polymer can be deduced from the appearance of the low BE C1s envelope with peak components centered at about 284.6 eV for the $\underline{C}$-H species and 287.7 eV for the $\underline{C}ONH$ species [24], as shown in Figure 2(c). The $\underline{C}H$ to $\underline{C}ONH$ peak area ratio in this case is somewhat higher than the theoretical ratio of 2 : 1 for the AAm polymer. The phenomenon is probably associated with presence of some adventitious carbon at the surface arising from the ionic nature of AAm. The low BE C1s envelope of the HEA-graft-copolymerized PTFE surface contains three main C1s peak components with BE's at 284.6 eV for the $\underline{C}$-H species, 286.2 eV for the $\underline{C}O$ species, and 288.5 eV for the $\underline{C}OO$ species [24], as shown in Figure 2(d). The spectral area ratio of the three species in this case is very close to the theoretical ratio of 2 : 2 : 1 for the HEA molecule.

3.2.1. *Effect of Monomer Concentration*

The effects of monomer concentration on graft yields and the T-peel adhesion strengths of the three types of the ITO/graft-modified PTFE assemblies involving the GMA, AAm and HEA-graft-copolymerized PTFE films are shown, respectively, in Figures 3, 4, and 5. For each type of the ITO/graft-modified PTFE laminates, the T-peel adhesion strengths of the laminates with thermal post-treatment, after metallization, at 170°C for 4 h are also reported.

For the GMA graft-copolymerized PTFE films, the Ar plasma pretreatment time and UV graft-copolymerization time were 60s and 1 h, respectively. As shown in Figure 3, the graft concentration increases gradually with increasing monomer concentration. The T-peel adhesion strength increases with increasing GMA monomer

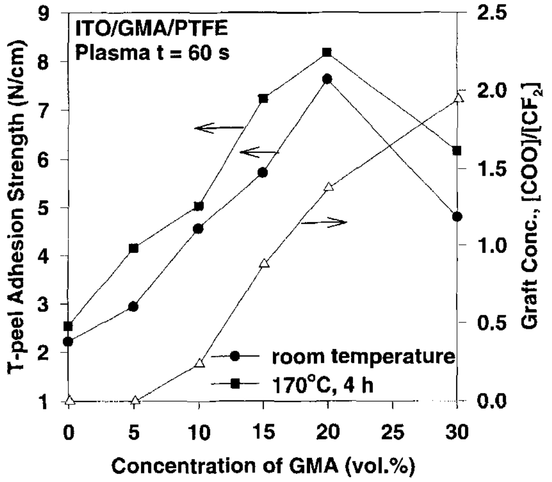


FIGURE 3 Effect of monomer concentration on the graft concentration and the T-peel adhesion strength of the ITO/GMA/PTFE assembly (Ar-plasma-pretreatment time = 60 s, UV time = 1 h, thermal post-treatment time at 170°C = 4 h).

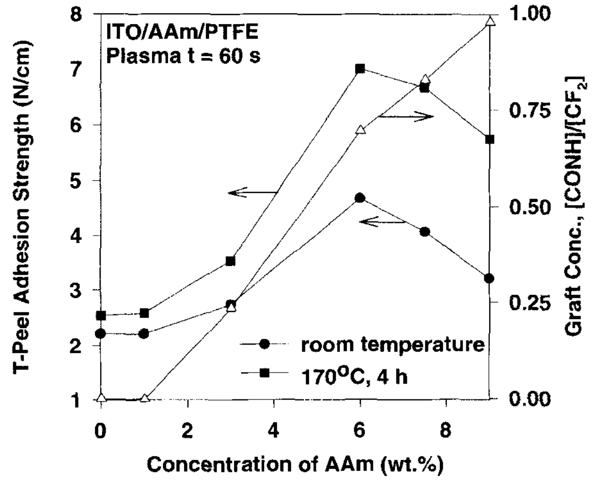


FIGURE 4 Effect of monomer concentration on the graft concentration and the T-peel adhesion strength of the ITO/AAm/PTFE assembly (Ar-plasma-pretreatment time = 60 s, UV time = 10 min, thermal post-treatment time at 170°C = 4 h).

concentration up to about 20 vol.% and reaches an optimum value of 7.4 N/cm before showing a decrease. From comparison with the T-peel adhesion strength of the assembly involving ITO and PTFE film

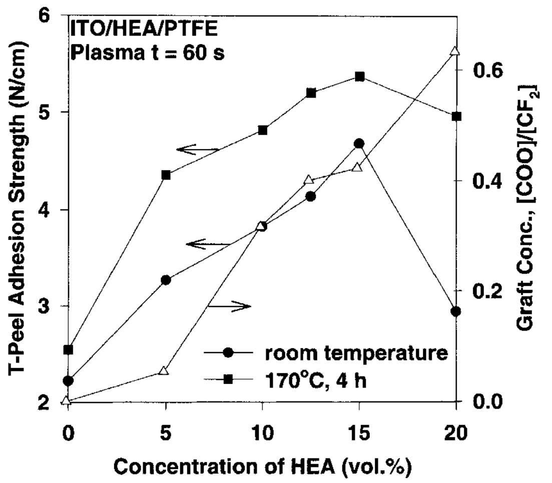


FIGURE 5 Effect of monomer concentration on the graft concentration and the T-peel adhesion strength of the ITO/HEA/PTFE assembly (Ar-plasma-pretreatment time = 60 s, UV time = 20 min, thermal post-treatment time at 170°C = 4 h).

with Ar-plasma treatment alone (Fig. 1), the effective contribution of the grafted GMA polymer in improving the adhesion strength with ITO is ascertained. However, it is interesting to note that increasing GMA monomer concentration above 20 vol.% does not result in the further enhancement of the T-peel adhesion strength, even though the graft yield continues to increase. The increase in the graft layer thickness apparently had resulted in a weaker ITO/polymer interface, probably due to the inefficient packing of the graft chains and the accompanying increase in spatial free volume at high graft concentration. In the earlier work, it had also been reported that the thickness of the grafted polymer layer could affect the adhesion strength of the evaporated metal [30]. The T-peel adhesion strength is enhanced by the thermal post-treatment of the ITO/polymer laminates. A maximum T-peel adhesion strength of about 8.2 N/cm was obtained with 4 h of curing at 170°C. The enhanced adhesion strength probably has resulted from the increased extent of charge transfer interaction between the GMA polymer and ITO and elevated temperature.

By increasing the AAm monomer concentration used for the UV-induced graft copolymerization, the concentration of grafted AAm polymer increases from 0.1 to 1.0, as shown in Figure 4. The graft copolymerization was carried out using the 60 s Ar-plasma-pretreated PTFE films and 10 min of UV graft copolymerization time. The T-peel adhesion strength of the ITO/AAm/PTFE assembly increases with increasing monomer concentration up to 4.7 N/cm. The increase in T-peel adhesion strength coincides with the increase in graft concentration up to about 6 wt.% AAm monomer concentration before showing a decrease. This phenomenon is similar to that observed for the ITO/GMA/PTFE assembly. The thermal post-treatment enhances the T-peel adhesion strength further to a maximum value of about 6.8 N/cm.

Figure 5 shows the concentration of grafted HEA polymer as a function of monomer concentration used for the graft copolymerization. The experiments were carried out using the 60 s Ar-plasma-pretreated PTFE films and 20 min of UV graft copolymerization time. The concentration of grafted HEA polymer increases with increasing monomer concentration. The corresponding T-peel adhesion strength also exhibits an increase with increasing monomer concentration up to about 4.7 N/cm at a monomer concentration of 15 vol.% before showing a decrease. An optimum T-peel adhesion strength of about 5.4 N/cm is achieved after 4 h of thermal curing at 170°C of the metallized film.

The formation of an ITO/PTFE assembly arising from the UV-induced graft copolymerization of a PTFE film is shown schematically in Figure 6. The enhanced adhesion in the present ITO/PTFE assemblies arises from the strong interactions between ITO and the functional groups of the graft chains, as well as the fact that the graft chains are covalently tethered on the PTFE surfaces.

3.2.2. Effect of Ar-plasma-pretreatment Time

Figure 7 shows the effect of Ar-plasma-pretreatment time of the PTFE film on the concentration of the surface-grafted GMA. The T-peel adhesion strengths of the corresponding ITO/GMA polymer-PTFE assemblies before and after thermal post treatment are also summarized in Figure 7. Similar dependence of the surface graft concentration and T-peel adhesion strength on the Ar-plasma-pretreatment time has also been observed for the assemblies involving AAm and HEA graft copolymerized PTFE films. The respective graft copolymerization conditions are 20 vol.% 1,4-dioxane solution of GMA for 1 h, 6 wt.% aqueous solution of AAm for 10 min, and 15 vol.% aqueous solution of HEA for 20 min. In each case, the concentration of surface-grafted

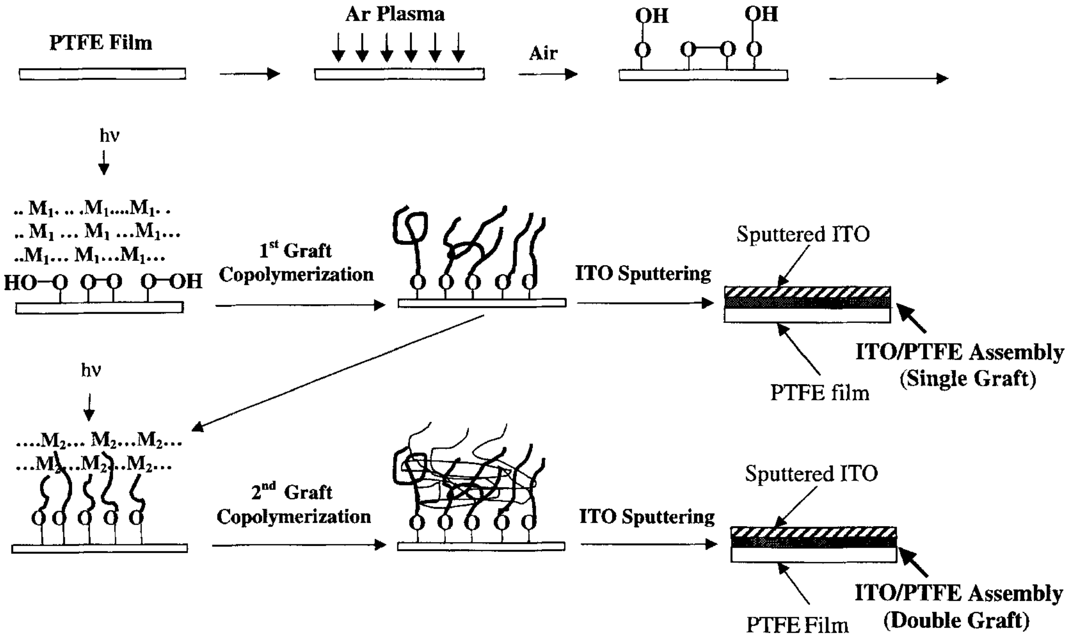


FIGURE 6 Schematic illustration of the formation of ITO/PTFE assemblies arising from UV-induced single and double graft copolymerization of the PTFE films.

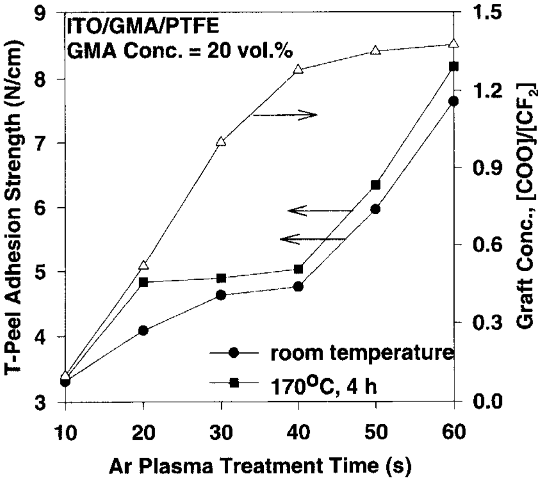


FIGURE 7 Effect of Ar-plasma-pretreatment time of the PTFE film on the graft concentration and the T-peel adhesion strength of the ITO/GMA/PTFE assembly (monomer concentration = 20 vol.%, UV time = 1 h, thermal post-treatment time at 170°C = 4 h).

polymer increases with increasing Ar-plasma-pretreatment time of the PTFE film, but exhibits a saturation phenomena at large plasma pretreatment time. These results, together with the increase in the surface [O]/[C] ratio of the PTFE film during plasma treatment (Fig. 1), are consistent with a peroxide or hydroxyl peroxide-initiated polymerization mechanism generally proposed for the UV-induced graft copolymerization [20]. The T-peel adhesion strengths for all three types of assemblies increase with increasing graft concentrations. Furthermore, the increase in the T-peel adhesion strength coincides approximately with the increase in surface graft concentration, suggesting that a graft-chain-induced adhesion mechanism is operative. Thermal post treatment of the ITO/graft-modified PTFE laminates again contributes to the enhancement of the adhesion strength in each case.

3.3. Surface Modification of PTFE Films *via* Double Graft Copolymerization: The ITO/GMA-AAm/PTFE and the ITO/GMA-HEA/PTFE Assemblies

Double graft copolymerization or double grafting in the present work is taken to mean that a second monomer is graft copolymerized onto the surface of the PTFE film which has been previously modified also by graft copolymerization.

Figures 8(a) and 8(b) show, respectively, the C1s core-level and wide scan spectra, obtained at an α of 75°, for a GMA-AAm doubly-graft-copolymerized PTFE film. The film was obtained *via* 10 min of UV-induced graft copolymerization in 3 wt.% aqueous solution of AAm with a 60 s Ar-plasma-pretreated PTFE film, followed by 30 s of Ar plasma treatment and further modified by graft copolymerization in a 10 vol.% 1,4-dioxane solution of GMA for 1 h. The corresponding spectra for a GMA-HEA doubly-graft-copolymerized PTFE film exhibit similar lineshape and features. The film was obtained *via* 20 min of UV-induced graft copolymerization in a 15 vol.% aqueous solution of HEA with a 60 s Ar-plamsa-pretreated PTFE film, followed by 30 s of Ar plasma treatment and further modified by graft copolymerization in a 10 vol.% 1,4-dioxane solution of GMA for 1 h. Comparison with the C1s core-level spectra of the PTFE films singly grafted with GMA, AAm, and HEA polymer, show that C1s core-level spectra of the doubly-graft-copolymerized films are similar in line shape to that of the GMA singly-graft-copolymerized PTFE surface. The results suggest that the coverage of the GMA polymer from the second graft copolymerization in each case is beyond the probing depth of the XPS technique. This conclusion is further supported by the fact that no N 1s signal is discernible in the wide scan spectrum of the GMA-AAm doubly-graft-copolymerized PTFE surface (Fig. 8(b)).

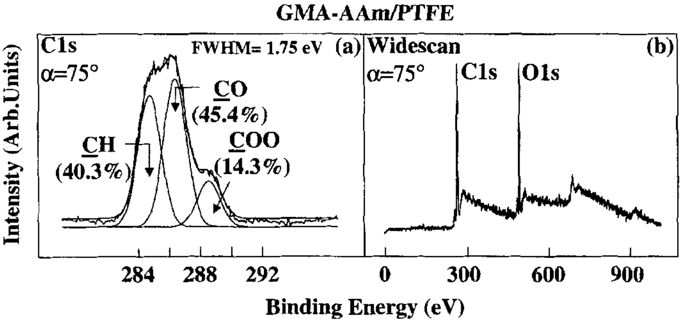


FIGURE 8 (a) C1s core-level and (b) wide scan spectra of the PTFE film surface after graft copolymerization in 3 wt.% aqueous solution of AAm for 10 min, followed by graft copolymerization in 10 vol.% 1,4-dioxane solution of GMA for 1 h.

Apparently, the surface graft copolymerization efficiency of GMA has been improved by the presence of the first graft on the PTFE surface, since the complete GMA polymer coverage was achieved at a substantially lower GMA monomer concentration. Previous works have also shown that the graft yield can be improved by the presence of a suitable swelling agent [31, 32]. The formation of the ITO/double-graft-modified PTFE assembly is also shown schematically in Figure 6.

3.3.1. Effect of the First Monomer Concentration

In the two cases of the double-graft-copolymerization process, the second graft copolymerization involves 1 h of UV-induced graft copolymerization in 10 vol.% 1,4-dioxane solution of GMA with 30 s of Ar plasma pretreatment of the AAm- or HEA-graft-copolymerized PTFE surface. Figure 9 shows the T-peel adhesion strength of the ITO/GMA-AAm/PTFE assembly as a function of the AAm monomer concentration used during first graft copolymerization. Optimum T-peel adhesion strengths of 6.0 N/cm (room temperature) and 8.2 N/cm (after thermal post-treatment) were obtained at 3 wt.% AAm concentration. Comparison of these optimum T-peel adhesion strengths with those corresponding to the singly-graft-copolymerization ITO/AAm/PTFE assembly at 3 wt.% AAm concentration (Fig. 4)

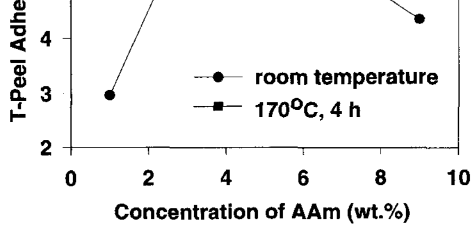


FIGURE 9 Effect of concentration of the first monomer (AAm) on the T-peel adhesion strength of the ITO/GMA-AAm/PTFE laminate.

and the ITO/GMA/PTFE assembly at 10 vol.% of GMA concentration (Fig. 3), show that each of these optimum T-peel adhesion strength is comparable with the sum of the T-peel adhesion strengths of the corresponding ITO/AAM/PTFE and ITO/GMA/PTFE asemblies. However, when considering the effect of the grafted GMA polymer on the T-peel adhesion strength, these optimum T-peel adhesion strengths are higher than the corresponding values of 4.5 N/cm and 5.0 N/cm for the assembly involving PTFE film from single graft copolymerization in 10 vol.% GMA (Fig. 3). This phenomenon is attributable to the increase in the efficiency of GMA graft copolymerization on the AAm polymer-modified PTFE surface, as well as to the cross-linking reaction between the functional groups of the grafted AAm and the GMA chains to enhance the bulk strength of the graft layer. At higher graft concentration, the T-peel adhesion strength involving the double-graft-copolymerized PTFE film again exhibits a decrease. This phenomenon is not unlike that observed in Figure 3, and provides further support to the earlier conclusion that the thickness of the graft layer can affect the T-peel adhesion strength. The thermal post treatment has an even greater effect on the T-peel adhesion strength of the double-graft-copolymerized surface, as shown in Figure 9, as the cross-linking reaction between the grafted AAm and GMA chains is promoted by thermal curing.

For the corresponding T-peel adhesion strength of the ITO/GMA-HEA/PTFE assembly as a function of the first monomer (HEA) concentration, results similar to those of the ITO/GMA-AAm/PTFE assemblies are observed. An optimum T-peel adhesion strength of 7.0 N/cm is obtained for the PTFE film first graft copolymerized in 15 vol.% HEA and then 10 vol.% GMA. This adhesion strength is also higher than that of the corresponding ITO/GMA/PTFE assembly with the 10 vol.% GMA singly-graft-copolymerized PTFE film. The thermal post treatment again readily contributes to the similar enhancement of the T-peel adhesion strength.

3.4. Surface Conductivity of the ITO/Graft-modified PTFE Assemblies

The electrical resistance of the sputtered ITO on all graft-modified PTFE surfaces before and after thermal post treatment remained almost constant at about 30 Ω/square, suggesting that the grafted layer and the thermal post-treatment did not have any significant effect on the electrical properties of the ITO.

3.5. The Failure Mode of the ITO and Graft-modified PTFE Interfaces

The locus of failure by peeling is expected to provide important clues to understanding the contribution of the grafted polymer to the observed adhesion phenomenon. The failure mode of the ITO and graft-modified PTFE interfaces was thus investigated. Essentially, the failure can take place in two modes: at the interface between the ITO and the polymer layer or within one of the layers. Figures 10(a) to 10(c) show the respective XPS wide scan spectra of the pristine PTFE surface, and the delaminated PTFE and ITO surfaces from an ITO/GMA/PTFE assembly having a T-peel adhesion strength of about 5.4 N/cm. The wide scan spectra of the delaminated PTFE and ITO

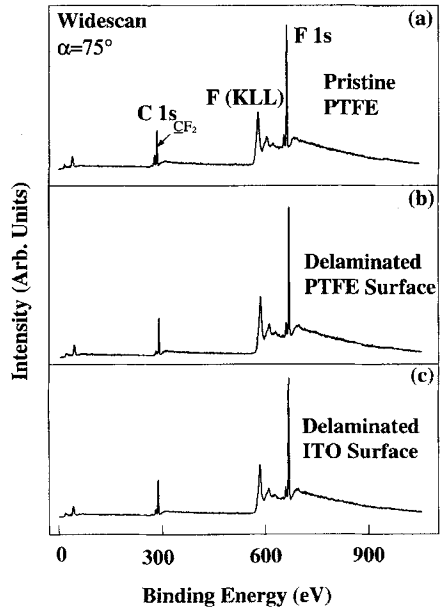


FIGURE 10 XPS wide scan spectra of (a) a pristine PTFE film, (b) and (c) the delaminated PTFE and ITO surfaces from an ITO/GMA/PTFE assembly having a T-peel adhesion strength of about 5.4 N/cm.

surfaces are similar to that of the pristine PTFE surface. The fact that the XPS wide scan spectra of the delaminated PTFE and ITO surfaces resemble each other and that of the pristine PTFE film, as well as the fact that no metal signal is discernible from the delaminated ITO surface, strongly suggest that the ITO/graft-modified PTFE assembly delaminated by cohesive failure inside the PTFE substrate. In fact, for all the ITO/graft-modified PTFE assemblies studied in the present work, clean cohesive failure inside the PTFE substrate is always observed when the T-peel adhesion strength exceeds 4 N/cm.

4. CONCLUSION

Ar-plasma-pretreated PTFE films were subjected to further surface modification *via* UV-induced graft copolymerization with GMA, AAm, and HEA. The compositions of the graft-copolymerized PTFE surfaces were characterized by XPS. In general, the graft yield increased with the monomer concentration used during the graft copolymerization, as well as with the Ar-plasma-pretreatment time. In each case, the T-peel adhesion strength between the graft-modified PTFE and sputtered ITO increase with graft concentration up to an optimum graft concentration and was further enhanced by thermal post-treatment of the laminates after ITO metallization. The double-graft-copolymerization process was also shown to be effective in enhancing the T-peel adhesion strength of the ITO/graft-modified PTFE assembly. A T-peel adhesion strength in excess of 8 N/cm was obtained. The present ITO/graft-modified PTFE assemblies delaminated by cohesive failure inside the PTFE films when the T-peel adhesion strength of the ITO/polymer assembly exceeded 4 N/cm. The strong adhesion in the present ITO/graft-modified PTFE laminates arises from the strong interaction between the sputtered ITO and the functional groups of the graft chains, as well as the fact that the graft chains are covalently tethered on the PTFE surfaces.

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