

Lamination of Conductive Polypyrrole Films to Poly(Tetrafluoroethylene) Films via Interfacial Graft Copolymerization

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ABSTRACT: A simple technique for the lamination of a conductive polymer film to an inert dielectric polymer film was demonstrated. The electrochemically synthesized and *p*-toluenesulfonic acid-doped polypyrrole (PPY) film was laminated simultaneously to the argon plasma-pretreated PTFE film during the thermally induced graft copolymerization of the PTFE surface with a functional monomer. The graft copolymerization was carried out using glycidyl methacrylate (GMA) monomer containing 20% v/v hexamethyldiamine (HMDA) and in the absence of any polymerization initiator. Thermally induced graft copolymerization of the GMA monomer on the PPY surface was minimal. The lap shear and T-peel adhesion strengths of the laminates were found to be dependent on the GMA graft concentration on the PTFE surface, which, in turn, was affected by the plasma pretreatment time of the film. To increase the GMA graft concentration for the enhancement of adhesion strength, the plasma-pretreated PTFE surfaces were premodified via UV-induced graft copolymerization with GMA prior to the simultaneous thermal graft copolymerization and lamination process. The modified surfaces and interfaces were characterized by X-ray photoelectron spectroscopy (XPS). Through XPS measurements of the delaminated surfaces, it was found that the PPY/PTFE laminates failed predominantly by cohesive failure inside the PTFE substrate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 716–727, 2001

Key words: polypyrrole; poly(tetrafluoroethylene); lamination; adhesion; graft copolymerization; XPS

INTRODUCTION

Conductive polymers are a novel class of electrically conducting organic solids. A common electronic feature of the pristine (undoped) conducting polymers is the π -conjugated system, which is formed by the overlap of carbon *p* orbitals and alternating C—C bond lengths.^{1,2} Conductive polymers combine the desirable properties of

polymers such as light weight, flexibility, ease of fabrication, etc., with the high electrical conductivity normally associated with metals and semiconductors. As a result of these attractive properties, the synthesis, characterization, and processing of conductive polymers have become an important research area in polymer and material science.³

Among the many conjugated polymers that are researched, polypyrrole (PPY) has emerged as one of the most extensively studied due to its high electrical conductivity, good environmental stability, interesting redox properties associated

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with the chain heteroatoms, and the ease of synthesis by chemical or electrochemical methods.⁴⁻⁸ Although both chemical and electrochemical methods of synthesis are commonly used in the laboratory, the electrochemical method offers several advantages over the chemical method. The distinct advantage being that the material can be produced *in situ* on the electrode with no further steps needed for intermediate treatment as in the chemical method of synthesis. Electrochemical synthesis thus offers a simple route for producing highly conductive PPY films.

Another polymer of interest is the highly insulating poly(tetrafluoroethylene) (PTFE). PTFE is an important engineering polymer due to its unique and useful properties, which include chemical resistivity, good thermal stability, wide service temperature range, and the absence of aging and embrittlement at very low temperatures (down to 4 K).⁹⁻¹² However, despite such superior properties, PTFE as an engineering polymer suffers from one major drawback. It possesses low surface energy that results in surface inertness, thereby making adhesion to any other surface difficult. This problem can be circumvented by a variety of pretreatment techniques that include the immersion of the polymer film in a solution of sodium in liquid ammonia¹³ or in a solution of sodium naphthalenide in tetrahydrofuran.¹⁴ Unfortunately, these methods usually alter the bulk properties of the film. Recently, two of the most commonly used methods dealing with surface modification of PTFE films are plasma treatment and surface graft copolymerization. A key advantage of the surface modification methods over the solution etching methods is that useful functionalities can be incorporated onto the film surface without altering the bulk properties of the polymer.¹⁵⁻¹⁸ Numerous works have been devoted to the activation of the PTFE surface by plasma treatment.¹⁹⁻²¹ Plasma treatment creates peroxides and hydroperoxides on the film surface through replacement of some of the C—F bonds,²¹ and can greatly enhance the adhesion property of the film. However, the physiochemical characteristics of the modified PTFE surface induced by plasma treatment are time dependent.²² To overcome this problem, plasma-treated films can be subjected to further surface modifications via, for example, graft copolymerization.²³⁻²⁶

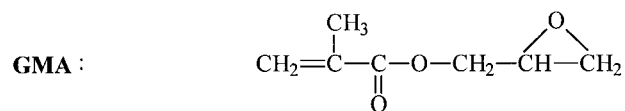
In sensor and microelectronic applications, multilayer structures consisting of laminated conductive and dielectric layers are of great importance.²⁷ In view of the potential applications of

conductive polymers in sensors, integrated circuits, and junction devices, the adhesion between a conductive polymer and a dielectric substrate is likely to become an important issue. In this study, a simple, one-step process of surface graft copolymerization of a plasma-pretreated PTFE film with concurrent lamination to a PPY film is demonstrated. The monomer mixture used for the graft copolymerization is glycidyl methacrylate (GMA) containing 20% v/v of hexamethyldiamine (HMDA), and no additional polymerization initiator is added. We further demonstrate the more effective lamination of a PPY film to a PTFE film when the latter is premodified via UV-induced surface graft copolymerization with GMA. The failure modes of the various assemblies are also investigated. The chemical composition of the surfaces and interfaces are characterized by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL PROCEDURES

Materials

Poly(tetrafluoroethylene) (PTFE) films, having a thickness of about 0.01 cm and a density of 2.18 g/cm³, were purchased from Goodfellow Ltd., UK. Prior to usage, the films were cleaned with acetone in an ultrasonic bath for approximately 10 min. Both the glycidyl methacrylate (GMA) monomer and the hexamethyldiamine (HMDA, 70% purity) curing agent were purchased from Aldrich Chemical Co., Milwaukee, WI. They were used as received, without further purification. The chemical structures of GMA and HMDA are shown below:



The *p*-toluenesulfonic acid-doped PPY films used in this study were prepared in the laboratory with the method as detailed in the following section.

Electrochemical Synthesis of Polypyrrole

Pyrrole monomer was purchased from Merck, Germany, and was vacuum distilled before use.

Acetonitrile and *p*-toluenesulfonic acid (TSA) were obtained from Aldrich Chemical Co., and were used as received. Nano-pure water was used as an additive solvent. Prior to the addition of the monomer, the electrolyte solution of the 0.1 M TSA in acetonitrile with 1% v/v water was purged for 25 min with dry argon gas. Pyrrole was added to the electrolyte solution to result in 0.1 M pyrrole concentration, and the solution was further purged with argon gas for another 5 min. The PPY film was electrodeposited galvanostatically on a stainless steel working electrode by applying a charge density of 10 Coulombs cm⁻² at 0°C.²⁸ The PPY film so obtained has an electrical conductivity of about 200 S/cm. The thermal stability of the PPY film was determined using a Netzsch Thermal Analysis unit (Model TASC 414/3).

Plasma Treatment

The plasma treatment of the PTFE films was carried out in an Anatech glow discharge quartz reactor (Model SP100 Plasma System). The plasma power applied was kept at 32 W at a radio frequency of 40 kHz. The pressure in the plasma chamber was maintained at an argon pressure of 0.58 Torr when the films were exposed to the plasma discharge for a predetermined period of time. Following the plasma treatment, the films were exposed to the atmosphere for a brief period of time to promote the formation of surface peroxides and hydroperoxides for the subsequent surface graft copolymerization process.²⁹

Thermally Induced Surface Graft Copolymerization with Simultaneous Lamination

The PTFE and PPY films strips used were about 1.5 × 0.5 cm in area for the lap shear strength measurements, and about 1.5 × 0.3 cm for the T-peel adhesion strength measurements. The PTFE film was treated with argon plasma for a predetermined period of 5 to 105 s before use. A small amount of GMA monomer containing 20% v/v of HMDA was introduced between the plasma-treated PTFE film and the PPY film. The PPY/monomer mixture/PTFE assembly was sandwiched between two glass slides with the aid of a set of mechanical clips, and placed in a constant temperature oven for 3 h under normal atmospheric conditions.

For the determination of surface graft concentration, a plasma-pretreated PTFE film and a pristine PTFE film were coated with pure GMA. They were lapped together and sandwiched be-

tween two glass slides. The assembly was subsequently heated for 3 h in a 170°C oven. As the pristine PTFE film is not susceptible to graft copolymerization, the two lapped PTFE films readily underwent self-delamination in acetone. They were then washed thoroughly with acetone before being subjected to surface analysis.

Adhesion of PPY Films to Surface-Modified PTFE Films from UV-Induced Graft Copolymerization with GMA

To obtain surface-modified PTFE films from UV-induced graft copolymerization with GMA, the PTFE films were first subjected to 60 s of argon plasma treatment. The plasma-pretreated PTFE films were then placed in a Pyrex® tube containing 20% v/v GMA in 1,4-dioxane solution. The reaction mixture was purged with dry argon gas for 30 min. The degassed Pyrex® tube containing the PTFE film-monomer mixture was sealed and then subjected to UV irradiation (wavelength greater than 290 nm) for 2 h in a Riko RH 400-10W photochemical reactor, manufactured by Riko Denki Kogyo of Chiba, Japan. Following the UV-induced graft copolymerization, the PTFE film was washed with copious amounts of 1,4-dioxane, followed by extraction with acetone to remove the residual monomer and adsorbed homopolymer.

The graft-modified PTFE film was lapped with the PPY film in the presence of a small amount of GMA monomer containing 20% v/v HMDA. To investigate the effect of post plasma treatment of the graft-modified PTFE films on their adhesion to PPY films, the GMA graft-copolymerized PTFE films (GMA-g-PTFE) were subjected to argon plasma treatment for a predetermined length of time. The PPY/GMA-HMDA/GMA-g-PTFE assemblies were sandwiched between two glass plates using a set of mechanical clips. The assemblies were then heated at 170°C for 3 h in a constant temperature oven.

For surface analysis of the effect of addition plasma treatment on the graft-modified PTFE films, the graft-copolymerized PTFE film with various extents of plasma post treatment were coated with HMDA and heated at 170°C for 3 h. The films were then washed with copious amounts of acetone to remove the excess HMDA.

Adhesion Strength Measurement

The adhesion strengths of the various PPY/PTFE laminates were determined by measuring the lap

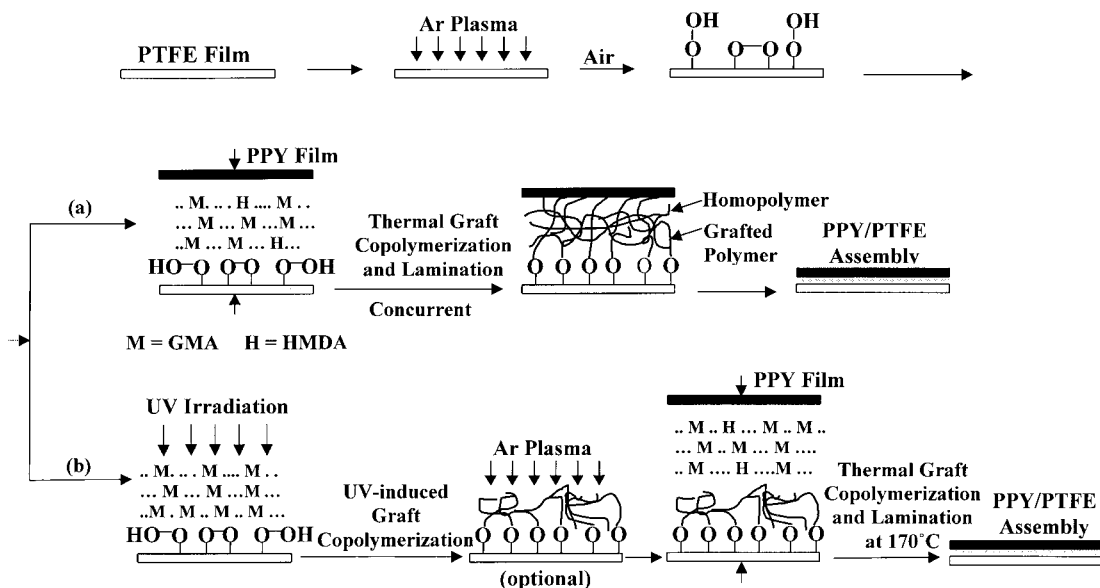


Figure 1 Schematic illustration of the processes of plasma treatment and the simultaneous thermal graft copolymerization and lamination involving surface-modified PTFE films from Ar plasma treatment [Path (a)], and UV-induced surface graft copolymerization [Path (b)].

shear and T-peel adhesion strengths with an Instron Model 5540 tensile tester from the Instron Corp., USA. Because the PPY film has a tendency to tear during the T-peel measurements, a poly(ethylene terephthalate) (PET) film (Goodfellow Inc., UK), used as the backing substrate, was adhered to the PPY film using a commercial epoxy adhesive (Araldite® Stand, Ciba-Geigy Chemical Co., Switzerland). All measurements were carried out at a crosshead speed of 10 mm/min. For every adhesion strength reported, at least five sample measurements were averaged.

Surface Characterization

X-ray photoelectron spectroscopy (XPS) analysis was used to determine the surface composition of the pristine, graft-modified, and delaminated PTFE and PPY film surfaces. The XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg K α X-ray source (1253.6 eV) at a constant retard ratio of 40. The polymer films were mounted on the standard VG sample stubs by means of double-sided adhesive tapes. The core-level spectra were obtained at a photoelectron take-off angle (α , measured with respect to sample surface) of 75°. The X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA) and the operating pressure in the analysis chamber was maintained at 10^{-9} Torr or lower

during the measurements. To compensate for surface charging effects, all binding energies (BEs) were referenced to the C(1s) neutral carbon peak at 284.6 eV. In the deconvolution of the spectra obtained, the line width (full width at half maximum, FWHM) for the Gaussian peaks were kept constant for all components in a particular spectrum. Surface elemental stoichiometries, reliable to $\pm 5\%$, were determined from the peak-area ratios after correcting with the experimentally determined sensitivity factors. These sensitivity factors were determined using stable binary compounds of well-defined stoichiometries.

RESULTS AND DISCUSSION

Thermally Induced Surface Graft Copolymerization with Simultaneous Lamination

The processes of the argon plasma pretreatment of the PTFE film and its subsequent thermally induced graft copolymerization with simultaneous lamination to a PPY film is illustrated schematically in Figure 1 [Path (a)].

The effect of plasma treatment of PTFE surfaces and the accompanied surface modification have been well documented.^{16,21,30,31} Argon plasma causes the breakage of C—F bonds, resulting in defluorination of the surface. When this

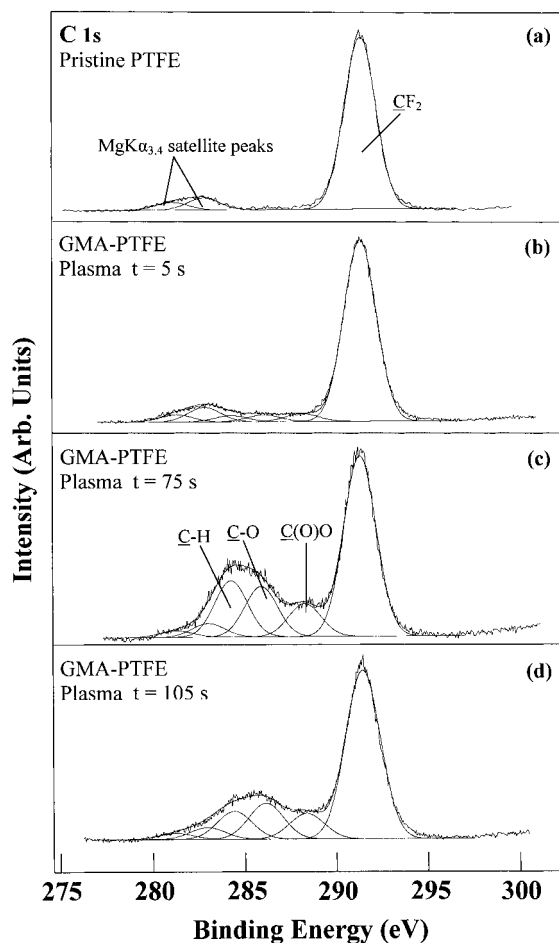


Figure 2 XPS C(1s) core-level spectra of (a) a pristine PTFE film, and PTFE films subjected to (b) 5 s, (c) 75 s, and (d) 105 s of argon plasma pretreatment before thermal graft copolymerization with pure GMA at 170°C for 3 h.

activated surface is subsequently exposed to the atmosphere, oxygen is incorporated onto the PTFE surface in the form of oxidized carbon species, including the peroxides and hydroperoxide species.³⁰

Figure 2(a) shows the XPS C(1s) core-level spectrum, obtained at the photoelectron take-off angle, α , of 75°, of a pristine PTFE film. The C(1s) spectrum comprises of a major peak component at the binding energy (BE) of 291.7 eV, attributed to the CF_2 species,²³ and a broad minor band at about 8 eV below the main peak arising from the contribution of the X-ray satellite peaks associated with the Mg $\text{K}\alpha_{3,4}$ radiation. The Mg $\text{K}\alpha_3$ satellite peak is shifted approximately 8.4 eV below the CF_2 peak, while the $\text{K}\alpha_4$ peak is about 10.1 eV below the major peak. They are about 8

and 4% of the main component area, respectively.³²

To investigate the extent of thermally induced graft copolymerization of GMA monomer on the PTFE surface as a function of the argon plasma pretreatment time, thermally induced graft copolymerization of GMA at 170°C for 3 h between an Ar plasma-pretreated PTFE film and a pristine PTFE film has been carried out. The assembly was allowed to self-delaminate in an appropriate solvent (acetone), and the delaminated films were subsequently washed thoroughly with acetone to remove the physically adsorbed GMA homopolymer. For the pristine PTFE film not subjected to any plasma pretreatment, subsequent XPS study does not reveal any discernible changes in the lineshape of the C(1s) core-level spectrum when compared to that of the C(1s) spectrum of the pristine film, to suggest the presence of any grafted GMA polymer. This outcome is not entirely unexpected, because PTFE surfaces have been known to be highly inert. Nevertheless, the surface of the PTFE film can be activated by plasma treatment. It has been proposed that the peroxide species generated by plasma treatment and air exposure are necessary to initiate the thermally-induced surface free radical polymerization³³ of the GMA monomer, similar to that suggested for UV-induced graft copolymerization process.^{25,34}

Figure 2(b)–(d) illustrates the changes in the C(1s) core-level spectra when the PTFE film is subjected to the increasing extent of Ar plasma pretreatment, followed by thermal graft copolymerization with pure GMA monomer. From Figure 2(b), it can be seen that with just 5 s of plasma exposure, a broad band emerges between the major CF_2 component peak and the satellite components. This new broad band can be curve-fitted into three peak components with BEs at 284.6 eV for the neutral C—H species, 286.2 eV for the C—O species and 288.5 eV for the C(O)O species.²³ The emergence of the C—H, C—O and C(O)O species indicates that the graft copolymerization of GMA on the PTFE film surface has occurred because all these species are characteristics of the GMA structure (see the Experimental section).

With increasing plasma pretreatment of the PTFE substrate, the peak areas assigned to the C—H, C—O, and C(O)O species are augmented until the plasma pretreatment time of 75 s when the maximum surface grafting of the GMA polymer is observed. Upon extending the plasma pre-

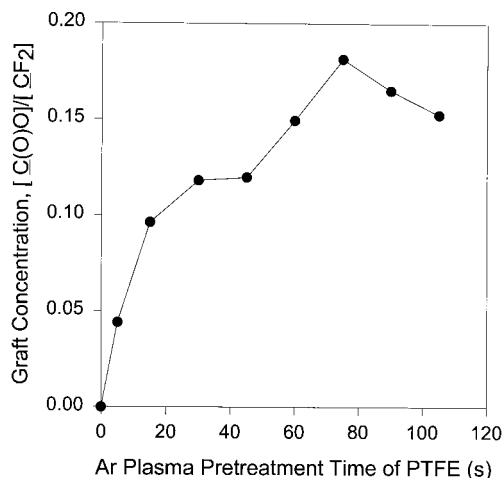


Figure 3 Graft concentration as a function of the argon plasma pretreatment time of the PTFE film.

treatment time to beyond 75 s, the concentrations of the C—H, C—O and C(O)O species are observed to fall slightly. The decline can probably be attributed to the excessive alteration of the PTFE surface at prolonged plasma exposure. Argon plasma treatment of the PTFE surface not only induces radical generation and surface oxidation, but also causes etching of the surface. The active species initially formed are etched away by prolonged plasma treatment.

Based on the chemical structure of GMA, the theoretical molar ratios of the C—H to C—O to C(O)O species should be 3.0 : 3.0 : 1.0. However, these ratios may not hold when the graft concentration is low (i.e., when the C—F₂ is still the dominant species in the C(1s) spectrum), as can be seen in Figure 2(b). This phenomenon is probably due to the presence of oxidized carbon species generated by the plasma pretreatment.³⁰ As the graft concentration of the GMA polymer increases, the peak area ratio of the C—H, C—O, and C(O)O species starts to approach the 3.0 : 3.0 : 1.0 ratio [Fig. 2(c)]. More efficient surface graft copolymerization is observed using the UV-induction process (see below). The graft concentration can be defined as the number of repeat units of the grafted GMA polymer per repeat CF₂ unit of the PTFE substrate. Thus, the graft concentration can be simply expressed as the following C(1s) component area ratio:

Graft Concentration

$$= \frac{[C(O)O]\{\text{Characteristic of GMA}\}}{[CF_2]\{\text{Characteristic of PTFE}\}}$$

A plot of the graft concentration from the thermally induced surface graft copolymerization vs. the plasma pretreatment time for the PTFE film is given in Figure 3. It can be seen that the graft concentration increases with plasma pretreatment until the maximum graft concentration is obtained at the plasma pretreatment time of 75 s. Increasing plasma pretreatment beyond 75 s then causes the graft concentration to fall.

Figure 4(a) shows the XPS C(1s) core-level spectrum of the pristine (as-synthesized) PPY salt film. The major peak component at the BE of 284.6 eV is assigned to the C—H species that arises from the carbon in the pyrrolylium ring. The high BE tail of the spectrum can be curve-fitted into two peaks. The first peak at 286.2 eV is due to C—O species, while the second peak at 287.9 eV corresponds to the carbonyl C=O species.³⁴ The C—O and C=O species probably have resulted from surface oxidation or charge-transfer complexing with oxygen.⁴ Hence, the surfaces of electrochemically synthesized PPY films are oxidized to some extent. For strong adhesion to occur between the PPY and PTFE films under the present lamination scheme, it is expected that the

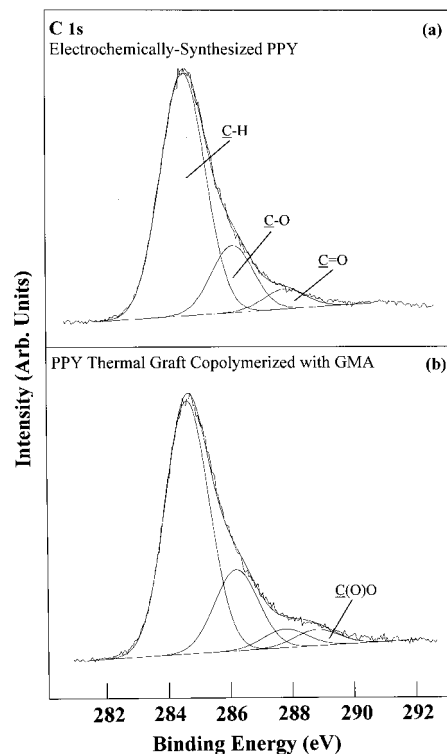


Figure 4 XPS C(1s) core-level spectra of (a) the as-synthesized PPY film, and (b) PPY film graft-copolymerized with GMA at the temperature of 170°C for 3 h.

surface of the PPY film should also undergo graft copolymerization with GMA. Figure 4(b) shows the C(1s) spectrum of a pristine (as-synthesized) PPY film that has been coated with pure GMA, heat treated at 170°C for 3 h and subsequently rinsed with copious amounts of acetone to remove the physically adsorbed GMA and GMA homopolymer. The emergence of a small C(O)O peak at 288.5 eV and the slight enhancement of the peak area assigned to the C—O species suggest the presence of a small amount of grafted GMA polymer on the PPY surface. The increase in C—O species can also be attributed to the curing of the GMA epoxy groups by the NH groups of polypyrrole. However, this minute amount of chemical bonds between the PPY film and the “adhesive layer” cannot account fully for the adhesion strength of the PPY/PTFE laminates observed (see below). Thus, the adhesive action on the PPY surface must be explained by an alternative mechanism. A plausible explanation is the thermal diffusion of the grafted GMA polymer chains on the PTFE surface across the PPY surface at elevated temperatures. These diffused GMA chains interlock with the PPY polymer network, inducing adhesion between the PPY and the PTFE films. Such a mechanism has been generally accepted to play a major role in polymer-polymer adhesion.^{36,37} Furthermore, charge transfer interactions and hydrogen bonding between the PPY surface and the grafted GMA polymer on the PTFE surface may also be responsible for augmenting the adhesion between the PPY and PTFE films. As can be seen from Figure 4(b), the amount of chemical bonds between the PPY and grafted layer formed by the thermal graft copolymerization and curing process are indeed minimal. However, it appears unnecessary to increase the amount of chemical interactions between these two entities through either plasma treatment or UV-induced graft copolymerization of the PPY surface, as it will be shown below that the PPY/PTFE laminate failed predominantly by cohesive failure inside the PTFE substrate.

The lap shear and T-peel adhesion strengths of the PPY/PTFE laminates as a function of the argon plasma pretreatment time of the PTFE films are shown in Figure 5. Both the lap shear and T-peel adhesion strengths are observed to increase with plasma treatment time of the PTFE films until the maximum strengths are reached at the plasma pretreatment time of 75 s. Following that, additional plasma treatment results in a decrease in adhesion strength. The trends of

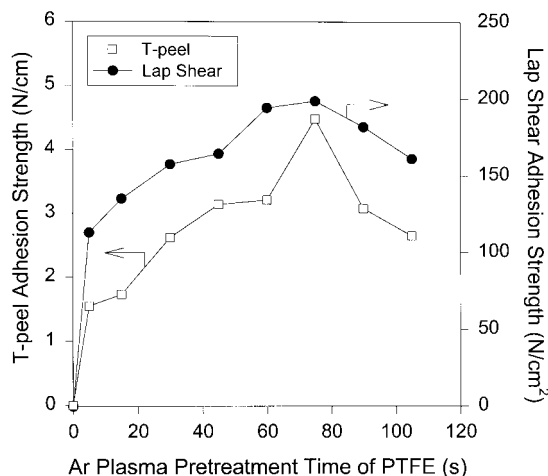


Figure 5 Plots of the T-peel and lap shear adhesion strengths of the PPY/PTFE laminates obtained from simultaneous thermal graft copolymerization and lamination as a function of the argon plasma pretreatment time of the PTFE film. The grafting/lamination was carried out at 170°C for 3 h using a GMA monomer mixture containing 20% v/v HMDA.

these plots are not unlike that of the graft concentration curve shown in Figure 3. As can be seen from Figures 3 and 5, the adhesion strength between PPY and PTFE is strongly influenced by the graft concentration of the GMA polymer on the PTFE surface. This observation is in excellent agreement with the fact that the interfacial adhesion process depends on the extent of chain entanglement and interaction which, in turn, are dependent on the concentration of the grafted polymer.³⁸

The effect of lamination temperature on the adhesion strengths of the thermally laminated assemblies is also investigated. The temperature at which the laminates are exposed will affect the graft copolymerization of GMA on the PTFE surface, as well as the polymerization and curing of the GMA–HMDA mixture. Figure 6 summarizes the lap shear adhesion strengths obtained at different argon plasma pretreatment times for a series of lamination temperatures. From the experimental results, the highest adhesion strengths are obtained for lamination carried out at the temperature of about 170°C. At the lamination temperature of 110°C, the polymerization appears to be incomplete and a sticky residue remained on the film surface even after 3 h of heat treatment. As such, the adhesion strengths obtained are low. The adhesion strengths of the laminates obtained at 200°C are found to be lower

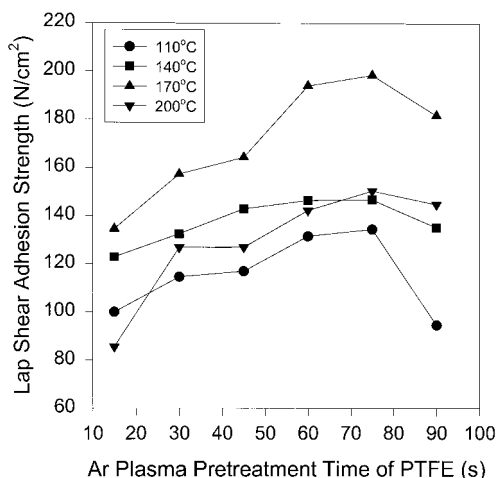


Figure 6 Plots of lap shear adhesion strength as a function of the argon plasma pretreatment time for the PTFE film at varying lamination temperatures.

than those cured at 170°C. Because the boiling point of the GMA monomer is about 190°C, a plausible explanation for this observation is that some of the GMA monomer may have evaporated before graft copolymerization, resulting in incomplete graft copolymerization and curing. Hence, the best lamination temperature, among the series of temperatures experimented upon, is in the order of 170°C for the GMA–HMDA mixture used in this study. This temperature coincides approximately with that of the exothermic peak observed in the differential scanning calorimetry (DSC) of the GMA–HMDA mixture. Thermogravimetric analysis (TGA) has also been used to analyze the stability of the PPY film at elevated temperatures. The TGA measurements show that at 170°C, minimal weight loss (and thus damage) occurs to the PPY film. For the electrochemically synthesized PPY–TSA salt film, the onset of weight loss occurs at temperatures above 300°C.

As can be seen from Figure 5, the adhesion strengths obtained from the simultaneous thermal graft copolymerization and lamination of the film surfaces are moderate. The maximum lap shear adhesion strength that can be achieved is about 200 N/cm², while the maximum T-peel adhesion strength is about 4.5 N/cm. Because it has been established that adhesion strength depends on the graft concentration of the GMA polymer on the PTFE surface, it follows that higher adhesion strengths can be obtained by increasing the GMA graft concentration on the PTFE surface to beyond the amount that can be achieved through thermal graft copolymerization. Thus, higher ad-

hesion strength is achieved through the two-step lamination process, involving the premodification of the PTFE film via UV-induced surface graft copolymerization prior to the simultaneous graft copolymerization and lamination of the PPY and the PTFE films [see Fig. 1, Path (b)].

Adhesion of PPY Films to Surface-Modified PTFE Films from UV-Induced Graft Copolymerization with GMA

The C(1s) core-level spectrum for a PTFE film subjected to 60 s of argon plasma pretreatment and UV-induced graft copolymerization in 20% v/v 1,4-dioxane solution of GMA for 2 h is shown in Figure 7(a). The presence of the $\underline{C}-H$, $\underline{C}-O$ and $\underline{C}(O)O$ peaks coupled with the fact that no $\underline{C}F_2$ component can be detected in the spectrum suggest that complete coverage of the PTFE surface by the GMA polymer to beyond the probing depth of the XPS technique (~ 7.5 nm for the organic matrix³⁴) has occurred. It has also been reported²³ that the full coverage of the PTFE surface by GMA polymer through UV-induced graft copolymerization can be easily obtained under slightly different conditions. The relative peak-area ratio for the three species are approximately 2.8 : 3.0 : 1.0, which is in good agreement with the theoretical ratio of 3.0 : 3.0 : 1.0 derived from the chemical structure of GMA.

Figure 7(b) shows the C(1s) core-level spectrum of the same GMA graft-copolymerized PTFE film after it has been coated with excess HMDA, subjected to 3 h of thermal treatment at 170°C and subsequently washed thoroughly with acetone to remove the unreacted HMDA. The appearance of the $\underline{C}-N$ peak component at 285.5 eV³⁹ and the decrease in the $\underline{C}-O$ peak component intensity suggest that curing of the epoxide groups of the grafted GMA polymer by the amine groups of HMDA has occurred. The curing reaction with HMDA is further confirmed by the appearance of a strong N(1s) peak component at the BE of 398.8 eV.²³ The crosslinking of the GMA polymer promoted by HMDA is effective in increasing the adhesive strength between the two films. The effect of plasma post treatment of the PTFE film after GMA graft copolymerization and prior to the simultaneous graft copolymerization and lamination with the PPY films has also been explored. To study the effect of plasma post treatment on the epoxide functional groups of the grafted GMA polymer on the PTFE surface, the changes in the [N]/[C] ratio arising from the reaction with

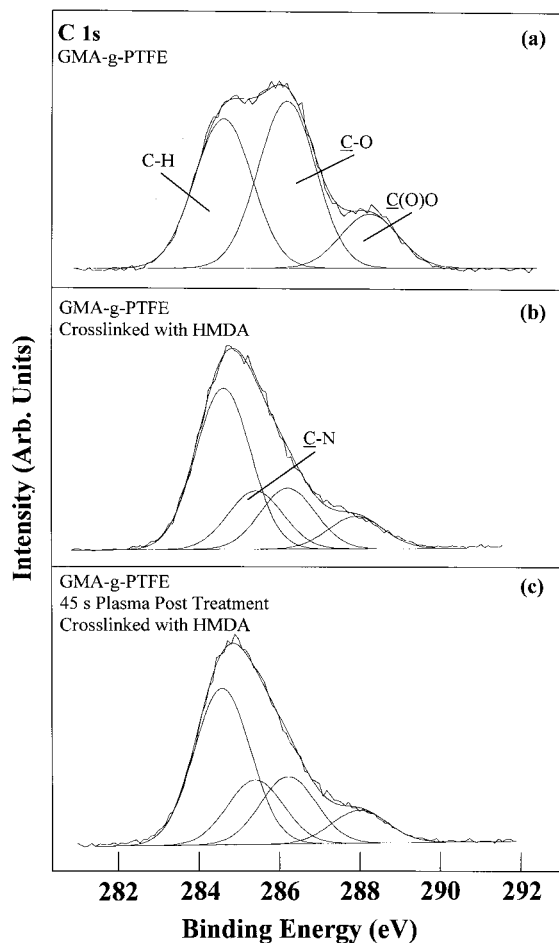


Figure 7 XPS C(1s) core-level spectra of (a) a PTFE film subjected to 60 s of argon plasma and UV-induced graft copolymerization in 20% v/v GMA in 1,4-dioxane solution for 2 h, and the modified PTFE films from UV-induced surface graft copolymerization when subjected to (b) 0 s and (c) 45 s of postargon plasma treatment before it was coated with HMDA and heat treated at 170°C for 3 h.

HMDA are tracked. The [N]/[C] ratio not only gives information on the extent of crosslinking, it also gives valuable insight into the number of epoxide groups present, because one HMDA molecule can attach itself to four epoxide groups of the GMA polymer. Hence, by tracking the changes in the [N]/[C] ratio after curing with HMDA for samples with and without the plasma posttreatment step, the effect of plasma exposure on the GMA graft-copolymerized PTFE surface can be quantified. The [N]/[C] ratio of the GMA graft-copolymerized PTFE surface not subjected to any argon plasma post treatment prior to the crosslinking step is found to be about 0.1. The [N]/[C] ratio does not change significantly even for the GMA graft-copoly-

Table I Effect of Ar Plasma Post Treatment on the Epoxide Groups of the Grafted GMA Polymer,^a as Evaluated by Treatment with Hexamethyldiamine

Ar Plasma Post Treatment Time	[N]/[C]
0 s	0.11
10 s	0.09
45 s	0.10
75 s	0.09

^a The GMA polymer concentration/coverage on the PTFE surface correspond to that shown in Figure 7.

merized surface with an extended plasma exposure of 75 s. The results are summarized in Table I. The C(1s) line shapes of the PTFE surfaces subjected to varying periods of plasma treatment prior to curing with HMDA do not exhibit any noticeable difference from those of the samples without the plasma post treatment, as shown in Figure 7(b) [cf. Fig. 7(c)]. Based on the above observations, it appears that post argon plasma exposure has no significant effect on the functional integrity of the epoxide groups of the grafted GMA chains.

Figure 1 shows schematically the processes of argon plasma pretreatment and UV-induced graft copolymerization of the PTFE films with GMA (GMA-g-PTFE) and their subsequent lamination to the PPY films. Figure 8 depicts the increase in the T-peel and lap shear adhesion strengths obtained with the GMA-g-PTFE films compared to

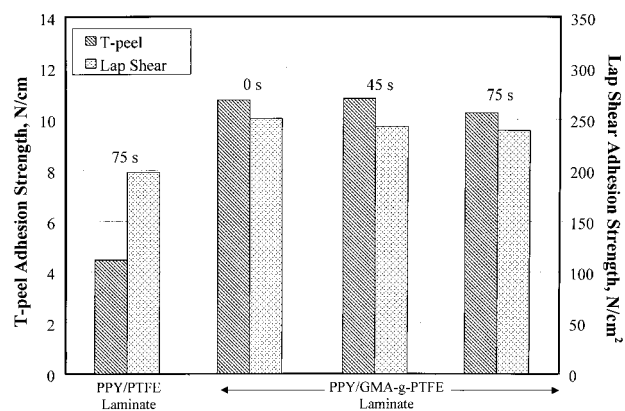


Figure 8 Comparison of the T-peel and lap shear adhesion strengths between PPY/PTFE and PPY/GMA-g-PTFE laminates. (The numbers above the bars represent the Ar plasma pretreatment time of PTFE for the PPY/PTFE laminate and the Ar plasma posttreatment time of GMA-g-PTFE for the PPY/GMA-g-PTFE laminates.)

the PTFE films subjected merely to argon plasma treatment. The T-peel and lap shear adhesion strengths of the laminates obtained from GMA-g-PTFE films subjected to post plasma treatments of 45 and 75 s are also depicted in Figure 8. As can be expected from the XPS analysis, post argon plasma exposure has no significant effect on the adhesion strength measured. From Figure 8, it can be seen that the PPY/GMA-g-PTFE laminates prepared with the GMA graft-copolymerized PTFE films have significantly higher adhesion strengths than the assembly obtained from the same simultaneous thermal graft copolymerization and lamination process involving only plasma-pretreated PTFE film (cf. Fig. 5). The T-peel adhesion strengths increase approximately by a factor of 2, while the lap shear adhesion strengths increase by approximately 30–50% for laminates prepared using the GMA-g-PTFE films. The reason for the smaller increase in the lap shear adhesion strength is as follows. At the higher loading employed in lap shear measurements, the yield strength of the 0.1 mm-thick PTFE is exceeded. Due to the yielding of the PTFE film, the measured adhesion strengths are lower than the actual adhesion strengths that could be obtained.

Failure Modes of the PPY/PTFE Laminates

The failure mode of the PPY/PTFE laminates from the simultaneous thermal graft copolymerization and lamination is also investigated. Figure 9(a)–(d) shows the respective wide-scan spectra of the as-synthesized PPY-TSA film, the pristine PTFE surface, and the delaminated surfaces from a PPY/PTFE laminate. The assembly was prepared from the simultaneous thermal graft copolymerization and lamination of a 60-s argon plasma-pretreated PTFE film with PPY at 170°C and had a T-peel adhesion strength of about 3.2 N/cm. The wide-scan spectra of the two delaminated surfaces are practically similar to each other. They also bear close resemblance to the wide-scan spectrum of the pristine PTFE film with the fluorine signals as the most prominent features in all the three wide-scan spectra. The C(1s) core-level spectra of both delaminated surfaces show the presence of CF_2 species, which are characteristic of the PTFE polymer. The lower BE component of the C(1s) spectrum indicates the presence of $\text{C}-\text{O}$, $\text{C}=\text{O}$, and $\text{C}(\text{O})\text{O}$ species. These species are due to the contribution from the grafted layer, as well as from PPY. The nitrogen

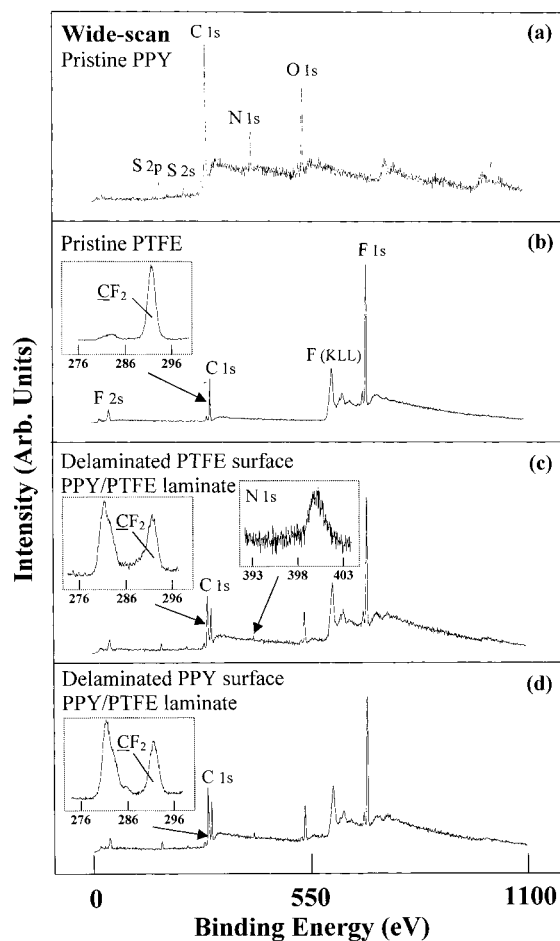


Figure 9 XPS wide-scan spectra of (a) an as-synthesized PPY-TSA film, (b) a pristine PTFE film, and (c,d) mechanically delaminated PTFE and PPY film surfaces from a laminate involving plasma-pretreated PTFE film (T-peel adhesion strength = 3.2 N/cm).

and the sulphur signals, which are associated, respectively, with the backbone and TSA dopant of PPY, are also discernible in both of the wide-scan spectra of the delaminated surfaces. Although the N(1s) signal may also have involved contribution from HMDA in the GMA polymer, the presence of a high BE N(1s) tail above 400 eV, attributable to the positively charged nitrogen, confirms the contribution of PPY-TSA to the N(1s) signal. Hence, based on the XPS data, the failure of the PPY/PTFE laminate involving PTFE film with Ar plasma pretreatment alone probably has proceeded via a mixed failure mode, including cohesive failure in the PTFE film, and to a lesser extent, cohesive failure in the PPY film.

The failure mode of the PPY/PTFE laminate involving the GMA graft-copolymerized PTFE

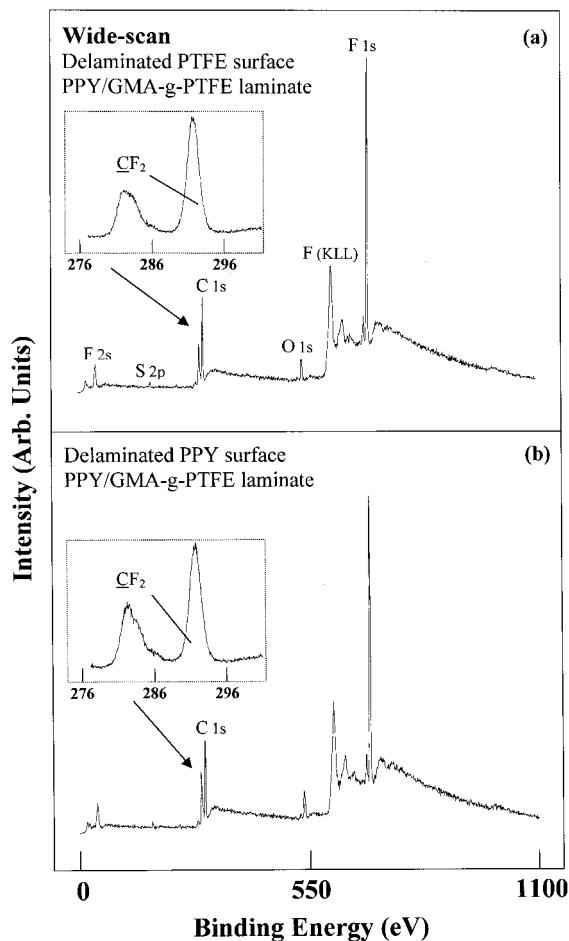


Figure 10 XPS wide-screen spectra of the mechanically delaminated PTFE and PPY surfaces from assembly involving GMA-g-PTFE film (T-peel adhesion strength 10.8 N/cm).

film is also investigated through XPS characterization of the two delaminated surfaces. Figure 10(a) and (b) show the wide-scan spectra of the delaminated PTFE and PPY surfaces, respectively, from a PPY/GMA-g-PTFE assembly having a T-peel adhesion strength of 10.8 N/cm. As with the assembly obtained through the same simultaneous thermal graft copolymerization and lamination involving PTFE films with plasma pretreatment alone, the fluorine signals, which are representative of the PTFE polymer, predominate. Although the sulphur signals are still discernible in the wide-scan spectra, the nitrogen signals become negligible. Hence, the cohesive failure of the assembly has occurred predominantly inside the PTFE substrate. The sulphur signals probably arise from the diffusion of TSA dopant of the PPY film into the interface. The

XPS result thus provide a strong support to the fact that higher adhesion strength, and thus a strong interface, in laminates involving the GMA graft-copolymerized PTFE surface has also given rise to a cleaner failure inside the PTFE substrate.

CONCLUSIONS

The extent of the argon plasma pretreatment of the PTFE films affected the concentration of the thermally grafted GMA polymer on the film surfaces. This in turn affected the lap shear and T-peel adhesion strengths of the laminates obtained from the simultaneous thermal graft copolymerization and lamination process involving PPY films with the Ar plasma-pretreated PTFE films. Because the adhesion strengths of the PPY/PTFE assemblies depended on the graft concentration of the GMA polymer on the PTFE surface, the surface graft concentration was increased by further modifications of the argon plasma-pretreated PTFE surface with UV-induced graft copolymerization prior to lamination. A full coverage of the PTFE surface by the GMA polymer was obtained. Consequently, a substantial increase in the lap shear and T-peel adhesion strengths was achieved for PPY/PTFE laminates obtained using the GMA graft-copolymerized PTFE films and the simultaneous thermal graft copolymerization and lamination technique. Ar plasma post treatment of the GMA-g-PTFE films before lamination had resulted in a slight decrease in adhesion strength, and thus should be avoided. The failure mode of the PPY/PTFE laminate arising from PTFE film with Ar plasma pretreatment alone was a mixed failure mode, involving cohesive failure in the PTFE film and, to a lesser extent, cohesive failure in the PPY film and adhesive failure in the graft layer. For the PPY/PTFE laminate involving the GMA graft-copolymerized PTFE film, the higher adhesion strength obtained gave rise to a cleaner cohesive failure inside the PTFE substrate.

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