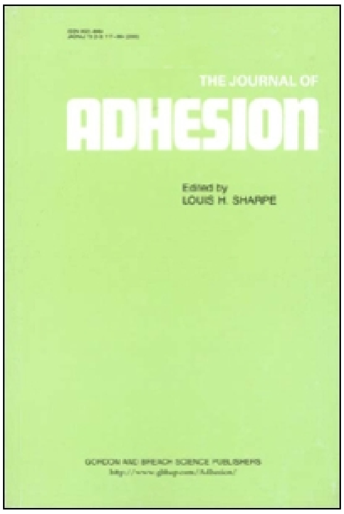

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Grafting of Epoxy Resin on Surface-modified Poly(tetrafluoroethylene) Films

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An epoxy/PTFE composite was prepared by curing the epoxy resin on the surface-modified PTFE film. Surface modification of PTFE films was carried out *via* argon plasma pretreatment, followed by UV-induced graft copolymerization with glycidyl methacrylate (GMA). The film composite achieved a 90°-peel adhesion strength above 15 N/cm. The strong adhesion of the epoxy resin to PTFE arose from the fact that the epoxide groups of the grafted GMA chains were cured into the epoxy resin matrix to give rise to a highly crosslinked interphase, as well as the fact that the GMA chains were covalently tethered on the PTFE film surface. Delamination of the composite resulted in cohesive failure inside the PTFE film and gave rise to an epoxy resin surface with a covalently-adhered fluoropolymer layer. The surface composition and microstructures of the GMA graft-copolymerized PTFE (GMA-g-PTFE) films and those of the delaminated epoxy resin and PTFE film surfaces were characterized by X-ray photoelectron spectroscopy (XPS), water contact angle and scanning electron microscope (SEM) measurements. The delaminated epoxy resin surfaces were highly hydrophobic, having water contact angles of about 140°C. The value is higher than that of the pristine PTFE film surface of about 110°. The epoxy resin samples obtained from delamination of the epoxy/GMA-g-PTFE composites showed a lower rate of moisture sorption. All the fluorinated epoxy resin surfaces exhibited rather good stability when subjected to the Level 1 hydrothermal reliability tests.

Keywords: Epoxy resin; PTFE; Graft copolymerization; Cohesive failure; Moisture sorption; Fluorination

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1. INTRODUCTION

Epoxy resins have been widely used in the packaging and encapsulation of semiconductors and microelectronic devices. They offer excellent combinations of the desirable physical, mechanical and electronic properties [1,2]. As established packaging materials, they exhibit good dimensional stability and excellent resistance to chemical attack. They also provide good dielectric properties and are mechanically strong. They exhibit low shrinkage and good adhesion to metals, and are resistant to mechanical and thermal shock [3]. At the same time, there is a need to improve the reliability of plastic encapsulated devices (PEDs) as they find further application in more stringent environments and certain military applications. Moisture is probably the single most detrimental factor in causing electrical or electronic failure in components [4]. Unfortunately, epoxy resins readily adsorb water because they inevitably possess hydroxyl groups in their molecular structure. Depending on the type of hardener used, the cured epoxy resin may also contain amine and carboxyl functional groups which are capable of undergoing hydrogen bonding with water. A film of moisture, once adsorbed on the insulating materials, is difficult to remove. Moisture films degrade the performance of electrical and electronic components not only by increasing their surface conductivity, but also through the chemical attack of these components. One of the major causes of failure in such devices is corrosion due to moisture permeating through the encapsulant, transporting a small amount of ionic impurity, and condensing at the chip surface to form an aggressive electrolyte [4]. As a consequence, corrosion occurs readily and can result in (a) disappearance of metallic thin films, (b) electrical opening of wirewound resistors, and (c) etching and dissolution of metal from anodic areas.

Recently, a number of studies on the interaction of epoxy resin with water [5], on the water sorption in epoxy resin [6], on the effect of adsorbed water on the properties of epoxy resins [7] and on the moisture degradation of epoxy resins and epoxy matrix composites have been carried out [8]. Ainger *et al.* [9] have attempted to improve plastic packaged semiconductor devices by adding corrosion-inhibiting chemicals in the encapsulating resin. Surface modification of polymers is a potentially useful method for reducing the moisture sorption in polymers, since the modification can impart hydrophobic properties to the surface and generate a barrier for the diffusion of water into the bulk of polymer. A variety of techniques have been proposed for improving the surface properties of polymers. It is well-known that fluorine-containing polymers, such as poly(tetrafluoroethylene) (PTFE), have low surface energy, low tendency for moisture uptake, high water repellency and low dielectric constant [10]. It has been reported that direct fluorination with fluorine gas can result in a marked decrease in the total surface tension of high-density polyethylene. Highly fluorinated compounds, such as CF_4, C_2F_6 and SF_6, have been used as plasma gases in the grafting of fluorine functionalities on the polymer surfaces [11–15]. Siloxane-containing block copolymers, which are composed of methyl methylacrylate (MMA), glycidyl methacrylate (GMA) and dimethylsiloxane methacrylate (SMA), have been blended in to an epoxy resin to improve the oil and water repellency [16]. The low surface energy segments orient toward the exterior surface of the blend to give rise to a low energy surface.

In the present work, we employ a model epoxy resin, *viz.*, the glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) with 4,4′-diaminodiphenyl methane as the curing agent. The epoxy resin is cast and cured on or between the surface-modified PTFE films from pretreatment by argon plasma, followed by UV-induced graft copolymerization with GMA. The composites are subsequently delaminated to result in the incorporation, *via* covalent linkages, of a thin film of PTFE on one or both sides of the cured epoxy resin surface. X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and contact angle measurements are used for the characterization of the surface-modified PTFE and epoxy resin. The validity of these fluorinating methods to minimize the water uptake of the epoxy resin is also evaluated in hydrothermal tests.

2. EXPERIMENTAL

2.1. Materials

Poly(tetrafluoroethylene) (PTFE) (Fig. 1(a)) films with a thickness of 0.25 mm and a density of 2.18 g/cm^3 were purchased from Goodfellow

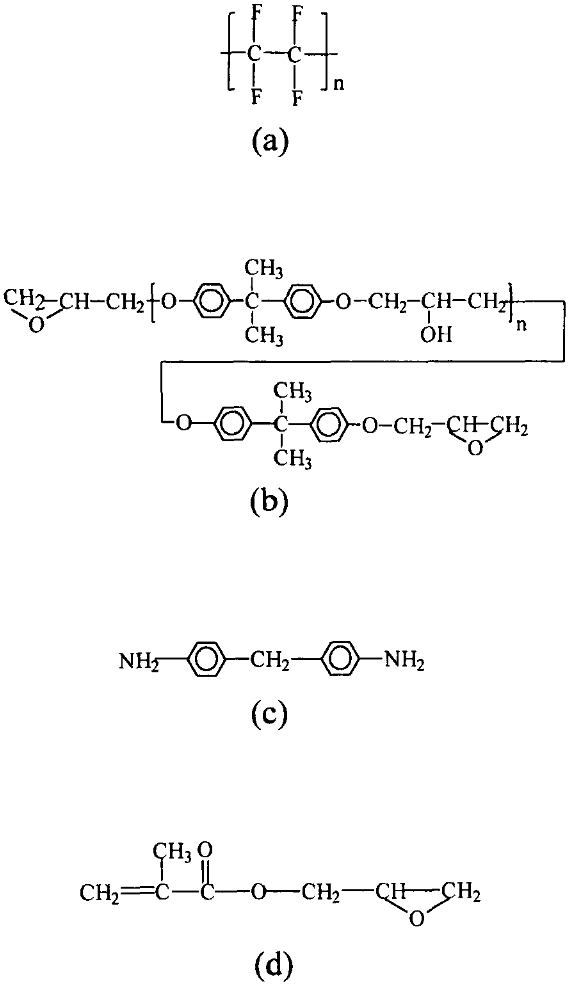

FIGURE 1 Chemical structures of (a) poly(tetrafluoroethylene) (PTFE), (b) glycidyl end-capped poly(bisphenol A-co-epichlorohydrin), (c) 4,4′-diaminodiphenyl methane and (d) glycidyl methacrylate (GMA).

Ltd. of Cambridge, UK. The surface of the PTFE film was thoroughly cleaned with acetone in an ultrasonic water bath before its use. The epoxy resin, glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (Average Mn = 377) (Fig. 1(b)) and the curing agent, 4,4′-diaminodiphenyl methane (Fig. 1(c)), were obtained from the Aldrich Chemical Company. Glycidyl methacrylate (GMA) (Fig. 1(d)) was also supplied by the Aldrich Chemical Company and was used without further purification for UV-induced surface graft copolymerization. The solvents, 1,4-dioxane and acetone, were of reagent grade and were purchased from the Aldrich Chemical Company.

2.2. Plasma Treatment

The plasma treatment of the PTFE films was performed between two parallel plate electrodes of 7 cm × 13 cm in area in a glow discharge quartz reactor (Model SP100 Plasma System), manufactured by Anatech Co. Ltd. The plasma power supply was set at 32 W at a radiofrequency of 40 kHz. The substrate was exposed to the glow discharge at an argon pressure of about 0.58 Torr for a predetermined period of time. The plasma-treated PTFE surface was subsequently exposed to the atmosphere for about 10 min to allow the formation of surface peroxide and hydroperoxide species for the subsequent UV-induced graft copolymerization [17, 18].

2.3. UV-induced Surface Graft Copolymerization of PTFE Films

The plasma-pretreated PTFE film, of dimensions about 2.0 cm × 7.2 cm, was placed in a Pyrex® tube containing 30 ml of 20 vol.% 1,4-dioxane solution of GMA. The reaction mixture was thoroughly degassed with argon before the glass tube was plugged with a silicone rubber stopper. The test tube was then exposed to the UV radiation from a 1000 W high-pressure mercury lamp in a Riko RH400-10W rotary photochemical reactor (manufactured by Riko Denki Kogyo of Chiba, Japan) at 30°C for 2 h. After the reaction, the PTFE film was extracted with copious amounts of 1,4-dioxane (a good solvent for both GMA homopolymer and monomer) for more than 12 h to remove the residual monomer and homopolymer physically adsorbed on the graft-modified PTFE film surface.

2.4. Surface Characterization

Static water contact angles of the sample surfaces were measured by the sessile drop method in a telescopic goniometer (Ramè-Hart, Model

100-0-230) at 25°C and 60% relative humidity. The telescope with a magnification power of 23 × was equipped with a protractor of 1° graduation. For each sample, at least five measurements on different surface locations were averaged. The measurements from each sample surface generally did not vary by more than 5 degrees.

The chemical compositions of the surfaces and interfaces were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out on a VG ESCALAB MkII spectrometer using a non-monochromatized Mg Kα X-ray source (1253.6 eV photon) at a constant retard ratio of 40. Samples were mounted on standard sample studs by means of double-sided adhesive tape. The XPS source was operated at a reduced power of 120 W (12 kV and 10 mA). The operating pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. The core-level signals were obtained at a photoelectron take-off angle (α, measured with respect to the sample surface) of 75°. All binding energies (BEs) were referenced to the Cls neutral carbon peak at 284.6 eV or to the $\underline{C}F_2$ peak component at 291.4 eV to compensate for surface-charging effects. Surface elemental stoichiometries were determined from core-level spectral peak area ratios, after correcting with the experimentally-determined sensitivity factors, and were reliable to ± 10%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Cross-sectional scanning electron microscopic (SEM) images were obtained from a Hitachi Model S-2150 SEM at a magnification power of 10000 × . The accelerating voltage was 15 kV. The samples were attached to the sample studs by means of conductive double-sided adhesive tape. A thin layer of gold was vacuum deposited on each sample before SEM observation.

2.5. Curing of Epoxy Resin on the Surface Graft-copolymerized PTFE Films

Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) was mixed by stirring with 4,4′-diaminodiphenyl methane powder to a homogeneous paste. The mixing ratio was 100 : 27 (w/w), based on the stoichiometric ratio of the functional group counts. After stirring, the mixture was heated at a temperature of 85°C for 3–5 min to achieve better mixing under reduced viscosity. The epoxy resin system was then degassed in a vacuum oven under a reduced pressure of 85 kPa. The epoxy mixture was subsequently cast onto the surface-modified PTFE film, or between two surface-modified PTFE films. The composite was allowed to cure at room temperature for 4–6 h before it was heated at 120°C for 4 h in a constant temperature oven. After the thermal curing, the epoxy/PTFE composite was allowed to cool down gradually over a period of 6 h in the well-insulated oven. Differential scanning calorimetry (DSC) studies showed that, under the above curing conditions, no further curing was detected in the subsequent DSC measurement.

2.6. Adhesion Strength Measurements

The adhesion strengths of the various epoxy/PTFE composites were determined by measuring the 90°-peel adhesion strengths on an Instron Model 5540 tensile tester. All measurements were carried out at a cross-head speed of 10 mm/min. For each measurement, the sizes of the samples were kept at 4–6 mm wide and 10–12 mm long. Each peel measurement was taken over a length of about 8 to 10 mm. Only measurements from samples which exhibited a constant maximum peel strength over a length of at least 5 mm were used. Each adhesion strength value reported was the average of at least three sample measurements. In general, the peel strengths among the three samples did not vary by more than 20%. Some of the epoxy/PTFE composites were mechanically delaminated by the 90°-peel and the delaminated surfaces were submitted to further analysis by XPS, SEM and water contact angle measurements.

2.7. Water Sorption Measurement of the Surface Fluorinated Epoxy Resin

The delaminated epoxy resin samples with the fractured PTFE material on their surfaces were subjected to the IPC Level 1 hydrothermal reliability test in a weathering chamber. The test was carried out at a constant temperature of 85°C and a relative humidity of 85% for 168 h. Before the test, the surface-modified samples were dried in a vacuum desiccator for at least 24 h and the weights of the dry resins were then recorded as the initial weight (W_0). After the test, the resin samples were dried superficially and the weights were determined again (W). The corresponding extent of water sorption was referenced to the original weight of the sample and was calculated as follows:

$$\text{Extent of Water Sorption} = (W - W_0)/W_0.$$

3. RESULTS AND DISCUSSION

The effects of the plasmas generated from various types of gases and under different glow discharge conditions on the surface characteristics of polymers have been widely reported [19–23]. The UV-induced surface graft copolymerization of GMA on the argon plasma-pretreated PTFE surface (GMA-g-PTFE) and the subsequent thermal curing of an epoxy resin on the GMA-g-PTFE surface are shown schematically in Figure 2.

3.1. UV-induced Surface Graft Copolymerization of GMA on PTFE Films

Figure 3 shows the C1s core-level spectra of the pristine PTFE film and the PTFE surface after 30 s, 60 s and 90 s of argon plasma pretreatment, followed by 2 h of UV-induced graft copolymerization in 20 vol.% GMA solution in 1,4 dioxane. The pristine PTFE surface (Fig. 3(a)) shows predominantly a major peak component at the binding energy (BE) of 291.4 eV, attributable to the $\underline{C}F_2$ species [24]. The spectral lineshape is consistent with the chemical structure of the PTFE molecule. The minor low BE components at about 281.2 eV and 283 eV, on the other hand, must have resulted from the contributions of the X-ray satellite peaks of the $\underline{C}F_2$ species arising from the Mg Kα_3 and α_4 radiation, respectively. A new C1s envelope at the BE of about 285 eV appears and increases in intensity with exposure, while the $\underline{C}F_2$ peak component shrinks in intensity with exposure, when the pristine PTFE films are subjected to argon plasma pretreatment and the UV-induced graft copolymerization with GMA. For the plasma

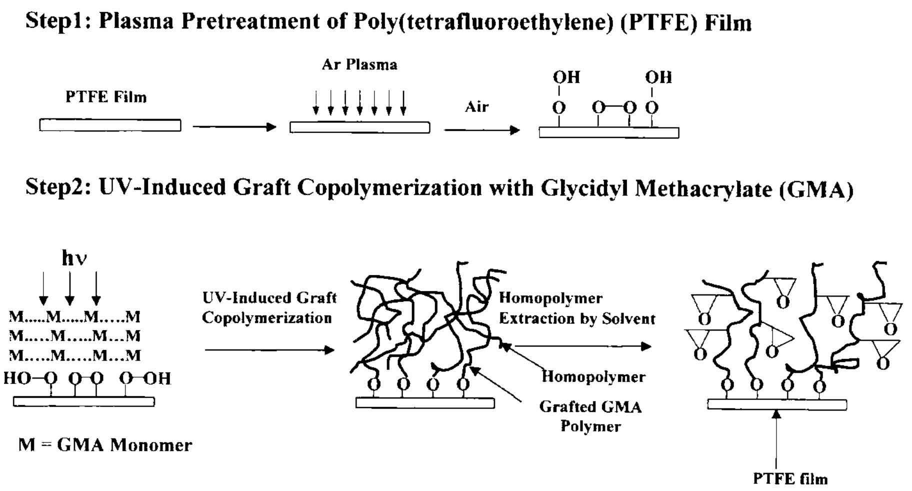

FIGURE 2 Schematic diagram illustrating the processes of plasma pretreatment of the PTFE substrate, UV-induced graft copolymerization with GMA and the crosslinking and curing reaction at the epoxy/GMA-g-PTFE interphase.

Step3: Cross-linking Reaction at the Surface of PTFE Film

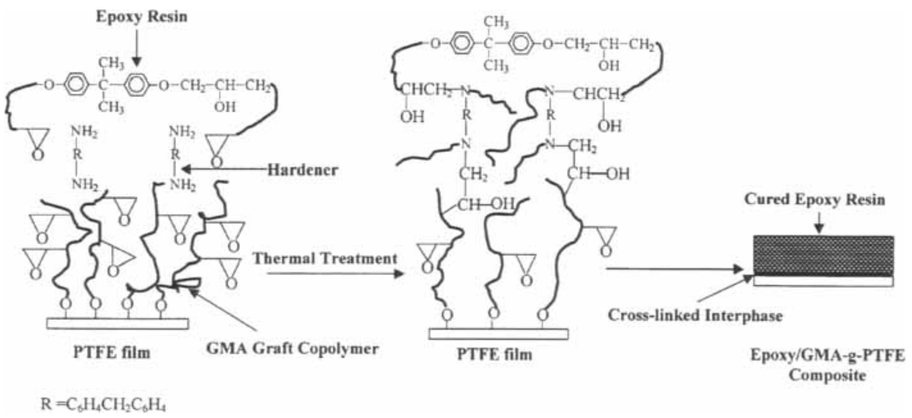

FIGURE 2 (Continued).

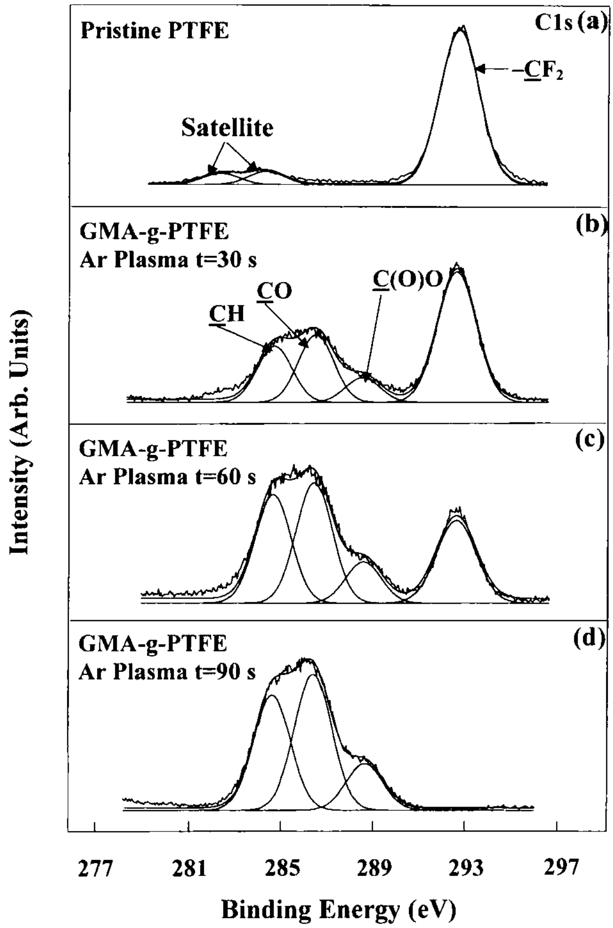

FIGURE 3 XPS C1s core-level spectra of (a) a pristine PTFE surface and the PTFE surfaces after (b) 30 s, (c) 60 s, (d) 90 s of argon plasma pretreatment, followed by 2 h of UV-induced graft copolymerization in 20 vol.% GMA solution in 1,4 dioxane.

pretreatment time of 90 s, the $\underline{C}F_2$ peak component of the PTFE substrate has disappeared completely after the UV-induced surface graft copolymerization with GMA (Fig. 3(d)). Under this condition, the PTFE surface is completely covered by grafted GMA copolymer which is thicker than the probing depth of XPS technique (about 7.5 nm in an organic matrix [17]). The C1s envelope at the BE of 285 eV can be curve-fitted with three peak components with BEs at

284.6 eV for the $\underline{C}-C$ species, 286.2 eV for the $\underline{C}-O$ species, and 288.5 eV for the $\underline{C}OO$ species [17]. The minor contribution from the $\underline{C}F_2$ satellite structure has been neglected in the related curve-fitting. The relative peak area ratios for the $\underline{C}-C$, $\underline{C}-O$, $\underline{C}OO$ species at high extents of graft copolymerization (Figs. 3(c) or 3(d)) are fairly close to the theoretical ratio of 3 : 3 : 1, dictated by the chemical structure of the GMA polymer (see Fig. 1(d)).

The water contact angles of the argon plasma-treated PTFE surface before and after graft copolymerization with GMA are shown in Figure 4. As the plasma treatment time increases, the contact angle for the PTFE surface decreases. Surface graft copolymerization with GMA results in the further decrease in water contact angle of the argon plasma-pretreated PTFE surface. The minimum water contact angles for the plasma-treated PTFE surfaces with and without surface graft copolymerization with GMA are about 55° and 95°, respectively. Plasma treatment and subsequent air exposure result in the oxidation of the PTFE surface and increase the wettability of the surfaces.

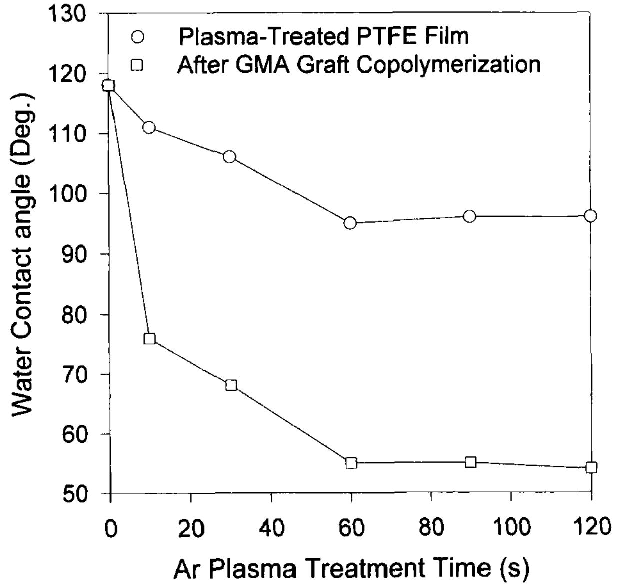

FIGURE 4 Dependence of water contact angles of the PTFE films on the argon plasma treatment time of the PTFE film in the presence and absence of surface graft copolymerization with GMA.

For the GMA-g-PTFE surface, the larger decrease in water contact angle is attributable to the fact that GMA polymer chains are covalently tethered on the PTFE surface, as well as the fact that GMA contains polar groups, such as ester groups and epoxide groups in its molecular structure. The contact angle does not decrease further at argon plasma treatment times above 60 s, due to the complete coverage of the PTFE surface by the GMA polymer.

3.2. Adhesion Strength of the Epoxy/PTFE Composites

Figure 5 shows the 90°-peel adhesion strengths of the various epoxy/PTFE composites as a function of the argon plasma treatment time of the PTFE film in the presence and absence of further modification *via* surface graft copolymerization with GMA. It is apparent that as the plasma treatment time increases, the 90°-peel adhesion strengths increase for both types of PTFE surfaces. The 90°-peel adhesion

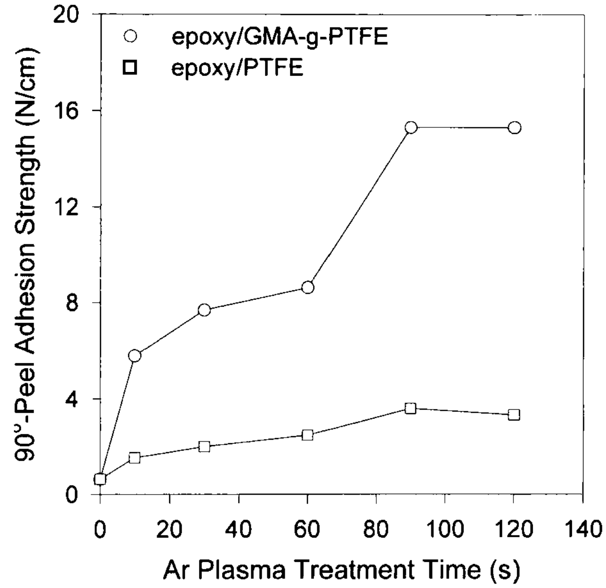

FIGURE 5 Dependence of the 90°-peel adhesion strength of various epoxy/PTFE composites on the argon plasma treatment time of the PTFE film.

strength of the epoxy/GMA-g-PTFE composite is always much higher than that of the corresponding epoxy/PTFE composite involving PTFE film with plasma treatment alone. At the plasma pretreatment time of 90 s, and with the complete surface coverage of PTFE film by the grafted GMA polymer, the 90°-peel adhesion strength of the epoxy/GMA-g-PTFE composite achieves a value in excess of 15 N/cm. The large increase in the adhesion strength of epoxy resin on the GMA-g-PTFE film must have resulted from the formation of covalent bonds between the epoxide groups on the grafted GMA polymer chains and the amino groups of the epoxy resin hardener. In this manner, the grafted GMA chains on the PTFE surface become covalently incorporated into the epoxy matrix, as shown schematically in Figure 2. Another factor influencing the interfacial adhesion is the surface wettability of the substrates. In Figure 4, the water contact angles of the GMA-g-PTFE surfaces are significantly lower than those of the pristine and argon plasma-treated PTFE surfaces. In addition, for the epoxy/PTFE composites involving PTFE films with plasma treatment alone, the 90°-peel adhesion strengths increase rather slowly, as surface oxidation is limited to only the top-most layer of the PTFE films.

3.3. Failure Mechanism at the Epoxy/PTFE Interface and the Formation of Surface Fluorinated Epoxy Resin

The failure modes of the thermally-cured epoxy/PTFE composites and the epoxy/GMA-g-PTFE composites were investigated through the characterization of the delaminated surfaces by XPS. Figure 6 shows the respective XPS wide scan spectra of the pristine epoxy resin surface cured in air (Fig. 6(a)), the pristine PTFE surface (Fig. 6(b)) and the delaminated epoxy resin surface (Fig. 6(c)) and PTFE surface (Fig. 6(d)) from an epoxy/PTFE composite involving PTFE film with 90 s of plasma treatment alone and having a 90°-peel adhesion strength of about 3 N/cm. The XPS wide scan spectrum of the delaminated epoxy resin surface is dominated by the F1s and F(KLL) signals while that of the delaminated PTFE surface resembles that of the pristine PTFE film. These results suggest that a thin PTFE layer remains on the delaminated epoxy resin surface and that the failure

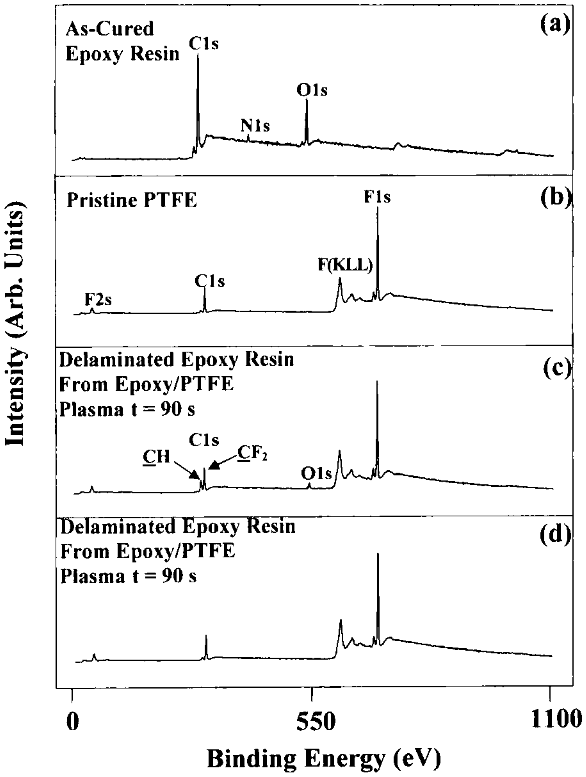

FIGURE 6 XPS wide scan spectra of (a) an as-cured epoxy resin, (b) a pristine PTFE film, and the delaminated (c) epoxy resin and (d) PTFE surfaces from an epoxy/PTFE composite involving PTFE film with 90 s of argon plasma treatment alone.

occurs inside the PTFE film. The fact that a weak O1s and C1s component signal associated with the underlying epoxy resin are still discernible in the wide scan spectrum of the delaminated epoxy resin surface, suggests that the thickness of the PTFE overlayer must be only in the order of the probing depth of the XPS technique, or less than 7.5 nm.

Figure 7 shows the characteristic XPS wide scan spectra of the delaminated epoxy resin surface and the delaminated PTFE surface from an epoxy/GMA-g-PTFE composite involving the GMA-g-PTFE film and having a 90°-peel adhesion strength of about 8 N/cm. The XPS wide scan spectra of both of the delaminated surfaces show complete resemblance to that of the pristine PTFE surface (Fig. 6(b)),

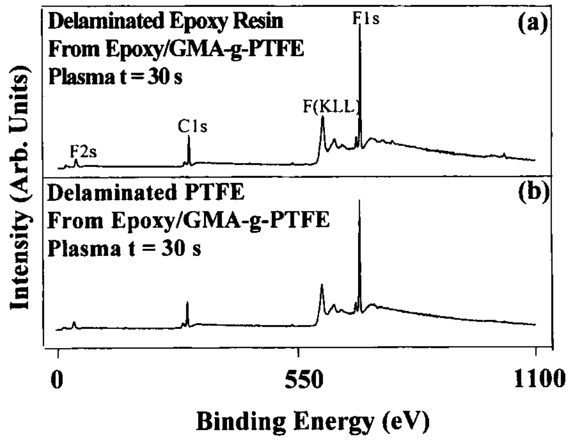

FIGURE 7 XPS wide scan spectra of the delaminated (a) epoxy resin surface and (b) PTFE surface from the epoxy/GMA-g-PTFE composite with a plasma treatment time of 30 s for the PTFE film.

suggesting the presence of a PTFE layer on the epoxy resin surface having a thickness greater than the probing depth of the XPS technique. These XPS results show that the failure of all the epoxy/PTFE composites must have occurred in the sub-surface layer of PTFE substrate. The clean cohesive failure inside the PTFE substrate is consistent with the poor mechanical strength of the PTFE polymer [10]. With further increase in adhesion strength at the interface, cohesive failure occurs further inside the PTFE substrate and the roughness of the delaminated surfaces increases significantly, as revealed by the cross-sectional scanning electron microscopic images and water contact angle results (see below).

The static water contact angles of the delaminated epoxy resin surfaces and the delaminated PTFE surfaces from all the epoxy/PTFE composites have been measured. As shown in Figure 8, the average water contact angle of the pristine epoxy resin cured against air is about 80°. On the other hand, the delaminated epoxy resin and PTFE surfaces from the epoxy/PTFE composites involving PTFE film with plasma treatment alone are comparable in magnitude with that of the pristine PTFE film surface. However, the water contact angles of the delaminated epoxy resin surface and PTFE surfaces from the epoxy/GMA-g-PTFE composites having 90°-peel adhesion strengths of at

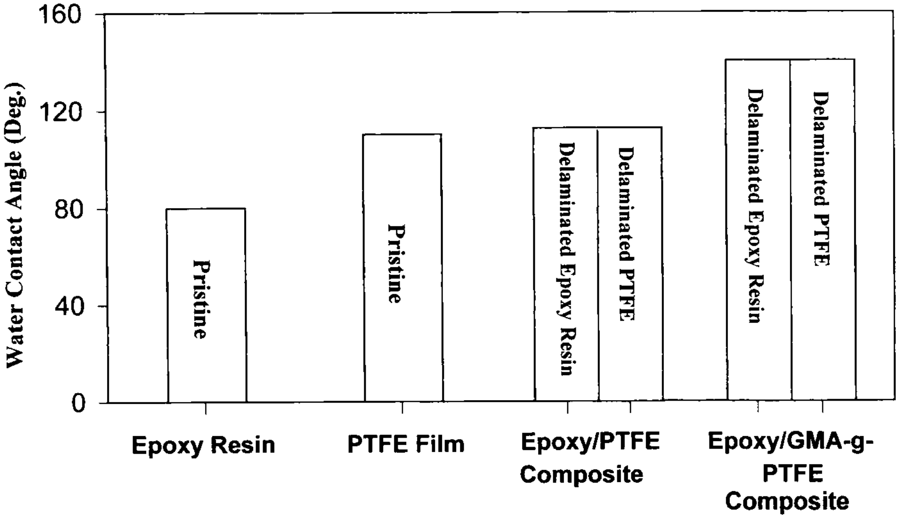

FIGURE 8 The water contact angle of the pristine and the delaminated PTFE and epoxy resin surfaces.

least 6 N/cm are in the order of 140 ± 5°. These angles are significantly larger than that of the pristine PTFE surface of about 110°. The AFM images reveal that the mean surface roughness (Ra) of the pristine PTFE used is in the order of 180 nm. However, the Ra's of the delaminated epoxy resin and PTFE surfaces from the epoxy/GMA-g-PTFE composites with 90°-peel adhesion strengths of at least 6 N/cm cannot be measured by AFM, due to the highly uneven topography of the surfaces, with Ra values exceeding the maximum upper limit of 1 μm. The surface of the delaminated epoxy resin is covered with PTFE material fractured from the sub-surface layer of the PTFE substrates due to the crosslinking and interlocking of the grafted GMA chains in the epoxy resin interphase. Thus, the surface topography of the delaminated epoxy resin and PTFE surfaces are highly uneven and have surface roughness values significantly larger than that of the pristine PTFE film. The surface roughness and the static water contact angle can be related by Wentzel's law, as proposed by Good [25],

$$\cos\theta_r = r \times \cos\theta_{\text{true}}$$

where θ_r, θ_{true} and r are the apparent static contact angle of a solid surface, the true static contact angle of the geometrically "smooth" surface, and the roughness factor of the surface, respectively. The roughness factor is, therefore, equal to 1 for a "smooth" surface and is always greater than 1 for a real surface. Thus, the hydrophobicity of a (hydrophobic) surface can be enhanced by increasing the roughness of the surface appropriately. The Ra values of the delaminated epoxy resin and PTFE surfaces are much greater than that of the pristine PTFE film. Thus, in accordance with the above equation, the water contact angles of the delaminated PTFE film surfaces are expected to increase significantly over that of the pristine PTFE film. This observation also implies that the epoxy resin surface is completely covered by the PTFE molecules to a depth greater than the sensitivity of the technique. The contact angle technique is sensitive to the chemical composition of 1 nm or less of the outmost molecular layer [26].

Surface modification of PTFE films by graft copolymerization with GMA causes a remarkable increase in the 90°-peel adhesion strength of the epoxy/GMA-g-PTFE composites and, thus, influences the thickness and topography of the PTFE layer peeled off from the PTFE substrate. The representative cross-sectional SEM images of the epoxy resin surfaces delaminated from the epoxy/GMA-g-PTFE composites involving PTFE films with plasma pretreatment times of 30 s and 90 s are shown in Figures 9(a) and 9(b), respectively. Apparently,

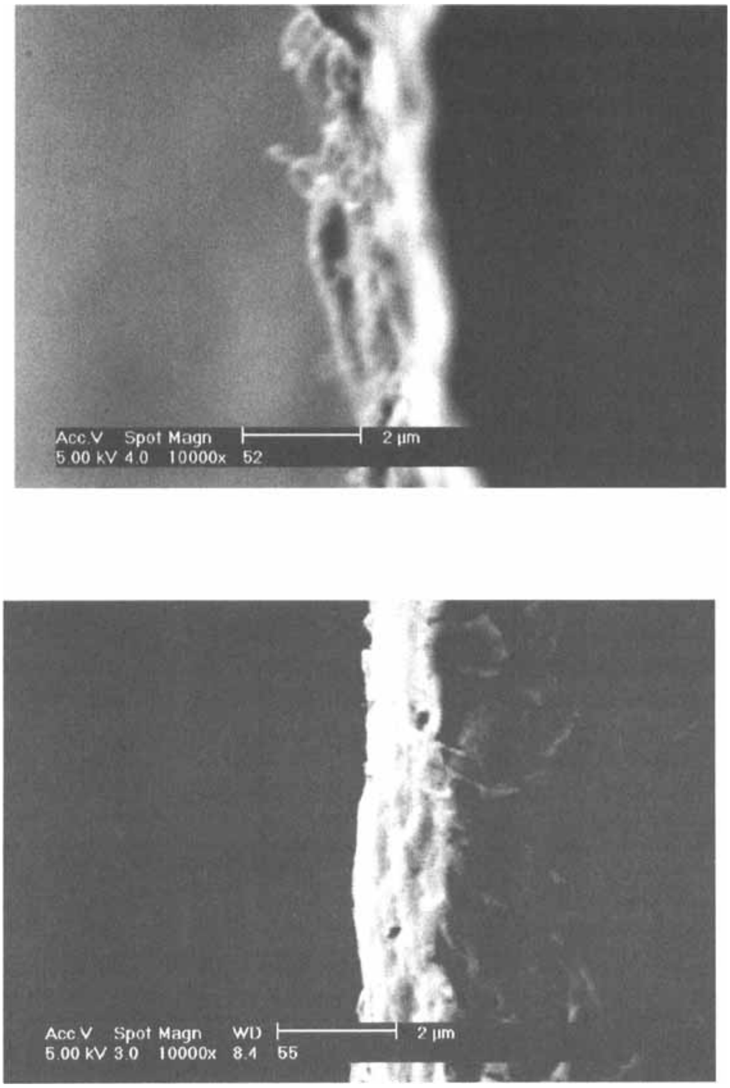

FIGURE 9 Cross-sectional SEM images of the delaminated epoxy resins from the epoxy/GMA-g-PTFE composites with the argon plasma pretreatment time of (a) 30 s and (b) 90 s for the PTFE film, followed by 2 h of UV-induced graft copolymerization with GMA.

the surface of each epoxy resin is covered with a rugged PTFE layer. The thicknesses of the adhered PTFE layer (light-colored area) are about 1 – 2 μm, which are much larger than those on the epoxy resin surface delaminated from the epoxy/PTFE composites involving PTFE film with plasma treatment alone. The thickness of the PTFE layer adhered to the delaminated epoxy surface from the latter composite is only in the order of the probing depth of the XPS technique, as suggested by the XPS wide scan spectrum of Figure 6(c).

3.4. Reliability and Moisture Sorption of the Fluorinated Epoxy

Table I shows the extents of moisture sorption, under the Level 1 hydrothermal test conditions, of the delaminated epoxy resin sheets with different thicknesses of surface-adhered PTFE layer. It is obvious that the extents of moisture sorption of epoxy resin samples from all the epoxy/PTFE composites with only one side cured against the 30 s, 60 s and 90 s plasma-treated PTFE surfaces are similar to each other and are in the order of 0.7 – 0.9 wt.%. Under the same test conditions, the average extent of moisture sorption of the as-cured epoxy resin is about 1.5 wt.%. The relatively high extent of moisture sorption arises from the presence of hydrophilic hydroxyl groups on the backbone of the cured epoxy resin. The extents of moisture sorption are much reduced when both sides of epoxy resin are cured against the surface-modified PTFE substrates. The extents of moisture sorption of the

TABLE I The extents of moisture sorption of various fluorinated epoxy resin samples under level 1 hydrothermal test conditions*

	*Extent of moisture sorption (wt.%)***			
Plasma pretreatment time	*From epoxy/PTFE composite*		*From epoxy/GMA-g-PTFE composite*	
of the PTFE film surface (s)	*One side fluorinated*	*Both sides fluorinated*	*One side fluorinated*	*Both sides fluorinated*
30	0.8	0.7	0.9	0.4
60	0.8	0.6	0.8	0.3
90	0.8	0.5	0.7	0.4

* Exposure to 85°C and 85% relative humidity for 168 h.

** The extent of moisture sorption for the pristine epoxy resin cured in the air is about 1.5 wt.%.

epoxy resin samples fluorinated on both sides *via* curing between two GMA-g-PTFE surfaces are in the order of 0.3–0.4 wt.%. As the moisture can permeate from the both sides of the epoxy resin, fluorination of only one side of the epoxy resin sample has a limited effect on the moisture sorption. Through comparison of the moisture sorption results of the epoxy resin samples delaminated from the PTFE surfaces modified by plasma treatment alone with those delaminated from the GMA-g-PTFE surfaces, it is also apparent that a thicker fluoropolymer layer is more effective in reducing moisture sorption.

The reliability and stability of the fluorinated epoxy resin surfaces were also evaluated by measuring the surface $[F]/[C]$ ratios and water contact angles of the fluorinated epoxy resin surfaces after the Level 1 hydrothermal test. The results reveal no significant difference in surface composition among the epoxy resin surfaces before and after the L1 test, suggesting the absence of any surface reconstruction. For the delaminated epoxy resin from the epoxy/PTFE composites involving PTFE film with plasma treatment alone, the PTFE chains must have been anchored or entrapped within the epoxy resin, which gives rise to the good stability in surface composition and hydrophobicity. The retention of hydrophobic PTFE chains on the epoxy resin surface is favored, as the configuration helps to minimize the free energy of the surface. The anchoring or entrapment of the PTFE chains on the epoxy resin from thermal curing on the pristine and plasma-treated PTFE surface is mainly a physical phenomenon arising from the inter-diffusion of the molecular chains. However, for the fluorinated epoxy resin surface from the epoxy/GMA-g-PTFE composites, the PTFE molecules are covalently tethered on the epoxy resin surface through the crosslinked GMA polymer network at the interphase. The chemical interaction and crosslinking at the interphase will contribute further to the stability and reliability of the adhered PTFE layer on the epoxy resin surface.

4. CONCLUSIONS

A novel method for fluorinating epoxy resin surfaces, *via* reverse grafting of the epoxides on fluorinated surfaces, to reduce moisture sorption was demonstrated. The method involved thermal curing of the epoxy resin on either argon plasma-treated PTFE films or argon plasma-pretreated and GMA graft-copolymerized PTFE (GMA-g-PTFE) films. Mechanical delamination resulted in the presence of a strongly-adhered, thin fluoropolymer layer on the epoxy surface. For the epoxy resin surfaces delaminated from the epoxy/GMA-g-PTFE composites, the fractured fluoropolymer on the epoxy resin surface gave rise to water contact angles as high as 140°. The strong and reliable adhesion of the epoxy/GMA-g-PTFE composite and the delaminated fluoropolymer on the epoxy resin surface arise from the synergistic effect of the interaction of the epoxide groups of the grafted GMA chains with the amine groups of the hardener of the epoxy resin during the thermal curing of the latter to form a highly crosslinked network at the interphase, as well as the fact that the GMA chains are covalently tethered on the PTFE surface.

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