number $\tau_s^{(i)}$ of graphs isomorphic to that given graph is defined by the relation:

$$\tau_s^{(i)} = \frac{\prod_{i=1}^{n} s_{A_i}! \prod_{j=1}^{m} s_{B_j}!}{|G_i|} \qquad (35)$$

Proof. Let $G_i = (Y,F)$ be a tree representative of an isomer, whose vertex set Y is partitioned in colors and types by Y_{A_i} ($1 \leq i \leq n$) and Y_{B_j} ($1 \leq j \leq m$) with $|Y_{A_i}| = s_{A_i}$ and $|Y_{B_j}| = s_{B_j}$.

On the other hand, let X be a set of labels, itself partitioned in colors and types by X_{A_i} ($1 \leq i \leq n$) and X_{B_j} ($1 \leq j \leq m$), with $|X_{A_i}| = s_{A_i}$ and $|X_{B_j}| = s_{B_j}$. We want to count the labeled trees on X isomorphic to G_i.

All these graphs can be obtained from the bijections $\sigma X \rightarrow Y$ such that $[\forall x \in X_{A_i} (X_{B_j}) \sigma(x) \in Y_{A_i} (Y_{B_j})]$ by putting in G_i the vertex x in the place of $\sigma(x)$. We note $G_i(\sigma)$, the tree associated to σ in that way. The set S of these bijections has cardinality:

$$\mathcal{S} = \prod_{i=1}^{n} s_{A_i}! \prod_{j=1}^{m} s_{B_j}!$$

However, two of these bijections can define the same tree. We must study the equivalence relation R in S defined by $\sigma R \sigma'$ if and only if $G_i(\sigma) = G_i(\sigma')$. We prove the next property of relation R, $\sigma R \sigma'$, if and only if $\varphi = \sigma' \cdot \sigma^{-1}$ is an automorphism of G_i. First we suppost that $\sigma R \sigma'$ is true. Clearly the function $\varphi = \sigma' \cdot \sigma^{-1}$ is a bijection from G_i to G_i, and we know that $G_i(\sigma) = G_i(\sigma')$ and $\sigma' = \varphi\sigma$. Then, from the property for every x,x' belonging to X, $[\sigma(x),\sigma(x')] \in F$ if and only if $[\sigma'(x),\sigma'(x')] \in F$; it follows that for every y,y' belonging to Y, $[y,y'] \in F$ if and only if $[\varphi(y),\varphi(y')] \in F$. This means that φ preserves adjacency.

Finally φ preserves colors because if $y \in Y_{A_i}$ then $\sigma^{-1}(y) \in X_{A_i}$ and $\varphi(y) \in Y_{A_i}$ and if $y \in Y_{B_j}$ then $\sigma^{-1}(y) \in X_{B_j}$ and $\varphi(y) \in Y_{B_j}$. So that φ is indeed an automorphism of G_i.

Conversely, it is obvious that for any automorphism φ of G_i and any $\sigma \in S$, $\sigma' = \varphi\sigma$ is an element of S which verifies $\sigma R \sigma'$. To obtain $\tau^{(i)}$, we must then divide the number of bijections belonging to S by the number of elements of each equivalence class, namely the cardinality of the automorphism group of G_i.

$$\tau_s^{(i)} = \mathcal{S}/|G_i|$$

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Surface Modification of Fluorocarbon Polymers by Radiation-Induced Grafting for Adhesive Bonding

Shinzo Yamakawa

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319-11, Japan.

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ABSTRACT: The mutual irradiation of polymers in methyl acrylate (MA) vapor followed by hydrolysis treatment is a surface grafting technique which had been developed originally for surface modification of polyethylene (PE). The technique now has been successfully applied to surface modification of two radiation-degradative fluorocarbon polymers, poly(tetrafluoroethylene) (PTFE) and poly(chlorotrifluoroethylene) (PCTFE). The adhesive bond strengths reach a maximum value when the grafted surface is covered with an outer homopolymer layer consisting only of the monomer component. Although this relationship between bond strength and homopolymer surface coincides with that suggested in PE grafts, it is shown more clearly by ESCA analysis of the modified fluoropolymer surfaces. The thickness of the homopolymer layer passes through a maximum and then decreases with irradiation time or dose. This decrease may reflect the radiation degradation of fluoropolymer chains. The peel strengths of grafted PTFE sheets are much higher than those of sodium (Na)-etched PTFE sheets. This difference in bond improvement is discussed in terms of mechanical strength of the modified surface layers.

In order to obtain strong adhesive joints of inert fluorocarbon polymers, the surfaces must be modified before bonding. The most extensively investigated pretreatments involve Na-etched treatments, using Na–ammonia[1-3] and Na–naphthalene–tetrahydrofuran[4-7] complex solutions, and CASING[8,9] or glow discharge treatments.[10-13] Though work has been done on the adhesive properties of radiation-grafted PTFE,[14,15] no detailed studies have been published on the relationship between the bond strength and the surface structure. Mutual irradiation of PE in MA vapor and subsequent hydrolysis treatment have been found to yield a surface graft having high adhesive bondability to epoxy adhesives.[16,17] Since the radiation grafting of radiation-degradative fluorocarbon polymers such as PTFE and PCTFE requires a low radiation dose to prevent the degradation, it is interesting that this surface grafting

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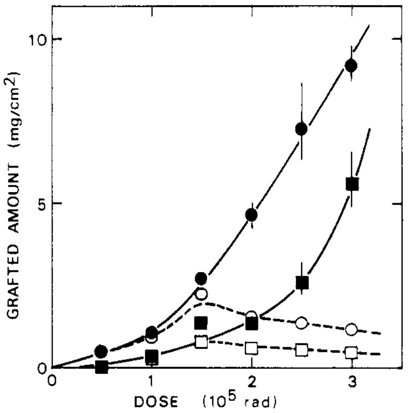


Figure 1. Amount of grafted monomer per surface area of the original polymer sheet (mg/cm^2) plotted against dose, irradiated at a dose of 5 × 10^4 rad/h: (●) PTFE; (○) PTFE, saponified; (■) PCTFE; (□) PCTFE, saponified.

technique,[16-20] developed originally for the surface pretreatment of radiation-cross-linkable PE, is also effective for the pretreatment of fluorocarbon polymers, which are especially difficult polymers to bond with conventional adhesives. The purpose of this paper is to characterize the surface structures and to relate them to the adhesive bond strengths of the MA-grafted PTFE and PCTFE. These results may also be informative for the preparation of synthetic hydrogels onto inert polymer surfaces for biomedical applications.[21,22]

Experimental Section

Heat-press-formed PTFE and PCTFE sheets (2.0 and 3.0 mm thick) and a skived PTFE sheet (1.5 mm thick), supplied by Nippon Valqua Industries Ltd., were cut to a rectangular shape measuring 25 mm wide and 115 mm long and then rinsed with acetone before use.

The vapor-phase mutual grafting of MA was carried out as described previously.[17] The PTFE and PCTFE sheets were irradiated in the saturated vapor pressure of MA at 15 °C. This dose rate from a ^{60}Co source was 5.0 × 10^4 rad/h. To remove occluded PMA homopolymer, the grafted sheets were extracted with acetone in a Soxhlet extractor until there was no further decrease in weight. The grafted sheets were partially saponified or hydrolyzed with a 1 N KOH solution in methanol at 50 °C for 4 h, rinsed with water, and then treated at 56 °C consecutively with a 1 N HCl solution in acetone–water (1:1, v/v), water, acetone–water (1:1), and acetone.

To characterize the grafted surface layers, four techniques were used: (1) attenuated total reflection (ATR) infrared spectroscopy,[16] (2) interference and polarizing microscopy,[17] (3) scanning electron microscopy (SEM),[17] and (4) X-ray photoelectron spectroscopy (ESCA).[20] ESCA spectra were taken with an AEI ES-200 electron spectrometer, using Al Kα radiation (1486.6 eV). The X-ray power supply was run at 12 kV and 20 mA. Pressure within the spectrometer during the scans was approximately 10^{-7} torr.

The two saponified grafts were bonded with an aminopolyamide-modified epoxy adhesive (epoxy:polyamide = 10:9, Cemedine No. 1500, Cemedine Co. Ltd.) to prepare a T-peel test specimen consisting of graft (2.0 mm)–adhesive (0.1 mm)–graft (2.0 mm) and a lap shear test specimen consisting of graft (2.0 or 3.0 mm)–adhesive (0.05 mm)–graft (2.0 or 3.0 mm). The assembly was lightly weighted (0.15 kg/cm^2), and the adhesive was allowed to cure for 4 h at 60 °C. The T-peel strength at 23 °C was measured according to ASTM D1876-61T. The cross-head speed was 100 mm/min. The lap shear strength at 23 °C was measured according to ASTM D1002-64T. The cross-head speed was 2 mm/min, and the overlap length was 12.7 mm.

Results and Discussion

Surface Structure of PTFE Grafts. Figure 1 shows the weight increase or the amount of grafted MA per surface area of polymer sheet plotted against dose. Figures 2 and 3 show the ATR spectra and the optical micrographs of a series of unsaponified PTFE grafts. From Figure 3, it is apparent that the grafted layer is confined to the surface region. The amount of grafted MA before saponification increases with irradiation (Figure 1). Corresponding to this increase in grafted MA, which is confined to the surface region, the ATR spectra of unsaponified grafts (Figure 2) show a rapid increase in surface graft composition with irradiation. The PMA bands (e.g., at 820 and 1720 cm^{-1}) increase with irradiation, and the PTFE bands (e.g., at 1207 cm^{-1}) decrease. Further, the grafts, irradiated to a dose of more than 1.5 × 10^5 rad (e.g., spectrum C in Figure 2), give the same ATR spectrum as that[16] of PMA. This result indicates that the grafted surface either consists of 100% MA or is covered with PMA homopolymer as a result of the rapidly increasing surface graft composition. In the interference micrographs of the grafts irradiated to a dose of more than 1.5 × 10^5 rad (Figure 3), it is noted that the interference fringe (i.e., graft composition) changes sharply in the direction of the surface from the inside and then levels off. The leveling-off point in the interference micrographs (D) coincides approximately with the boundary between optically isotropic (dark) and anisotropic (bright) layers in the polarizing micrographs (B, C). Apparently, the outer leveled-off layer corresponds to the isotropic layer, and the inner composition-gradient layer corresponds to the anisotropic layer.

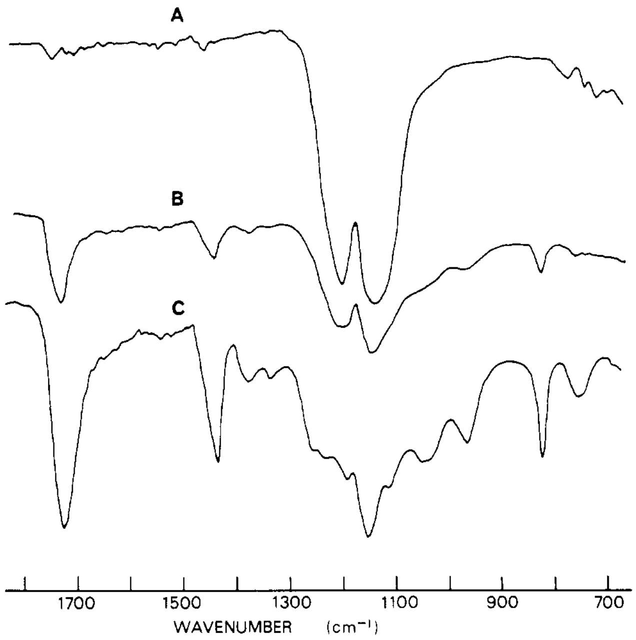
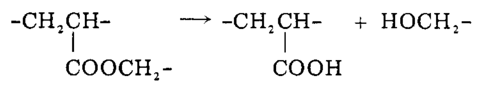


Figure 2. Typical ATR infrared spectra of unsaponified PTFE grafts: (A) unmodified PTFE; (B) irradiated to 0.5 × 10^5 rad; (C) irradiated to 1.5 × 10^5 rad.

In PE–MA grafts,[17] hydrolysis or saponification treatment gives a greater weight loss than that due to the change from OCH_3 to OH. This additional decrease has been suggested to result mainly from the partial removal of PMA chains in the isotropic layer, whose removal is due to cleavage of ester side chain links by saponification:



$$\underset{\displaystyle COOCH_2-}{-CH_2\overset{}{C}H-} \longrightarrow \underset{\displaystyle COOH}{-CH_2CH-} + HOCH_2-$$

In PTFE–MA grafts, the treatment gives a more significant decrease in the amount of grafted MA (Figure 1). Figure 4 shows the interference micrographs of a series of saponified PTFE grafts. Figure 5 summarizes the isotropic and anisotropic layer thicknesses (T_i and T_a) before and after

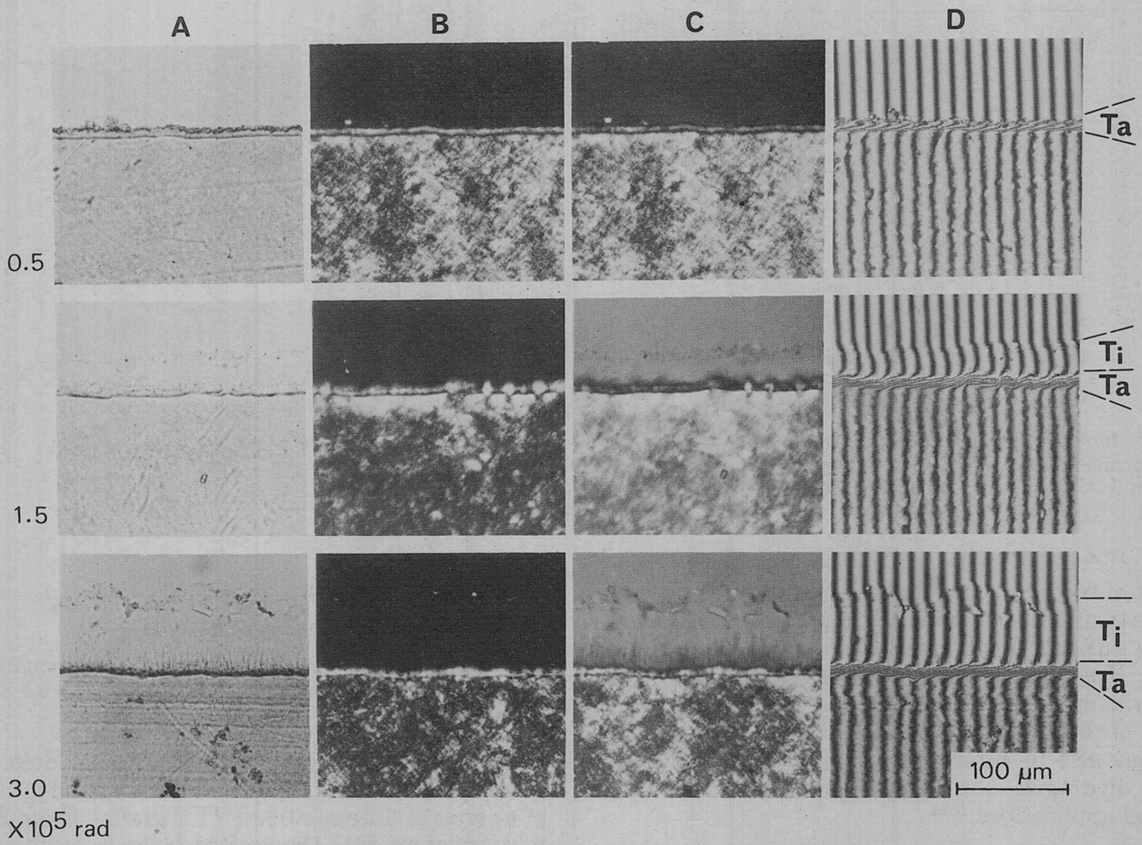


Figure 3. Optical micrographs of a section of unsaponified PTFE grafts. An identical area in a cross section of the grafts was photographed under four different conditions: (A) under an unpolarized white light; (B) between crossed polarizers at a 45° angle between the original surface plane and the vibration planes of crossed polarizers; (C) at an 85° angle between polarizer and analyzer and at 0 or 90° between the original surface plane and the vibration planes; and (D) under an interference microscope.

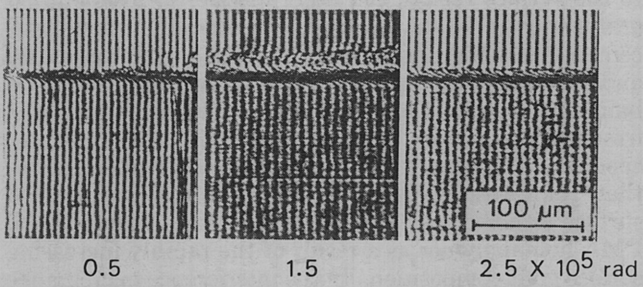


Figure 4. Interference micrographs of a section of saponified PTFE grafts.

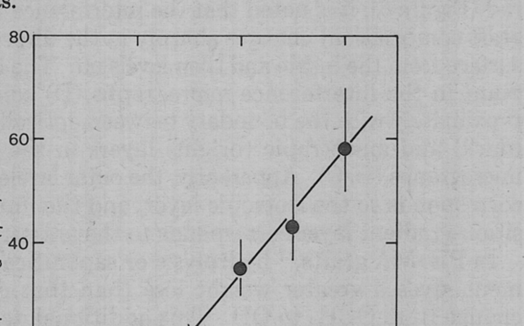


Figure 5. Isotropic and anisotropic layer thicknesses (T_i or T_a) vs. dose of unsaponified and saponified PTFE grafts: (●) T_i; (○) T_i, saponified; (■) T_a; (□) T_a, saponified.

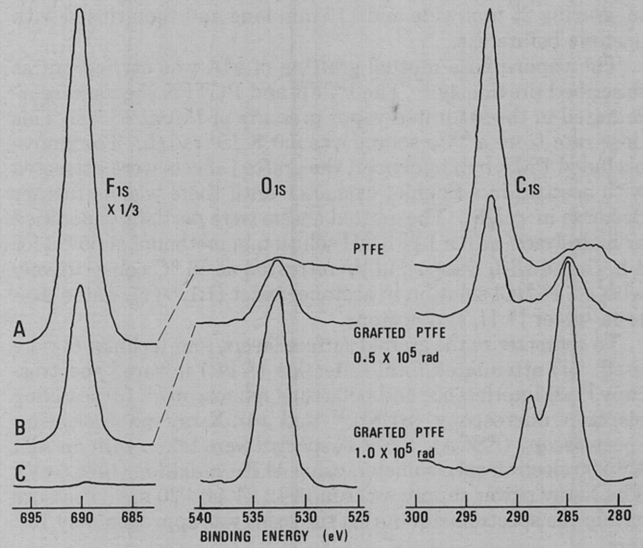


Figure 6. ESCA spectra of saponified PTFE grafts.

saponification vs. dose of PTFE grafts. From Figure 5, it is seen that the treatment gives a significant decrease in T_i, whereas it gives no change in T_a.

Figure 6 shows the F_{1s}, O_{1s}, and C_{1s} ESCA spectra of saponified PTFE grafts. Untreated PTFE gives a sharp F_{1s} peak[23] with a binding energy of 689.6–689.8 eV and a sharp C_{1s} peak of $-CF_2-$[23] with a binding energy of 292.4–292.6 eV. These binding energies are in good agreement with the values reported by other workers.[2,13,23] On the other hand, PMA homopolymer gives two C_{1s} peaks at 284.8–288.6 eV and two O_{1s} peaks at 532.4–533.9 eV,[20] whose values are also in good agreement with those reported by Clark et al.[24] The O_{1s} peaks are observed as a wide unresolved single peak with a shoulder in the case of poly(acrylic acid).[24] In saponified PTFE grafts, the F_{1s}

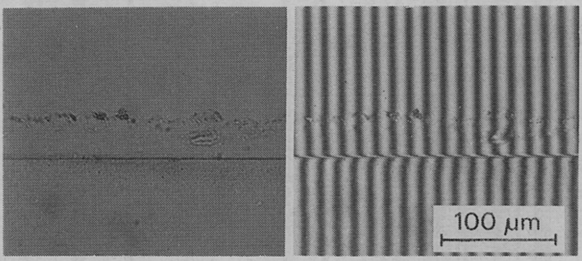


Figure 7. Typical surface structure of unsaponified PCTFE grafts. An identical area in a cross section of a graft (irradiated to 3.0 × 10^5 rad) was photographed under unpolarized white light (left) and under an interference microscope (right).

peak and the C_{1s} peaks of PTFE decrease with irradiation, and the O_{1s} peak and the C_{1s} peaks of hydrolyzed PMA increase with irradiation. The ESCA spectra from the saponified grafts, irradiated to a dose of more than 1.0 × 10^5 rad (e.g., spectrum C), have no F_{1s} and C_{1s} peaks of PTFE and coincide with those[20] from PMA and partially hydrolyzed PMA homopolymers. Abrasion of the grafted surfaces reformed the F_{1s} peak. These results indicate that the grafted surface after saponification reaches 100% monomer at 1.0 × 10^5 rad. The attainment of 100% monomer according to ESCA indicates that the grafted surface is covered with a homopolymer layer (consisting only of the monomer component) at least as thick as the ESCA sampling depth, which is less than 100 Å.[25] From comparison of the T_i value (Figure 5) and the ESCA spectrum (Figure 6) of saponified PTFE grafts, it can be seen that the thickness of the homopolymer layer coincides approximately with the thickness (T_i) of the isotropic layer in polarizing micrographs or the leveled-off layer in interference micrographs. In PTFE grafts, accordingly, it is concluded that the isotropic or leveled-off layer consists of PMA homopolymer and that the anisotropic or composition-gradient layer consists mainly of graft copolymers of PTFE and MA.

The saponified grafts were extracted with acetone and acetone–water (1:1) solution until there was no further decrease in weight. As suggested in the PE grafts,[17] the high stability of the residual homopolymer to solvent extraction may indicate that this homopolymer is not only cross-linked but is also linked by chemical bonds to the PTFE and grafted PMA chains in the contiguous inner copolymer layer.

Most surface grafts of PTFE have been prepared by mutual irradiation of PTFE sheets in liquid monomer or monomer solution (liquid-phase mutual grafting).[14,15,26–32] Detailed investigations of effects of monomer diffusion on mutual grafting are limited to the liquid-phase mutual grafting of styrene.[28–30] The results[28–30] from the PTFE–styrene grafting system indicate that the grafting zone proceeds gradually from the surface to the inner region with irradiation time. The surface graft composition, determined by interferometry, remained less than 60 wt %.[30] On the other hand, in the vapor-phase mutual grafting of MA onto PTFE, the inner copolymer or anisotropic layer thickness (T_a, Figure 5) and the composition distribution (Figures 3 and 4) remain unchanged while the homopolymer layer is forming on the inner copolymer layer. This result indicates that the grafting or monomer consumption zone moves outward from the original surface rather than being confined to the surface region. This difference in growth processes of the grafting layers of both PTFE–MA and PTFE–styrene systems can be explained in terms of a difference in the grafting rate (R_p) and its change with time ($\partial R_p/\partial t$). The growth process of the grafting layers of PE–MA systems has already been explained in terms of R_p and $\partial R_p/\partial t$.[19]

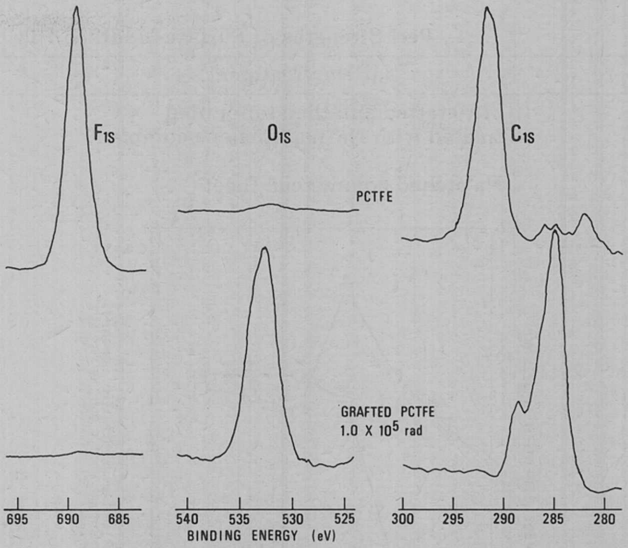


Figure 8. ESCA spectra of saponified PCTFE grafts.

Surface Structure of PCTFE Grafts. Figure 7 shows a typical surface structure of unsaponified PCTFE grafts. Note that the thickness of the inner copolymer layer is much thinner (several micrometers) than that of PTFE grafts (10–14 μm). Microscopic observations showed that saponification treatment removed almost all of the homopolymer or isotropic layer (e.g., compare the closed and open circles of Figure 10). However, the ESCA spectra of the saponified grafts show that the grafted surfaces, irradiated to a dose of more than 1.0 × 10^5 rad, are still covered with a homopolymer layer (consisting only of the MA component) at least as thick as the ESCA sampling depth (Figure 8). The coverage is evident from complete disappearance of the F_{1s} and C_{1s} peaks of PCTFE and from good agreement with the ESCA spectrum from the PMA homopolymer.

Radiation Degradation of PTFE and PCTFE during Grafting. In PTFE grafts, the T_i value after saponification passes through a maximum and then decreases with irradiation, whereas the T_i value before saponification increases monotonously (Figure 5). This decrease in T_i corresponds to the decrease in the amount of grafted MA (Figure 1). The PCTFE grafts give a similar decrease in grafted MA with irradiation. In PE grafts,[17] on the other hand, the amount of grafted MA and the T_i value after saponification gradually level off but do not decrease with irradiation. This decrease in PTFE and PCTFE grafts may be due to the radiation degradation of fluoropolymer chains in the graft copolymer layer, whose degradation occurs concurrently with the grafting reactions.

It is well known that PTFE and PCTFE are typical radiation-degradative polymers, whereas PE is a radiation-cross-linkable polymer.[26,27] Irradiation of PTFE and PCTFE in air causes a rapid deterioration of the mechanical properties due to chain scission. The chain scission can also occur by irradiation under vacuum and subsequent exposure to air,[33] an irradiation condition similar to that in grafting. The maximum values in T_i and grafted MA occur at 1.5 × 10^5 rad (Figures 1 and 5). It should be noted that the dose range is much lower than the doses at which the mechanical properties appreciably deteriorate.[26,27]

Relationship between Bond Strength and Surface Structure. In PE grafts,[17] it has been suggested that the grafted surface yields a maximum bond strength at 100% grafted monomer, i.e., when formation of the MA surface

Table I
Peel Strengths of Surface-Modified PTFE Sheets Bonded with an Epoxy Adhesive

surface treatment	PTFE sheet	peel strength, kg/25 mm
MA-grafted and then saponified	heat press formed	>50
treated with Na-naphthalene complex	heat press formed, 2.0-mm thick	0.5-1.2
	skived, 1.5-mm thick	4.2-5.5
Na-etched commercial sheet	skived, 1.5-mm thick	5.0-7.0

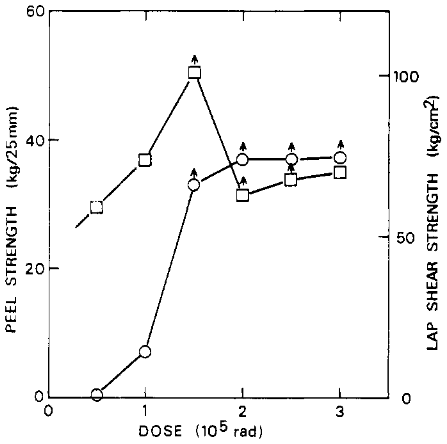


Figure 9. Peel strength and lap shear strength vs. dose of PTFE grafts corresponding to Figure 5: (○) peel strength; (□) lap shear strength; and (↑) necking or failure of the PTFE adherend.

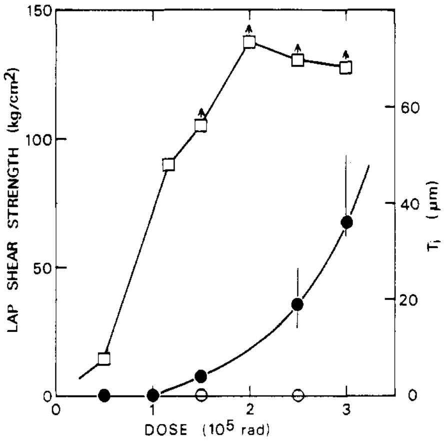


Figure 10. Lap shear strength and isotropic layer thickness (T_i) vs. dose of PCTFE grafts: (□) lap shear strength; (●) T_i, unsaponified; (○) T_i, saponified; and (↑) necking of the PCTFE adherend.

layer is complete. This relationship between bond strength and surface structure is shown more clearly in PTFE and PCTFE grafts by the relationship between bond strength and ESCA spectrum. Figure 9 summarizes the peel and lap shear strengths vs. dose of saponified PTFE grafts corresponding to Figure 6. By comparing the peel strength (Figure 9), the T_i value (Figure 5), and the ESCA spectrum (Figure 6), it can be seen that the peel strength increases abruptly with formation of the homopolymer layer (at 1.0 × 10^5 rad) and reaches adherend failure. The formation of the homopolymer layer is evident from the complete disappearance of the F_{1s} and C_{1s} peaks of PTFE. The lap shear strength shows a similar increase, although it is not sensitive to surface changes.

Figure 10 shows lap shear strength and T_i values vs. dose for saponified PCTFE grafts. Since the PCTFE sheet was rigid, no meaningful value of peel strength was obtained. Although the optical micrographs show no detectable isotropic or homopolymer layers, the ESCA spectra show the formation, at doses of more than 1.0 × 10^5 rad, of a surface homopolymer layer whose formation is evident from complete disappearance of the F_{1s} and C_{1s} peaks of PCTFE (Figure 8). Therefore, it is concluded that the adhesive bond strength in PCTFE grafts also (Figure 10) increases abruptly with the formation of homopolymer layer.

According to the above relationship between bond strength and surface structure, the attainment of maximum bond strength requires the presence of a homopolymer layer on the surface. This requirement of a surface homopolymer for maximum bond strength cannot be explained in terms of the weak boundary layer theory[34] and the wettability criteria for maximum adhesion.[35] The water contact angle decreased with grafting and became constant at lower stages of grafting than the stage at which the homopolymer formation occurs. The homopolymer surface may reflect an optimum surface state for penetration of the epoxy adhesive into the modified surface layer. An adhesion mechanism, involving penetration of the epoxy adhesive into the homopolymer layer, has been proposed.[36,37]

Comparison with Sodium-Etched PTFE Joints. Among many surface pretreatments proposed, the most extensively used techniques[6,7] are Na-etched treatments using Na–ammonia and Na–naphthalene–tetrahydrofuran solutions. Table I gives a comparison in peel strength between MA-grafted and Na-etched PTFE joints, bonded with an epoxy adhesive. The MA-grafted joints yield much higher peel strengths (more than 50 kg/25 mm) than the Na-etched joints (less than 7 kg/25 mm). In the latter joints, skived sheets give higher peel strengths than heat-pressed-formed sheets. This is probably due to a greater surface area caused by the rough, microporous nature of the skived sheets.

In the peel test of Na-etched joints, failure occurred at the interface between the outer modified layer and the inner unmodified PTFE bulk and partly in the modified layer. The locus of failure was apparent from a difference in color between the modified layer (brown) and unmodified PTFE bulk (white). Therefore, the limited peel strength of Na-etched PTFE joints derives from the low mechanical strength of the modified layer itself and from the low interfacial force between modified and unmodified layers. In this case, a prime factor limiting the adhesive bond strength is the mechanical strength of the modified layer but not the surface-chemical properties at the modified surface–adhesive interface. The unstable natures of the modified layer have been shown by other workers.[3] The modified layer consists of a rough, porous hydrocarbon containing unsaturation and carbonyl and carboxyl groups. The layer can be removed by abrasion, heat aging, and artificial weathering.

On the other hand, the MA-graft joints yielded adherend failure, corresponding to the extremely high peel strength. The high peel strength reflects a high mechanical strength of the surface homopolymer layer itself and a high interfacial force between the homopolymer layer and the unmodified PTFE bulk. The high interfacial force results probably from chemical linkages through the graft copolymer layer between the homopolymer layer and the unmodified PTFE bulk. The stabilized homopolymer layer in the PE grafts is stable to abrasion, heat aging, and artificial weathering.[18] The homopolymer layer in the PTFE grafts showed a high stability similar to that in the PE grafts.

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Notes

A New Technique for Determining Polymer–Polymer Miscibility

S. ANAVI and M. T. SHAW*

Department of Chemical Engineering and Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06268

J. F. JOHNSON

Department of Chemistry and Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06268. *Received June 25, 1979*

Two-component polymer blends have long been attracting considerable interest both because of their commercial utility and their scientific importance. From either viewpoint, the phase behavior of these systems is of direct significance, considering that partial or complete solubility usually gives rise to improved properties,[1-6] and systems exhibiting high solubility are likely to provide valuable clues about the interactions between unlike macromolecules. Therefore, it is interesting to know to what extent two polymers are mutually soluble; that is, at what composition does phase separation occur. Upon correlating this with the structure, two-component systems with specific properties can be designed with greater facility, and more data will be available for testing and improving the theory[7,8] of phase behavior for polymer–polymer systems.

There are several techniques for determining the presence of two phases (e.g., glass transition temperature, microscopy, scattering methods, ternary solution methods)[7-9] but few methods for determining the extent of the miscibility of one polymer in another, particularly when the degree of miscibility is very low and the molecular weights are high. The technique we present here involves a novel method of measuring directly the solubility of one polymer in another and is applicable for systems exhibiting low solubility and high viscosity. Basically, one polymer is added to another until two phases are detected by light scattering; in a sense it is a melt titration.

The first polymer, in the melt form, is fluxed on a two-roll mill, and the second polymer is gradually added from a buret in a volatile solvent. As the milling proceeds the solvent evaporates and the polymers mix thoroughly. At certain intervals during the titration, small samples (about 1% of the total mixture) are taken from the mill and placed on a ferrotype plate. The mill rolls, running at 30 rpm, thoroughly disperse the added component in seconds, but several minutes of mixing are allowed before the sample is removed by scraping with a microspatula across the rolls. This procedure completely removes the chance of inhomogeneous sampling, as was demonstrated by replication trials.

After the air bubbles were removed, the samples are pressed under a glass plate to a constant thickness of 125 μm. These thin circular films are then observed for scattered light at room temperature to detect the presence of two phases. A "reflection" meter is used (Photovolt 670 color and gloss meter), where the search unit is placed on the glass above the film. The light coming perpendicularly

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