

Functionalization and Metallization of Fluoropolymer Surfaces Through Reduction^{1,2}

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SYNOPSIS

Fluoropolymer films, such as Teflon[™]-TFE [poly(tetrafluoroethylene)], Teflon[™]-FEP [copolymer of tetrafluoroethylene and hexafluoropropylene], Teflon[™]-PFA [copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether)], and PCTFE [poly(chlorotrifluoroethylene)], are reduced by the mild reducing agent benzoin dianion/DMSO, while Teflon[™]-AF [copolymer of tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxole] is unreactive. The reduction makes the films adherable toward epoxy resins, the adhesive strength decreasing in the order PCTFE > PFA ≥ FEP > PTFE. Surprisingly, Teflon[™]-AF films are totally inert except when the TFE content is high, and in these cases, the adhesive strength of Teflon[™]-AF is close to that of PTFE. The surfaces of PTFE, FEP and PFA films are further modified by first treating these films with the benzoin dianion/DMSO reagent and then with an excess of sodium salts of mercaptans. Reactive PTFE films that are light colored with a metallic luster are formed rather than the dark, metallic color typical of PTFE surface reduction without mercaptan treatment. These films have poor adhesion toward epoxy resins but good adhesion toward gold applied by sputtering. FEP and PFA films behaved similarly. These results are attributed to the incorporation of sulfur onto the reduced surface. Unreduced fluoropolymer films reacted with only sodium mercaptan fail to show C—S bond incorporation. This newly developed method can be used to selectively metallize the fluoropolymer film surface with gold layers and affords very high conductivity of the metallized regions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Fluoropolymers are distinguished by chemical inertness, low surface energy, high temperature stability, and low dielectric constant.^{3,4} Nevertheless, some applications require good adhesion to fluoropolymers while retaining desirable bulk properties such as dielectric constant.⁵ We have studied mild chemical reagents that promote adhesion of metals or other polymers to fluoropolymers while leaving the bulk unchanged.

Reaction of polytetrafluoroethylene (PTFE) with strong reducing agents, such as alkali metals, is

widely used to promote adhesion to other materials, but these harsh conditions are poorly controlled.⁶ Recent reports⁷⁻¹⁰ describe use of potassium *t*-butoxide (*t*-BuOK)/benzoin/dimethyl sulfoxide (DMSO) as a mild reducing agent for fluoropolymer reduction and also the use of sodium thiophenolate (PhSNa) for C—F bond cleavage in small molecules,¹¹ such as perfluorodecalin.^{12,13} We now report a systematic study of the reaction of various fluoropolymer films with the mild reducing agent *t*-BuOK/benzoin/DMSO, comparing the reactivity of various fluoropolymers and showing the utility of the mild reducing agents for functionalization of fluoropolymer surfaces for the selective enhancement of adhesion to other materials. We also demonstrate a new process for the direct metallization of fluoropolymer surfaces to give a durable, highly conductive metal layer on fluoropolymer substrates.

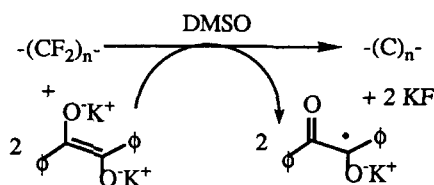
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RESULTS AND DISCUSSION

Strong reducing agents, such as alkali metals or sodium naphthalide, are well known to react readily with fluoropolymers to give dark, carbonaceous fluoropolymer surfaces, but the reactions are difficult to control and the reagents are difficult to handle and typically pyrophoric. These reactions presumably occur by electron-transfer mechanisms: electrons migrate into the $(-\text{CF}_2-)_n$ backbone inducing ionization of fluoride from the carbon-fluorine bonds. After initial electron transfer, the process proceeds rapidly, eventually giving a graphitic or polyene-like surface. It was proposed that the reduced fluoropolymer surfaces are unsaturated frameworks of sp^2 or sp hybridized carbon atoms with some carbon atoms bonded to small amounts of hydrogen or oxygen arising from solvent, the reductants themselves, or the atmosphere during workup.⁷ The net reaction is shown in Scheme 1. Costello and McCarthy have speculated on the structure of the reduced polymer.⁷⁻⁹ These reduced surfaces have higher surface energy than the virgin fluoropolymer surfaces and, therefore, should be more reactive toward other chemical reagents and adhere better to other materials.

Scope of the Fluoropolymer Reduction Reaction

Nearly all previous studies of fluoropolymer reduction reactions have been limited to PTFE, despite the fact that other fluoropolymers are widely used in many applications requiring adhesion to other materials. We have studied the reduction of commercially available fluoropolymer films, including Teflon[™]-TFE (PTFE), Teflon[™]-FEP (TFE/hexafluoropropene copolymer), Teflon[™]-PFA¹⁴ (TFE/perfluoropropyl vinyl ether copolymer), Teflon[™]-AF¹⁴⁻¹⁶ (TFE/perfluoro-2,2-dimethyl-1,3-dioxole copolymer), and PCTFE [poly(chlorotrifluoroethylene)]. Clean, dry strips of these films were reacted with *t*-BuOK and benzoin (in 25–30 : 1 mol ratio) in DMSO under inert atmosphere at ambient temperature at 60°C for fixed periods of time. The reduced fluoropolymer films were washed thoroughly



Scheme 1

with water and THF, then dried before characterization, all under an inert atmosphere. In general, the reduced PTFE films show a shiny, metallic luster after drying, while the other films are dark with little or no metallic luster. PTFE, FEP, PFA, and PCTFE are all readily reduced by the benzoin dianion in DMSO, while, surprisingly, Teflon[™]-AF is unreactive. In our hands, Teflon[™]-AF is unreactive even toward much stronger reducing reagents such as sodium naphthalene and sodium benzophenone radical anions, as gauged by visual appearance and contact angle studies.

Fluoropolymer/Epoxy Resin Adhesion

Fluoropolymer adhesion to epoxy resins reflects the extent of fluoropolymer surface reduction. The epoxy resin is applied to the fluoropolymer surface, cured, and then the adhesion of the laminate is measured by peel strength. With the exception of Teflon[™]-AF, all the fluoropolymer substrates reacted with benzoin dianion/DMSO solutions show strong adhesion to epoxy resins, as shown by the data in Table I. By contrast, the unreduced fluoropolymer films show no adhesion.

For PTFE, PFA, FEP, and PCTFE, the adhesive strength maximizes in 24 h or less, with longer reaction times giving little improvement. Because the reaction starts from the fluoropolymer film surface, then gradually penetrates into the lower layers, highly reduced carbonaceous surface layers may block penetration of the reagents deeper in the films. Furthermore, the adhesive strength of the epoxy resins to the fluoropolymer films is probably determined by the interfacial strength between the two materials. Therefore, it is reasonable to assume that, once the interfacial region is fully reduced, further reduction gives no improvement in adhesive strength. The PTFE, PFA, FEP laminates failed at the fluoropolymer–epoxy interface, while the PCTFE–epoxy laminates were too brittle for measurement when the reaction times are longer than 6 h.

The data in Table I also shows that the adhesive strength of the reduced fluoropolymer films toward epoxy resins decreases in the order PCTFE > PFA ≥ FEP > PTFE > Teflon[™]-AF. The high reactivity of PCTFE is presumably due to the weak C–Cl bond in the $-\text{CF}_2\text{CFCl}-$ repeat unit compared to the more robust C–F bonds. Therefore, the rate of reduction is much higher for PCTFE than for the other fluoropolymers, and the long reaction periods may cause over reduction of the PCTFE films, causing embrittlement. The reactivity of Teflon-PFA

Table I Epoxy Adhesion Tests of Reduced Fluoropolymer Films

| Rx. Time (h) | 6 | 18 | 24 | 48 |
|-----------------------------|------------------|----------------|----------------|----------------|
| PTFE | 6.0 ^a | 6.5 | 6.7 | 5.7 |
| Teflon-FEP | 8.0 | 10.5 | 7.9 | 11.5 |
| Teflon-PFA | 7.5 | 13.2 | 15.0 | 15.0 |
| PCTFE ^b | 12.4 | — ^c | — ^c | — ^c |
| Teflon-AF (10) ^d | 0 | 0 | 0 | 0 |
| Teflon-AF (40) | 0 | 0 | 0 | 0 |
| Teflon-AF (82) | 0 ^e | not tested | 0.5 | not tested |
| Teflon-AF (91) | 2.4 | not tested | 1.8 | not tested |
| Teflon-AF (95) | 5.8 | not tested | 6.3 | not tested |

^a Peel tests measured by Instron (ASTM D-903); all units are in lbs/inch.

^b Poly(chlorotrifluoroethylene).

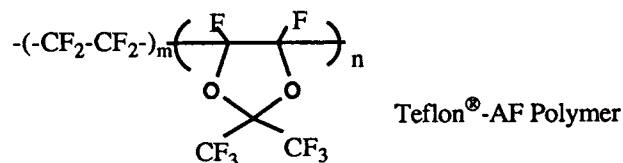
^c These films were strongly reduced and therefore, too brittle for testing.

^d The numbers in parentheses are mol % tetrafluoroethylene in the TFE/perfluoro-2,2-dimethyl-1,3-dioxole copolymers.

^e This film was weakly reduced.

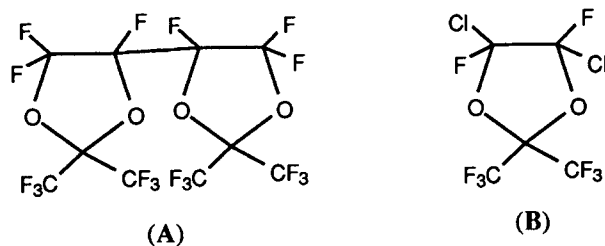
and FEP are similar at short reaction times, but PFA shows higher strength with longer reaction time. Both PFA and FEP show enhanced reactivity compared to PTFE. PTFE is much more crystalline than either PFA or FEP, and the amorphous regions of PFA and FEP may allow diffusion of the reducing agents throughout the film, rather than localizing it at the surface.

Most importantly, we find that the reactivity of the various Teflon[®]-AF compositions depends on the TFE:perfluoro-2,2-dimethyl-1,3-dioxole ratio. When the TFE content in the polymer is low, the polymers show no sign of reduction even though these polymers are totally amorphous.¹⁶ The crystallinity of perfluoro-2,2-dimethyl-1,3-dioxole/TFE copolymers depends on the TFE content, becoming crystalline when the TFE content is ≥ 80 mol %. The perfluoro-2,2-dimethyl-1,3-dioxole/TFE copolymers are reduced only when the TFE composition is $\geq 80\%$. The perfluoro-2,2-dimethyl-1,3-dioxole/TFE copolymers have essentially the same reactivity toward reduction as PTFE when the TFE content is ~ 95 mol %.



Another effect is that compounds containing tertiary carbon-fluorine bonds are much more suscep-

tible to reduction than those containing only primary or secondary carbon-fluorine bonds. Therefore, PFA and FEP are much more readily reduced than is polytetrafluoroethylene. For example, cyclic voltammetry of model compounds¹⁷ shows that fluoroaliphatics with tertiary carbon-fluorine bonds have significantly lower reduction potentials than do perfluorocarbons without tertiary carbon-fluorine bonds. We have found that cyclic voltammetry of model compounds shows the perfluorodimethyl dioxolane unit is much more resistant to reduction reactions than even simple fluoroaliphatic compounds, despite the fact that the perfluoro dimethyl dioxolane unit has tertiary carbon-fluorine bonds. For example, cyclic voltammetry of perfluoro-2,2-dimethyl-1,3-dioxole dimer (A) showed no reduction out to the potential limit of -2.90 V.¹⁸ Similarly, cyclic voltammetry on 4,5-dichloro-4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxolane (B), despite having carbon-chlorine bonds, showed no reduction out to the reduction limit of -2.70 V.¹⁹



No reduction occurs when the PTFE film is reacted with *t*-BuOK/benzoin in 1,3-dimethyl-2-imidazolidinone solution rather than DMSO solution, as judged by the appearance of the film, infrared spectrum, and the poor adhesion to epoxy resins. This result is surprising because 1,3-dimethyl-2-imidazolidinone is a polar, aprotic solvent, like DMSO.

We have found that treatment of PTFE with the benzoin dianion in DMSO show enhanced adhesion to polyethylene films or Mylar[®] films, with peel strengths of approximately 0.15 lbs/in and 0.24 lbs/in, respectively. By contrast, the virgin fluoropolymer films show no adhesion to these substrates. The reduced fluoropolymer films could not be laminated to other fluoropolymers or other reduced fluoropolymers by hot pressing at 200°C , 25000 psi. Attempts to isolate the products of reduction of perfluorodecalin and perfluorocyclohexane with *t*-BuOK/benzoin/DMSO were unsuccessful.

Fluoropolymer Metallization

The reduced fluoropolymer films can be metallized in several ways. Reduced fluoropolymer films treated

with silver nitrate solutions followed by a sodium borohydride solution give a conductive fluoropolymer film with a silver metallic appearance. The resulting film can then be plated with metals such as copper by electroless plating methods to give a laminate with micron-thick coatings of copper. Similar results are obtained with films from any method of fluoropolymer surface reduction, including potassium t-butoxide/benzoin/DMSO solutions, sodium benzophenone/THF solutions, or sodium naphthalene/THF solutions. PTFE, PFA, and FEP films metallized in this way pass the adhesive tape test, but qualitatively the adhesion is best to PTFE, with adhesion to PFA and FEP being somewhat lower. A micrograph of the cross-section of a PTFE film metallized in this way is shown in Figure 1.

A variation of this technique is to directly sputter gold or palladium/gold on the reduced fluoropolymer surface. This metallized fluoropolymer can also be electrolessly plated with copper to give copper-fluoropolymer laminates. A sample of PFA that was electrolessly plated with copper in this way was subsequently electroplated with copper to give a laminate with a peel strength of 7 lb/in, as determined by T-peel test.

Fluoropolymer films are conventionally metallized by lamination with metal foils, although metallization by metal sputtering on unactivated (unreduced) fluoropolymers is also known.²⁰⁻²² Our approach is an improvement over conventional metallization in the following respects: it relies solely on chemical reactions with no need for heat treatment or metal vapor deposition. The combination of chemical reduction with metallization improves adhesion, giving a laminate that is resistant to boiling water and organic solvents. As a chemical method of metallization, this approach offers a substantially more versatile metallization technology. In principle, it should allow metallization of via holes in fluoropolymer-based electronic circuitry and it should provide a method for image-wise metallization of thin conductor lines for greater circuit miniaturization.^{23,24}

Reduced fluoropolymer surfaces are known in the literature to undergo doping with iodine to become electrically conductive.⁸ We have found that the iodine doping is reversible: the iodine is readily extracted out with organic solvents to re-form electrically insulating films. Exposure to iodine a second time does not regenerate electrical conductivity.

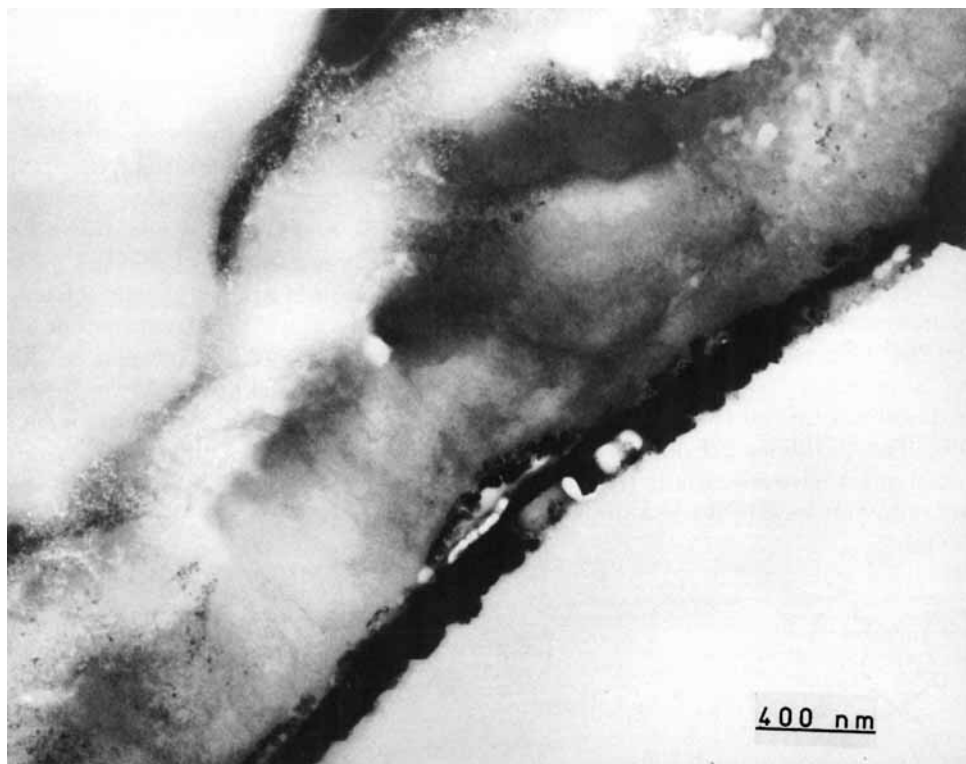


Figure 1 Transmission electron micrograph of the cross-section of a copper Metallized PTFE film revealing the metal-fluoropolymer interface.

Doping with nitrosonium tetrafluoroborate rather than iodine did not give a conductive film. Attempts to electrolessly plate and/or electroplate copper metal on the iodine-doped reduced PTFE films were unsuccessful.

Fluoropolymer Surface Functionalization

Previous models of reduced fluoropolymer surfaces have a polyene-like surface of sp or sp^2 hybridized carbon atoms and a high density of unsaturated carbon-carbon bonds. This model suggests that the reduced fluoropolymer surface should be highly susceptible to attack of nucleophiles or electron transfer agents. Salts of alkyl- or aryl-mercaptans are good nucleophiles, and the aryl-mercaptans are also excellent electron transfer reagents,²⁵ especially toward highly unsaturated frameworks. To this end we have studied the reduction of fluoropolymer films with the benzoin dianion to generate the activated fluoropolymer surface followed by reaction with thiolates, giving thiolates covalently bonded to the fluoropolymer surface. Because sulfur has a high affinity for metals, we expect such a derivatized surface to give especially high adhesion to metals.

Potassium *t*-butoxide, sodium thiophenolate, and benzoin (in a 25–30 : 10–15 : 1 molar ratio) in DMSO react with fluoropolymer films, yielding films identical in appearance to those from the reaction with the benzoin dianion in the absence of sodium thiophenolate. Unexpectedly we found that large excesses of sodium thiophenolate (> 35 : 1 sodium thiophenolate to benzoin dianion molar ratio) do not reduce the fluoropolymer films, suggesting that large amounts of thiolate may trap radical species necessary for the reduction reaction. Sodium thiophenolate and benzoin in DMSO without added base show no evidence for reaction with the fluoropolymer films nor did the distinct purple-red color form that is indicative of the benzoin radical anion. FEP and PFA films behaved similarly to PTFE films. Sodium thiolates alone do not react with the fluoropolymer films, suggesting that they are not sufficiently reducing, although they do discolor PCTFE films.

In an alternative experiment, PTFE films were treated with *t*-BuOK/benzoin in DMSO solvent at 60°C for 24 h, then sodium methylthiolate (MeSNa) was added (as a DMSO suspension) and the reaction was continued at 60°C for another 24 h. This sequential addition of thiolate to reduced fluoropolymer films gave a light-colored film with a slight metallic lustre. This is very different from the dark, highly metallic appearing PTFE films obtained by the benzoin dianion treatment alone. ATR-IR spec-

tra of these films showed that the absorptions at 1590–1600 cm^{-1} for polyene species formed from the reaction with the benzoin dianion had decreased after the sodium methyl thiolate treatment, and two new absorptions at 896 and 962 cm^{-1} appeared, which are consistent with C—S and C—O bond formation. The C—O bonds could arise from reaction of the graphitic surface with atmospheric water or oxygen during workup.

These light-colored films have excellent adhesion to metals applied by sputtering but surprisingly poor adhesion to epoxy resins. A gold layer, applied to the fluoropolymer surface by sputtering, is stable to boiling water and organic solvents (methylene chloride or acetone). Adhesive tape does not remove metal. Qualitatively, use of sodium methylthiolate gives better metal adhesion than use of sodium thiophenolate salts. A similar treatment of FEP and PFA films gives fluoropolymer films that are much less dark in color but, again, show very good adhesion with gold applied by sputtering techniques. These results show that this two-step sequential treatment of fluoropolymer films is useful for the chemical functionalization of fluoropolymer surfaces, providing control over the fluoropolymer surface chemistry.

To study the scope of this process, disodium salts of 1,6-hexanedithiol was used instead of MeSNa or PhSNa in the PTFE reduction reaction. After workup, the resulting films had a somewhat dark appearance, not as dark as that from the treatment with the benzoin dianion alone, also lighter than that from the reaction of the benzoin dianion followed by MeSNa. The 1,6-hexanedithiol functionalized PTFE film adheres well not just to gold but also now has improved adhesion toward epoxy resins, with a peel strength of 7.6 lbs/in, and the metal remains firmly adhered to the fluoropolymer film even after boiling in water or organic solvents. Other difunctional reagents behave similarly. The reduced PTFE films graft with 1,3-diaminopropane, the disodium salt of 3-mercaptopropionic acid ($NaS-CH_2CH_2-COONa$) and the disodium salt of 2-mercaptoethanol ($NaS-CH_2CH_2-ONa$), in addition to MeSNa, PhSNa, and $NaS-(CH_2)_6-SNa$. As expected, the PTFE films reacted with these reagents all show good adhesion to both epoxy resins and sputtered gold. These results suggest that the improved adhesion to epoxy resins is due to the difunctional nature of the thiol reagents. The full utility of this broad range of functional groups on fluoropolymer surfaces is under investigation. Data from ESCA analysis of the fluoropolymer films after reduction and subsequent reaction with thiols are in

Table II, showing the uptake of both oxygen and sulfur.

Scanning electron microscopy reveals morphological changes resulting from reduction of the fluoropolymer films with the benzoin dianion and subsequent reaction with thiolate reagents. Figures 2 and 3 illustrate the changes on the surface of FEP film, first from the reaction with the benzoin dianion and then after MeSNa treatment. The benzoin dianion reduction etches the film surface, but these features are diminished upon reaction with MeSNa. Etching may contribute to enhanced adhesion of the reduced fluoropolymer films to epoxy or metals simply through interdigitation.²⁶ Figures 4 and 5 describe the same processes for PFA film, but now the effect of the MeSNa reaction is more pronounced, the etched sites now being covered with agglomerations. Figures 6 and 7 show the same effects for PTFE films. Etching is less deep for PTFE than for FEP and PFA, and this may be reflected in the weaker adhesion of reduced PTFE films to epoxy compared to reduced FEP and PFA films. The NaS—(CH₂)₆—SNa reagent gives larger agglom-

erations on the surface and, correspondingly, the NaS—(CH₂)₆—SNa reagent gives better adhesion than the MeSNa reaction toward both epoxy resins and metals.

Summary

A variety of fluoropolymers are reduced by the benzoin dianion to give a reactive surface that is presumably graphitic or polyene-like in composition and reactivity. The reactive surface is further functionalized by chemical reagents: addition of sulfur nucleophiles gives a surface that is especially reactive toward metals, while reaction with difunctional reagents enhances fluoropolymer adhesion toward metals or toward reactive resins such as epoxys. Through choice of reagents, fluoropolymers that form especially strong laminates with epoxys or metals can be prepared, yet the bulk of the film remains unaffected. Amorphous TFE/perfluoro-2,2-dimethyl-1,3-dioxole fluoro-copolymers appear inert to reduction.

Table II ESCA Analysis of Fluoropolymer Films After Reactions

| Film | Scan Degree ^a | Rx. Conditions | Element Distributions | | | |
|------|--------------------------|---------------------------------|-----------------------|------|------|-----|
| | | | C | F | O | S |
| PTFE | 0 | Control ^b | 68.9 | 4.9 | 22.6 | 3.6 |
| | 0 | | 68.1 | 5.3 | 22.9 | 3.7 |
| | 60 | | 68.4 | 6.3 | 22.0 | 3.3 |
| PTFE | 0 | 2 , 24/24 h ^d | 60.3 | 7.5 | 25.9 | 6.3 |
| | 0 | | 62.5 | 5.9 | 24.1 | 6.6 |
| | 0 | | 65.1 | 8.5 | 20.7 | 5.7 |
| FEP | 0 | Control ^b | 65.7 | 14.7 | 17.4 | 2.2 |
| | 0 | | 67.1 | 16.0 | 14.1 | 2.8 |
| | 60 | | 67.3 | 15.7 | 14.6 | 2.3 |
| FEP | 0 | 1 , 6/17 h ^c | 60.9 | 14.2 | 19.8 | 5.1 |
| | 0 | | 59.5 | 19.2 | 12.4 | 8.8 |
| | 60 | | 63.1 | 18.5 | 10.8 | 7.6 |
| PFA | 0 | Control ^b | 73.3 | 3.5 | 20.8 | 2.3 |
| | 0 | | 70.9 | 4.4 | 22.0 | 2.7 |
| | 60 | | 65.7 | 5.8 | 26.4 | 2.2 |
| PFA | 0 | 1 , 6/17 h ^c | 69.9 | 3.8 | 20.9 | 5.4 |
| | 0 | | 68.7 | 4.9 | 21.6 | 4.8 |
| | 60 | | 71.0 | 6.3 | 19.0 | 3.8 |

^a Photoelectron takeoff angle.

^b Control means the fluoropolymer films were treated with *t*-BuOK/benzoin in DMSO solvent only. The reaction periods are the same as those of two-step reactions.

^c **1** = MeSNa, reaction time 24 h with *t*-BuOK/benzoin in DMSO, then 24 h with MeSNa or 6/17 h in two-step reaction for FEP and PFA.

^d **2** = NaS—(CH₂)₆—SNa was used instead of MeSNa.

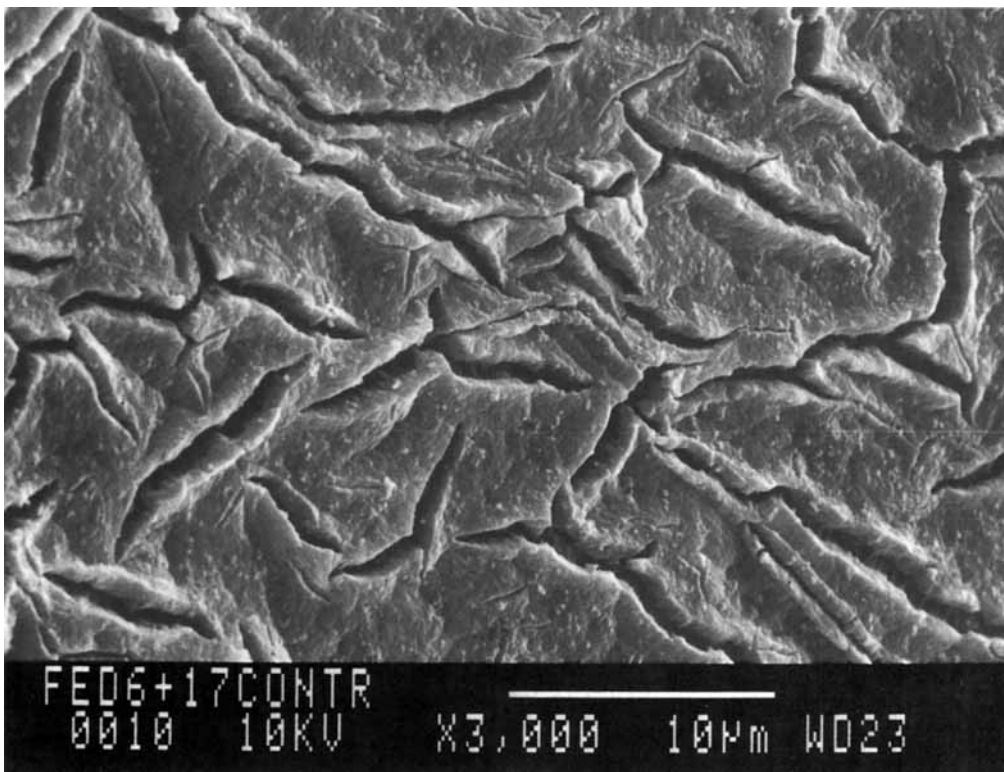


Figure 2 Scanning electron micrograph (SEM) of the surface of a Teflon[®]-FEP film after reaction with t-BuOK/benzoin at 60°C for 23 h, showing the surface etching resulting from reduction.

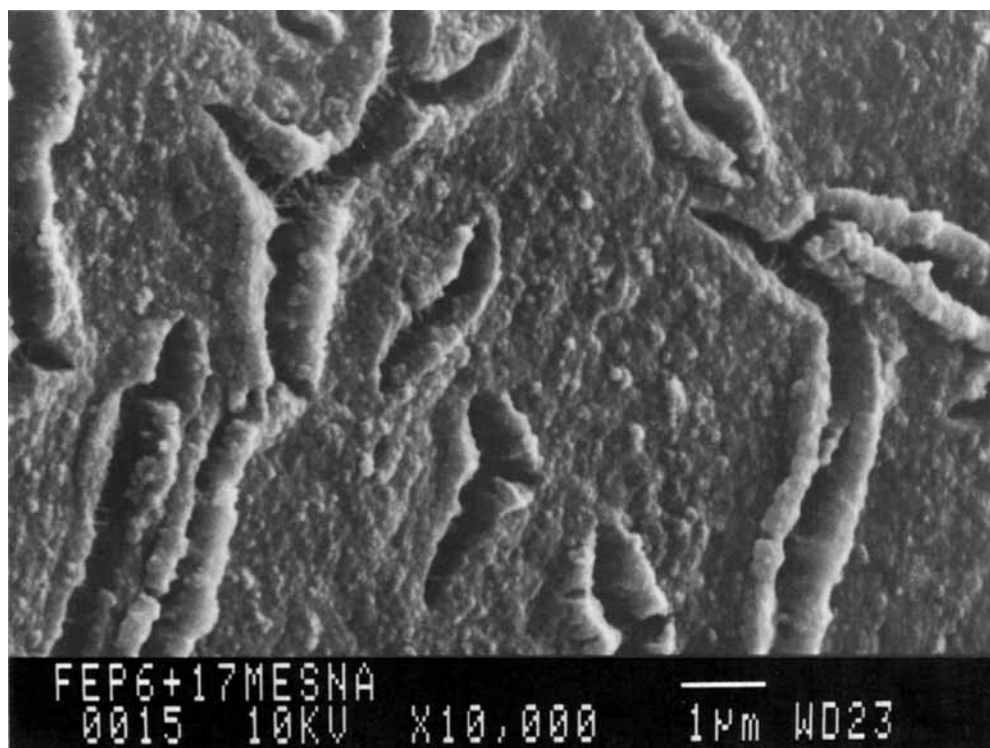


Figure 3 SEM of the surface of a Teflon[®]-FEP film after reaction with t-BuOK/benzoin/DMSO at 60°C for 23 h, followed by reaction with MeSNa/DMSO at 60°C for 17 h. The depth of the etches are diminished upon MeSNa treatment.

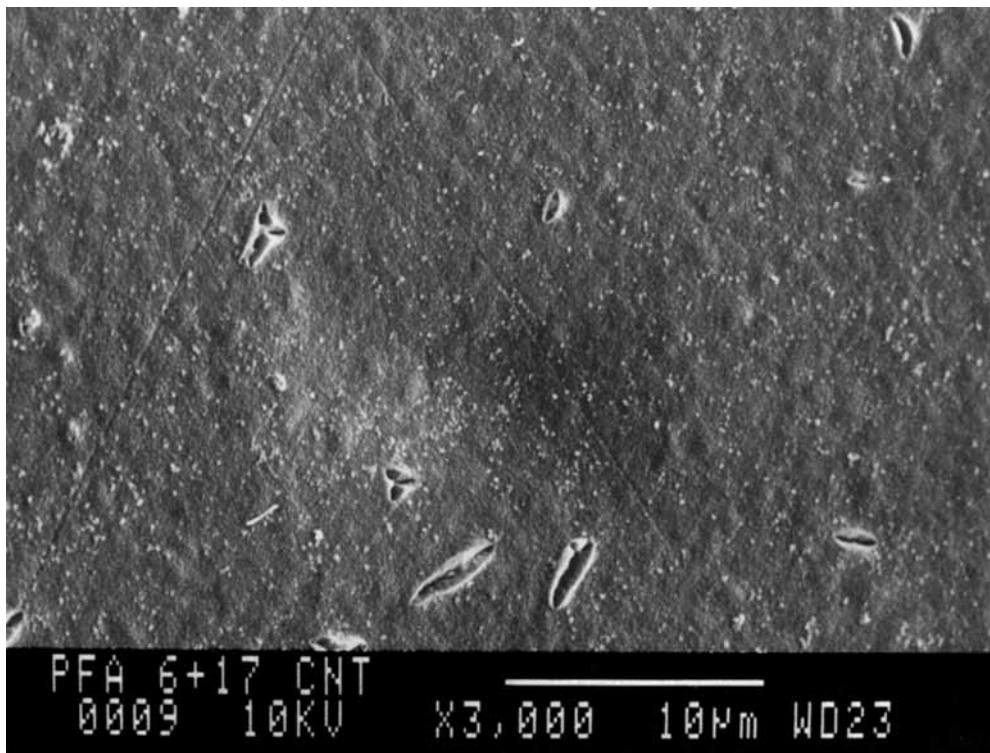


Figure 4 SEM of the surface of a Teflon[®]-PFA film after reaction with t-BuOK/benzoin at 60°C for 23 h, showing the surface etching resulting from the reduction.

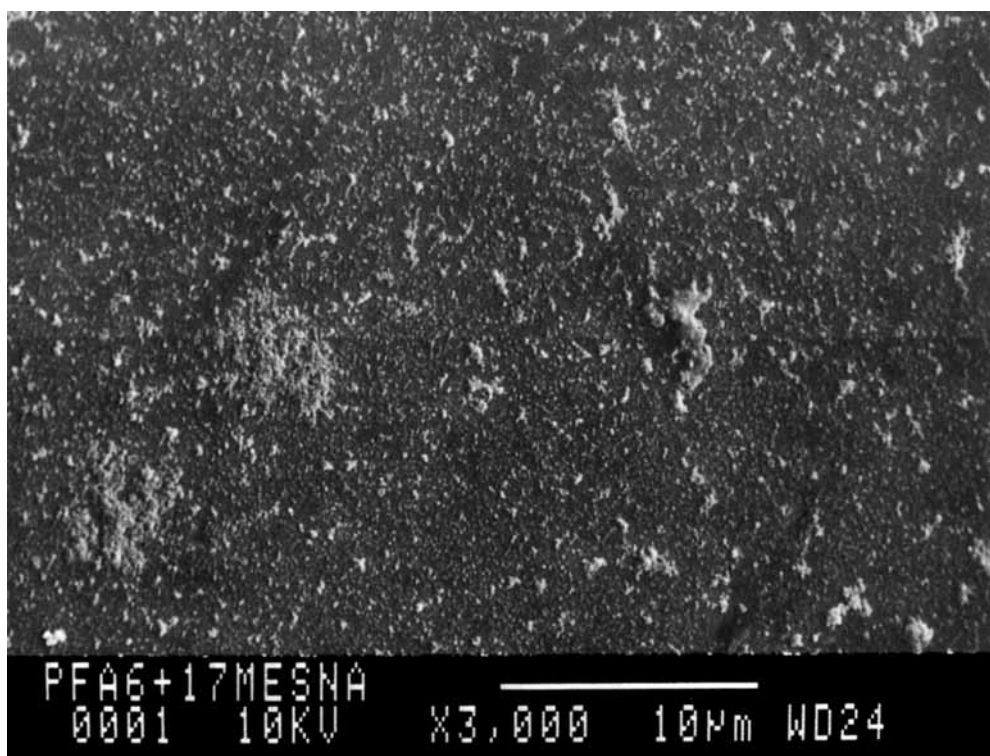


Figure 5 SEM of the surface of a Teflon[®]-PFA film after reaction with t-BuOK/benzoin/DMSO at 60°C for 23 h, followed by reaction with MeSNa/DMSO at 60°C for 17 h. The effect of the MeSNa treatment on the depth of the etches is more pronounced than for the Teflon[®]-FEP Film.

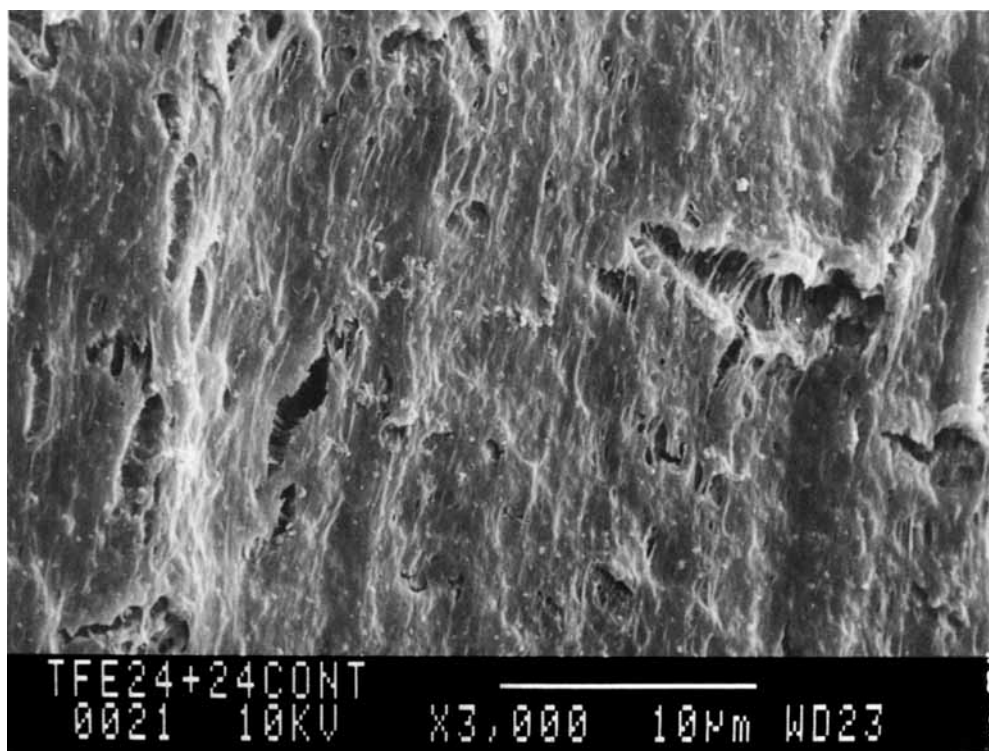


Figure 6 SEM of the surface of a Teflon[®]-TFE film after reaction with t-BuOK/benzoin at 60°C for 23 h, showing the surface etching resulting from the reduction.

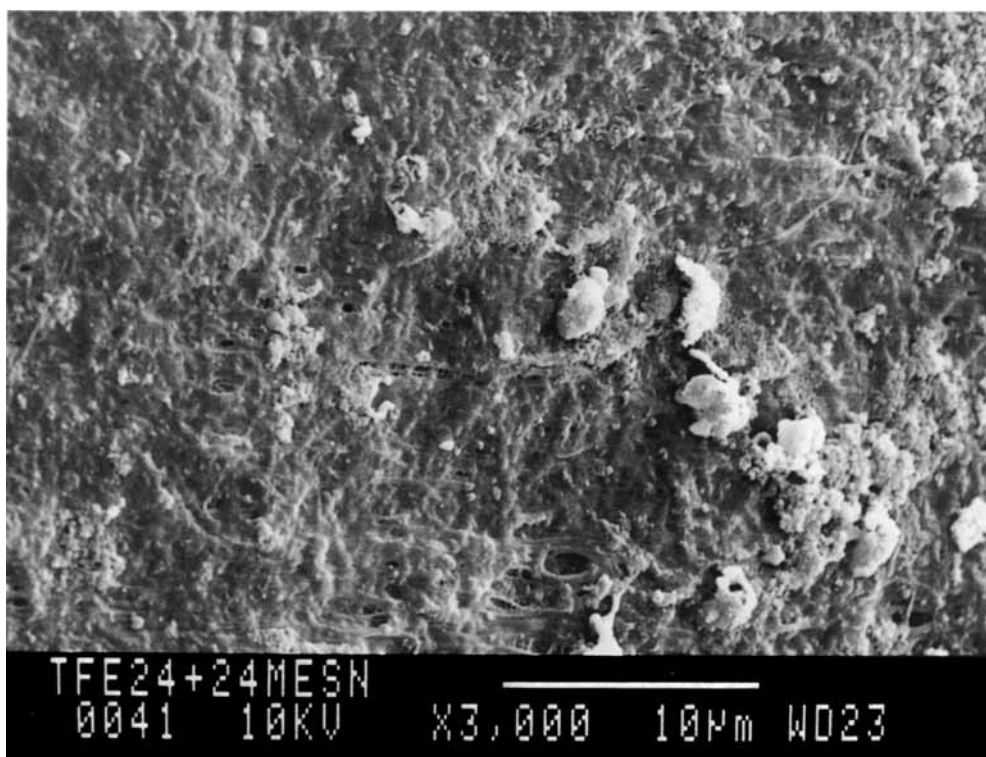


Figure 7 SEM of the surface of a Teflon[®]-TFE film after reaction with t-BuOK/Benzoin/DMSO at 60°C for 24 h, followed by reaction with MeSNa/DMSO at 60°C for 24 h.

EXPERIMENTAL

General Procedures

PTFE, PCTFE (from 3M Company), Teflon-PFA, Teflon-FEP, Teflon-AF films are cut into the size of 1" × 2–3" and in 3 to 7.5 mil thickness. The fluoropolymer films except PCTFE were washed with predried THF in Soxhlet extractor at refluxing temperature for 24 h, then were dried in high vacuum in a desiccator and were kept under inert atmosphere. PCTFE was washed with methylene chloride in a similar treatment. Benzoin was recrystallized from 95% ethanol and was stored in desiccator. DMSO and DEMU solvents were distilled first, then degassed by bubbling nitrogen. The fluoropolymer films after reactions were washed successively with water and THF, sometimes washed with additional 1,1,2-trichloro-1,2,2-trifluoroethane. The films after washing were kept under inert atmosphere before analysis. Most chemicals were purified before use.

MeSNa was purchased from Aldrich Chemical Co. PhSNa was prepared from PhSH with sodium methoxide in methanol and toluene. The sodium salts of NaS—(CH₂)₆—SNa, HO—CH₂CH₂SH, and HS—CH₂CH₂COOH were prepared similarly. A typical example is illustrated below:

Sodium methoxide (54 g, 1.0 mol) was suspended in anhydrous methanol (300 mL) at 5–10°C. 2-Mercaptoethanol (39 g, 0.5 mol) was introduced slowly via syringe. After addition, the mixture was stirred at ambient temperature for 2 h. MeOH solvent was removed *in vacuo* at 70°C, and the residual salt was dried under high vacuum, a very pale-brown salt NaS—CH₂CH₂ONa was obtained in almost quantitative yield. ¹H NMR (D₂O): δ2.56 (t, J = 15.3 Hz, 2H), 3.52 (t, J = 15.3 Hz, 2H). ¹H NMR (D₂O) for NaS—CH₂CH₂COO—Na: δ2.52 (t, J = 14 Hz, 2H), 2.73 (t, J = 14 Hz, 2H).

ESCA analysis used a Kratos 300 instrument in the Mg anode.

Reduction of Fluoropolymer Films With t-BuOK/Benzoin

A typical procedure follows: a prewashed and dried PTFE film was placed in a sealed bottle with t-BuOK (4.0 g, 35 mmol) and benzoin (0.27 g, 1.3 mmol) in DMSO solvent (40 mL) (all the materials were charged under inert atmosphere) with a glass-wrapped stirring bar. The purple-red color reaction was allowed to proceed at designed temperature for a period of time. The reaction mixture was then cooled, the solution was decanted and the film was washed with water thoroughly (25 mL × 8–10) and

THF (25 mL × 5). The film was allowed to dry under inert atmosphere. A metallic luster typically develops as the PTFE film dries. The film was stored in a sealed vial before further characterization.

Reaction of Reduced Fluoropolymer Film With SodiumThiolates

A typical example is illustrated as follows: The PTFE film was first reacted as described above with t-BuOK/benzoin. Before isolation, sodium salt of the mercaptan compounds (50 mmol) was added either in DMSO as a suspension or solution or as a solid (all carried out in a dry box). The reaction was continued under the designed conditions, then the film was worked up in the same way as the above experiment.

Fluoropolymer Adhesion With Epoxy Resins

The epoxy resin used in these experiments are "Epoxy-Patch" made by Dexter Corporation. The epoxy resin was made ready to use before the test according to manufacturer's instructions. Then the reacted and dried fluoropolymer films (two pieces) were taken out from the storage vial. The epoxy resin was applied to the interface of these two films and the fixed films were placed between two glass plates that were held together by clamps. The films were allowed to cure for 24 h before adhesion peel strength tests by Instron instrumentation.

Fluoropolymer Metallization

A sample of PTFE film (21.8 g) was washed with THF and dried at 50°C under vacuum. The film was then soaked in a solution of benzoin (6 g), and potassium t-butoxide (22 g) in anhydrous DMSO (600 mL) for 20 h at room temperature under an inert atmosphere. The benzoin/potassium t-butoxide/DMSO solution was cannulated out of the reaction vessel, which was recharged with fresh benzoin/potassium t-butoxide/DMSO solution. The reaction was continued for an additional 24 h at room temperature. At the end of the reaction, the benzoin/potassium t-butoxide/DMSO solution was removed from the vessel, and the film was rinsed with THF and dried, leaving a shiny bronze-colored film, which was stored under inert atmosphere.

The reduced film was soaked for 1 h in a solution of AgNO₃ (1.7 g) in deoxygenated water (100 mL). During this time, the shiny bronze color of the reduced PTFE film was replaced by a silvery gray color. The film was rinsed briefly with deoxygenated

water and then placed in a solution of NaBH_4 (0.38 g) in deoxygenated water (100 mL) for ~ 2 min. The film was then rinsed sequentially with water, isopropanol, and acetone, and then finally dried in open air. The conductivity of the resulting film approximated that of bulk metal. FEP and PFA films were treated similarly. These films, as well as reduced fluoropolymer films sputtered with gold or palladium, could be electrolessly plated as described below.

Sputtering was done with a Denton Vacuum, Inc., table top sputter coater, equipment such as is used for preparing samples for electron microscopy. Copper electroless plating solutions were prepared by mixing a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (22.7 g), Na_2CO_3 (12.5 g), sodium potassium tartrate (70 g), and EDTA (9.0 g) in deionized water (400 mL) with a solution of NaOH (20.0 g) and of 37% formaldehyde (75.0 g) in deionized water (100 mL). Nickel electroless plating solutions were prepared by mixing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (5.0 g) and dimethylamine borane (0.2 g) in dimethyl formamide (50 mL)/deionized water (50 mL). This plating solution required heating to about 50°C for nickel deposition to proceed.

Electrochemistry Experiments

Cyclic voltammetry was run with a 2 mm diameter platinum working electrode and a platinum counter electrode using a Ag/Ag^+ reference with 0.1 M $\text{Et}_4\text{N}^+\text{BF}_4^-$ and 0.01 M AgClO_4 in distilled acetonitrile (+0.292 V vs. SCE). The total solution volume was 3 mL, which was further deoxygenated by bubbling with nitrogen for 10 min. The cyclic voltammograms were performed under a constant nitrogen blanket, starting at 0 V and ramping at 10 mV/s to -2.90 V, the limit in this solvent. The experiments were performed first without the perfluoro-2,2-dimethyl-1,3-dioxole dimer to determine the background current, and the total reduction charge was determined for the blank. Ten microliters of sample was added and the cyclic voltammogram was run again. No additional current was observed. An additional 10 μL was added but, again, no current was observed in the cyclic voltammogram. For a molecular weight of 526 and an approximate density of 1.8, the solution concentration was 0.023 M, certainly high enough to detect electrochemical activity. Therefore, no reduction of the fluorodioxanes was observed in this system up to a potential of -2.90 V (vs. Ag/Ag^+).

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