Photolithography of Polytetrafluoroethylene for Adhesion

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Synopsis

Irradiation of polytetrafluoroethylene (PTFE) with Mg(Kα) X-rays is shown to protect the surface against the chemical etching steps used to prepare PTFE for adhesion. Preirradiated etched samples of PTFE have adhesion strengths to epoxies of less than 3% of that for nonirradiated etched samples. The major portion of this decrease in adhesion strength occurs for X-ray exposures of less than 10 min and failure in every case occurs in PTFE and not in the bonded transition region. XPS measurements (20 Å sampling depth) show little difference in F content between irradiated and nonirradiated samples, but thermal desorption shows increasing short chain fluorocarbon desorption with irradiation time. These results are consistent with previous studies showing that irradiation produces free radicals that lead to branching and/or crosslinking, and a surface rich in low molecular weight fluorocarbons. The crosslinked surface is resistant to deep (10,000 Å) chemical attack and rich in short chain fluorocarbons; both effects are expected to lead to weak adhesive bonding.

INTRODUCTION

Due to the chemical and physical inertness of polytetrafluoroethylene (PTFE), drastic methods are usually employed to prepare such surfaces for adhesion. The most widely used method is a chemical etch[1,2] involving sodium, either as sodium in liquid ammonia or as a 1 : 1 sodium–naphthalene complex (Tetra-Etch, W. L. Gore & Associates, Newark, DE). This chemical etching process is characterized[1,2] by a loss of surface F and etching to a depth of up to 10,000 Å. The highly porous, thermally unstable etched surfaces have an extremely large surface area (> 1200 cm^2/g) compared to untreated PTFE (< 25 cm^2/g). Bond strengths to such etched surfaces using epoxy resins are so large that cohesive failure usually occurs in the PTFE and not in the boundary layer.

We have shown recently[3] that exposure of PTFE to X-rays prior to chemical etching leads to a dramatic increase in its resistance to the chemical etching process. Regions of PTFE exposed to Mg(Kα) X-rays for 1 h and then etched appear only slightly discolored by the etching process, as compared to the usual dark brown appearance of nonirradiated etched surfaces. The protection afforded by X-ray preirradiation was interpreted[3] as resulting from radiation-induced branching and/or crosslinking, which produces a more rigid structure resistant to deep attack. An additional consequence of the crosslinking process is the production of low molecular weight fluorocarbons in the surface region. Consistent with this, thermal desorption measurements show a monotonic increase in the desorption of low molecular weight fluorocarbons with increasing irradiation times.

Journal of Applied Polymer Science, Vol. 37, 2529–2536 (1989)
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In this present report we will present a quantitative measure of the effect of X-ray irradiation on the adhesive yield strength. Irradiation with Mg(Kα) X-rays (1254 eV) for up to 1 h followed by chemical etching is shown to result in adhesion strengths using epoxy resins that have decreased to only 3% of the adhesive strength of nonirradiated samples. The major portion of this loss in adhesion strengths occurs for X-ray exposure times of less than 10 min. The decrease in adhesion strength is discussed in terms of the two major consequences of irradiation: crosslinking and/or branching, and the production of short chain fluorocarbon fragments. The more rigid structure resulting from crosslinking could limit the depth of chemical attack and bonding to a surface while an increasing fraction of short chain species is expected to produce a weak boundary layer; both effects would decrease adhesion strength. These results define a photolithographic process for adhesion control and open the possibility for tailored adhesion strength.

EXPERIMENTAL

Experimental details of the ultrahigh vacuum (UHV) system have been presented in previous publications[3,4] and will not be repeated here. The system consists of two interlocked vacuum chambers which allow rapid transfer of samples to the UHV chamber containing an XPS spectrometer with its associated X-ray source and a mass spectrometer for line-of-sight thermal desorption experiments.

After X-ray exposure, the samples were first chemically etched for 30 s in Tetra-Etch (W. L. Gore & Associates) followed by ultrasonic rinses with, in sequence, water, acetone, and methyl alcohol. Adhesion strength measurements were made using a Sebastion I adherence tester. Before bonding, the aluminum tensile test plugs were freshly etched using a sulfuric acid/sodium dichromate solution to produce a surface insuring that failure did not occur in the bond to the test plug. The tensile test plugs were bonded to the PTFE samples using a quick setting nonamine epoxy-cured at 100°F for $2\frac{1}{2}$ h. Special attention was paid to maintaining a constant procedure and time sequence for all the steps following X-ray exposure. In contrast to the known instability of etched surfaces of PTFE, the X-ray exposed surfaces of PTFE are stable, yielding the same etching results after weeks of storage.

RESULTS

Because of their importance to the present adhesion results we will summarize the XPS and thermal desorption results from Ref. (3). Figure 1 contains a photograph of two PTFE samples which illustrate the effect of X-ray irradiation.[3] One half of each sample was covered with 5 mil Ta foil, exposed to Mg(Kα) X-rays for 10 min (4800 mrads) and 60 min (29,000 mrads), respectively, and then chemically etched. The radiation dose values given here and subsequently in the text are estimates based on the dose rate of 8 mrads/s reported by Wheeler and Pepper[5] for a similar X-ray source. Visually, those portions of the PTFE surface exposed to X-rays are markedly less etched than the nonirradiated surfaces; this is especially the case for the sample receiving 29,000 mrads, where the irradiated half is only slightly tinted compared to the normal dark, discolored result.

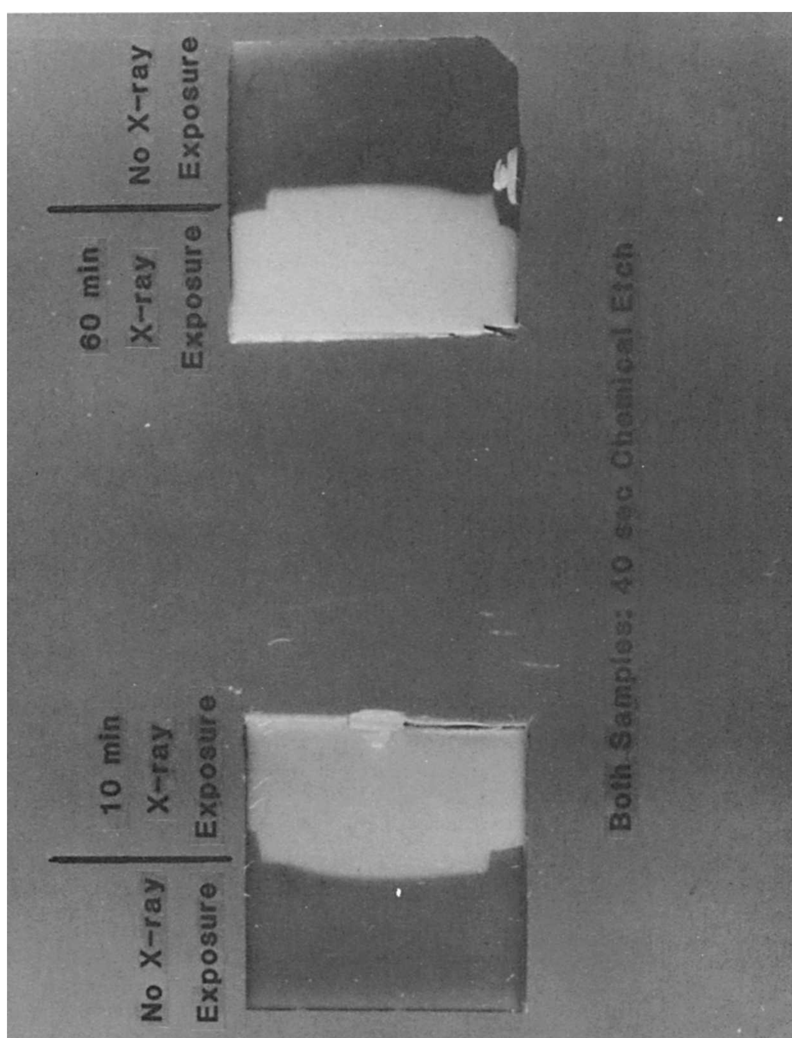

Fig. 1. Photographs of PTFE chemically etched for 40 s. Prior to etching, one half of each sample was covered with 5 mil Ta foil and exposed to Mg(Kα) X-rays (1254 eV) for 10 min (4.8×10^3 mrads) and 60 min (2.9×10^4 mrads), respectively. Sample dimensions are $1.2 \times 1.2 \times 0.79$ mm.

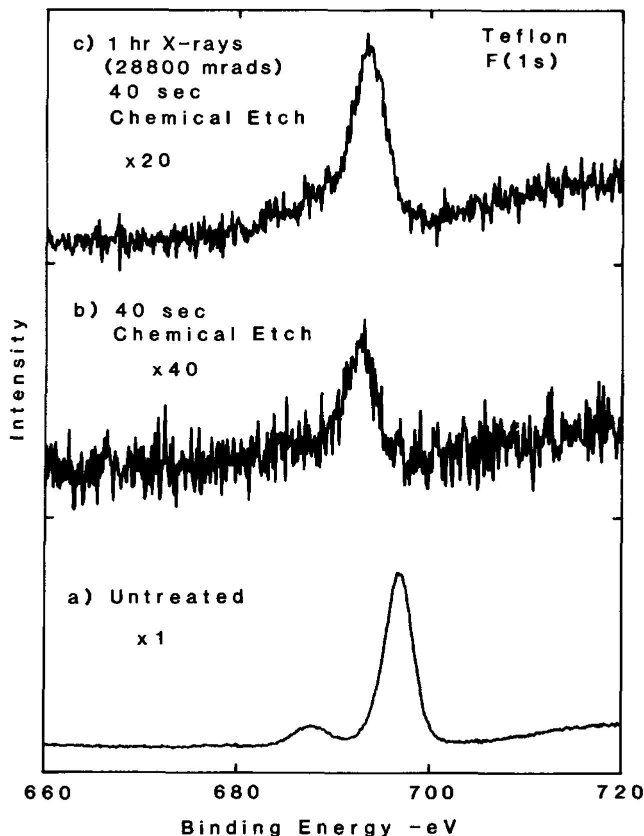

Fig. 2. F(1s) XPS spectra for (a) untreated PTFE, (b) PTFE etched for 40 s in Tetra-Etch, and (c) PTFE etched for 40 s after a 1-h exposure to Mg(Kα) X-rays (2.9×10^4 mrads). All three are for the same total data accumulation time. No corrections were made for charging. The small peak at lower binding energy is due to an X-ray satellite.

While dramatic differences in the appearance of the etched PTFE surfaces can result from X-ray preirradiation, XPS (C or O) indicates very little difference before or after etching. As Wheeler and Pepper[5] pointed out earlier, Mg(Kα) exposures of many hours are required to observe radiation induced changes in the XPS spectrum of PTFE, and no changes in the XPS spectra ascribable to radiation effects were observed in the present experiments. The XPS F results[3] after chemical etching are summarized in Figure 2. For a 40 s etch, both a 290,000 mrad preexposure to X-rays and no X-ray predose indicate major defluorination of the surface and a shift to lower binding energy. For the X-ray predosed surface the extent of defluorination is less than for the sample that was just etched, but the difference between the two etched surfaces is small compared to that between either of the etched surfaces and virgin PTFE. Similar small differences are seen in the C XPS spectra between irradiated and nonirradiated samples; in both cases the C(1s) peak increases in intensity and shifts to lower binding energy indicative of defluorination. The thermal desorption results in Figure 3 led to an interpretation of the X-ray induced protection in terms of radiation damage effects.[3]

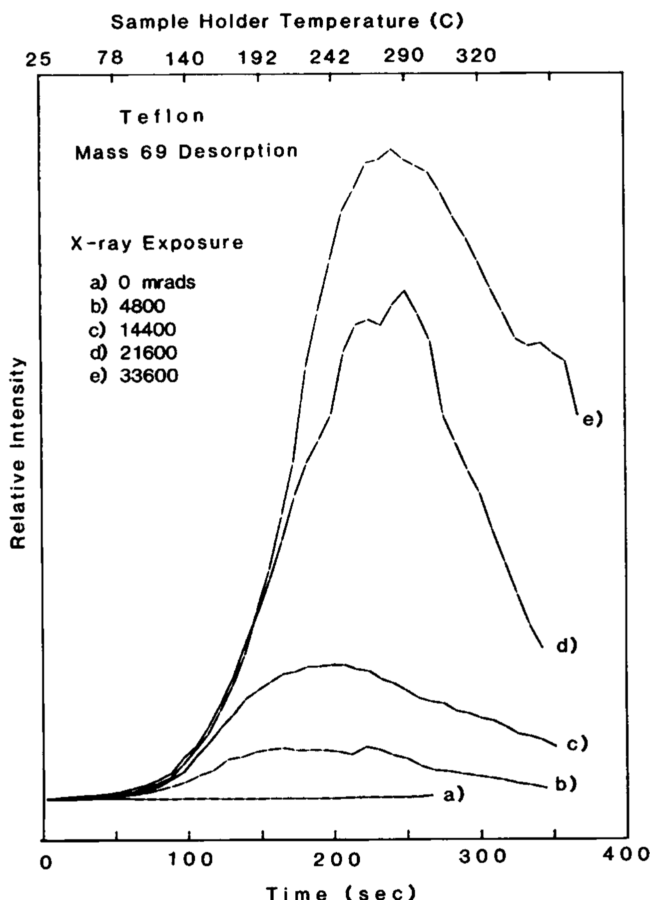

Fig. 3. Mass 69 (CF_3^+) thermal desorption as a function of X-ray exposure (mrads): (a) 0; (b) 4800; (c) 14,400; (d) 21,600; (e) 33,600. An isolated mass 69 species is a fingerprint of linear, saturated fluorocarbons.

The only mass species that desorbs to any appreciable extent is mass 69 (CF_3^+); an isolated mass 69 species is the characteristic mass fragment of low molecular weight fluorocarbons.[6] Desorption of these low molecular weight fluorocarbons (Fig. 3) shows a monotonic increase with increasing X-ray exposure to the extent that after a 34,000 mrad exposure mass 69 is the dominant desorbing species.

While only small X-ray dose effects are seen in the XPS spectra, even after etching, differences more dramatic than the visual evidence in Figure 1 are seen in the adhesive yield strength data as a function of X-ray exposure contained in Figure 4. The changes induced by X-ray exposure are stable with qualitatively similar results being obtained weeks after irradiation. Three separate samples were run for each X-ray exposure, along with a single nonirradiated control sample, and the solid line in Figure 4, used as a guide for the eye, connects the average value for each exposure. It is clear that exposure of PTFE to X-ray radiation prior to chemical etching leads to a dramatic decrease in adhesion strength. For longer radiation exposures, the yield

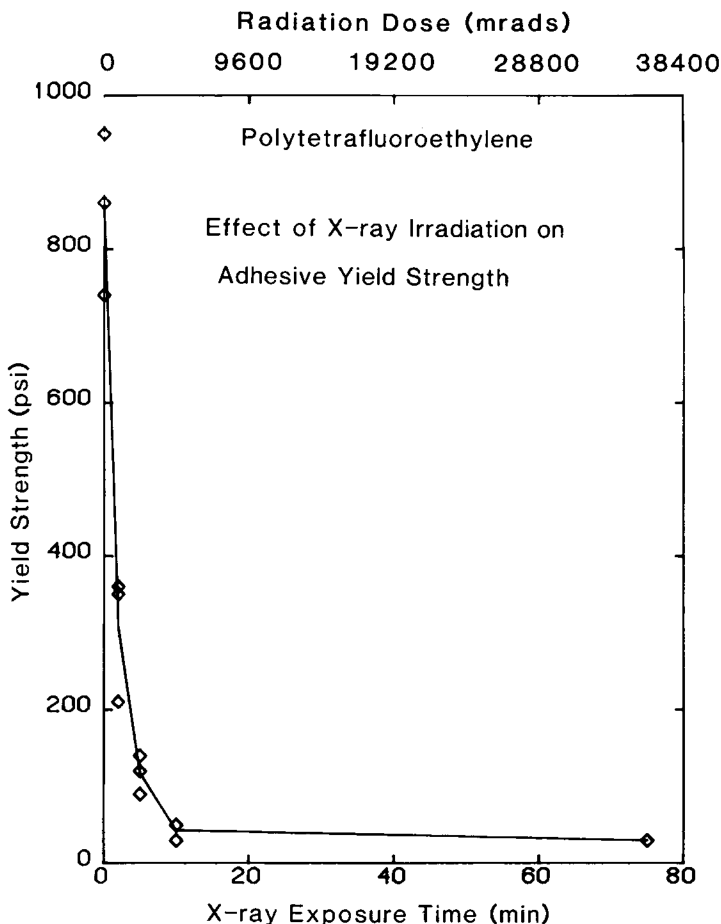

Fig. 4. Yield strength as a function of X-ray exposure time (and radiation dose). Freshly etched aluminum test plugs were bonded to the PTFE samples with epoxy. Failure in each case occurs in PTFE and not in the boundary layer.

strength is only 3% of the value or the control samples which received no irradiation. There are additional observations that one can make about the yield strength data. First, the decrease in yield strength is essentially complete for an exposure of only 4800 mrads while visual differences are seen between 4800 mrads and 29000 mrads exposures) (see Fig. 1). Second, for every point in Figure 4 failure is observed to occur in PTFE and not in the adhesive layer. In each case failure resulted in removal of the entire boundary layer leaving behind a white spot visually similar to PTFE.

DISCUSSION

The radiation-induced protection of PTFE against chemical etching has been interpreted[3] in terms of radiation damage which produces branching and/or crosslinking and a more rigid PTFE surface resistant to deep etching. This interpretation was based on the direct correlation of increased desorption of low molecular weight fluorocarbon products with increased X-ray exposure

(see Fig. 3) and is consistent with radiation damage studies suggesting[7,8] that effective C—C bond scission occurs near the chain ends. The present radiation dose rates are clearly capable of producing radiation damage effects since the radiation dose rates from the X-ray source (estimated to be 8 mrads/s by Wheeler and Pepper[5] for a similar source) are much larger than those used by Fisher and Corelli (< 100 mrads)[7,8] in a study of radiation induced crosslinking.

It is clear that chemical etching leads to loss of fluorine, but the important question is what chemical or physical changes (or combination of such changes) are important for adhesion. The loss of fluorine is a consequence of modifying the surface for increased adhesion but is not necessarily the reason for the increased adhesion. Present results suggest that enhanced adhesion may also be associated with the thick porous layer that results from chemical etching, and probably reflects a contribution from physical interlocking. Heating of an etched surface is known to lead to an increase in surface *F* as indicated by XPS and a corresponding loss of adhesion strength.[2] We have shown that heating leads to a loss of surface area, and suggested that this reflects a surface melting process in which the increase in *F* results from mixing of defluorinated surface species with more highly fluorinated material from deeper in the modified region.[3]

Irradiation of PTFE leads to two main changes in the surface region: branching and/or crosslinking and the production of low molecular weight fluorocarbon products. The effect of the branching and/or crosslinking is the production of a rigid structure in which diffusion of the active sodium is more limited. As a consequence, the crosslinked PTFE should have a greater resistance to deep chemical attack. Defluorination of such surfaces does occur, but the depth of attack is limited. A second major consequence for adhesion comes from the production of low molecular weight fluorocarbons. With increasing X-ray exposure times, chemical etching occurs with a surface increasingly rich in short chain fluorocarbons. Subsequent bonding to these short chain species would form a weak boundary layer to the underlying PTFE. The loss of adhesive strength is thus not necessarily due to weak bonding to the modified layer, but to a weak interaction between the modified layer and the underlying PTFE. Thus, the known effects of radiation are sufficient to explain the apparent visual lack of chemical etching in Figure 1, the XPS evidence for chemical etching in Figure 2, and the loss of adhesion strength in Figure 4.

For adhesive applications involving PTFE, the present results allow two potentially important new capabilities: (1) the ability to tailor a specific adhesion strength and (2) the development of photolithographic techniques for patterned adhesion. Figure 4 defines a calibration curve for adhesive strength whereby one should be able to use the preirradiation step to "dial in" any desired fraction of the maximum yield strength. The results in Figure 1 are photolithographic patterns, however simple. The ultimate complexity of the pattern is only limited by the complexity of the mask used.

Finally, we should note that in preliminary experiments we have shown that electron irradiation gives the same basic photolithographic result as X-rays. If, as we propose, these etching and adhesion results simply stem from the introduction of radiation damage effects, similar results for electrons and

other forms of ionizing radiation should be expected insofar as the radiation damage can be localized to the surface region. The use of electrons, however, has fundamental and practical consequences. From the practical standpoint no mask is required; using the deflection capabilities with electrons we have shown that one can write desired patterns on the surface. From the fundamental standpoint the ability to vary parameters such as beam energy and beam current allows one to probe properties such as energy thresholds and depth dependence. Work is currently in progress in this direction.

We acknowledge the help of Dave Zamora with innovative attachment schemes and the mechanical testing. We acknowledge support of the Department of Energy (Contract DE-AC02, 80ER10746).

References

1. A. A. Benderly, *J. Appl. Polym. Sci.*, **20**, 221 (1962).
2. D. W. Dwight and W. M. Riggs, *J. Colloid Interface Sci.*, **47**, 650 (1974).
3. R. R. Rye, *J. Polym. Sci., Polym. Phys. Ed.*, to appear.
4. R. R. Rye and J. A. Kelber, *Appl. Surface Sci.*, **29**, 397 (1987).
5. D. R. Wheeler and S. V. Pepper, *J. Vac. Sci. Technol.*, **20**, 226 (1982).
6. H. Budzikiewiez, C. Djerassi, and D. H. Williams, *Mass Spectroscopy of Organic Compounds*, Holden-Day, San Francisco, 1967, p. 441.
7. W. K. Fisher and J. C. Corelli, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2465 (1981).
8. W. K. Fisher and J. C. Corelli, *J. Appl. Polym. Sci.*, **27**, 3769 (1982).

Received March 29, 1988
Accepted June 13, 1988