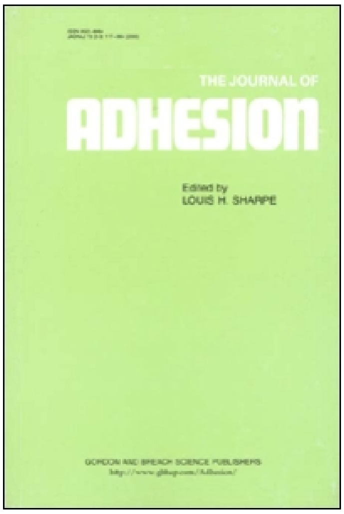

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D. J. Barker[a][b]; D. M. Brewis[a]; R. H. Dahm[a]; J. D. Gribbin[a]; L. R. J. Hoy[a]
[a] School of Chemistry, Leicester Polytechnic, Leicester, LEI 9BH. Imperial Chemical Industries Ltd, Plastics Division, Welwyn Garden City, Hertfordshire, England [b] Raychem Ltd., Wiltshire, U.K.

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Surface Pretreatments of Polytetrafluoroethylene

D. J. BARKER,† D. M. BREWIS, R. H. DAHM, J. D. GRIBBIN
and L. R. J. HOY

School of Chemistry, Leicester Polytechnic, Leicester, LE1 9BH, and Imperial Chemical Industries Ltd, Plastics Division, Welwyn Garden City, Hertfordshire, AL7 1HD, England

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PTFE as normally processed contains a highly sheared atypical surface layer. If this layer is removed then the naphthalenide treatment is not effective, although the surface may be reactivated by various means. However, the direct electrochemical reduction and sodium/liquid ammonia treatment, being more severe, readily attack PTFE without this atypical layer. The mechanisms of the above treatments are discussed.

INTRODUCTION

Adhesion to polytetrafluoroethylene (PTFE) is greatly improved by treating the surface of the polymer with solutions of naphthalenide ion in aprotic solvents[1,2] or with solutions of alkali metals in liquid ammonia.[3] In addition to these well established methods, exposure of solid perfluoropolymers to an electrical discharge[4] also leads to improvements in joint strengths. Neither the mechanism of the surface reactions nor the nature of the reaction products are fully understood although such knowledge is important for a proper understanding of the molecular basis of adhesion in general and of PTFE in particular. We have been studying the reduction of PTFE by a new electrochemical method which has helped to shed some light on the mechanism of the reduction. The starting point for this investigation was the realisation that the reduction of PTFE to carbon and fluoride ion is

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† Present address: Raychem Ltd., Faraday Road, Dorcan, Swindon, Wiltshire, U.K.

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thermodynamically feasible according to the following equation:

$$1/n(CF_2)_n + H_2 \rightarrow C_{(s)} + 2HF \qquad \Delta G = -176.94 \text{ kJ mol}^{-1}$$

The standard reduction potential E is therefore 0.917 V or about 0.67 V w.r.t. the saturated calomel electrode (SCE). PTFE is therefore thermodynamically unstable when in contact with nearly all metals, the exception being the noble metals such as gold and platinum. Reactions between PTFE and the common metals are of course not usually observed at room temperature due to the presence of inert oxide or possibly passivating fluoride films. However under tribological conditions such films are readily broken down and this may account for the formation of metallic fluorides when PTFE is rubbed in contact with stainless steel or nickel surfaces.[5] Schonhorn *et al.*[6] obtained greatly enhanced joint strengths after vapour depositing aluminium onto fluorinated ethylene-propylene copolymer. Removal of the aluminium with sodium hydroxide left a surface with similar X-ray Photoelectron Spectroscopic (XPS) characteristics as that obtained after treatment with sodium naphthalenide. Interestingly, deposition of gold followed by its removal with mercury did not produce an activated surface. On the other hand in a recent publication Schonhorn and Vogel[7] found no increase in wettability when a number of metals were vapour deposited onto PTFE. However Jansta and Dousek[8,9] showed that PTFE is reduced by alkali metal amalgams.

EXPERIMENTAL

Electrochemical pretreatment

The three compartment cell used in the electrochemical studies is shown in Figure 1. The working electrode (WE) consists of a short piece of platinum wire firmly held in contact with the PTFE ("Fluon" G163 skived tape†) which was placed on a small glass table. The potential of the WE was controlled potentiostatically with respect to an aqueous saturated calomel reference electrode (SCE). The electrolyte consisted of a solution of vacuum dried tetrabutylammonium tetra-fluoroborate of concentration 0.1 mol dm^{-3} in dimethylformamide dried by standing over Type 4A molecular sieves for 48 hours followed by distillation under reduced pressure and storage over molecular sieves. This procedure gave a specific resistance of 3×10^5 Ωm and a moisture content as determined by Karl Fischer titration of 0.02–0.07%. The solutions were further dried immediately before use by the addition of activated alumina (BDH Type, neutral, Brockmann grade 1) to the electrochemical cell. Potentiostatic transients were recorded after stepping the

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†PTFE sheet pared from a cylindrical billet by rotating this against a stationary knife on a lathe.

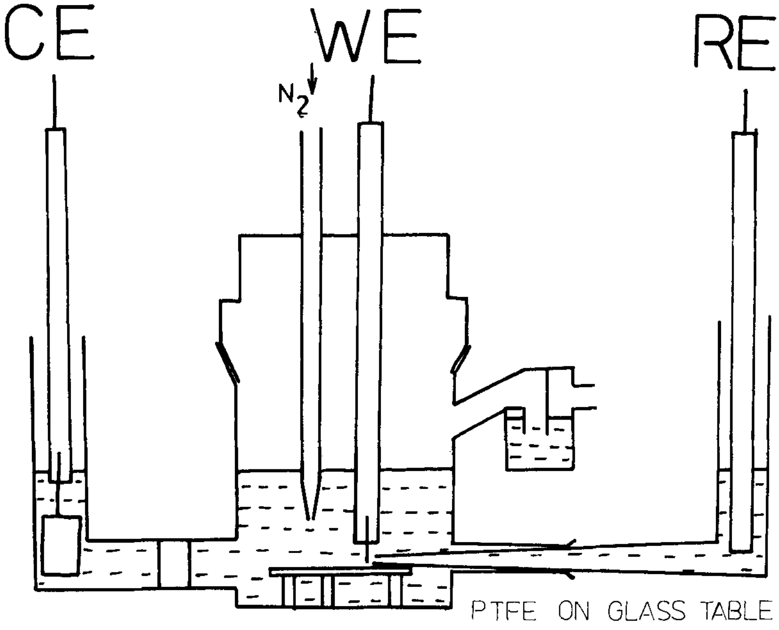


FIGURE 1 Electrochemical cell for the reduction of PTFE skived tape.

potential from −1 V, a potential too low for the reduction of PTFE, to the values indicated in Figure 2. Samples of tape were prepared for adhesive bonding by repeatedly contacting the film with the polarised electrode until the required area of the film had been blackened. The treated film was washed in the same way as the chemically treated films.

Chemical pretreatments

A solution of sodium naphthalenide of concentration 1 mol dm^{-3} was prepared by stirring an equimolar mixture of naphthalene and 1 mm diameter sodium wire in sodium dried THF until all of the sodium had dissolved (*c.* 3 hours).

A solution of sodium in liquid ammonia of concentration 2.4×10^{-2} mol % was prepared by adding small pieces of sodium to liquid ammonia cooled to −50° in a carbon tetrachloride–carbon dioxide slush bath.

The atypical surface layer produced by the skiving process was removed by immersion in one of the above solutions (*c.* 30 seconds for sodium in liquid ammonia, 1 hour for naphthalenide) followed by removal of the carbonaceous film by immersion first in fuming nitric acid and heating to 50°. This solution

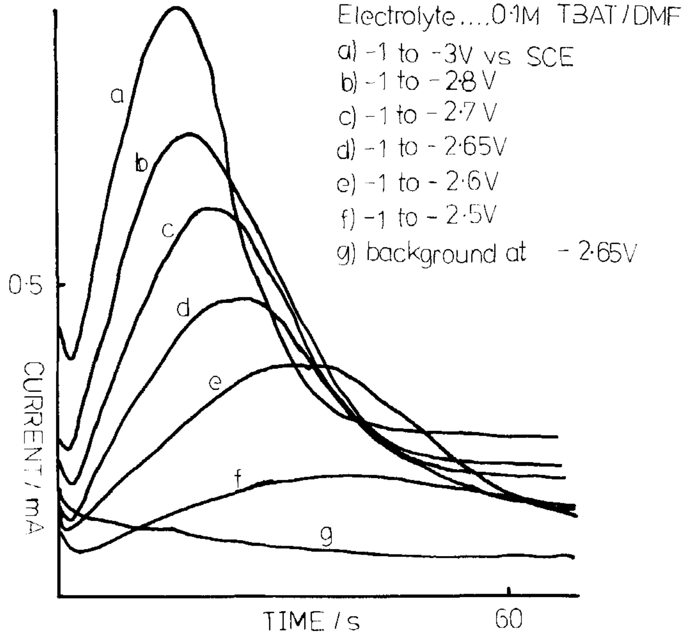


FIGURE 2 Potentiostatic current time transients for skived tape in contact with a platinum electrode.

was then allowed to cool naturally to room temperature and the whole process was repeated using acid dichromate ($Na_2Cr_2O_7 . 2H_2O$ 5 p.b.w., H_2O 8 p.b.w., H_2SO_4 100 p.b.w. in place of the nitric acid. The sample was then washed in cold water and allowed to dry at room temperature. This sample was then subjected to the thermal cycling regime described in Table 2 before reimmersion in the naphthalenide solution.

Joint strength determination

Samples of skived tape (thickness 0.25 mm) were bonded between aluminium strips 12 mm wide, 3 mm thick with a 12 mm overlap using a standard epoxide adhesive [100 p.b.w. Epikote 828 and 60 p.b.w. tris(dimethylaminoethyl)phenol] cured for 16 hours at 60°. Lap shear strengths were then determined using a Monsanto W Type tensometer at a crosshead speed of 5 mm/min^{-1}.

ELECTROCHEMICAL REDUCTION OF PTFE

The authors find that the surface of PTFE held in contact with a cathodically polarised point contact electrode placed in an aprotic solvent such as dimethylformamide (DMF) containing an inert support electrolyte such as 0.1 M tetrabutylammonium tetrafluoroborate (TBAT) is reduced to form a black coherent carbonaceous layer growing outwards from the point of contact and covering an area of up to 2 cms^2 in approximately 15–30 s.[10] The apparatus required to carry out the reduction is simple and is shown in Figure 1.

The major features of this treatment may be summarised as follows:

i) The reduction does not take place at a measurable rate at 0.64 V (SCE) but requires large overpotentials. The reaction is electrochemically highly irreversible and the rate of reduction becomes detectable at potentials more cathodic than −1.5 volts (SCE) and the rate as measured by the reduction current increases with increasingly cathodic potentials as seen from the potentiostatic current-time transients shown in Figure 2. The maxima in these curves can be accounted for if it is assumed that the carbonaceous reduction product of PTFE is an electronic conductor.

ii) Prolonged application of the polarising potential produces a slow thickening of the treated layer to give values of 40 μm in 5 days.

iii) The extent to which the surface of PTFE is reduced is greatly dependent on the processing history of the sample.[11] Thus skived tape and ram extruded rod with their highly sheared atypical surface layers are much more readily reduced than are samples without such layers such as dispersion cast films or samples from which such layers have been removed chemically.

iv) The appearance of an electrochemically treated surface is a useful indicator of molecular orientation. Thus etching becomes anisotropic when samples of PTFE are stretched prior to treatment.

v) In common with chemically produced etched surfaces[12],[13] complete removal of the carbonaceous film is possible by oxidation with for example acid dichromate, sodium hypochlorite solution or exposure to light. The XPS spectra of these regenerated polymer surfaces are identical with those of the original surface so that PTFE is unique in that the treated surface layer can be removed completely by purely chemical means.

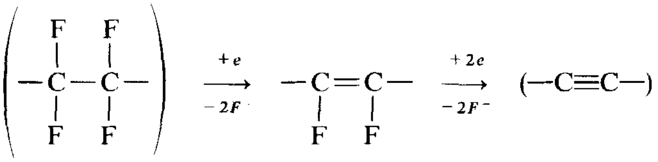
THE COMPOSITION OF THE REDUCTION PRODUCT

The appearance of electrochemically treated PTFE is similar to material treated with naphthalenide except for the anisotropic effects mentioned earlier. The most likely reduction product of PTFE is carbon[14] requiring a total of four electrons per—C_2F_4—repeat unit. However coulometric measurements show that the number of electrons required is always slightly but consistently greater than four. We interpret this in terms of a two-step mechanism involving:

i) The reduction of PTFE at the electrode-PTFE-electrolyte interface to yield a form of carbon according to:

$$(C_2F_4)_n + 4ne \rightarrow (C_2)_n + 4nF^-$$

In common with the electroreduction of the alkyl halides[15] the reaction probably proceeds via the intermediate radical anion.



$$\left(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right) \xrightarrow[-2F^-]{+e} -\underset{F}{C}=\underset{F}{C}- \xrightarrow[-2F^-]{+2e} (-C\equiv C-)$$

The exact form of the carbonaceous product is as yet unknown and the above polyacetylide structure is only one possibility.

ii) The formation of an intercalation compound according to

$$(C_2)_n + pe + pR_4N^+ + \rightarrow (C_2)_n^{p-}\ p(R_4N)^+$$

where the ratio of $n:p$ is approximately 10. Intercalation compounds of natural graphite and tetraalkylammonium ions have been reported by Simonet and Lund[16] and by Besenhard *et al.*,[17] and their results are in substantial agreement with ours.

The fact that the electrochemical treatment proceeds radially outwards from a point contact cathode implies that the carbonaceous reaction product is an electronic conductor. Direct measurement of the conductivity of the treated layer proved difficult but was eventually achieved using a special vacuum cell to yield a value of 2.1×10^{-3} Ωm for a freshly formed intercalated film. However exposure to traces of air or protic solvents caused an immediate and irreversible rise to *c.* 1.6×10^4 Ωm. Examination of the defluorinated layer by XPS revealed the presence of large amounts of oxygen as well as carbon even when attempts were made to introduce the sample into the spectrometer without exposure to air. Pure carbon is known to be highly reactive towards oxygen[18] and the formation of the intercalation compound is likely to increase the reactivity even further.

COMPARISON OF CHEMICALLY WITH ELECTROCHEMICALLY TREATED PTFE

Because the electrochemical treatment leads to preferential reduction of the highly orientated atypical layer found on skived tape and ram extruded rods, experiments were carried out in order to determine whether or not the presence of these atypical layers would effect bond strength particularly in the case of skived tapes. The results in Table I clearly show that the presence of the atypical layer has no effect on the bond strength and that the joint strength for

TABLE I

A comparison of the joint strength obtained for chemically and electrochemically treated PTFE

Sample	Treatment	Joint strength
		kN ± S%
Skived tape	Untreated	0.4
Skived tape	Sodium naphthalenide for 10 s	2.42 ± 12
Skived tape	Sodium naphthalenide for 30 s	2.73 ± 11
Skived tape	Sodium naphthalenide for 4 hours	2.76 ± 10
Skived tape atypical layer removed	Sodium naphthalenide for 5 min	2.40 ± 10
Skived tape	Electrochemical[a]	3.24 ± 5

[a] Repeated contacting with a platinum cathode at −2.9 V (SCE) in DMF 0.1 M TBAT.

electrochemically treated material are if anything slightly superior to those obtained for naphthalenide treated surfaces. This may well be due to the greater severity of the electrochemical treatment resulting in the formation of a slightly thicker carbonaceous film. In the following section we present some evidence which suggests that sodium naphthalenide is a relatively mild reducing agent.

THE SURFACE REDUCTION OF PTFE BY SOLUTIONS OF SODIUM NAPHTHALENIDE

The much lower reduction potential of naphthalene *c.* −2.6 V (SCE)[19] compared with the formation potential of solvated electrons *c.* −3 V (SCE)[20] suggests that sodium naphthalenide is a much milder reducing agent than the other widely used chemical etchant sodium in liquid ammonia. As shown in Table II sodium naphthalenide can only be reliably used to treat PTFE exhibiting the atypical surface layer. Once this layer has been removed further treatment is only possible if the surface is first reactivated either thermally, (electro) chemically or mechanically.

The results summarised in Table II present a number of puzzling features and only partial and tentative explanations are possible at the present stage. The results obtained for the electrochemical reduction of PTFE show that the highly orientated atypical surface on skived tape or ram extruded rod are reduced preferentially. This suggests that the crystalline regions may be more reactive than the amorphous regions in complete contradiction to the reactivity of the polyolefins where the amorphous regions are known to exhibit the higher reactivity, for example to oxidation.[21] This view however is not unreasonable because the formation of a relatively ordered graphitic or polyacetylenic carbonaceous material should be aided by the high degree of

TABLE II

Reactivity of PTFE towards reduction by sodium naphthalenide (1 m in THF) after removal of the atypical layer

Test no.	Type of sample	Treatment of sample after removal of carbonaceous film	Reactivity towards sodium naphthalenide[a]
1	0.25 mm skived tape	Quenched in THF at 10° followed by naphthalenide at 10°	High
2–25	Sample 1	Sample 1 treated as above a further 24 times	High
26	Sample 25	Same sample as above after 25 treatment cycles	Low
27	Sample 1	Cooled slowly over 1.5 h to 10° followed by naphthalenide at 10°	Low
28	Sample 1	No cooling. Direct treatment with naphthalenide at 50°	High
29	Sample 1	Cooled rapidly to 28° naphthalenide at 28°	High
30	Sample 26 treated with sodium in liquid ammonia	No thermal treatment required	High[b]

[a] Surfaces classified as possessing high reactivity produce a coherent brown deposit which yield joint strengths similar to those reported in Table I. Surfaces classified as possessing low reactivity produced a light, off white, non coherent "greasy" deposit giving rise to bonds with very low joint strength, typically 0.5 kN.

[b] All samples could be reduced by sodium in liquid ammonia or electrochemically. Such treatment reactivated the surface for a further 3–6 treatments with naphthalenide.

order existing in the crystalline regions of the starting material. This view is supported by the fact that unsintered PTFE with a crystallinity in excess of 90% readily reacts with naphthalenide for a large number of times without apparent loss in reactivity. If we further assume that reduction commences at certain activated sites for example dislocations within these crystalline regions we may account for the lack of reactivity of PTFE towards naphthalenide and its thermal and chemical reactivation. Thus the atypical layer formed in the skiving process has within it a large number of active sites which can act as nuclei for the reduction. Once these defects have been used up (usually 5–6 treatments for 0.25 mm skived tape or 1–2 treatments for 6 mm ram extruded rod) no further treatment with sodium naphthalenide is possible. If the polymer is now heated to 50° and rapidly quenched to below 10°, the active sites formed at the higher temperature, for example by the rotational changes occurring when the polymer passes through the 19° or 30° transitions,[22] are "frozen in" and further treatment is now possible until after about 25 treatment cycles, all reactive material near the surface has been consumed and no further treatment is possible unless new crystalline regions are exposed by, for example, treating the surface with the highly reactive sodium in liquid ammonia which will indiscriminately attack both the crystalline and the amorphous regions. If however the films are cooled slowly the crystal defects present at the higher temperatures have sufficient time to relax thus leaving a surface of low reactivity. Further work is in progress in order to clarify the situation.

CONCLUSIONS

i) The electrochemical, naphthalenide and sodium/liquid ammonia treatments involve reduction of PTFE to form a discrete carbonaceous layer. This layer can be completely removed subsequently by strong oxidising agents.

ii) PTFE after normal processing, *e.g.* skiving, possesses an atypical layer.

iii) The naphthalenide process, unlike the electrochemical or sodium/liquid ammonia treatments, is not effective with PTFE from which the atypical layer has been removed.

iv) PTFE from which the atypical layer has been removed can be reactivated towards naphthalenide by various methods *e.g.* heating to above 50° followed by quenching to below 10°.

v) In contrast to the treatment of polyolefins with oxidising solutions, the crystalline regions of PTFE are preferentially attacked.

References

1. A. A. Benderley, *J. Appl. Polym. Sci.* **6,** 221 (1962).
2. D. M. Brewis, R. H. Dahm and M. B. Konieczko, *Angew. Makromol. Chem.* **43,** 191 (1975).
3. Minnesota Mining & Manufacturing Co. GB 765284 (1957).
4. E.I. Du Pont de Nemours US 3296011 (1967).
5. P. Cadman and G. M. Gossedge, *Wear* **54,** 211 (1979).
6. R. F. Roberts, F. W. Ryan, H. Schonhorn, G. M. Sessler and J. E. West, *J. Appl. Polym. Sci.* **20,** 255 (1976).
7. S. L. Vogel and H. Schonhorn, *J. Appl. Polym. Sci.* **23,** 495 (1979).
8. J. Jansta, F. P. Dousek and J. Riha, *J. Appl. Polym. Sci.* **19,** 3201 (1975).
9. J. Jansta and F. P. Dousek, US 3967018 (1976).
10. R. H. Dahm, D. J. Barker, D. M. Brewis and L. R. J. Hoy, *Adhesion 4* Ed K. W. Allen (Applied Science, London, 1979), Chap. 4.
11. D. M. Brewis, D. J. Barker, R. H. Dahm and L. R. J. Hoy, *J. Mater. Sci.* **14,** 749 (1979).
12. D. W. Dwight, W. M. Riggs, *J. Coll. Interface Sci.* **57,** (3), 650 (1974).
13. H. Brecht, F. Mayer and H. Binder, *Angew. Makromol. Chem.* **33,** 89 (1973).
14. D. J. Barker, D. M. Brewis, R. H. Dahm and L. R. J. Hoy, *Electrochim. Acta* **23,** 1107 (1978).
15. M. R. Rifi, *Technique of Electroorganic Synthesis*, Vol. V, Part II, Ed by N. L. Weinberg (Wiley-Interscience, London, 1975).
16. J. Simonet and H. Lund, *J. Electroanal. Chem.* **75,** 719 (1977).
17. J. O. Besenhard and H. P. Fritz, *J. Electroanal. Chem.* **53,** 329 (1974).
18. S. Mazur, T. Matusinovic and K. Cammann, *J. Amer. Chem. Soc.* **99,** 3888 (1977).
19. H. Siegerman, *Technique of Electroorganic Synthesis*, Vol. V, Part II, Ed by N. L. Weinberg (Wiley-Interscience, London, 1975).
20. H. Lund, *Organic Electrochemistry*, Ed by M. M. Baizer (Marcel Dekker, New York, 1973).
21. R. P. Palmer and A. J. Cobbold, *Makromol. Chem.* **74,** 174 (1964).
22. H. Starkweather, *J. Polym. Sci.* Polymer Phys. ed, **17,** 73 (1979).