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Int. J. Adhesion and Adhesives 16 (1996) 173–178
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0143-7496/96/$15.00

0143-7496(95)00042-9

Influence of chemical and plasma treatments on the adhesive properties of PTFE with an epoxy resin

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(Accepted 29 September 1995)

Poly(tetrafluoroethylene) (PTFE) films and fibres were surface modified by different methods (chemical and plasma treatments) to improve their wetting and adhesion properties. Both chemical and, to a lesser extent, ammonia and hydrogen plasma treatments have been shown to greatly enhance the adhesion between PTFE and an epoxy resin. In the last case (ammonia and hydrogen plasma treatments), the adhesion increase has been related to the degree of defluorination rather than to the presence of polar functions at the surface. In the case of the chemical treatment, in addition to the defluorination, the incorporation of a large amount of oxygen moieties can play an important role in adhesive properties. In all cases the failure zones, observed by X-ray photoelectron spectroscopy after pull-off tests, are characteristic of a cohesive failure. The differences between the chemical and the plasma treatments have been attributed to the modified depth, which is more important in the former case. Fibre wettability is enhanced by a previous ammonia plasma treatment making easier the formation of an epoxy microdroplet for microbond tests. For ammonia-plasma-treated PTFE fibres the ultimate load increases; this cannot be attributed to a debonding process since either the droplet or the fibre breaks.

(Keywords: poly(tetrafluoroethylene); remote microwave plasma; surface modifications; epoxy resin adhesion; pull-off test; microbond test)

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) has excellent chemical resistance and low moisture absorption but exhibits poor adhesion to a thermoset matrix. Much effort has focused on the surface modification of PTFE, primarily by chemical treatment[1–6] (etching treatment) and radio-frequency plasma treatments[7–17]. All of these modification techniques tend to improve the PTFE wettability and to optimize PTFE–matrix interactions[18]. Very few studies[19] are concerned with the remote microwave plasma treatment, the main advantage of which is to prevent the electrons and ions of the plasma hitting the surface to be treated. In previous studies[20,21], we have investigated the surface modifications of PTFE induced by a microwave plasma treatment, by means of contact angle measurements and X-ray photoelectron spectroscopy (XPS) analysis. We have shown that, under our conditions (remote treatment), oxygen or oxygen/nitrogen mixtures were inefficient to modify the surface of PTFE and thus to improve the adhesion properties. However, ammonia or hydrogen plasma treatments produced significant surface modifications depending, in the case of ammonia treatment, on various parameters such as exposure time, power and gas flow. The surface modifications included an important defluorination, the appearance of C=C or C–H groups for both hydrogen and ammonia treatments and, in addition, the incorporation of nitrogen-containing groups for the ammonia treatment, rendering the PTFE surface more hydrophilic. This paper is now concerned with adhesion measurements. The influence of hydrogen and ammonia remote microwave plasma treatment on PTFE–epoxy resin adhesion will be described and compared with the results obtained after a chemical treatment of the PTFE surface. Both PTFE films and fibres will be considered.

EXPERIMENTAL

Two kinds of PTFE substrate were used in this study: a 4 mm thick sheet from Gaflon and fibres from Du Pont (monofilament diameter in the 20–26 μm range).

The PTFE sheets and fibres were treated in the

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plasma apparatus previously described[20], using a 2.45 GHz microwave generator. Two gases — hydrogen and ammonia — were employed. In all cases, the samples were placed 30 cm from the centre of the discharge.

The chemical treatment consisted of a commercial Tetra-Etch treatment (Gore). The sample was covered with the sodium-naphthalene complex in solution in ethylene glycol dimethyl ether. After 1 min, it was washed with water and then with methanol.

All the modifications carried out to PTFE sheets were evaluated by contact angle measurements and XPS analysis. The contact angle θ was evaluated from the height and the base diameter of a sessile drop, by assuming the contour to have a circular shape. Measurements using water and methylene iodide allowed the calculation of both the dispersive and the non-dispersive components of the surface energy[20]. XPS analyses were carried out using an ESCASCOPE apparatus (Vacuum Generators) with an unmonochromatized Al-X-ray source ($h\nu = 1486.6$ eV). The X-ray source power was set to 300 W to prevent degradation of the sample during the measurements. The binding energies were calibrated against the value of the aliphatic C 1s component centred at 285.0 eV.

Two tests were used for the adhesion measurements: the pull-off test performed on the sheets and the microbond technique on the fibres. For the pull-off test (*Figure 1*), an aluminium stud (diameter 20 mm) was adhesively bonded with an epoxy resin to the PTFE substrate and a 4.9 N load applied to the stud for 12 h at 50°C. After curing, the excess adhesive due to flow around the stud was removed by trimming. This operation was made easier because an exactly 20 mm diameter area was plasma-treated and the untreated PTFE shows very poor adhesion to the epoxy resin. The test was performed using an Instron tensile testing machine at 5 mm min^{-1} displacement rate. The average of the ultimate load (L_u) values is reported and, after testing, the failure zone was studied by XPS to find out whether the failure was cohesive or adhesive type.

Following the microbond technique developed by Miller *et al.*[22], a small amount of resin was deposited on a single fibre to form discrete microdroplets. Following appropriate curing, the droplets were debonded in shear away from the fibre at 0.1 mm min^{-1} displacement rate.

RESULTS AND DISCUSSION

Adhesive properties and PTFE sheets

*_Chemical treatment._ Defluorination resulting in the formation of unsaturated bonds is deduced from the colour change of the PTFE, which becomes brown after the chemical treatment. Such behaviour has been already reported in the literature[1–4]. The defluorination is confirmed by the XPS results (*Table 1*) which show a decrease of the F/C atomic ratio from 2.5 to 0.2. At the same time, incorporation of a large amount of oxygen and a small amount of nitrogen can be noticed.

A large decrease of the contact angles of water and methylene iodide, from 115 to 52° and from 84 to 23°, respectively, is observed. This leads to an increase of both the dispersive (γ^D) and non-dispersive (γ^P) components of the surface energy (*Table 1*).

This treatment leads to an increase of the ultimate load which reaches a value of 800 ± 100 N. Before treatment it is 31 ± 17 N.

Ammonia plasma treatment. It has been shown[21] that the surface modifications induced by ammonia plasma are dependent on power, gas flow and treatment time. As confirmed by the evolutions of the defluorination rate, the oxygen and nitrogen contents, and the dispersive and non-dispersive components of the surface energy, the treatment is more efficient:

- when the gas flow decreases;
- when treatment time is longer than 120 s;
- when the power is larger than 350 W.

In *Table 1* are reported the F/C, O/C, N/C atomic ratios and the values of dispersive and non-dispersive components of the surface energy for optimized plasma treatment conditions (500 W, 30 sccm (standard cubic centimetre per minute), 120 s). As previously observed with the chemical treatment, the ammonia treatment is accompanied by a large amount of defluorination, incorporation of oxygen and nitrogen species, and by an increase of both γ^D and γ^P.

The adhesive properties of the treated samples are presented in *Figures 2* and *3*. Although the standard deviations are large, we notice a significant increase of the ultimate load as the power of the treatment increases. Furthermore, the adhesive properties are much better when the samples are treated with a low gas flow. With regard to the influence of the treatment time, the ultimate load increases rapidly for plasma

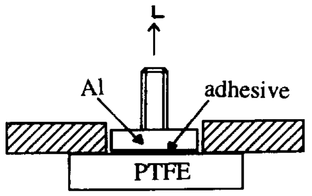

Figure 1 Schematic illustration of the pull-off test

Table 1 F/C, O/C and N/C atomic ratios, dispersive (γ^D) and non-dispersive (γ^P) components of the surface energy of the PTFE after various treatments and ultimate load at break (L_u) measured by the pull-off test between PTFE and an epoxy resin

Treatment conditions	F/C	O/C	N/C	γ^D (mN m^{-1})	γ^P (mN m^{-1})	L_u (N)
Untreated	2.50	0.06	–	16.2	0.2	31 ± 17
NH_3 plasma[a]	0.74	0.10	0.18	35.0	13.8	195 ± 42
H_2 plasma[b]	0.78	0.10	–	33.0	3.8	189 ± 21
Tetra-Etch	0.22	0.19	0.04	49.0	13.2	800 ± 100

[a] Treatment conditions: 500 W, 30 sccm, 120 s
[b] Treatment conditions: 350 W, 100 sccm, 120 s

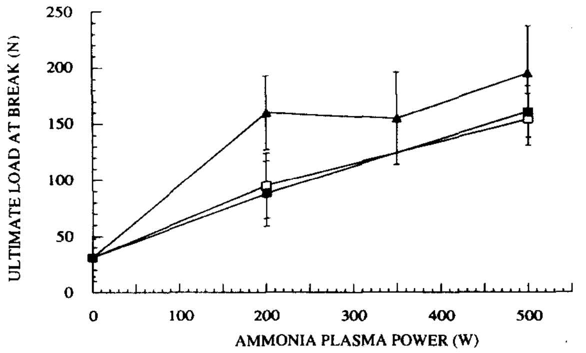

Figure 2 Ultimate load at break as a function of the ammonia plasma power for different gas flows: ▲, 30 sccm; □, 110 sccm; ■, 200 sccm

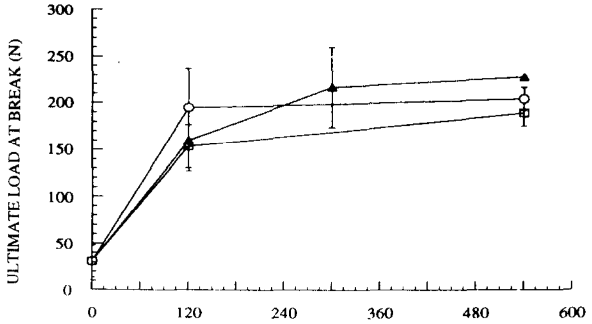

Figure 3 Ultimate load at break as a function of the ammonia plasma exposure time for different gas flows: ▲, 200 W–30 sccm; ○, 500 W–30 sccm; □, 500 W–110 sccm

exposure times less than 120 s and then it stays roughly constant. The adhesion properties are thus well related to the chemical surface modifications. Finally, the ammonia plasma treatment leads, under optimized conditions, to a sixfold increase of the ultimate load (*Table 1*).

**Hydrogen plasma treatment.* Unlike the ammonia plasma treatment, the hydrogen plasma treatment is not dependent on power, gas flow or exposure time[21]. Like ammonia treatment, it leads to a decrease in fluorine content (the F/C ratio is equal to 0.78, thus similar to that obtained after NH_3 plasma treatment) and to incorporation of a small amount of oxygen on the surface; however, no nitrogen species are introduced. Consequently, no great increase of the non-dispersive component of the surface energy is evidenced (*Table 1*). In spite of this difference, the ultimate load measured with the pull-off test is similar to that obtained for NH_3 optimized treatment conditions (*Table 1*).

**Comparison between the different treatments.* To summarize, all of the tested treatments lead to a high defluorination rate, more important, however, in the case of the chemical treatment. A noticeable amount of oxygen is incorporated mainly with the Tetra-Etch treatment. Nitrogen-containing species are mostly present with ammonia plasma treatment.

All the treatments increase the surface energy. The dispersive components are similar whatever the treatment, but the non-dispersive ones are better enhanced with ammonia plasma treatment and Tetra-Etch than with the hydrogen plasma treatment, due to a higher amount of polar moieties on the surface.

Hydrogen and ammonia plasma treatments increase the ultimate load by a factor of six relative to the untreated PTFE surface. This improvement seems to be more related to the degree of defluorination rather than to the presence of polar species at the surface. However, this load remains low compared with the one obtained with Tetra-Etch, as observed by Kaplan *et al.*[11]. Indeed, in addition to the defluorination, the oxygen uptake induced by the chemical treatment may also contribute to an increase of adhesion.

To obtain more information about the failure type of the specimens, the failure zones (PTFE side and stud side) were analysed by XPS. *Table 2* displays the C, F, O and N percentages as well as the F/C, O/C and N/C atomic ratios measured on untreated, chemically, NH_3 and H_2 plasma treated PTFE, and epoxy resin. From these results, the F/C atomic ratio appears a good indicator of the failure zone: failure in the epoxy matrix will lead to an F/C ratio of 0; failure in the bulk PTFE will be indicated by an F/C ratio near 2.5; and failure in the plasma-modified layer will give an intermediate value.

After chemical treatment and debonding, failure occurs in the PTFE near the modified zone: the F/C ratio is equal to 1.6 on the stud and equal to 2.1 on the PTFE sheet. Yamakawa[23] reached the same conclusion. According to him, the adhesion properties of chemically treated PTFE are limited by the poor properties of the modified layer and by the slight interfacial stress between this modified layer and the bulk PTFE.

With respect to the ammonia and hydrogen plasma treated samples, the same conclusions are reached. The F/C ratios measured on the stud and on the PTFE sample after NH_3 plasma treatment are both equal to 2.5. Similar results are obtained after hydrogen plasma treatment where an F/C ratio of 2.4 is obtained on the PTFE side.

Table 2 XPS chemical composition of all components used to realize the PTFE/epoxy matrix composite

	C(%)	F(%)	O(%)	N(%)	F/C	O/C	N/C
Untreated PTFE	27.7	70.5	1.8	0.0	2.5	0.07	0.00
Chemically-treated PTFE	68	14.7	13.2	2.7	0.22	0.19	0.04
NH_3-treated PTFE[a]	49.4	36.6	4.9	9.1	0.74	0.10	0.18
H_2-treated PTFE[b]	53.4	41.4	5.2	0.0	0.78	0.10	0.00
Epoxy matrix	78.4	0	9.9	11.7	0	0.13	0.15

[a] Treatment conditions: 500 W, 30 sccm, 120 s
[b] Treatment conditions: 350 W, 100 sccm, 120 s

Thus, in all cases, the locus of failure is between the modified layer and the bulk PTFE and never between the epoxy and the treated PTFE sample. The adhesion properties seem then to be limited by the presence of a weak boundary layer. The differences that we have observed between ultimate loads for chemically treated samples and for plasma-treated samples can be explained by the width of the modified layer. It is well known that chemical treatment induces modifications to greater depths than plasma downstream treatment[5,24]. Thus the modifications are probably more gradual than in the case of plasma treatment, explaining the better cohesion between the modified layer and the bulk material.

Adhesive properties of the PTFE fibres

The pull-off test results have shown an increase of the adhesion properties of the plasma-treated PTFE and they allow a better understanding of the failure mechanism. Nevertheless, this kind of test is not at all representative of what happens in a composite. Indeed, in the pull-off test, the specimens are loaded in tensile mode whereas in a composite the interface is loaded in shear mode. In the following, the effects of an ammonia plasma treatment on the adhesion properties between a single fibre and the epoxy resin is investigated by the microbond technique.

To make microdroplet formation easier, we chose an epoxy system with a low viscosity: it is composed of bisphenol A diglycidyl ether and methyl tetrahydrophthalic anhydride with $r = 0.85$ and 1% by weight of methyl imidazole. The glass transition temperature of the network is 135°C after the curing cycle (1 h at 100°C and 5 h at 160°C).

The treatment conditions applied to the fibres (500 W, 30 sccm, 120 s) were chosen following the results obtained from the pull-off test, where this treatment led to a six-fold increase of the pull-off ultimate load.

Before any treatment, it was very difficult to deposit correctly a microdroplet on the untreated fibres as observed in *Figure 4*. Nevertheless, some axisymmetrical microdroplets were obtained and they allowed measurement of the microdebonding load as a function of the embedded length (*Figure 5*). The type of load–displacement curve obtained is presented in *Figure 6a* and is representative of a debonding process. Due to the great difficulty in depositing large axisymmetrical microdroplets on untreated PTFE fibres, we will restrict our discussion to embedded lengths smaller than 200 μm. In this region, the debonding load is directly proportional to the embedded length and a mean interfacial shear stress can be calculated following:

$$\tau = F_d / \pi D_f L$$

where F_d is the debonding load (*Figure 5*), D_f the fibre diameter and L the embedded length. A mean value of 1.5 MPa is obtained from the initial slope.

Figure 4 Non-axisymmetric resin droplet on an untreated PTFE monofilament

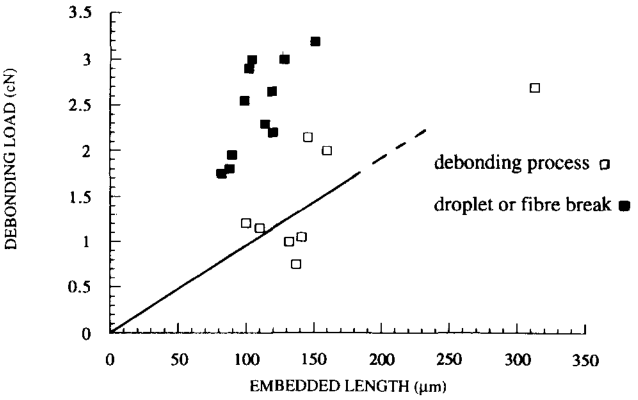

Figure 5 Debonding load as a function of the embedded length for untreated PTFE fibres (□) and for NH_3 plasma (500 W, 30 sccm, 120 s) treated PTFE fibres (■)

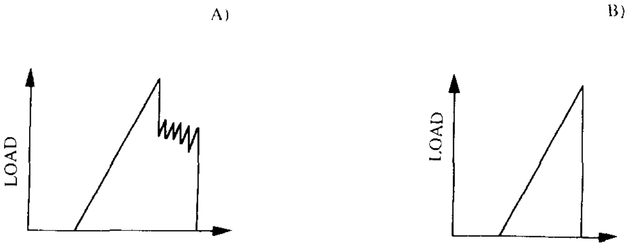

Figure 6 Various types of load–displacement curve obtained during the microbond test, indicative of (a) a debonding process and (b) fibre or matrix failure

After microwave plasma treatment the fibre wettability increased, making microdroplet formation easier. The evolution of the debonding load as a function of the embedded length is presented in *Figure 5*, underlining a significant increase of the adhesion properties after plasma treatment. In this case, the load–displacement curve obtained is represented in *Figure 6b*. The maximum load in this case is not representative of a debonding process but corresponds to the droplet or even to the fibre breaking as shown in *Figures 7* and *8*. After the plasma treatment, the adhesion properties are enhanced so that the droplet or the fibre breaks before the debonding process occurs.

CONCLUSION

The pull-off test results have shown a significant increase of the adhesion properties of PTFE surfaces treated by both hydrogen and ammonia plasmas, and by chemical treatment. These properties are mostly attributed to defluorination of the surface and the incorporation of a large amount of oxygen moieties in the case of chemical treatment. Hydrogen and ammonia plasma treatments increase the ultimate load by a factor of six, but their efficiencies remain low compared with the Tetra-Etch treatment. In all cases, failure appears in the weak boundary layer. Since the chemical treatment penetrates more in depth than the plasma treatments[5,24], the modifications are more gradual in the former case and lead to better cohesion between the modified layer and the bulk material.

The adhesion results obtained by the microbond technique demonstrate the increased adhesive properties of the ammonia-plasma-treated PTFE fibres. Furthermore, such a treatment leads to an enhanced wettability of the fibres by the epoxy resin.

Figure 7 Matrix failure during the microbond test applied to an NH_3-treated PTFE fibre/epoxy assembly

Figure 8 Fibre failure during the microbond test applied to an NH_3-treated PTFE fibre/epoxy assembly

ACKNOWLEDGEMENTS

The authors wish to thank DRET (Direction des Recherches Etudes et Techniques) for supporting this work and Région Rhône Alpes for providing a scholarship to one of us (J.P. Badey).

REFERENCES

1 Siperko, L.M. and Thomas, R.R. *J. Adhes. Sci. Technol.* 1989, 3(3), 157
2 Purvis, R.J. and Beck, W.R. *US Patent 2789063*, to 3M Company
3 Dwight, D.W. and Rigs, W.M. *J. Colloid Interf. Sci.* 1974, **47**(3), 650
4 Costello, C.A. and McCarthy, T.J. *Macromolecules* 1984, **17**, 2940
5 Rye, R.R. *J. Polym. Sci., Part B: Polym. Phys.* 1988, **26**, 2133
6 Benderley, A.A. *J. Appl. Polym. Sci.* 1962, **6**, 221
7 Yasuda, H., Marsh, H.C., Brandt, E. and Reilley, C.N. *J. Polym. Sci: Polym. Chem. Edn* 1977, **15**, 229
8 Momose Y, Tamura, Y, Ogino, M., Okazaki, S. and Hirayama, M. *J. Vac. Sci. Technol.* 1992, **A10**(1), 229
9 Dekker, A., Reitsma, K., Ceugeling, T., Bantjes, A., Feijen, J. and Van Aken, W.G. *Biomaterials* 1991, **12**, 130
10 Hirotsu, T. and Ohnishi, S. *J. Adhes.* 1980, **11**, 57

11 Kaplan, S.L., Lopata, E.S. and Smith, J. *Surf. Interf. Anal.* 1993, **20**, 331

12 Hollahan, J.R., Stafford, B.B., Falb, R.D. and Payne, S.T. *J. Appl. Polym. Sci.* 1969, **13**, 807

13 Collins, G.C.S., Lowe, A.C. and Nicholas, D. *Eur. Polym. J.* 1973, **9**, 1173

14 Inagaki, N., Tasaka, S. and Kawai, H. *J. Adhes. Sci. Technol.* 1989, **3**(8), 637

15 Mora, M., Occhiello, E. and Garbassi, F. *Surf. Interf. Anal.* 1990, **16**, 412

16 Golub, M.A., Wydeven, T. and Cormia, R.D. *Langmuir* 1991, **7**, 1026

17 Youxian, D., Griesser, H.J., Mau, A.W.H., Schmidt, R. and Liesegang, J. *Polymer* 1991, **32**(6), 1126

18 Mascia, L., Carr, G.E. and Cember, P. *Plastics Rubber Process Applic.* 1988, **9**, 133

19 Egitto, F.D. and Matienzo, L.J. *Polym. Degrad. Stabil.* 1990, **30**, 293

20 Badey, J.P., Urbaczewski-Espuche, E., Jugnet, Y., Sage, D., Tran Minh Duc and Chabert, B. *Polymer* 1994, **35**(12), 22472

21 Badey, J.P., Espuche, E., Jugnet, Y., Batier, C., Sage, D., Tran Minh Duc and Chabert, B. *Polymer* to be published

22 Miller, B., Muri, P. and Rebenfeld, L. *Compos. Sci. Technol.* 1987, **28**, 17

23 Yamakawa, S. *Macromolecules* 1979, **6**, 1222

24 Rye, R.R. and Arnold, G.W. *Langmuir* 1989, **5**, 1331