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Plasma-treatment of polyetheretherketone (PEEK) for adhesive bonding

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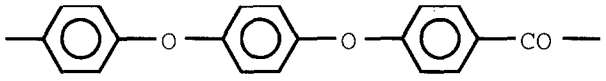
Polyetheretherketone (PEEK) has been treated with oxygen-, air-, argon- and ammonia-plasmas, which greatly improve adhesion to an epoxide film adhesive. Treated surfaces can be stored under laboratory conditions for up to 90 days without significant loss of the improved adhesion properties. Contact angle measurements show that the surface energy of PEEK is much increased by plasma-treatment. X-ray photoelectron spectroscopy shows that the plasmas increase the amounts of oxygen and in some cases the amounts of nitrogen, and that new surface groups include —OH and —CO—. Wiping treated surfaces with acetone can reverse the effects of plasma-treatment.

(Keywords: B. Plastic, B. Surface treatment by excited gases, C. Infrared spectra, C. X-ray photoelectron spectroscopy)

INTRODUCTION

Polyetheretherketone (PEEK) is an engineering thermoplastic with outstanding heat-resistance, having the structure shown below. The glass transition temperature is 144°C, the melting point 335°C and it is typically melt processed at 370°C[1]. A major use of PEEK is as matrix–polymer for carbon-fibre reinforced composites.



polyetheretherketone

There has been a number of reports involving treating the surface of PEEK, or composites containing a PEEK matrix, with the intention of improving adhesive bonding. Kinloch and Taig[2] showed that solvent-cleaning is ineffective, and Hadman and Evans[3] when using silicon carbide paper to abrade the surface, obtained weak joints which failed adhesively. Silverman and Griese[4] blasted PEEK with an alumina grit and then cleaned the surface with deionized water, the small increase in adhesion to an epoxide film adhesive was ascribed to an increase in surface area. Carbon-fibre PEEK composites have been claimed to have been successfully treated for adhesive bonding and blasting, by Yoon and McGrath[5], but Davies *et al.*[6] found that sandblasting gave low joint strengths. Corona-discharge treatment in air can also improve adhesion to PEEK composites[7–9].

Chemical methods which have been used to treat the surfaces of PEEK composites include sodium naphthalenide in tetrahydrofuran[3], permanganate–sulfuric acid[7], nitric–sulfuric acid[3] and chromic–sulfuric acid[4,6,10], the latter appearing to be the most effective.

The use of plasma to treat polymers has been known for more than 20 years and all the major reactions are thought to involve free radicals or ions[11]. Polymer surfaces can be cleaned, etched or chemically modified, but only the topmost 2–3 mm is affected. Plasmas from several gases have been found to enhance the adhesive bonding of PEEK composites[3–6,8,13]. Surface characterization of plasma-treated PEEK has been reported by several authors[3–6,8,12–16]. Blackman, Kinloch and Watts[17] used oxygen-plasma and corona discharge in air to improve adhesion to PEEK composites.

We now report the use of oxygen-, air-, argon- and ammonia-plasmas to treat PEEK for improved adhesive bonding. We considered it possible that oxygen-, air- and ammonia-plasmas might introduce polar chemical groups to the PEEK surface which would enhance adhesion. Additionally chemical groups might be formed (e.g. —COOH, —NH_2) which chemically react with epoxide adhesives.

EXPERIMENTAL

Materials

PEEK film (Stabar K200) 0.25 mm thick was supplied by ICI. The adhesive used was the epoxide film with a carrier, AF-163-2K (3M). Gases were obtained from BOC and had the following purities (oxygen 99.5%, argon 99.95%, ammonia 99.98%). HPLC grade acetone of at least 99.9% purity was used.

Plasma-treatment

All PEEK films were initially cleaned with a tissue soaked in acetone. Plasma-treatment was carried out in a Plasma Technology "System 80" apparatus, which operated at a frequency of 1×10^5 Hz and had a maximum power of about 1 kW. A rotary vacuum pump permitted the pressure to be lowered to about 35 Pa in a few minutes. Samples were mounted in the middle of the chamber using a clip, so that both sides were equally treated. After pumping the chamber to the base-pressure it was filled with test gas and then again pumped to the base-pressure. This was repeated twice and then chamber was then filled with the test gas to the required pressure. After plasma-treatment the chamber was vented with air.

Joint preparation and testing

Joints for T-peel tests were prepared with two pieces of PEEK measuring 125 mm by 25 mm bonded along 75 mm. Curing of the adhesive was at 100°C for 30 min under vacuum to minimize the formation of voids, and then for 90 min at 120°C between steel platens, and under weights to give a pressure of about 17 kPa; the samples were allowed to cool to room temperature in this condition. Joints were tested at room temperature in a Lloyd 1000 testing instrument using a crosshead speed of 254 mm min^{-1}. Three replicate samples were used.

Lap shear joints consisted of two steel adherends which had been treated with abrasive paper, with an adhesive–PEEK–adhesive sandwich in the overlap region which measured 25×12 mm. They were held together with clips during curing which was under the same conditions for the peel joints. Here the crosshead speed for testing was 3 mm min^{-1}, and five replicates were used.

Contact angle measurement

The liquids used for the contact-angle measurements were triply distilled water and special grades of ethanediol (ED), dimethylsulphoxide (DMSO) and dimethylformamide (DMF) obtained from Romil Chemicals Ltd, Shepshed, Leicestershire. Some contact angles were measured using BDH pH 4.0 and pH 10.0 phthalate buffer solutions. The syringes which were used to place small drops of the liquids on the film surfaces were each dedicated to handle only one of the liquids. Each syringe was rinsed five times before being finally filled. The volumes of the drops were about 3 μl, at least four were used. Contact angles were measured using a Krüss G40 Contact Angle Measuring System, which is a microscope with a goniometer in the eyepiece. A sample of adhesive was cured in a laboratory oven and then used for measurements of contact angle.

X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained using a VG Escalab Mark II at Loughborough Consultants Ltd, or a Surface Sciences M-Probe at CSMA Ltd. The primary beam in both cases was AlK_α X-rays.

Trifluoracetic anhydride (TFAA) and 2,2,2-trifluoroethanol (TFE) were used as specific reagents to tag hydroxyl and carboxylic acid groups[18–20], on treated PEEK surfaces, using the following chemical reactions.

$$(CF_3CO)_2O + HO— = CF_3COO— + CF_3COOH$$

TFAA

$$CF_3OH_2OH + HOOC— = CF_3OH_2OOC— + H_2O$$

TFE

These have the advantage of substituting one —OH or —COOH group with three fluorine atoms, which have high relative atomic sensitivities. The reactions were carried out by exposing PEEK films to vapours of the reagents at room temperature, on a vacuum line for 24 h. XPS spectra were obtained within a further 24 h.

Scanning electron microscopy

Fractured joints were sputter coated with gold, and examined in a Cambridge model 300 scanning electron microscope.

Acetone-treatment and Fourier transform infrared spectroscopy (FTIR)

Films of treated and untreated PEEK measuring 100 mm × 90 mm were immersed in 2 cm^3 acetone for one week and the resulting solutions were examined by transmission FTIR. Spectra were obtained using a Galaxy series 3000 FTIR made by Mattson Instruments.

RESULTS AND DISCUSSION

The standard conditions for plasma-treatment were for 60 s at a power of 500 W and a gas pressure of 40 Pa. These conditions were used throughout, unless otherwise stated.

Joint strengths

Peel test results for PEEK treated with oxygen-plasmas are shown in *Table 1*, where the following codes are used to indicate locus of failure:

I, internal failure between adhesive and PEEK as judged by eye;

Table 1 Peel strengths for PEEK after oxygen-plasma treatment

Treatment conditions			Mean peel strength and range ($kN\,m^{-1}$)	Locus of failure
Time (s)	Power (W)	Pressure (Pa)		
untreated			0±0	I
Effect of treatment time				
30	300	40	0.84 ± 0.04	I + C
60			4.23 ± 0.36	C + M
120			4.18 ± 0.09	C + M
360			3.90 ± 0.03	C
600			4.03 ± 0.20	C + M
1800			4.07 ± 0.08	C
Effect of power				
60	300	40	4.23 ± 0.36	C + M
	400		4.29 ± 0.04	C
	500		4.64 ± 0.02	C + M
	600		4.84 ± 0.11	C + M
600	300	40	3.80 ± 0.35	C + M
	400		3.88 ± 0.06	C
	600		3.72 ± 0.29	C + M
Effect of pressure				
60	600	40	4.84 ± 0.11	C + M
		53	4.13 ± 0.10	C
		67	4.42 ± 0.16	C + M
Effect of over-treatment, i.e. high power for long time				
600	600	53	3.77 ± 0.35	C

C, cohesive failure in the adhesive, and
M, material failure by tearing of the PEEK.

Errors shown are the maximum and minimum values. It can be seen that adhesion to the untreated material is very low, and that all oxygen-plasma treatments give considerable increases in peel strength, reaching a maximum value of about $4\,kN\,m^{-1}$ after 1 min at 300 W. Treatment beyond this time offers no increase in peel strength. Increasing the power from 300 to 600 W at 60 s treatment time gives a further increase in peel strength with failure passing from the adhesive to PEEK. Increasing the gas pressure at 60 s tends to lower peel strength, but at 600 s it is unaltered. Apart from the first two entries in *Table 1*, all peel strengths and loci of failure are quite similar. This is very similar to what was observed by Blackman *et al.*[17], namely that joints with untreated PEEK–composite adherends failed interfacially at low loads, but oxygen-plasma treatment increased strengths to a maximum.

Peel strengths of joints treated with oxygen-, air-, argon- and ammonia-plasmas are given in *Table 2*. It shows that all joints with plasma-treated PEEK have similar strengths, the only possible exception being those which used argon-plasmas.

Strengths of lap joints are given in *Table 3*, where errors shown are standard deviations. In comparing these results with those in *Table 1*, it is noted that whilst untreated PEEK gives zero peel strengths, lap-shear strengths are fairly high, and all are approximately doubled as a result of plasma-treatment.

Contact angles

The dispersion (γ_S^d) and polar force (γ_S^p) contributions to the surface energy of the polymeric solid are related

Table 2 Peel strengths of PEEK treated with plasmas

Plasma gas	Treatment conditions			Peel strength $kN\,m^{-1}$	Failure mode
	Time (s)	Power (W)	Pressure (Pa)		
Oxygen	60	500	40	4.64 ± 0.02	C + M
Oxygen	60	600	53	4.13 ± 0.10	C
Air	60	500	40	4.19 ± 0.07	C + M
Air	60	600	53	4.00 ± 0.38	C
Argon	60	500	40	3.36 ± 0.32	C
Argon	300	500	40	3.85 ± 0.27	C
Ammonia	60	500	40	4.05 ± 0.11	C
Ammonia	60	600	53	4.00 ± 0.09	C

Table 3 Lap shear strength for joints with PEEK with a standard plasma-treatment

Plasma gas	Joint strength (MPa)	Failure mode
Untreated	16.9 ± 1.3	I + C
Oxygen	34.0 ± 1.4	C + M
Air	29.1 ± 1.2	C + M
Argon	33.4 ± 1.0	C + M
Ammonia	32.2 ± 2.1	C + M

Table 4 Surface energy parameters of test liquids

Liquid	γ_L^d ($mJ\,m^{-2}$)	γ_L^p ($mJ\,m^{-2}$)	Ref.
Water	21.8 ± 0.7	51.0	22
Ethane diol	29.3	19.0	23
Dimethyl sulphoxide	34.86	8.68	24
Dimethyl formamide	32.42	4.88	24

to the contact angle (Θ) made by liquid droplets placed on the solid by equation (1), where γ_S^d and γ_S^p are the dispersion and polar force contributions to the surface energy of the liquids, and γ_{LV} is the surface free energy of the liquids when in equilibria with their saturated vapours.

$$\gamma_{LV}(1 + \cos\Theta)/2(\gamma_L^d)^{1/2} = (\gamma_S^d)^{1/2} + (\gamma_S^p\gamma_L^p/\gamma_L^d)^{1/2}. \quad (1)$$

This means that if $\gamma_{LV}\ (1 + \cos\Theta)/2(\gamma_L^d)^{1/2}$ is plotted against $(\gamma_L^p/\gamma_L^d)^{1/2}$, (A Fowkes plot) the graph should be linear with intercept $(\gamma_S^d)^{1/2}$ and slope $(\gamma_S^p)^{1/2}$, so permitting the determination of γ_S^d and γ_S^p. The subject of contact angles and adhesive bonding has been reviewed by Comyn[21]. Values of γ_L^d and γ_L^p for the liquids used are given in *Table 4*.

Contact angles on various surfaces are given in *Table 5*. The standard oxygen-plasma treatment for PEEK gives zero contact angles with all the four liquids, and this remains so if the treatment is increased in any way.

A Fowkes plot for untreated PEEK film appears in *Figure 1*, and the values of γ_S^d and γ_S^p obtained from this, and other plots (which are not shown here), are given in *Table 6*. Details of the estimation of errors are given by Comyn *et al.*[25] The reliability of these values may be further reduced because spreading pressure is likely to be significant when contact angles are low, but it is reasonable to conclude from the data, that the treated PEEK surfaces are very polar. Contact angles

Table 5 Contact angles on PEEK and adhesive surfaces

Surface	Treatment conditions			Contact angles (degrees)			
	Time (s)	Power (W)	Pressure (Pa)	Water	ED	DMSO	DMF
PEEK							
Untreated				71	51	42	8.5
Oxygen-plasma	60	300	40	25	0	0	0
Oxygen-plasma	60	500	40	0	0	0	0
Ammonia-plasma	60	500	40	37	28	26	<5
Cured adhesive				73	58	54	50

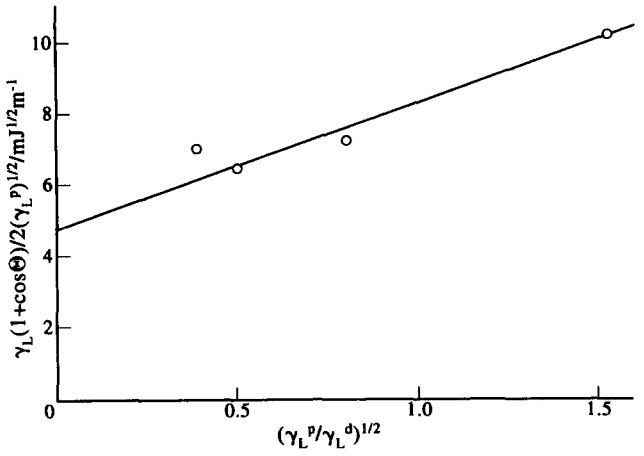


Figure 1 Fowkes plot for liquids on the surface of untreated PEEK

Table 6 Surface energy components of PEEK and adhesive surfaces

Surface	γ_S^d (mJ m^{-2})	γ_S^p (mJ m^{-2})
PEEK		
Untreated	12.5 ± 3	23 ± 4
Oxygen-plasma	10 ± 4	63 ± 10
Ammonia-plasma	14 ± 4	44 ± 8
Cured adhesive	14 ± 1	17 ± 2

Table 7 Thermodynamic work of adhesion between epoxide adhesive and PEEK

PEEK surface treatment	W_A (mJ m^{-2})
Untreated	66 ± 5
Oxygen-plasma	89 ± 8
Ammonia-plasma	83 ± 7

of pH 4 and pH 10 buffer solutions on oxygen-plasma treated PEEK were less than 5°.

The values of γ_L^d and γ_L^p are at some variance with others given in the literature for epoxide adhesives. Kinloch[26] gives values of about 40 mJ m^{-2} for γ_L^d and 5–8 mJ m^{-2} for γ_L^p.

The thermodynamic work of adhesion between the adhesive and PEEK W_A can be calculated from equation (2), where the subscripts now denote A = adhesive and S = substrate. Values calculated for some of the interfaces are shown in *Table 7*, such large and positive values indicate stable adhesive interfaces

$$W_A = 2[(\gamma_A^d\gamma_A^d)^{1/2} + (\gamma_S^p\gamma_S^p)^{1/2}]. \quad (2)$$

XPS

Information from XPS survey spectra for PEEK subjected to standard plasma-treatments is given in *Table 8*. The results show that the amount of oxygen is untreated material is close to what is expected from the molecular structure of PEEK, and there is a small amount of nitrogen which is difficult to account for. Ammonia- and argon-plasmas increase the amount of nitrogen, and oxygen- and air-plasmas reduce it. Oxygen-, air- and argon-plasmas increase the amount of surface oxygen by the same amount while ammonia gives a lesser increase. The method which we have used to fill the plasma-chamber is not expected to rigorously exclude air, and it is evident from the XPS data that residual oxygen in argon- and ammonia-plasmas is highly reactive. Desorption of oxygen from the chamber walls may be particularly important.

Table 8 Atomic analyses per 100 carbon atoms from survey spectra

Plasma gas	Nls	Ols
Untreated PEEK	3.8	16.3
Oxygen	1.3	28.6
Air*	2.2	31.0
Argon*	9.0	30.2
Ammonia	9.5	21.4

*LCL instrument. The level of oxygen in the repeat unit of PEEK is 15.7.

There are four peaks which occur in the high resolution carbon 1s spectra of PEEK, these are illustrated for the untreated and oxygen-plasma PEEK in *Figure 2*. Details of the relative amounts of these, obtained from curve-fitting appear in *Table 9*.

The assignment of the three peaks of lowest binding energy are those given by Beamson and Briggs[27] and Pawson *et al.*[16], i.e. 285.0 eV aromatic carbon not bonded to oxygen, 286.7 eV aromatic carbon bonded to oxygen and 288.0 eV carbonyl. The peak at 289.3 eV which is produced by all the plasma-gases, and which is removed or much reduced by acetone, is due to —COO groups in either an ester or an acid. This is evident from the assignments for polymethylmethacrylate and polymethacrylic acid by Beamson and Briggs. The increase in intensity of the 286.7 eV peak on treated surfaces could be due to an increase in the amount of C—O or C—N bonds.

There are two peaks in the high resolution oxygen 1s

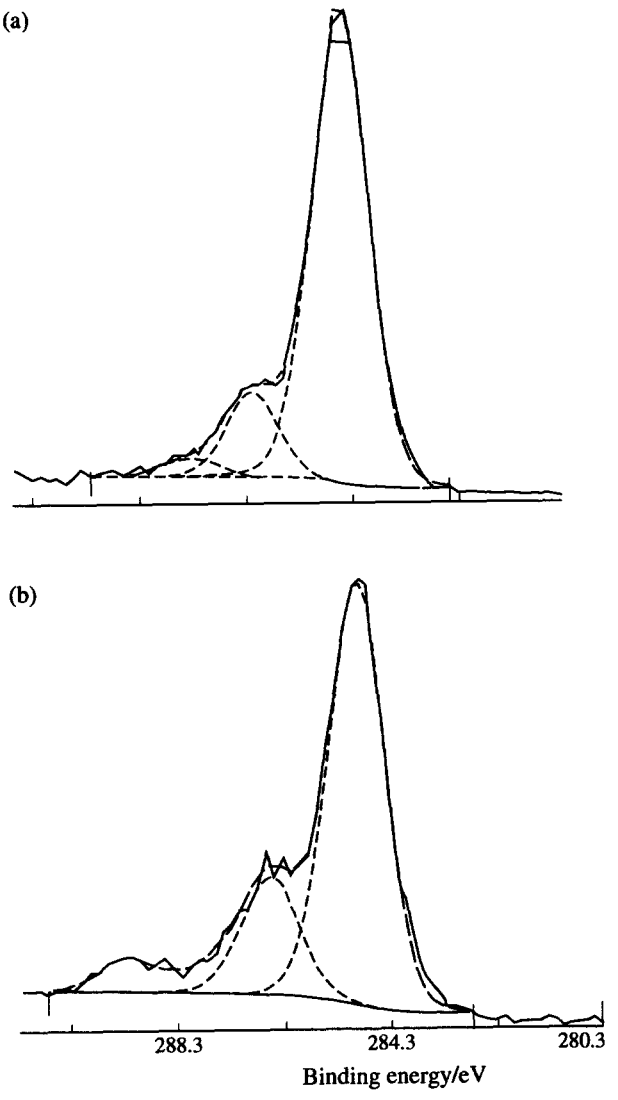


Figure 2 High resolution carbon 1s spectra of (a) untreated PEEK and (b) PEEK after treatment with standard oxygen plasma

spectra of PEEK and details of the relative amounts of these, obtained from curve-fitting appear in *Table 10*. The peak at 531.2 eV is due to carbonyl and that at 533.5 eV to ether. Ammonia-plasma does not alter the ratio of C—O to C=O ratio, but oxygen-plasma increases the amount of C=O.

Nitrogen 1s spectra were obtained for the three samples treated with ammonia, all were of poor quality but indicated two components in roughly equal quantities at about 399.5 eV and 400.6 eV.

XPS analyses of PEEK surfaces treated with the fluorinated reagents TFAA and TFA are given in *Table 11*. They show that large amounts of hydroxyl and carboxylic acid groups are introduced by plasma-treatment.

Scanning electron microscopy

The surfaces of the PEEK films, before and after treatment in standard plasmas were smooth and featureless, showing that changes in surface roughness cannot account for any increases in joint strengths.

Table 9 Relative intensities (%) of components in high resolution carbon 1s spectra

Gas	Solvent wipe	Binding energy (eV)			
		285.0	286.7	288.0	289.3
Molecular structure		75	21	5	0
Untreated PEEK	None	84	14	3	
Oxygen	None	71	20	4	6
Oxygen	Acetone	78	19	2	1
Ammonia	None	71	20	6	2
Ammonia	Acetone	76	18	5	

Table 10 Relative intensities (%) of components in high resolution oxygen 1s spectra

Gas	Solvent wipe	Binding energy (eV)	
		531.2	533.5
Molecular structure		33	67
Untreated PEEK		50	50
Oxygen	None	43	57
Oxygen	Acetone	45	55
Ammonia	None	68	32
Ammonia	Acetone	63	37

Table 11 Atomic analyses of fluorinated PEEK surfaces, atoms per 100 C atoms

Plasma gas	Tagging reagent	O	N	F	% Total oxygen as	
					—OH	—COOH
Oxygen	TFAA	30.1	0	9.9	12.3	
Air	TFAA	35.3	3.3	13.7	14.8	
Argon	TFAA	32.0	0.7	9.6	11.1	
Oxygen	TFE	35.6	0	8.7		16.3
Air	TFE	32.0	0	7.5		15.6
Argon	TFE	32.5	0	4.6		9.4

Aging treated PEEK in ambient conditions

Some samples of PEEK which had been treated with an oxygen-plasma were stored in the laboratory at room temperature for up to 90 days before being bonded. Results of peel tests are given in *Figure 3*; experimental scatter was less than the size of the points and failure was C + M. Clearly peel strength is not affected by aging for 30 days, but there is then a slight fall.

Other samples which had been treated with an ammonia-plasma were aged for up to 90 days before being incorporated into lap-joints. Strengths fell steadily from 35.5 ± 1.1 MPa to 30.8 ± 1.3 MPa over 90 days and failure was a mixture of C + M. It is clear that even after 90 days storage in laboratory air, strong adhesive bonds can be made to plasma-treated PEEK.

Effect of solvent wiping on the surface of PEEK

Table 12 shows the effect of wiping plasma-treated PEEK surfaces with acetone, on peel strength, water contact angles, and the amounts of surface oxygen and nitrogen as revealed by XPS. Data on the effect of acetone on high resolution carbon 1s and oxygen 1s spectra appear in *Tables 9* and *10*.

Table 12 Effect of solvent wiping on the surface of PEEK

Plasma gas	Solvent	Peel strength (kN m^{-1})	Failure mode	Θ^0_{water}	Atoms per 100 C	
					O	N
Oxygen	None	4.65 ± 0.03	C + M	<5	28.6	1.3
	Acetone	very low	I + C	77	24.1	0
Air	None	4.19 ± 0.07	C + M	<5	31.0	2.2
	Acetone	very low	I + C	76	28.7	0
Argon	None	3.36 ± 0.20	C	<5	30.2	9.0
	Acetone	3.80 ± 0.15	C	76	33.3	0
Ammonia	None	4.05 ± 0.15	C	37	21.4	9.5
	Acetone	3.99 ± 0.14	C	57	19.3	6.7

Figure 3 Effect of ageing in laboratory conditions on peel strengths to PEEK, which had first been treated with a standard oxygen plasma

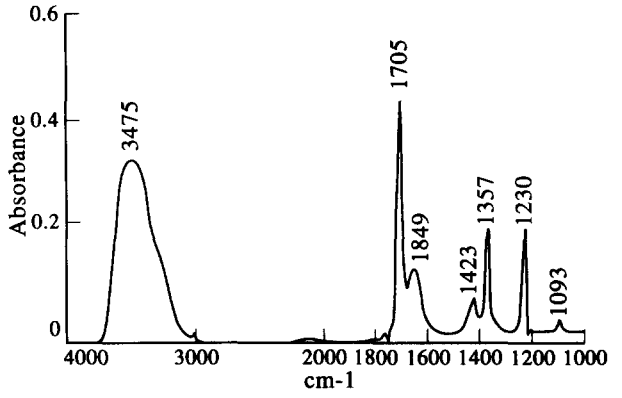


Figure 4 FTIR difference spectrum of acetone which had been in contact with plasma-treated PEEK

The effect of acetone on PEEK which has been treated with oxygen- and air-plasmas is severe, in that peel strength is reduced almost to zero, the locus of failure returns to the interface, the contact angle of water resumes high values, and levels of oxygen and nitrogen are reduced. The data suggest that the treatment produces small molecules which are acetone-soluble. From the peel strength results it would seem that surfaces treated with argon- and ammonia-plasmas are not so strongly affected by acetone wiping.

Pawson *et al.*[16] recorded the secondary ion mass spectra (SIMS) of PEEK which had been treated by oxygen plasma and then rinsed in methanol. The effect of methanol was to remove or reduce the intensity of most of the peaks which had been introduced by the plasma-treatment.

FTIR spectra of acetone which had been in contact with PEEK treated with air-, oxygen- and ammonia-plasmas were markedly different from that of the solvent, but those treated with an argon-plasma were not. An FTIR difference spectrum (acetone used to immerse oxygen-plasma treated PEEK minus solvent) is shown in *Figure 4*, and the peaks can be assigned in the following manner[28].

3475 cm^{-1}, —OH stretching mode.
1705 cm^{-1}, >C=O stretching mode, the range for carboxylic acids is 1700–1725 cm^{-1}.
1649 cm^{-1}, asymmetric stretching mode of carboxylate anion.
1423 cm^{-1}, —C—O stretching mode in carboxylic acid.
1367 cm^{-1}, symmetric stretching mode of carboxylate anion.
1230 cm^{-1}, C—H in plane bending mode for 1,4-substituted benzene ring.

This indicates that the substance removed by acetone is 4-substituted benzoic acid, which could be formed when PEEK chains are attacked by plasmas. A difficulty however is to account for the presence of carboxylate anions, which cannot occur without a counterion. Because cations from the commoner metals such as sodium and calcium are clearly absent, the only possible common counterion is the ammonium ion, which seems likely from the SIMS spectrum of PEEK treated by oxygen-plasma reported by Pawson *et al.*[16] where a positive ion of mass 18 was attributed to the ammonium ion.

Effect of heat treatment on PEEK

Samples of untreated and plasma-treated PEEK were aged in an oven for 1 h at 180°C, before constructing lap-joints. Joint strengths are given in *Table 13*. With untreated PEEK, strengths are the same within the experimental scatter, but those which were plasma-treated are both weakened. The effect of aging PEEK, which has been treated with oxygen-plasma, at lower temperatures is shown in *Table 14*,

Table 13 Effect of heating PEEK films prior to adhesive bonding

Plasma gas	Lap-shear strength (MPa) and mode of failure	
	Unheated PEEK	PEEK heated for 1 h at 180°
Untreated	16.9 ± 1.6 (I + C)	13.0 ± 5.0 (I + C)
Oxygen	34.8 ± 0.8 (C + M)	15.2 ± 6.9 (I + C + M)
Ammonia	33.2 ± 1.4 (C + M)	26.4 ± 1.0 (C + M)

Table 14 Effect of heating oxygen-plasma PEEK films at different temperatures prior to adhesive bonding

Temperature (°C)	Lap-shear strength (MPa)	Mode of failure	Water contact angle
Ambient	34.8 ± 0.8	C + M	<5
120	33.1 ± 1.0	C + M	59
150	31.5 ± 1.4	C + M	74
180	15.2 ± 6.9	I + C + M	73

Table 15 Effect of annealing PEEK at 180°C on strengths of lap-joints

Anneal time (h)	Degree of crystallinity	Joint strength (MPa)	
		Untreated (a)	Oxygen plasma (b)
0	0	16.9 ± 1.5	34.8 ± 0.8
0.5	0.31	15.5 ± 4.3	30.8±1.7
1.0	0.32	13.0 ± 4.0	31.3 ± 1.0
2.0	0.32	12.6 ± 3.3	30.9 ± 2.4
4.0	0.34	9.3 ± 0.2	32.1 ± 0.4

(a) failure was I + C. (b) failure was C + M.

showing that the phenomenon which causes weakening takes place between 150 and 180°C. These changes are probably due to the volatilization of substances from the PEEK surface. An alternative explanation is that the ammonium carboxylate moiety postulated above decomposes on heating first to an amide and then to a nitrile, with the elimination of water at both steps, i.e.

$$—COONH_4 = —CONH_2 = —CN$$

Heat-treatment can cause PEEK to crystallize. The effect that this has on adhesive bonding was examined by heating films at 180°C for up to four hours, measuring degree of crystallinity by DSC, and then using films to make single lap-joints. Degree of crystallinity was measured from peak areas using a value of $130\,J g^{-1}$ for the heat of fusion[29,30]. Joint strengths are shown in *Table 15*. It can be seen that there is a possible slight weakening as untreated material crystallizes, but subsequent treatment with oxygen-plasma removes these differences.

POSSIBLE MECHANISMS OF PLASMA-TREATMENTS

A possible explanation of the above observations is that oxygen attacks carbonyl groups in PEEK to give —Ph—COOH groups. Further attack may release small molecules such as benzoic acid or 4-hydroxybenzoic acid, both of which are soluble in acetone[31] and volatile at 180°C. This is supported by the following observations.

(i) All plasma-gases increase the amount of surface oxygen.
(ii) The carbon 1s peak at 289.3 eV which is due to —COO— is produced by all plasma-gases, and is removed or much reduced by acetone.
(iii) Derivatization with TFA and TFE indicate the formation of both —COOH and —OH groups.
(iv) The surface energy of PEEK is $35\,mJ m^{-2}$ which is very close to that for polyethylene which is $36.1\,mJ m^{-2}$ [32]. Holmes-Farley *et al.*[33] have introduced specific chemical groups to the surface of polyethylene and observed the effect on contact angles for water. That for untreated polyethylene is about 100° and introducing polar groups can lower this to 70° —$COOCH_3$ and —CH_2OH can lower this to about 70°. The introduction of —COOH groups lowers water contact angle to about 53° but if the droplet is an alkaline aqueous buffer solution the angle drops to about 20° as the groups ionize. With PEEK the water contact angle is 71° and it is tempting to think that the very low values after plasma-treatment are due to the formation of ionizable groups, or charged groups. Contact angles with acid and alkaline buffers on oxygen-plasma treated PEEK are also very low, indicating that both acidic (—COOH) and basic (e.g. —NH_2) groups are formed.

Predictions about adhesion which are based on contact angle measurements can only be valid if the mechanism of adhesion is physical adsorption. If —COOH groups are formed on the PEEK surface they would be expected to react with epoxide groups in the adhesive so that covalent bonds are formed between adhesive and polymer. Chemical bonding would then be a significant mechanism of adhesion. Carboxylic acid anhydrides are a major group of hardeners for epoxides[34]; the initial reaction produces —COOH groups which then react with further epoxide groups. Such hardeners are only effective at elevated temperatures.

Should 4-hydroxybenzoic acid or a similar substance be formed by air- and oxygen-plasmas, it could act as a coupling agent by hydrogen-bonding to >C=O groups in PEEK by its —OH groups.

CONCLUSIONS

(1) PEEK surfaces are smooth and not roughened by treatment with plasma or subsequent treatment with acetone.
(2) Treatment with the plasma-gases markedly increase peel and lap-shear adhesion to PEEK. Peel

strengths after treatment are all about $4\,kN\,m^{-1}$, whereupon the PEEK film ruptures instead of the interface. Lap joints fail at about 33 MPa with rupture of both adhesive and PEEK.

(3) The overall indications are that plasma-treated surfaces can be stored for at least 90 days in laboratory conditions, without significant loss of bondability.

(4) The polar component of the surface free energy of untreated PEEK is $23 \pm 4\,mJ\,m^{-2}$ and the dispersive component is $12.5 \pm 3\,mJ\,m^{-2}$. The polar component is much increased by plasma-treatments.

(5) XPS shows that —COO— groups are formed by plasma-treatment.

(6) The effect of acetone on air and oxygen plasma-treated PEEK is to remove the advantages of treatment. Heat treatment at 180°C has a similar effect with oxygen-plasma.

(7) FTIR analysis on acetone which had been in contact with treated PEEK is consistent with the formation of a small molecule such as 4-hydroxybenzoic acid.

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