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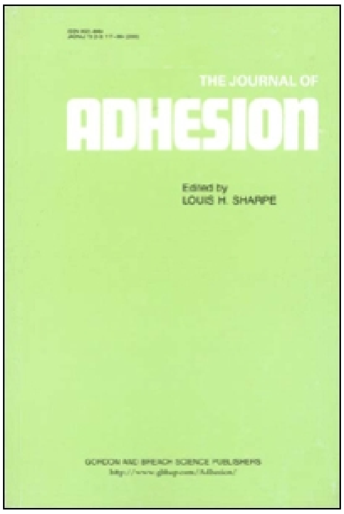

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Surface Treatment of Polyetheretherketone (PEEK) Composites by Plasma Activation*

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Carbon-fiber-reinforced PEEK composites (APC 2, ICI plc) were plasma treated for adhesive bonding. This was done in a microwave plasma in argon or oxygen. An epoxy-based film adhesive (AF 191, 3M) was employed for adhesive bonding (1 h curing at 175°C, 30 N/cm^2). Both plasma treatments resulted in a high level of lap shear strength (Ar: >40 MPa, 25°C). The environmental behaviour (42 d, 70°C hot water) of the adhesively bonded composites has also shown that good bonds could be obtained. Regarding the stability of the freshly-treated surfaces against exposure to the surrounding atmosphere only a small decrease in lap shear strength was observed. After storage for 4 weeks in air the strength was still almost 85% of that when the bonding was done directly after the treatment.

ESCA measurements revealed an increase in carbon-oxygen groups by the plasma treatment and a strong cleavage of the PEEK chemical structure.

KEY WORDS surface treatment; plasma activation; polyetheretherketone (PEEK); adhesive bonding; composites; lap shear strength.

INTRODUCTION

The selection of a joining technology which is equivalent to the specific material properties of fibre-reinforced composites is a prerequisite for their optimum technical application. Regarding this, adhesive bonding technology has been of great interest in the joining of fibre composites and is widely used.

In the field of composites, thermoplastic PEEK represents one of the most interesting engineering materials. PEEK shows processing flexibility associated with many advantages such as: chemical stability, a good fibre-matrix compound and excellent thermal and mechanical behaviour.

Adhesive bonding of this material is a useful technique, but an effective pretreatment procedure is necessary to produce good bonds. Low pressure R.F. plasma[1] and corona discharge[2] as well as other treatments have been tested. Although the plasma treatment has been shown to be attractive, the stability of the freshly-treated

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surface against exposure to air is unsatisfactory.[1] Furthermore, plasma chemical reactions are complex and mostly not well known. The type of plasma discharge (DC, AC, RF, MW) is often important for the reactions going on and particular parameters must be used to obtain certain reactions.

In this investigation a microwave plasma was employed for the pretreatment. This type of discharge is highly effective (high degree of ionisation) and, in addition, a more gentle treatment of the surface is attained due to the less important effects of ion bombardment.

EXPERIMENTAL

Materials

The material used was a 1 mm thick, 8-ply stack of carbon-fibre-reinforced PEEK. This material, of the type Fiberite APC 2/AS 4, was supplied by ICI plc. For some ESCA measurements additional samples from injection moulded bars of compact PEEK-thermoplastic material, type TK-PEEK, produced by Enzinger GmbH, Germany were employed.

All adhesive bonding tests were performed with an epoxy-based structural adhesive. A film adhesive (AF 191 K 0,08) from 3M Company that was used was cured at 175°C for 1 hour at a pressure of 30–35 N/cm^2 (Heating rate: 2–3°C/min). Prior to the application of the different surface pretreatments that were tested, all samples were degreased by an ultrasonic cleaning with methyl ethyl ketone (MEK) for 10 min.

The APC 2 composites, as well as special-sized samples, were prepared for ESCA studies. The special-sized samples were made from the compact thermoplastic material by breaking notched samples in liquid nitrogen. The obtained fracture surfaces were smooth in a sufficiently large region for the ESCA measurements. By this preparation method the influence of any contaminating species from release agents could be excluded.

Surface Treatment

A diagrammatic view of the experimental equipment is shown in Figure 1. The plasma reactor consists of a cylindrical quartz vessel (50 l) sited under a microwave source. A vertical gas flow exists in the reaction chamber due to the gas inlet at the top and the pumping port at the bottom. A well-defined gas flow is obtained by mass flow controllers (MKS, type 147B) and pressure measurement is performed by a MKS Baratron.

The power of the microwave (2.45 GHz) plasma discharge could be adjusted continuously up to 1000 W; mostly a level of 500 W was used. Exposure time of the PEEK samples to the plasma was between 10 seconds and 5 minutes. Commercial argon (99.999%, Messer Griesheim) or oxygen (99.995%, Messer Griesheim) were used. During the plasma treatment a pressure of 20 Pa was maintained.

The treatment in chromic sulphuric acid (CSA) was performed in accordance

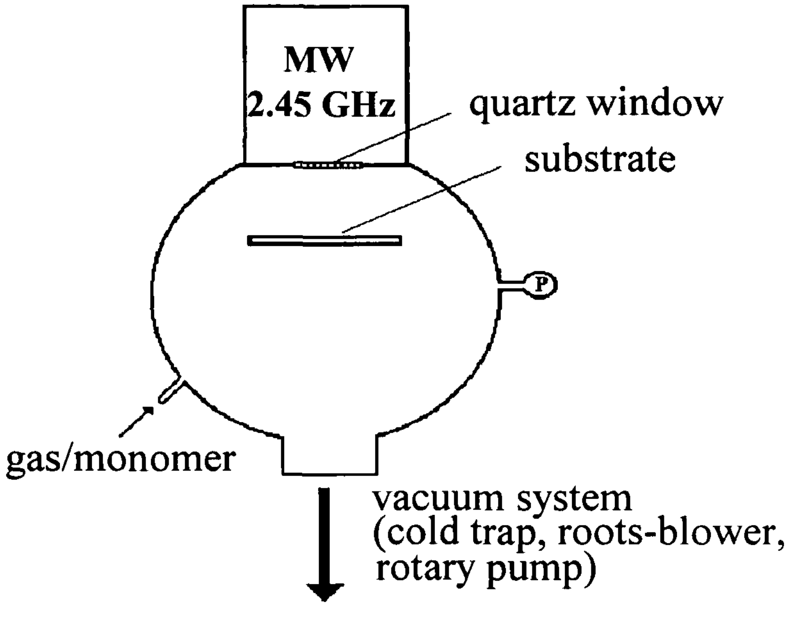

FIGURE 1 Plasma equipment.

with the specification of the standard practice in DIN 53281, part 1 for 30 min at 60°C.

A commercial corona facility (CEE 42-0-1MD, SOFTAL electronic GmbH, Hamburg, Germany) was used for the corona treatment. This treatment was carried out for 20 cycles at a level of 15kV high voltage with a controlled speed of 2 m/min.

Lap Shear Test

The lap shear tests were performed at two test temperatures, 25°C and 150°C, in a temperature-controlled test environment in an atmosphere of dried air. The test was done in accordance with DIN 53283, using 25 × 100 mm test samples of the specified APC 2 material. The adhesively-bonded overlap region was 3 cm^2. Using a film adhesive ensured a constant film thickness of 0.33 mm for the adhesive.

ESCA

The test specimens were wrapped in aluminium foil with a free surface of 5 × 5 mm^2 and then mounted on the sample holder. This method of embedding nonconducting specimens in a metal foil is well established to give reasonable results regarding static charge buildup. The sample holder could be rotated to change the emission angle. Energy resolution of the analyser was set to 1.25 eV for survey scans and to 0.25 eV for detail scans.

Contact Angle Measurements

For the determination of the surface tension the sessile drop method was used (apparatus by Krüss GmbH). Testing liquids were water, glycerol and ethylene glycol with well known surface energies. The resulting surface energies (Table I) were calculated from the experimental data using the method of Wu.[6]

RESULTS AND DISCUSSION

Lap Shear Strength

In Figures 2 and 3 the results of the lap shear measurements are given for 25°C and 150°C. The results of the plasma-treated samples are compared with some other pretreatment methods such as degreasing with MEK, corona discharge, etching in chromic sulphuric acid (CSA) and SACO coating (silicate like). In the SACO process (ESPE Co., Munich, Germany) a silicate-containing film is generated on the sample surface by blasting with silicate-covered particles of corundum.

The best results are obtained by the plasma-based treatments in argon or oxygen. They greatly exceed the results of the chromic sulphuric acid treatments. This holds for the test results at 25°C and 150°C without conditioning the samples, as well as

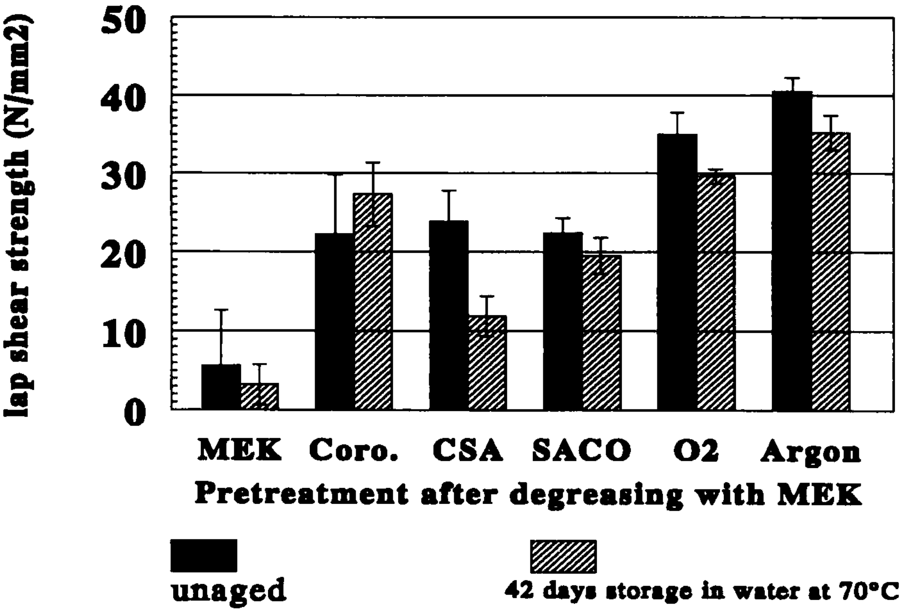

FIGURE 2 Lap shear strength at 25°C for different surface treatments: methyl ethyl ketone (MEK), corona (Coro.), chromic sulphuric acid (CSA), SACO coating (SACO), and plasma treatment in oxygen or argon.

TABLE I
Surface energy measurements of MW-plasma treated surface
(500 W, 20 Pa)

Treatment	Surface energy (mN/m)
untreated (degreased)	41.3
10 sec O_2-plasma	68.2
10 sec O_2-plasma, 1 day storage in air	57.8
30 sec O_2-plasma	>72.0
30 sec O_2-plasma, 1 week storage in air	>72.0
120 sec O_2-plasma	>72.0
10 sec Ar-plasma	66.5
30 sec Ar-plasma	>72.0
120 sec Ar-plasma	>72.0

after storing them in hot water (70°C) for 42 days. After this storage the decrease in shear strength is small, indicating a good environmental behaviour of the adhesively-bonded composite. Except for the plasma treatments, the failure mechanism in the bonded composite for the other pretreatments was adhesive at the interface of the joint for the measurements at 25°C, whereas the failure mode for the plasma-treated samples was mainly cohesive (~90%) in the adhesive itself. At 150°C test temperature, where the strength of the adhesive decreases, the plasma-treated samples

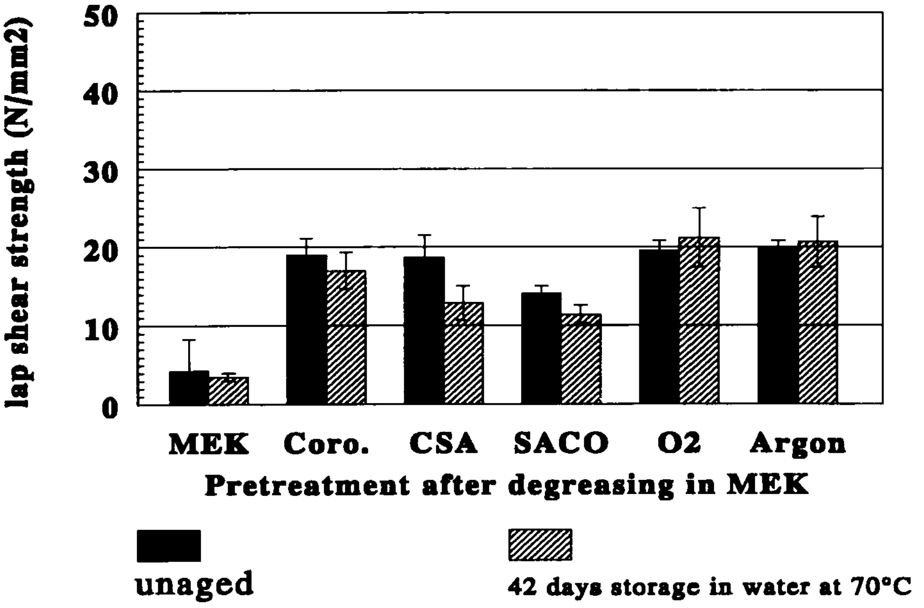

FIGURE 3 Lap shear strength at 150°C for different surface treatments: methyl ethyl ketone (MEK), corona (Coro.), chromic sulphuric acid (CSA), SACO coating (SACO) and plasma treatment in oxygen or argon.

show only cohesive failure. At this temperature, some of the samples with other pretreatment procedures that exceed a sufficiently high level of activation also have shown a partly-cohesive failure. Therefore, these treatments may also give a sufficiently high level of activation.

Another point of interest is the stability of the plasma-treated surface against the surrounding atmosphere. This is of great importance for practical bonding operations. Surface activation processes and treatments of polymers are often known to be highly sensitive to the atmosphere. For example, the reaction of oxygen or moisture with radicals formed on the surface is a well-known phenomena.

Davies *et al.*[1] have reported some results on the stability of R.F. plasma treated PEEK-surfaces. They found a strong decrease in shear strength when the treated samples were stored in air for 10 days prior to adhesive bonding. Even after storing them for only some hours a dramatically-reduced strength was found.

In order to study the discussed stability effect, a series of plasma-treated (O_2 plasma, 120 sec) samples were stored in the laboratory atmosphere for time intervals of up to 4 weeks prior to adhesive bonding. This was done by storing the samples directly after the plasma treatment in an open environment. Just before adhesive bonding of the samples dust was removed from the surface using a stream of dry air. The results of the lap shear tests of these samples are shown in Figure 4. The decrease in lap shear strength with increasing storage time in air is rather small. A level of almost 30 MPa remains even after 4 weeks of exposure to air after the plasma treatment.

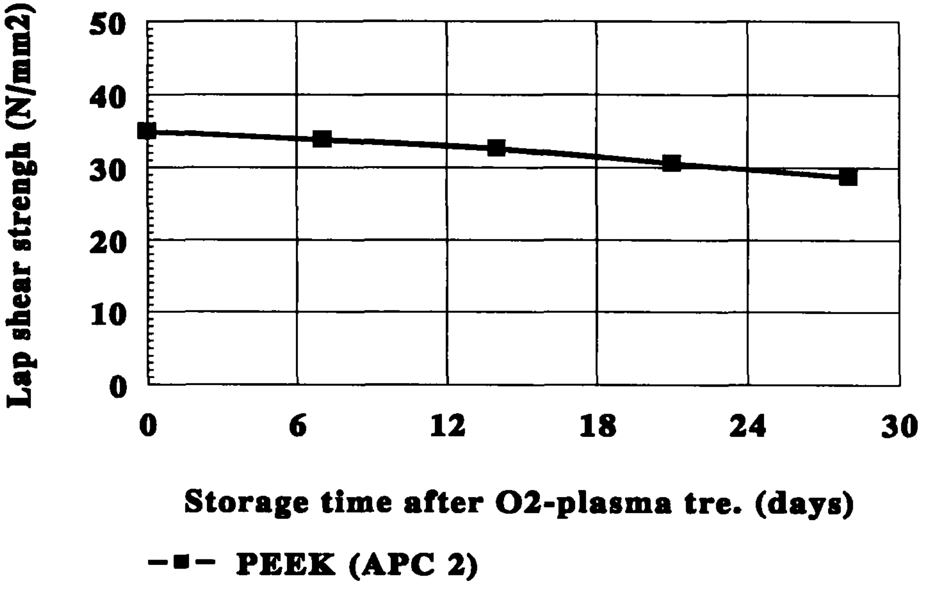

FIGURE 4 Time stability of the O_2 plasma treatment.

Measurement of Surface Energy

In order to see if there was a correlation between the results of the lap shear tests of the adhesively-bonded specimens and their surface free energies, the contact angles of the plasma-treated surfaces were determined with different liquids and the surface free energies computed as stated previously.

The results of these measurements are given in Table I. The time dependency, as well as the influence of the gas composition, was investigated. It should be noted that a plasma treatment of 10 seconds results in a significantly increased surface energy. The maximum value of >72 mN/m is obtained after 30 seconds of plasma treatment. This shows that, on a well-prepared (degreased) PEEK surface, a plasma treatment of only some ten seconds is sufficient to change the surface properties, *e.g.*, the surface energy, dramatically.

The influence of the surrounding atmosphere was noticed quite clearly for the short treatment of 10 seconds after one-day storage in air. For this, a decrease in surface energy was recorded (see Table I). Compared with the 10-second treatment, for the longer treatment of 30 seconds (resulting in a surface energy >72 mN/m) no change in surface energy could be detected, even after a storage of one week. Hence, the surface state obtained by this longer treatment seems to be stable, confirming the lap shear tests.

ESCA

Surface analysis of untreated and plasma-treated PEEK was performed by ESCA. On the MEK-degreased PEEK the elements C, O, and Si were detected. The Si was not expected but the content is only 3.5 atomic %. This element most likely belongs to the mold release agent.

ESCA measurements were performed as well on freshly-fractured surfaces of the compact PEEK to study the plasma treatment also on Si-free PEEK. However, apart from the small content of Si, no difference was recorded compared with the ESCA results on the PEEK composites. In order to eliminate the influence of silicon, all results which are presented have been obtained on pure PEEK (fracture surface).

In Figure 5 and Table II the results of the untreated PEEK are given. The theoretical values are based on the ideal chemical structure of PEEK. According to this, three C 1s environments (aromatic carbon, C—O ether group, C═O ketone group) and two O 1s environments (ether, ketone) are considered. For the peak fit, a procedure with Tougaard background subtraction was applied.

The contribution of the well known $\pi-\pi^*$ shake-up satellite, which is characteristic of the aromatic ring structure, is added to the accompanying aromatic C 1s contribution to compare theory and experiment. A reasonable accordance is obtained for this comparison. In addition, the measured C/O ratio is in good agreement with the theoretical value, indicating that the untreated surface consists of pure PEEK without any contamination. Similar results have been obtained by Jama *et al.*[4] on thin films of PEEK.

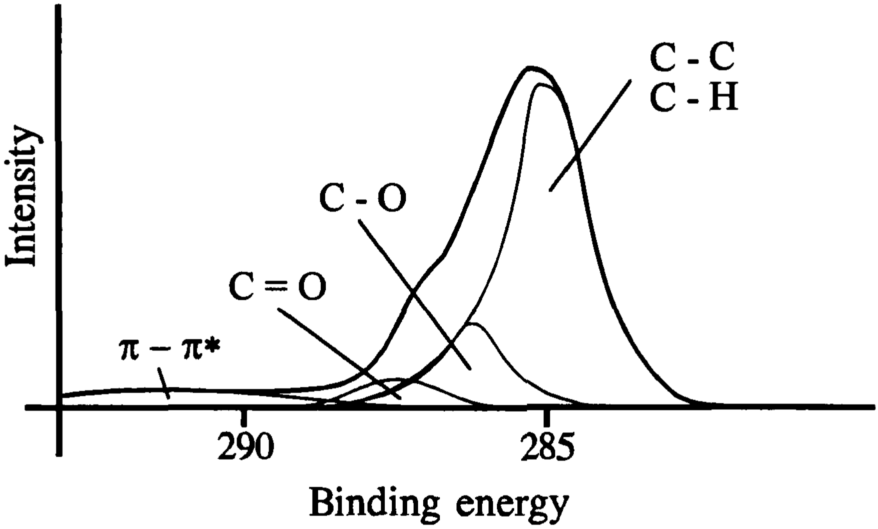

FIGURE 5 ESCA results for untreated PEEK.

TABLE II
ESCA results of untreated PEEK ($\theta = 0°$, normal emission)

	Theory	Experiment
C/O ratio	6.3	6.5
carbon 1s		
C—C	74	76 (66 + 10)
C—O	21	19
C═O	5	5
$\pi - \pi^*$	—	10
oxygen 1s		
O—C	67	64.5
O═C	33	35.5

The effect of plasma treatment for 120 sec in an argon atmosphere on the PEEK surface is shown in Figure 6 and Table III. It can be seen that the characteristic $\pi - \pi^*$ shake-up satellite has disappeared almost completely after this treatment. For shorter treatment times of 10 and 30 sec the intensity of the peak is higher, nearly 8% and 4%, respectively. This result is in accordance with the measurements of surface energy, where a treatment of 10 sec was not sufficient to give the full effect.

For the peak fit procedure of the C ls peak, four different carbon environments were involved. In addition to the three environments of the untreated PEEK, the O—C═O group was included in the calculation. By the plasma treatment a higher oxidized surface is generated and the C/O ratio changes from 6.5 to 4.4. The content of carbon-oxygen functional groups on the surface is increased. This effect can also be observed by surface treatment with a remote plasma discharge.[4]

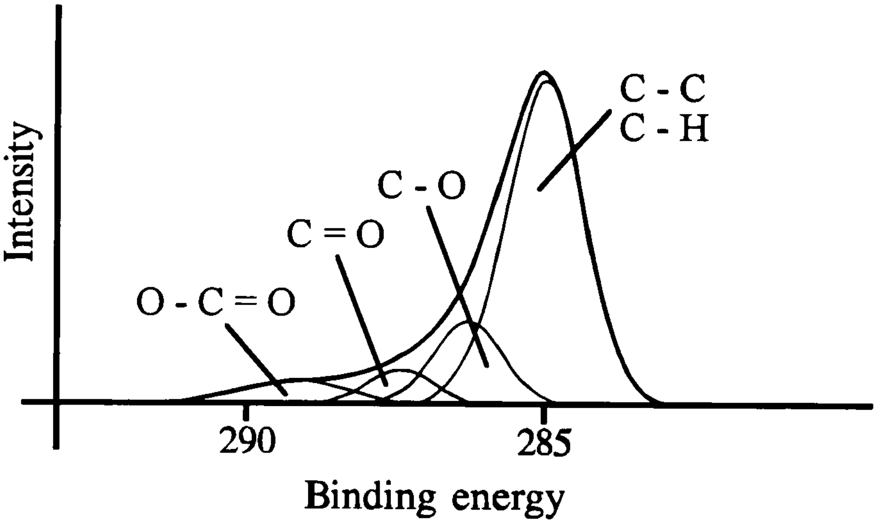

FIGURE 6 ESCA results after Ar-plasma treatment.

TABLE III
ESCA results of Ar-plasma-treated PEEK
($\theta = 0°$, normal emission)

	120 s Ar plasma	Untreated
C/O ratio	4.4	6.5
carbon 1s		
C—C	70	76 (66 + 10)
C—O	16.5	19
C═O	6.7	5
O—C═O	7.2	—
$\pi-\pi^*$	—	10

A removal of the PEEK matrix material from the composite was clearly observed for long plasma treatments (10 min) in argon or oxygen. For the argon treatment, at least, this cannot be attributed to a reaction with oxygen or oxygen-containing species, which may be present in the reactor but surely to a much smaller extent than would be necessary for the observed ablative effect.

Therefore, it is concluded that, for the applied microwave plasma treatment, the gas species is not the important factor. The emitted UV light, namely the very energetic vacuum ultraviolet (VUV) radiation, is probably the most important component of the plasma for the PEEK ablation as well as for the observed surface activation. Shard and Badyal[5] have reported on this subject for polyethylene, polystyrene and PEEK, using an oxygen R. F. plasma discharge. The significance of this radiation and the importance of photochemical reactions for plasma-induced chemical reactions has also been pointed out in some work of Corbin *et al.*[7] and in a review by Liston.[8]

The take-up of additional oxygen on the PEEK surface, especially for the argon treatment, takes place possibly after the plasma treatment, when the specimen is exposed to air. Thereby, the observed carbon-to-oxygen functional groups are formed.

Instead of the VUV radiation, in principle, other species of the plasma, such as active Ar* or energetic electrons, also may be responsible for the surface activation.

A detailed study of the plasma chemical modification of PEEK surfaces is currently in progress for further clarification.

CONCLUSIONS

Surface activation for adhesive bonding of PEEK-based carbon fiber composites can be performed very effectively by a microwave plasma treatment in oxygen as well as in argon. For both plasma treatment procedures high levels of lap shear strength were obtained, exceeding 40 MPa (at 25°C) for the argon treatment. Good ageing behaviour was observed. After a storage test in hot water (42 d, 70°C), the decrease of lap shear strength was quite low.

The surface state generated by the plasma processes is very stable to air exposure. Even when the freshly-treated surface was exposed to air for four weeks prior to adhesive bonding, the decrease of lap shear strength was fairly small (~15%) compared with adhesive bonding immediately after the plasma treatment.

The characterisation of the PEEK surface by ESCA shows an almost complete cleavage of the aromatic ring structure and an uptake of oxygen, which is present in different functional carbon-oxygen groups. The plasma-chemical mechanism of the activation process is not known exactly and needs to be studied in detail.

References

1. P. Davies, C. Courty, N. Xanthopoulos and H. J. Mathieu, *J. Mater. Sci. Letts.* **10,** 335 (1991).
2. G. K. A. Kodokian and A. J. Kinloch, *J. Mater. Sci. Letts.* **7,** 625 (1988).
3. B. R. K. Blackman, A. J. Kinloch and J. P. Dear, *Proc. 15th Annual Meeting of The Adhesion Socy.*, p. 109 (1992).
4. C. Jama, O. Dessaux, P. Goudmand, L. Gengembre and J. Grimblot, *Surf. Inter. Anal.* **18,** 751 (1992).
5. A. G. Shard and J. P. S. Badyal, *Macromolecules* **25,** 2053 (1992).
6. Souheng, Wu, *J. Adhesion* **5,** 39 (1973).
7. G. A. Corbin, R. E. Cohen and R. F. Baddour, *Macromolecules* **18,** 98 (1985).
8. E. M. Liston, *J. Adhesion* **30,** 199 (1989).