

SURFACE PROPERTIES AND INTERFACIAL ADHESION STUDIES OF ARAMID FIBRES MODIFIED BY GAS PLASMAS

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Abstract

The surface of aramid (Kevlar 49) fibre was modified by NH_3 , O_2 or H_2O plasmas in order to improve the adhesion to epoxy resin. Electron spectroscopy for chemical analysis (ESCA) and static secondary ion mass spectroscopy (SSIMS) were used to identify the chemical compositions and functional groups of the plasma-treated fibre surface, respectively. The surface topography and mechanical properties of plasma-treated fibres were also investigated. After plasma treatments, the interfacial shear strength (IFSS) of aramid-fibre/epoxy-resin composites, as measured by the microbond pull-out technique, was markedly improved (43–83% improvement) and the fibre strength was only little affected (less than 10% loss). Significant improvement in the IFSS principally resulted from forming the covalent bonds between the newly reactive functionalities at the modified fibre surfaces and the epoxides of the resin.

Keywords: aramid fibre, plasma treatment, surface analysis, microbond pull-out test, interfacial shear strength

1 INTRODUCTION

Aramid fibres have a unique combination of stiffness, high strength and low density that rivals the properties of inorganic reinforcing fibres such as glass and carbon fibres.¹ However, the off-axis properties of aramid composites are limited by low fibre/matrix adhesion by comparison with that of inorganic-fibre-reinforced composites.² In order to improve the fibre/matrix interfacial bond, a variety of fibre surface modifications, such as plasma treatments^{3–6} and chemical modifications,^{7–10} have been developed. Among others, plasma treatment has an important advantage in comparison with other methods, which is that the surface modification can be achieved with the

minimum alteration of the bulk characteristics of the substrate polymer.¹¹ Excluding our previous studies,^{5,6,9} a combination of ESCA (electron spectroscopy for chemical analysis) and SSIMS (static secondary ion mass spectroscopy) to elucidate the adhesive behaviours has never been reported, although aramid fibre modifications have been studied by several workers.^{3,4,7,8}

In the present study, Kevlar 49 fibres were modified by NH_3 , O_2 or H_2O plasmas, in order to improve the adhesion to epoxy resin. The microbond pull-out technique was then used to measure the interfacial shear strength between the fibre and epoxy resin. The chemical compositions and functional groups on the fibre surfaces were quantitatively and qualitatively analysed by ESCA and SSIMS, respectively. Both the surface topography of the treated fibres and the fracture surfaces of microbond pulled-out specimens were examined by SEM (scanning electron microscopy). The effect of plasma treatment on the fibre strength was also investigated.

2 EXPERIMENTAL

2.1 Materials

Kevlar 49 fibres (1420 denier) made from poly(*p*-phenylene terephthalamide) (PPTA) were supplied by the Du Pont Company. The epoxy resin was Epon 828 and the curing agent was 4,4'-diaminodiphenylmethane (DDM), which were supplied by the Shell Chemical Co. and Merck, respectively. Anhydrous ammonia (99.99%), oxygen gas (99.99%), and distilled water were used for plasma treatments.

2.2 Plasma treatments

The fibres were cleaned successively with 1,2-dichloroethane, methanol, and de-ionized water, followed by drying overnight at 110°C in a vacuum oven before plasma treatments. Some of the cleaned fibres without plasma treatment served as 'control' samples.

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The plasma treatments were carried out in a SAMCO Model BP-1 bell jar plasma reactor. The gases used for plasma treatments were ammonia, oxygen and water vapour. After evacuating to a pressure lower than ~ 0.1 Pa, the reactor was purged with each gas three times and then the pressure was maintained at ~ 20 Pa throughout the plasma treatment processes. The fibres were treated at 30 W of radio frequency (13.56 MHz) plasma power in each gas plasma environment for 15 s–10 min treatment time. At the end of each treatment, the plasma power was turned off and the treated fibre was left there for 30 min post-treatment.

2.3 Fibre tensile tests

Tensile tests of Kevlar 49 fibres were performed by using the modified ASTM D3379-75 (1982) procedure. A gauge length of 10 mm at a crosshead speed of 1 mm/min was used to test the fibres. Altogether 40 single filament specimens were tested for each treated sample.

2.4 Scanning electron microscopy

The surface topography of the plasma-treated and control fibres were observed by scanning electron microscopy (SEM). Micrographs of single filaments were used to determine the fibre diameter. The filament diameter was the average of more than 60 measurements from SEM micrographs. The fracture surfaces of the fibres pulled-out from the resin droplets were also examined by SEM.

2.5 Electron spectroscopy for chemical analysis

A Perkin-Elmer PHI 590 SAM/ESCA instrument was used for ESCA measurements. The spectra were collected using a MgK_{α} ($h\nu = 1253.6$ eV) X-ray source (12 keV) operated at 250 W and at a pressure below 5×10^{-8} Pa. High-resolution spectra were obtained at a pass energy of 25 eV. The atomic sensitivity factors (ASF) for core levels were used to calculate the atomic concentration of the fibre surfaces.

2.6 Static secondary ion mass spectroscopy

The SSIMS experiments were performed by using a Cameca IMS-4f ion microscope equipped with a Cs^+ ion source and magnetic sector mass analyzer. The primary ion source was 10 keV Cs^+ operated at a current of 10 pA and at a pressure lower than 1.5×10^{-9} Pa. An electron flood gun set at 4.5 keV was used to minimize sample charging.

2.7 Microbond specimen preparation and test

The Epon 828 epoxy and DDM were mixed in 4:1 weight ratio to make small droplets on Kevlar 49 fibres. After curing the resin, then measuring the length of the resin droplets by an optical microscope, microbond specimens were tested at 25°C on an

Instron tester (Model 4302) at a crosshead speed of 0.5 mm/min. Details have been described in a previous study.⁹ The interfacial shear strength (IFSS), τ , was calculated using the relationship:

$$\tau = F/\pi dL \quad (1)$$

where F is the pull-out force, d is the diameter of the fibre and L is the embedded length of the resin droplet. Each reported IFSS value is the average of more than 40 successful measurements.

3 RESULTS AND DISCUSSION

Assuming round fibres, the average fibre (Kevlar 49) diameter measured from SEM micrographs was $12.35 \mu\text{m}$. No significant difference in diameter was found for the fibre with these plasma treatments.

3.1 Fibre surface topography

The SEM micrograph of the control monofilament reveals it to be quite smooth, as shown in Fig. 1(a). Figure 1(b) shows that after treatment in O_2 plasma at 30 W for 10 min, many particle-like structures are clearly visible in the fibre surface. This may be the result of the bombardment of the fibre surface with high-energy species (e.g. ion, neutral and metastable particles) in the plasma environment.^{11,12} During these processes, the structure of the fibre skin was etched out and some of the fragments would be precipitated on the fibre surface. In the case of NH_3 and H_2O plasma treatments, the surface topography of these treated fibres (not shown) are similar to that observed for the O_2 plasma treatment; with shorter treatment time, the changes in the surface topography of the fibres are smaller or quite negligible for all the three gas plasma treatments.

3.2 Fibre tensile strength

Individual filaments of the control and plasma-treated samples were tested in tension to determine the effect of these surface treatments on the mechanical properties of the fibres. The mean tensile strengths of the control and plasma-treated fibres are reported in Table 1.

The strengths of Kevlar fibres have been shown to be well fitted to a two-parameter Weibull distribution.^{8,13,14} The distribution function is described by the cumulative distribution function $F(x)$:

$$F(x) = 1 - \exp[-(x/a)^b]; \quad a > 0; \quad b > 0 \quad (2)$$

where x is the load experienced by the fibre, a and b are called the scale and shape parameters, respectively. A plot of $\ln(-\ln(1 - F))$ versus $\ln(x)$ should

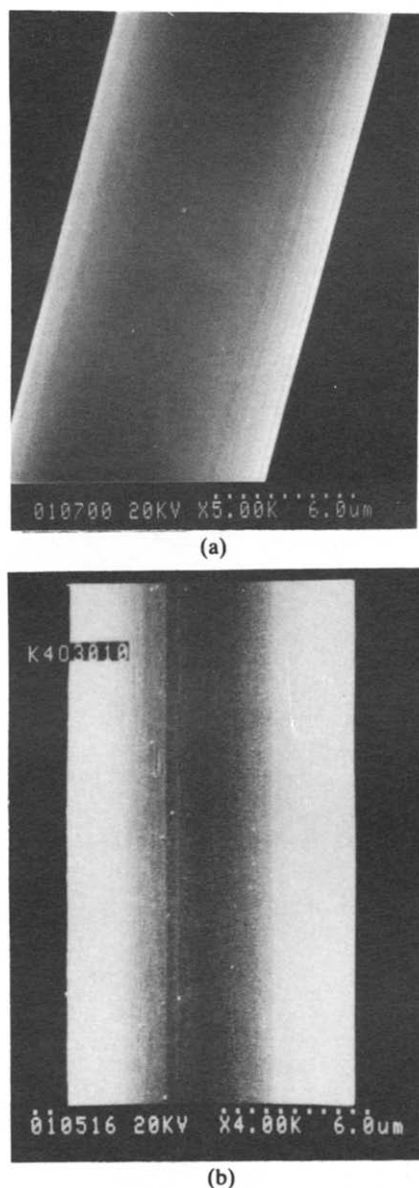


Fig. 1. SEM micrographs of Kevlar-49 fibre surfaces: (a) control; (b) treated by O_2 plasma at 30 W for 10 min.

produce a straight line of gradient b and intercept $b \ln(a)$. For differently treated samples, the Weibull plot for the tensile strength is shown in Fig. 2.

Although Weibull parameters (a, b) could be evaluated from Fig. 2, a more popular method to estimate Weibull parameters was obtained by using the method of maximum likelihood estimation (MLE), as described by Cohen.¹⁵ Table 1 contains a summary of the shape and scale parameters which are calculated by the method of MLE.

The effect of the treatment time in different gas plasmas on the relative fibre strengths (for the control fibre equal to 1.00) is demonstrated in Fig. 3. It can be seen that there is no significant difference in the tensile strength between the control and plasma-treated Kevlar 49 fibres. The reductions in fibre

strengths are less than 10% (3–9%) when the fibres exposed to 30 W power level of NH_3 , O_2 or H_2O plasma for 15 s–10 min. It has been postulated¹⁶ that plasma treatment is a surface phenomenon that causes both chain scissions and crosslinking between polymer chains, probably within a few hundred angstroms of the fibre surface layer. Crosslinking and chain scission are cited as the main cause of the changes in tensile strength.¹⁷

3.3 ESCA analysis of fibre surfaces

Kevlar 49 fibre surfaces modified by NH_3 , O_2 and H_2O plasma exposure were analysed by ESCA. Table 2 summarizes the atomic percentages of carbon, oxygen and nitrogen, and the atomic ratios of N/C and O/C for the control and modified fibre surfaces. The chemical composition of the control fibres examined by Perkin-Elmer Model 240C elemental analyser is also given in Table 2.

Table 2 shows that there is a significant difference in chemical composition between the bulk (EA data) and the surface (ESCA data) of the control fibre. At the control fibre surfaces, there is about four times as much oxygen as that in the bulk. The abundance of oxygen may be caused by surface oxidation during the processing.^{3,7,18}

After treatment with NH_3 plasma at 30 W for 3 min, more than twice as much nitrogen content as that of the control fibres is detected; in addition, an increase in carbon content and decrease in oxygen content are also found at the same time. All the results suggest that the ablation of the oxidized layer from the fibre surfaces and the incorporation of nitrogen atoms into the fibre surfaces occurred simultaneously during NH_3 -plasma discharge processes.

It can be seen from Table 2 that a decrease in carbon content is accompanied by an increase in oxygen content for the fibres treated by O_2 plasma at 30 W for 3 min. This result indicates that the fibre surfaces were oxidized further. It also implies that oxygen atoms were incorporated into the fibre surfaces by O_2 -plasma treatment.

Although a high concentration of atomic oxygen could be generated in H_2O plasma,¹⁹ there is no significant increase in oxygen content for H_2O plasma treated fibres. It is surprising to find marked increases in the N/C atomic ratio after the fibres were treated by H_2O plasma at 30 W for 3 min. The result proposes that the ablation of part of the oxidized layer by H_2O plasma causes the appearance of a PPTA structure and that will be responsible for a nitrogen-rich surface compared with the oxidized layer.

The results of ESCA analysis evidently show that these plasma treatments effectively change the chemical composition of Kevlar 49 fibre surfaces and these changes in chemical composition are highly

Table 1. Tensile strength and Weibull parameters of plasma-treated Kevlar 49 fibres

Treatment	Treatment time	Mean fibre strength (MPa)	CV ^a (%)	Shape parameter	Scale parameter (MPa)
Control		3418	7.2	17.1	3526
NH ₃ plasma	15 s	3303	7.2	16.3	3412
	1 min	3292	7.5	16.0	3402
	3 min	3274	7.6	16.1	3383
	10 min	3203	6.7	18.5	3297
O ₂ plasma	15 s	3286	6.9	17.9	3385
	1 min	3203	8.5	14.5	3320
	3 min	3196	7.0	17.7	3294
	10 min	3116	6.1	20.3	3200
H ₂ O plasma	15 s	3291	7.2	17.2	3394
	1 min	3285	6.6	18.6	3380
	3 min	3175	8.0	15.3	3286
	10 min	3163	6.2	19.9	3250

^a Coefficient of variation.

dependent on the type of gas used for the plasma discharge.

3.4 SSIMS analysis of fibre surfaces

Generally, SSIMS has very high sensitivity, and information about the chemical structure can be derived from molecular fragment ions.²⁰ Many workers²¹⁻²⁴ have concluded that the negative ion spectra of polymers are more reliable for analysis than the positive ion spectra. In this study, the negative ion spectra of the control and plasma-treated fibres are shown in Figs 4-7. Although a 1-280 amu mass scan is

performed during spectra acquisition, all the spectra of the Kevlar 49 fibres are dominated by peaks which appear in the mass range less than 100 amu.

The negative ion spectrum of the control fibres is shown in Fig. 4. The principal peaks of interest here occur at 16, 17, 26, 32, 42, 72-76, 84-86, 92, 96-98, 118 and 142 amu which can be ascribed to the moieties O⁻, OH⁻, CN⁻, O₂⁻, CON⁻, C₆H_n⁻ ($n=0-4$), [C₆H_n-C]⁻ ($n=0-2$), [C₆H₄NH₂]⁻, [C-C₆H_n-C]⁻ ($n=0-2$), [C₆H₄-CON]⁻ and [CO-C₆CON]⁻, respectively. The relatively high intensity of the oxygen-containing fragments (O⁻, OH⁻ and OH₂⁻) in the spectrum indicates that the control fibre surfaces contain abundant oxygen. The result is very consistent

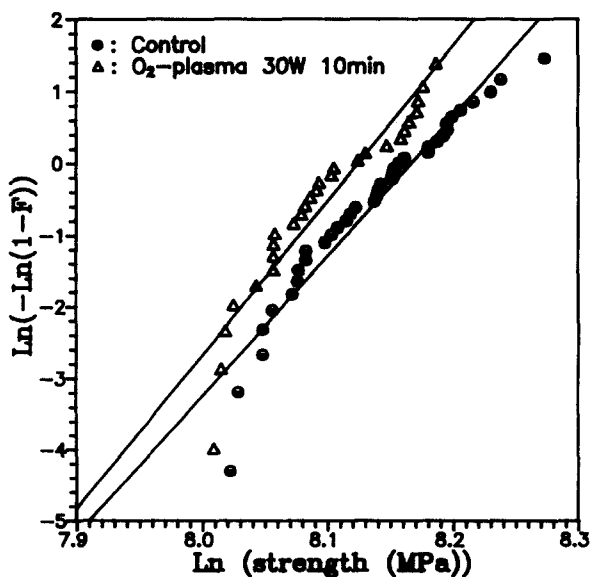


Fig. 2. Weibull distribution from the tensile strength data of the untreated (control) and O₂ plasma treated Kevlar-49 fibres.

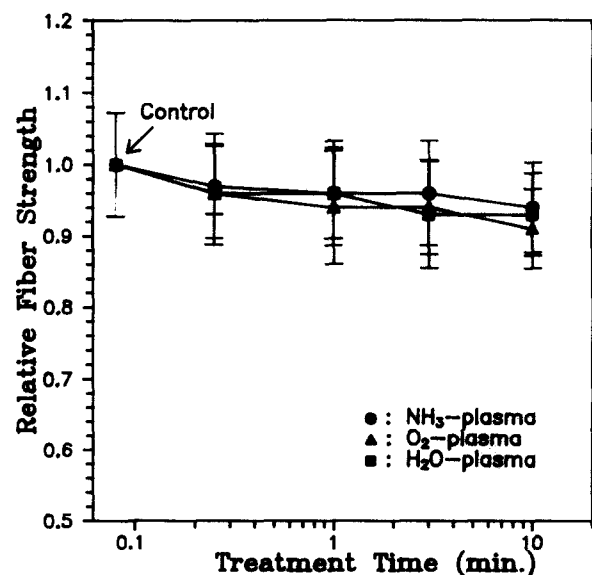


Fig. 3. Effect of the treatment time in various plasmas on the relative tensile strength of Kevlar-49 fibres.

Table 2. ESCA analysis results of surface composition for plasma-treated Kevlar 49 fibres

Treatment	Treatment time	Atomic percentage			Atomic ratio	
		C	O	N	N/C	O/C
EA ^a		79.4	14.4	10.7	0.143	0.192
Control		37.4	57.0	5.6	0.150	1.524
NH ₃ plasma	3 min	42.2	45.2	12.6	0.299	1.071
O ₂ plasma	3 min	34.8	61.0	4.2	0.121	1.753
H ₂ O plasma	3 min	38.2	53.5	8.3	0.217	1.401

^a Elemental analysis results of the control fibres.

with the result of ESCA analysis (Section 3.3) and it also proves further that the oxidized layer truly existed at the surfaces of the control fibres. Other peaks, as assigned above, are apparently capable of providing structural information about the repeating unit of poly(*p*-phenylene terephthalamide) (i.e. $(-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-)_n$).

No significant difference in the negative ion spectra between the control and NH₃ plasma treated samples (Fig. 5) is found. However, the peaks which have arisen at 108 and 112 amu for NH₃ plasma (30 W for 3 min) treated surfaces, shown in Fig. 5 are newly formed ion fragments after the NH₃ plasma treatment and can be ascribed to $[\text{C}_6\text{H}_4(\text{NH}_2)_2]^-$ and $[\text{C}-\text{C}_6(\text{NH}_2)-\text{C}]^-$, respectively. Both peaks contained amino groups and are direct evidence of plasma amination during the NH₃ plasma discharge. This result is also in agreement with ESCA analysis data (i.e. an increase in nitrogen content). Further, oxygen can still be detected from peaks at 16, 17 and 32 amu due to O⁻, OH⁻ and O₂⁻, respectively. This should be the result of the fact the radicals formed during plasma treatment are long-lived, and can react with oxygen upon exposure to the air after treatment.¹⁶

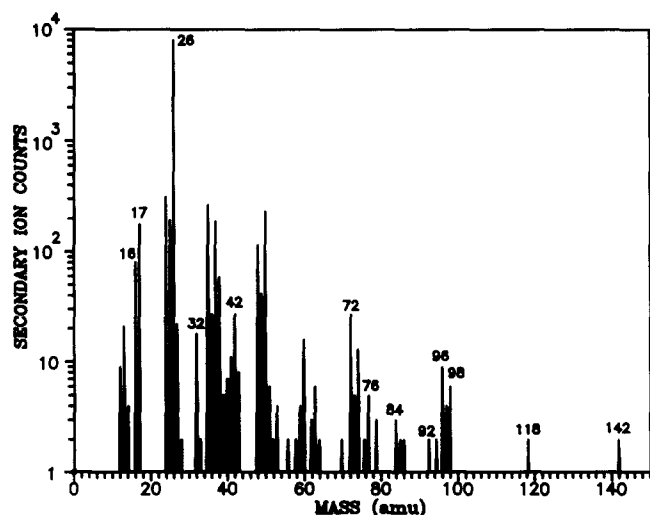


Fig. 4. Negative ion spectrum of the untreated (control) Kevlar-49 fibres.

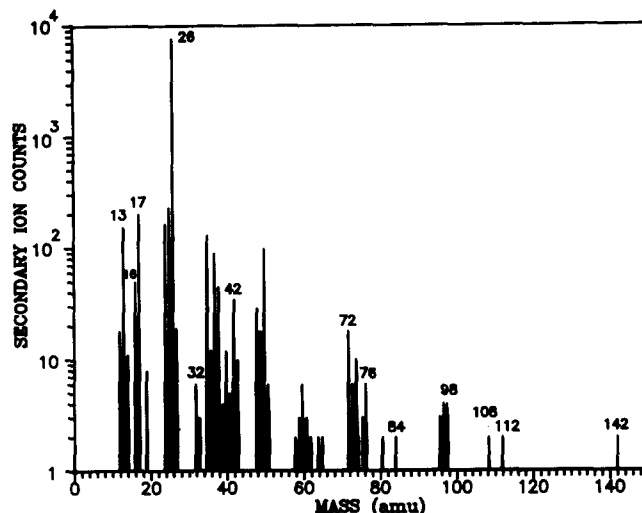


Fig. 5. Negative ion spectrum of Kevlar-49 fibres treated by NH₃ plasma at 30 W for 3 min.

Figure 6 shows the negative ion spectrum of Kevlar 49 fibres treated by O₂ plasma at 30 W for 3 min. Comparison of Fig. 4 with Fig. 6 shows that after O₂ plasma treatment, many of the ion fragments contained aromatic rings so that peaks at 76, 84–86, 92, 96–98, etc., are absent from the spectrum (Fig. 6); furthermore, decreases in the intensities of the ion signals at the lower mass ranges of 35–43 and 48–64 amu are observed. However, these results are not seen in NH₃ plasma treated fibres. This obviously shows that the O₂ plasma treatment led to extensive damage of the aromatic ring^{5,25} and the polymer backbone.⁵ It also indicates that the O₂ plasma exhibited a more powerful destruction of the surface polymer chains than the NH₃ plasma. In the higher mass range, only one new peak at 102 amu can be seen in Fig. 6, this peak can be ascribed to the

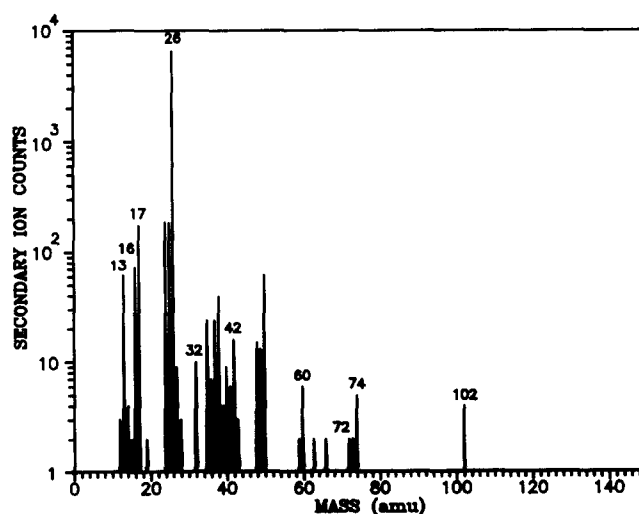


Fig. 6. Negative ion spectrum of Kevlar-49 fibres treated by O₂ plasma at 30 W for 3 min.

$[\text{C}_6\text{H}_2\text{—CO}]^-$ or $[\text{C—C}_6\text{H}(\text{OH})]^-$ species because both of them will contribute to the peak. As the result of ESCA analysis, a high oxygen content at the fibre surfaces is detected when the fibres are exposed to the O_2 plasma, therefore $[\text{C—C}_6\text{H}(\text{OH})]^-$ is likely to form because the fragment expresses the incorporation of oxygen atoms into the fibre surfaces by the O_2 plasma treatment.

After treatment with the H_2O plasma at 30 W for 3 min, the negative ion spectrum becomes more complicated, as shown in Fig. 7. New peaks occur at 107, 109, 110, 114, 119, 121 and 136 amu which may arise due to the formation of the species $[\text{C}_6\text{H}(\text{OH})_2]^-$, $[\text{C}_6\text{H}_3(\text{OH})_2]^-$, $[\text{C}_6\text{H}_4(\text{OH})_2]^-$, $[\text{C—C}_6\text{H}(\text{OH})\text{—C}]^-$, $[\text{C—C}_6\text{H}(\text{OH}_2)]^-$ and $[\text{C—C}_6\text{H}(\text{OH})_3]$, respectively. Ferrerio *et al.*¹⁹ reported that the major ions found in the H_2O plasma environment are H_2O^+ , H_3O^+ , O_2^+ , $\text{H}(\text{H}_2\text{O})_2^+$ and $\text{H}(\text{H}_2\text{O})_3^+$. According to Ferreiro's study, assignments of these new chemical structures containing hydroxyl groups are quite reasonable in this study. It is evident that the abundant hydroxyl ions formed in the H_2O -plasma environment¹⁹ were incorporated into the fibre surfaces during the plasma treatment. Furthermore, there are still relatively high intensities of the oxygen-containing ion fragments (O^- , OH^- and O_2^-) and the fragments containing aromatic rings in the mass range from 78 to 98 amu.

It is anticipated that, with plasma treatment, a wide variety of new chemical structures are created in the polymer surfaces. Due to the fact that probably several new structures are formed during the plasma treatment and there is a lack of reference structures for spectra, it is very difficult to assign all these peaks. In this study, significant differences in the SSIMS results are found in the negative ion spectra of the plasma-treated Kevlar 49 fibre surfaces. It is known

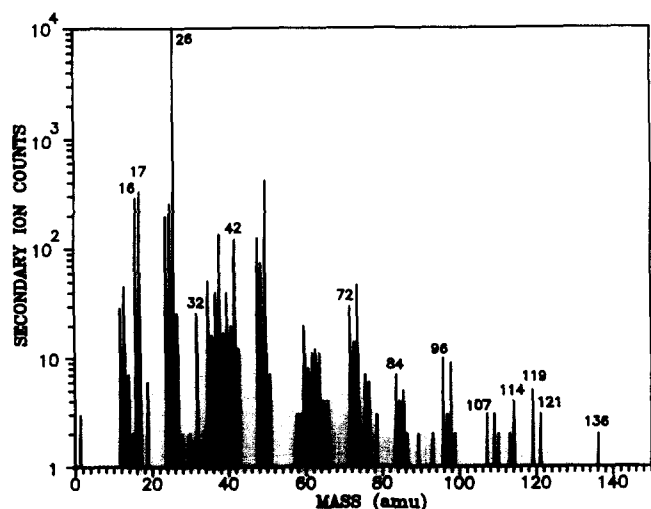


Fig. 7. Negative ion spectrum of Kevlar-49 fibres treated by H_2O plasma at 30 W for 3 min.

that plasma-treated surfaces contain a high density of free-radical sites.²⁶ These sites will react with the gases and ions present in the reactor. This can reasonably account for the incorporation of amino and hydroxyl groups into the fibre surfaces treated by the NH_3 plasma and H_2O plasma, respectively; furthermore, evidence for such groups is provided by the negative ion spectra.

3.5 Interfacial shear strength of aramid-fibre/epoxy-resin composites

The interfacial shear strength (IFSS) determined by the microbond pull-out test can give a reliable evaluation of the strength of the adhesive bond. The results are presented in Table 3.

The IFSS of the control sample, 28.1 MPa, is somewhat smaller than the value in the literature. Biro *et al.*⁴ reported the strength to be 32.8 MPa which was measured for an acetone-washed Kevlar 49 fibre with the bisphenol-A epoxy resin (Epon 828). In this study, a higher oxygen concentration on the fibre surfaces is found compared to that reported by Biro.⁴ The slight difference in the IFSS is therefore reasonable. The poor adhesion for the control sample may be due to the existence of an inert oxidized layer at the fibre surfaces, as in the results analysed by ESCA and SSIMS.

The effects of the treatment time in different discharge gases on the IFSS for a discharge power level of 30 W are demonstrated in Fig. 8. The results show that even with a very short time treatment (15 s), a remarkable improvement in the IFSS is found for all the three plasma treatments. With an increase in the treatment time, there is an apparent increase in the IFSS for NH_3 and H_2O plasma treatments. However, the treatment time has no significant effect on the IFSS of a O_2 plasma treated sample. For short treatment

Table 3. Interfacial shear strength (IFSS) of plasma-treated Kevlar-49-fibre/epoxy-resin composite as determined by the microbond pull-out test

Treatment	Treatment time	IFSS ($\pm 95\%$ confidence) (MPa)	Improvement of IFSS (%)
Control		28.1 (0.9)	—
NH_3 plasma	15 s	43.3 (1.8)	54
	1 min	43.6 (1.9)	55
	3 min	47.6 (1.9)	69
	10 min	48.0 (1.8)	71
O_2 plasma	15 s	41.6 (1.6)	48
	1 min	42.2 (1.5)	50
	3 min	42.8 (1.9)	52
	10 min	43.4 (1.7)	54
H_2O plasma	15 s	41.6 (1.8)	48
	1 min	43.5 (1.6)	55
	3 min	45.2 (1.6)	61
	10 min	51.4 (1.9)	83

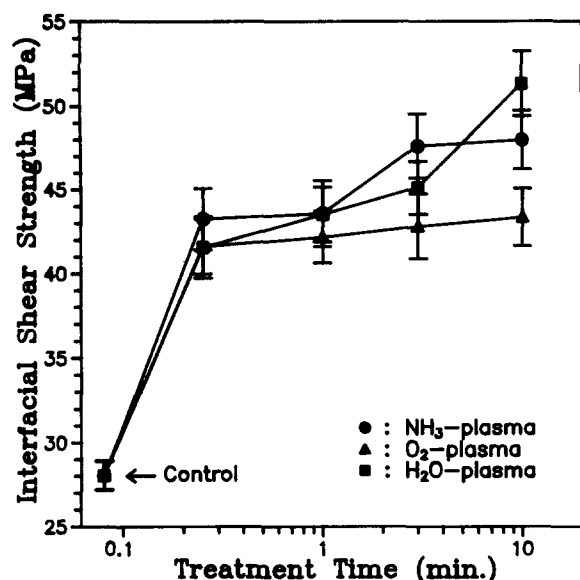


Fig. 8. Dependence of the interfacial shear strength of Kevlar-49 fibre/epoxy-resin composite on the time of fibre treatment by various plasmas at 30 W power level.

times there is little difference in the IFSS value obtained for fibres treated in different gas plasmas. However, for longer treatment times a difference becomes apparent, with the H₂O plasma yielding the greatest improvement in IFSS (after 10 min) having a value of 51.4 MPa.

After plasma treatments, the improvement in adhesion may be primarily due to the introduction of reactive functionalities into the fibre surface and the removal of the inert oxidized surface layer of the Kevlar 49 fibres. With the NH₃ plasma treatment, the amino groups on the fibre surface introduced by the plasma, as identified by the negative ion spectrum (Fig. 5), can react with the epoxides, the same as with the amine curing agents. This will result in the formation of covalent bonds between the fibre and epoxy resin, causing an improvement in the IFSS. Although there are no amino groups introduced by the H₂O plasma, the newly formed hydroxyl groups at the fibre surface could covalently bond to the amine-type curing agents²⁷ or the epoxides.²⁸ This should be the main factor causing a stronger adhesion between the H₂O plasma treated fibre and the epoxy resin. The result of the ESCA analysis (Table 2) shows that the O₂ plasma treatment increases the oxygen content of the fibre surfaces. This might suggest that O₂ plasma treatment creates more oxygen functionalities at the fibre surfaces, which would increase the surface polarity leading to better fibre wet-out.⁵ Furthermore, O₂ plasma treatment could generate reactive groups, namely, hydroxyl and carboxyl groups,¹⁰ which could chemically bond with the epoxides^{27,28} improving the strength of the adhesive bond.

From the results of the IFSS, ESCA and SSIMS, we can conclude that the newly formed functionalities at the fibre surfaces by plasma treatment is the principal factor in improving the adhesion between Kevlar 49 fibre and epoxy resin. Besides the chemical (or covalent) bonding formed between the newly reactive functionalities at the fibre surface and epoxy resin, other possible factors such as the physical bonding may also be contributing to the increase in the IFSS. As shown in our previous study,⁵ the plasma treatment could introduce polar groups into the surface of PPTA prepared from Kevlar fibres, increasing the wettability and leaving the surface with a higher surface energy. The introduction of the polar functionalities presumably resulted in an increase in the van der Waals forces and/or hydrogen bonding. Both bonding forces should make some contribution to the adhesive strength.

3.6 Fracture surface examination of microbond pulled-out specimens

The fracture surfaces of microbond specimens were examined by SEM after testing. As shown in Fig. 9(a), the fracture surface of the control sample is relatively clean. However, significantly different fracture surfaces compared with that of control sample for samples treated by NH₃, O₂ and H₂O plasmas at 30 W for 3 min are illustrated in Figs 9(b)–(d), respectively. Obviously, epoxy resin adhering to the fibre surfaces is found in all the plasma-treated samples, and the wave-like resin at the fibre surfaces arises due to the shear friction between the resin adhered to the fibre surface and the debonding resin droplet during the microbond pull-out process. It is very interesting that after different gas-plasma treatments at 30 W for 3 min, higher values of the IFSS are always accompanied by a larger amount of epoxy resin adhering to the fracture surface (NH₃ > H₂O > O₂ plasma treatment).

From the results of the IFSS and fracture surface observation, it is clear that the bonding failure occurred at the interface in case of the control sample (lower IFSS); however, resin adhering to the fibre surfaces are found in the case of the plasma-treated samples (higher IFSS). The higher IFSS causing the resin to adhere to the fibre surface also indicates that the bonding strength between the plasma-treated fibre and the epoxy resin is larger than the cohesive strength of the epoxy resin.

4 CONCLUSIONS

Gas plasma treatment offers an effective and rapid method for modifying the Kevlar 49 fibre surface and improving the adhesion between the fibre and epoxy resin. After the plasma treatments, the losses in fibre tensile strength are less than 10%. A combination of

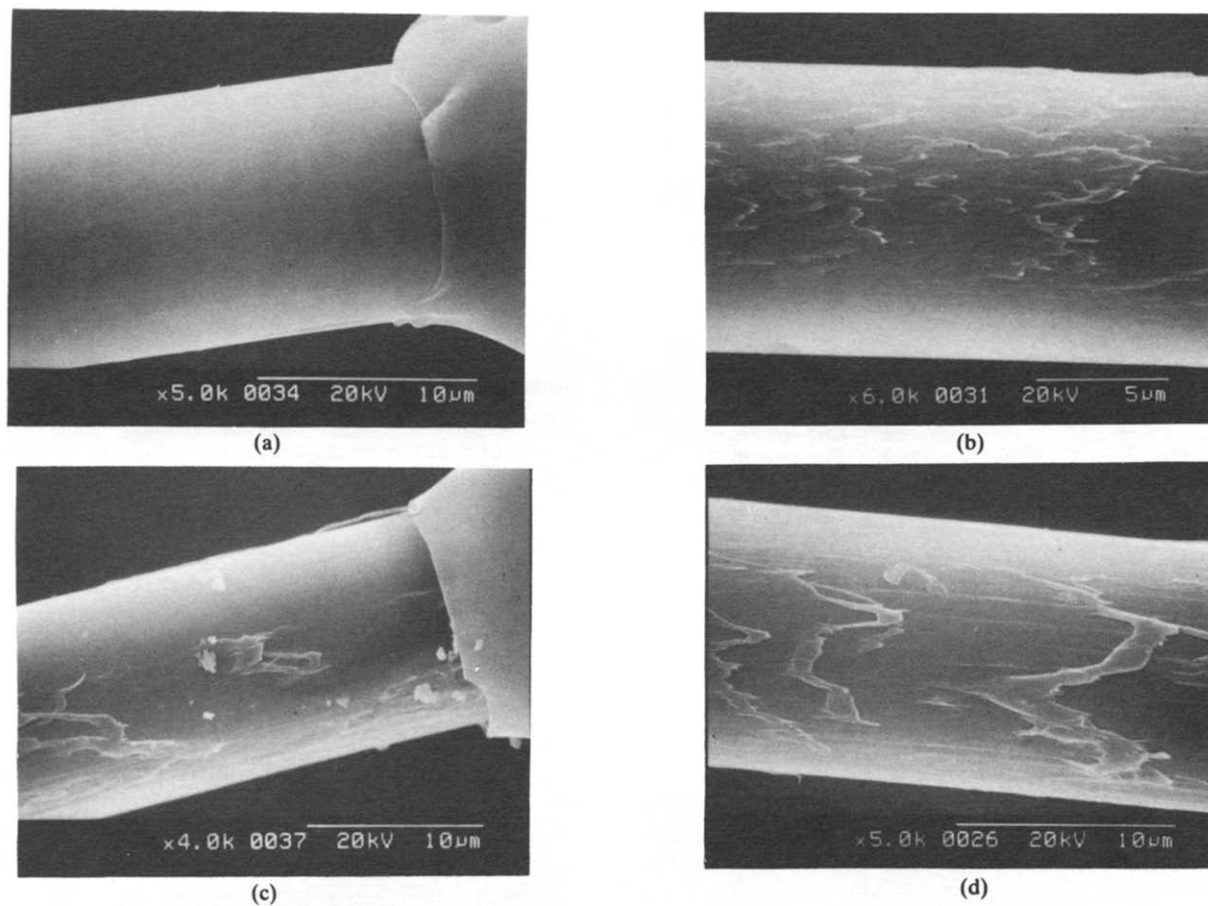


Fig. 9. Fracture surfaces of microbond pull-out specimens: (a) control; (b) treated by NH_3 plasma at 30 W for 3 min; (c) treated by O_2 plasma at 30 W for 3 min; (d) treated by H_2O plasma at 30 W for 3 min.

SEM, ESCA and SSIMS has been used efficiently to described the changes in the fibre surface properties caused by these plasma treatments. Removal of an inert oxidized layer from the fibre surfaces and the introduction of reactive functionalities into the fibre surfaces occur simultaneously during plasma discharge. The newly formed functionalities such as amino and hydroxyl groups are clearly identified by the negative SSIMS spectra. The remarkable improvement in the IFSS of Kevlar 49 fibre epoxy resin principally results from a covalent bond formed between the newly reactive functionalities at the modified fibre surfaces and the epoxides of the resin. The improvement in the IFSS is accompanied by a change in the fracture mode from the failure in the interface to a location within the epoxy resin.

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