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Argon plasma treatment of glass surfaces

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The effect of argon plasma treatment of glass surfaces is studied by FTIR and SEM. The argon plasma on cleaned glass surfaces resulted in increased surface area due to microetching and surface rearrangement of the silicate network as indicated by the observed changes in the Si–O stretching infrared absorption. The result was a relative increase in surface hydrophilicity which could be optimized by the plasma reaction conditions. The etching action of the argon plasma on the substrate surfaces facilitated the removal of the micrometre thick sizing from the commercial fibres accompanied by little loss in tensile strength. Plasma was also used to graft selected monomers to the surface of glass fibres for enhancement of bond compatibility in a composite system. This grafting treatment was followed by an argon etching step. The argon-plasma action on the coated surfaces improved the wettability further and increased the surface area. Changes in surface chemistry that accompanied the argon etching treatment were very subtle in the case of the plasma polymer of allylamine, but proved significant in the case of the plasma polymer of hexamethyldisiloxane. On the latter surfaces, rearrangement of the siloxane (Si–O–Si) bonds to silylmethylene (Si–$(CH_2)_n$–Si) groups is suggested.

1. Introduction

Glow discharges (cold plasmas) have been widely used for surface modification of materials [1]. Fluorine-containing plasmas are used in the semiconductor industry for surface cleaning and etching. Sterilization of biological tissues can be achieved by a short oxygen or nitrogen plasma treatment. Cold plasmas have also been used to graft functional groups on surfaces for post-plasma grafting of biomolecules, e.g. ammonia plasma [2, 3], or to improve adhesive properties by increasing surface polarity, e.g. oxygen plasma [4, 5].

Improved chemical compatibility between glass fibres and high-temperature thermoplastic matrices like polyphenylene sulphide (PPS) and polyetheretherketone (PEEK) is being investigated by plasma modification of the glass-fibre surfaces [6]. The proposed plasma-treatment scheme consists of an initial argon-plasma treatment followed by plasma polymerization of selected monomers on to the surfaces. The plasma-grafted layer is flawless highly cross-linked film and has excellent adhesion to the substrate [7]. Functional groups on this organic layer will act as coupling agents and help improve the bond between the glass-fibre surface and the organic matrices. The argon plasma treatment is performed to clean the substrates of molecular level contaminants and to modify the surface chemistry to facilitate grafting of the monomer introduced into the plasma field.

In polymer matrix composites, the fibres are usually given surface treatments to improve their bondability to the polymer matrices. This could either be an oxidative treatment [8] or a chemical etching of the fibre surface [9], both of which are accompanied by a loss in fibre strength. The plasma treatment proposed to modify the surface functionality and the surface energy could prove better than the furnace or chemical treatments [8, 9] by creating the desired changes in the surfaces without a significant reduction in the strengths.

The effects of argon plasma on glass surfaces, both cleaned and coated are the subject of the present investigation. Changes in surface chemistry, surface energy and morphology are studied by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

2. Experimental procedure

The equipment used in this study was an inductively coupled plasma reactor (Branson/IPC 3000) operating at the r.f. frequency of 13.56 MHz. The reactor chamber was evacuated to 0.02 to 0.05 torr and purged well with argon before initiation of the discharge at the desired pressure level. This was done to minimize the presence of oxygen in the chamber during the treatment.

The argon plasma was initiated at a pressure of 0.5 torr at the required power level. To determine the optimum plasma power level, contact angles were determined on glass slides exposed to the argon plasma for a duration of 10 min. The glass slides were cleaned in 5% NaOH solution and rinsed in distilled water and acetone to remove any grease during handling of these samples. The contact angles were the average of five measurements. The plasma power was varied from 30 to 150 W.

The effect of argon plasma on the cleaned glass surface was studied using commercial glass fibres (E-glass, Owens Corning – type 497 225) which were

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furnace cleaned (650° C for 1 h in air) to remove the sizing. The fibres were separated and mounted on a frame and plasma treated at 100 W (determined to be the optimum from the wettability measurements) for 10 min and viewed under the SEM. In addition, attenuated total reflectance (ATR) infrared spectra (Perkin Elmer 1800, MCT detector) of cleaned glass slides treated at 100 W for 15 min were used to study the molecular level changes resulting from the plasma modification.

Removal of the sizing on the commercial fibres by the argon plasma as an alternative to furnace cleaning was also studied by exposing the as-received fibres to the plasma action (0.5 torr, 100 W) for extended periods (1 to 2 h). To determine the resultant loss in tensile properties, single-fibre breaking loads were measured on the as-received and the plasma-treated fibres. A testing speed of $1\,\mathrm{mm\,min^{-1}}$ over a gauge length of 25.4 mm was used. Ten samples were tested to obtain an average value.

The argon plasma treatment was followed by plasma polymerization of selected monomers – allylamine and hexamethyldisiloxane (Aldrich Chemicals) – on the substrates. This was done to introduce specific functionality on the surfaces. The effect of a second argon plasma treatment on the plasma-coated glass surfaces was also studied to modify further the chemistry of the plasma grafted layer. Wettability values were determined on glass slides coated with these monomers both in the as-coated condition and after exposure to the argon plasma. Scanning electron micrographs were used to study the changes in surface texture and transmission spectra of NaCl plates coated with these monomers and exposed to the argon plasma were used to determine the changes in the structure of the plasma polymers.

TABLE I Argon plasma treatment of glass slides

Treatment	Water contact angle (deg)
Cleaned glass slides	53
Argon plasma (0.5 torr, 10 min):	
30 W	44
50 W	45
100 W	36
150 W	39

3. Results and discussion

The modification of surfaces as a result of the plasma action can be attributed to bombardment of the substrates by a variety of active species, e.g. electrons, ion, free radicals, etc. ([10] p. 4, [11]). The result of an inert non-polymer forming gas plasma treatment (argon or helium) is to clean the surfaces at the molecular level. However, the substrates have to be solvent cleaned prior to this to remove the grease due to handling as the plasma action penetrates to only a few molecular layers. In addition, with polymer surfaces, reactive sites are created by chain scissioning and bond rearrangement. The activated surface can react with the activated gas (oxygen, nitrogen or ammonia) and leads to an altered surface chemistry by the introduction of functional groups, e.g. peroxides, nitrite, etc. As a result, the surfaces can be made more wettable which is particularly useful in adhesive applications.

Table 1 lists the contact angles obtained on glass slides after the argon plasma treatment at different

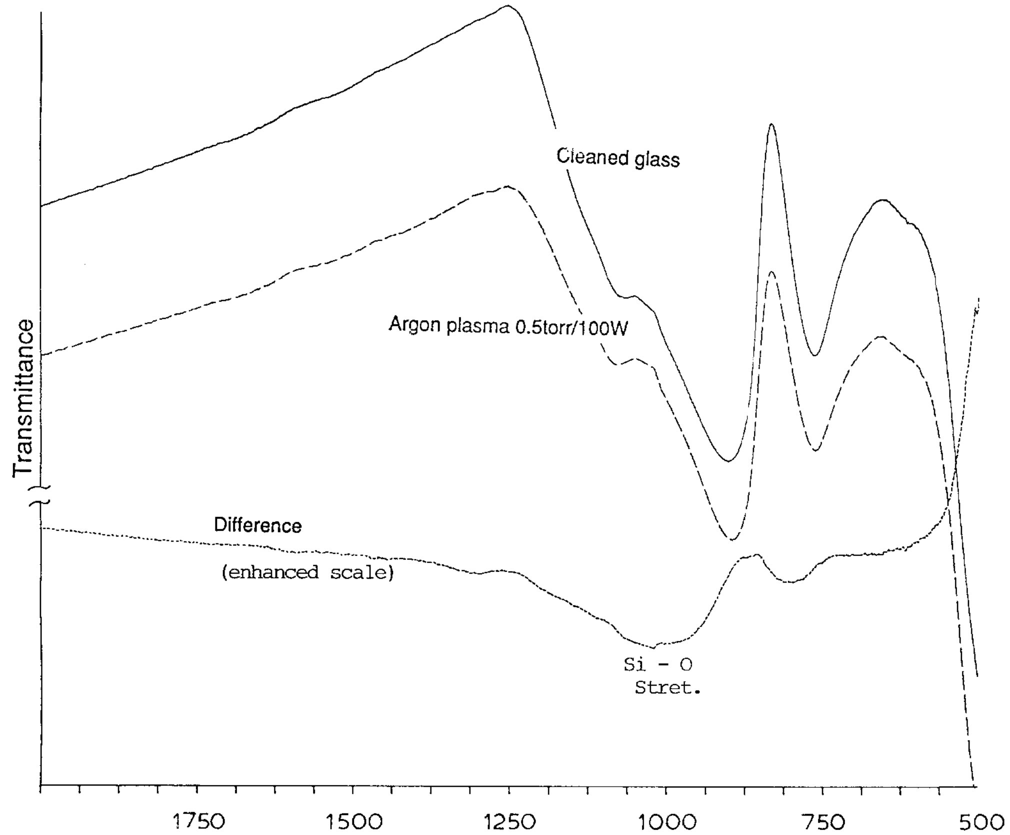

Figure 1 FTIR–ATR spectra of untreated and plasma treated glass slides.

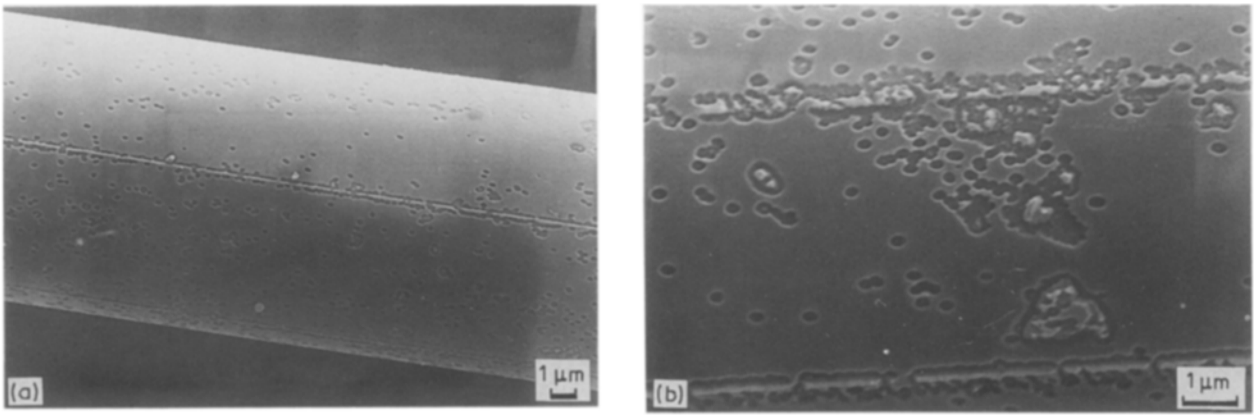

Figure 2 Furnace-cleaned glass fibre treated in argon plasma (0.5 torr, 100 W) for 10 min.

power levels. The values indicate that the treatment makes the surface more hydrophilic and that 100 W seems to be the optimum power level. To study the effects of the operational conditions on gas plasma treatments, Yasuda [12] has proposed the use of a composite parameter, W/F, where W is the plasma power level, F is the gas flow rate which, in effect, represents the energy input per molecule. Thus the plasma treatment can be performed under two conditions: (i) insufficient power, (ii) insufficient flow rate. In the present case, because only the power level is changed keeping the gas flow rate constant, there will be an optimum wattage for the given flow rate. This power level represents input of that amount of energy for the optimum bombardment of the surface. Lower power levels probably mean an insufficient number of active species and/or insufficient energy per particle. Higher power levels may result in an undesirable or drastic breaking of the glass surface.

The argon plasma treatment was performed not only to clean the substrates of molecular level contaminants but also to modify the surface chemistry by the creation of active sites on the surfaces for further grafting with the monomer species introduced into the reactor. Because the plasma polymerized layer has the role of a coupling agent, the plasma polymer has to be grafted to the fibre surface for optimum strength at the interface. Such grafting will only be achieved by breaking covalent bonds and creating active sites on the glass surfaces onto which the monomer can polymerize.

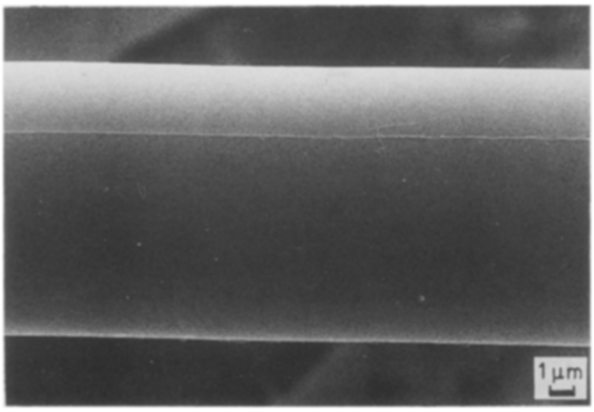

Figure 3 Furnace-cleaned glass fibre.

The wettability values indicate that the argon plasma treatment causes the contact angles to reach a minimum before rising again. If the removal of contaminants only was taking place without any chemical change, the contact angle values would reach a minimum and not change further. To detect the molecular level changes taking place in the glass surface, a typical ATR spectrum of glass slides exposed to the argon plasma (0.5 torr, 100 W) is compared with that of untreated glass slides (Fig. 1). Some differences are evident in the Si–O stretching absorption region (1250 to 900 cm^{-1}). The change in the absorption of the Si–O stretching region (1250 to 900 cm^{-1}) may be due to breaking and reforming of the bonds in the silicate networks of the glass surface ([13] p. 274, [14]) and may be indicative of surface rearrangement similar to that observed with polymeric substrates [11]. It should be noted that the changes will be subtle in comparison to polymer substrates due to the high viscosity and low mobility of the chains in the glass surface.

To detect the changes in the texture on the cleaned glass surfaces, furnace-cleaned glass fibres were exposed to the argon plasma (0.5 torr, 100 W) for different durations and viewed under the SEM. Fig. 2 shows the resultant surface after exposure to the plasma for 10 min and can be compared with the cleaned glass-fibre surface shown in Fig. 3. These micrographs show material removal from the surface due to plasma active species bombardment resulting in microetching. The plasma action also seems to be concentrated on the preexisting defects on the surfaces, e.g. the lip on the fibres. Flat glass substrates treated in the argon plasma at the same operational conditions and viewed under the SEM at these magnifications showed no detectable changes. This is due to the fact that the plasma action is a strong function of the morphology and relative stability of the surface. Significant changes in surface textures have been reported for polyethylene terephthalate fibres [15] as well as for natural and man-made fibres like cotton, cellulose, nylon, etc. [16] as a result of gas plasma treatments.

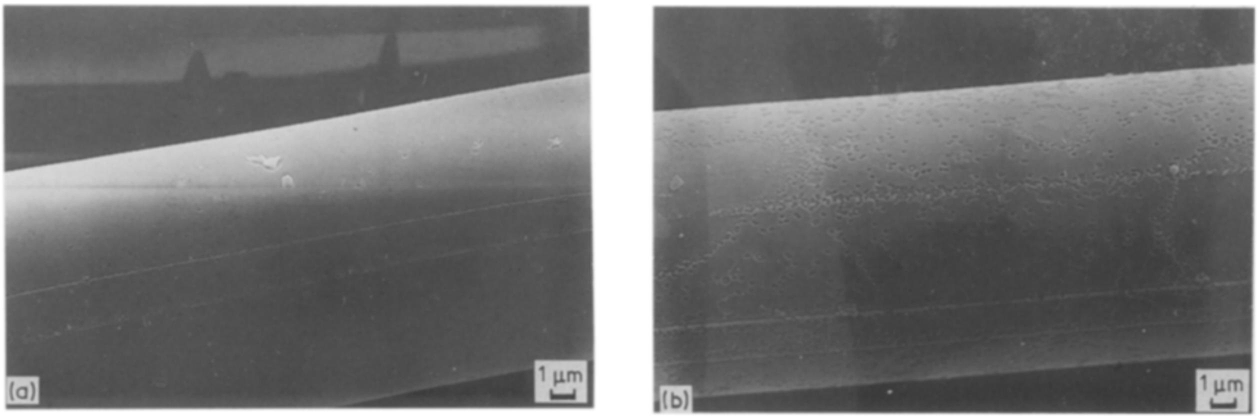

Figure 4 Furnace-cleaned glass fibre treated in argon plasma (0.5 torr, 100 W) for 10 min at two locations in the reactor.

The plasma action was also a function of the position in the reactor as shown by the scanning electron micrographs (Figs 4a and b) at two different locations. Fig. 4a represents the surface near the centre of the reactor chamber and Fig. 4b the surface towards the reactor walls. This is the direct result of the variations in the r.f. field and can only be avoided by proper equipment design. The plasma action will also depend on various other factors, e.g. geometry of the flow of gas, residence time of the gas and the type of gas used, etc. [12].

To see if the ablation of the surface observed could be utilized to remove the sizing from the fibres, as-received fibres were treated in the argon plasma for extended periods of time (1 to 2 h). It should be noted that a furnace treatment (650° C which was a manufacturer-recommended temperature) to remove the sizing will reduce the strength of the glass fibres (glass softens above 250° C). Figs 6 and 7 show the resultant surfaces after 60 and 90 min argon plasma treatment, respectively, and can be compared with the starting surface in the as-received fibres, Fig. 5. Fig. 6 shows that the sizing removal is not complete and that the ablation proceeds by removal of circular segments. The fibre surface treated for 90 min (Fig. 7) is similar to the cleaned fibres treated for 10 min (Fig. 2) and shows that the sizing can, indeed, be completely removed by the argon plasma. The temperature rises during extended treatment, but was no more than 100° C which results in a final temperature significantly below the softening point of glass (250° C) and as such should not reduce the fibre strength. The temperature rise is a function of the plasma reaction conditions: plasma power level, gas flow rate and duration of treatment.

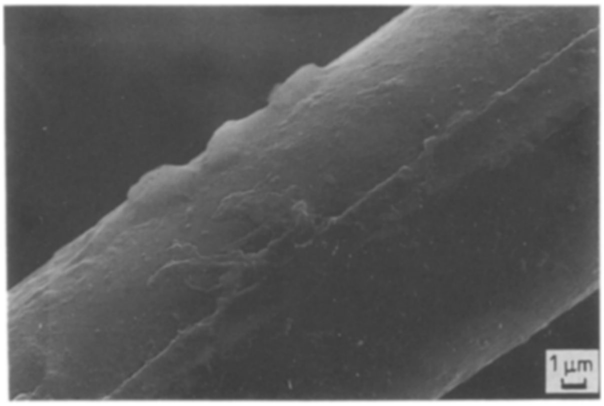

Figure 5 As-received commercial glass fibre.

Single-fibre breaking loads measured on the as-received commercial fibres and the fibres exposed to the argon plasma for 120 min and coated with plasma polymer of allylamine showed that the plasma treatment resulted in minimal loss of tensile properties. The strengths were not calculated from the breaking loads as the diameter of the fibres varied from 8 to 14 μm. The as-received fibres had an average breaking load of 54.2 g and an extension at failure of 2.1 per cent. For the plasma-treated fibres the effect was a function of the position in the reactor (due to variations in the r.f. field within the reactor). The fibres were taken from three positions: centre, middle and towards the walls. The fibres in the centre had the least reduction in strength with an average breaking load of 51.25 g and extension at break of 1.8% and the values for the fibres in the intermediate position were similar at 50 g and 1.6%. The fibres close to the reactor walls had a drastic reduction in strength with values of 28 g and 1.2% extension at break which is attributed to excessive surface etching near the electrodes. The reduction in the extension at break is a direct result of the etching of the surface creating significant defect size (glasses are sensitive to the surface conditions). It should be emphasized that these values are based on very limited tests, the fibre strengths usually vary within a wide range and demand averaging over a significant number (at least 30 for statistical analysis) but the measured values are a reasonable estimate of the process effect on the glass surfaces. In comparison, the furnace-cleaned fibres had a tendency to break on handling and thus their breaking loads could not be evaluated.

A common way to improve bondability of the fibres to the matrices is to increase interfacial or fibre surface area through etching thus increasing the frictional forces. However, such an increase in surface area should not result in any significant reduction in

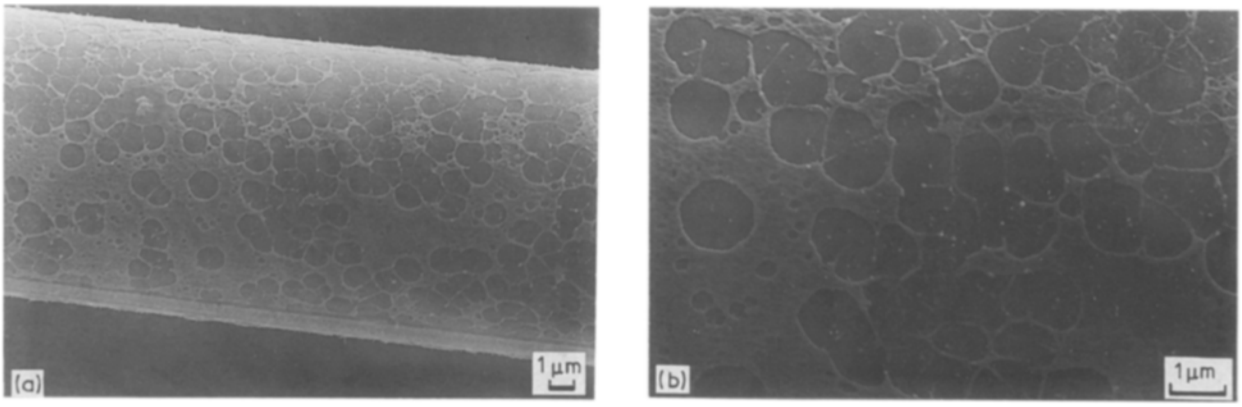

Figure 6 As-received fibre treated in argon plasma (0.5 torr, 100 W) for 60 min.

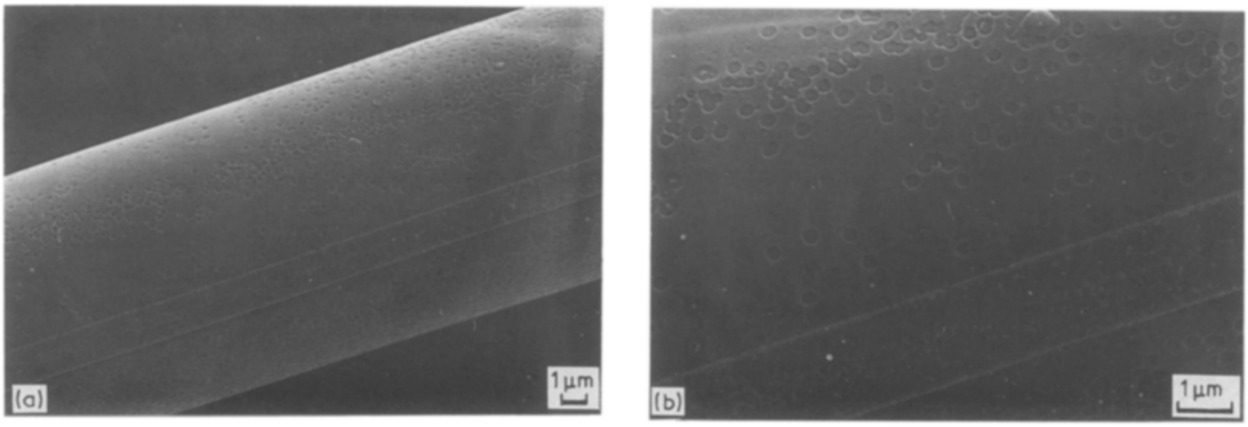

Figure 7 As-received fibre treated in argon plasma (0.5 torr, 100 W) for 90 min.

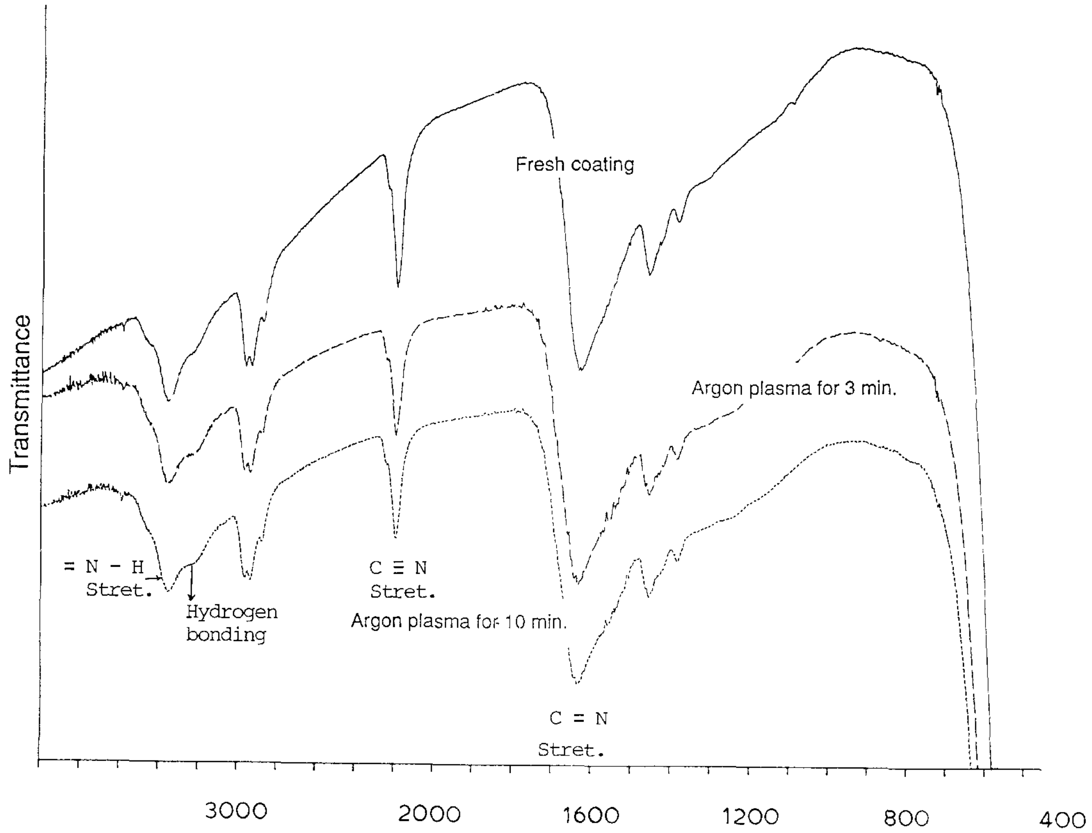

Figure 8 Argon plasma treatment (0.5 torr, 50 W) on the plasma polymer of allylamine.

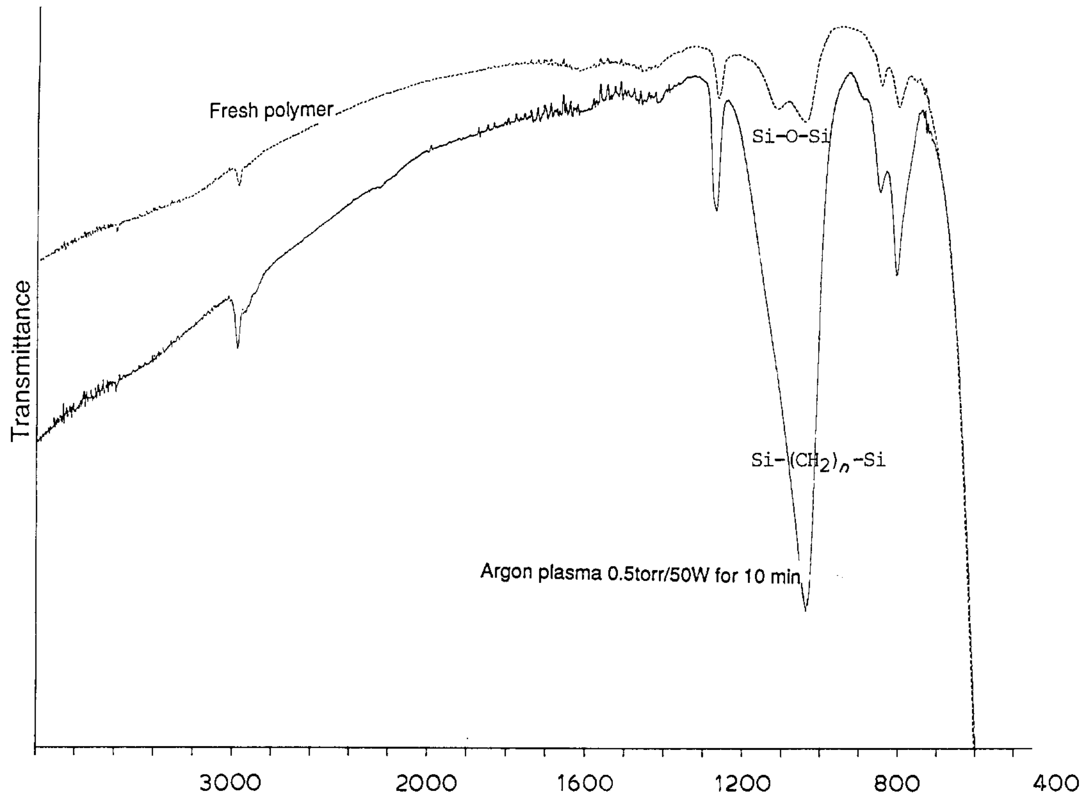

Figure 9 Argon plasma treatment (0.5 torr, 50 W) on the plasma polymer of hexamethyldisiloxane.

the strength of the fibres. The etching time (10 min) selected in this study was chosen to dramatize the effects and to facilitate viewing under the SEM. The plasma processing parameters (gas flow rate, plasma power level, duration of the treatment) can easily be controlled to optimize the surface etching while avoiding any loss in fibre strength.

The plasma treatment scheme proposed to modify the fibre surfaces includes a plasma-induced grafting of selected monomers (monomer discharge) following the argon plasma treatment. The purpose is to increase the fibre's organic compatibility by introducing resin-compatible functional groups on the surface. A second argon plasma treatment to modify further the wettability and structure of the plasma grafted polymer was also studied. Tables II and III list the water contact angles obtained after a post-grafting argon plasma treatment for the two monomers: allylamine and hexamethyldisiloxane, respectively. The values indicate that the effect of the argon etching is to make the surfaces more hydrophilic. The water contact angle value which was 20° for the as-coated

TABLE II Argon plasma etching of allylamine coatings on glass surfaces

Treatment	Water contact angle (deg)
As-coated (0.5 torr, 50 W, 20 min)	
Post-plasma treatment:	
left in vacuum for 15 min after discharge power off	20
air-purged immediately after discharge power off	21
Etched in argon plasma (0.5 torr, 50 W, 3 min)	
Post-plasma treatment:	
left in vacuum for 15 min after discharge power off	13
air-purged immediately after discharge power off	15

TABLE III Argon plasma etching of hexamethyldisiloxane coatings on glass surfaces

Treatment	Water contact angle (deg)
As-coated (0.5 torr, 100 W, 15 min)	
Post-plasma treatment:	
left in vacuum for 15 min after discharge power off	103
air-purged immediately after discharge power off	106
Re-etched in argon plasma (0.5 torr, 50 W, 3 min)	
Post-plasma treatment:	
left in vacuum for 15 min after discharge power off	90
air-purged immediately after discharge power off	77

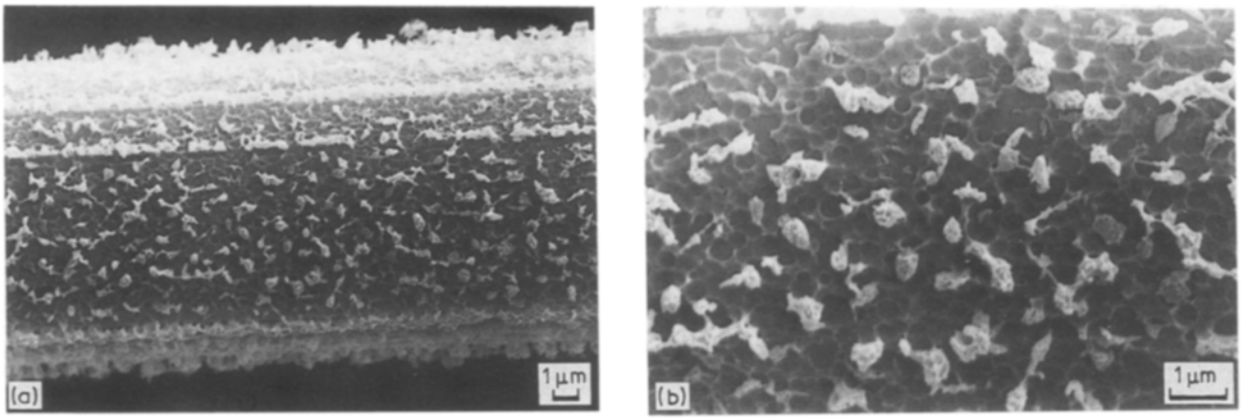

Figure 10 Allylamine coating after argon plasma treatment (0.5 torr, 100 W, 5 min).

plasma polymer of allylamine reduced to 13° for the argon plasma etching of the polymer. Similar effect was also observed for the argon etching of hexamethyldisiloxane (a hydrophobic coating) where the water contact angle value dropped from 103° to 90°.

In the plasma reactor, a substrate surface remains chemically active for some time after turning off the discharge. This is due to the presence of long-lived free radicals and other active species on the surfaces which do not die down immediately. The effect of how the active surfaces are quenched after the plasma modification may be observed through examination of surface energy or contact angle measurements (Tables II and III). Two post-plasma treatments were considered in this study: (i) chamber left in vacuum for 15 min, and (ii) air purged immediately after turning the power off. In Table II with an allylamine coating, there was no change in the contact angles for the two post-plasma treatments, both in the as-coated condition and in the post-coating argon plasma treatment. For the plasma polymer of hexamethyldisiloxane (Table III) there was no significant change in the wettability of the coated polymer by the above post-plasma treatments. But, after the post-coating argon plasma modification, the wettability value significantly dropped from 90° to 77° when the reactor was air purged immediately after turning off the discharge. This can be attributed to the formation of peroxides ([10] p. 41) on the surfaces and may be beneficial for improving the interfacial bonding. The tendency of the peroxide group formation seems to be a function of the plasma polymer. The siloxane bonds in the plasma polymer of hexamethyldisiloxane can probably incorporate oxygen within the surface structure easier than the plasma polymer of allylamine.

To study the changes in the structure of the plasma polymers as a result of the post-grafting plasma treatment, coatings on NaCl plates were exposed to the argon plasma (0.5 torr, 50 W). Fig. 8 shows the infrared spectra of the plasma polymer of allylamine both in the as-coated condition and after the argon plasma treatment. It was expected that either the nitrile stretching absorption ($C{\equiv}N$) near 2200 cm^{-1} or the absorption of $C{=}N$ near 1630 cm^{-1} due to the imine group ($-CH{=}NH$) will change as they are unsaturated sites and hence unstable. But the spectra show that the only difference between the two spectra is the broadening of the N–H stretching absorption in the 3400 to 3200 cm^{-1} region with the increase in intensity of a second peak. This may be attributed to a hydrogen bonding effect ([13] p. 212) between the nitrogen of one chain with the hydrogen of another chain and is thus indicative of the surface rearrangement expected of argon plasma. The results are also indicative of the highly cross-linked state of the nitrile and imine groups.

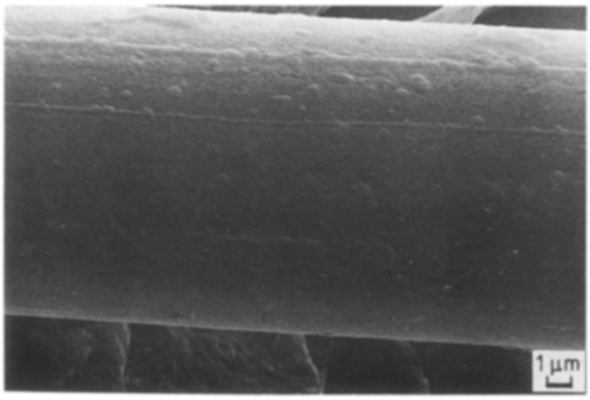

Figure 11 Glass-fibre surface coated with the plasma polymer of allylamine.

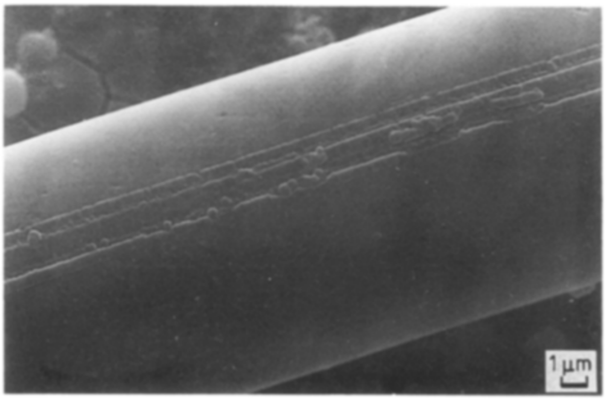

Figure 12 Glass-fibre surface coated with the plasma polymer of hexamethyldisiloxane.

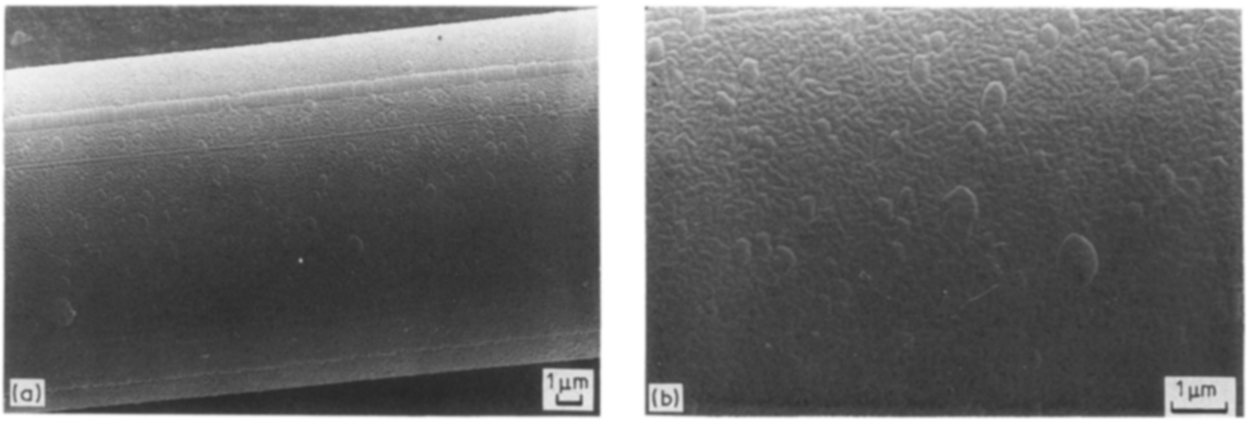

Figure 13 Hexamethyldisiloxane coating after argon plasma treatment (0.5 torr, 100 W, 10 min).

The post-coating argon plasma can also have drastic effects as shown in Fig. 9. The Si–O stretching absorption in the siloxane (Si–O–Si) bonds is replaced with the absorption due to silylmethylene (Si–$(CH_2)_n$–Si) groups as a result of the plasma action [14]. This conversion is also confirmed by the increase in the Si–Me stretching absorptions due to the Si–$(Me)_2$ and Si–Me at 800 cm^{-1} compared to the absorption due to Si–$(Me)_3$ groups at 837 cm^{-1}. This effect, though undesirable in terms of thermal stability (silylmethylene groups will have lower stability than the siloxane groups), improved the surface wettability.

The change in surface texture of the grafted plasma coatings as a result of the argon plasma (0.5 torr, 100 W) once again increases the surface area by microetching. Figs 10a and b show the drastic etching of the surface on allylamine coatings when compared to the as-coated surface in Fig. 11. Under similar argon plasma conditions the hexamethyldisiloxane coatings were not as drastically affected as shown in Figs 12 and 13a and b. The effect of the argon plasma on the polymer coatings will depend on their chemical structure and stability. The plasma polymer of hexamethyldisiloxane is less affected by the argon plasma than the plasma polymer of allylamine probably because of its relatively low organic content and high thermal stability due to a higher degree of crosslinking.

4. Conclusions

The effect of argon plasma on glass surfaces is to modify the surface chemistry by affecting the silicate network and to increase the surface area by microetching. This microetching, which is due to ablation of the material, can also be utilized effectively to clean the fibre of its sizing. Such a process, although time consuming, has the advantage of little or insignificant loss in tensile strength. Argon plasma etching of plasma-coated surfaces can further increase the wettability, the surface area and modify the chemistry of the surface layer.

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