Surface modification of aramid fibre by graft polymerization

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To modify the surface properties of aramid fibre, graft polymerization of acrylamide (AAm) and glycidyl methacrylate (GMA) was performed onto the surface of Kevlar 49. Following plasma treatment and subsequent exposure to air to introduce peroxides onto the fibre surface, the polymer peroxides were decomposed in the monomer solution containing riboflavin by ultra-violet (u.v.) irradiation to effect graft polymerization of the monomers onto the fibre. The monomer solution was prepared from water and dioxane for AAm and GMA, respectively. After removal of homopolymers, the grafted fibre was subjected to surface analysis with attenuated total reflection Fourier-transform infra-red spectroscopy and X-ray photoelectron spectroscopy (XPS). It was found that grafted PAAm and PGMA chains were present in the surface region of the fibre. Graft polymerization was greatly affected by u.v. irradiation time, monomer concentration and plasma treatment time. The reaction of propylamine with the PGMA-grafted surface was accompanied by the appearance of a new nitrogen peak in the XPS spectrum, suggesting the presence of epoxy groups on the surface of PGMA-grafted fibre.

(Keywords: aramid fibre; surface graft polymerization; argon plasma treatment)

INTRODUCTION

Aramid fibres have frequently been utilized for composite material fabrication because of their high thermal stability in addition to their high modulus, high strength, vibration damping and resistance to chemicals. However, aramid is poor in terms of the interfacial adhesion between the fibre and a polymer matrix, although the surface properties are a key factor governing the performance of the composites. Therefore, many surface modifications have been attempted on aramid fibres to improve their adhesion to polymer matrices. Takayanagi *et al.* subjected a metallated aramid fibre to reaction with alkyl halides and bisphenol A type epoxy resin[1,2]. As a result of this reaction, the surface layer of aramid fibre was partly given functional groups. Evaluation of the interfacial adhesion between the modified fibre surface and an epoxy–amine resin by a pull-out test showed that surface modification of the aramid fibre by polyfunctional epoxy resin gave the highest adhesive strength.

Andreopoulos performed the surface treatment of aramid fibre with various compounds and found that methacryloyl chloride was an effective coupling agent with possible grafting to the aramid fibre[3]. Wertheimer and Schreiber modified an aramid fibre by plasma treatment to enhance the bond strength between the aramid and triazine[4]. Eagles *et al.*[5] performed two different surface treatments to improve the adhesion of aramid fibre to thermoplastic polymers, and showed that the sized aramid fibre had the greatest interfacial bond strength and frictional shear strength. Penn and Jutis[6] attached amine-terminated pendent groups to the surface of aramid fibre by a chemical reaction. A single-filament pull-out test used to assess the effect of the pendent groups on the fibre–epoxy matrix bond strength revealed that the presence of the pendent groups increased the adhesive performance. Wu and Tesoro[7] incorporated amine functional groups into aramid fibre surfaces by bromination followed by ammonolysis and also by nitration followed by reduction. The presence of amine groups on the aramid fibre provided remarkably improved peel strength and apparent interlaminar shear strength in epoxy laminates, suggesting a significant role of covalent bonding in improving the adhesion in aramid–epoxy composites.

All the reports mentioned above modify the aramid fibre surface by introducing polymer moieties such as oxidized and amine groups through conventional polymer reactions. It is, however, conceivable that good interfacial properties of aramid fibre would be obtained if the fibre surface carried graft chains, which can be molecularly incorporated into the matrix polymer when a composite is made from the modified fibre. Recently we have improved the surface of ultra-high-modulus polyethylene fibre by graft polymerization of vinyl monomers to render the very hydrophobic surface permanently wettable and to introduce reactive groups on the fibre surface[8]. The objective of the present study is to explore whether or not any surface graft polymerization can proceed onto aramid fibre. For this purpose, acrylamide (AAm) and glycidyl methacrylate (GMA) are employed as monomers for the graft polymerization. To generate active species on the fibre surface for initiation of the graft polymerization, aramid fibre is pretreated with an argon plasma, followed by ultra-violet irradiation in the presence of monomer.

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EXPERIMENTAL

Materials

Kevlar 49 (E. I. Du Pont de Nemours & Co.) was employed as the aramid fibre for surface modification. It was purified by Soxhlet extraction with a mixture of benzene and methanol (1:1) for 20 h and then vacuum-dried at 30°C. AAm monomer of electrophoresis grade was used as obtained. GMA of extra-pure grade was purchased from Tokyo Kasei Co., Ltd, Tokyo, Japan, and used after purification by conventional distillation. 1,4-Dioxane of chromatographic grade, propylamine of guaranteed reagent grade and other reagents were used without further purification.

Plasma treatment

The plasma treatment of the fibre was performed in a bell-jar-type reaction cell (model LCVD 12, manufactured by Shimadzu Co., Kyoto, Japan)[9]. The distance between the two electrodes was kept at 6.5 cm. The frequency and voltage applied were 5 kHz and 270 V, respectively. After fixing the fibre on a stainless-steel sample holder placed between the two electrodes, the pressure in the bell jar was reduced to 10^{-3} Torr, followed by introduction of Ar gas into the bell jar at a flow rate of 20 ml min^{-1}. When the Ar pressure in the bell jar became 3×10^{-2} Torr, low-temperature plasma was generated and the fibre was exposed to the plasma for 30 s, unless otherwise noted. After plasma treatment, the fibre was exposed to air for 30 min at room temperature prior to graft polymerization.

Graft polymerization

Approximately 10 mg of plasma-treated fibre was placed in a Pyrex glass tube containing 5 ml of 20 mg l^{-1} aqueous solution of riboflavin and 20 ml of various concentrations of aqueous AAm solution or 1,4-dioxane GMA solution. The mixture was briefly purged with nitrogen and then plugged with a silicone stopper. The tube containing the fibre/monomer mixture was exposed at 30°C to u.v. light from a 1000 W high-pressure mercury lamp (Riko rotary photochemical reactor, model RH400-10W). The PAAm-grafted fibre was taken out of the tube and placed in distilled water at 65°C under continuous stirring for longer than 15 h, whereas the PGMA-grafted fibre was subjected to Soxhlet extraction with acetone for 7 h to remove the residual monomer and homopolymer. The removal of homopolymer was repeated until the extract solution contained no trace of homopolymers. Generally it took 5 to 10 h.

Characterization

Infra-red spectra were obtained with a Nicolet 20 DXB Fourier-transform infra-red (*FT*i.r.) spectrometer equipped with an attenuated total reflection (a.t.r.) holder. A Ge prism was used as an internal reflection element at the incident angle of 45° to measure a.t.r.-*FT*i.r. spectra. X-ray photoelectron spectra were recorded with an Ulvac-phi 5500 MT X-ray photoelectron spectrometer using an Mg Kα X-ray source. Scanning electron micrographs were taken with a Hitachi S-800 scanning electron microscope (SEM). Prior to SEM observation, the fibre surface was coated with Pt–Pd. The grafted amount of PAAm was determined by the ninhydrin method described elsewhere[9].

Reaction with amine

The PGMA-grafted fibre was reacted with propylamine by immersing the fibre in ethanol solution containing 1 mol l^{-1} propylamine at 60°C for 4 h. Following the amine treatment, the fibre was subjected to Soxhlet extraction with acetone for 7 h to remove propylamine remaining unreacted.

RESULTS

Graft polymerization

To avoid the time-consuming degassing process, graft polymerization was carried out in the presence of riboflavin without degassing, because this compound consumes oxygen dissolved in the monomer solution upon u.v. irradiation[10].

Acrylamide. *Figure 1* shows the dependence of u.v. irradiation time on the graft polymerization of AAm onto the fibre pretreated with Ar plasma for 30 s. It is clearly seen that the graft amount increased almost linearly with u.v. irradiation up to 50 min.

A.t.r.-*FT*i.r. and XPS spectra of PAAm-grafted fibre are shown in *Figures 2* and *3*, respectively, along with those of virgin fibre, when graft polymerization was conducted in 10 wt% AAm solution by u.v. irradiation for 50 min after plasma treatment. As can be seen, the grafted surface exhibited i.r. and XPS spectra different from those of the virgin fibre. The strong i.r. peak at 1656 cm^{-1} seen in *Figure 2b* is assigned to the amide bond of PAAm grafted onto the fibre. Comparison of *Figure 3a* with *3b* clearly reveals an increase of nitrogen and oxygen peaks relative to the carbon peak by graft polymerization of AAm. *Table 1* shows the atomic ratios determined by the XPS spectra for these fibres. The result also supports the occurrence of graft polymerization of AAm on the surface region of aramid fibre.

Glycidyl methacrylate. *Figures 4* and *5* show a.t.r.-*FT*i.r. and XPS spectra of the aramid fibres, respectively, when GMA was graft polymerized at 30°C in 10 vol% dioxane solution by u.v. irradiation for 2 h after Ar plasma

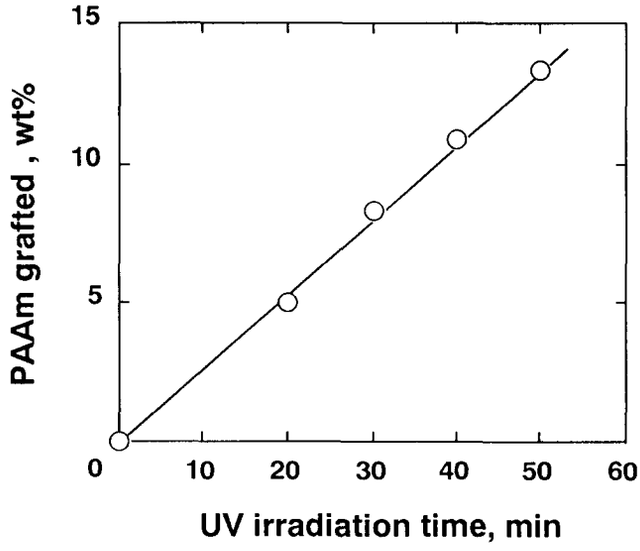

Figure 1 Weight increase by AAm graft polymerization induced by u.v. irradiation at 30°C in 10 wt% AAm solution onto the aramid fibre pre-exposed to Ar plasma for 30 s

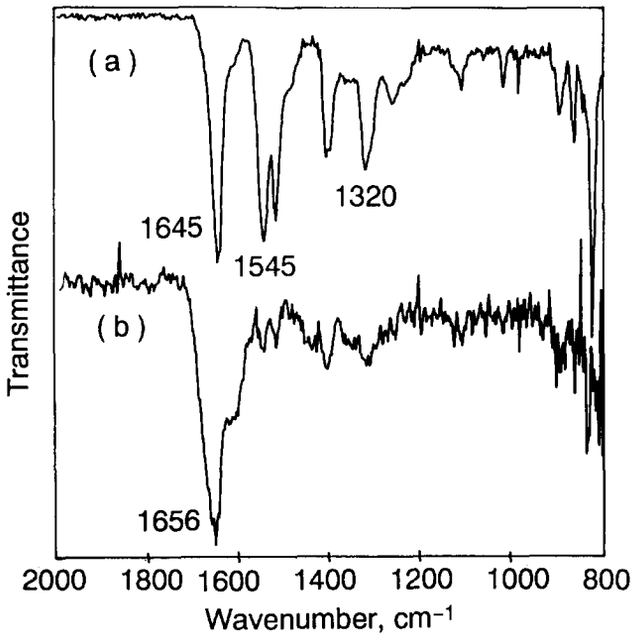

Figure 2 A.t.r.–*FT*i.r. spectra of (a) the virgin aramid fibre and (b) the PAAm-grafted aramid fibre (30 s plasma exposure, 10 wt% AAm solution, 30°C and 50 min u.v. irradiation)

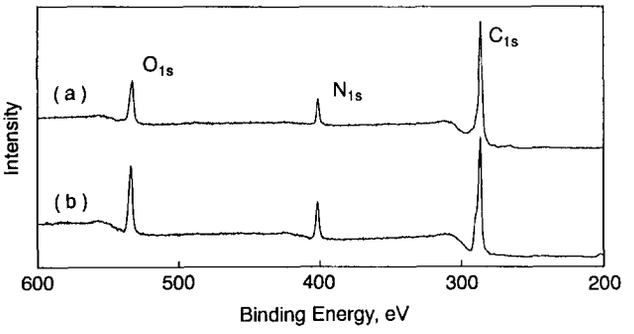

Figure 3 XPS spectra of (a) the virgin aramid fibre and (b) the PAAm-grafted aramid fibre (30 s plasma exposure, 10 wt% AAm solution, 30°C and 50 min u.v. irradiation)

treatment for 30 s. In *Figure 4*, the carbonyl peak of GMA is clearly seen at 1730 cm^{-1}, indicating that the surface of aramid fibre was modified by graft polymerization of GMA. It is obvious from *Figure 5* that the nitrogen peak disappeared while the oxygen peak significantly increased by graft polymerization of GMA. This again supports the presence of PGMA graft chains covering the fibre surface.

Amide I, amide II and amide III bands at 1645 cm^{-1} (C=O), 1545 cm^{-1} (CNH) and 1320 cm^{-1} (CNH), which are assigned to the aramid fibre, can be observed in the a.t.r.-*FT*i.r. spectrum in *Figure 4*[1], but the nitrogen peak assigned to the aramid fibre disappeared from the XPS spectrum in *Figure 5* upon graft polymerization. The spectroscopic evidence indicates that the graft polymerization of PGMA is restricted to the fibre surface.

Compared to the graft polymerization of AAm, it was too difficult to determine quantitatively the absolute amount of grafted PGMA because of its very low surface concentration. Besides, no sensitive analytical means such as the ninhydrin method is available for the GMA polymer. Therefore, the relative absorbance of the carbonyl peak of GMA at 1730 cm^{-1} against the amide peak at 1645 cm^{-1} as internal standard was employed as a measure of graft amount, similar to the graft polymerization of GMA to polyethylene fibre[8]. The result of the a.t.r.-*FT*i.r. measurement is shown in *Figure 6* for the fibres exposed to Ar plasma for different times, followed by graft polymerization of GMA in 10 and 20 vol% dioxane solution by u.v. irradiation for 2 h. Apparently, the i.r. ratio increased with the plasma treatment for both concentrations of GMA, but graft polymerization of 20 vol% GMA seemed to be higher in yield than that of 10 vol% GMA. *Figure 7* shows the effect of u.v. irradiation on the graft polymerization of GMA onto the fibre treated with plasma for 60 s using 10 and 20 vol% monomer solution. The absorbance ratio increased with the u.v. irradiation, and graft polymerization with 20 vol% GMA was higher in yield than that with 10 vol% GMA, similar to *Figure 6*.

To get additional evidence for the surface graft polymerization of GMA, we attempted to react the

Table 1 Atomic surface concentration of virgin, PAAm-grafted and PGMA-grafted aramid fibres

	Concentration (%)		
	C	N	O
Theoretical			
Aramid	78	11	11
PAAm	60	20	20
PGMA	70	0	30
Experimental			
Virgin aramid fibre	80	8	12
PAAm-grafted aramid fibre[a]	73	11	16
PGMA-grafted aramid fibre[b]	74	0	26

[a] 30 s plasma exposure, 10 wt% AAm solution, 30°C and 50 min u.v. irradiation

[b] 30 s plasma exposure, 10 vol% GMA solution, 30°C and 2 h u.v. irradiation

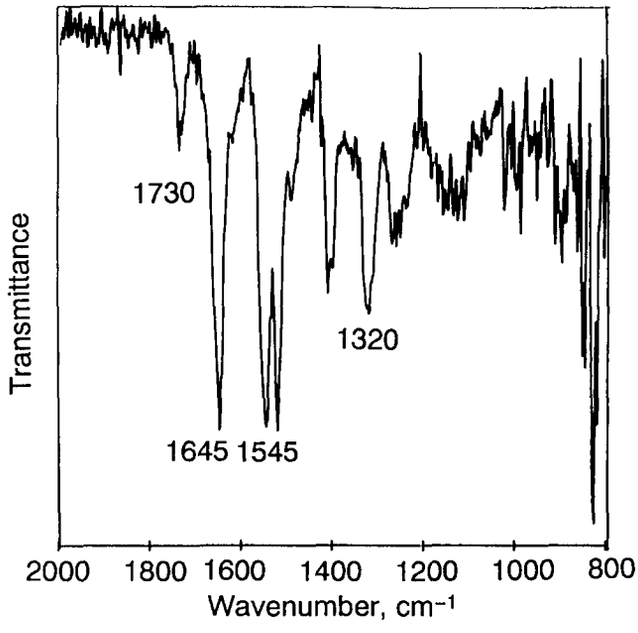

Figure 4 A.t.r.-*FT*i.r. spectrum of the PGMA-grafted aramid fibre (30 s plasma exposure, 10 vol% GMA solution, 30°C and 2 h u.v. irradiation)

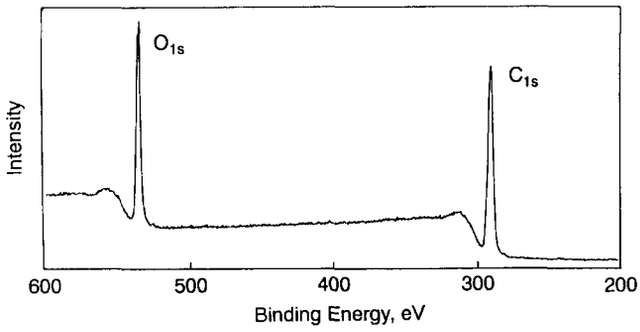

Figure 5 XPS spectrum of the PGMA-grafted aramid fibre (30 s plasma exposure, 10 vol% GMA solution, 30°C and 2 h u.v. irradiation)

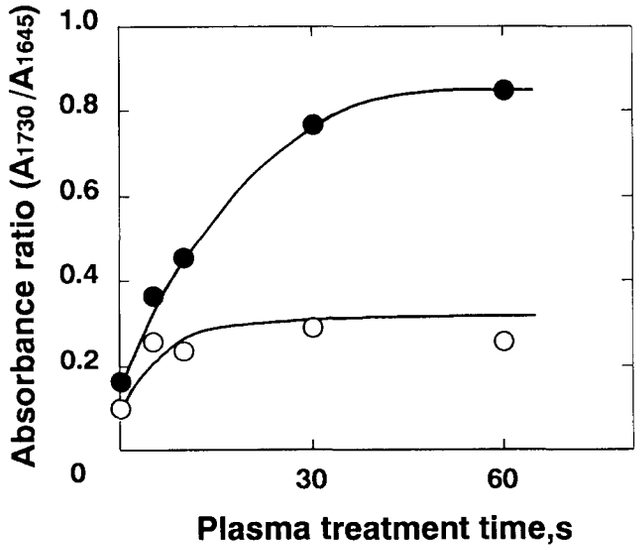

Figure 6 Changes in the absorbance ratio of the carbonyl peak at 1730 cm^{-1} to the amide peak at 1645 cm^{-1} for the aramid fibre grafted with PGMA by u.v. irradiation for 2 h after plasma treatment for different times: (○) 10 vol% GMA; (●) 20 vol% GMA

PGMA-grafted aramid fibre with propylamine, which is a small aliphatic amine reactive with epoxide. The specimen was graft polymerized at 30°C in 10 vol% GMA solution by u.v. irradiation for 2 h after plasma treatment for 30 s. *Figure 8* shows the XPS spectrum of PGMA-grafted fibre after reaction with propylamine for 4 h at 60°C. Comparison with the XPS spectrum in *Figure 6* clearly indicates that the oxygen peak decreased while the nitrogen peak appeared upon reaction with propylamine. This spectral change must be due to the covalent coupling of propylamine with the epoxy group of PGMA.

Surface topography

Figure 9 shows SEM micrographs of the virgin and the grafted aramid fibres. Apparently, the surface of the virgin fibre is very smooth, whereas that of the grafted fibres is much rougher. It is unclear to us why graft polymerization makes the fibre surface irregular, but it seems to be due to the existence of grafted polymer chains. This may be supported by the finding that more extensive graft polymerization yielded a rougher surface.

DISCUSSION

As described above, the results of a.t.r.-*FT*i.r. and XPS have revealed that the graft polymerization could introduce PAAm and PGMA chains onto the surface region of the fibre, because the depth of penetration in the a.t.r.-*FT*i.r. and XPS measurements is 0.2–0.8 μm and about 2 nm, respectively[11]. Unfortunately, no direct evidence for localization of the grafted region to the fibre surface was obtained, as the Kevlar fibre is very strong and thin. However, the fact that there was no significant change in bulk properties and diameter of the fibre after graft polymerization strongly supports the localization of the graft polymerization to the fibre surface. These findings are very similar to our previous surface modification by graft polymerization onto polymers such as poly(ethylene terephthalate)[12], polyethylene[9,13,14], silicone[15], polypropylene[16], ethylene–vinyl acetate copolymer[17], polyurethane[18], poly(methyl methacrylate)[19] and cellulose[20]. The pretreatment of their surface prior to graft polymerization to introduce polymer radicals or peroxides that are capable of initiating graft polymerization of vinyl monomers is different among these polymers. It includes high-energy radiation[21], glow

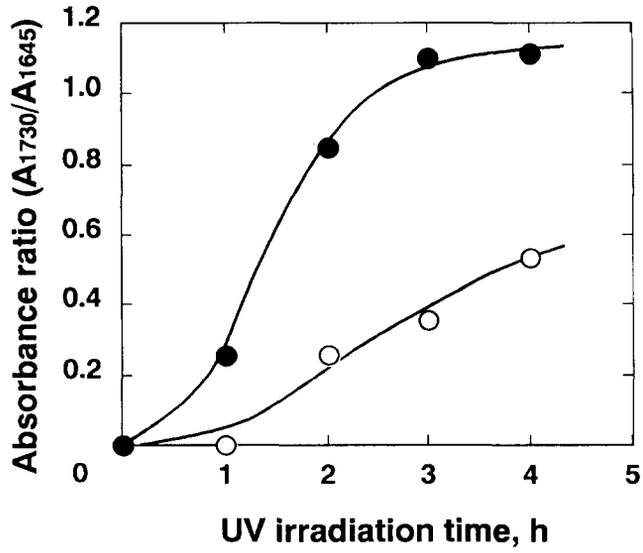

Figure 7 Changes in the absorbance ratio of the carbonyl peak at 1730 cm^{-1} to the amide peak at 1645 cm^{-1} for the aramid fibre grafted with PGMA by u.v. irradiation for different times after plasma treatment for 60 s: (○) 10 vol% GMA; (●) 20 vol% GMA

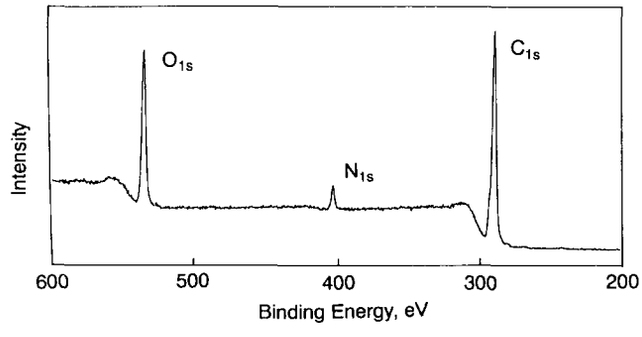

Figure 8 XPS spectrum of the PGMA-grafted aramid fibre after reaction with propylamine for 4 h (graft polymerization: 30 s plasma exposure, 10 vol% GMA solution, 30°C and 2 h u.v. irradiation)

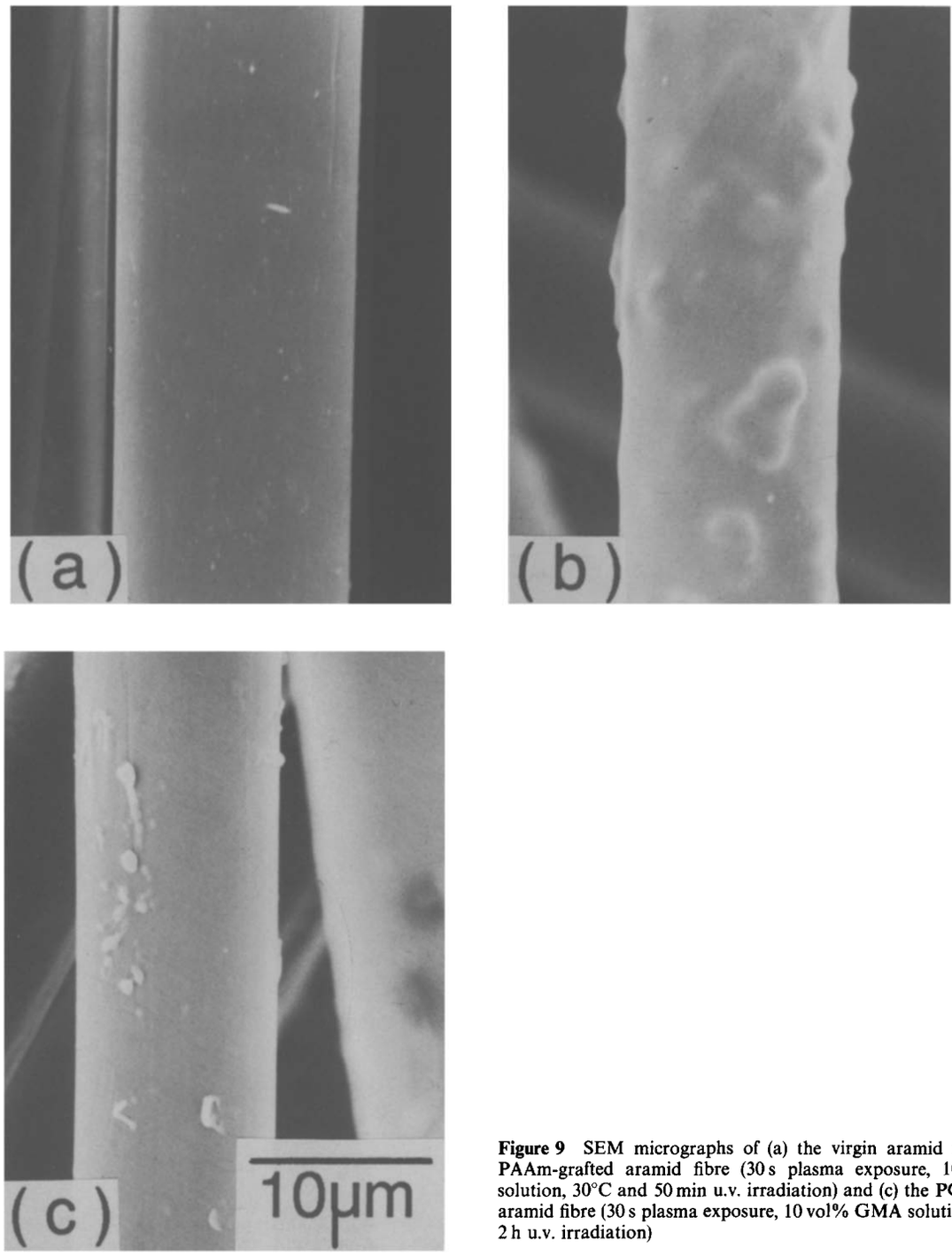

Figure 9 SEM micrographs of (a) the virgin aramid fibre, (b) the PAAm-grafted aramid fibre (30 s plasma exposure, 10 wt% AAm solution, 30°C and 50 min u.v. irradiation) and (c) the PGMA-grafted aramid fibre (30 s plasma exposure, 10 vol% GMA solution, 30°C and 2 h u.v. irradiation)

discharge[9], corona discharge[13,15], u.v. irradiation[16,17] and ozone[20].

An advantage of these graft polymerization methods is to introduce functional groups onto the polymer surface region if a monomer with functional groups is used for the graft polymerization. This is in marked contrast to the low-temperature plasma treatment, which generally produces only oxidized polar groups on the treated polymer surface. It should also be stressed that the modification by plasma-induced graft polymerization is limited only to the surface region of the treated material without impairing the mechanical properties of the fibre, because plasma treatment yields oxidized groups only in the surface region. Staining of the cross-section of grafted materials with dye proved that plasma-induced graft polymerization is actually restricted to the surface region of material[9].

U.v. irradiation was performed on the monomer solution containing the plasma pretreated fibre in the present graft polymerization.

There are two reasons for this u.v. irradiation. One is to cleave at 30°C the polymer peroxide bond produced by the plasma treatment and the other is to reduce the oxygen concentration in the monomer solution virtually to zero. Indeed, riboflavin added to the monomer solution could consume most of the oxygen molecules present in the monomer solution by photo-induced reactions associated with riboflavin[10].

For the surface graft polymerization to the aramid fibre, AAm was chosen in the present study because of

high potentiality of the surface graft polymerization of this monomer and the established quantitative analysis of amide by the ninhydrin method. Although PAAm is a water-soluble hydrophilic polymer, it exhibits strong adhesion against another substrate when grafted and brought into direct contact in the presence of water and subsequently dried[22]. It should also be pointed out that the amide group of grafted PAAm can be converted to reactive moieties such as amino and carboxyl groups by Hofmann degradation and alkaline hydrolysis, respectively[14].

In contrast to AAm, GMA monomer has an epoxy group that can readily react with many functional groups such as amine, carboxyl, acid anhydride and so on. It is widely accepted that formation of covalent bonds between fibre surface and resin matrix can improve the interfacial adhesion in fibre-reinforced composites[7]. Therefore, graft polymerization of GMA seems very promising for the surface modification of aramid fibre when it is to be used for composite material fabrication with polymer matrices having reactive groups such as amine.

Evaluation of the effectiveness of our surface-modified Kevlar in composite fabrication will be published in the near future.

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