The effects of ionization and epoxy reaction on the surface and mechanical properties of poly(*p*-phenylene terephthalamide) fibres

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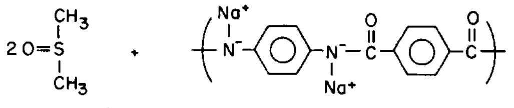
The effects of ionization and epoxy reactions on the bulk and surface properties of poly(*p*-phenylene terephthalamide) (PPTA), namely Kevlar 149, fibres were studied. When the ionized Kevlar 149 fibres were quenched in water, their tensile properties were significantly lowered with increasing ionization time. The lowered tensile strengths were attributed to the reactions between the residual sodium ions in the fibres and water, and possibly the subsequent hydrolytic chain scissions of the PPTA molecules. The tensile properties of the fibres were only slightly lowered with increasing NaH concentrations. With increasing ionization time, the epoxy reaction first significantly lowered and then began to compensate for the tensile properties of the fibres. The interfacial shear strength of the Kevlar 149 fibres with the epoxy was slightly higher and was associated with better wetting property of Kevlar 149 fibres and surface compositional differences between the two PPTA fibres. The ionization and epoxy reaction conditions employed for Kevlar 49 fibres did not affect the interfacial shear strengths with the epoxy resin. The interfacial shear strength for Kevlar 149 fibres was increased from 4.35×10^{-3} g μm^{-2} for the untreated to 5.29×10^{-3} g μm^{-2} for the ionized and epoxy-reacted fibres, a 22% increase.

(Keywords: poly(*p*-phenylene terephthalamide); fibres; ionization; epoxy reaction; tensile strength; surface topography; interfacial shear)

INTRODUCTION

The ionization or metallization of poly(*p*-phenylene terephthalamide) (PPTA) molecules is possible by reacting the PPTA polymer with sodium methylsulphinyl carbanion from mixing sodium hydride (NaH) in dimethylsulphoxide (DMSO). The formation of methylsulphinyl carbanions and the formation of the polyanions, Na^+PPTA, are illustrated as follows:

Formation of methylsulphinyl carbanion



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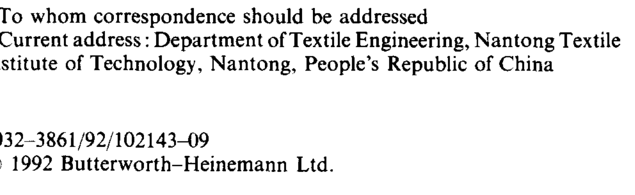
Ionization or metallization of PPTA



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The ionized PPTA powders can be dissolved in DMSO[1] at low concentrations (ca. 1–3 wt%) and have improved solubility in other solvents[2]. Soluble polyanions are produced only when the extent of deprotonation exceeds 60%[3]. The ionized PPTA molecules are also capable of further bonding with aliphatic and arylalkyl halides[1,4] and copolymerization[5]. Chemical bondings to ionized PPTA fibres, specifically Kevlar fibres, have also been reported. These reports include the reactions of ionized Kevlar 29 fibres with monobromoacetic acids and acrylonitrile[6], of ionized Kevlar 49 fibres with epichlorohydrin[7], and of ionized Kevlar 49 fibres with epoxy[2,7].

As manufacturing methods influence the micro- and macrostructure of fibres strongly, the different spinning and the subsequent processing for PPTA fibres are expected to cause structural differences among Kevlar 29, 49 and 149 fibres. For instance, the structural differences between Kevlar 49 and 149 fibres have been indicated by their different moisture sorption properties[8]. For hydrophilic and semicrystalline polymers, moisture sorption is a diffusion process and is dependent upon both the chemical and internal structure of the materials. Equilibrium moisture content in Kevlar 49 fibres is close to linearly proportional to the relative humidity[9] whereas a third-order polynomial dependence of moisture regains with increasing humidity has been reported for Kevlar 149 fibres[8]. The non-linear moisture sorption isotherm found on Kevlar 149 fibres is typically observed on semicrystalline polymers. The higher and nearly linear moisture sorption isotherm of Kevlar 49 fibres is attributed to the interfibrillar microvoids and the hygro-

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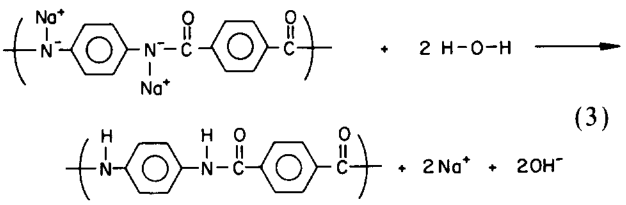
scopic Na_2SO_4 in the fibres[9–11]. It has been suggested that the microvoids in the fibres allow moisture to penetrate into the fibre freely to be absorbed by Na_2SO_4 (ref. 10) and the amide linkages in the PPTA chains[11].

Structural differences can also affect the accessibility of functional groups in the fibres for chemical reaction. It has been shown that less than 30% of the N–H groups in Kevlar 49 fibres were accessible for chemical bonding due to the high molecular order and extensive inter- and intramolecular hydrogen bonding[12,13]. Previous ionization studies on PPTA fibres, which assumed that reaction occurred at the fibre surfaces, focused on changes in the surface and adhesive properties of the subsequently grafted Kevlar 29 and 49 fibres. Whether the ionization and the subsequent reactions affect the bulk properties of the fibres was not verified.

This study focused on the much less studied Kevlar 149 fibres with some comparison made on the Kevlar 49 fibres. The effects of the ionization reaction and the subsequent reaction with an epoxy resin on the bulk as well as the surface properties were studied separately. The ionization reaction followed equations (1) and (2). The effects of ionization alone were studied by reversing the reaction by quenching in water. Ideally, this reaction would replace the Na^+ ion on the ionized PPTA molecules with H^+ ion:

Quenched reaction with H_2O



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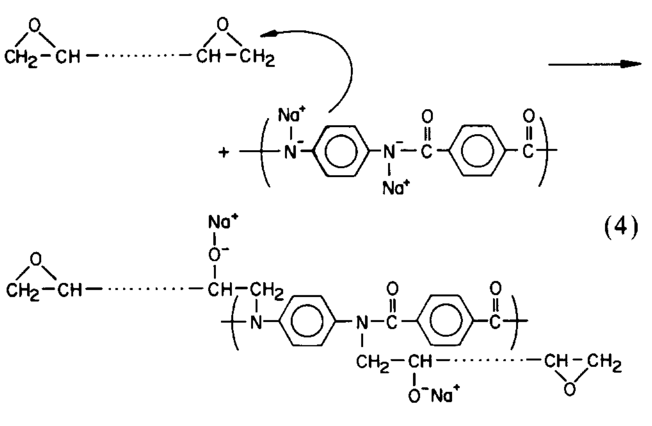
Reaction with an epoxy resin. In the subsequent epoxy reaction, both the ionization reaction time and the NaH concentration were included in the investigation. The negatively charged nitrogen of the ionized PPTA (from equation (2)) attacked the primary carbon of the epoxide[3]:



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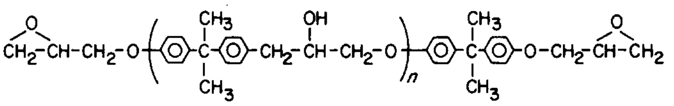
EXPERIMENTAL

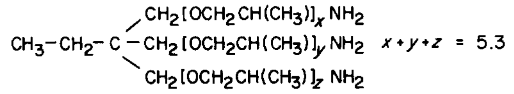
Fibres and reagents

The poly(*p*-phenylene terephthalamide) fibres used in this study were Kevlar 49 and 149 filaments from E.I. du Pont de Nemours Inc. For each treatment, continuous filaments were wound into a loop with a circumference of about 20 cm. The filament loops were cleaned in carbon tetrachloride for 10 min using bubbling nitrogen for agitation. The rinsed fibres were then oven dried at 100°C for 2 h and stored in a desiccator under vacuum before use.

The chemicals used were reagent-grade and were used without further purification. The epoxy was diglycidyl ether of bisphenol A (Dow's DER 332):



with epoxide equivalent molecular weight of 172–176 g mol^{-1}. A primary triamide (Jefferson Chemical's Jeffamine T-403) shown below was added as the curing agent at a 40:100 weight ratio:



$$CH_3{-}CH_2{-}C{\left\{\begin{array}{l} CH_2[OCH_2CH(CH_3)]_xNH_2 \\ CH_2[OCH_2CH(CH_3)]_yNH_2 \\ CH_2[OCH_2CH(CH_3)]_zNH_2 \end{array}\right.} \quad x+y+z = 5.3$$

Reactions

The reaction conditions and reagent concentrations for the experiments reported in this paper are listed in *Table 1*. The ionization bath was prepared by stirring NaH into dimethylsulphoxide (DMSO). The dissolution was aided by heating the solution to about 40–45°C in a nitrogen atmosphere with continuous stirring for 40 min. After cooling the solution to 23°C, the fibres were added to the reaction solution. Agitation was provided by bubbling nitrogen through the solution during the ionization reaction. The reaction varied in length from 0.5 to 4 h.

When the effects of the ionization reaction were evaluated, the ionized fibres were quenched with water. Two quenching procedures were examined. One involved rinsing the ionized fibres with an excessive amount of flowing water. The other included two consecutive rinses in DMSO followed by rinsing in excessive amounts of water. Quenching in water lasted up to about 1 min whereas the DMSO rinse took about 20 s.

For reactions with the epoxy resin, the ionized fibres were rinsed with DMSO before being added to a DMSO bath containing the epoxy resin. The epoxy was added to DMSO in a bubbling nitrogen atmosphere. For studying the length of ionization time, a concentration of 0.083 g ml^{-1} epoxy/DMSO was used initially. This ratio was then reduced to 0.0083 g ml^{-1} epoxy/DMSO for the rest of the study. After the reaction with epoxy, the fibres were washed with acetone until the rinsing acetone became clear. The fibres were placed in a vacuum desiccator.

Tensile and interfacial shear strengths

The tensile properties of the untreated and treated fibres were measured by an Instron tensile tester. Specimens for single fibre test were prepared according to a fibre mounting procedure previously described[14]. All fibres were tested with a 25.4 mm gauge length at 20 mm min^{-1} cross-head speed under constant temperature (21°C) and humidity (65% relative humidity). The adhesive bonding force between fibre and epoxy resin was measured by the microbond method described previously[15]. All fibres were dried over desiccant in vacuum at 21°C.

Table 1 Reaction conditions for ionization and epoxy reactions

	Ionization		Reaction with epoxy	
Experiment	NaH/DMSO concentration (g ml^{-1})	Time	Epoxy/DMSO concentration (g ml^{-1})	Time
I. *Fibre size and surface morphology*				
Kevlar 49	0.008	1[a,e] and 4 h[a]	0.083	16 h
Kevlar 149	0.008	0.5[b], 1[b] and 4 h[c]	0.083	16 h
II. *Quenched ionization reaction*				
Water alone	0.008	1, 2, 5, 10 min	–	–
DMSO and water	0.008	0.5, 1, 2, 10, 30 min	–	–
III. *NaH concentration*	0.0004, 0.0008, 0.004, 0.008	1 min	0.0083	1 h
IV. *Ionization time*	0.008	0.5[f], 1, 5, 10, 30[d], 60 min	0.0083	1 h

[a] Condition for fibres shown in *Figure 2*
[b] Condition for fibres shown in *Figure 5*
[c] Condition for fibres shown in *Figure 4*
[d] Condition for fibres shown in *Figure 7*
[e] Condition for treated Kevlar 49 fibres shown in *Figure 11*
[f] Condition for treated Kevlar 149 fibres shown in *Figure 12*

Scanning electron microscopy

Cut segments of fibres were mounted on sample stubs and sputtered with gold.

RESULTS AND DISCUSSION

Fibre size and surface morphology

The surface features of the untreated Kevlar 49 fibres including irregular particles and elongated voids were detailed by scanning electron microscopy in our previous paper[15]. Similar surface appearance was also observed on the untreated Kevlar 149 fibres. In addition, peeled surface fibrils (*Figure 1a*) and continuous spiral gaps along the fibre axis (*Figure 1b*) were frequently observed. These gaps ranged from approximately 1.6 to 2.0 μm in width and were bridged by fibrils at constant intervals (*Figure 1c*). The spiral defects were thought to be of manufacturing origin[16]. The cause and significance of these macrostructural features on fibre properties are yet to be determined.

The reaction variables in the ionization and the epoxy reactions were first examined by varying the ionization times at a fixed 0.008 g ml^{-1} NaH/DMSO concentration (I in *Table 1*). This concentration was identical to that used in the ionization of PPTA powder[1,2]. The Kevlar 49 fibres were ionized for 1 and 4 h and then reacted with epoxy for 16 h. The fibres ionized longer had very granulated and rough surfaces (*Figure 2a*). The fibre size estimated from the SEMs was about 15.4 μm as compared to the average 12.4 μm diameter of the untreated fibres[8]. The 1.5 μm thick epoxy coating on the fibre surfaces suggested substantial epoxy deposition on fibre surfaces. For the 1 h ionization treatment, the fibre surfaces also appeared granulated, but were not nearly as rough (*Figure 2b*). The 13.5 μm fibre diameter estimated from the SEMs showed a reduced epoxy thickness of about 0.5 μm. The fracture ends of the epoxy-reacted fibres (4 h ionization) showed a clearly differentiated sheath–core structure (*Figures 3a* and *3b*). The fracture of the coated sheath appeared to be brittle with a fibrillated fracture of the fibre core. The core dimension was slightly smaller than the dimension of the original fibre.

The same conditions studied on the Kevlar 49 fibres, i.e. 0.008 g ml^{-1} NaH/DMSO ionization and 16 h reaction in a 0.0883 g ml^{-1} epoxy/DMSO concentration, were used for treating Kevlar 149 fibres. Similarly coated and granulated surfaces were observed on the epoxy-reacted Kevlar 149 fibres after a 4 h ionization reaction (*Figure 4a*). The estimated diameter from SEM examination on the modified fibres was 14.7 μm as compared to the 12.9 μm diameter of the untreated fibres[8]. The surface coating on fibres was about 0.9 μm thick. Surface peeling of the reacted fibres (*Figure 4b*), though not often observed, was thought to be related to the segregated and fibrillated fibre skin shown on the untreated fibres (*Figure 1a*). As the ionization reaction time decreased to 1 h and 0.5 h, the surfaces became less granulated and more uniform (*Figures 5a* and *5b*). The fibre diameters were also reduced to 14.2 and 13.3 μm, respectively. For the 0.5 h reaction, the spiral gaps on fibres (untreated in *Figures 1b* and *1c*) were nearly filled by the epoxy coating (*Figure 5c*).

The thickness of the epoxy coating on these PPTA fibres appeared to be closely associated with the ionization times. Under the same ionization conditions, the thickness of epoxy coating on Kevlar 49 fibres showed continuous increases whereas that on the Kevlar 149 fibres levelled off as ionization time increased (*Figure 6*). This difference suggested that the extent of ionization on these two Kevlar fibres may be different.

The epoxy thickness may also be reduced by lessening the epoxy concentration and the length of the epoxy reaction. After a 30 min ionization, smooth surfaces (*Figure 7a*) were observed on fibres treated at a reduced epoxy concentration (0.0083 g ml^{-1} epoxy/DMSO) and epoxy reaction time (1 h). The gaps on fibres were mostly concealed with occasional unfilled holes along the spirals (*Figure 7b*). At this reduced epoxy concentration, surface coating was a minimum with no change in fibre size.

As discussed earlier, the surface epoxy coating thickness could be reduced by shortening the ionization reaction

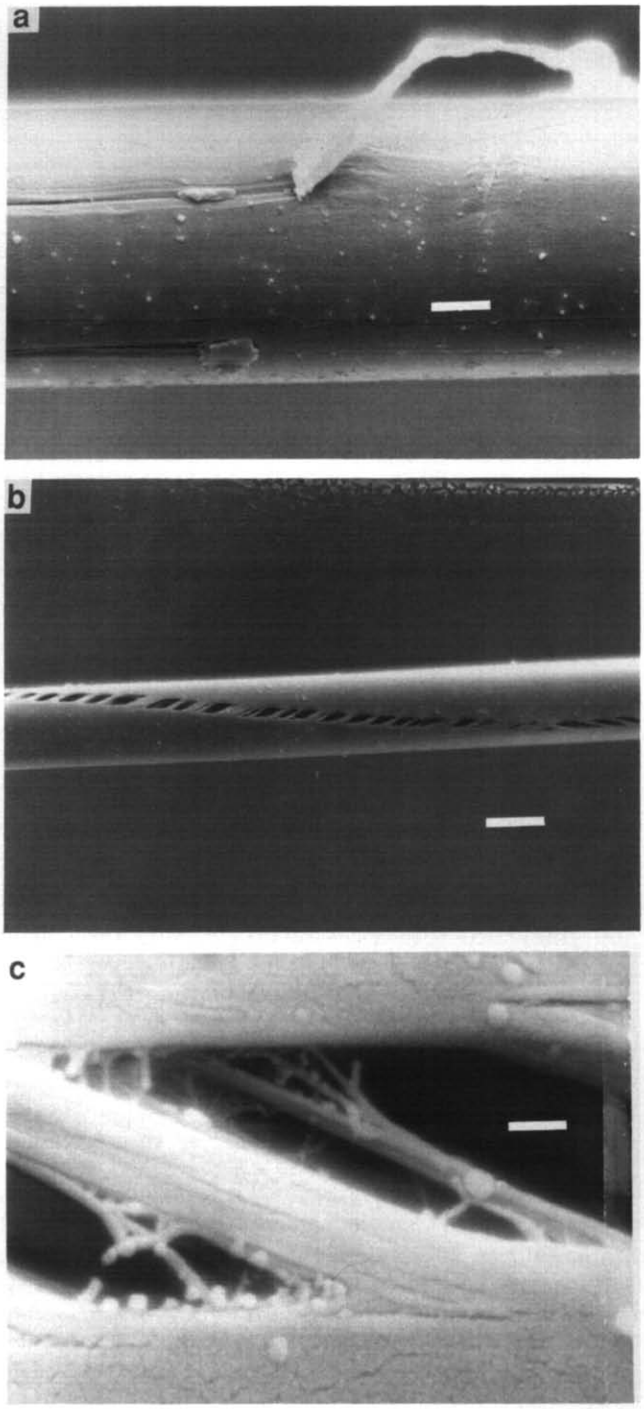


Figure 1 Surface defects on Kevlar 149 fibres: (a) peeled fibril on the surface (bar = 2.56 μm); (b) spiral gap along fibre (bar = 9.34 μm); (c) fibrillar connection across the gap (bar = 0.39 μm)

time (*Table 1*). The epoxy-reacted Kevlar 149 fibres that were ionized for 5 min or less show no observable surface effects. Those fibres appear the same as the untreated fibres (*Figure 1*). In the rest of this study, reduced reaction conditions were used to study the effects of the quenched ionization reaction (shorter ionization times as II in *Table 1*) and the NaH concentration (reduced epoxy concentration as III in *Table 1*).

Quenched ionization reaction

The effects of the ionization reaction alone on the PPTA fibres were evaluated by quenching the ionized fibres without the subsequent reaction with epoxy (II in *Table 1*). Upon quenching in water, the tensile properties of the Kevlar 149 fibres decreased with increasing ionization time (*Figure 8*). The decreases in breaking load and strain were most significant during the first few minutes of reaction. A low plateau about half of the original tensile properties was reached on fibres ionized for 5 min and longer.

When the ionized fibres were rinsed in DMSO prior to being quenched in water, the tensile properties of Kevlar 149 fibres were not affected by short ionization reactions up to 2 min (*Figure 8*). For ionization reactions lasting 10 min or longer, the tensile properties of fibres rinsed in DMSO were significantly lowered to the same low level as those quenched directly in water.

The solubility of ionized PPTA polymer in DMSO could be increased by adding a substantial amount of proton donors, such as alcohols[3]. The large amount of water used in quenching the ionized PPTA could serve as a proton donor to facilitate dissolution of the polymer. However, the weights of the quenched fibres remained unchanged after either quenching process, indicating no dissolution. Since dissolution of ionized PPTA in DMSO occurs only if 60% of the PPTA molecules are protonated[3], the lack of dissolution suggests that protonation on the Kevlar 149 fibres was below that level under the reaction conditions studied. An even lower level of protonation may be expected if only 30% of the N–H groups are accessible for chemical bonding[12,13] in the

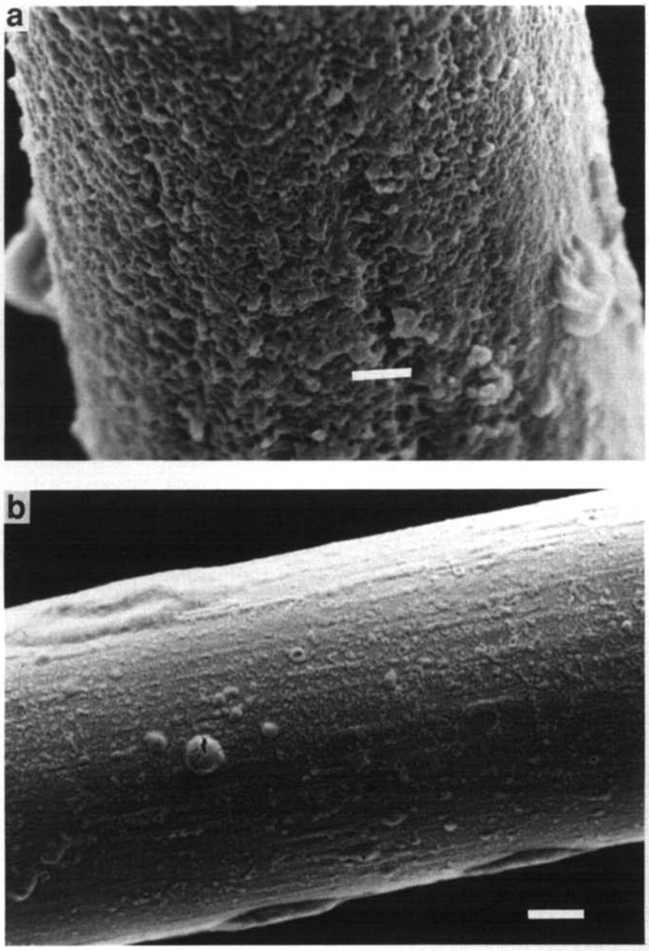


Figure 2 Fibre surfaces of the epoxy-reacted (0.083 g ml^{-1} epoxy/DMSO for 16 h) Kevlar 49 fibres at different lengths of ionization (0.008 g ml^{-1} NaH/DMSO concentration): (a) 4 h ionization (bar = 1.65 μm); (b) 1 h ionization (bar = 2.13 μm)

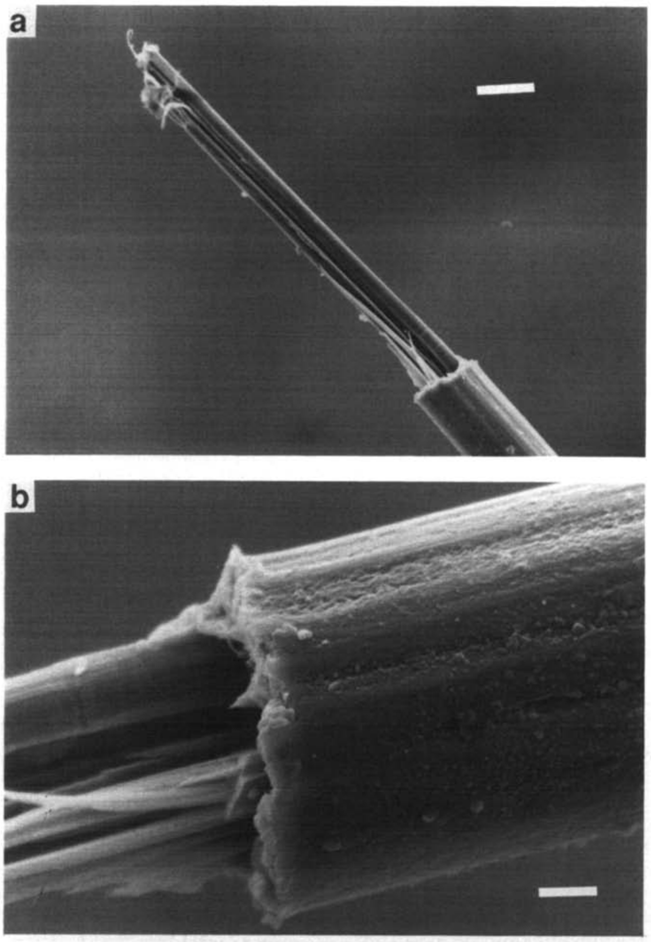


Figure 3 Tensile fracture end of the epoxy-reacted Kevlar 49 fibres as in *Figure 2b*: (a) bar = 12.0 μm; (b) bar = 2.38 μm

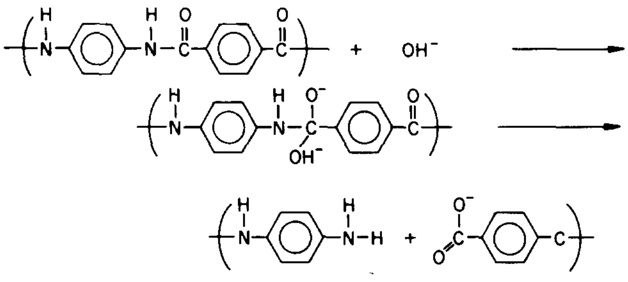
highly crystalline and hydrogen-bonded PPTA fibre structure.

Ideally, quenching in water replaces the Na^+ ions on the ionized PPTA molecules with the hydrogen ions as expressed in equation (3). Experimentally, the quenching reactions by water alone caused extreme temperature increases and large amounts of gas. Heat generation is expected from quenching the ionized sites on the PPTA molecules as well as from the reactions between water and NaH or methylsulphinyl carbanions. The generation of gas was believed to be H_2 from the reaction between NaH and water. The observation of extreme heat and gas suggests the existence of residual sodium salts on the ionized fibres. The significantly deteriorated tensile properties of the quenched fibres could be attributed to the heat and/or the gas generation.

When two DMSO rinses were employed prior to water quenching, significant reduction in heat and gas was observed in the reaction with water. During the DMSO rinse, replacement of the Na^+ ions on ionized PPTA molecules with the H^+ in DMSO as expressed in reversed equation (2) was thermodynamically unfavourable. DMSO can, however, react with NaH and help to carry away methylsulphinyl carbanions in the fibres. This is supported by the less deteriorated tensile properties of the fibres rinsed in DMSO after short ionization periods (up to 2 min). It is reasonable to believe that only fibre surfaces were affected by shorter ionization reactions, and the DMSO rinses were effective in removing the sodium salts on the fibre surfaces.

Ionization that lasted 10 min or longer significantly lowered the tensile properties of the fibres regardless of the quenching process. It appeared that the sodium salts penetrated deeper into the fibre with increasing ionization time. The sodium hydride and sodium methylsulphinyl carbanions entrapped in the fibre interior could not be completely removed by the DMSO rinses. When these sodium salts and ions react with water during the quenching process, the production of heat and gas could cause internal damage in the fibres.

In addition to heat, by-products such as Na^+ and OH^- ions can also be generated from these reactions in the fibres. The strongly nucleophilic hydroxide ions can attack the amide linkages in the PPTA chains, leading to hydrolytic chain scissions:



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The chain scission reactions could lead to major reduction in fibre tensile strength as well. It is not known

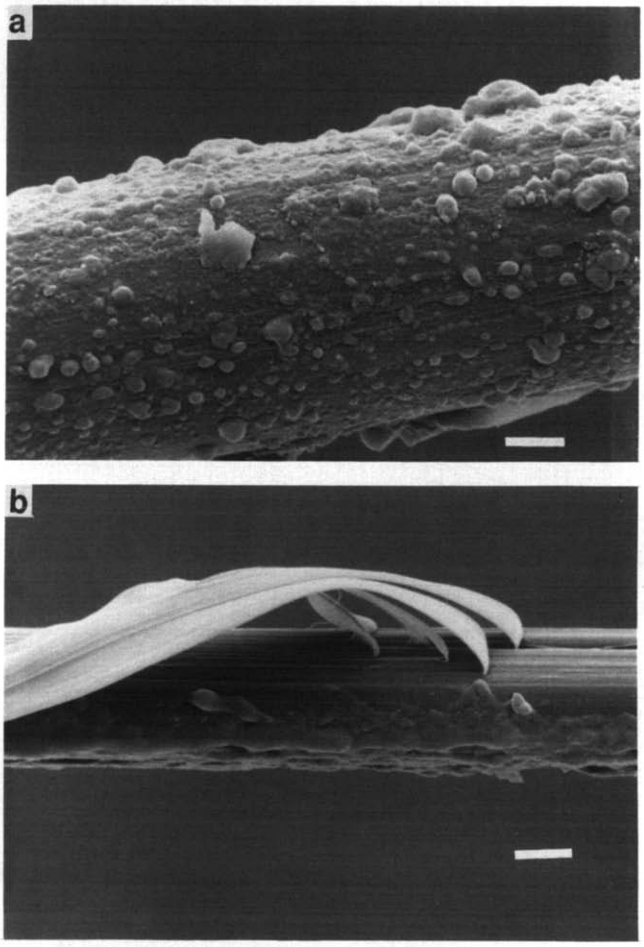

Figure 4 Surface features of the epoxy-reacted Kevlar 149 fibres with same treatment conditions as in *Figure 2*: (a) 4 h ionization (bar = 2.76 μm); (b) 4 h ionization (bar = 5.53 μm)

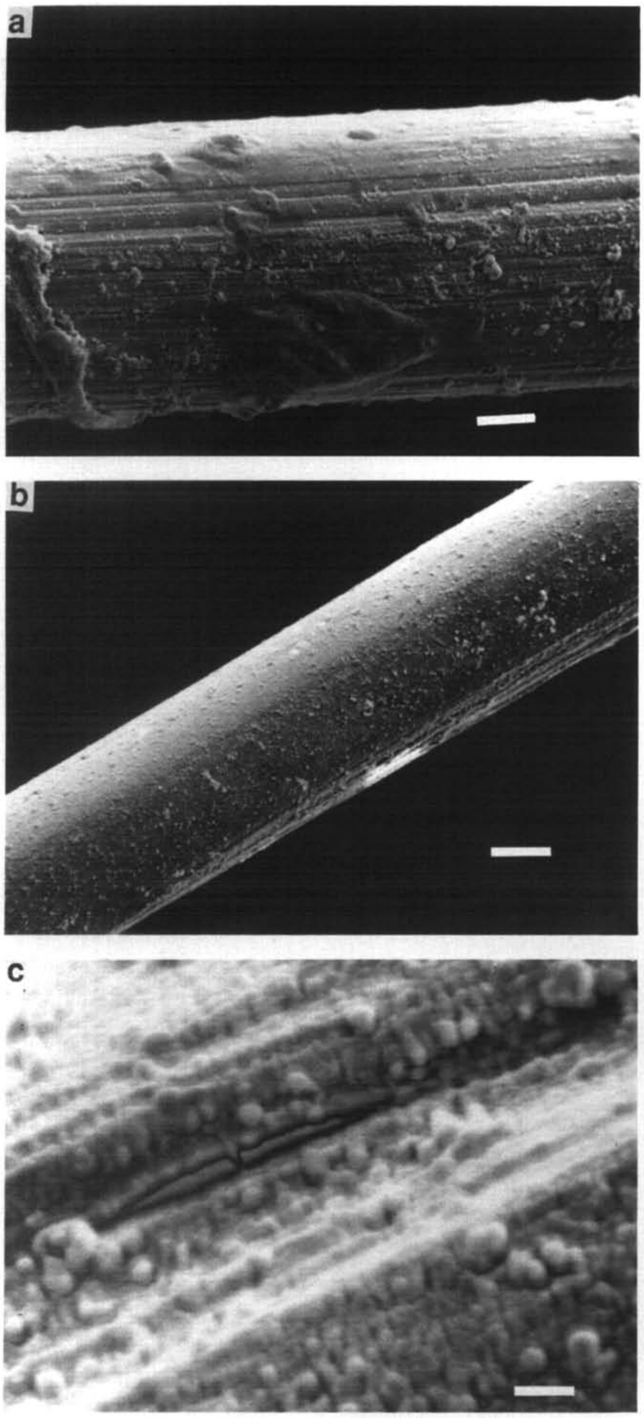

Figure 5 Surface features of the epoxy-reacted Kevlar 149 fibres with same treatment conditions as in *Figure 2*: (a) 1 h ionization (bar = 2.69 μm); (b) 30 min ionization (bar = 4.20 μm); (c) 30 min ionization (bar = 0.42 μm)

whether both the heat/gas generation and hydrolytic chain scissions contributed to the lowered tensile properties of the ionized PPTA fibres.

NaH/DMSO concentration and ionization reaction time

The effects of varying ionization conditions were evaluated on the ionized and epoxy-reacted fibres. Two ionization variables were studied including the NaH concentrations and the reaction time. Varying NaH/DMSO concentrations from 0.0004 to 0.008 g ml^{-1} were used at the constant 1 min reaction time. The highest concentration was the same as that used in the earlier quenching experiments and that reported on the PPTA powder[1]. The lowest NaH/DMSO concentration was close to the 0.00047 g ml^{-1} reported on reacting Kevlar 49 fibres with bisphenol A type epoxy (Dow's DER 383)[6]. A decreasing trend in tensile properties was clearly indicated with increasing NaH concentrations (*Figure 9*). The differences among the selected concentrations were small, however. The only significant difference (at

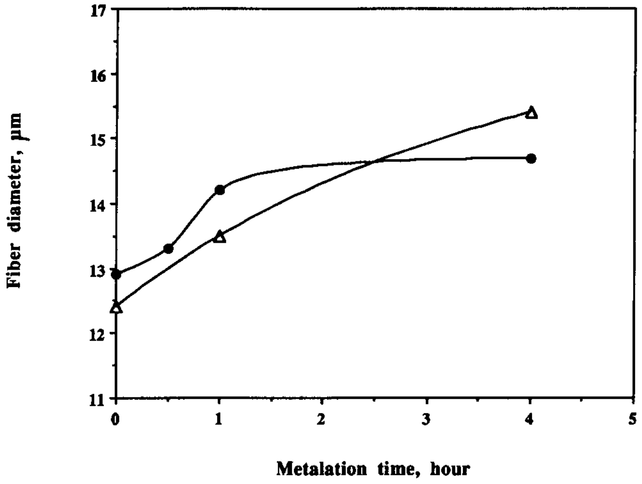

Figure 6 Diameter changes of ionized and epoxy-reacted Kevlar fibres: Kevlar 49 (△), Kevlar 149 (●)

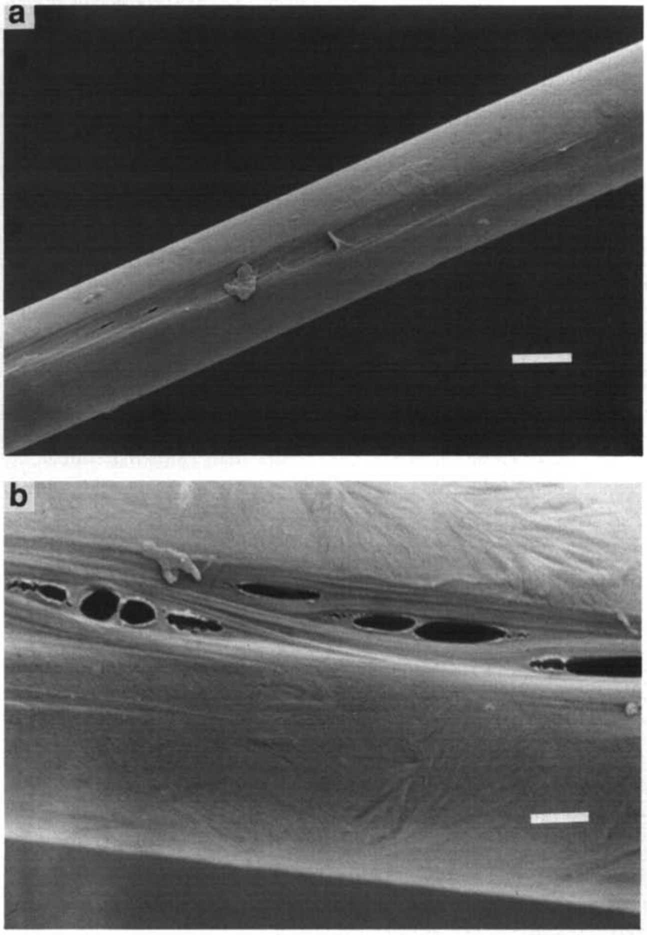

Figure 7 Fibre surfaces of the epoxy-reacted (0.10 or 0.083 g ml^{-1} epoxy/DMSO) Kevlar 149 fibres after 30 min ionization (0.008 g ml^{-1} NaH/DMSO): (a) bar = 5.62 μm; (b) bar = 1.68 μm

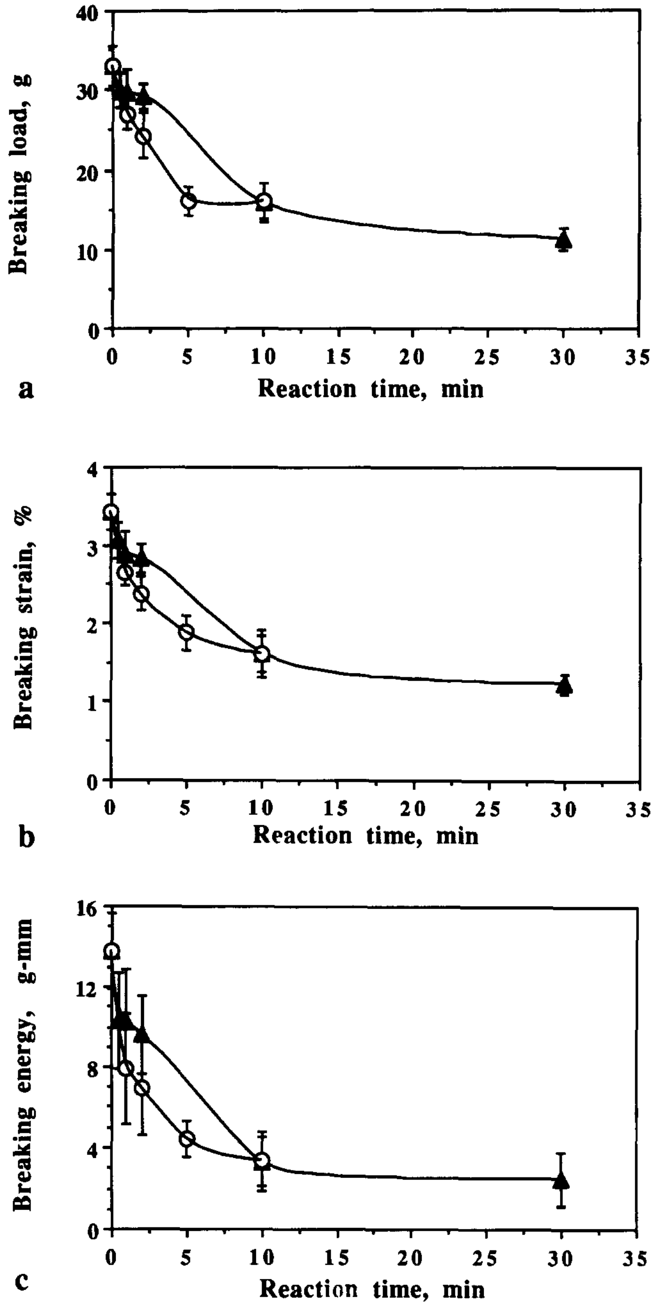

Figure 8 Tensile properties of ionized Kevlar 149 fibres quenched in water (○) and DMSO then water (▲)

0.05 confidence level) was between the ionized fibres treated at the lowest and those at the highest NaH concentrations.

The effects of ionization reaction times were evaluated at a constant 0.008 g ml^{-1} NaH/DMSO concentration. The lengths of ionization varied from 0.5 to 60 min followed by the same reaction with the epoxy. The tensile properties of the ionized and epoxy-reacted fibres were drastically reduced to a minimum after 1 min of ionization (*Figure 10*). As the ionization reaction time increased further, the tensile properties were improved somewhat. A region of higher tensile properties was reached between the 10 and 30 min ionization reactions before lowering again for the 60 min reaction.

For ionization lasting up to 5 min, the tensile properties of the epoxy-reacted fibres were much lower than for the quenched fibres with the DMSO rinse and those quenched directly in water (*Figure 8*). During the ionization and epoxy reaction processes, the PPTA fibres were ionized, rinsed in DMSO and then reacted in the epoxy/DMSO solution. Hydrolytic chain scission resulting from reaction with the minute amount of water in the hygroscopic DMSO was unlikely and was not believed to have caused such severely reduced tensile properties.

Even though the sheath–core structure has been observed on the ionized and reacted fibres under the most extreme reaction conditions (*Figure 2*), the thickness of the epoxy-reacted layer was minimized by reducing the NaH concentration and reaction time. Without the surface coating, the significant changes in tensile properties with increasing ionization times indicate internal structural changes by these ionization and epoxy reactions.

A possible explanation for the drastically reduced tensile strength was that the ionization and reaction with

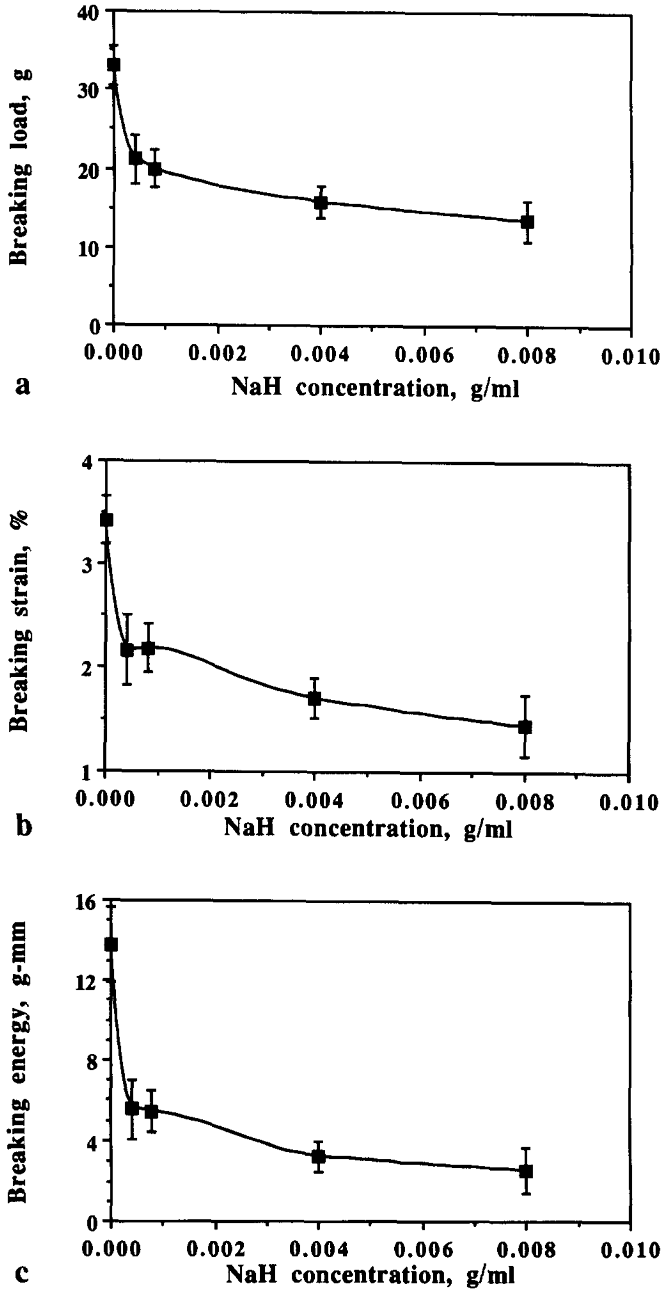

Figure 9 Tensile properties of ionized and epoxy-reacted Kevlar 149 fibres at varying NaH/DMSO concentrations

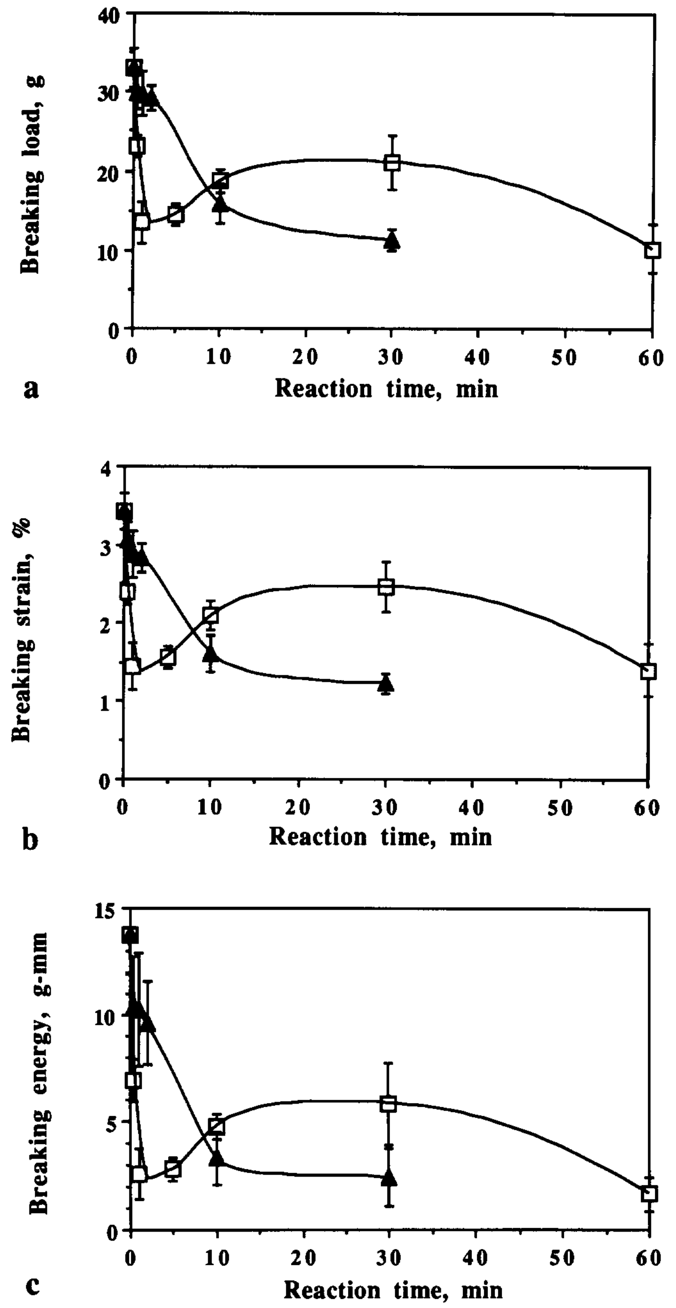

Figure 10 Tensile properties of reacted Kevlar 149 fibres at varying ionization times: DMSO quenched ionization reaction (▲) and epoxy-reacted (□)

epoxy occurred predominantly in these more accessible defect regions. The PPTA fibres contain extended chain crystallites with defect regions in between. The defect regions contain chain ends as well as the load-bearing chains extending through the defect regions along the axial direction of the fibre. It is possible that the reaction with epoxy destroyed additional load-bearing linkage in addition to the effects from the quenching process, thus accelerating the breakage of the PPTA fibres. As ionization of PPTA molecules became more extensive with longer reaction time, chemical bonding with epoxy in the defect regions began to compensate for the loss in load-bearing linkages.

Interfacial shear strength

The interfacial strengths between the PPTA fibres and the epoxy resin are shown by the shear force *versus* interfacial area plots (*Figures 11* and *12*). For Kevlar 49 fibres, the ionization was performed at a 0.008 g ml^{-1} NaH/DMSO concentration for 1 h, and the epoxy reaction was conducted at a 0.0083 g ml^{-1} epoxy/DMSO concentration for 16 h. The interfacial shear strengths for the untreated and the modified fibres were 3.93×10^{-3} and 4.04×10^{-3} g μm^{-2}, respectively. Under these reaction conditions, the interfacial shear strengths of the Kevlar 49 fibres were not affected.

The interfacial shear strength with epoxy was 10% higher for the untreated Kevlar 149 fibres than for the untreated Kevlar 49 fibres. In our previous study, resin wettability on dried Kevlar 149 fibres was also found to be higher than that on Kevlar 49 fibres[8]. The higher interfacial shear strength of the Kevlar 149 fibres can thus be attributed to their better wettability in the epoxy resin. Kevlar 49 fibres are known to contain an oxidized

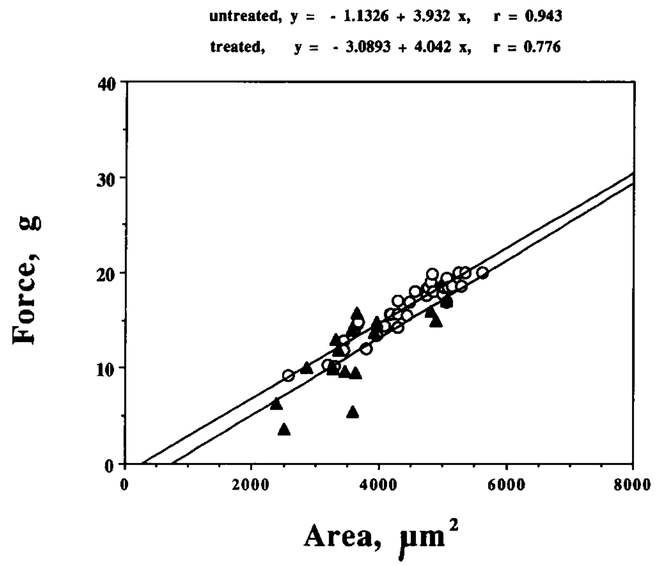

Figure 11 Interfacial shear strengths of Kevlar 49 fibres: (○) untreated; (▲) ionized (1 h in 0.08 g ml^{-1} NaH/DMSO) and epoxy-reacted (0.083 g ml^{-1} epoxy/DMSO)

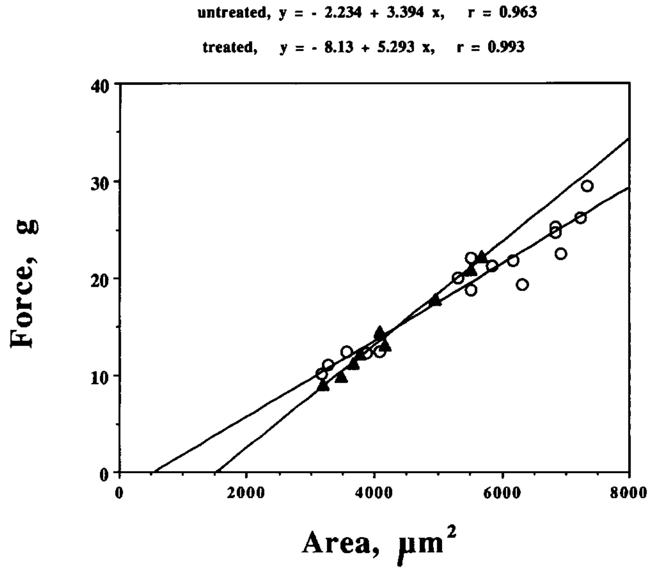

Figure 12 Interfacial shear strengths of Kevlar 149 fibres: (○) untreated; (▲) ionized (35 s in 0.008 g ml^{-1} NaH/DMSO) and epoxy-reacted (0.0083 g ml^{-1} epoxy/DMSO)

surface layer, which could be reduced by heating at 350°C[17]. The surface compositions of Kevlar 149 fibres are probably different because of the additional heating to above 500°C during fibre processing. The surface compositional differences could in part explain the observed differences in the adhesion and wetting properties[8] of these two PPTA fibres.

For the epoxy-reacted Kevlar 149 fibres, the interfacial shear measurements were made on fibres treated under the condition from which no loss in fibre tensile strength occurred. The fibres were ionized ($0.008\ \mathrm{g\ ml^{-1}}$ NaH/DMSO) for 35 s and reacted with epoxy ($0.0083\ \mathrm{g\ ml^{-1}}$ epoxy/DMSO) for 1 h. The interfacial shear strength of the fibres was increased from $4.35 \times 10^{-3}\ \mathrm{g\ \mu m^{-2}}$ for the untreated to $5.29 \times 10^{-3}\ \mathrm{g\ \mu m^{-2}}$ for the epoxy-reacted Kevlar 149 fibres, a 22% increase.

On Kevlar 49 fibres, our interfacial shear data on single fibres did not show the same level of improvement as those reported on similarly modified Kevlar 49 fibre composites[7]. The difference may be explained by several contributing factors. The interfacial shear strength tests were performed on Kevlar 49 fibres ionized much longer (1 h) than those for the Kevlar 149 fibres (35 s). As previously shown, the effects of ionization on the bulk properties of Kevlar 149 were reaction-time-dependent. The specific reaction condition studied on Kevlar 49 fibres may not produce the level of ionization on the fibre surfaces for optimal bonding with the epoxy.

Also, there are some intrinsic differences between the adhesion test for single fibres and those for the composites. The adhesive forces of the single fibres should be different from fibre bundles or composited materials owing to the lack of shear forces imposed by the neighbouring fibres. Without these shear forces, the surface layers on single fibres may be more readily separated than those on bundled fibres in composites. Therefore, the single shear force data for both PPTA fibres may underestimate the adhesive properties of these modified fibres in composites.

SUMMARY

In establishing reaction conditions initially, the PPTA fibres were ionized with methylsulphinyl carbanions in a $0.008\ \mathrm{g\ ml^{-1}}$ NaH/DMSO solution and reacted with epoxy at a $0.083\ \mathrm{g\ ml^{-1}}$ epoxy/DMSO concentration. Very rough surfaces and a sheath–core fracture structure were observed for those ionized for 4 h. By reducing the ionization time to 1 h and the epoxy/DMSO concentration to $0.0083\ \mathrm{g\ ml^{-1}}$, respectively, surface coating thickness and roughness were minimized.

The deterioration in the tensile properties of the fibres quenched directly in water was believed to be associated with the residual sodium salts, e.g. NaH and methylsulphinyl carbanions, in the fibres. The sodium salts from short ionization reactions were thought to be limited to the fibre surfaces and were removed by the two DMSO rinses. As ionization time increased, the sodium salts penetrated into the fibre interior, making removal of these salts incomplete. Heat and gas were generated from the reaction between the interiorly entrapped sodium salts and water. Quenching of the ionized fibres can also generate strongly nucleophilic hydroxide ions, which attack the amide linkages in the PPTA chains, in turn leading to hydrolytic chain scissions. All these factors could contribute to internal damage to the fibres, causing significantly lowered tensile properties.

Increasing NaH/DMSO concentrations only had a slightly lowering effect on the tensile properties in the 0.0004 to $0.008\ \mathrm{g\ ml^{-1}}$ concentration range. With ionization up to 5 min at a fixed NaH concentration, the tensile properties of the epoxy-reacted fibres were much lower than the quenched fibres. A possible explanation for the drastically reduced tensile strength was that the epoxy reaction occurred predominantly in the more accessible defect regions, destroying the load-bearing linkage in the fibre core. With more thorough ionization, extensive epoxy crosslinking in these defect regions eventually compensated for part of the strength loss.

The interfacial shear strength of the Kevlar 149 fibres with the epoxy was slightly higher than that of the Kevlar 49 fibres. The higher interfacial adhesion on Kevlar 149 fibres was associated with better wetting property of the fibres and was attributed to surface compositional differences between the two PPTA fibres. The ionization and epoxy reaction conditions employed for Kevlar 49 fibres did not affect their interfacial shear strengths with the epoxy resin. For Kevlar 149 fibres under slightly different reaction conditions, the interfacial shear strength was increased from $4.35 \times 10^{-3}\ \mathrm{g\ \mu m^{-2}}$ for the untreated to $5.29 \times 10^{-3}\ \mathrm{g\ \mu m^{-2}}$ for the ionized and epoxy-reacted fibres, a 22% increase.

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