The effects of ionization on the structure of poly(*p*-phenylene terephthalamide) fibres

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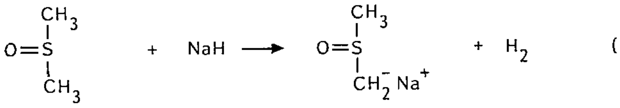
(Received 14 September 1992; revised 26 March 1993)

Extended periods of ionization of poly(*p*-phenylene terephthalamide) (PPTA), namely Kevlar 149, fibres by sodium methylsulfinyl carbanions leads to a significant deterioration in the fibre tensile properties. The non-chain-breaking nature of the ionization suggests that hydrogen bonds among the PPTA chains in the intercrystalline regions also contribute to the axial strength of the fibres. Rinsing with dimethylsulfoxide (DMSO) following the ionization initially improves the tensile strength. With DMSO immersions of 10 h or longer, the tensile strength loss resumes, and can be explained by hydrolytic chain scission of the PPTA molecules in the intercrystalline regions. Ionization which does not affect the fibre strength of Kevlar 49 is effective for structural differentiation between Kevlar 49 and 149 fibres. In a similar fashion to ionization, etching by argon glow discharge produces little change in Kevlar 49 fibre structure and strength. The fact that both ionization and glow discharge treatment affect PPTA fibre properties similarly demonstrates that both reactions depend on the accessibility and precise microstructure of these fibres.

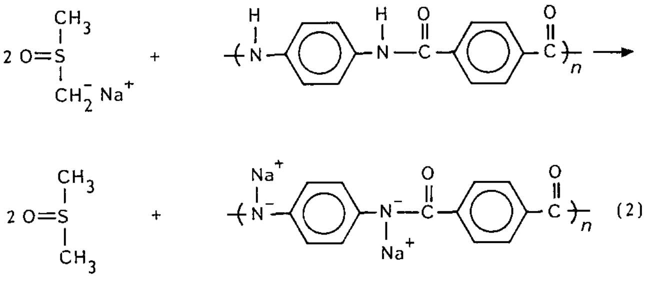
(Keywords: poly(*p*-phenylene terephthalamide); ionization; tensile properties)

INTRODUCTION

The ionization of poly(*p*-phenylene terephthalamide) (PPTA) can be achieved by using sodium methylsulfinyl carbanions, produced by mixing sodium hydride (NaH) in dimethylsulfoxide (DMSO). The formation of sodium methylsulfinyl carbanions (equation (1)) and the polyanions Na^+PPTA^- (equation (2)), are illustrated as follows:



$$CH_3-S(=O)-CH_3 + NaH \longrightarrow CH_3-S(=O)-CH_2^-\,Na^+ + H_2 \qquad (1)$$



(2)

Short ionization reaction times followed by reactions with epoxy resin, have been shown to be very effective in improving the adhesive properties of Kevlar 149 fibres[1]. Although the effects of ionization on the fibre strength can be minimized, a significant deterioration of the fibre tensile properties can result if ionized PPTA fibres are quenched in water instead of reacting with epoxy. The loss of strength of water-quenched fibres after short ionization treatment can be lessened by rinsing the ionized fibres with DMSO prior to quenching. It is believed that a DMSO rinse removes any residual sodium methylsulfinyl carbanions from the fibre surfaces, thus reducing their potential reactions with water. However, the fibre strength deterioration increases with increasing ionization time. The fact that brief DMSO rinses cannot recover the tensile strength loss of fibres that have been ionized for extended lengths of time suggests that both diffusion of sodium methylsulfinyl carbanions and ionization occur inside the fibres.

Chemical diffusion and reactions of polymers are structure-dependent, and thus further understanding of the effects of ionization on PPTA fibres should provide additional information on their microstructure. This paper reports the effects of extended DMSO immersions on the structure and properties of ionized PPTA fibres, including differentiating the structural differences between Kevlar 49 and 149 fibres. Accessibility of these fibres to ionization are also compared with the effects of a base on its own and argon glow discharge.

EXPERIMENTAL

The two types of poly(*p*-phenylene terephthalamide) fibres used in this study were Kevlar 49 and 149 filaments, obtained from E. I. du Pont de Nemours Inc. Approximately 0.3 g of continuous filaments were wound into a loop with a circumference of about 20 cm. The wound filaments were cleaned in carbon tetrachloride for 10 min using bubbling nitrogen for agitation, and then oven dried at 100°C for 2 h. The filaments were cooled, weighed and stored in a desiccator under vacuum before use.

The chemicals were reagent grade, and were used without further purification. Each ionization bath was prepared by stirring 0.24 g of NaH into 30 ml of DMSO at a 8 mg ml^{-1} NaH/DMSO concentration, or

0032-3861/94/06/1216-06

a 0.024 molar ratio. The dissolution was aided by heating the solution to about 40–45°C with continuous stirring for 40 min. After cooling the solution to 23°C, the cleaned and dried fibres were added to the reaction solution. All reactions were carried out under nitrogen and were agitated by bubbling nitrogen through the solution.

All of the ionized fibre samples were rinsed in three 10 ml DMSO baths before immersion in 30 ml of DMSO. The effects of the DMSO immersions were evaluated at various lengths of time, ranging from 30 s to 70 h. Following removal from DMSO, the fibres were finally rinsed in three, fresh, acetone baths.

Specimens for single fibre tensile testing were prepared according to a fibre mounting procedure that has been previously described[2]. All fibres were tested with a fixed gauge length of 25.4 mm, employing a 20 mm min^{-1} cross-head speed under constant temperature (21°C) and humidity (65% relative humidity). Twenty-five specimens were tested for each reaction.

Glow discharge of PPTA fibres was performed at a 50 W level for 4 and 8 min using a previously established technique[3]. Fibres were sputter coated with gold at a thickness of ~ 300 Å, and the fibre surfaces were examined by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

In order to study the effects of extended DMSO immersions, significant changes in the PPTA fibre properties have first to be achieved. Such ionization conditions can be identified by varying the extent of ionization, including the reactant concentration and the length and temperature of the reaction. Our previous work shows the effects of the NaH/DMSO concentration on the fibre strength to be insignificant[1]. If the ionization temperature is raised, a dissolution of the Kevlar 149 fibres is observed at 45°C. It was therefore decided to vary the lengths of the reaction time. Thus, Kevlar 149 fibres were ionized for varying times at a 0.024 NaH/DMSO molar ratio at 25°C, rinsed twice in DMSO, and then dried over a desiccant at 21°C. Both the breaking strength and the breaking elongation of Kevlar 149 fibres are reduced with increasing ionization time (*Figure 1*). A significant reduction in tensile properties begins when the ionization lasts longer than 2 min. Following the 10- and 30-min ionization reactions, both the breaking strength and the breaking elongation of the ionized fibres are reduced to less than one half of the original values. The significantly reduced tensile properties indicate that major stress-bearing mechanisms of the fibres are affected by the longer ionization reactions. Ionization reactions, at the selected NaH/DMSO concentration, for 10 min at 25°C, were therefore selected for examining the effects of DMSO immersions.

A previous report has indicated that polyanions of PPTA become soluble in DMSO if over 60% of the amide groups are deprotonated[4]. Polymer dissolution through improved solubility in DMSO is possible only if large portions of the PPTA molecules are ionized. Because of the highly crystalline structure of the PPTA fibres, high levels of ionization are not expected to occur throughout the fibres. It is, however, possible that PPTA molecules in the more accessible intercrystalline regions can be ionized to a greater extent and become dissolved, therefore leading to strength reduction.

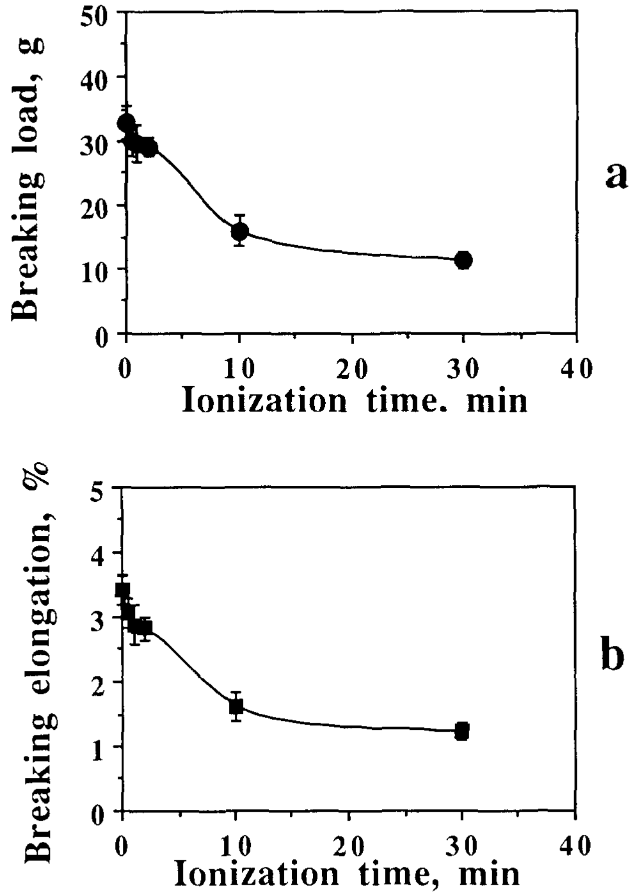


Figure 1 Tensile properties of DMSO rinsed Kevlar 149 fibres ionized for various lengths of time: a, breaking load; b, breaking elongation

The ionized PPTA fibres were rinsed in DMSO three times and then immersed in DMSO for varying lengths of time, ranging from 20 s to 70 h. Fibres after a 20-s DMSO immersion have a much reduced breaking strength and elongation, with values of about one half of those of the untreated fibres (*Figure 2*). The fibre tensile properties are not significantly improved by changing from rinses of a few seconds (10-min reaction in *Figure 1*) to a 20-s immersion. However, with increasing lengths of DMSO immersion times, the fibre tensile properties are improved, reaching their peaks between 10 min at 4 h, and then returning to the same low level as those with only brief DMSO rinses.

It is also observed that the weights of the ionized PPTA fibres vary with the length of immersion time (see *Figure 3*). A weight gain of 5.6% is observed in fibres immersed in DMSO for 20 s. These weight gains decrease with increasing immersion time and become negligible for values between 10 min and 4 h. Upon further DMSO immersion, fibre weights increase, reaching their peak values after 24 h, before finally decreasing again with continuing immersion.

The axial strength of PPTA fibres has been explained by molecular linkages in the less ordered regions of the fibres, such as crystallites extending through two or more crystalline lamellae[5] or extended chains passing through defect spacings[6]. The lateral strength of PPTA fibres has been attributed to intermolecular and intramolecular hydrogen bonds between amide linkages in the PPTA[5]. Since ionization is not a chain-breaking reaction for these polymers, neither of the molecular linkages mentioned

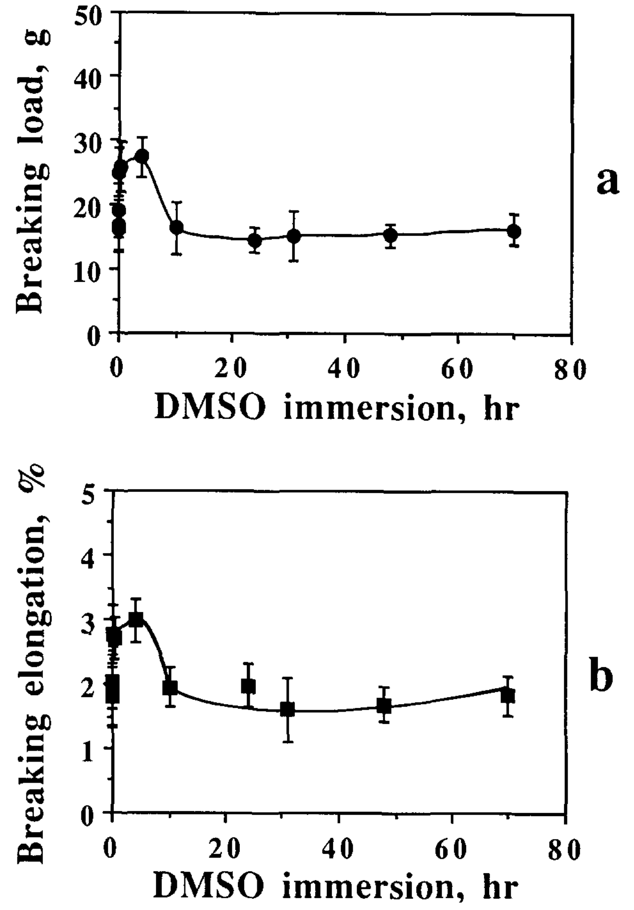


Figure 2 Tensile properties of ionized (10 min) Kevlar 149 fibres as a function of the immersion time in DMSO: a, breaking load; b, breaking elongation

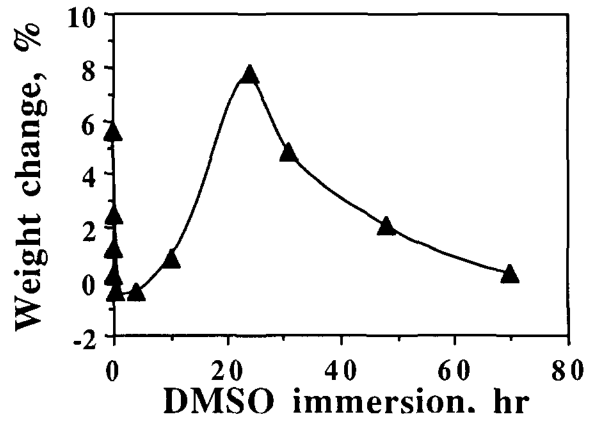


Figure 3 Weight changes of ionized (10 min) Kevlar 149 fibres as a function of the immersion time in DMSO

above should be affected. However, the reduced tensile properties of the ionized fibres show that the stress-bearing mechanism in the PPTA fibres was significantly affected by the ionization reactions. The effects of ionization suggest that other factors may also contribute to the stress-bearing mechanism in this case.

Ionization of PPTA molecules involves the formation of polyanions (see equation (2)) on the amide groups in the less ordered regions of the fibres. Deprotonated amide linkages in PPTA cannot contribute to either intermolecular or intramolecular strength through hydrogen bonding. It is well documented that the strength of crystalline domains is enhanced by strong intermolecular and intramolecular hydrogen bonding among the amide groups. Ionization can affect the load-bearing structure if hydrogen bonding also takes part in the stress-transfer mechanism which occurs in the intercrystalline regions. Significantly reduced fibre tensile strengths as a result of ionization indicate that intermolecular and intramolecular hydrogen bonds in the intercrystalline regions may be partly responsible for the axial strength of the PPTA fibres.

Weight changes in the ionized PPTA fibres can be attributed to both the ionization reaction and the DMSO immersion process. Fibre weight gains may include the replacement of hydrogen with sodium in the PPTA structure, sodium salt retention in the fibre, and the redeposition of sodium salts on the fibre surfaces. Weight reduction of ionized PPTA fibres, on the other hand, could result from the loss of associated salts and ions, and PPTA molecules.

Ionization would be expected to increase the fibre weight as a result of diffusion of sodium salts into the fibres and the replacement of hydrogen with sodium in the PPTA molecules. Subsequent DMSO immersions can reduce the weights of the ionized fibres by removing the unreacted sodium salts from within the fibres. For DMSO immersion times up to 4 h, the fibre weight losses are accompanied by a substantial recovery in strength. This suggests that a plasticizing effect of the unreacted salts could be responsible for the initial loss in strength.

With immersion times of 10 h and longer, the ionized fibres exhibit further weight changes (see *Figure 3*) while their tensile properties remain at a constant low level (see *Figure 2*). An increasing surface roughness was observed for fibres immersed in DMSO for more than 4 h (*Figure 4*). The surface roughness, which is thought to result from salt deposition, appears similar for all fibres immersed in DMSO for longer than 4 h. The reason for the additional weight gains following extended DMSO immersion is therefore not obvious. The major loss in strength and the associated weight loss are likely to be due to loss of polymer through hydrolysis reactions.

Weight loss can also be caused by hydrolysis of PPTA by NaOH, the latter generated by reaction with water. Small amounts of water in the reaction mixtures are expected because of the hygroscopic nature of DMSO, and particularly during extended DMSO immersion

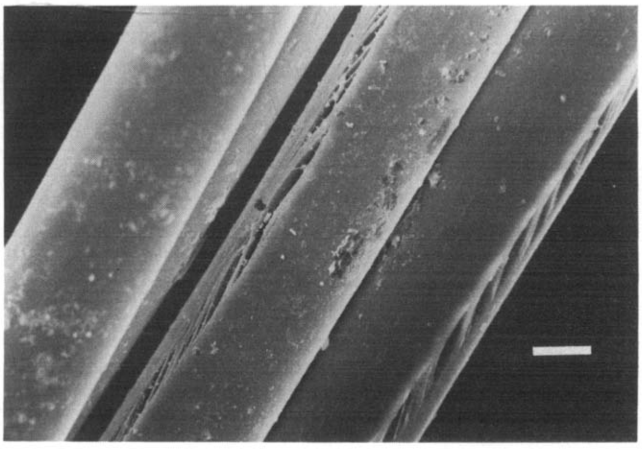
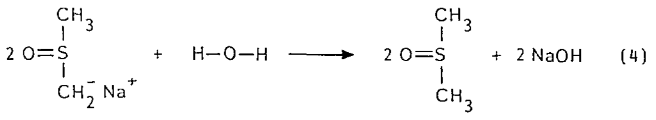


Figure 4 Scanning electron micrograph of ionized Kevlar 149 fibres after 70 h of immersion in DMSO (bar = 4.39 μm)

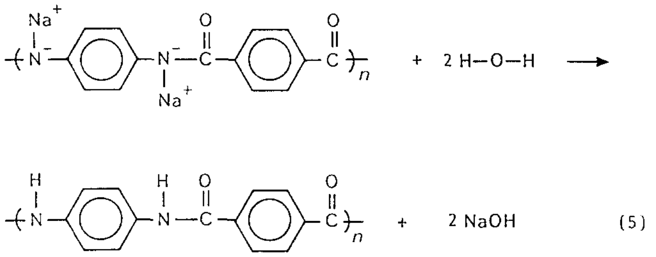
experiments. Residual NaH on the ionized fibres can react with water to generate NaOH and hydrogen gas:

$$\mathrm{NaH} + \mathrm{H{-}O{-}H} \longrightarrow \mathrm{NaOH} + \mathrm{H_2} \qquad (3)$$

This reaction is characterized by a rising reaction temperature and the formation of gas bubbles. Such phenomena have been observed for ionized fibres directly quenched in water. Although neither heat nor gas was observed in experiments when fibres were rinsed with DMSO, the possibility of such a reaction inside the ionized fibres cannot be ruled out. Water also reacts with methylsulfinyl carbanions and the polyanions to generate NaOH:



$$2\,\mathrm{O{=}S(CH_3)(CH_2^-\,Na^+)} + \mathrm{H{-}O{-}H} \longrightarrow 2\,\mathrm{O{=}S(CH_3)CH_3} + 2\,\mathrm{NaOH} \qquad (4)$$



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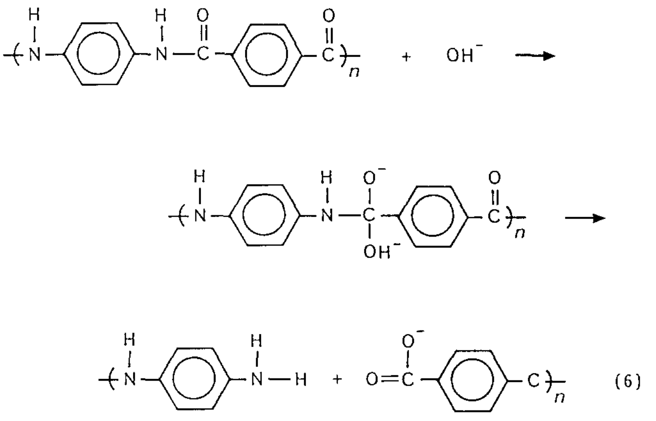
The hydroxide ions, which can be generated by either of the above reactions, are strongly nucleophilic and can attack the amide linkages in the PPTA chains, causing hydrolytic chain scissions:



(6)

These hydrolysed chain scission reactions lead to the separation and loss of PPTA chain length.

As hydrolytic chain scission may be responsible for the strength loss in PPTA fibres, the effects of a base (such as sodium hydroxide) on its own, on the tensile properties of Kevlar 149 fibres, were studied. Sodium hydroxide solutions ($\leqslant 1$ M) were employed for treatments lasting 2 h. As shown in *Figure 5*, the effects of this base on Kevlar 149 fibre strength and elongation are insignificant. The minor effects of sodium hydroxide, when compared to ionization, may be related to the lower reactivity of the NaOH solutions and a poor accessibility of NaOH into the fibre.

Sodium methylsulfinyl carbanions are more effective in penetrating into the fibre interior and in reacting with the amide groups to form polyanions. These internally located sodium ions and polyanions react with water

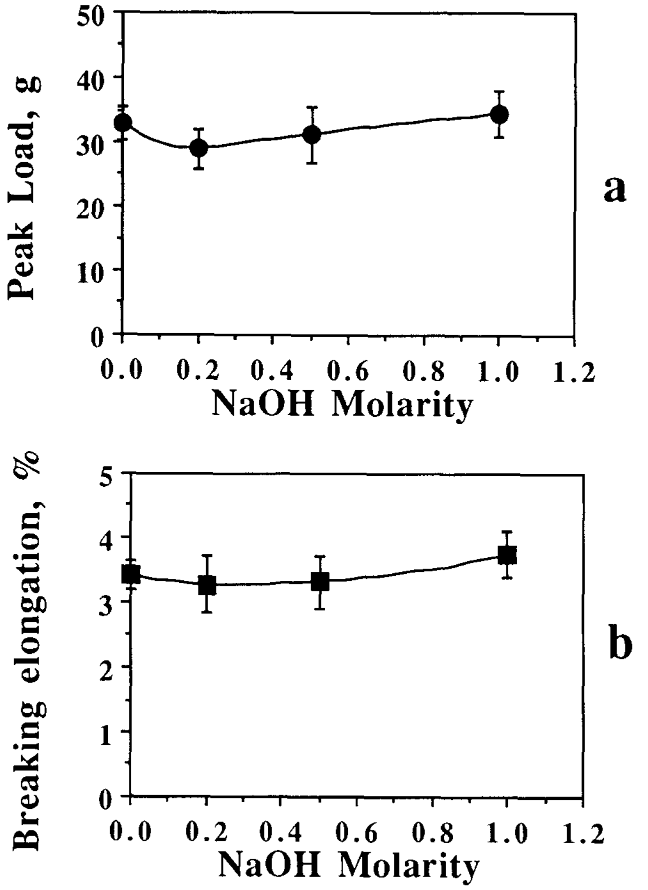


Figure 5 Tensile properties of NaOH treated Kevlar 149 fibres: a, breaking load; b, breaking elongation

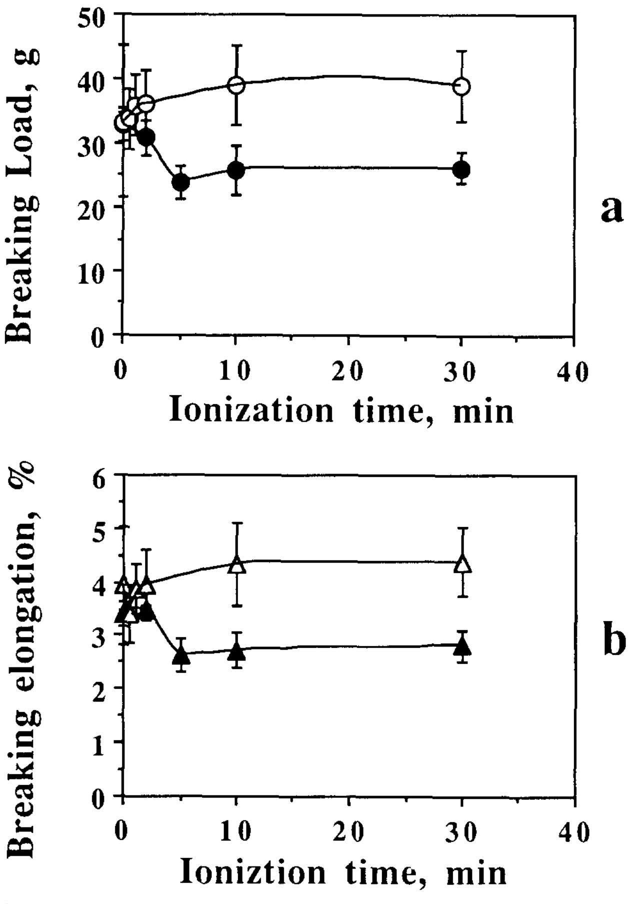


Figure 6 Tensile properties of ionized Kevlar 49 and 149 fibres after 30-min DMSO immersions: a, breaking load; b, breaking elongation (●, ▲, Kevlar 149; ○, △, Kevlar 49)

during the DMSO immersion, thus generating NaOH inside the fibres. Due to the proximity of the hydroxyl ions, internal damage at the ionized sites is found to occur.

The ionization effects on two types of PPTA fibres, i.e. Kevlar 49 and 149, under the conditions as described, were compared. The ionized fibres were rinsed with DMSO three times and then immersed in DMSO for 30 min. In fact this is the actual immersion condition which results in the optimum strength and minimal weight change in Kevlar 149 fibres. Neither the breaking strength nor the breaking elongation of the Kevlar 49 fibres are affected by any of these ionization reactions (*Figure 6*). The breaking strength and elongation of Kevlar 149 fibres, on the other hand, are substantially reduced with increasing ionization time.

Possible morphological differences between these two types of fibres have been indicated by their different moisture sorption properties[7,8]. Equilibrium moisture content in Kevlar 49 fibres has been found to increase almost linearly with the relative humidity[7], whereas that in Kevlar 149 fibres follows a third-order polynomial dependence[8]. Higher moisture absorption in Kevlar 49 fibres has been explained by the existence of interfibrillar microvoids. The moisture sorption behaviour of Kevlar 149 fibres, which is similar to that of most other semicrystalline polymers, suggests a lack of the microvoids that are found in the Kevlar 49 material. When compared to the latter, Kevlar 149 fibres are found to have higher crystalline orientation, larger crystallite size, and/or reduced crystalline disorder[9]. However, none of these structural differences can explain, or is consistent with the greater ionization effects that have been observed on Kevlar 149 fibres.

Further differentiation between the structures of Kevlar 49 and 149 fibres is aided by argon plasma etching. Low-temperature glow discharge attacks the less ordered non-crystalline regions of the fibres, thus helping to elucidate the more chemically accessible pathways. Argon glow discharge does not significantly change the fibre diameters of either fibre (at a 0.05 significance level). On Kevlar 49 fibres that were glow discharged for 8 min, the surfaces appear to be etched (*Figure 7*). The etching effects are similar between the 4 min and 8 min lengths of glow discharge. The only observable surface effects on Kevlar 49 fibres are the areas in slight relief (indicated by arrows in *Figure 7*) on the fibre surface, when using a longer glow discharge. These domains indicate heterogeneity in surface crystallinity which may be related to the skin–core structure reported by others[6,10,11].

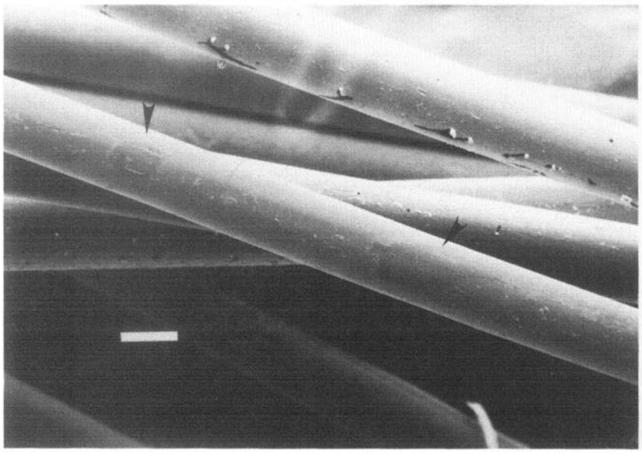


Figure 7 Scanning electron micrograph of Kevlar 49 fibres after argon glow discharge treatment for 8 min (bar = 9.17 μm)

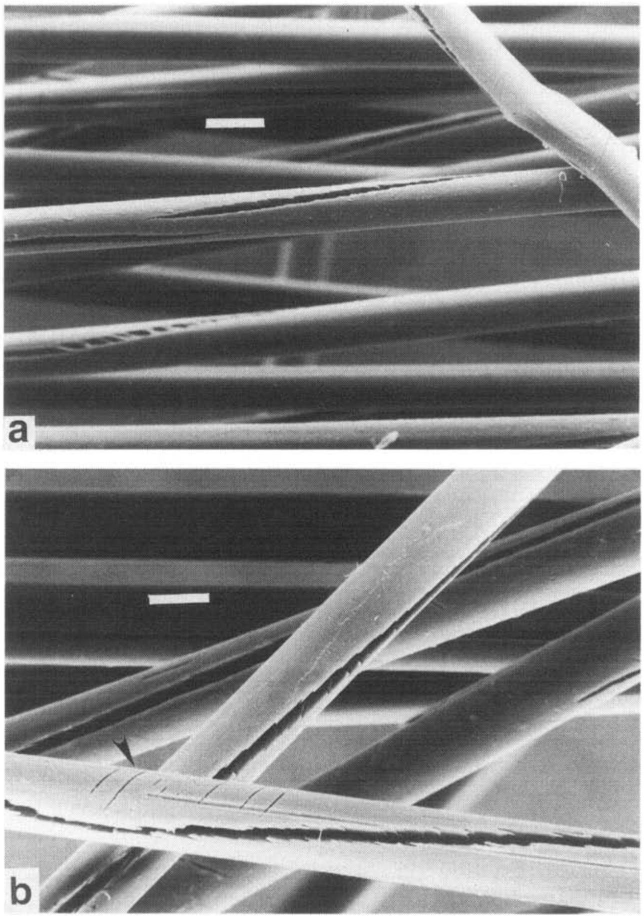


Figure 8 Scanning electron micrographs of Kevlar 149 fibres after argon glow discharge treatment: a, 4 min (bar = 15.5 μm); b, 8 min (bar = 9.17 μm)

Argon-etched Kevlar 149 fibres, on the other hand, have large gaps spiralling along the length of the fibre (*Figure 8a*). Longer etching times (e.g. 8 min) also reveal cracks perpendicular to the fibre axis direction (indicated by an arrow in *Figure 8b*). This observation strongly indicates that this macrostructural differentiation in the Kevlar 149 fibres may be responsible for the greater overall chemical accessibility. In fact, there is a remarkable similarity between the tensile properties of the two PPTA fibres resulting from ionization (see *Figures 1* and *6*) and from the low-temperature plasma (*Figure 9*).

CONCLUSIONS

In polymeric solids, chemical diffusion and reactions such as those that occur in the ionization of PPTA begin in the less ordered intercrystalline regions. The effects of chemical reactions, therefore, can serve to depict the morphological structure of the polymers. In highly crystalline fibre structures, such as those found in PPTA, the less ordered regions are also responsible for stress-bearing. This study shows that the stress-bearing capacity of Kevlar 149 fibres can be significantly reduced by ionization. Since ionization by itself is not a chain-breaking reaction in the case of PPTA,

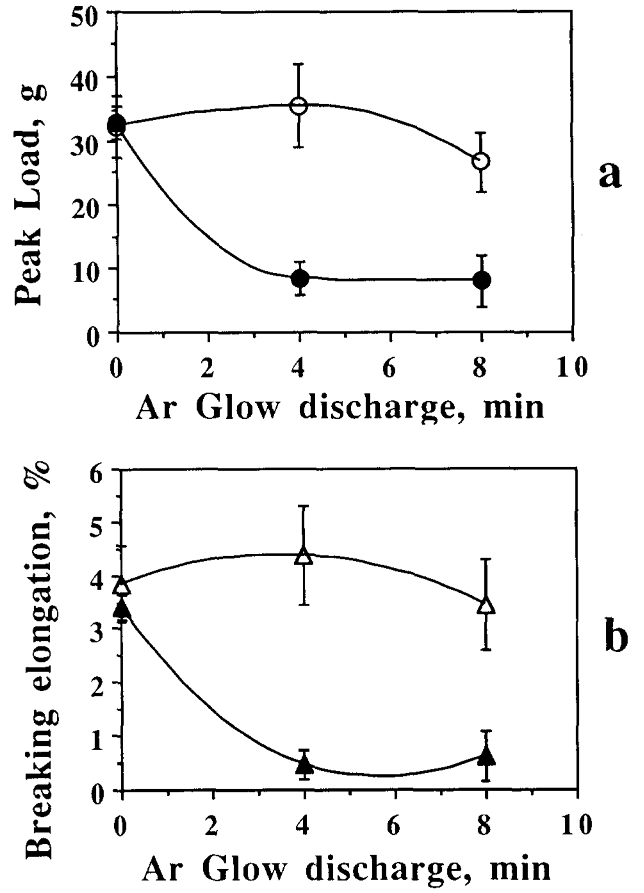


Figure 9 Tensile properties of Kevlar 49 and 149 fibres as a function of the time of argon glow discharge treatment: a, breaking load; b, breaking elongation (●, ▲, Kevlar 149; ○, △, Kevlar 49)

the significantly reduced fibre strength resulting from ionization suggests that hydrogen bonds among the PPTA chains in the intercrystalline regions partially contribute to the axial strength of the fibres, Strength reduction can also be attributed to extraction of PPTA molecules, through extended deprotonation of the amide linkages, from the intercrystalline regions in the fibres following extended ionization reactions.

With extended times of immersion in DMSO, further reductions in tensile strength can be attributed to reduction in the polymer molecular weight through the hydrolytic chain scission of PPTA molecules in the intercrystalline regions. The differences in accessibility between the two PPTA fibres can be clearly indicated by the ionization and etching effects on their structures. The microvoids in Kevlar 49 fibres which allow better moisture sorption do not facilitate the diffusion of sodium methylsulfinyl carbanions. The lower moisture sorption behaviour of Kevlar 149 fibres may be indicative of a higher crystalline content in the solid. However, the spiral and longitudinal macrostructure observed for the argon glow discharged Kevlar 149 fibres shows the large-scale pathway by which the sodium salts and methylsulfinyl carbanions can reach the interiors of the fibres, thus affecting the bulk properties more significantly.

ACKNOWLEDGEMENT

The participation and assistance of the United States Department of Agriculture Summer Research Apprentices, Luis Arellano and Maria L. D. de Leon, are greatly appreciated.

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