The characterization of the chemical impurities in Kevlar 49 fibres*

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The impurities in Kevlar 49 fibres (poly(*p*-phenylene terephthalamide), PPTA) are reported from chemical analyses. The interrelationships between the fibre impurities, microvoid characteristics, moisture sorption and chemical degradation are discussed. The chemical nature of the impurities and their distribution within the fibre are considered in relation to the physical and chemical processes involved in fibre fabrication. From chemical analyses, together with C, N, H elemental analyses, we show Kevlar 49 fibres contain 1.5 wt% impurities of which ~50% are in the form of Na_2SO_4. The Na_2SO_4 resides in the fibre interfibrillar regions, which are paths for preferential moisture diffusion. During fibre fabrication, these Na_2SO_4 impurities generate osmotic pressures and microvoids in the fibre. There are three benzenesulphonic acid side groups and one COOH end group per PPTA macromolecule. Sixty per cent of these acid groups are neutralized and are in the from of the Na salt. Other metallic compounds at concentrations of ~350 ppm are also present in Kevlar 49 fibres. There is evidence of trace quantities of mobile H_2SO_4 in Kevlar 49 fibres that will accelerate hydrolytic and oxidative Kevlar 49 degradation.

(Keywords: Kevlar 49 fibres; impurities; microvoids; moisture sorption; degradation)

INTRODUCTION

Kevlar 49 and 29 fibres (registered trademark of E. I. DuPont de Nemours and Co.) are generally considered to be composed of poly(*p*-phenylene terephthalamide) (PPTA)[1-11]. Analyses by Gan *et al.*[1] and Burchill[8] showed that Kevlar 49 fibre is solely a condensation polymer, PPTA, formed from terephthalic acid and *p*-phenylene diamine.

Kevlar 49 fibres are utilized in critical structures in the aerospace industry in the form of high-performance fibrous epoxy composites. Such composites will have to maintain their structural integrity over prolonged time periods. An understanding of the microscopic phenomena that control the mechanical properties of these composites and the modification of these properties during service environment exposure is critical for any durability predictions. Previously we have studied the physical structure and deformation and failure processes of bare Kevlar 49 yarns and single filaments in a variety of Kevlar 49–epoxy composites to ascertain the critical molecular and microstructural parameters that control the deformation and failure processes of the fibre and its composite and how such phenomena are modified by service environment conditions[12-17].

The residual impurities in Kevlar 49 fibres, as a result of the fibre fabrication processes, can influence the fibre oxidation and hydrolytic stability and its microvoid and moisture sorption characteristics. In this paper we report our analyses of the chemical impurities in Kevlar 49 fibres. The chemical nature of the impurities and their distribution within the fibre are considered in relation to the physical and chemical processes involved in fibre fabrication. The interrelationships between the fibre impurities and the microvoid and moisture sorption characteristics are also discussed.

EXPERIMENTAL

Materials

Twenty-five Kevlar 49 spools produced over a period of 10 years were analysed in this study. The Kevlar 49 yarns were of 380 denier, consisting of 267 filaments with a twist of approximately three turns per metre. The Kevlar 49 yarn had no additional finish or sizing applied to the yarn after fibre processing. Three spools of preproduction Kevlar 49 fibres, PRD 49, were also included in these studies. Prior to analyses the spools had been stored in either dry metal containers or in dark cupboards.

Method

Kevlar 49 fibres were ashed at 700°C for 8 h and the weight percentage ash was determined. From the ash, the Na content was determined by atomic absorption (Perkin–Elmer) and the total sulphate SO_4^{2-} was determined by a Technicon Autoanalyzer. The total S in the fibre was determined by a Fisher 475 S Analyzer. Minor impurities in the fibres were determined by inductively coupled plasma atomic emission spectrom-

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Table 1 Ash, Na, SO_4^{2-} and S in Kevlar 49 fibres

Impurity	Average (ppm)	Range (ppm)
Ash	10950	6200–15700
Na	3750	2000–5100
SO_4^{2-}	5050	800–8650
S	4050	3600–4600

Table 2 C, N, H analyses of Kevlar 49 fibres

Element	Theoretical (wt%)	Dried outside analyser (wt%)	Dried inside analyser (wt%)
C	70.59	68.71	69.39
N	11.77	11.51	11.66
H	4.20	4.53	4.29

etry (ISA, model JY38) and optical emission spectrometry (3.4 m Jarrel–Ashe Ebert Spectrograph) of the ash.

Studies were conducted to ascertain if the impurities can be leached out of Kevlar 49 fibres by contact with water. Five gram samples of the fibres were placed in HNO_3-washed glass beakers and were covered with deionized water for periods of 6 h, 11 and 15 days at 23°C, and 30 days at 100°C. At the end of the allotted time the fibres were separated by filtration and were washed. The samples were dried in a desiccator for several days and then ashed and the impurities were analysed.

C, N, H analyses were performed on Kevlar 49 fibres with a Perkin–Elmer Elemental Analyzer, model 240. Fibre samples dried at 100°C prior to introduction into the analyser and samples dried at 100°C directly inside the analyser were investigated.

Electron microprobe X-ray spectroscopy (EMP) (Applied Research Laboratories) with a beam diameter of 1 μm was used to monitor the impurity distributions in the filament cross section. For these studies Kevlar 49 filaments were encapsulated in a resin and subsequently were polished to expose the cross sections of individual filaments.

RESULTS AND DISCUSSION

Impurity analyses

The average values of the ash, Na, SO_4^{2-} and S in parts per million by weight (ppm) and the range of these values observed in the 25 Kevlar 49 spools that were studied are documented in *Table 1*. We observed that rare, larger-diameter (~18 μm) fibres contained considerably more impurities (i.e. Na content of 27 500 ppm) compared to the normal 12 μm diameter fibres.

Emission spectroscopy of the ash revealed the presence of ~200 ppm of other impurities in Kevlar 49 fibres. The impurities are Al, Fe, Si, Cl, Ca and K and are present in concentrations in the 10–100 ppm range. If we assume that these impurities are present as their oxides, their concentration in the fibre is ~350 ppm. (These minor impurities are probably present as a mixture of sulphates and oxides rather than exclusively as oxides.)

These impurity analyses of Kevlar 49 fibres were consistent with previous studies conducted by Thompson, Powell and Lever[18] and Penn and Larsen[19].

C, N, H values for Kevlar 49 samples dried at 100°C prior to introduction into the analyser and for samples dried at 100°C inside the analyser are compared in *Table 2* with the theoretical values for pure PPTA. The lower C value for samples dried outside the analyser indicates that Kevlar 49 fibres readily sorb moisture during transfer into the analyser. The C values previously reported in the literature were in the 67–68 wt% range[18,19], well below the theoretical value of 70.59 wt%. We assume that insufficient drying precautions were followed in these studies. The maximum C value of 69.39 wt% obtained when specimens were dried inside the analyser indicates that Kevlar 49 fibres contain 17 000 ppm impurities, which is a larger value than the ash content of 10 950 ppm reported in *Table 1*.

We attempted to determine the distribution of Na and S in the cross section of Kevlar 49 fibres by EMP studies with a beam diameter of 1 μm. No evidence indicating any segregation to produce Na- and S-rich areas within the fibres was obtained and these elements appeared to be uniformly dispersed. Any Na or S inclusions with dimensions significantly less than the electron beam diameter would have escaped identification. However, from laser vulnerability studies of Kevlar 49–epoxy composites[20] we may have indirect evidence of nonuniform impurity distributions in Kevlar 49 fibres. We observed that fractured Kevlar 49 fibres upon exposure to a heat pulse with associated temperatures of 3000°C preferentially degraded and volatilized within the fibre interior, resulting in hollow fibres as illustrated in *Figure 1*. Such a phenomenon could be caused by a high concentration of impurities in the fibre interior, which preferentially catalyse chemical degradation.

The Na and SO_4^{2-} impurities can be partially leached out of Kevlar 49 fibres upon immersion in water. Our analyses of the impurities that remained in the fibres indicated that Na_2SO_4 was the principal impurity leached from the fibres. At 23°C after 6 h, ~15 wt% of the fibre impurities can be leached out, with little additional loss of impurities occurring after 15 days of further water immersion. However, over 50% of the impurities can be leached out upon exposure to the boiling water for 30 days.

Preproduction Kevlar 49 fibres, PRD 49, were found to contain 10–60% fewer impurities than Kevlar 49 fibres and to exhibit ash contents in the 1500–4200 ppm range. Lower Na contents of 60–550 ppm and higher Ca contents of 300–375 ppm relative to Kevlar 49 fibres

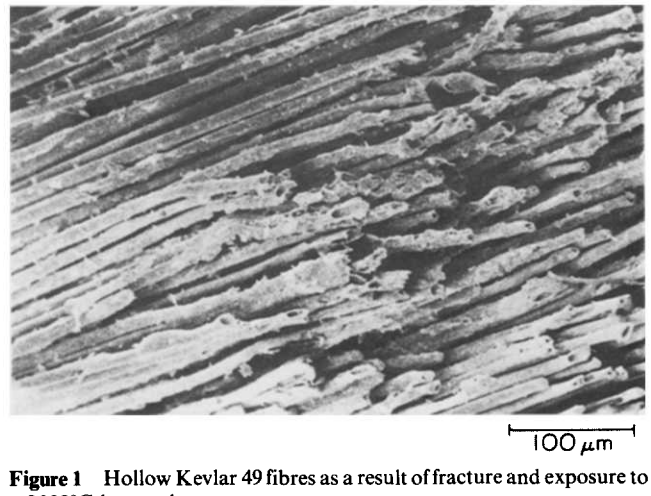


Figure 1 Hollow Kevlar 49 fibres as a result of fracture and exposure to a 3000°C heat pulse

indicate that these PRD 49 fibres were either more thoroughly washed than Kevlar 49 fibres and/or neutralized by chemicals other than NaOH and/or spun from a solvent other than H_2SO_4. PRD 49 fibres have been reported to be of two types: (1) polybenzamide (PBA)[4] and (2) PPTA[7]. PBA can be spun from solvents other than H_2SO_4 such as dimethylacetamide.

Chemical and physical processes involved in fibre fabrication

To ascertain the chemical and physical characteristics of the impurities in Kevlar 49 fibres and to identify the microscopic and molecular environments in which they reside within the fibre, the chemical and physical processes involved in fibre fabrication must be understood.

Kevlar 49 fibres have been characterized as PPTA[1-11]. The polymerization and fibre fabrication of PPTA have been described in the patent literature[21-23], and we have discussed these processes in a previous publication[14].

In *Figure 2*, we illustrate the PPTA fibre fabrication processes and the corresponding chemical and physical structures that result from these processes.

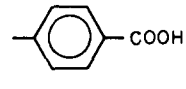
The PPTA fibres are extruded at ~80°C in the form of liquid-crystalline PPTA–H_2SO_4 (~20 wt% PPTA) dopes from a spinneret at 0.1–0.6 m s^{-1}. The spinneret face is separated from a 1°C water bath by an air gap of ~5 mm. When PPTA macromolecules are exposed to 80°C in 100% H_2SO_4 during the fibre spinning operation, sulphonation of the PPTA phenyl groups can occur to produce impurities in the form of benzenesulphonic acid side groups (*Figure 2*). The sulphonating power of the H_2SO_4 is a maximum at this stage of the fibre fabrication process. The addition of water in the later stages of fibre fabrication will dramatically decrease the potential for sulphonation of the PPTA macromolecules[24,25]. The phenyl group attached to the NH_2 macromolecular end will be most susceptible to electrophilic attack, and thus sulphonation, because of the partial delocalization of the lone pair of electrons of the N atom into this phenyl ring. The delocalization of N electrons into the phenyl ring is not as strong in the case of the PPTA amide groups because of the competing delocalization across the C–N bond that results in their partial double bond character[26].

The macromolecular orientation within a filament is determined by the extensional stresses imposed on the dope as it enters the spinneret die and, also, in the air gap after the dope exits the spinneret orifice. The fibre exterior is more oriented because of the additional shear stresses imposed on that portion of the dope that is adjacent to the wall in the spinneret capillary[14].

The solidification process of the PPTA–H_2SO_4 is critical in determining the ultimate impurity distribution within the fibre. The PPTA–H_2SO_4 (~20 wt% PPTA) dope at 80°C is situated near a minimum in the viscosity (η)–polymer concentration plot[27]. This minimum results from two phenomena that affect the η of a liquid-crystalline dope as a function of polymer concentration. The η of the liquid-crystalline dope decreases with increasing concentration as the anisotropic phase forms at the expense of the isotropic phase. However, at higher concentrations, solid polymer phase separation occurs in the dope, causing a subsequent upturn in the η[14,28]. Hence, the PPTA–H_2SO_4 (20 wt% PPTA) dope at 80°C is at a polymer concentration just below the concentration at which solid polymer precipitation would occur. The lowering of the dope temperature under stress in the air gap and then in the water bath should favour PPTA phase separation. In the wet-spinning process, in which the air gap is absent and the dope and coagulation bath are at the same temperatures, dope solidification occurs as a result of H_2SO_4–H_2O coagulation. In this case, phase separation of the PPTA does not occur and the structural integrity of the fibres is poor compared to that of those produced by the dry-jet wet-spin process, where the presence of the air gap allows the dope temperature to be greater than that of the coagulation bath. In the dry-jet wet-spin process it is suggested that the PPTA phase separates prior to significant diffusion of water into the dope[14].

From structural studies of hydrolytically degraded Kevlar 49 fibres we believe that PPTA macromolecules phase separate into 60 nm diameter fibrils. These fibrils are clearly evident in the fracture topographies of Kevlar 49 fibres that have been swollen in superheated steam and hydrolytically degraded[17], as illustrated in *Figure 3*. We observe that the fibril diameter is constant in fibres that originated from a variety of Kevlar 49 spools. Careful control of the PPTA–H_2SO_4 dope concentration and initial temperature in the spinneret, the air gap length and the water bath temperature would produce PPTA phase-separated fibrils of similar diameters.

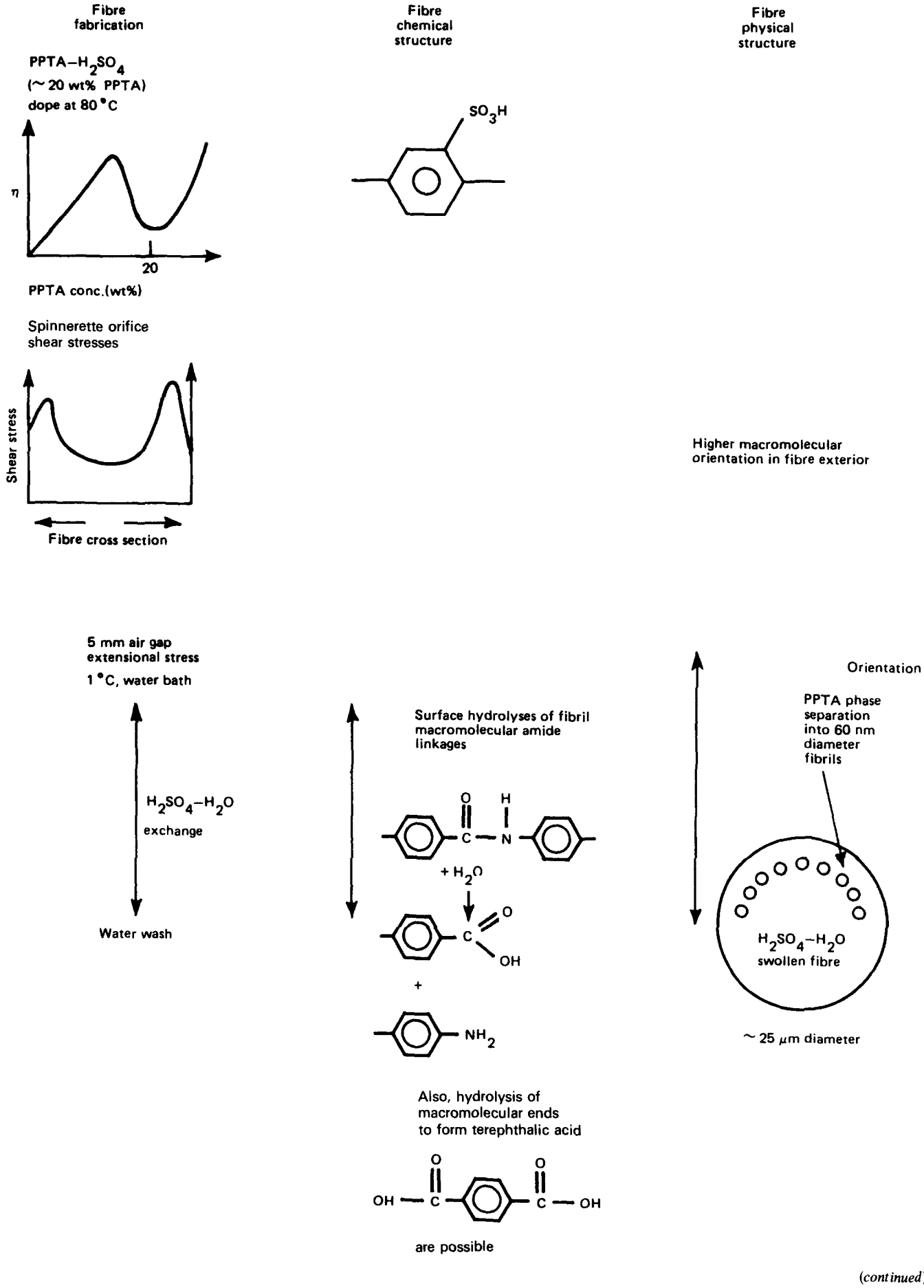
Ideally we assume that in the PPTA phase separation process the H_2SO_4 is completely excluded from the solid PPTA phase. Upon this separation the PPTA fibrillar crystallite boundaries are spaced 130 nm apart in a continuous H_2SO_4 medium. A large portion of the H_2SO_4 is washed out from the swollen fibre by the water in the coagulation bath and then by water and/or dilute NaOH sprays[22,23]. When acidic water mixtures are in the swollen fibre, acid-catalysed hydrolyses of the PPTA macromolecular amide linkages can occur at the PPTA fibril surfaces (*Figure 2*). In our recent studies on the characterization of the H_2SO_4-catalysed hydrolysis species of PPTA, we found that terephthalic acid was readily formed[29]. H_2SO_4-catalysed hydrolysis studies of model aromatic amine compounds indicate that terephthalic acid formation results from the preferential hydrolysis of the PPTA amide linkage adjacent to the



macromolecular end group.

A dilute 1% NaOH spray is used to neutralize the H_2SO_4 that resides between the PPTA fibrils resulting in the formation of Na_2SO_4. The copious quantities of Na_2SO_4 formed upon neutralization are washed from the fibre by water. The PPTA COOH macromolecular end groups and SO_3H side groups will also be neutralized by NaOH to form the corresponding Na salts if the NaOH can penetrate the polymer fibrils and the volume in the local molecular environment of the acid groups is sufficient sterically to allow the neutralization reaction to occur. In this regard, the spacing in PPTA crystals based on the reported unit cell lattice constants[4] allows H_2O and NaOH molecules to penetrate the PPTA fibrillar crystals but sterically prohibits penetration or mobility of Na_2SO_4 or H_2SO_4 within these crystals.

After the neutralization–washing process, the fibre still contains significant quantities of water, which is then



(*continued*)

Figure 2 PPTA fibre fabrication processes and the corresponding chemical and physical structures that result from these processes

Figure 2 (*continued*)

Fibre fabrication	Fibre chemical structure	Fibre physical structure
NaOH spray	Na_2SO_4 $-SO_3Na$ $-CO_2Na$	
Dry fibre (65 °C) under tension		Microcracks Cross section Fibre direction
Stressed, 550 °C, 1–5 s		Microbuckling Fibre direction Fibrillar crystallite orientation

removed from the fibre by slowly drying the yarn under slight stress in the 65–130°C range over a period of days. To produce a higher-modulus PPTA fibre, such as Kevlar 49, the still partially moist fibre is oriented at ~550°C for 1–6 s.

The distribution of any residual Na_2SO_4 impurities throughout the fibre and the fibre microvoid characteristics will depend intimately on the dynamics of the fibre drying process. The diameter of the H_2SO_4 swollen fibre is reduced by one-half upon final fibre drying and 'solidification'. This shrinkage causes skin–core radial and hoop stresses and longitudinal kinking of the fibrillar crystallites under compressional forces that are more severe in the fibre skin (*Figure 2*).

Impurity model

To ascertain the characteristics of the impurities in Kevlar 49 fibres we assume that (1) complete PPTA polymer phase separation occurs and all H_2SO_4 is completely excluded from the fibrillar crystallites, (2) all measured SO_4^{2-} is in the form of Na_2SO_4, (3) S in excess of that associated with SO_4^{2-} is in the form of $-SO_3H$ PPTA side groups, and (4) Na in excess of that associated with Na_2SO_4 is in the form of COO^-Na^+ PPTA end groups or $SO_3^-Na^+$ side groups. Based on these assumptions, together with the average values of the impurity analyses data in *Table 1*, we calculated the nature of the chemical impurities in Kevlar 49 fibres, and these are documented in *Table 3*.

Fifty per cent of the impurities in Kevlar 49 fibres are in the form of Na_2SO_4 situated between the fibrillar, 60 nm diameter crystallites. If this Na_2SO_4 was uniformly distributed on the crystallite surfaces, a Na_2SO_4 molecule would be spaced every 45 Å along each surface PPTA macromolecule (*Figure 4*). The Na_2SO_4 molecules are more likely to exist in the form of small clusters that get trapped upon shrinkage during the fibre drying stage at molecular 'log-jams' in the preferential diffusion paths that develop within the three-dimensional aggregating fibrillar crystallite array. Such Na_2SO_4 clusters will be a source of microvoid formation, particularly in the later stages of drying when trapped aqueous Na_2SO_4 concentrations will impose osmotic pressures upon their surroundings resulting in spherical defects. Small-angle X-ray scattering (SAXS) studies[30] indicate that Kevlar 29 fibres contain 0.8% of 10 nm diameter spherical microvoids. This concentration of microvoids is equivalent to 10 microvoids per 250 nm length of each 60 nm diameter PPTA fibrillar crystal. The presence of

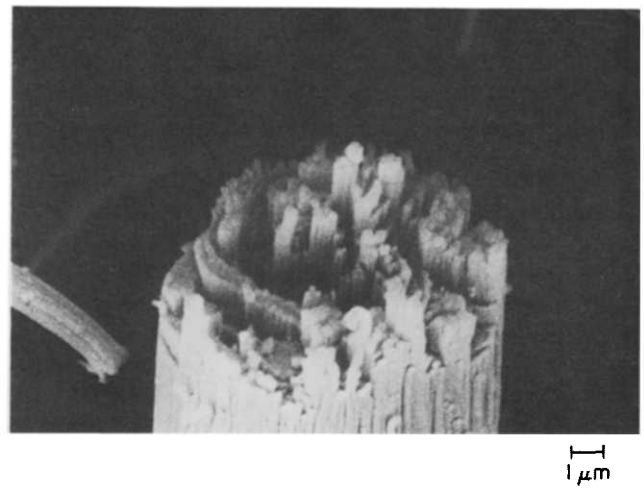


Figure 3 Scanning electron micrograph of hydrolytically degraded Kevlar 49 fibre exhibiting a 60 nm diameter fibrillar morphology

Table 3 Chemical impurities in Kevlar 49 fibres

Chemical	Concentration (ppm)
Na_2SO_4	7450
$-SO_3^-Na^+$	4550
$-SO_3H$	2400
$-Na^+$ (COO^-Na^+ end groups)	350
Metallic oxides	350
Total	15100

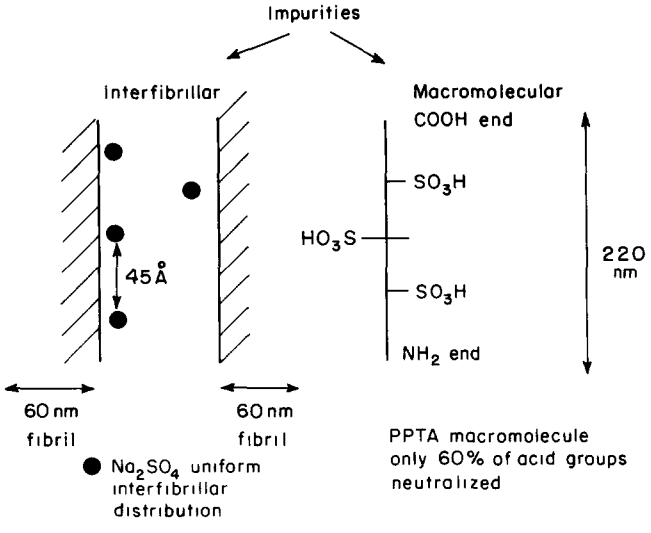


Figure 4 Impurities in Kevlar 49 fibres

spherical microvoids in a highly anisotropic structure indicates that their formation is governed by osmotic pressure effects rather than by structural effects. Upon orienting Kevlar 29 fibres to form Kevlar 49 fibres the anisotropic structural changes cause the microvoids to change shape to $10 \times 5 \times 5$ nm ellipsoids aligned along the fibre axis. Treating Kevlar 49 fibres with superheated steam[17] causes the ellipsoidal microvoids to revert to their original spherical shape. Absorbed moisture within a Kevlar 49 fibre will preferentially accumulate at hygroscopic Na_2SO_4 concentrations. Superheated steam exposure clearly reveals the 60 nm diameter crystallites in fractured fibres (*Figure 3*), which suggests that H_2O preferentially accumulates in the interfibrillar regions in which the Na_2SO_4 clusters and their associated microvoids reside and forces the crystallites apart.

Kevlar 49 fibres, whose density indicates they contain 3.4% voids, do contain larger needle-shaped microvoids (up to $>10\,\mu m$ in length) than those observed by SAXS studies[31,32]. These larger voids are a result of fibre handling, sample preparation techniques and shrinkage stresses, and we do not associate such voids with Na_2SO_4 impurities, although such voids could have propagated initially from Na_2SO_4-induced smaller spherical microvoids.

The chemical impurity analyses in *Table 3* indicate that there are three $-SO_3H$ groups per PPTA macromolecule, which together with the one COOH macromolecular end group results in four acid groups per PPTA macromolecule (*Figure 4*). The Na present in the fibre in excess of that associated with Na_2SO_4 is only sufficient for 60% of the acid groups to be in the form of their Na salts $SO_3^-Na^+$ and COO^-Na^+. (In our calculations we assume an equal probability of the –COOH and $-SO_3H$ acid groups being neutralized by NaOH.) Thus 1.6 acid groups per PPTA macromolecule are not neutralized.

Electron paramagnetic resonance studies on Kevlar 49 fibres[16] indicate that paramagnetic impurities, such as Fe, are oriented within crystalline regions, which suggests that such impurities may be trapped in the fibrillar crystals.

The average impurity total of 15 100 ppm in *Table 3* is larger than the average ash content of 10 950 ppm because, upon ashing Kevlar 49 fibres, the $-SO_3H$ side groups and, also, possibly a portion of their Na salts will volatilize. However, the impurity total in *Table 3* is lower than the impurity level of 17 000 ppm implied by the C value from C, N, H analyses. We believe this discrepancy is a result of experimental scatter from the various techniques used in these analyses.

Effect of impurities on fibre durability

The impurities in Kevlar 49 fibres, in addition to creating inherent microvoids in the fibre, can catalyse chemical degradation and enhance moisture sorption.

Critical small quantities of mobile H_2SO_4 could seriously affect long-term fibre strength. In reality, the characteristics of the impurities in Kevlar 49 fibres may be more complex than implied by our analyses. Possibly H_2SO_4 is (1) not completly excluded from the PPTA crystals upon phase separation, particularly that in the form of $NH_3^+HSO_4^-$ macromolecular end groups, and (2) not neutralized or completely washed from the fibre. Any mobile residual H_2SO_4, specifically that residing in the interfibrillar regions, will accelerate hydrolytic and oxidative degradation of PPTA. Penn and Larsen[19] have detected traces of H_2SO_4 in Kevlar 49 fibres by mass spectrometry. Acid-catalysed oxidative degradation of Kevlar 49 yarns is used to identify yarns with 'unacceptable' acid levels. In this procedure bare Kevlar 49 yarns are placed in a calibrated air convection oven for 3 h at 240°C and their residual strengths are determined at 23°C as twisted bare yarns[33]. A loss in strength of $>10\%$ is considered indicative of the presence of an unacceptable concentration of H_2SO_4.[34] Residual strength reductions were found to be in the 0.3–7.1% range for spools used in some of our impurity analyses[33].

Our most recent data indicate that the rate of hydrolysis of Kevlar 49 fibres under ambient conditions is small and is in the order of 0.2% per annum[35]. However, studies on the H_2SO_4-catalysed hydrolytic-induced strength degradation of Kevlar 49 yarns indicate that the acid increases the hydrolysis rate constant of PPTA by $\sim 10^5$ (ref. 29). Therefore, small quantities of mobile H_2SO_4 could have a significant effect on the long-term strength of the fibre. The presence of excess NaOH in the fibre would not be such a serious concern, because, although it increases the hydrolysis rate constant of PPTA by $\sim 10^3$ (ref. 29), it converts to the relatively stable COO^-Na^+ salt upon hydrolysis, thus essentially eliminating itself from further catalytic behaviour.

The moisture sorption characteristics of Kevlar 49 yarns will be affected by hygroscopic Na_2SO_4 clusters. Penn and Larsen[19] reported enhanced moisture sorption in Kevlar 49 yarns with increasing ash content. Moisture readily diffuses through Kevlar 49 fibres. From residual gas analyses–mass spectroscopy studies at 10^{-7} Torr vacuum as a function of temperature, we determined an activation energy for moisture diffusion in Kevlar 49 fibres of 6.0 kcal mol^{-1} (ref. 36). This value is about one-third that of 18.5 kcal mol^{-1} reported for moisture diffusion in epoxies[37]. We suggest that preferential moisture diffusion occurs through Na_2SO_4-rich regions that exist between the PPTA 60 nm diameter fibrils.

CONCLUSIONS

Kevlar 49 fibres contain 15 000–17 000 ppm impurities. Fifty per cent of these impurities are Na_2SO_4 situated in impurity-rich regions between 60 nm diameter fibrils.

These regions are paths for preferential moisture diffusion. During fibre fabrication these Na_2SO_4 impurities generate osmotic pressures that cause 10 nm diameter spherical microvoids in the fibre. There are three benzenesulphonic acid side groups and one COOH end group per PPTA macromolecule. Sixty per cent of these acid groups are neutralized and in the form of the Na salt. Other metallic compounds at concentrations of ~350 ppm are also present in Kevlar 49 fibres. Trace quantities of mobile H_2SO_4 accelerate hydrolytic and oxidative Kevlar 49 fibre degradation.

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