

EFFECT OF ENVIRONMENTAL EXPOSURES ON THE ARAMID FIBRE KEVLAR

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Abstract: The effects of exposure of Kevlar 49 fibres to thermal, ultrasonic and chemical environments have been analysed. Both the tensile strength and the tensile modulus deteriorate with thermal exposures. However, the former is more sensitive than the latter. The prominent crystal structural changes induced by thermal exposures are reduction in crystallinity, molecular misalignment about the fibre axis, increase in the inter layer distance, changes in crystallite size and/or microstrain. Thermally induced macro changes include introduction of surface holes, partial hollowness near the core, localised thinning, material loss in the vicinity of surface impurities etc. The structural changes could be satisfactorily correlated with the corresponding changes in tensile properties. All the thermally induced effects are controlled by two parameters, viz., the temperature (T) and the duration of the cumulative exposure to T, $t_{cum}(T)$. The $T-t_{cum}(T)$ effect leads to the observation of isothermal decomposition of Kevlar over a range of temperatures which include T's, far below the reported decomposition temperature of 500/550 °C. A hitherto unknown direct correlation between X-ray diffraction peak positions and the tensile strength has also been identified. Exposure to ultrasonic waves introduces axial compression, evinced by the formation of kink bands, fibrillation and macro buckling. The unit cell of axially compressed fibres manifests an anisotropic deformation. The process of moisture uptake by Kevlar 49 fibres is controlled by the relative humidity (RH) of ambient atmosphere. The saturation moisture content is, however, determined by structural characteristics such as the degree of crystallinity, molecular alignment etc. The uptake of common organic solvents by Kevlar is dependent on the molar volume of the former.

Key words: Kevlar 49 fibres, environmental exposures, structure, tensile

1. INTRODUCTION

Kevlar (Kevlar is the commercial name given by DuPont Inc., USA) is an aramid made up of poly(*p*-phenylene terephthalamide)¹ or PPTA. Kevlar fibres are characterised by high tensile modulus, strength, good thermal stability and low density. On account of these exceptional combination of properties, Kevlar fibres have an extensive range of applications which include sports goods to aerospace structures. Different versions of Kevlar fibres have been introduced by DuPont, viz., Kevlar 29, Kevlar 49, Kevlar 149, Kevlar 981 etc. each one being an improvement over the previous versions. Table I presents a comparison of relevant properties of some versions of Kevlar^{2,3}. It may be noted that of these, Kevlar 149 and Kevlar 981 represent the high modulus and high strength versions respectively. However, the most extensively studied and used version is Kevlar 49. While in use, Kevlar fibres or components made up of Kevlar fibres are likely to be exposed to different types of environments. Do such environmental exposures affect the initial exceptional properties of this high performance fibre? This question was addressed by exposing Kevlar 49 fibres to thermal, ultrasonic and chemical environments. Of these, the effect of thermal exposures was studied in an extensive fashion and a satisfactory correlation between thermally induced changes have indeed been worked out. An account of the major features which characterise environmentally exposed Kevlar fibres is presented in this paper.

2. EXPERIMENTAL METHODS

Kevlar 49 fibres made commercially available by DuPont Inc., USA, have been used in the present study. X-ray diffraction, scanning electron microscopy, optical microscopy,

Table I. A comparison of the properties of different versions of Kevlar fibres^{2,3}

Version → ↓Properties	Kevlar 29	Kevlar 49	Kevlar 68	Kevlar 119	Kevlar 129	Kevlar 149	Kevlar 981
Tensile strength (GPa)	2.9	2.9	3.1	3.1	3.4	2.3	3.5
Tensile modulus (GPa)	70	135	99	55	99	143	120
Diameter (μm)	12 - 15	12	15	12 - 15	12	12	9.5
Breaking strain (%)	3.6	2.8	3.3	4.4	3.3	1.5	2.8
Density (Kgm ⁻³)	1440	1450	1440	1440	1450	1470	-
Specific strength (GPa/Kgm ⁻³)	2.0	2.0	2.2	2.2	2.3	1.6	-

tensile testing and weight analysis were the major techniques used in these investigations. Details of the experiments have been presented elsewhere⁴⁻¹⁶ and are not repeated here.

3. RESULTS AND DISCUSSION

3.1 Exposure to thermal environments

Thermal exposures of Kevlar fibres were carried out in the temperature (T) range 50 to 550 °C. It must be pointed out that Kevlar 49 fibres are recommended for use upto 250/300 °C^{3,18}. With the view to accelerate the data collection and possibly extrapolate to lower T's, exposures to temperatures well above the recommended service range were deliberately included. The durations of cumulative exposures, $t_{cum}(T)$, ranged from few seconds to few thousands of hours. Interestingly these exposures, without any exception, influenced the structural as well as the tensile characteristics of the fibre, the details of which are presented below.

3.1.1 Tensile characteristics: Both the tensile strength and the modulus of Kevlar 49 fibres are influenced by thermal exposures. However, the tensile strength is more sensitive than the modulus^{5,6,9}. Such a preferential response of the former parameter may be associated with corresponding preferential, thermally induced structural changes^{5,6,11}, the details of which will be presented in the subsequent section. The deterioration in tensile characteristics increase with increase in T as well as the duration of cumulative exposure, $t_{cum}(T)$ ^{6,9}. The activation energy, E, required for 50% reduction in tensile strength was found to be 54 kJ/mole⁹. This value is less than the energy needed to disrupt a covalent bond and higher than that required to disrupt a single hydrogen bond. It appears therefore that partial disruption of van der Waals forces and/or few hydrogen bonds in the crystal structure can lead to 50% reduction in the tensile strength of the fibre. Further experimental evidence supporting such weakening of van der Waals forces in the crystal structure has been obtained. Apart from the above mentioned crystallographic changes, thermally induced macro structural changes can also reduce the tensile strength of the fibre. Details of these structural changes are described in the ensuing section.

It must also be mentioned that heat treatment altered the fracture mechanism of the fibres. Prior to heat treatment, individual filaments fractured in tension were characterised

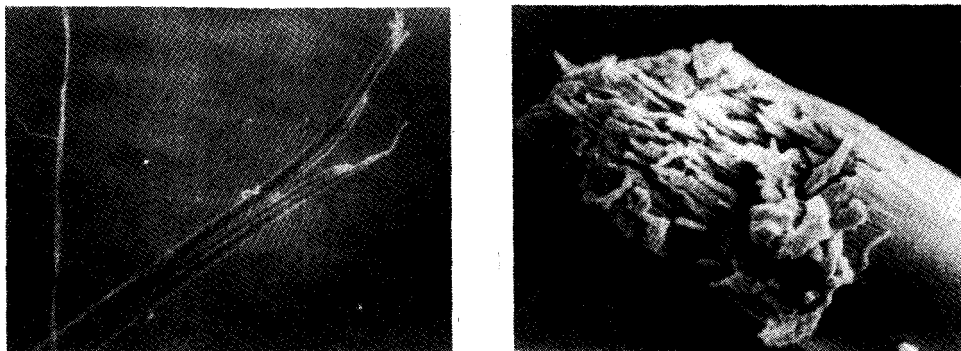


Fig.1. Scanning electron micrographs from filaments fractured in tension (a). Longitudinal splitting prior to heat treatment. (b). Brittle fracture after heat treatment.

by longitudinal splitting (Fig.1a) whereas after the thermal exposures, the fracture was conspicuously brittle in nature (Fig.1b). The degree of brittleness increased with T and $t_{cum}(T)$.

3.1.2 Structural characteristics : Thermal exposures are found to influence the crystal as well as the macro structural characteristics. To appreciate the extent of these thermally induced changes, a brief description of the initial structural characteristics of Kevlar 49 fibres have been included here.

3.1.2.1 Crystal structural characteristics: Kevlar fibres crystallise in the monoclinic space group $P2_1/n$ or Pn ¹⁹. Figure 2 presents the arrangement of PPTA chains in the crystallographic bc - plane.

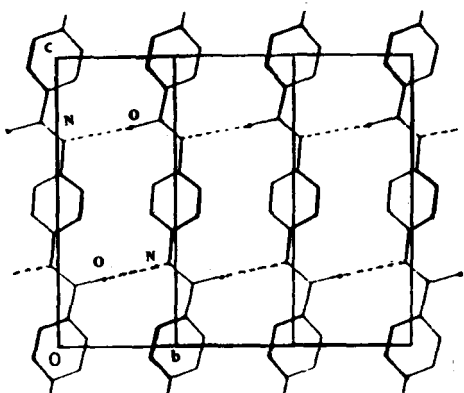


Fig. 2. Arrangement of the PPTA chains in the crystallographic bc - plane. Dashed lines indicate the hydrogen bonds.

The chains which assume an all trans, fully extended conformation are oriented along the crystallographic c - direction. Adjacent chains interact by means of hydrogen bonds formed between the CO and the NH groups. Interestingly, all the CO and all the NH groups in the chains are involved in the formation of hydrogen bonds. Consequently, the hydrogen bonds in the crystallographic bc -plane assume a periodic network like pattern. The layer structure in the bc - plane is stabilised, primarily, by this periodic network of inter chain hydrogen bonds. Such hydrogen bonded layers are stacked along the crystallographic a -direction. On account of the presence of the n -glide, adjacent layers are staggered with respect to each other.

The distance between adjacent layers along the a - direction is $a/2$ and the interaction between them is primarily of the van der Waals type and to some extent, π -electron interactions also exist.

It may be pointed out that the crystal structure of Kevlar is characterised by specificity of bonds along each of the crystallographic axis. The crystallographic c - axis which is also the fibre axis, corresponds to a concentration of covalent bonds. The inter chain hydrogen bonds run nearly parallel to the crystallographic b - direction and the a - direction is represented by a concentration of the weak van der Waal's interactions. Such a specificity has been correlated with the exceptional tensile properties of the fibre. For example, the high tensile strength may be associated with the ability of the polymer chains to transfer the applied tensile load from chain to chain, via the weak link in each layer, which in this case, are the inter chain hydrogen bonds²⁰. The weak van der Waal's

forces facilitate transfer of load between adjacent layers. It is well known that the tensile modulus of a fibre is related to its degree of crystallinity. The X-ray diffraction pattern from Kevlar 49 fibres includes ~ 44 observable reflections¹⁹ which indeed is a high number for a synthetic polymer. Kevlar is among the few polymers which manifest good degree of initial crystallinity. The high initial modulus of Kevlar can also be associated with the initial good alignment of polymer chains about the fibre axis. The azimuthal spread of X-ray reflections is an indication of the chain alignment. For Kevlar fibres in the as received state, this value is as low as 6° .

Thermally exposed Kevlar fibres manifest interesting structural changes^{5,6,11}. X-ray diffraction patterns show that the initial monoclinic structure is retained till decomposition. Absence of diffuse intensities further indicates that structural disorders are not introduced by thermal exposures. The conspicuous effect of thermal exposures concerns the initial crystallinity of the fibre. Reductions in diffraction intensities indicate that the overall crystallinity of the fibre decreases with thermal exposure. A progressive reduction in crystallinity with increase in T as well as the $t_{cum}(T)$ values has been observed. Such a reduction may be expected to lead to deterioration in the initial tensile modulus. It was also found that in heat treated fibres, the initial molecular alignment was substantially disturbed. Such a misalignment suggests further reduction in tensile modulus. It appears therefore that the observed reduction in the tensile modulus of heat treated fibres is primarily due to reduction in crystallinity and molecular misalignment.

Another conspicuous change indicated by the X-ray diffraction patterns is the preferential sharpening of the equatorial (110) reflection, in the early stages of thermal ageing^{6,11}. Such a sharpening suggests thermally induced crystallite growth and / or reduction in microstrain i.e., a sort of annealing type of effect occurring in the early stages of ageing. Growth of crystallites and / or reduction in microstrain can only be expected to improve the initial tensile modulus. This feature, obviously, is in striking contrast with the deterioration in modulus suggested by reduction in crystallinity and molecular misalignment mentioned above. It appears therefore that the beneficial effect arising from crystallite growth and / or reduction in microstrain on the tensile modulus annuls, at least partially, the deterioration caused by the reduction in crystallinity and molecular misalignment. It must also be mentioned that the preferential sharpening of the (110) reflection has been associated with the concentration of non bonded inter molecular interactions in the crystallographic (110) set of planes^{5,11}.

Examination of the unit cell dimensions of heat treated fibres showed that the most sensitive parameter is the a - dimension. The preferential increase in the a - dimension is indeed understandable because the a - direction represents a concentration of weak van der Waal's interactions. The already weak interactions appear to get further weakened by thermal exposures. Such a weakening of inter layer interactions may be expected to affect the layer-to-layer transfer of load and hence influence the tensile strength of the fibre. The b - axial length, which represents the inter chain distance is, however, less affected by thermal exposures. Any increase in b - value will be an indication of weakening of the inter chain interactions and consequently, the proposed load transfer mechanism between the chains. However, in striking contrast with the a - dimension, the b - length of the unit cell was little affected by thermal exposures. Thus, the changes in unit cell dimensions, viz., the increase in the a - dimension and the near-retention of the b - length were not commensurate with the observed, substantial reduction in tensile strength. This anomaly could, however, be explained satisfactorily by taking into account the thermally induced macro changes, the details of which follow.

3.1.2.2 Macro structural changes : Examination of fibres under scanning electron and optical microscopes revealed that thermal exposures led to the introduction of severe structural damages^{6,14,17}. In particular, the surface showed the formation of large number of holes (Fig.3). The size and the number of these holes increased progressively with increase in T as well as $t_{cum}(T)$. In addition to the formation of holes, the heat treated fibres were also characterised by localised thinning and heavy loss of material. The loss of material was conspicuously intense in regions where surface impurities were present. It has been established that commercially available Kevlar fibres, in the as received state, include large quantities of impurities in the form of sodium salts²¹ (Fig.4). In the vicinity of such impurities, large crater like features were introduced during thermal ageing, leading to shallow pits on the surface. All these structural changes introduced during

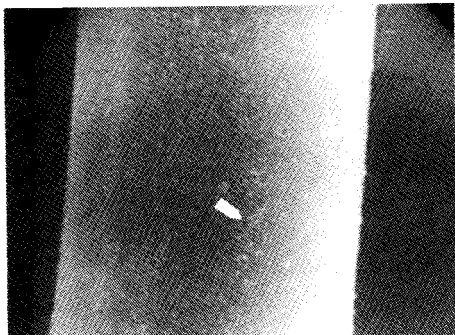


Fig. 3. Holes formed on the surface of heat treated fibre. Arrow shows a typical hole.

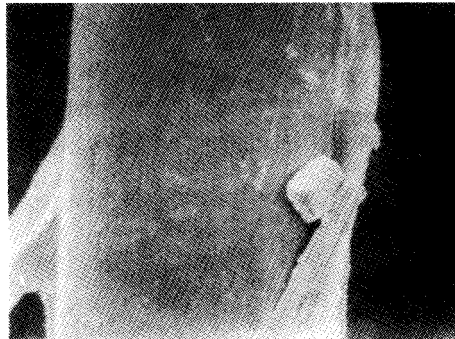


Fig. 4. Scanning electron micrograph showing the presence of surface impurity in the form of a salt.



Fig. 5. Partial hollowness in a heat treated fibre.

thermal exposures are indeed conducive to reduction in the tensile strength of the fibre.

In addition to the above mentioned structural changes introduced on the surface, the core of the heat treated fibres also manifest loss of material and consequently turn partially hollow (Figure 5). Kevlar, as is well known, has a skin-core structure with the skin being ~ 0.1 - 0.6 μm thin²²⁻²⁴. Introduction of hollowness suggests that the molecular

arrangement in the interior of the core is comparatively, thermally less stable than on the skin. As in the case of surface damages, the thermally induced hollowness also favours reduction in the tensile strength of the fibre. Taking into account these macro features and the crystallographic changes mentioned earlier, it is clear that the thermally induced reduction in tensile strength is a combined effect of changes from the initial macro as well as crystallographic characteristics. It must be emphasised that as in the case of the tensile and the crystallographic characteristics, the severity of the macro changes were also dependent on the parameters T as well as $t_{cum}(T)$.

3.1.3 Weight loss : Thermally aged fibres manifest weight loss the magnitude of which also increases with T as well as $t_{cum}(T)$. The weight loss may be associated with evolution of volatile components from within the fibre, formed due to chemical reactions induced in the PPTA chains, during heating. The earlier mentioned observation on the formation of surface holes supports the concept of evolution of components from within,

via the surface. It must be mentioned that below 250 °C, the weight loss as well as the formation of surface holes were not conspicuous. It appears therefore that the threshold temperature required for initiating the chemical reactions which are responsible for the weight loss is >250 °C.

It must be mentioned that fibres subjected to few seconds of thermal exposures also manifest deterioration in tensile and structural characteristics, very similar to those following prolonged thermal exposures.

3.1.4 The T - $t_{cum}(T)$ effect : The above mentioned data on tensile characteristics, crystallographic parameters, macro features and the weight loss, collected from thermally exposed Kevlar fibres led to an interesting observation concerning the combined role of two parameters, viz., T and $t_{cum}(T)$ which characterise any thermal exposure. It was found that changes which occurred at any temperature $T_2 (> T_1)$ recurred at T_1 also, if the exposure to the lower temperature T_1 was long enough. Interestingly, the T - $t_{cum}(T)$ effect was common to all the thermally induced effects. For example, a 50% reduction in crystallinity could be observed over a range of temperatures. The distinguishing factor at each temperature was the duration of the cumulative exposure which led to the 50% reduction. Similarly, after 3h of exposure to 350 °C, the tensile strength was found to reduce by 60%. Reduction by nearly the same amount was found to occur at 150 °C also when the $t_{cum}(T)$ value was as high as 250 h⁹. Thus the thermally induced effects were common to all the temperatures; their magnitudes were, however, controlled by two parameters, viz., T and $t_{cum}(T)$. The two parameters T and $t_{cum}(T)$ were found to act, always in unison⁶.

The T- $t_{cum}(T)$ effect identified from experimentally measured changes in the tensile properties, structural characteristics and weight loss led to the identification of the isothermal decomposition behaviour of Kevlar fibres. Kevlar fibres are reported to decompose at $T_d = 500 / 550$ °C^{25,26}. Changes which characterise decomposition at the stipulated decomposition temperatures were found to recur at temperatures far below T_d also, the controlling factor at any temperature being the duration of the cumulative exposure $t_{cum}(T)$. Kevlar fibres thus manifest decomposition characteristics over a range of temperatures, which include T's far below T_d ⁶.

3.1.5 The $\Delta t(T)$ effect : Thermally induced changes in Kevlar fibres were found to be controlled by a third parameter too viz., $\Delta t(T)$, the duration of an individual exposure to any T. A single long exposure ($t_{cum}(T)$) causes more damage to the fibre than several short exposures which together add up to a cumulative exposure of the same duration viz.,

$$t_{cum}(T) = \Delta t_1(T) + \Delta t_2(T) + \dots$$

Detailed study^{6,15} of the effect of $\Delta t(T)$ established that while using the fibre at elevated temperatures, the onset of thermally induced deterioration can be delayed or slowed down by judiciously selecting the $\Delta t(T)$ value.

3.1.6 Direct correlation between tensile strength and X-ray diffraction peak positions : In the course of the study on thermally aged Kevlar fibres, a hitherto unknown direct correlation between tensile strength and X-ray diffraction peak positions has been identified⁸. Reduction in tensile strength was found to be accompanied by closing up the equatorial planes (110) and (200), which are also the load bearing planes. This new correlation provides a fast method of assessing the tensile strength of large batches of Kevlar fibres, by a cursory examination of the equatorial X-ray diffraction pattern.

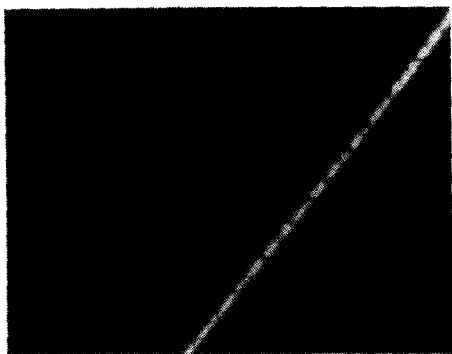


Fig. 6. V- and X-shaped kink bands on the surface of Kevlar exposed to ultrasonic waves.

3.2 Exposure to ultrasonic waves

Exposure of Kevlar 49 fibres to ultrasonic waves led to an interesting mechanical deformation. Ultrasonically agitated Kevlar fibres were characterised by the introduction of V- and X- shaped kink bands (Fig. 6), dispersion of fibrils and macro buckling all of which are manifestations of axial compression^{6,13}. Application of subsequent tensile load, however, removed the kink bands thereby showing that the structural

deformation responsible for the formation of kink bands was not permanent.

In contrast to their exceptional tensile characteristics, the compressive properties of Kevlar are rather poor. In the past, attempts have been made to understand the deformation mechanism underlying the compression of the rigid rod like molecules of PPTA²⁷⁻³¹. The basic difficulty in these studies concerned the introduction of pure axial compression to fibres which are $\approx 11\mu\text{m}$ thin. The methods which were used in the past include the elastica loop test³², ber.ding beam method, recoil method³³, single filament composite test³⁴ etc. The present study has shown that exposure to ultrasonic waves offers a new method for introducing axial compression in this high performance fibre.

It must be pointed out that the earlier studies on the compressive behaviour of Kevlar fibres were based primarily on optical and electron microscopic observations. The macro characteristics derived from these investigations established that buckling of the fibrils and the resultant formation of kink bands are the prominent manifestations of axial compression. Surprisingly none of these earlier investigations concerned the crystal structural characteristics of axially compressed Kevlar fibres. As is well known, Kevlar has a fibrillar structure and in the architecture of fibre morphology, fibrils include several crystallites; each crystallite includes several unit cells. When fibres undergo axial compression, how does it affect the unit cell? X-ray analysis of Kevlar fibres axially compressed by ultrasonic agitation, showed^{6,16} that the most prominent effect of axial compression was the anisotropic deformation of the unit cell. Whereas the c-length which corresponds to the axial length of a PPTA monomer undergoes contraction, the basal plane dimensions manifest enlargement. The observed changes in the unit cell dimensions of compressed fibres could be accounted for, at least qualitatively, by proposing a wave-like deformation along the chain axis.

In addition to the changes in unit cell dimensions, axially compressed Kevlar fibres manifest progressive broadening of the meridional reflections with increase in the extent of compression. Such a broadening suggests fragmentation of crystallites and/or introduction of microstrain along the axial direction. Introduction of such microstrain is in keeping with the above mentioned axial deformation.

Another conspicuous feature observed in the X-ray diffraction patterns from axially compressed Kevlar fibres is the increase in the azimuthal spreads of reflections. Such an increase is an indication of molecular misalignment about the fibre axis which in turn suggests reduction in the initial tensile modulus of compressed fibres. Estimation of tensile modulus and strength of the axially compressed fibres did indeed provide

qualitative evidence for such deterioration in the tensile properties of axially compressed Kevlar fibres^{6,16}.

3.3 Exposure to moisture and other chemical environments

On account of the polarity of the amide group in the PPTA molecule, Kevlar fibres have an inherent propensity for moisture uptake^{4,7,10,12}. In addition, features such as the presence of microvoids³⁵⁻³⁷ and hydrophilic sodium salts²¹ on the surface, can also facilitate easy uptake of solvents or extraneous molecules by Kevlar fibres. The above mentioned features are essentially the characteristics of the sample. It has been found that in addition to these sample characteristics, the relative humidity (RH) of ambient atmosphere also controls the process of moisture uptake by Kevlar fibres. When left in an atmosphere with higher RH value or moisture content, the process of moisture uptake by the fibre is faster. Interestingly, the saturation moisture content of fibres belonging to a batch, is constant and is independent of the RH value. The RH value of ambient atmosphere influences only the process of moisture uptake and not the saturation moisture content^{4,10}.

The process of moisture uptake as well as the saturation moisture content are, however, influenced by sample characteristics such as the degree of crystallinity and the extent of molecular alignment. Comparative analysis of the process of moisture uptake by Kevlar, the unoriented and the less crystalline polymer PPTA and also treated Kevlar fibres which are less crystalline and the less oriented than the as received fibres, provided quantitative evidence for the role of structural characteristics on moisture uptake. For a chosen value of RH, at any stage of moisture uptake, the less oriented and less crystalline samples were found to retain more moisture than their better oriented and more crystalline counterparts^{4,7,10}. It was also observed that the saturation moisture content in the former was conspicuously high. For example, in the case of the fibres with 60 % reduction in crystallinity, the moisture content had increased to 24 weight percent whereas for Kevlar fibres, in the as received state, the equilibrium saturation moisture content is only ~ 5 weight %. X-ray examination of fibres with various levels of moisture content further revealed that the water molecules did not enter the unit cell of the crystal lattice^{5,7,12}.

When exposed to alkali halide solutions, increase in the size of the alkali metal ion and decrease in the electronegativity of the halogen ion led to increase in the equilibrium weight gain^{5,12}. Kevlar fibres respond to common laboratory solvents also. The uptake of solvents, both aliphatic and aromatic, by the fibre manifested an inverse dependence on the molar volume of the former i.e., the bigger the size of the molecule, more difficult is the entry into the fibre^{6,12}. Retention of these solvents was found to be a temporary phenomenon; no permanent damage to the fibre was found except in the case of DMSO which was hostile to the fibre.

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