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Effect of thermal spikes on the structural characteristics of Kevlar fibres

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The effect of upto six cumulative exposures to thermal spikes, each of 10 s duration, on Kevlar 49 fibres has been analysed. X-ray data show that exposures to spikes corresponding to T's $\geq$ 400°C cause changes at the level of the crystal lattice. At and above 500°C, severe surface damages such as introduction of longitudinal openings, peel-offs and extraneous material are found to occur. The tensile properties of the spike-exposed fibres manifest changes which conform well with the structural changes. As in the case of prolonged thermal exposures, the spike induced effects are also controlled by two parameters, viz., the temperature and the duration of the cumulative exposure. The data from spike exposed fibres indicate that the thermally induced changes in the structural and tensile characteristics get initiated at the very early stages of thermal exposure viz., of the order of 10 s.

1. Introduction

It was shown earlier [1, 2] that prolonged thermal exposures of the order of few hundreds of hours lead to changes in the tensile as well as the structural characteristics of Kevlar 49 fibres. The changes in the tensile properties were found to conform with the corresponding changes in the structural characteristics. The present study concerns the effect of thermal spikes on Kevlar 49 fibres. A thermal spike may be defined as a sudden shooting up of temperature from ambient conditions and lasting for very short durations of the order of few seconds. Suffering thermal spikes could be accidental. As is well known, Kevlar 49 fibres are recommended for use at elevated temperatures [3]. In the course of any high temperature application, any unprecedented fluctuation in the line voltage which is beyond the controlling capabilities of a stabiliser, can cause a corresponding thermal spike. Also, while handling, accidental proximity to a high temperature source such as a furnace or flame can also have the effect of a thermal spike. Quite apart from the above mentioned accidental exposures to thermal spikes, if it is required to use a component made of Kevlar fibres beyond the recommended highest temperature for only 10 or 20 s, what sort of losses will be incurred? These questions were addressed by us and this paper reports the effect of exposure to such thermal spikes, accidental or intentional, on Kevlar 49 fibres with focusing of attention on the structural characteristics. A preliminary report concerning the effect of thermal spikes on Kevlar's tensile characteristics and some aspects of micrographs has recently appeared as part of a conference proceedings [4]. This paper presents the details of the structural changes occurring at the level of the crystal lattice, derived from X-ray diffraction experiments. Detailed information on the macro changes deciphered from both optical and scanning electron microscopy (SEM) have also been included. Correlation between tensile and structural characteristics has been examined. It must be emphasised that the present study concerns primarily with the physical changes which accompany exposure of Kevlar 49 fibres to thermal spikes.

2. Experimental details

In the present study, the temperature (T) of the spike was chosen, deliberately, to be close and beyond the recommended limit of the service range viz., from 300 to 700°C. The duration of a pulse was chosen, arbitrarily, to be 10 s. Production of a spike/pulse with precisely controlled temperature and duration is indeed a formidable task. Hence, to achieve the effect of a thermal spike, a slightly different procedure was followed. Instead of producing a spike corresponding to temperature T, a thermal environment maintained at T was created and the fibre retained at ambient temperature was suddenly exposed to this environment for precisely 10 s. Thus, the fibre experiences a sudden shooting up of temperature for durations characteristic of a spike. To create the thermal environment, a tubular resistance furnace with nichrome wire as the heating element was used. By employing a proportional integral differential (PID) controller, the temperature of the furnace could be controlled and maintained to an accuracy of $\pm 1^\circ$ C. The temperature was measured using a chromel alumel thermocouple. For each experiment, a bundle of Kevlar 49 fibres, $\approx$50 mm long and $\approx$1 mm thick was used. To ensure that all the filaments in the

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bundle experienced the required thermal exposure, they were laterally spread on the outer surface of a quartz tube and thus, overlap between filaments which in turn, can lead to partial shielding from the heat source, was minimised. Also to avoid displacement of fibres during the exposure, one end of the bundle was clamped on to the tube with the help of a metallic clip. The fibres which were held under such partial constraint occupied the region near one end of the quartz tube. The quartz tube was inserted into the furnace held stabilised at the required temperature. The fibres reaching the centre of the constant temperature zone of the furnace were allowed to stay there for precisely 10 s after which the quartz tube was pulled out of the furnace and air cooled. It must be emphasised that in order to minimise thermal exposures other than the required 10 s, the processes of inserting the quartz tube and subsequent removal were carried out very fast. Typically, it took <2 s to carry out these operations. The fibres were exposed to upto six cumulative spikes.

Equatorial X-ray diffraction patterns from fibres, both prior to and at various stages of the cumulative exposure to spikes, were recorded using a manually operated Philips powder diffractometer. Copper K_α radiation and a graphite monochromator in the diffracted beam were used. Samples were rotated at the rates of 1/4 and 1° per minute for the slow and the fast scans respectively. The chart speed was 10 mm per minute. The diffraction patterns were restricted to the 2θ range of 15 to 27° which included the two most intense reflections in the diffraction pattern from Kevlar. viz., (200) and (110). The 2θ values were estimated by the mid point chord extrapolation method [5]. The total integrated intensity in the 2θ range 15 to 27° was measured using a digitiser. Values of the full width at half maximum (FWHM) were estimated manually using a scale. As in this analysis, only relative values were being examined, no attempt was made to separate the slightly overlapping profiles. For some of the heat treated samples, in addition to the diffractometer scans, transmission Laue photographs were also recorded to identify the changes in molecular alignment.

For examining the surface characteristics, a Neophot optical microscope and a Jeol scanning electron microscope were used. Tensile testing of single filaments was carried out on a Zwick universal testing machine. Filaments ≈25 mm in gauge length were pulled in tension at the rate of 2.5 mm per minute. The chart speed used was 60 mm per minute. For each experiment, at least 50 filaments were examined and the average value was worked out. For each of the chosen temperatures, tensile testing was carried out only for samples which have experienced one and six spikes respectively. It must be mentioned that to avoid artefacts arising from handling, special care was exercised to ensure that the fibres were not twisted, bent etc. In particular, the samples examined in microscope were carefully handled.

3. Results and discussion

3.1. Crystallographic data

Examination of the X-ray diffraction patterns showed that at T's < 400° C, thermal spikes had negligible influence on the overall characteristics of the pattern. Figs 1 and 2 compare the diffraction profiles recorded from samples prior to heat treatment with those exposed to one and six thermal spikes respectively. The most conspicuous feature is that in all the patterns, the reflections (200) and (110) occur close to the expected 2θ values thereby showing that the initial crystal structure of Kevlar is substantially unaffected by the thermal spikes. The patterns, however, include minor changes in their characteristics, the details and implications of which are described in the following sections.

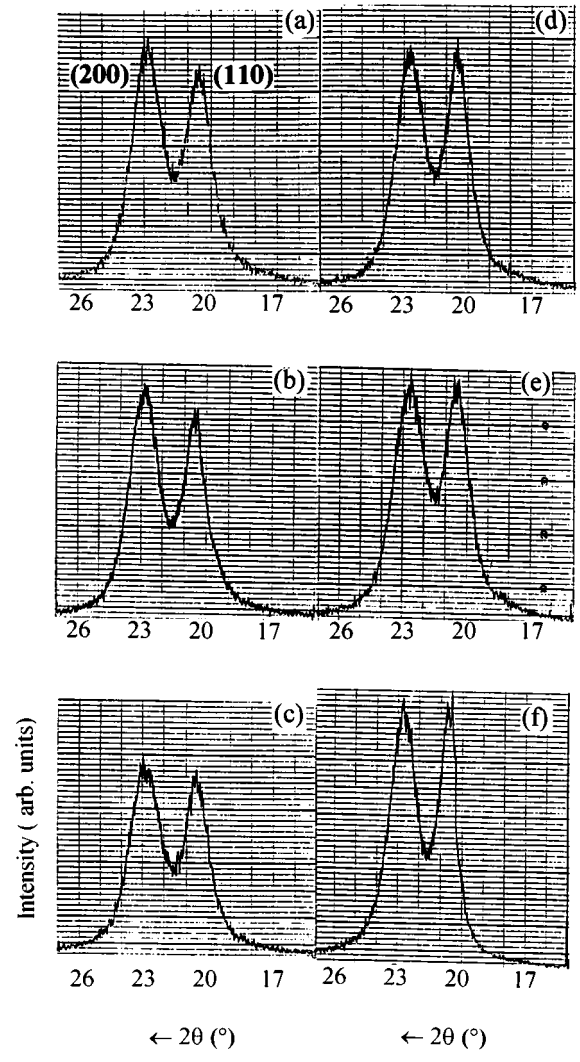


Figure 1 The (110) and (200) diffraction profiles from Kevlar 49 fibres (a) prior to exposure to spikes and after exposure to a single spike (10 s) at (b) 300 (c) 400 (d) 500 (e) 600 and (f) 700°C.

3.1.1. 2θ values

Fig. 3 shows the spike - induced shifts in the 2θ values. For both the reflections, the shifts, though small, are towards the lower angle side, indicating an increase in the corresponding d values. Fig. 3 also shows that for any value of $t_{cum}(T)$, the 2θ values exhibit a progressive decrease with increase in T. The effect of the number of spikes on the 2θ values is conspicuous only at 600 and 700°C. In any case, the observed shifts indicate that the residual effect of exposure to thermal spikes is an increase in the basal plane dimensions of

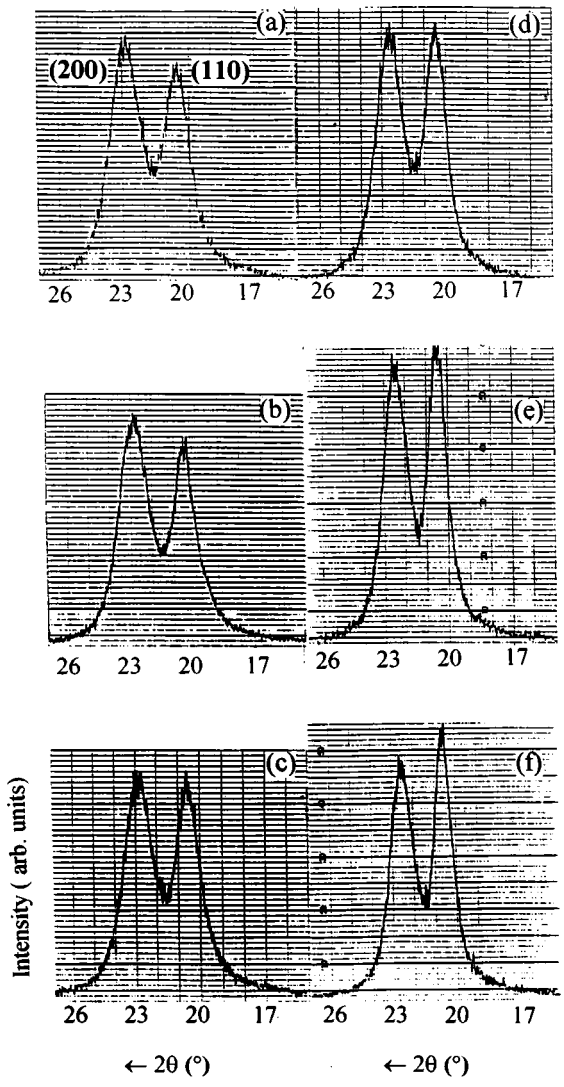


Figure 2 The (110) and (200) diffraction profiles from Kevlar 49 fibres (a) prior to exposure to spikes and after cumulative exposure to six spikes at (b) 300 (c) 400 (d) 500 (e) 600 and (f) 700°C.

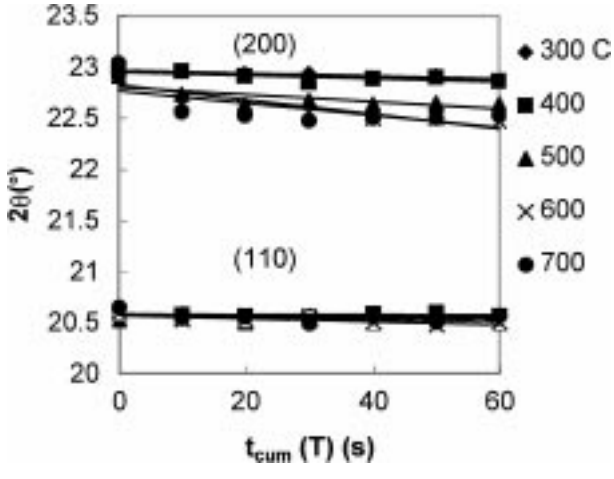


Figure 3 Observed shifts in the 2θ values.

the crystal lattice. Another interesting feature is that at any stage of exposure to the spikes, the shift in the $2\theta_{(200)}$ value is more than that in the 2θ value of the other equatorial reflection, viz., (110). This difference may be attributed to the comparatively weak van der Waal's forces which exist between adjacent (h00) planes, in the crystal structure [6]. Thermal pulses of 10 s duration appear to be sufficient to weaken further these already weak interactions and increase the $d_{(200)}$ spacing. Thus, the increase in the basal plane dimension arises primarily from the increase in the a dimension. Fig. 4 depicts the progressive increase in the ratio a/a_0, where a_0 and a represent the values of the unit cell dimension prior to and after thermal exposure, respectively. It is observed that exposure to six spikes at 700°C increases the dimension by ≈2.4%.

The parameter which is closely related to the 2θ values is the angular separation, $\Delta(2\theta) = (2\theta)_{(200)} - (2\theta)_{(110)}$. Fig. 5 depicts the influence of both T as well as $t_{cum}(T)$ on the angular separation. The correlation between the decrease in the angular separation of these equatorial reflections and reduction in the tensile strength of Kevlar fibres has been reported earlier [7]. Combining this information with the data in Fig. 5, it

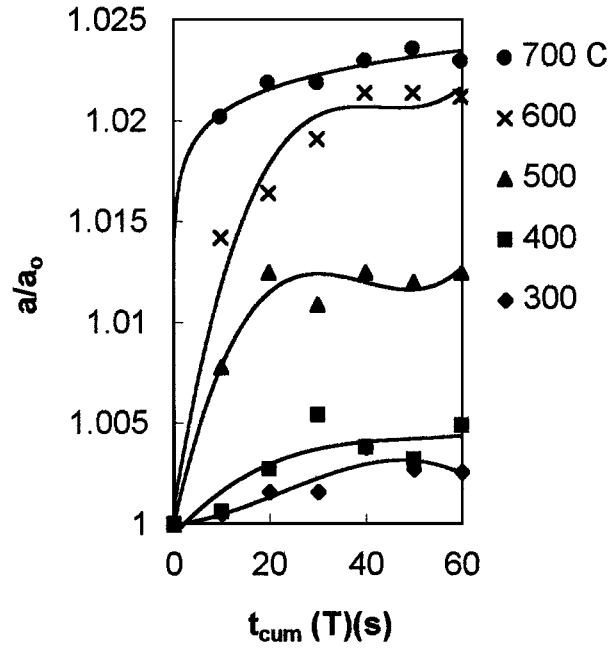


Figure 4 Fractional variation in the unit cell dimension a. Here, a_0 refers to the value, prior to exposure to spikes.

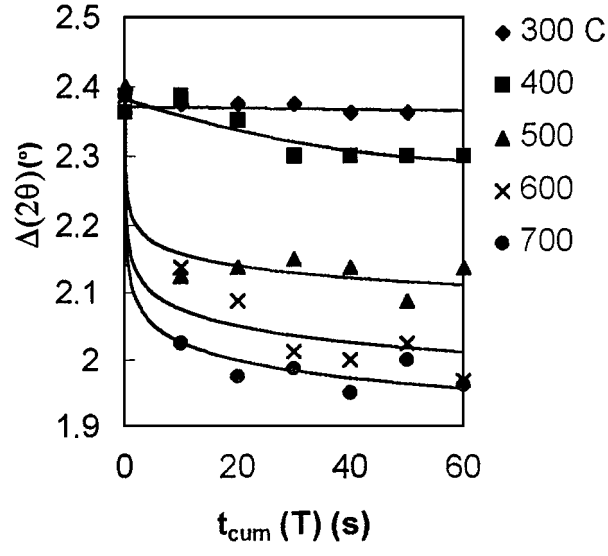


Figure 5 Observed variation in the $\Delta(2\theta)$ values.

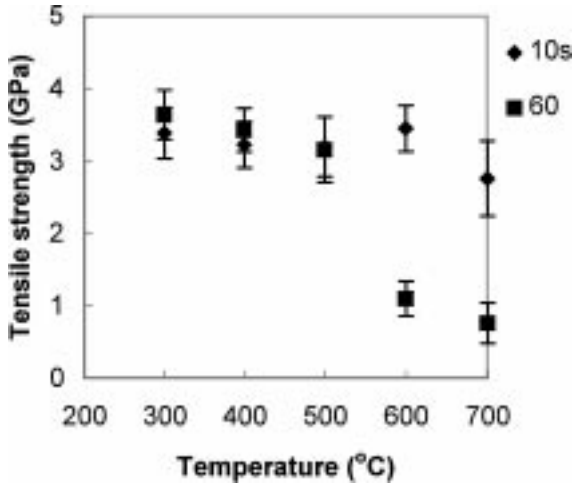


Figure 6 Observed variations in the tensile strength, with e.s.d's marked as error bars.

may be surmised that the tensile strengths of the spike - exposed fibres are reduced. Such a reduction has indeed been confirmed experimentally. Fig. 6 shows the decreasing trend in the tensile strength. It is also conspicuous that at both 600 and 700°C, the effect of six cumulative spikes is strikingly more than that of a single spike.

3.1.2. FWHM

In addition to the shifts in the 2θ values, the full width at half maximum (FWHM/half widths) of the diffraction profiles are also influenced by exposure to spikes. Fig. 7 presents the fractional variation in the half widths (b) which exhibit a progressive sharpening at T's $>$ 400°C. It is interesting to note that at these temperatures even a single spike can cause detectable sharpening of the reflections. The effects of both T and $t_{\text{cum}}(T)$ can be appreciated from Fig. 7. The half width values illustrate a difference in the behaviour of the equatorial reflections. It is found that the reflection (110) sharpens more than (200). As pointed out earlier [2], the difference may be attributed to the concentration of non-bonded intermolecular interactions in the crystallographic (110) set of planes. It is well known [8] that sharpening of reflections is associated with growth of crystallites and/or reduction in the microstrain in the crystal lattice, both of which in turn, can improve the tensile modulus of the fibre. The observed sharpening thus suggests that exposure to thermal spikes could have a beneficial, annealing type of effect which in turn, can improve the tensile modulus of the fibre. Values of the tensile modulus presented in Fig. 8 show that within the errors of experimental measurement, for $t_{\text{cum}}(T)$ of 10 s, the modulus tends to increase with T. This feature is in keeping with the sharpening of reflections observed at 10 s. However, for $t_{\text{cum}}(T) = 60$ s, the modulus exhibits a decreasing trend, a feature not in agreement with the sharpening which persists after exposure to six spikes also. The structural change which contributes to such a decrease in modulus will be described in the following section.

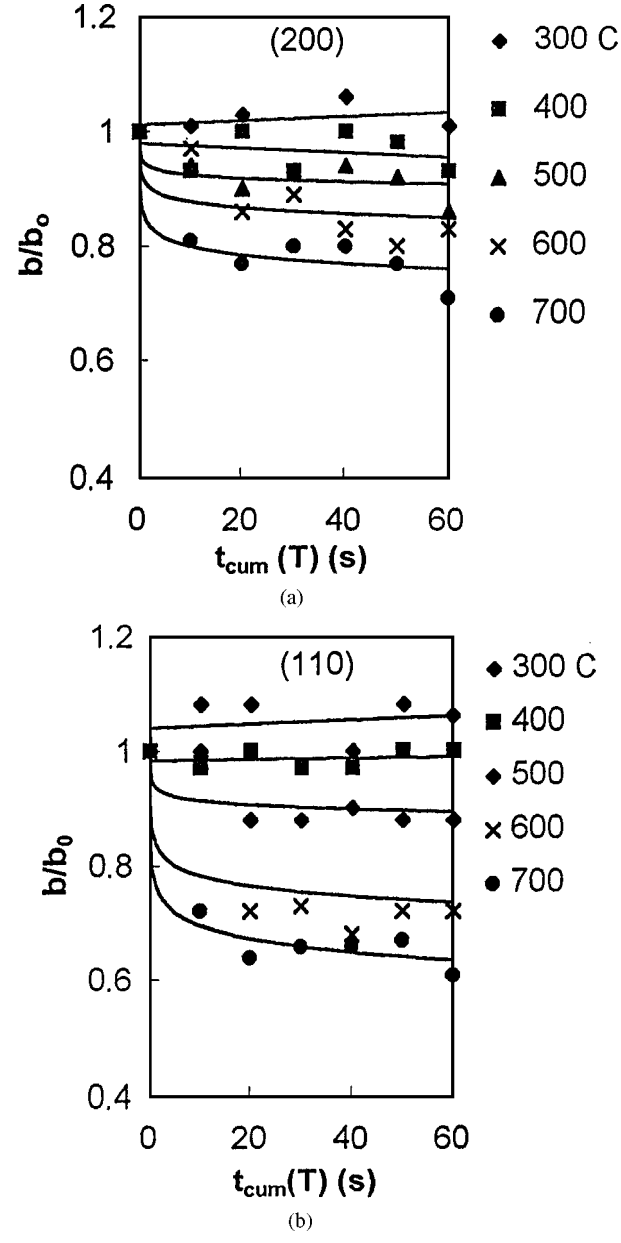


Figure 7 Fractional variation in the half width of (a) (200) and (b) (110) reflections. Here, b_0 and b refer to the values of the half width, prior to and after heat treatment respectively.

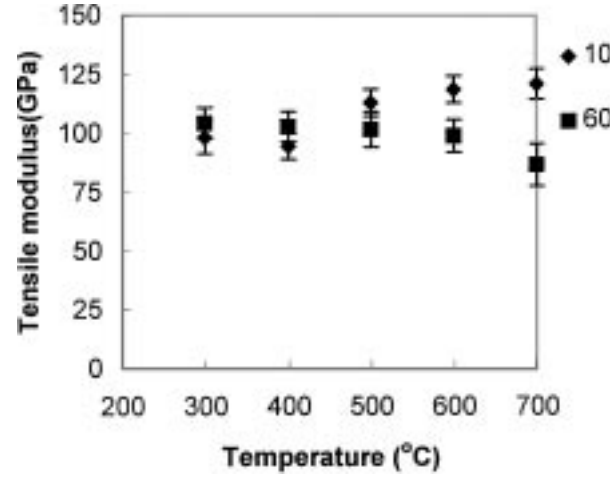


Figure 8 Observed variation in the tensile modulus with e.s.d's marked as error bars.

3.1.3. Azimuthal spread

In Kevlar fibres, the average angle of misalignment of polymer chains about the fibre axis is reported to be ≈14° [9]. Fig. 9 compares the azimuthal spread of reflections from fibres prior to heat treatment with those exposed to spikes at 700°C. The increase in the azimuthal spread is a clear indication of spike - induced molecular misalignment about the fibre axis. Such molecular misalignment can be expected to reduce the initial tensile modulus of the fibre. It appears therefore that the beneficial effects on the tensile modulus, arising out of crystallite growth/reduction in microstrain, described earlier, are annulled at least partially, by the adverse effect of molecular misalignment. The tensile modulus of the spike - exposed fibres thus reflect the combined effect of molecular misalignment and crystallite growth/reduction in microstrain. The reduction in tensile modulus accompanying 60 s of exposure show that at this stage, the effect of molecular misalignment overrides the beneficial effect of crystallite growth/reduction in microstrain.

Examination of Figs 6 and 8 further shows that as in the case of prolonged thermal exposures, the tensile strength is more sensitive to the spikes than the modulus.

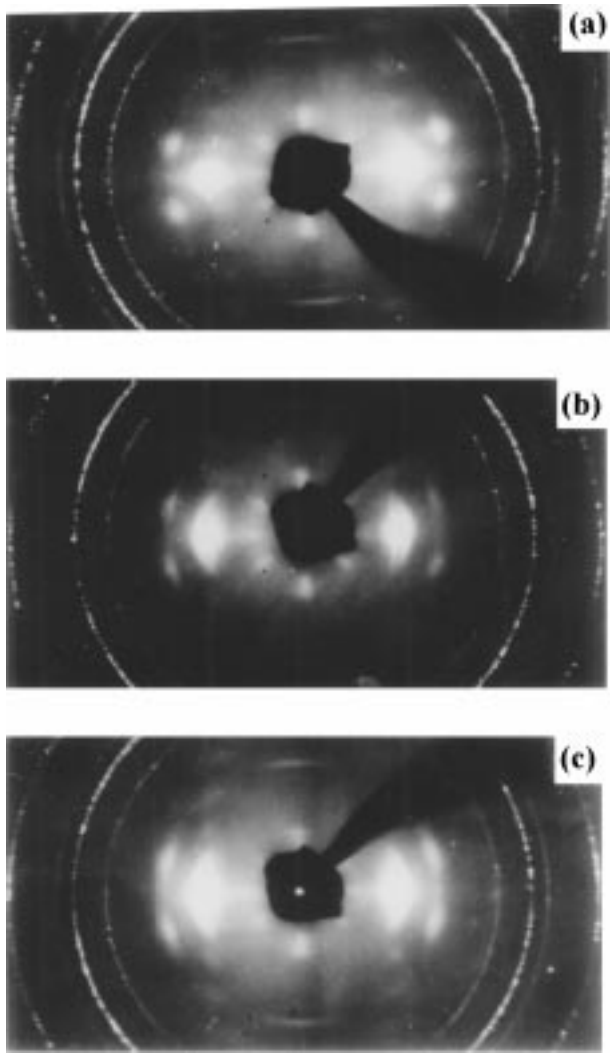


Figure 9 Comparison of the azimuthal spread of reflections (a) prior to exposure to spikes; (b) after exposure to a single spike at 700°C; (c) after exposure to six spikes at 700°C.

3.1.4. Intensities

Examination of the integrated intensities measured from the areas under the diffraction profiles shows that the effects of neither T nor $t_{\mathrm{cum}}(T)$ is significant (Fig. 10). The nearly invariant integrated intensity suggests that the crystallinity of the fibre is not affected by exposure to spikes. It is, however, noticed from Figs 1 and 2 that the relative intensities of the equatorial reflections are influenced by the spikes. Prior to heat treatment, as is expected [6], the reflection (200) is more intense than (110). After exposure to a single spike, the difference between the peak intensities of these two reflections reduces (Fig. 1c). The patterns in Fig. 1d–f show that after exposure to a single spike at 500, 600 and 700°C respectively, the peak intensities are nearly equal. Similar effects are found in the patterns from fibres exposed to six cumulative spikes also (Fig. 2). At 300°C, the initial inequality $I_{(200)} > I_{(110)}$ persists. At 400 and 500°C, $I_{(200)} \approx I_{(110)}$, whereas at 600 and 700°C, $I_{(110)} > I_{(200)}$ i.e. a reversal of the peak intensities occur. These subtle changes in the intensity distribution suggest the occurrence of similar subtle changes in the atomic or molecular arrangement in the crystal structure, the details of which have not been worked out at present.

It must be pointed out that the above mentioned changes in the crystal structural characteristics and also the tensile properties introduced by exposure to spikes are very similar to those accompanying prolonged thermal exposures of the order of few hundreds of hours [1, 2]. This striking similarity throws light in identifying, on the time scale, the initiation of the thermally induced changes. The present data strongly suggest that the thermally induced changes get initiated at the very early stages of thermal exposure, viz., of the order of few seconds and they progress with further continuation of thermal exposures.

3.2. Macro changes

In addition to the above mentioned features introduced at the level of the crystal lattice, exposure to thermal

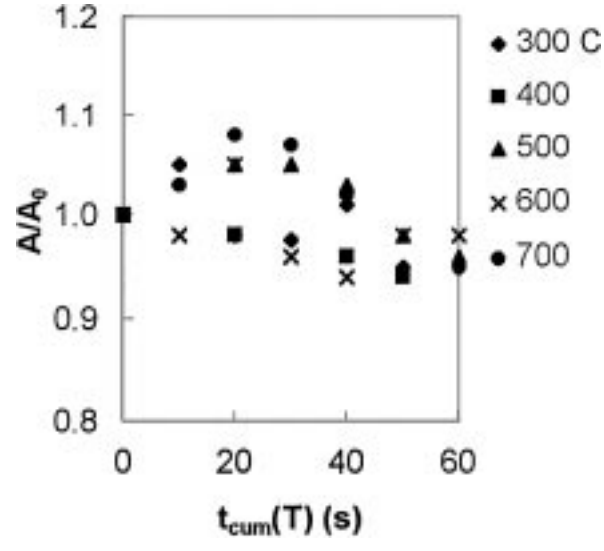


Figure 10 The near invariance of the equatorial diffraction intensity. A_0 and A represent the areas under the diffraction profiles in the 2θ range of 15 to 27°, prior to and after exposure to spikes respectively.

spikes lead to macro changes also. Optical and SEM examination of the spike - exposed fibres showed that the macro features are primarily, the extensive changes introduced on the surface of the fibre. The micrographs in Figs 11–21 present the relevant details. The most striking features are the introduction of (i) longitudinal openings on the surface (ii) localised openings resembling nodes (iii) ribbonlike peel offs (iv) extraneous material on the surface and (v) black discoloration. Details of these observations are presented below. It must be mentioned that as in the case of the crystallographic changes, the macro effects are also significant only at T's $> 400^{\circ}$C. In particular, at both 600 and 700°C, the macro changes are prominent with both 10 and 60 s of exposures. At 500°C, although the macro changes are detectable, they are comparatively less severe than at 600 and 700°C.

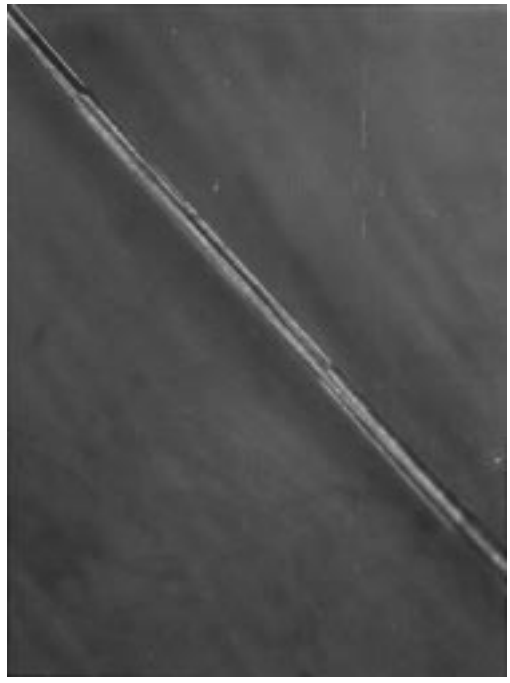


Figure 11 Optical micrograph showing a longitudinal opening, 700°C, 60 s.

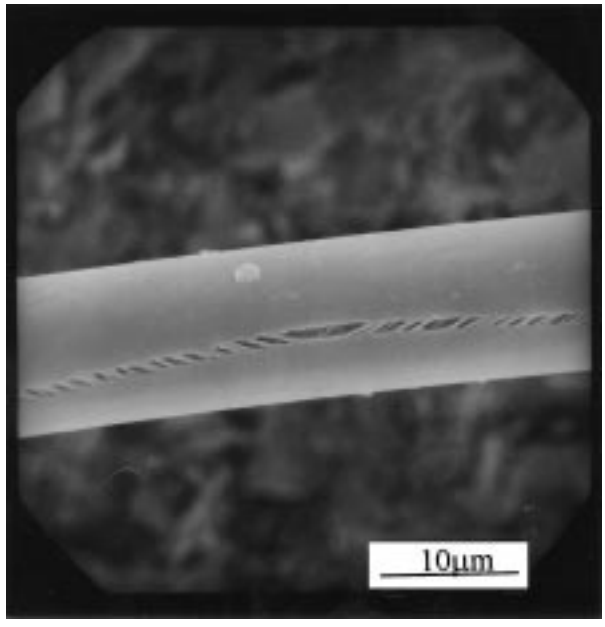


Figure 12 The ellipse-like openings, 700°C, 60 s.

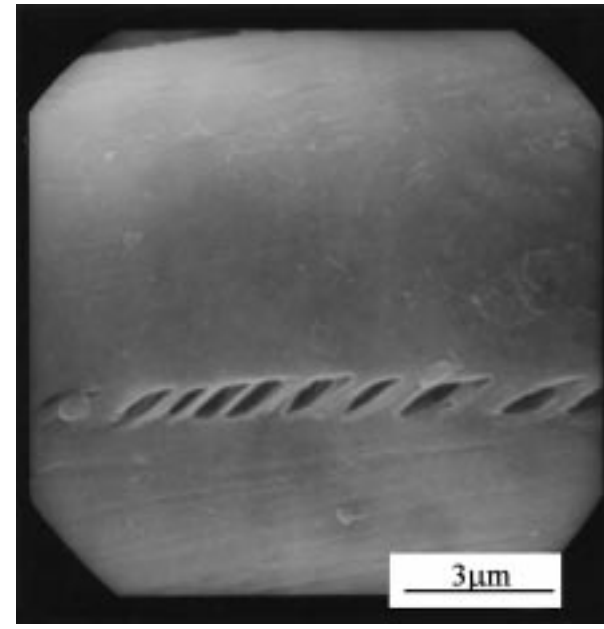


Figure 13 Portions of the surface interconnecting adjacent elliptical openings, 700°C, 60 s.

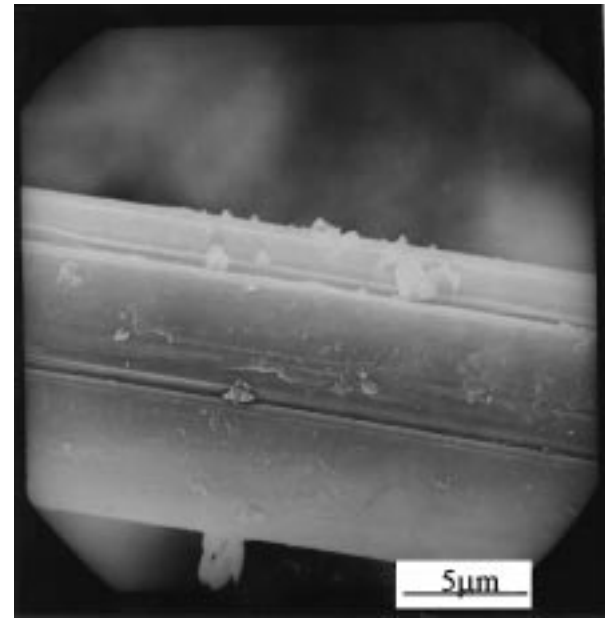


Figure 14 Occurrence of multiple openings in a single fibre, 700°C, 10 s.

The optical micrograph in Fig. 11 shows a typical longitudinal opening introduced at 700°C. Although the line representing the opening appears continuous, it is really not so. The SEmicrograph (Fig. 12) shows that the seemingly continuous opening in Fig. 11 is actually made up of several small, ellipse-like openings. Portions of the fibre surface which interconnect adjacent, elliptical openings can be seen in Figs 12 and 13. These micrographs further show that the longitudinal opening is not quite parallel to the fibre axis. The openings follow a helical path. The pitch of the helix is found to be $\approx$350 μm. It must be mentioned that in the case of Kevlar 149 fibres Dobb and Robson [9] have observed a

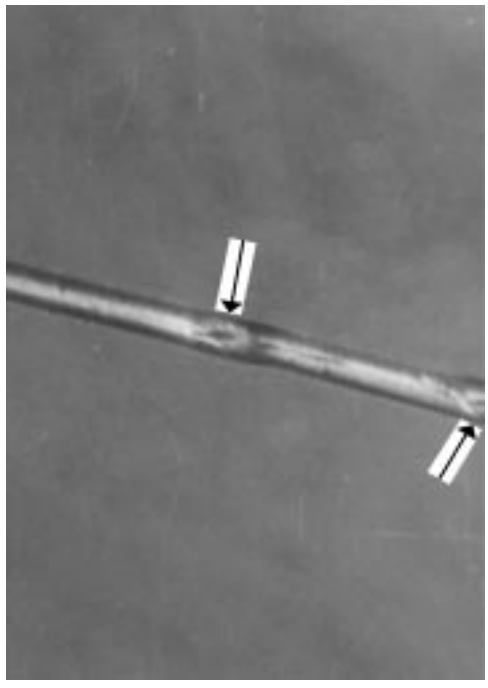


Figure 15 Localised node like openings indicated by arrows, 700°C, 10 s.

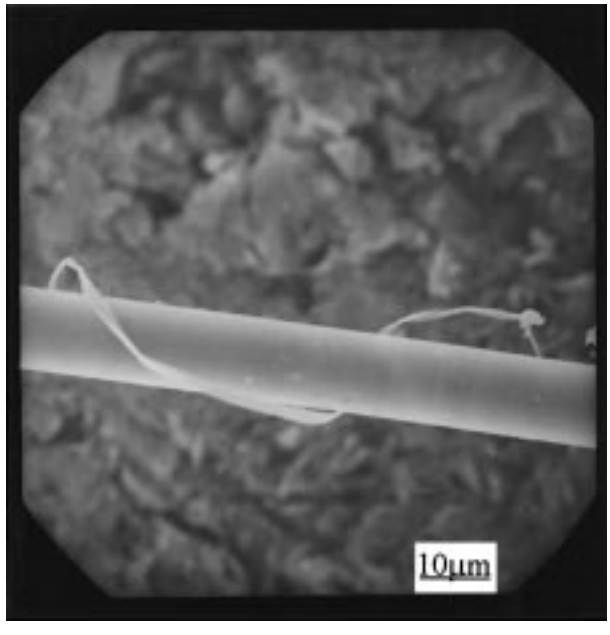


Figure 16 Formation of ribbon-like peel offs, 700°C, 10 s.

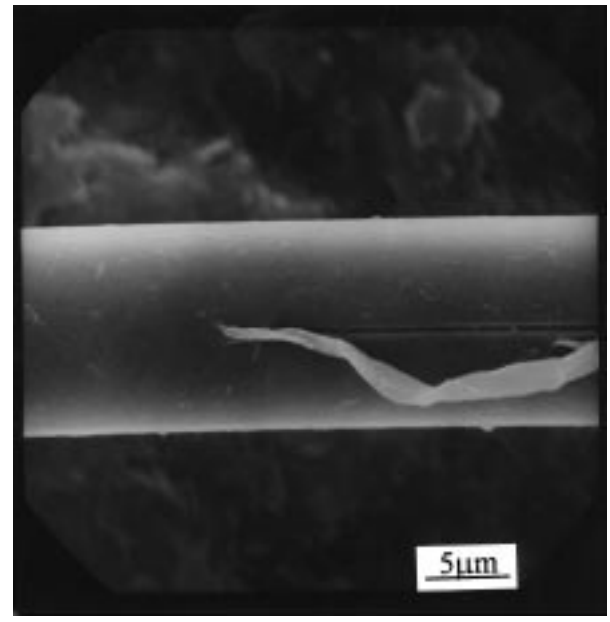


Figure 17 One end of a peel-off is attached to the surface of the fibre, 600°C, 60 s.

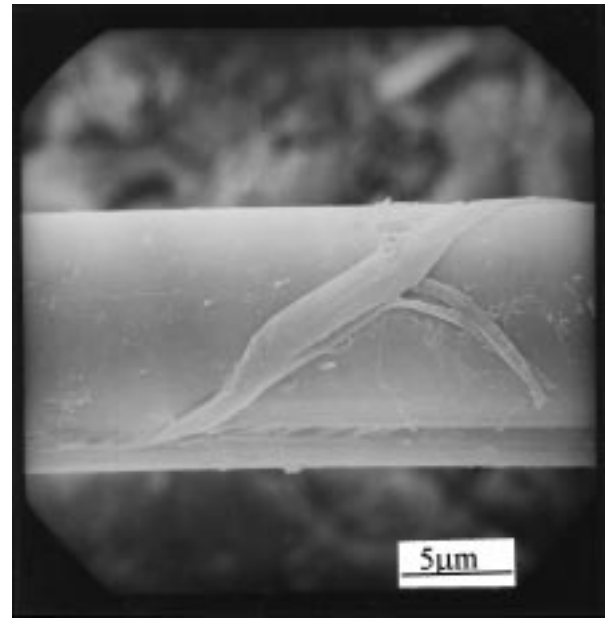


Figure 18 The elliptical openings seen under a peeled-off ribbon, 700°C, 60 s.

sinusoidal distribution of elliptical holes on the surface of the fibre. In some parts, helical distribution has also been observed by them. They have associated the occurrence of these voids with the processing conditions. It must be pointed out that the shape and the orientation of the openings in Figs 12 and 13 are very similar to those observed by Dobb and Robson on Kevlar 149 fibres. This remarkable similarity suggests that Kevlar fibres, whether they are 49 or 149, have an inherent tendency to open up on the surface along a line made up of the elliptical voids. This feature is perhaps related to some processing conditions which are common to both the 49 and the 149 versions of Kevlar. From Fig. 12, it may be seen that the ellipses on the helical path are quite regularly spaced. The relative orientation of the ellipses, however, changes in every half turn of the helical path. Fig. 12 clearly depicts the change in orientation of the major axis of the ellipse by $\sim 90^{\circ}$, after crossing a turn of the helix. These regularities in the characteristics of the ellipses suggest that their occurrence is perhaps closely related to the development of stress concentration along a helical path, during the fabrication of the fibre. With the availability of the external energy, which in this case is thermal, localised regions corresponding to stress concentration appear to open up.

As seen in the micrograph in Fig. 14, often, multiple longitudinal openings are also introduced in the same fibre. In addition to the above mentioned nearly continuous, longitudinal openings, several localised nodelike features have also been observed on the surface of the

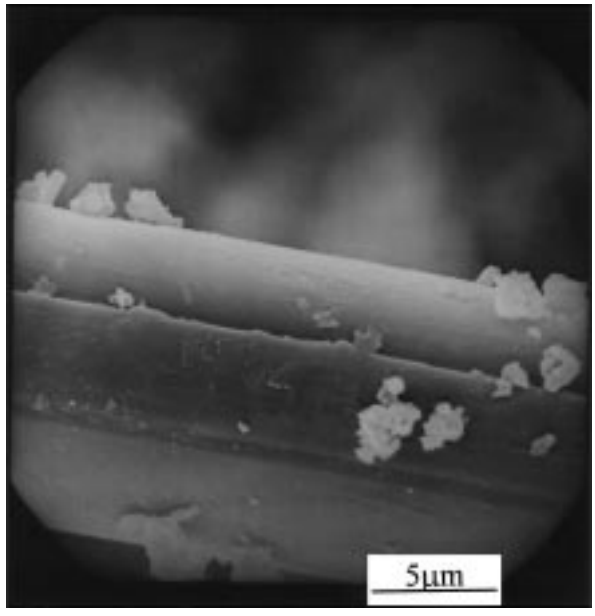
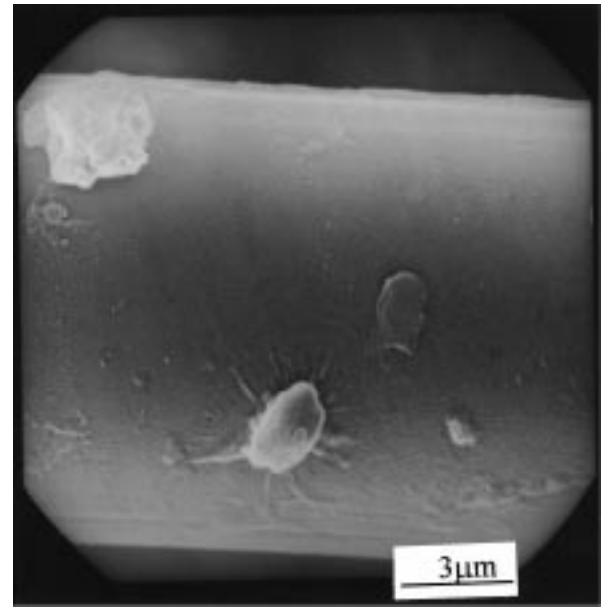
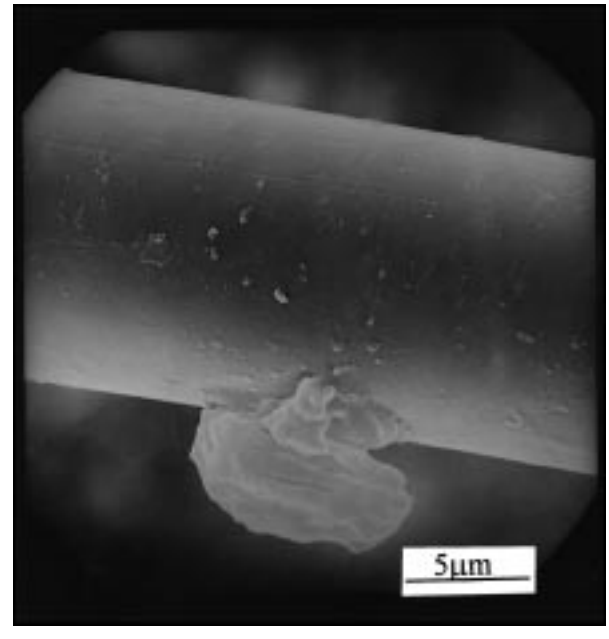


Figure 19 Introduction of extraneous material, close to the longitudinal openings, 700°C, 10 s.



(a)



(b)

Figure 20 (a) and (b) Extraneous material found away from the longitudinal opening, 700°C, 10 s.

spike - exposed fibres. The distribution of two of these has been shown in Fig. 15.

Fig. 16 depicts the formation of ribbonlike peel-offs on the surface. The micrograph in Fig. 17 shows a typical peel-off one end of which is seen attached to the fibre. Often, the peel-offs are found to wind round the fibre (Figs 16 and 18). The width of the peel-offs ranges from 0.6 to 2μm. The micrograph in Fig. 18 also records the interesting feature of the elliptical openings seen under a peeled off ribbon. Kevlar fibres are known to have a skin - core structure [10, 11]. It is not unlikely that the peel-offs introduced by the thermal spikes are connected with the skin part of the fibre.

Another interesting observation concerns the introduction of substantial amount of extraneous material on the surface of fibres exposed to spikes at $T = 700$°C (Fig. 19). Conspicuously, most of these material are concentrated in the vicinity of the longitudinal opening described earlier. Such a proximity strongly suggests the possibility that these extraneous material have evolved from within the fibre. It appears that exposures to temperatures of the order of 700°C for durations as small as 10 s can trigger chemical reactions in the polymer which in turn can lead to the formation and evolution of components from within, via the surface of the fibre. The deposits seen in Fig. 19 may be correlated with such components which have solidified on the surface. The micrographs (Fig. 20) show two pieces of similar extraneous material which are lying away from the longitudinal opening. In both the cases, dark, crater like features were observed right below, suggesting that the material has just come out of these openings. These craters have, unfortunately, been not clearly reproduced in the micrographs. It must be admitted that no attempt was made to identify chemically, the extraneous material. It must also be mentioned that Kalashnik *et al.* [12] have reported the formation of benzonitrile, aniline, terephthalo nitrile etc. when the aramid was exposed to 510°C for about 10 minutes. It is not unlikely that the same or similar compounds are formed by exposure to the spikes. It must be mentioned that commercially available Kevlar fibres include surface impurities in the form of crystalline salts [13, 14]. They are, however, much less in number compared to the spike induced surface material observed in the present set of experiments.

Some of the spike - exposed fibres were also found to be characterised by localised charring/blackening (Fig. 21). Such a blackening is not very surprising because the temperature of the spikes which lead to the blackening is high, viz.,700°C. The optical micrograph (Fig. 21) further shows that blackening is concentrated near the openings described earlier. It is likely that loss of solid material near the openings lead to easy and enhanced, localised charring.

It must be pointed out that the features presented in the micrographs (Figs 11–21) pertain to 600 and 700°C.

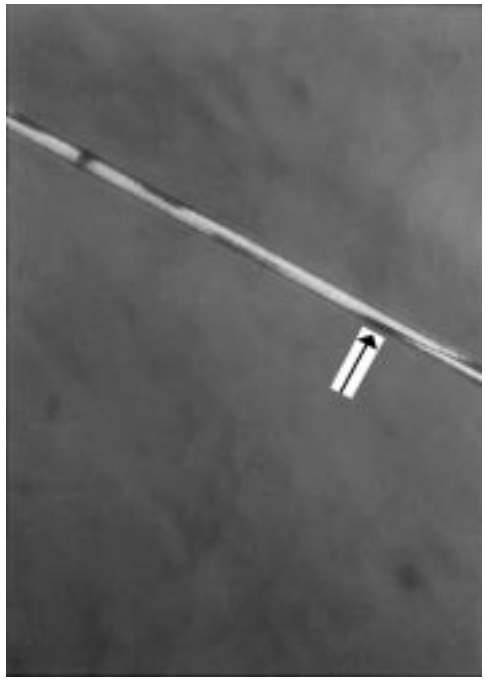


Figure 21 Blackening/charring along the surface openings, 700°C, 60 s.

As mentioned earlier, at 500°C, similar surface damages are found to occur but they are very much less severe. For example, the peel-offs and surface openings are very few in number and there are no deposits. Thus, the severity of the surface damages appears to get enhanced almost dramatically, for spikes at 600 and 700°C. This behaviour is very consistent with the observed changes in the tensile strength (Fig. 6) which also manifests a conspicuous drop at 600 and 700°C.

It is likely that many of the surface features of heat treated fibres are closely associated with chemical reactions which follow the thermal exposures. However, as the present study does not include the chemical aspects, further correlation between the physical and chemical changes cannot be provided with the existing data.

4. Conclusion

Exposure to thermal spikes, accidental or not, could be detrimental to the initial, exceptional characteistics of Kevlar 49 fibres. Spikes corresponding to T's ≥ 400°C cause changes at the level of the crystal lattice. In addition, macro changes such as the introduction of longitudinal openings, peel offs and extraneous material on the surface also get introduced. Changes in the structural characteristics of the spike - exposed fibres conform well with the corresponding changes in the tensile properties. The present data provide evidence that the thermally induced changes in the structural characteristics and the tensile properties get initiated at the very early stages of thermal exposures, viz., exposures of the order of few seconds. As in the case of prolonged thermal exposures of the order of several hundreds of hours, the tensile strength of the fibre is found to be more sensitive to thermal spikes than the modulus. The spike induced effects are controlled by two parameters viz., T and $t_{\text{cum}}(T)$.

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