Effects of annealing on the crystallinity and microparacrystallite size of Kevlar 49 fibres

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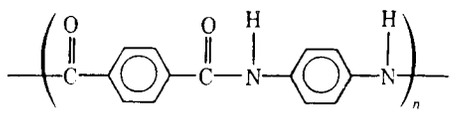
The effects of annealing in the range 20–500°C on the crystallinity and microparacrystallite (mPC) size of Kevlar 49 fibres were studied by X-ray diffraction techniques. The crystallinity (75.5%) remained constant until 350°C; at 400°C it reached its maximum value (81%), and at 500°C it decreased to 51%. The mPC size ($\bar{D}_{110}=4.23$ nm and $\bar{D}_{200}=3.85$ nm) remained constant until 250°C, then reached the maximum values ($\bar{D}_{110}=4.89$ nm and $\bar{D}_{200}=4.22$ nm) at 400°C, after which they decreased. The netplane spacings were not affected until 400°C, but the relative peak intensities of the (200) and (110) reflections increased by 10% at 400°C. The TGA thermogram indicated a weight loss <1% below 350°C, 3.9% at 450°C, 5.5% at 500°C and 20.4% at 657°C. The DTA curve showed a peak melting point at 536.7°C and six transition temperatures. The shrinkage of Kevlar 49 fibres is about 1%; in effect the constant-length annealing and the free-length annealing produced similar results for crystallinity. Thermal ageing in static air at 150°C for periods ranging between 1 and 150 days showed no change in the crystallinity within the first 7 days, but an increase in the lateral mPC sizes occurred.

(Keywords: annealing; crystallinity; Kevlar 49)

INTRODUCTION

Kevlar 49 fibres are aromatic polyamide fibres, produced by Du Pont de Demours and Company from the polymer poly(p-phenylene terephthalamide):



The polymer is spun into continuous multifilament yarn of 1400 denier, containing 1000 filaments, 12 μm in diameter. The chain molecules are linear and rigid. Small-angle X-ray diffraction patterns indicated that Kevlar fibres have no chain folding[1–4]. Wide-angle X-ray diffraction investigations showed that Kevlar fibres have a paracrystalline structure[1,2,5,6], a monoclinic (pseudo orthorhombic) unit cell with dimensions $a=7.87$ Å, $b=5.18$ Å, c (fibre axis)$=12.9$ Å and $\gamma\simeq 90°$ [7] and a Maxwellian size distribution of microparacrystallites (mPC)[5,8]. High-resolution transmission-electron micrographs revealed an ordered lattice[3] and a radially arranged pleated-sheet structure[9]. Scanning electron microscopy revealed a skin-core differentiation[10] and the formation of kinks on the compression side of the fibre[11].

Kevlar fibres are classified as high-strength high-modulus fibres, useful for a wide range of applications such as cables, tyre-cords, sporting goods, circuit boards, fan blades, low-weight panels for aircraft interiors, fire-fighting clothing, body armour and fibre-reinforced composites[12–15].

The present study is concerned with the effects of thermal treatments in the temperature range 20–500°C on the structure in terms of the crystallinity and microparacrystallite size.

EXPERIMENTAL

Annealing

Annealing of Kevlar 49 fibres was performed in nitrogen gas atmosphere in the temperature range 150–500°C. The sample was admitted to the oven at 20°C; the temperature was raised at the rate of 5°C min^{-1}, and the sample was annealed for 15 min at the selected temperature level. Finally the sample was transferred for quenching at room temperature. Two sets of samples were prepared: in one set the length of the yarn was constrained (constant-length annealing), while in the second set the fibre was annealed freely (free-length annealing).

Thermal ageing

A third set of samples was thermally aged at constant length in static air at 150°C for periods ranging between 1 and 150 days.

Wide-angle X-ray diffraction (WAXS)

The WAXS pattern was recorded in a flat-plate X-ray diffraction camera using Ni-filtered Cu K_α X-ray radiation. The equatorial intensity in the range 10–35° 2θ was recorded in a Philips X-ray diffractometer PW1050 operated in the reflection mode. Ni-filtered X-ray radiation was used. The diffractometer incorporated a sample rotator for eliminating the effect of orientation. A step scan at intervals of 0.1° 2θ was made. The azimuthal-intensity scan was achieved in a diffractometer operated in the transmission mode.

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Crystallinity

The equatorial scan of Kevlar 49 fibres contains two overlapping peaks, representing the (110) and (200) reflections in the angular range 10–35° 2θ. After 35° the scan is flat. To determine the crystallinity quantitatively the scan was first corrected for air scatter, polarization, Compton scatter and Lorentz factor, and finally normalized to a convenient area. The corrected scan was then resolved into two peaks and background scatter using the Multipeak Resolution procedure developed by Hindeleh and Johnson and applied to the X-ray investigation of natural and synthetic polymers[2,16–19]. The crystallinity X_{Cr} is considered as a structural parameter defined as the ratio of the total scatter under the resolved peaks to the total scatter under the normalized intensity scan:

$$X_{cr}=\frac{\sum_{t=1}^{B}\int_{2\theta_1}^{2\theta_2} I_t(2\theta)\mathrm{d}(2\theta)}{\int_{2\theta_1}^{2\theta_2} I_{(\mathrm{norm})}(2\theta)\mathrm{d}(2\theta)} \quad (1)$$

where B is the number of resolved peaks.

Microparacrystallite size (mPC)

The resolved peaks were then corrected for instrumental broadening using Stokes' deconvolution method[20]. The X-ray diffraction profile of hexamethylene tetramine crystals, compacted at 85°C, was used to correct for beam width[18]. The integral breadth of the corrected peak-profile was used to calculate the mean mPC size $\bar{D}_{hkl}$ normal to a set of {hkl} netplanes according to Scherrer's equation:

$$\bar{D}_{hkl}\approx\frac{1}{\delta b}=\frac{K\lambda}{\cos\theta\,\delta(2\theta)} \quad (2)$$

where K is a constant ≈ 1, (2θ) is the integral breadth expressed in radian, λ is the wavelength of radiation, and θ is the Bragg angle.

Thermogravimetric analysis (TGA)

A 5 g sample of Kevlar 49 fibres was inserted in a weighing bottle and dried at 105°C in a vacuum oven. TGA in the temperature range 105–675°C was then achieved in a muffle oven in the presence of dry nitrogen gas. The reduction in weight relative to the dry weight of the sample was determined at 50°C intervals.

Differential thermal analysis (DTA)

The DTA curve was recorded in a Netzch Thermal Analyser STA 409/429 in static air in the temperature range 20–770°C. The temperature was increased at the rate of 10°C min^{-1}. The reference material was Alumina, and the mass of the Kevlar 49 sample was 40 mg.

RESULTS

The effects of annealing on the colour and brittleness of Kevlar 49 fibres

The untreated Kevlar 49 filaments are flexible and their colour is light yellow. As a result of annealing, the colour changed to dark yellow at 350°C, light brown at 400°C, brown at 450°C and black at 500°C. The filaments became slightly brittle at 450°C, charred and highly brittle after 500°C.

The degree of change in the colour of organic fibres at high temperatures can be attributed to various thermochemical possibilities, but it would be informative to mention major contributing factors in the case of Kevlar 49. Kevlar 49 multi-filament yarns are spun from PPTA-conc. H_2SO_4 dope by extrusion through spinnerets. Although the yarn is then washed with water and neutralized with NaOH or Na_2CO_3, residuals of H_2SO_4, as well as other compounds such as Na_2SO_4, $NaHSO_4$, $NaHCO_3$ and Na_2CO_3 in quantities ranging from 0.1 to 1.2% by weight of the fibre may remain trapped within the fibre[21]. Traces of H_2SO_4 accelerate hydrolytic and oxidative degradation of Kevlar 49 fibres and cause chain scission, and the fibres will darken at elevated temperatures (>75°C) with associated losses in strength[21–25]. Spectroscopic outgassing analysis of Kevlar 49[21] revealed the presence of some sulphur oxides, sulphuric acid and hydrochloric acid. Emission spectroscopy of the ash from Kevlar 49 fibres revealed the presence of ~200 p.p.m. impurities which included Al, Fe, Si, Cl, Ca and K in concentrations in the 10–100 p.p.m. range. These impurities could be in the form of oxides or sulphates[23]. Spark source mass spectroscopy revealed the presence of Na, Mg, Al, Si, S, Cl in quantities in the range 100–600 p.p.m. and P, K, Ca and Fe in the range 20–50 p.p.m., and about 60 other trace elements with concentrations <5 p.p.m.[21].

X-RAY DIFFRACTION

Wide-angle X-ray diffraction pattern (WAXS)

Figures 1a–d show WAXS patterns of Kevlar 49: (a) untreated, (b) annealed at 400°C, (c) annealed at 450°C and (d) annealed at 500°C. The principal diffraction maxima are the innermost equatorial reflections (110) and (200), and the meridional reflections (002), (004) and (006), which have mean netplane spacings of 0.423 nm, 0.380 nm, 0.645 nm, 0.320 nm and 0.214 nm, respectively. The mean relative peak-intensities are 6.6:10:1:4:2.8, respectively. *Figure 1a*, where the sample was exposed to X-rays for a relatively shorter time, shows the two equatorial reflections (110) and (200) and the most intense meridional reflection (004). The diffraction pattern reveals a high degree of mPC orientation; the azimuthal spread of the (200) reflection at half amplitude is 12.3° and that of the (004) reflection is 14.8°. *Figure 1b*, where the sample was exposed to X-rays for a longer time, shows the two equatorial reflections, the three meridional reflections (002), (004) and (006) and the off-equatorial reflections. The diffraction pattern in *Figure 1c* shows a larger spread of the azimuthal distribution of the intensity in the equatorial reflections, which indicates the onset of disorientation at 450°C. *Figure 1d* indicates that many reflections had faded at 500°C, and the mPCs are more disorientated.

Resolution of the equatorial X-ray diffraction scan

Figure 2 illustrates the equatorial X-ray diffraction scan of Kevlar 49 fibres annealed at 400°C, corrected for air scatter, polarization, Compton scatter and Lorentz effect. The scan is in the angular range 10–35° (2θ) which

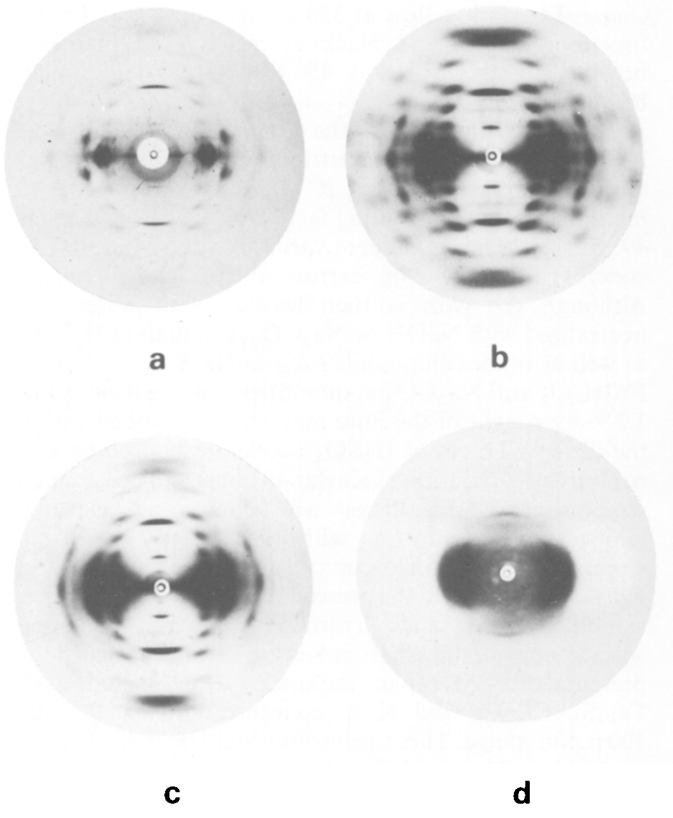

Figure 1 Wide-angle X-ray diffraction patterns of Kevlar 49. (a) Untreated fibres; (b) annealed at 400°C; (c) annealed at 450°C; (d) annealed at 500°C

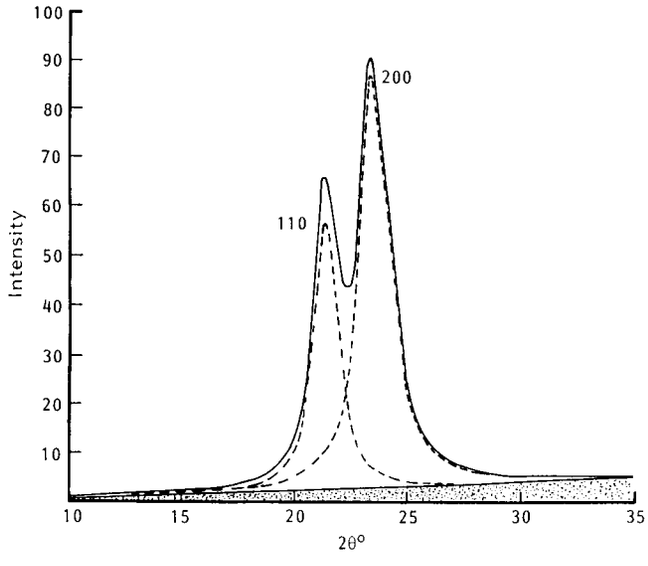

Figure 2 Normalized equatorial X-ray diffraction intensity scans of Kevlar 49. (a) Untreated fibres; (b) fibres annealed at 400°C. Each scan (———) is resolved into two peaks (– – –) and a background scatter (·····)
Crystallinity (a) 75.5%; (b) 81.0%.
mPC size (a) $\bar{D}_{110}=4.23$ nm, $\bar{D}_{200}=3.85$ nm; (b) $\bar{D}_{110}=4.89$ nm, $\bar{D}_{200}=4.27$ nm

contains two overlapping peaks corresponding to the (110) and (200) reflections superimposed on a background scatter. After 35°, the scan is almost flat. The scan has been resolved into two peaks and a background scatter. Compared with the resolved scan of the untreated sample, *Figure 2* indicated that after annealing the fibres at 400°C, the resolved peaks had narrower profile widths, their amplitudes increased, and the background scatter under them decreased. These phenomena meant larger mPC lateral sizes and a higher 'crystallinity', respectively.

The effect of annealing on the lattice dimensions

The resolved scan proved clearly that annealing Kevlar 49 fibres below 450°C did not cause a change in the netplane spacing, but an approximately 10% increase in the relative intensities of I_{200}/I_{110} which is 1.47 for the untreated fibre and 1.55 for the annealed fibre at 400°C (*Figure 2*).

The effect of annealing on the crystallinity

Using equation 1, the crystallinity of the untreated sample was found to be 75.5%. Annealing the sample at constant length in the temperature range 150–350°C did not cause any change in the crystallinity. At 400°C the maximum crystallinity was obtained; it amounted to 81%. At 450°C the crystallinity decreased to 64%, and at 500°C it dropped to 51%. After 500°C the two reflections (110) and (200) overlapped severely (fused); their intensities were low, and it was difficult to resolve them for the determination of crystallinity.

After free-length annealing, there was also no change in the crystallinity in the temperature region 150–350°C. At 400°C, the crystallinity increased slightly to 77%; at 450°C it decreased to 64% and at 500°C it dropped to 49%.

The results of the crystallinity investigation in the two

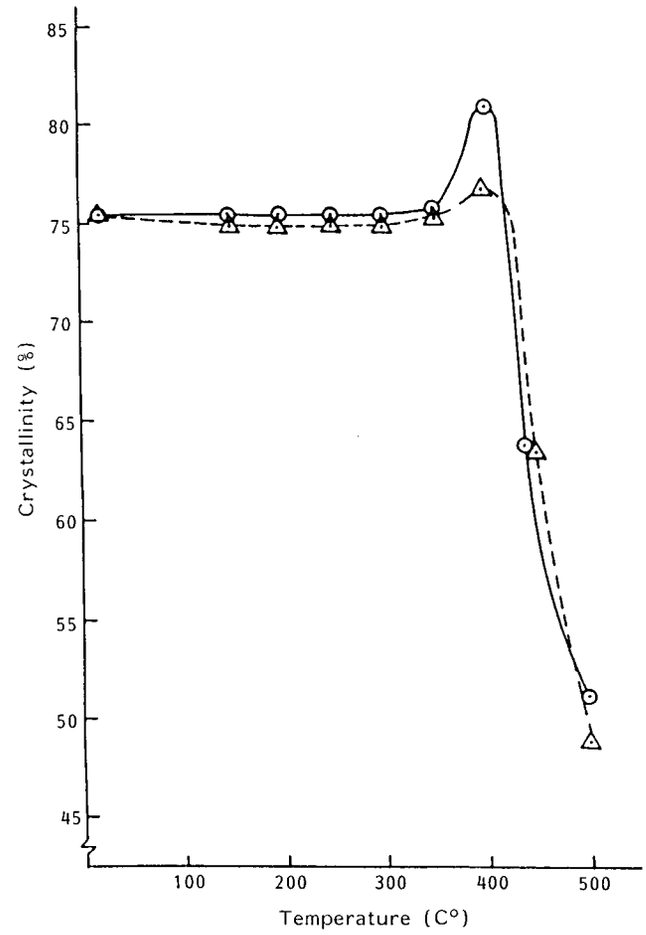

Figure 3 The effect of the annealing temperature on the crystallinity of Kevlar 49 fibres after: constant-length annealing (——⊙——) and free-length annealing (---△---)

modes of annealing are illustrated in *Figure 3*. The similarity in the results, regardless of the mode of annealing, can be interpreted by a subsidiary fibre-shrinkage experiment.

Many types of materials shrink when they are subjected to thermal treatments if the dimensions of the sample were not constrained during the treatment. On the other hand, free-length annealing allows more freedom for the molecular structure to be rearranged and may cause a shrinkage of the sample. In the present experiment the yarn 'denier' of the constrained and unconstrained samples were compared after annealing. It was then found that after free-length annealing the denier was higher by about 1% than after constant-length annealing, which implied a shrinkage of about 1%. It was concluded that, in the absence of a significant shrinkage due to thermal treatment, any mode of annealing will yield close values of crystallinity at any selected temperature level.

The effect of annealing on the microparacrystallite (mPC) size

The results are shown in *Figure 4*. The mean mPC size of the untreated Kevlar 49 fibres had the following values: $\bar{D}_{110}=4.23$ nm and $\bar{D}_{200}=3.85$ nm. In the temperature range 20–250°C there was practically no change in the mPC size of the samples which were annealed at constant length; while in the case of free-length annealing $\bar{D}_{110}$ and $\bar{D}_{200}$ increased gradually and reached the values 5.18 nm and 4.72 nm, respectively. This increase can be interpreted as follows: when the filaments are not constrained, they are given freedom to shrink; and although the shrinkage in Kevlar 49 fibres is only ~1%, during the shrinking and simultaneous annealing processes the mPCs can be more mobile and hence, small mPCs may join together to form larger ones.

As the annealing temperature was increased above 250°C, the mPC size increased, and the optimum values were attained at 400°C: for constant-length annealing $\bar{D}_{110}$ became 4.89 nm and $\bar{D}_{200}$ became 4.27 nm; and for free-length annealing $\bar{D}_{110}$ became 5.30 nm and $\bar{D}_{200}$ became 5.03 nm. After 400°C, the sizes decreased in both directions.

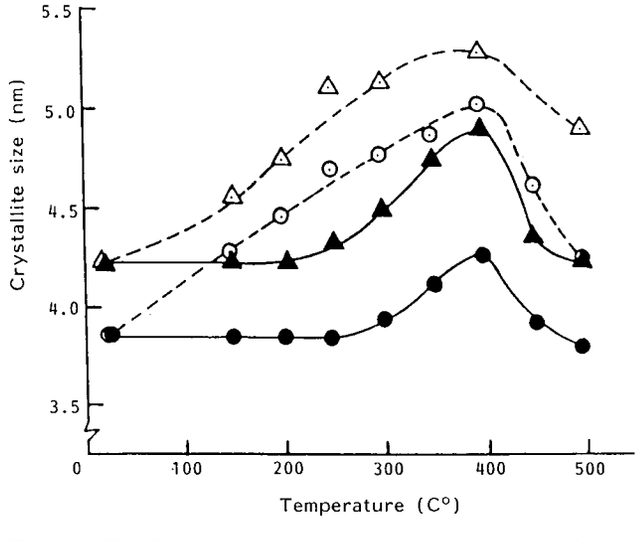

Figure 4 The effects of the annealing temperature and mode of length constraint on the lateral mPC sizes of Kevlar 49 fibres. Constant-length annealing, ▲ $\bar{D}_{110}$, ● $\bar{D}_{200}$; free-length annealing, △ $\bar{D}_{110}$, ⊙ $\bar{D}_{200}$

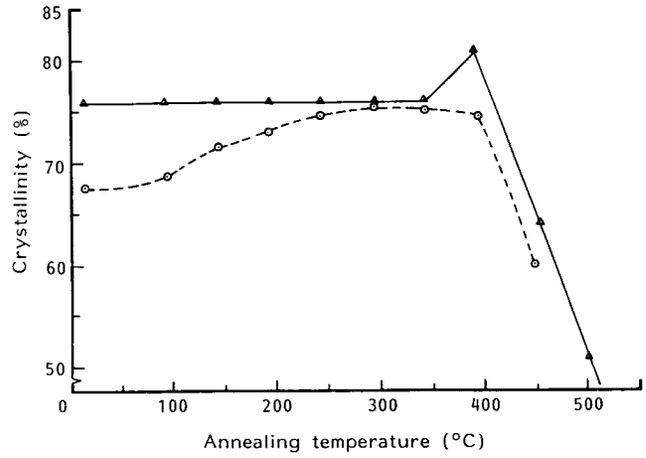

Figure 5 Comparison between the effect of annealing temperature on the crystallinity of Kevlar 49 and Kevlar 29 fibres. ⊙ Kevlar 29; △ Kevlar 49

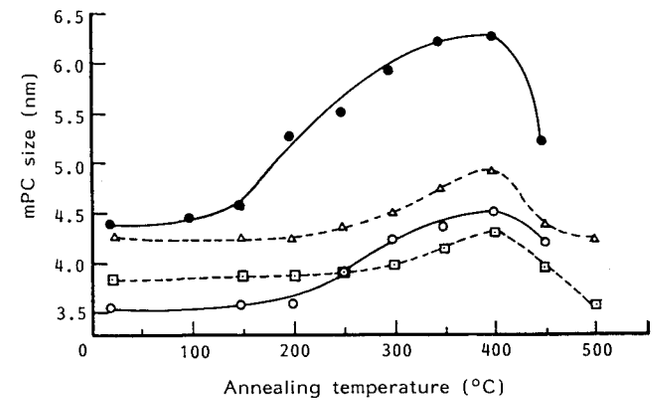

Figure 6 Comparison of the effect of annealing temperature on the lateral mPC sizes of: Kevlar 29 (———) $\bar{D}_{110}$, (●); $\bar{D}_{200}$, (○); Kevlar 49 (- - - -) $\bar{D}_{110}$, (△); $\bar{D}_{200}$, (□)

Comparison between Kevlar 49 and Kevlar 29

A comparison of the effect of annealing at constant length on the crystallinity of Kevlar 49 and Kevlar 29[2] fibres is illustrated in *Figure 5*, which shows clearly that the crystallinity of Kevlar 29 started to increase gradually at 100°C and reached its maximum value at 400°C. In Kevlar 49 the maximum crystallinity was also obtained at 400°C as discussed earlier, but below this temperature no change in the crystallinity over that of the untreated fibre was detected. *Figure 6* compares the mPC lateral sizes of Kevlar 49 and Kevlar 29[2] in the temperature range 20–500°C. In Kevlar 29 the mPC sizes started to increase at 100°C, while in Kevlar 49 the increase started at 250°C. In both types of fibres, the maximum mPC sizes were obtained at 400°C, after which they decreased.

The anomaly in the behaviour of Kevlar 29 and Kevlar 49 fibres at temperatures below 250°C can be understood with reference to their fabrication procedures. Chemically the two Kevlars are the same, poly(p-phenylene terephthalamide). They are also spun from the PPTA-H_2SO_4 dope, neutralized and washed similarly. Both types of fibres are dried slowly in the temperature range 65–130°C over a period of days. But to obtain better orientation and higher modulus, Kevlar 49 fibres are given an additional step while they are slightly wet, during which the fibres are heated at 250°C for 1 to 6 s

under a tension of 6g denier^{-1} to an elongation of 0.5%[25]. Other references mention a temperature of 550°C[23]. However, if we considered a threshold heating temperature of 250°C, then one would expect that annealing, as described in this paper, should have no appreciable effect in changing the crystalline parameters (crystallinity and mPC size) at temperatures below 250°C.

The effect of thermal ageing on the crystallinity and mPC size

The crystallinity of Kevlar 49 fibres (75.5%) was practically unaffected by thermal ageing for a period of 7 days at 150°C in static air. Between 7 and 44 days the crystallinity decreased gradually until it reached a value of 62.3%. Between 44 and 150 days there was no further change in the crystallinity as shown in *Figure 7a*.

Thermal ageing helped the lateral mPC sizes to grow; within 32 days, $\bar{D}_{110}$ increased from 4.23 nm to 5.2 nm, and $\bar{D}_{200}$ increased from 3.85 nm to 4.27 nm. After 32 days the sizes started to decrease gradually; after 150 days

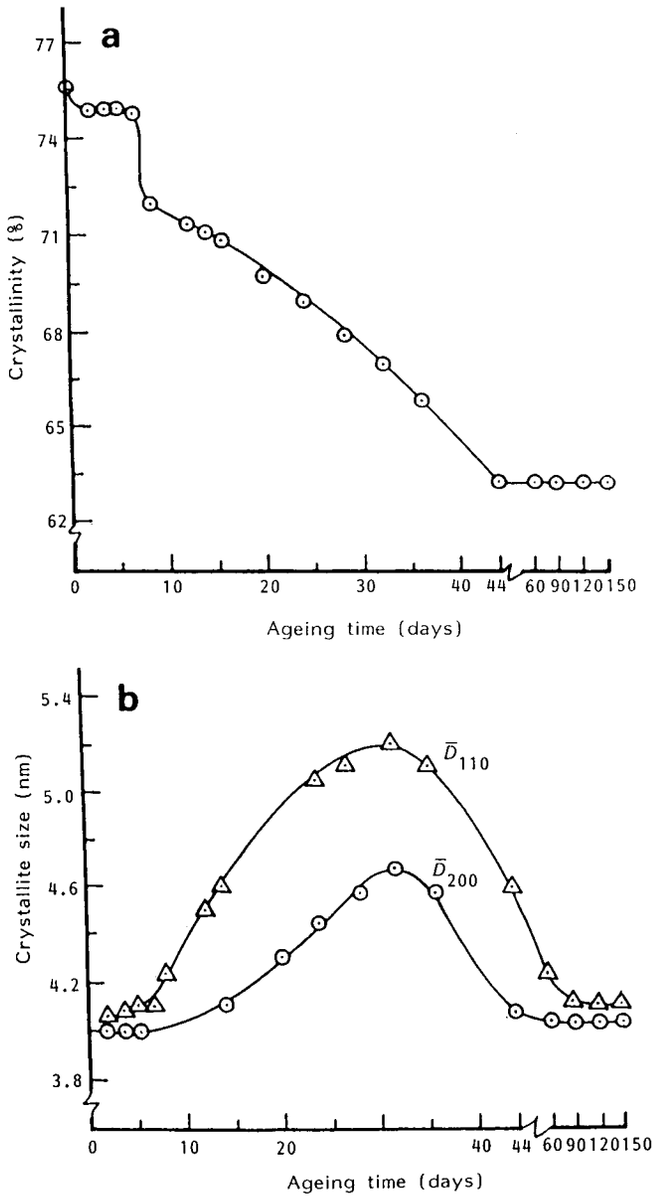

Figure 7 The effect of thermal-ageing time at 150°C in static air on (a) the crystallinity and (b) the lateral mPC sizes of Kevlar 49 fibres

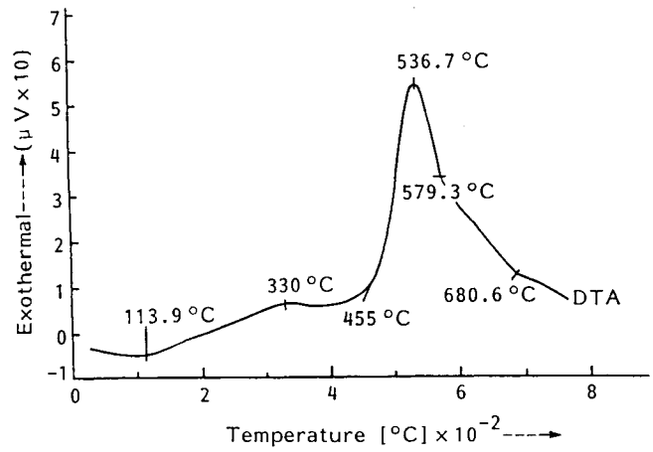

Figure 8 The DTA curve of Kevlar 49 fibres

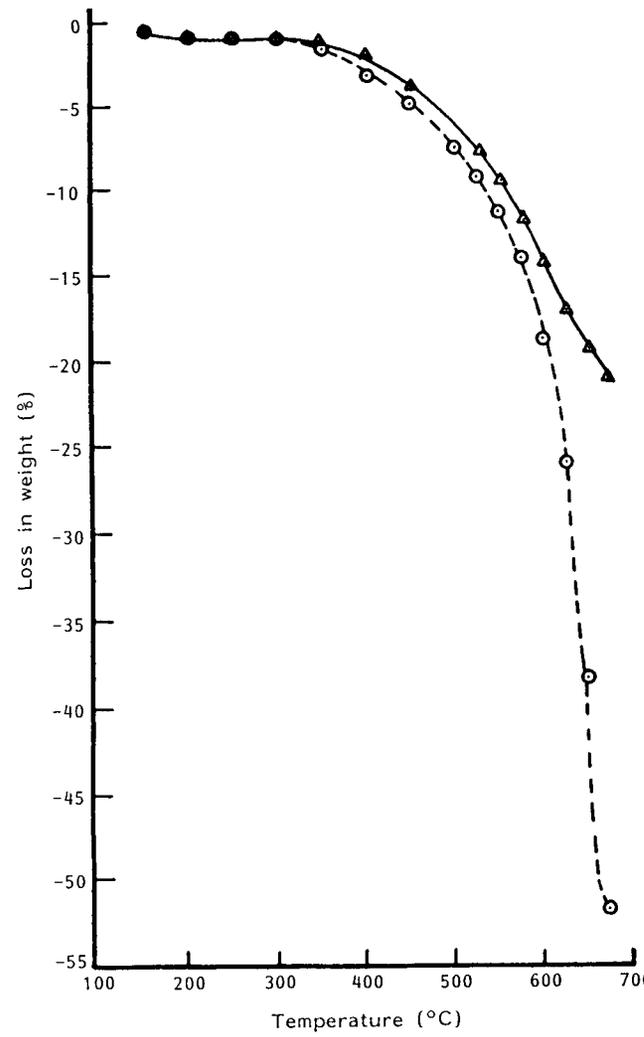

Figure 9 The TGA curve of Kevlar 29 and Kevlar 49 fibres. Kevlar 29 (⊙---⊙); Kevlar 49 (▲——▲)

$\bar{D}_{110}$ reached 4.12 nm and $\bar{D}_{200}$ reached 4.04 nm. The results are illustrated in *Figure 7b*.

The implications of why crystallinity decreased while there had been an increase in the lateral mPC sizes during the ageing time 7–32 days has been explained by Hindeleh[26] through further experiments on the mPC size and lattice distortion parameter in the direction of the fibre axis: the lattice distortion parameter increased

during this ageing period and the mPC size decreased in the direction of the fibre axis due, probably, to chain scission caused by residual H_2SO_4 in the fibres as discussed earlier in this paper. Such factors may cause a reduction in the crystallinity. Moreover, a reduction in the mechanical properties of these samples was detected[27].

The decrease in the crystallinity and lateral mPC sizes of the Kevlar fibres after annealing at temperatures above 400°C can be well related to the results of two subsidiary investigations of the DTA and TGA properties of Kevlar 49 fibres. *Figure 8* shows the DTA scan of Kevlar 49 in the temperature range 20–770°C containing several transition temperatures and a peak profile extending mainly between the two transition temperatures 455 and 680°C, with a peak temperature 537.6°C, which is assumed to indicate the peak melting point of Kevlar 49. A close value for the melting point, 540°C, obtained from a d.s.c. study, was reported by Morgan *et al.*[28]. The melting point of polymers is often reported as a single temperature at which a transition from the solid phase to the liquid phase is complete. Kevlar fibres do not exhibit a real melting behaviour, but charring and brittleness of the fibres were observed at temperatures above 450°C. Regarding the WAXS diffraction patterns (*Figure 1*), the DTA transition temperature 455°C represents a transition temperature at which disorientation was observed (*Figure 1c*); and the peak melting point region in the DTA curve corresponds to the diffraction pattern (*Figure 1d*) where the equatorial reflections started to become diffuse. If one considers that smaller crystals melt earlier than larger crystals in polymers[29], and that Kevlar fibres have a wide statistical size distribution[5], and that the DTA scan has also a wide temperature-distribution, one would essentially contemplate the large spread of the melting and/or degradation of Kevlar fibres over a wide range of temperatures. This is certainly compatible with the continuous decrease of the crystallinity and the mean mPC size after 400°C.

The TGA investigation (*Figure 9*) showed that, for Kevlar 49 fibres, the weight loss was $<1\%$ at temperatures below 350°C, 3.9% at 450°C and 5.5% at 500°C, after which the rate of weight-loss was rapid, and at 675°C the loss amounted to 20.4%. For Kevlar 29 fibres, the weight loss was also $<1\%$ at temperatures below 350°C, 4.8% at 450°C and 7.0% at 500°C, after which the loss was more rapid than in the Kevlar 49 sample, and at 675°C the loss amounted to 51%. In this respect, investigations were made by Brown and Power[30] by pyrolysis/gas chromatography/mass spectrometry of the commercial Kevlar 49 fibres. They found that between 300 and 500°C, CO_2 and H_2O were evolved. Between 500 and 540°C the pyrolysis products included 1,4 phenylene diamine, benzonitrile, aniline, benzanilide and N-(4-amino-phenyle benzamide), which indicated that the degradation reactions were initiated by the homolytic cleavages of the CO–NH and aromatic –NH bonds with subsequent decarboxylation of carbonyl end groups; at higher temperatures many other pyrolysis by-products were detected.

The degradations occurring at high temperature can disturb the three-dimensional order of the structure of Kevlar fibres and increase the lattice distortions. Distortions cause an increase in the background X-ray scatter and hence reduce the integral scatter under the resolved peaks, which, according to equation 1, will show reduced crystallinity values.

CONCLUSIONS

Kevlar 49 fibres are highly crystalline and the mPCs are well orientated. The crystallinity did not change after annealing at temperatures below 350°C. The maximum crystallinity occurred at 400°C. The mean mPC size remained unaffected by annealing until 250°C, then increased and reached the maximum value at 400°C. After 400°C, the crystallinity and mPC sizes decreased due to the onset of melting of smaller mPCs and thermochemical degradation effects.

The crystallinity of the samples which were aged for 7 days in static air at 150°C did not change. A decrease from 74.8% to 62.3% occurred in the period between 7 and 44 days, after which no further change occurred. Thermal ageing helped the mPC size to grow, but after 44 days of ageing the sizes decreased slightly.

The resolution of the overlapping (110) and (200) reflections showed that the annealing of Kevlar 49 fibres up to 400°C did not cause a change in the netplane spacing, but a small increase from 1.47 to 1.55 in the relative intensities of the (200) and (110) reflections was detected at 400°C.

The DTA scan showed a peak melting point at 536.7°C and six transition temperatures. The TGA thermogram showed a weight reduction $\sim 1\%$ at temperatures below 350°C, 3.9% at 450°C and 5.5% at 500°C. The reduction was more remarkable after 500°C and reached 20.4% at 675°C due to the melting of mPCs and degradation. The DTA and TGA results after 400°C correlate well with the changes in the WAXS patterns and the results of the crystallinity.

In comparison with Kevlar 29[2], the present untreated sample of Kevlar 49 fibres has a higher crystallinity.

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