

Moisture uptake by Kevlar fibres

M. SHUBHA*, H. V. PARIMALA, K. VIJAYAN†

Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

Kevlar fibres are known to have a propensity for moisture [1]. It is an accepted view that, in polymers, interactions with moisture are often confined to the less-crystalline or the amorphous fractions. In the case of Kevlar fibres, to date there has been no experimental evidence for the presence of an amorphous fraction. In the absence of an amorphous component the prominent structural features that can favour moisture uptake by Kevlar fibres are as follows. First, the inherent polarity of the amide group in the molecule of *p*-phenylene terephthalamide (PTA), of which Kevlar fibres are made [2]. X-ray data have shown [3] that the water molecules from moisture uptake do not enter the unit cell of the crystal lattice. Hence, the amide-water molecular interactions are likely to be confined to the polymer chains on the surface. Secondly, the presence of microvoids on the surface [4-6]. It must be mentioned that the existing data on the possible filling up of the microvoids by moisture are contradictory. Whereas the fraction of microvoids in Kevlar 149 fibres is substantially higher than in Kevlar 49 fibres [7], the moisture content in the former is reported to be less than that in the latter [8]. Thirdly, the presence of hydrophilic sodium salts [9]. The above-mentioned factors connected with moisture uptake are, essentially, characteristics of the sample. In this letter we report the details of observations concerning the effect of the relative humidity (RH) of ambient atmosphere on moisture uptake by Kevlar 49 fibres. Data from the unoriented polymer poly-PTA (PPTA) has also been included.

The samples used in this study were approximately 1 g in weight. The effect of RH was analysed using the chamber of an electronic balance as the humidity chamber. The RH value within the chamber was monitored using appropriate chemicals, namely calcium chloride for the range 3-50%, and saturated solutions of sodium nitrate, sodium chloride and potassium bromide for 60, 70 and 80%, respectively. Small glass containers with the required chemicals were placed within the chamber, along with a hygrometer and a thermometer. The RH within the chamber stabilized to the required value within 1-1.5 h and thereafter remained stable within $\pm 1\%$, over a period of 1 h. Within a span of 24 h the fluctuations increased to $\pm 2\%$. The temperature within the chamber was $26 \pm 2^\circ\text{C}$.

The samples were initially dried for about 20 h in an electric oven maintained at 150°C . The dry

specimens were cooled for 1 min in a desiccator containing silica gel, after which they were quickly transferred to the humidity chamber and the changes in the sample weight were followed. In this analysis the observed changes in the weight of the initially dry sample were attributed entirely to the entry of moisture from the ambient atmosphere into the sample. The balance used to identify the change in weight of the sample was capable of reading down to 0.0001 g. In the early stages, when the change in weight was rapid, readings were taken at intervals of 30 s. With the progressive reduction in the rate of change of weight, the time interval was increased appropriately. For each sample the changes in weight induced during approximately the first 6 h exposure to a chosen atmosphere were followed closely. After 6 h the moisture content, w_{22} , corresponding to 22 h exposure was estimated. The saturation moisture content, w_s , corresponding to 1 week exposure to a chosen RH value was also determined using a bell-jar as the humidity chamber. It must be mentioned that each value reported in this letter represents an average obtained from at least three experiments.

The sample referred to as "unoriented polymer PPTA" represents the polymer before spinning into fibres. Qualitative characterization of both Kevlar fibres and the unoriented PPTA sample was done by recording the X-ray diffraction patterns in the 2θ range $15-27^\circ$ using CuK_α radiation and a Philips powder diffractometer with a graphite monochromator in the diffracted beam. The samples were rotated at the rate of $0.25^\circ\text{min}^{-1}$ and the chart speed was 10 mm min^{-1} . The density of the unoriented polymer was estimated by flotation in a mixture of carbon tetrachloride and absolute ethyl alcohol.

Fig. 1 compares the diffraction profiles of the equatorial reflections (1 1 0) and (2 0 0) recorded from Kevlar fibres and the unoriented polymer. The marked reduction in the overall intensity of the diffraction pattern from the latter suggests a reduction in its crystallinity. Further direct evidence for the reduction in crystallinity of the unoriented polymer is obtained from its density value of 1.33 g cm^{-3} , which is significantly lower than the value of 1.48 g cm^{-3} reported for PPTA fibres [10]. Thus, the polymer used was not only unoriented, but also less crystalline than the fibre. The conspicuously broadened profiles from the unoriented sample (Fig. 1) further suggest that the crystallites in this sample were smaller than those in Kevlar fibres and that they were also likely to include some micro-strain.

In Fig. 2 the percentage change in the weight of

* Present address: Graphite India Ltd, Bangalore, India.

† Author to whom all correspondence should be addressed.

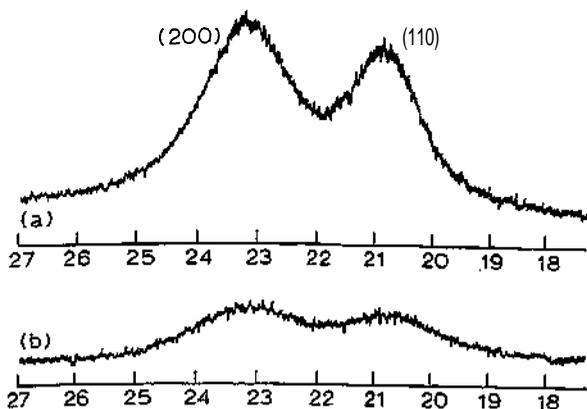


Figure 1 Comparison of the X-ray diffraction profiles of the equatorial reflections (110) and (200) from (a) Kevlar 49 fibres and (b) the unoriented polymer PPTA.

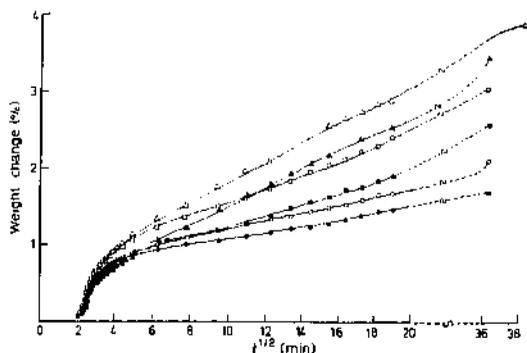


Figure 2 Percentage change in the weight of initially dry Kevlar 49 fibres versus $t^{1/2}$. RH: (A) 80%, (A) 70%, (\square) 60%, (1) 50%, (O) 30% and (\bullet) 20%.

Kevlar fibres, calculated as $(\Delta w/w_d) \times 100$ versus $t^{1/2}$ is plotted. Here

$$\Delta w = w_m(t) - w_d \quad (1)$$

where w_d is the weight of the dry sample and $w_m(t)$ is the weight after exposure to a chosen RH value for t min. Fig. 2 shows that for the range of RH values chosen in this study the increase in weight was rapid and non-linear up to about 40 min exposure, beyond which the gain in weight was progressively slowed until eventual stabilization representing saturation occurred. Fig. 2 also shows that the initial rapid uptake of moisture is not significantly dependent on the RH value. This stage represents the presence of a sharp gradient in the RH value, between the atmosphere in the chamber and the sample. It appears that, irrespective of the RH value, the sites that permit entry of moisture into the sample tend to become filled up rapidly. After the initial gain of approximately 1 wt %, the process of moisture uptake by the less-dry fibres exhibited a detectable dependence on the RH value of the atmosphere. Fig. 3 shows that the moisture content w_{22} estimated by using the value of w_m corresponding to $t = 22$ h in Equation 1 varies linearly with the RH value. In striking contrast with the w_{22} values, the w_s value did not exhibit any significant dependence on the RH value. Within the range 20-80% RH the saturation moisture content varied from 4.3 to 4.9 wt %. These observations suggest that the saturation moisture content may be a constant for

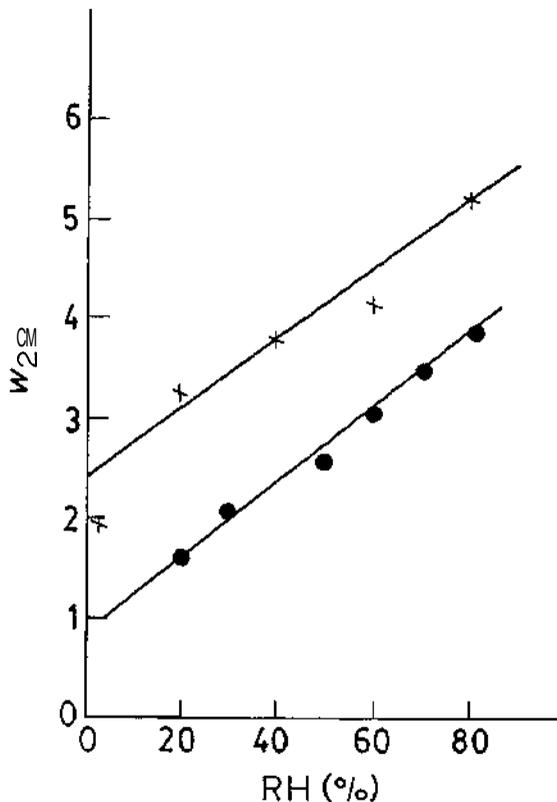


Figure 3 Linear dependence of w_{22} values on RH for (\bullet) Kevlar 49 fibres and (\times) the unoriented polymer PPTA.

the sample and that the RH value of the atmosphere affects only the process of moisture uptake, not the saturation moisture content.

Quantitative evidence for the effect of sample characteristics on moisture uptake was obtained from the data collected from the unoriented PPTA samples. Fig. 4 shows the percentage increase in weight of the initially dry samples versus $t^{1/2}$. The similarities between the curves in Figs 2 and 4, and the linear dependence of the w_{22} values characterizing the unoriented samples on the RH of the atmosphere shown in curve b of Fig. 3, suggest that, despite the differences in the degree of crystallinity and the molecular orientation, the overall nature of the process of moisture uptake is very similar both in Kevlar fibres and in the unoriented polymer. However, the distinct difference that was observed between the two sets of samples pertains to the amount of moisture uptake. It was found that at any time, for the chosen values of RH, the unoriented polymer contained more moisture than the Kevlar fibres. The saturation moisture content of approximately 9 wt % characterizing the unoriented polymer was also nearly twice that in the fibre. The observed enhancement in the moisture content is admittedly not commensurate with the reduction in the crystallinity (about 10%) of the unoriented sample. Hence, the increase in the propensity for moisture exhibited by the unoriented polymer cannot be attributed entirely to the presence of less-crystalline regions. It appears that lack of molecular alignment and diminution in the crystallite size are also likely to be factors that contribute to the enhanced moisture content.

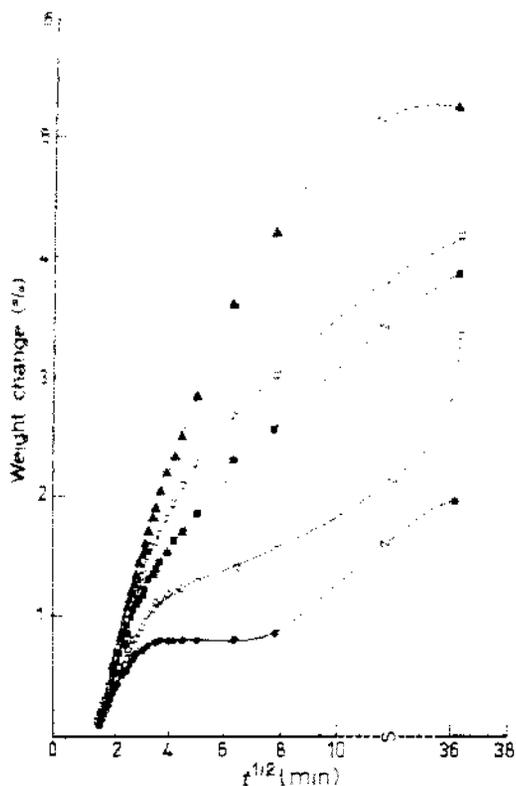


Figure 4 Percentage in the weight of initially dry unoriented polymer PPTA versus $t^{1/2}$. (▲) 80%, (□) 60%, (■) 40%, (○) 20% and (●) 3%.

It has been found that when Kevlar fibres are exposed to thermal environments, structural changes occur such as misalignment of polymer chains about the fibre axis [3, 11] and reduction in interlayer interactions [3]. These structural changes have been satisfactorily correlated with the thermally induced reduction in the tensile strength of the fibre [12]. Combining these factors with the present data on moisture uptake, an interesting correlation between thermal exposure and moisture uptake emerges, i.e. when Kevlar fibres suffer thermal exposures that induce appropriate structural changes, not only does the tensile strength deteriorate, the moisture content is also likely to become enhanced. It is believed that such an effect can have serious consequences, especially in composite structures which include Kevlar fibres. With the enhanced moisture content in thermally exposed components, the weight percentage of the fibre in the composite, and consequently its properties and performance, are likely to change. Adequate caution should be exercised under such circumstances.

It must be mentioned that earlier we analysed [13] the effect of RH on moisture uptake with a different batch of Kevlar fibres, and found that the initial increase in weight was followed by a conspicuous reduction which persisted until about 60 min exposure. Although the data presented in this letter appear to be physically meaningful, an acceptable explanation for the reduction in weight observed earlier has not yet been obtained.

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References

1. R. G. GARZA, C. O. PRUNEDA and R. J. MORGAN, Unpublished work.
2. B. G. CARTER and V. T. J. SCHENK, in "Structure and properties of oriented polymers", edited by I. M. Ward (Elsevier Applied Science, London, 1975) Ch. 13.
3. M. SHUBHA, MPhil dissertation, Mangalore University (1989).
4. K. TASHIRO, M. KOBAYASHI and H. TADOKORO, *Macromolecules* **10** (1977) 413.
5. M. G. DOBB, D. J. JOHNSON, A. MAJEED and B. P. SAVILLE, *Polymer* **20** (1979) 1284.
6. J. S. LEE, J. S. FELLERS, M. Y. TANG and J. S. LIN, *J. Compos. Mater.* **19** (1985) 114.
7. M. G. DOBB and R. M. ROBSON, *J. Mater. Sci.* **25** (1990) 459.
8. S. L. KWOLEK, W. MEMEGER and J. E. VAN TRUMP, in "Polymers for advanced technologies", edited by M. Lewin (VCH, USA, 1988) p. 443.
9. K. VIJAYAN, *Current Sci.* **56** (1987) 1055.
10. M. G. NORTHOLT and J. J. VAN AARTSEN, *Eur. Polym. J.* **10** (1974) 799.
11. A. M. HINDELEH and SH. M. ABDO, *Polymer* **30** (1989) 218.
12. H. V. PARIMALA, MPhil dissertation, Mangalore University (1991).
13. K. VIJAYAN, H. V. PARIMALA and M. SHUBHA, in "Polymer Science - contemporary themes", edited by S. Sivaraman, Vol. 2 (Tata-McGraw-Hill, New Delhi, 1981) p. 666.

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