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Investigations on the Problem of Moisture Absorption by Kevlar Fibres

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Abstract

Kevlar fibres are known to have affinity for moisture. We have investigated (i) the effect of relative humidity (RH) of ambient atmosphere and (ii) the effect of crystallinity of fibres on the process of moisture uptake. For RH values ranging from 3 to 80% variation of moisture content of initially dry fibres with time has been measured. It is found that saturation moisture content varies with RH value. Specimens in which crystallinity has been reduced by appropriate treatment exhibit a marked increase in moisture content. Experiments on the effect of soaking the fibres in water at 26°C and 98°C have also been carried out. The site of moisture absorption has been studied using X-ray of dry Kevlar 49 fibres and those with different levels of moisture content. The results suggest that water molecules do not enter the unit cell.

Introduction

It is well known that Kevlar fibres have great affinity for moisture. Moisture absorption by Kevlar has many consequences. If the water molecule directly interacts with the fibre crystal lattice, changes in the moelcular and crystal structure can occur which in turn can lead to changes in fibre properties. When composite structures containing Kevlar fibres are used at low temperatures, the volume expansion of absorbed water molecules can lead to cracking of the composite. In case of polymer blends, the additional weight due to moisture absorbed by Kevlar fibres can alter the proportion of fibre in the blend. For successful applications of the fibre a detailed knowledge of the effect of moisture on the fibres is essential. Literature information on moisture absorption by Kevlar is quite contradictory. Fukuda et al (1) using CP/MAS ^{13}C NMR spectra and ^{13}C spin lattice relaxation suggested that water molecules do not interact with the amide groups. In contrast, Kim et al (2) ascribed the decrease in the intensity of the N-H stretching vibration in IR to the interaction of water molecules with the amide band. Penn and Larsen (3) related moisture absorption with the sodium salts in the fibre. The cylindrical voids on the surface of the fibre have also been associated with moisture absorption (4).

The present work was undertaken to study the effect of atmospheric humidity on moisture absorption by Kevlar. The effect of moisture on fibre crystallinity was also studied.

Experimental

Kevlar 49 fibres used in this investigation were supplied by Du Pont, USA. The effect of RH on the fibre has been studied using the chamber of an elect-

ronic balance as the humidity chamber. The RH within the chamber was monitored by the use of appropriate chemicals. Table 1 lists the chemicals used for obtaining RH values of 3, 20, 40, 60 and 80%. Small dishes containing the required chemicals were placed within the chamber along with a air hygrometer and a thermometer. It was found that in about 1 to 1½ hours, RH value within the chamber stabilized at the expected value. The variation in RH value within a duration of 1 hour was found to be ± 1% whereas over a day's time the fluctuations corresponded to ± 4%.

Table 1 Chemicals used for controlling the RH values at 26°C

RH (%)	Chemical
3	Calcium chloride
20	Calcium chloride
40	Calcium chloride
60	Sodium nitrate
80	Potassium bromide

Kevlar fibres were initially dried for 20 hrs in an oven maintained at 150°C. The dry specimens were transferred to a dessiccator containing silica gel. After cooling in air for ~1 minute, the fibres were transferred to the humidity chamber. The moisture absorbed by the sample was estimated by measuring the change in weight of the sample at chosen intervals of time. When change in weight was rapid, readings were taken at intervals of 30 seconds. With progressive decrease in the rate of change of weight, the time interval was increased. For each dry sample, the variation in weight during the first one hour of exposure to the environment and the saturation moisture content corresponding to 22 hours of exposure, were meausred. The balance used in these experiments was capable of reading up to 0.0001g and the temperature within the chamber was 26±2°C.

For identifying the role of crystallinity on moisture absorption, fibres wherein crystallinity had been reduced by heat treatment were used. Unconstrained Kevlar fibres were exposed to 350°C for 30 hours and 500°C for 1/2 hour in air using a tubular, resistance furnace. The crystallinities of the heat-treated fibres were determined by X-ray method of Wakelin et al (5). The saturation moisture contents of the fibres with reduced crystallinities were determined by the weighing procedure. In addition to the diffusion of water molecules in the form of vapour, penetration of water due to soaking the fibres in water at 30°C for 70 hours and at 98°C for 1 hour, were studied. Before weighing the soaked samples they were thoroughly dried by pressing between filter papers.

X-ray diffraction patterns from the fibre were recorded by the diffractometric as well as photographic method. For the determination of correlation crystallinity index (5) the diffraction pattern in the 2θ-range of 15 to 27° was recorded on a Philips powder diffractometer using $CuK\alpha$ radiation, a proportional counter and a graphite monochromator in the diffracted beam. Sample rotation speed of 1/4 degree per minute and chart speed of 10 mm per minute were employed. The intensity values at various points along the diffraction profile were estimated using a digitizer and the AD-380 graphics system. The unit cell constants

were determined from the photographs recorded in the transmission Laue geometry. The incident CuKα beam was normal to the length of the fibre. In order to calibrate the sample to film distance, a thin copper wire was mounted along with the tautly held fibre sample. In case of dry fibres and those with different levels of moisture content, the calibrant as well as the fibre were sealed taut within a Lindemann capillary tube. Visually measured distances on the photographs were used to calculate the unit cell constants.

Results and Discussion

Fig 1(a) shows the percentage variation in the weight obtained expressed as $w/w_d \times 100$, with t. Here w is the change in weight at time t and w_d is the weight of the dry fibre. It is found that for all RH values chosen the change in weight is rapid and non-linear in early stages followed by a progressively slow variation and an eventual stabilization. From Fig 1(a) it is also observed that during first 60 minutes of exposure, the effect of RH on moisture absorption is statistically not significant. In contrast, the saturation moisture content, w_s, exhibits a significant dependence on the RH value (Table 2). By fitting a polynomial it has been found that the w_s values exhibit a dependence on RH expressed as $w_s = 0.72 + 0.033(RH)$

Table 2 Observed values of the saturation moisture content w_s

Sample	w_s %
Kevlar fibres as received	
At 26°C, RH = 3%	0.74 (8)
20%	1.48 (4)
40%	2.07 (3)
60%	2.35 (8)
80%	3.2 (1)
Soaked in water at 26°C for 70 hours	3.5 (1)
Soaked in water at 98°C for 1 hour	3.8 (1)
Kevlar fibres with reduced crystallinity at 26°C and RH = 65%	
Reduction in crystallinity 40%	20
Reduction in crystallinity 60%	24

The humps in the curves in Fig.1 suggest that after the initial rapid absorption of moisture, slight reduction in weight occurs. Table 2 also lists the saturation moisture content in fibres soaked in water, (100% RH). It is observed that the w_s values corresponding to both 26°C and 98°C, are not statistically different. They are, however, higher than the w_s values obtained for diffusion of water vapour from the atmosphere.

Estimation of the correlation crystallinity index (CCI) has shown that for fibres exposed to 350°C for 30 hrs and 500°C for 1/2 hr, the value of CCI is

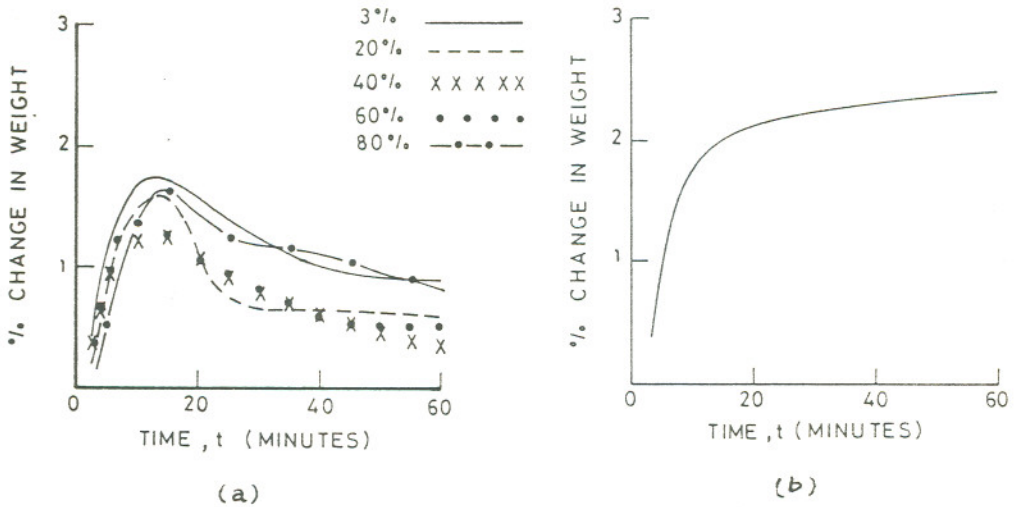

Fig 1(a) and (b) : Percentage variation in the weight of the fibre with time

reduced by 60 % and 40 % respectively. The saturation moisture content in these fibres, corresponding to 26°C and 65 % RH (Table 2) are significantly higher than that in the as-received samples in which the crystallinity has not been disturbed. This feature suggests that in Kevalar fibres the presence of less crystalline regions enhances moisture absorption. However, Kevlar fibres are known to be highly crystalline and to-date, there has been no evidence for the presence of an amorphous component in the fibre(6,7). It may therefore be concluded that although in the as-received fibres the moisture content may be low, any treatment which may reduce the crystallinity is likely to enhance the moisture absorption capacity of the fibre.

The unit cell data obtained for dry Kevlar fibres and for those with different levels of moisture content are shown in Table 3. Within limits of experimental error the unit cell constants of dry and wet fibre do not differ significantly. This observation indicates that water molecules do not enter the unit cell of the crystal lattice of Kevlar. Based on the volume of water molecule, 20 $A^{\circ 3}$(8) and the unit cell volume of Kevlar, 526 $A^{\circ 3}$(9)the expected increase in the unit cell volume of Kevlar by inclusion of one water molecule in the crystal lattice can be calculated as 4 %, which is well within the capacity of XRD to detect.

Table 3 Unit cell data of Kevlar fibres with different levels of moisture absorption

Sample condition	Unit cell a Å	b Å
Dry	7.79 (3)	5.26 (3)
Saturated with moisture	7.73 (3)	5.28 (3)
Moisture absorption corresponding to		
i) 1.2 wt %	7.83 (3)	5.27 (4)
ii) 2.4 wt %	7.75 (3)	5.33 (3)

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References

1. Fukuda M, Kawaii H, Horii F and Kitamaru R (1988) Polym Commun 29:97
2. Kim P K, Change C and Hsu S L (1986) Polymer 27:34
3. Penna L and Larsen F (1979) J Appl Poly Sci 23:59
4. Dobb M G, Johnson D J, Majeed A and Saville B P (1979) Polymer 20:1284
5. Wakelin J H, Virgin H S and Crystal E (1959) J Appl Phys 30:1654
6. Dobb M G, Johnson D J and Saville B P (1977) J Polym Sci Polym Symp 58:237
7. Panar M, Avakian A, Blume R C, Gardner K H, Gierke T D and Yang H H (1983) J Polym Sci Polym Phys Ed 21:1955
8. Kitaigorodskii A I (1955) Organic chemical crystallography, Acad Sci USSR p 13.
9. Northolt M G and Van Aartsen J J (1974) Eur Polym J 10:799.