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Thermally induced changes in Kevlar* fibre surface evidenced by inverse gas chromatography

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Inverse gas chromatographic analysis of Kevlar yarns reveals a major surface property difference between free-length annealed fibres and constant-length annealed fibres. The deviation in the retention diagram is studied and discussed along with four possible hypotheses. A surface microstructure change is the most realistic explanation of the observed phenomena.

(Keywords: PPTA; fibre surface; annealing; inverse gas chromatography)

Introduction

Inverse gas chromatography (i.g.c.) is a suitable technique for detecting changes in the morphologic structure of polymers, for determining interaction parameters (e.g. polymer–solvent or polymer–polymer), and, more generally, for the characterization of the surface physicococochemical properties of advanced materials in various forms[1].

This paper describes a modification in the surface microstructure of the poly(*p*-phenylene terephthalamide) (PPTA) based fibres (Kevlar) during annealing as revealed by i.g.c. analysis. A very similar phenomenon, namely the increase of the crystallinity rate and the growth of the microparacrystallites during annealing, was observed by Chatzi *et al.*[2] and by Hindeleh and Abdo[3]. These authors refer to i.r. spectroscopy analysis, after hydrogen exchange with D_2O (ref. 2), and X-ray diffraction observation[3] to support their findings.

Annealing of Kevlar fibres provides a means to tailor the molecular orientation which directly affects the crystalline parameters. This annealing effect is observed at a lower temperature (100°C) in the case of Kevlar-29 than for Kevlar-49 fibres. In both cases, the degree of orientation is larger when fibres are free-length annealed than when these fibres are annealed at constant length.

Experimental

Material. Finish-free Kevlar-29 fibres, supplied by E.I. DuPont de Nemours and Co., are used as received. These fibres are produced from the PPTA polymer. The yarn is made of 1000 filaments of 12 μm diameter and its specific linear density is 1670 dtex (equivalent to 0.167 g m^{-1}).

Annealing. Skeins of Kevlar yarn are treated for 24 h in an oven at 130°C under atmospheric pressure in order to eliminate most of the sorbed water—5–6% by weight. During this fibre preconditioning, two types of annealing are performed:

(i) The skein of yarn is hung freely in the oven ('free-length annealed fibres').
(ii) The yarn is wound on a glass tube and placed in the oven ('constant-length annealed fibres').

Column preparation. A treated skein of 160 fibre ends is pulled into a stainless steel column (internal diameter, 4.7 mm; length, 80 cm). The packing factor of the column is 0.55–0.60, which guarantees an optimum reproducibility of the method. Usual precautions are taken to avoid moisture and dust contamination of the fibres.

Chromatographic measurements. The column is inserted in an Intersmat IGC 16 chromatograph equipped with a catharometer detector. The flow rate of carrier gas (helium) is carefully regulated at 25 ml min^{-1} (measured at 20°C) using a constant flow Brooks valve (model 8744). A purge of the column is performed at 60°C, in order to eliminate all molecules able to desorb at this temperature.

For this study, the saturated linear hydrocarbon, n-dodecane from Fluka, is used as a non-polar probe. The retention time is given by the maximum value of the peak, corresponding to the injected probe molecule. Its net value, t_r, is obtained by subtracting the retention time of air. The specific retention volume V_g is given by:

$$V_g = j\frac{Dt_r}{m}$$

where j is the James and Martin correcting factor which takes into account the pressure drop ΔP along the column, D is the flow rate of carrier, and m is the mass of the stationary phase (Kevlar fibres) in the column.

At a given temperature, several injections of the probe

* DuPont's registered trademark for its high strength para-aramid fibres
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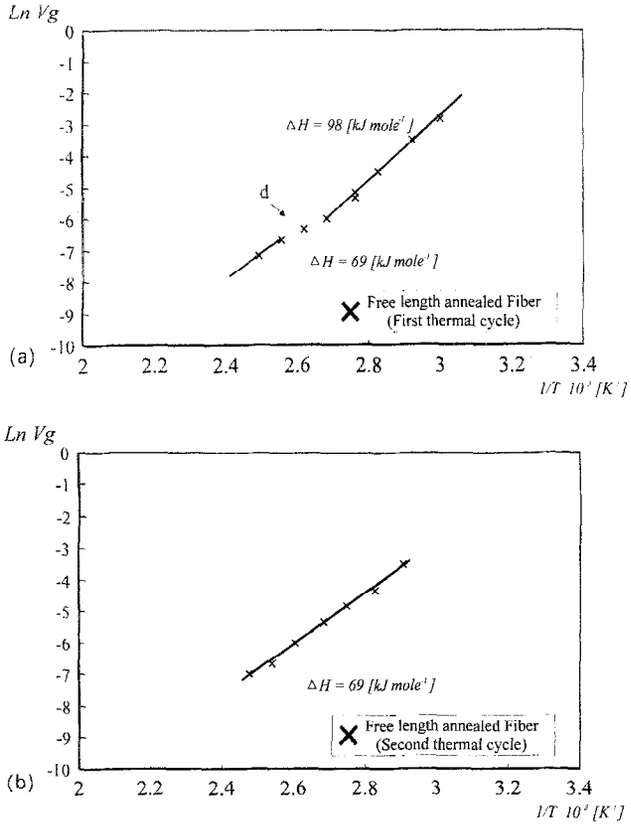

Figure 1 Variation of $\ln V_{g0}$ for n-dodecane with reciprocal of the temperature (column packing: free-length annealed Kevlar-29 fibres): (a) first temperature rise, (b) second temperature rise

molecule at different concentrations are performed using a micro-syringe. The smallest possible amount of probe has to be injected (using the head-space technique). V_{g0}, corresponding to the theoretical retention volume at 'nil concentration', is obtained by extrapolation of the collected data.

According to Clapeyron's equation, there is a linear relationship between $\ln V_{g0}$ and $1/T$. The slope gives access, in our case, to the enthalpy of adsorption of the probe molecule on the fibre surface. By comparing this value with the liquefaction energy of the gaseous probe molecule, one can estimate the specific interactions between the probe and the fibre surface[1].

Consequently, the calculation of the specific interactions requires the measurements of a fairly large number of retention times at different isothermal stages. Between 60 and 130°C, measurements were done for each 10°C step. Since, for each step, several days are needed to obtain a good stabilization of the baseline, one can easily appreciate the large time period of the technique.

Results and discussion

Figure 1 represents the variation of $\ln V_{g0}$ with the reciprocal of the temperature for the selected Kevlar fibre after free-length annealing. *Figure 1a*, which corresponds to the first temperature rise, shows two straight segments with a discontinuity (d) between 95 and 120°C. On the contrary, a single straight line (*Figure 1b*) is obtained for the second temperature rise. The experiments are conducted at intervals of 10°C in order to produce the data within a reasonable time scale. It is possible that shorter temperature intervals would lead to a better defined, eventually smaller, discontinuity step, d. A straight line with the same slope as in *Figure 1b* is also obtained when the columns are prepared with unpreconditioned, unannealed fibres.

Different hypotheses can be envisaged to explain the curve discontinuity:

(i) Such a discontinuity is often observed by i.g.c. for polymers which exhibit a glass transition temperature, T_g, or a second order transition in the studied range of temperature. It is not the case here since a 'T_g' value of Kevlar is given around 345–375°C[4,5], which is confirmed by a baseline change around 360°C on a d.s.c. thermogram. On dried Kevlar, no other phenomenon is observed at 100°C (ref. 5) on the d.s.c. curve. Furthermore, this discontinuity would be reversible, which is not the case since a single segment is observed for the second temperature rise (*Figure 1b*).

(ii) Another explanation would involve the desorption (at temperatures between 95 and 120°C), of fairly strongly sorbed water molecules located onto highly active sites. In order to verify this hypothesis, Kevlar fibres are rehydrated in the column using helium gas saturated with water. After another period of stabilization, a single straight line (as in *Figure 1b*) is obtained. This means that during the preconditioning, all the water molecules were desorbed, and the curve discontinuity is not due to new accessible sites created during the desorption of water.

(iii) A third hypothesis may be related to the dimensional modifications of the column packing with the temperature, which are well evidenced by monitoring the pressure drop ΔP between the inlet and the outlet of the column. However, as the flow rate of carrier gas is rigorously maintained constant, the discontinuity cannot be due to dilatation phenomena.

(iv) A fourth hypothesis involves a morphological modification of the material. This modification, concerning at least the surface of the fibres, would be due to the free annealing. As described by Hindeleh and Abdo[3], the annealing above 100°C increases the degree of orientation, especially for free-length annealed fibres, and involves the growth of microparacrystallites which can generate changes at the surface.

In order to verify this hypothesis, a new set of measurements is conducted comparing free-length and constant-length annealed fibres (*Figure 2*). A discontinuity is observed in the two cases. *Figure 2* shows the remarkable reproducibility of the phenomenon observed in *Figure 1a*. It is also worth noting that the curve interruption is markedly reduced for constant-length annealed fibres. The crystallinity parameters are also affected, as confirmed by X-ray diffraction measurements (WAXS)—the (2 0 0) reflection peak increases by 14% for free-length annealed fibres and only by 11% for constant-length annealed fibres. This difference may appear small, but remember that the Kevlar superficial zones are more ordered than the core[2], and the modifications are always developed from the surface to the core.

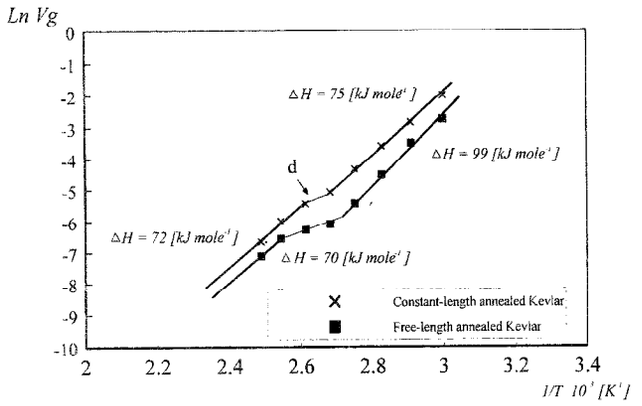

Figure 2 Variation of $\ln V_{g0}$ for n-dodecane with reciprocal of the temperature (column of Kevlar-29 fibres, first temperature rise) for (■) free-length annealed fibres, and (×) constant-length annealed fibres

Consequently, one can expect that the difference in surface crystallinity is higher than the mean bulk value given by X-ray measurements. It is then logical to consider that such a variation of surface orientation would be observable by i.g.c., a well respected technique in terms of surface analysis.

This hypothesis, as outlined in paragraph (iv), is also supported by the energy values obtained prior to and after the curve discontinuity. As exhibited in *Figures 1a* and *2*, the enthalpic variations, ΔH, corresponding to the adsorption of n-dodecane on the Kevlar surface, are different before and after the curve discontinuity. This is especially noticeable for the free-length annealed fibres.

For temperatures above 120°C, after the curve discontinuity, ΔH is in the range 69–72 kJ mol^{-1}, i.e. ≈ 20 kJ mol^{-1} above the liquefaction energy of n-dodecane (52 kJ mol^{-1}), although no specific interactions between the hydrocarbon molecules and the poly-aramid chains are expected. A similar result was previously described[6] for the adsorption of n-alkanes on Kevlar fibres, and was interpreted in terms of specific interactions with the aromatic rings of Kevlar polymer. The results obtained in the present study correlate very well with the n-dodecane adsorption energy obtainable by extrapolation of the data published by Gozdz *et al.*[6] (69–72 *versus* ≈ 66 kJ mol^{-1}).

For temperatures below 95°C, i.e. before the appearance of the curve discontinuity, the measured energy of interaction is much higher, especially for the free-length annealed fibres (98 kJ mol^{-1}, *Figure 1a*). Such a significant difference in the case of a non-polar molecule, may involve the condensation of n-dodecane in the surface micropores. These micropores would have to be of a size relatively close to the size of the condensate.

The need then remains for an explanation of the disappearance, after the first thermal cycle, of this energy phenomenon and of the curve discontinuity d. The complete thermal cycle consist of 8 isothermal steps, from 60 to 130°C, each lasting several days. It is then possible that these prolonged periods, which, due to the column compactness, could be considered as equivalent to the constant-length annealing conditions, are favourable to a relaxation of internal stresses[7] leading to a further modification or even a disappearance of the previous orientation increase. As a result, the behaviour becomes similar to that of unannealed fibres or to the constant-length annealed fibre as shown in *Figure 2*.

Conclusion

A modification of the microstructure of Kevlar-29 fibres during annealing was evidenced by i.g.c. The observed phenomena are not only in agreement, but further complete the previously described effects of annealing. For example, the increase of the size of the microcrystallites generates micropores at the surface, where molecules such as n-dodecane may condense with high interaction energies. This effect is accentuated by the annealing method. Free-length annealed fibres are more clearly subject to these microstructural modifications.

References

1 Lloyd, D. R., Ward, T. C. and Schreiber, H. P. 'Inverse Gas Chromatography', ACS Symp. Ser. 391, American Chemical Society, Washington DC, 1989
2 Chatzi, E. G., Urban, M. W., Ishida, H. and König, J. L. *Polymer* 1986, **27**, 1850
3 Hindeleh, A. M. and Abdo, S. M. *Polymer* 1989, **30**, 218
4 Butta, E., de Petris, S., Frosini, V. and Pasquini, M. *Eur. Polym. J.* 1971, **7**, 387
5 Yang, H. H. 'Aromatic High-Strength Fibres', Wiley, New York, 1989, Ch. 2, p. 191
6 Gozdz, A. S. and Weigmann, H. D. *J. Appl. Polym. Sci.* 1984, **29**, 3965
7 Wu, Z., Zhang, A., Cheng, S. Z. D., Huang, B. and Qian, B. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 2565