The potential for using alkaline hydrolysis to study the fine structure of fibres manufactured from a thermotropic liquid crystalline copolyester

S. H. Zeronian*, G. Buschle-Diller and M. K. Inglesby
Division of Textiles and Clothing, University of California, Davis, CA 95616, USA
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The possibility of utilizing alkaline hydrolysis for studying changes in the properties of thermotropic liquid crystalline copolyester fibres is evaluated. The copolyester fibre manufactured from 4-hydroxybenzoic acid (HBA) and 2-hydroxy 6-naphthoic acid (HNA) in a molar ratio of 73/27 HBA/HNA was hydrolysed at 21°C with 2.5 M NaOH, 0.1% cetyltrimethylammonium bromide solution. After hydrolysis the shape of the HBA/HNA fibre cross-section changed from round to polygonal, unlike the cross-section of poly(ethylene terephthalate) fibre which does not change in shape after a similar treatment. Although heat treatment markedly increased the tenacity of HBA/HNA fibre, the tenacity fell steadily with increasing weight loss by hydrolysis. In contrast, the tenacity of the non-heat-treated fibre remained constant up to a weight loss of 58%, indicating that hydrolysis was occurring at the fibre periphery and leaving its core unaffected. For both the heat-treated and non-heat-treated products the initial modulus of the fibres fell progressively with increasing weight loss. Significant change in brittleness did not appear to occur when either form of HBA/HNA fibre was hydrolysed to a weight loss of 38%.

(Keywords: fibres; hydrolysis; copolyester)

INTRODUCTION

The invention and manufacture of fibres from thermotropic liquid crystalline copolyesters began in the 1970s[1] and there have been reviews of the formation and properties of such fibres[1-3]. The liquid crystal copolyester fibre we studied is formed from 4-hydroxybenzoic acid (HBA) and 2-hydroxy 6-naphthoic acid (HNA) in a molar ratio of 73/27 HBA/HNA. Fibre manufactured from this copolyester can be heat treated. It has been observed that before heat treatment the X-ray fibre diagrams of HBA/HNA fibres are characteristic of highly oriented parallel arrays of polymer chains with poor lateral registry of atoms normal to the chain direction[3]. After heat treatment fibre tenacity increases markedly but the tensile modulus is little affected[3]. The increase in strength has been attributed primarily to an increase in molecular weight due to solid-state polymerization rather than to a structural perfecting process[3,4]. Nevertheless, the diffraction pattern of HBA/HNA copolyesters does sharpen after heat treatment[1,3]. Two hypotheses have been considered, without resolution so far, to explain the manifested effects[1,3], namely: (a) the chains become locked into an orthothombic arrangement from the less ordered pseudo-hexagonal oriented nematic structure associated with as-spun fibres; (b) there is a redistribution of crystal sizes. Other models are also being considered.

As we described in a comprehensive review of the literature[5], it has been well established that alkaline hydrolysis of poly(ethylene terephthalate) (PET) fibres with aqueous sodium hydroxide is confined to their surfaces. As the reaction proceeds successive layers of the polymer are dissolved. We have developed techniques to use this reaction to study the fine structure of PET fibres[6].

The objective of this study was to determine whether the alkaline hydrolysis technique could be applied to thermotropic liquid crystal copolyester fibres.

EXPERIMENTAL

Materials

The starting materials were 1500/300 Vectran HS (VHS) multifilament yarn and 750/150 Vectran M (VM) multifilament yarn supplied by Hoechst-Celanese Corporation (Charlotte, NC, USA). These samples were formed from 73/27 HBA/HNA, and VHS had been heat-treated. The heat treatment involved heating at close to the fibre melting point under nitrogen for several hours. All chemicals were of reagent grade.

Procedures

Alkaline hydrolysis. Yarn samples were treated with 2.5 M NaOH, 0.1% cetyltrimethylammonium bromide solution in sealed jars at 21°C (±2°C) with mild mechanical agitation utilizing a 2.5 w/v (g/l) ratio. The reaction was terminated by rinsing in distilled water then immersing in 1% aq. hydrochloric acid for 2 min and finally rinsing in distilled water to neutrality. The samples were dried to constant weight by exposure to the ambient atmosphere at 21°C and 65% relative humidity (r.h.).

* To whom correspondence should be addressed

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Characterization of products. Conditioned samples were weighed before and after hydrolysis.

Filament tex of the non-hydrolysed samples was calculated from the yarn tex. The tex of the hydrolysed filaments was calculated using the weight loss suffered by the samples and the tex of the starting material.

Density determinations were made in duplicate with a density gradient column prepared with n-heptane and carbon tetrachloride and maintained at a temperature of 21°C (±2°C). Samples were in the form of bundles of fibres tied into small knots and the loose ends cut off. Duplicate determinations varied only in the fourth decimal place and results are presented to the third decimal place.

Scanning electron microscopy (SEM) was performed with an International Scientific Instruments model DS 130 microscope operating in the secondary mode at an accelerating voltage of 10 kV. The samples were mounted on standard specimen stubs with silver paint and the stubs were then sputtered with gold.

Measurements of filament tensile properties were made on single filaments at 65% r.h. and 21°C on a table model Instron Universal Testing machine set for a constant elongation rate of 20 mm min^{-1}. A gauge length of 10.16 cm was used. Results given are for an average of 20 tests.

Breaking twist angles (BTA) were measured in the manner described previously at 65% r.h. and 21°C using a sample length of 1.27 cm[7]. The fibres were pretensioned to 0.5 g tex^{-1} in order to avoid snarling during testing. The samples were twisted at a rate of 100 rev min^{-1}. Fifteen tests were performed each time. Standard deviations were about 0.027 rad. By definition, the higher the BTA value the greater the brittleness of the sample.

RESULTS AND DISCUSSION

Both the non-heat-treated (VM) and heat-treated (VHS) samples progressively lost weight when immersed in the alkaline solution at room temperature (*Tables 1* and *2* and *Figure 1*). VHS lost weight more slowly than VM. It appears from the density measurements that the molecular order of VHS was higher than that of VM since the former product had the higher density (*Table 3*); this may be associated, at least in part, with the reduction in rate of weight loss after heat treatment. A similar effect is found with PET fibres. To enable comparisons to be made, the time for 25% weight loss to occur was calculated for VM, VHS and a PET sample that had been hydrolysed before and after heat setting[6] (*Table 3*). It may be observed that the rate of hydrolysis of the PET dropped markedly as its density increased.

Table 1 Properties of non-heat-treated HBA/HNA 73/27 fibre (VM)[a]

Hydrolysis time (h)	Weight loss (%)	Tenacity (GPa)	Breaking extension (%)	Initial modulus (GPa)
0	–	1.36 (0.17)	2.33 (0.22)	62.2 (7.0)
24	8.77	1.35 (0.24)	2.45 (0.27)	54.8 (7.6)
96	25.6	1.40 (0.22)	2.26 (0.27)	51.0 (4.7)
168	37.2	1.38 (0.26)	2.24 (0.34)	44.6 (5.1)
337	57.7	1.40 (0.23)	1.95 (0.24)	33.3 (5.1)
504	76.3	1.11 (0.30)	1.61 (0.28)	17.4 (3.0)
672	85.4	1.09 (0.36)	1.31 (0.23)	12.4 (2.8)

[a] Standard deviations in parentheses

Table 2 Properties of heat-treated HBA/HNA 73/27 fibre (VHS)[a]

Hydrolysis time (h)	Weight loss (%)	Tenacity (GPa)	Breaking extension (%)	Initial modulus (GPa)
0	–	3.13 (0.51)	3.62 (0.47)	69.5 (6.6)
24	5.11	2.73 (0.60)	3.23 (0.37)	61.6 (6.6)
96	15.5	2.16 (0.43)	2.69 (0.35)	57.2 (6.0)
168	22.8	2.14 (0.70)	2.63 (0.63)	53.7 (6.2)
337	38.0	1.79 (0.79)	2.21 (0.75)	46.5 (8.8)
504	47.2	1.51 (0.74)	2.11 (0.82)	32.6 (3.0)
672	58.0	1.00[b] (0.57)	1.40 (0.71)	29.0 (3.6)

[a] Standard deviations in parentheses
[b] After hydrolysis for 672 h the fibres were very brittle and only one out of 15 was strong enough and of sufficient length to be mounted and tested. Therefore, this value can only be considered as representing the stronger (smaller) portion of the sample

Table 3 The time required to hydrolyse[a] various samples to 75% of their starting weights (75% life) and sample densities

Sample	Description	Density (g cm^{-3})	75% life[b] (h)
VM	Non-heat-treated 73/27 HBA/HNA	1.402	93.6
VHS	Heat-treated VM	1.408	192.4
PET-1	Non-heat-set bright PET[6]	1.370	13.5
PET-2	PET-1 heat set at 197°C for 30 min[6]	1.389	80.8

[a] Hydrolysis conditions given in the Experimental section
[b] Obtained by data interpolation

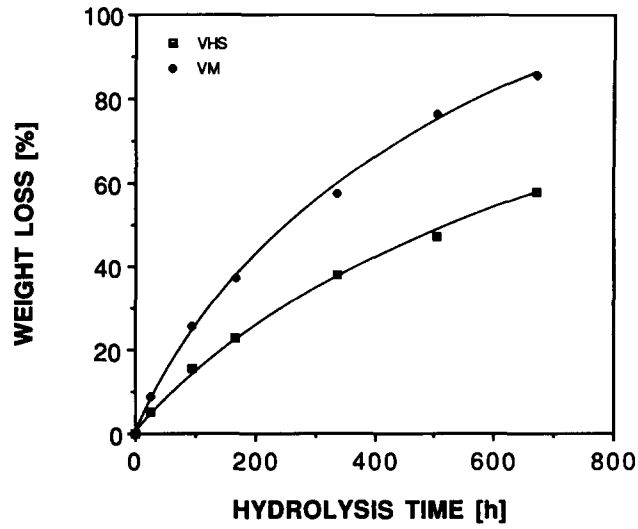

Figure 1 Weight loss of VM and VHS after hydrolysis

A second factor which may be associated with the slower weight loss of the HBA/HNA fibre after heat treatment is the concomitant increase in molecular weight[3,4]. A molecular weight increase is not found when PET is heat set.

The relation between weight loss and time of hydrolysis was curvilinear for both VM and VHS samples. In contrast, a linear relation is found for PET hydrolysed under the same conditions[5,6]. In the case of the hydrolysis of HBA/HNA fibres, weight loss occurs at a faster rate initially and then becomes slower. One explanation would be that the molecular order is less at the fibre surface, allowing the hydrolysis to occur more rapidly at first. It is interesting to note that when VM or VHS is hydrolysed the shape of the fibre cross-section changes from generally

round to polygonal. The angularity of the fibres can be observed in scanning electron micrographs (*Figures 2–5*). Similar changes in cross-ectional shape have not been observed with PET fibres[5,6,8]. It is therefore feasible that certain segments of the fibre periphery are more prone to hydrolysis than other parts, and the initial rapid reaction rates are due to the attack of these segments. It is speculated that the change in fibre shape reflects the underlying microstructure.

Upon hydrolysis, the tenacity of the non-heat-treated fibre (VM) remained constant until the weight loss exceeded 58% (*Table 1*, *Figure 6*), which is an indicator that hydrolysis had occurred at the fibre surface and had not affected its core. It is interesting to note that in the case of PET, where several tests have indicated that aqueous sodium hydroxide attacks at the fibre surface[5,6], fibre tenacity of a variety of fibres starts to decrease when weight loss exceeds 30%[6,8]. Fibre fracture initiates at imperfections or weak points along the fibre length. It therefore appears that the structure of the HBA/HNA fibre remains uniform well into the fibre core. The fibre loses only 20% of its tenacity after a weight loss of 85%.

When the HBA/HNA fibre was heat treated its strength more than doubled (cf. *Tables 1* and *2*). However, unlike the non-heat-treated counterpart, its tenacity progressively fell as the time of hydrolysis increased. At a weight loss of 58% VHS was weaker than VM. Thus it appears that the heat treatment markedly improved the strength of the fibre in the peripheral region and left the core relatively weak. Generally, a drop in breaking

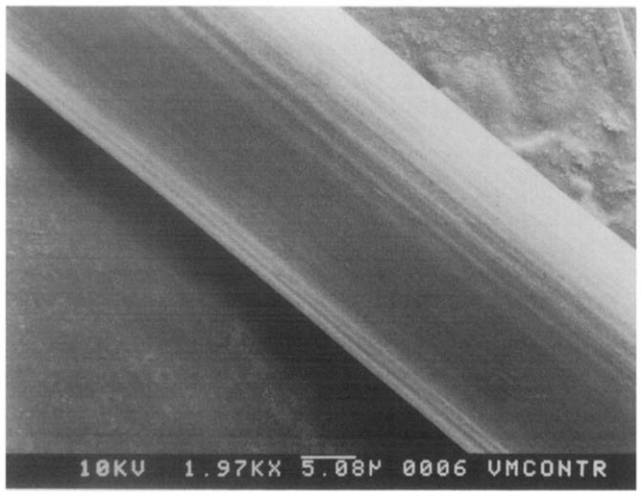

Figure 2 Scanning electron micrograph of VM

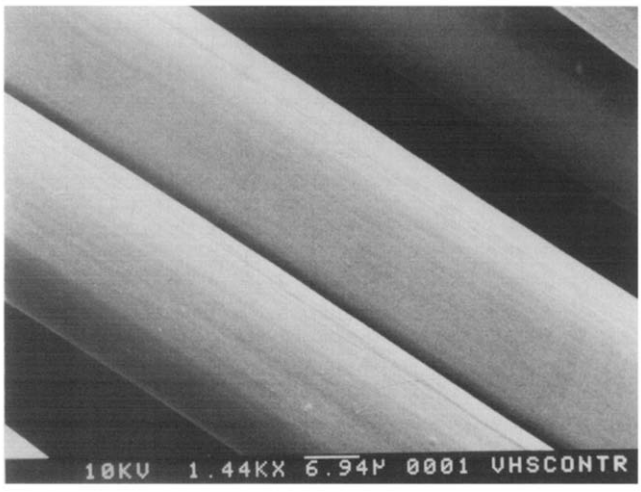

Figure 3 Scanning electron micrograph of VHS

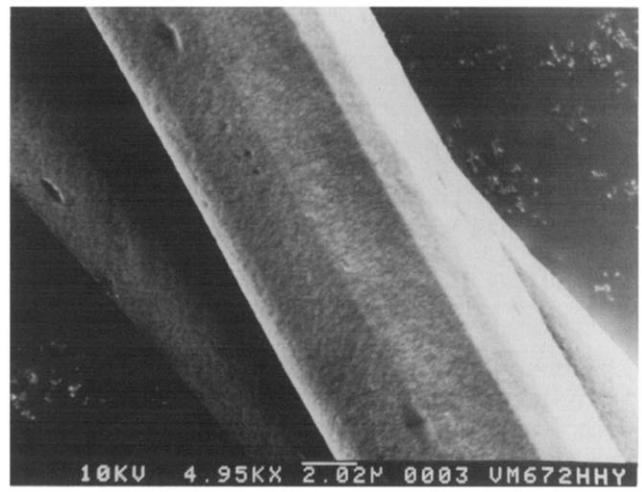

Figure 4 Scanning electron micrograph of VM after 672 h hydrolysis

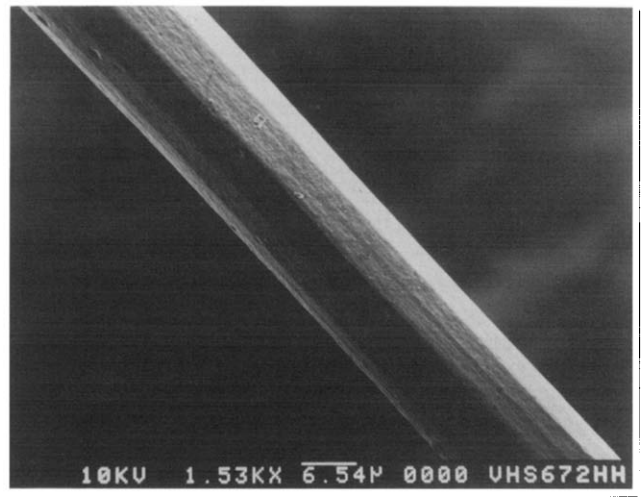

Figure 5 Scanning electron micrograph of VHS after 672 h hydrolysis

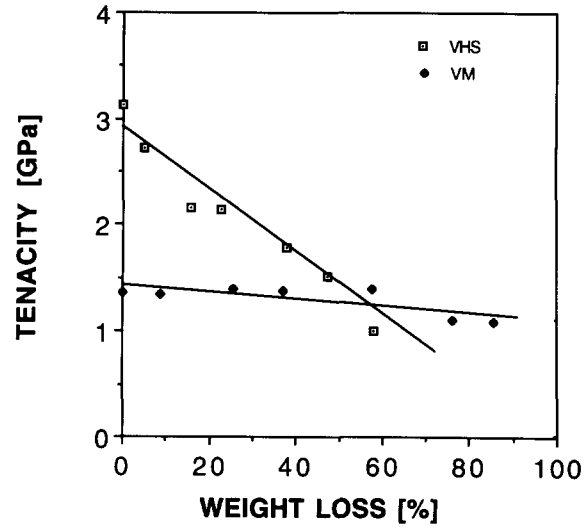

Figure 6 Relation between tenacity and weight loss for VM and VHS

Table 4 Breaking twist angle (BTA) of selected samples

Sample	Weight loss (%)	BTA (rad)
VM	–	1.25
VM	37.2	1.27
VHS	–	1.23
VHS	38.0	1.23

extension coincided with the fall in tenacity for both VM and VHS.

As expected[1], the initial modulus of VHS fibre was only slightly higher than that of VM fibre (cf. *Tables 1* and *2*). In both cases initial modulus fell progressively and markedly with increasing hydrolysis time. For VHS the drop in initial modulus paralleled the lowering in tenacity as weight loss increased. However, in the case of VM, while tenacity remained constant until a weight loss of 58%, initial modulus had already dropped to 54% of the starting value. It is interesting to observe that the initial moduli of VM and VHS samples are similar when compared at equal weight losses (cf. *Tables 1* and *2*). The difference in behaviour of tenacity and initial modulus for hydrolysed VM may be related to the weak forces present between the highly oriented parallel array of polymer chains. Such forces may be more irregular towards the fibre centre. In the case of oriented and partially crystalline PET fibres marked drops in initial modulus have not been observed on hydrolysis[8]. Thus the interchain forces present in PET, which would be stretched in the initial modulus region as well as the intrachain bonds, may be more uniform throughout the transverse direction of the fibre.

The BTA test measures the maximum resistance to shear of a fibre and gives a measure of fibre brittleness[9]. Values in the range 0.22–1.27 rad have been observed for organic fibres, depending on their chemical and fine structure[10]. BTA was determined for non-hydrolysed VM and VHS and for their hydrolysed counterparts of about 38% weight loss (*Table 4*). Both VM and VHS are brittle as measured by this test and there is little, if any, change in brittleness after the hydrolysis in each case.

CONCLUSIONS

It appears that alkaline hydrolysis can be a useful tool for studying any differences that may occur in HBA/HNA fibre properties in the radial direction. Unlike PET, the relation between weight loss and hydrolysis time is not linear for HBA/HNA fibre. The rate of weight loss decreases if the HBA/HNA fibre has been heat treated. The tenacity of the non-heat-treated HBA/HNA product remains constant up to a weight loss of 58% whereas the heat-treated product loses strength progressively on hydrolysis, indicating major differences in the skin/core properties of the latter product. For both the non-heated and heat-treated samples the initial modulus decreases steadily with increasing weight loss and appears to be a reflection of the distribution of the secondary valence forces in HBA/HNA fibres. Significant changes in brittleness do not appear to occur when non-heat-treated or heat-treated HBA/HNA fibre is hydrolysed to a weight loss of 38%.

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