JOURNAL OF MATERIALS SCIENCE 18 (1983) 2517–2530

Chemical stress cracking of acrylic fibres

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The generation of periodic microscopic transverse cracks in oriented acrylic fibres immersed in hot alkaline hypochlorite solution is described in detail and shown to be a variety of chemical stress cracking. It is greatly accelerated by external tensile stress, high fibre permeability, moderate fibre orientation, and water-plasticization. The proposed mechanism for bond cleavage involves cyclization of nitrile groups (similar to the "prefatory reaction" in pyrolysis of acrylic fibres), followed immediately by *N*-chlorination and chain scission. Mechanical retractile forces (internal or external) then cause chain retraction and crack growth. Despite the remarkable regularity of the crack pattern, which typically resembles a series of stacked lamellae, the process is independent of any such underlying fibre morphology, The cracking process does, however, appear to be a sensitive indicator of residual latent strain in the fibre, which may persist even after high-temperature annealing.

1. Introduction

An earlier study by Warner *et al.* [1] on the cryogenic ion etching of the oriented acrylic fibres, stabilized acrylic fibres, and carbon fibres made from acrylic fibres, reported the observation of periodic transverse striations on a submicron scale. Care was taken to ensure that the observed striations were not artifacts reflecting the process of ion etching. The regular orientation normal to the fibre axis and the periodicity of the striations led to the proposal that the original acrylic fibres were heterogeneous and that heterogeneities persisted throughout the process as the acrylic fibre was converted to carbon fibre.

Dr William Watt (private communication) drew our attention to the similarity in scanning electron micrographs between acrylic fibres subjected to cryogenic ion etching and acrylic fibres subjected to hot hypochlorite solutions.

These striking similarities warranted further investigation to obtain insight into the heterogeneities and the chemical interactions between etching solution and fibre. The present paper reports on the chemical etching of acrylic fibres by hot hypochlorite solutions in relation to the fibre orientation, the tensile stress, the chemical composition, plasticization, and other factors. It will be shown that the etching behaviour does not reflect underlying heterogeneities in the fibres, as originally thought, but represents a form of chemical stress cracking.

The present work differs from that previously reported on the decolouration of stabilized acrylic fibres [2] in two important aspects. The material under investigation in the present study is as-received acrylic fibre exposed to alkaline hypochlorite at the boil. The material used in the decolouration study had undergone partial stabilization reactions by heating the as-received fibres at about 230° C in air for various periods of time. The stabilization process causes both chemical and colour changes in the fibres. The partially stabilized fibres were exposed to the same concentration of alkaline hypochlorite solutions as used in the present study, but at 50° C.

Before considering the present results, it seems appropriate to consider the various types of environment-related cracking which have been reported in the literature. These have been the subject of several reviews during the past two

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decades [3–6]; and the interested reader is referred to them for extensive bibliographies as well as in-depth commentary.

Neglecting the situations where cross linking from environmental factors causes a decrease in ductility (observed even when the environmental interactions occur in the absence of stress), stress cracking can conveniently be divided into two categories: (a) environmental factors leading primarily to physical but not permanent chemical changes in the polymer; and (b) chemical stress cracking, where permanent chemical changes (most notably chain scission) are produced.

1.1. Environmental stress cracking (ESC)

Environmental stress cracking includes several types of phenomena:

1. The cracking of highly crystalline polymers (e.g. the polyolefins) by materials which do not swell, dissolve, or react with the polymer (e.g. detergents or alcohols). In this case, the cracks typically propagate along boundaries between spherulites and also along boundaries between lamellae within spherulites [4]. Non-spherulitic but highly crystalline materials can also exhibit such cracking. For example, highly oriented cold-drawn polyethylene may develop stress cracks running parallel to the direction of orientation. But these materials are extremely resistant to such cracking transverse to the orientation direction [3].
2. The crazing and cracking of glassy polymers by organic liquids, which is sometimes termed solvent cracking [3, 4]. The cracking agents here solvate and swell the bulk polymer at the crack tip. Typical examples include the crazing and cracking of polycarbonate by acetone or benzene and of polystyrene by hydrocarbons or esters. Such cracking can also be modified by cold drawing: crazes due to simple tensile stress do not form or propagate easily in cold-drawn polymers when the axis of stress coincides with the orientation direction [7].
3. The crazing/cracking of glassy or partially crystalline polymers by gases at low temperature or high pressure. In these cases, "crazing can be so profuse as to produce the phenomenon of craze yielding, whereby the overall strain rate of the sample due to crazing actually exceeds the imposed strain rate so that the applied stress drops" [6].

While there are significant differences among these various types of ESC, there seems to be a central similarity, namely the advance of the crack seems to occur by localized plastic failure, with a zone of craze-like features developing ahead of the crack tip. Chain scission or effective dissolution of polymer at the crack tip are not observed with this type of stress cracking.

1.2. Chemical stress cracking (CSC)

In contrast to ESC, chemical stress cracking involves the cleavage of bonds in the backbone of the polymer chains.

1.2.1. Ozone cracking of rubber

The classic example of CSC is the ozone cracking of rubber. In unstressed rubber, no cracks develop, despite the fact that the ozone readily cleaves the rubber molecules. Rather, the degraded rubber molecules simply merge into a continuous, oily surface layer, which retards the access of ozone to uncleaved polymer chains.

A mechanical retractile stress is required to generate polymer chain extension at the crack tip. The total strain at the crack tip in ozone cracking of rubber is low; about 30% for ozone cracking compared with 700% for ordinary tensile cracking [8]. The attacking reagent weakens the material at the crack tip by chemically cleaving the load-bearing bonds, so that low mechanical stresses are sufficient to pull the broken chains apart.

The rate of CSC and the microscopic appearance of the polymer vary markedly during the attack [8, 9]. In the early stages, the molecular weight of the surface material is still high and cracking is restructed to the vicinity of stress concentrators (surface flaws). Only etch pits and very short cracks appear (stage I). Later, when the molecular weight of the surface material has been reduced, cracks initiate in seemingly flaw-free regions and grow laterally at a high rate of speed. This results in the appearance of long seams, long thin cracks approximately 50 nm or less in width (stage II). Still later, the molecular weight of the surface material is severely degraded to produce a tacky residue. This layer tends to flow rather than produce cracks and impedes further attack by the chemical agent (stage III).

1.2.2. Amine cracking of PET

Amine stress-cracking of polyethylene terephthalate (PET) fibres is similar in many respects to ozone cracking of rubber; but the appearance of the affected polymer surface is markedly different.

TABLE I Cracking data for PET fibres in 40% methylamine (no external stress), based on information given in [10]

Fibre draw ratio	Estimated permeability	Rate of overall weight loss	Rate of stress-crack development	Ultimate crack density	Regularity of spacing (Degree of transverse orientation)
×1	High	Moderate	Zero	–	–
×2	High	High	High	Low	Low
×3	Moderate	Moderate	Moderate	Moderate	Moderate
×4	Low	Low	Low	High	High

Sweet and Bell [10] etched 14-denier PET filaments in 40% aqueous methylamine. Undrawn filaments which were loaded to 15% of the yield stress developed shallow, narrow cracks which girdled the filament at irregular intervals. These cracks resulted in failure after just 3 min. Undrawn filaments which were not loaded showed much greater resistance to cracking. After 4 h in the reagent solution, they suffered an 80% weight loss, but no cracks developed. The filaments simply decreased in diameter due to generalized surface attack.

The effects of fibre orientation on the development of stress cracks in methylamine-treated PET are summarized in Table I, which is based on information presented in [10]. While higher tensile loading dramatically speeded up cracking, higher internal retractile force arising from higher chain extension had the opposite effect: the induction time for crack formation increased by 150% with an increase in draw ratio (DR) from ×2 to ×4. This very likely reflects a decreased permeability of the fibres, and an increased concentration of load-bearing chains, with increasing DR.

Increasing the fibre orientation produced a higher density of cracking, i.e. a smaller axial spacing of cracks. This was associated [10] with a higher residual stress which required a greater number of cracks for relaxation to be achieved. Marked variations in cracking behaviour were observed on apparently identical filaments from the same yarn, subjected to identical treatments; and notable variations were also observed for separate regions of a single fibre. This was suggested to correspond with variations in the fibre spinning or drawing processes.

1.2.3. Other types of chemical stress cracking

Hinton and Keller [11] made a definitive study of the CSC of compression-molded HDPE (high-density polyethylene) immersed in fuming nitric acid at 60° C. Unoriented material held under 25% of the yield stress showed fine transverse surface cracks and failed after 2 h. Oriented material held under 25% of the yield stress reacted more slowly, with a time-to-failure of 20 h. Hinton and Keller ascribed this effect to a slower rate of diffusion of the CSC agent due to orientation. An increase in the concentration of load-bearing chains in the oriented samples would also presumably have been involved.

Unoriented unstressed material showed no transverse cracking, but became brittle and fragmented after 20 h. Oriented unstressed material developed cracks parallel to the direct of orientation. This is not CSC (by definition), but rather a "structural etch". Polyethylene chains in oriented amorphous regions apparently do not develop sufficient freedom of motion for the necessary retractile stress to develop under these conditions. This is consonant with the relatively ordered character of the amorphous regions in oriented HDPE, and with the absence of plasticization in the HDPE/HNO_2 system.

1.3. Comparison of chemical stress cracking and environmental stress cracking

The major distinction between CSC and ESC is that the former involves actual chemical changes in the polymer whereas the latter involves physical phenomena. One distinctive aspect of CSC is the simultaneous production, in many instances, of a surface layer of degraded material. Polymers with quite small levels of orientation can exhibit CSC: the chemical chain-cleavage reaction progressively degrades the molecular weight until even the chain extension inherent in production spinning of "undrawn" fibres is sufficient to cause chain retraction and stress-cracking. In contrast, ECS requires a significant level of axial stress; below this critical level, no cracking occurs, even for long immersion times. Partially cross-linked polymers (e.g. irradiated PE) are immune to ESC; and highly-drawn polymers are immune to ESC in the transverse direction [8]. Such materials are, however, susceptible to CSC.

2. Experimental procedures

2.1. Hypochlorite reagent

The stress cracking reagent used for all experiments was a 5.25% aqueous solution of sodium hypochlorite, sold commercially as Clorox® bleach. It is used as a mild oxidizing agent in chemical synthesis [12]. The reagent consists of the following ingredients: 0.76 M sodium hypochlorite ($NaOCl$), 0.76 M sodium chloride, and sufficient sodium carbonate to produce a pH of 10.9 (approximately 10^{-3} M). The solution is filtered to remove traces of transition metal oxides which will catalyse decomposition of the hypochlorite.

The reagent slowly disproportionates to chlorate and chloride during storage through the reactions

$$2NaOCl \xrightarrow{k_1} NaClO_2 + NaCl \qquad (1a)$$

$$NaOCl + NaClO_2 \xrightarrow{\text{fast}} NaClO_3 + NaCl \qquad (1b)$$

The rate constant for disproportionation is given [13]:

$$k_1 = 0.94 \times 10^{12} \exp(-24\,000/RT) \qquad (2)$$

at an ionic strength of 1.52 and a pH of 10.9. With an initial concentration of 0.76 M hypochlorite, the decomposition rate is approximately 3.19% per month at 25° C or 18% per hour at 100° C.

Most of the present experiments were conducted at the boil, slightly greater than 100° C. The decomposition products, chlorine, chlorate, plus oxygen originating from the slow disproportionation of hypochlorite, are much weaker than hypochlorite in terms of nucleophilicity or oxidizing power. Hence they should not interact significantly with acrylic fibres.

Since the decomposition of hypochlorite is greatly accelerated by transition metal ions, all reaction equipment was thoroughly rinsed with deionized water before use. Hot hypochlorite also is extremely corrosive to most metals. According to Wojtowics [14], gold, titanium, and platinum are resitant to hypochlorite attack. In the present study, the following materials were resistant to corrosion under operating conditions: gold, platinum, glass, polyethylene, polypropylene, polyvinylidene chloride, and the fluoropolymers. Adhesives suitable for short time use in boiling reagent include RTV silicone rubber adhesive (about 1 h) and Hysol oven-cured "Epoxi-Patch" (about 3 h).

Standard etching conditions involved roughly 1/2 g of acrylic fibre immersed in 250 ml reagent at the boil. Under these conditions, there are 21 moles of hypochlorite for every acrylonitrile or other mer unit in the fibre. With such an excess of hypochlorite, the effective concentration should not be diminished by reaction with the fibre during the course of the reaction. Owing to the rapid depletion of hypochlorite at 100° C, the solution was replaced every two hours to maintain an excess concentration of hypochlorite.

The evolution of gaseous degradation products from the hot solution and their entrapment in the loose fibres caused the fibres to float on the top of the hot solution. To keep the fibres submerged in the reacting system, they were tied to a short length of pyrex rod.

It was suggested above that only the hypochlorite ion would attack the acrylic fibres in the alkaline solutions. To verify this suggestion, CH-type fibres (see Table II for identification) and heat-treated stabilized acrylic fibres were held under tension for several hours in a concentrated solution of boiling sodium chlorate ($NaClO_3$). Scanning electron micrographs of the products showed no detectable change from the untreated fibres.

Hypochlorous acid ($HOCl$) solutions were produced by acidification of hypochlorite with hydrochloric acid to pH of 5.4. Since HOCl has a pK_a of 7.53, 99.3% of the hypochlorite ions should be protonated at this pH. The solution turned yellow-green and evolved chlorine gas. Due to the rather rapid decomposition of hot hypochlorous acid ($2HOCl \rightarrow H_2O_2 + Cl_2\uparrow$), hot solutions were replaced every 30 min. No observable effects resulted from exposure of the fibres to HOCl solutions for 130 min at 98° C.

Fibres were also boiled for 210 min in 1.5 M NaCl without observable etching, although the fibres were plasticized by this treatment. Other fibres were boiled in 1.5 M NaCl containing sufficient KOH to give a solution with pH about 11.2, or roughly double the hydroxide concentration of commercial hypochlorite solution (pH about 10.9). These fibres became reddish in colour and somewhat gelatinous to the touch after 210 min exposure to the boiling alkali solution. Again, no obvious etching had occurred; although some dissolution of surface material may have taken place.

TABLE II Acrylic fibres investigated

Designation	Trade name	Manufacturer	Composition*	Spinning conditions
CC	Courtelle	Courtaulds	6% methyl acrylate 1% itaconic acid	Wet spun from a conc NaCNS solution into dilute NaCNS solution; draw ratio approx. 6.5; denier per filament (dpf) ~ 4.
CH	Courtelle	Courtaulds	same	High tenacity Courtelle. Draw ratio approximately 11. ~ 1.5 dpf.
O43	Orlon 43	Du Pont	6% methyl acrylate 1% sodium styrene *p*-sulphonate	Dry spun from organic solvent. 6 dpf
M	Experimental	Monsanto	6% vinyl acetate	Wet spun from organic solvent into aqueous solvent. Highly oriented. 1.23 dpf.
N	Experimental	Monsanto	6% vinyl acetate	Wet spinning conditions varied to produce different draw ratios while maintaining reasonably constant filament diameter.
	Sample N draw ratio N1, N2, N3, N4, N6	Filament denier 24.0, 3.8, 3.7, 3.9, 3,8, respectively		
DT	Dralon T	Bayer	100% acrylonitrile	Dry spun from organic solvent, undrawn, 2.1 dpf.

*Remaining component is acrylonitrile.

2.2. Fibre samples

The acrylic fibre samples are described in Table II. The nominally undrawn Nl fibre contained a slight orientation, observed by a first order white birefringence under cross polarizers and by wide angle X-ray scattering [15], but exhibited no measurable shrinkage after immersion in boiling water.

Drawn fibre D was prepared by extending the fibre while submerged in hot (155° C) glycerol. Control samples were subjected to hot glycerol treatment for 2 min without tension.

2.3. Scanning electron microscopy (SEM)

After immersion in hot hypochlorite solution, small sections of etched yarn were excised with scissors, rinsed twice in hot deionized water, then rinsed in methanol. This procedure removed both the inorganic salts and any removable organic decomposition products from the fibres. A small section was then mounted with silver paint onto an aluminium SEM tab. The mounted fibres were dried overnight in a desiccator then coated at two different angles to give a gold layer several tens of nanometres thick.

To ensure that the cracks were not caused by the drying process (i.e. mud cracking where severe tensile stresses are imposed on partially dried material), a sample of CC fibre was carefully freeze-dried after 60 min etching at 100° C, then gold coated. The freeze dried material would not experience tensile stresses during drying. The fibre appearance was indistinguishable from a similarly etched fibre dried at room temperature.

3. Results and discussion

Etching of oriented acrylic fibres by boiling alkaline hypochlorite solution appears to be a classical stress cracking. The reagent causes a slow chain scission in the exposed surface regions of the polymer; retractile force is provided by the tendency of the extended chains to return to an equilibrium conformation, especially when the mobility is increased by plasticization, and also by an externally applied tensile load.

3.1. Stressed CC and CH fibres

The initial stages of hypochlorite cracking are very similar to those observed in ozone/rubber cracking [8, 9]. CC fibres (DR $\approx$ 6.5) and CH fibres (DR $\approx$ 11) were stretched tightly over a glass frame (effective strain 0.7 to 0.8%) and subjected

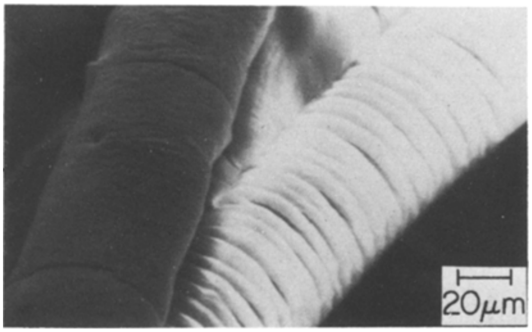

Figure 1 Fibre CC held at constant strain in boiling hypochlorite solution for 45 min.

to boiling hypochlorite solution. Under such constant-strain conditions, both types of fibre have an induction period for stress-cracking of about 35 min. The appearance of the fibres remains unchanged throughout this period, except for a barely-discernible surface roughening.

In CC fibres, stress-cracking typically begins with the appearance of transverse seams (fine superficial lines near the SEM limit of detection) or more prominent crack lines. Once initiated, these crack lines propagate very rapidly in the circumferential direction (see the left hand fibre in Fig. 1 where only a few cracks have been initiated). The cracks then deepen and widen during further exposure.

Under different etching conditions, stress-cracking begins with the formation of tiny pinholes or pits, plus short superficial crack lines (see Fig. 2). Here the sample was loaded with a constant stress of about 5.5 MPa. These pinhole pits and short seams rapidly deepen, widen and lengthen to give an interleaving network of sharp cracks (see the fibres on the left side of Fig. 3). Note the difference in appearance between the fibre furthest to the left and the fibres on the right. The last are more extensively degraded, resembling water-plasticized fibres (see below).

After 70 min under tension in boiling hypochlorite, CC fibres are covered with deep stress cracks, as in Fig. 4. Extensive plasticization of the

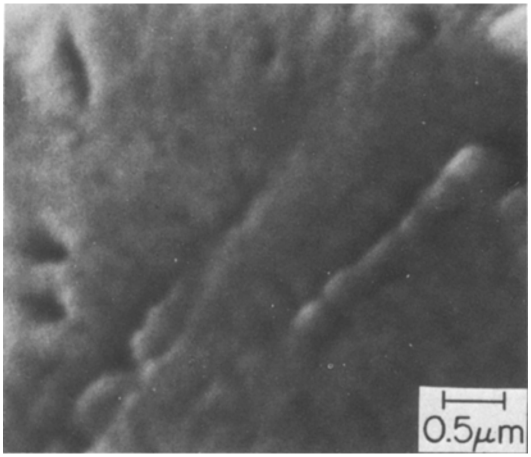

Figure 2 Fibre CC held at constant stress in boiling hypochlorite solution for 27 min.

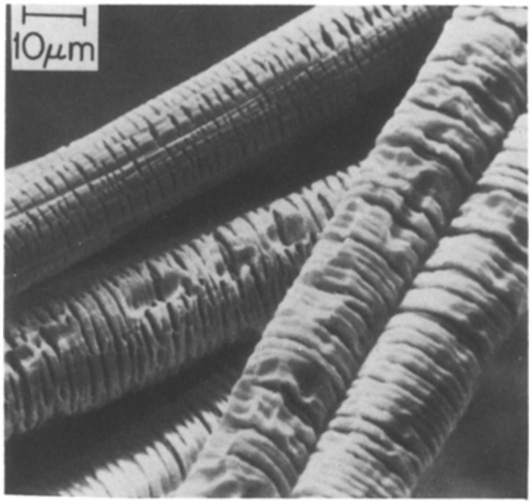

Figure 3 Fibre CC held at constant stress in boiling hypochlorite solution for 40 min.

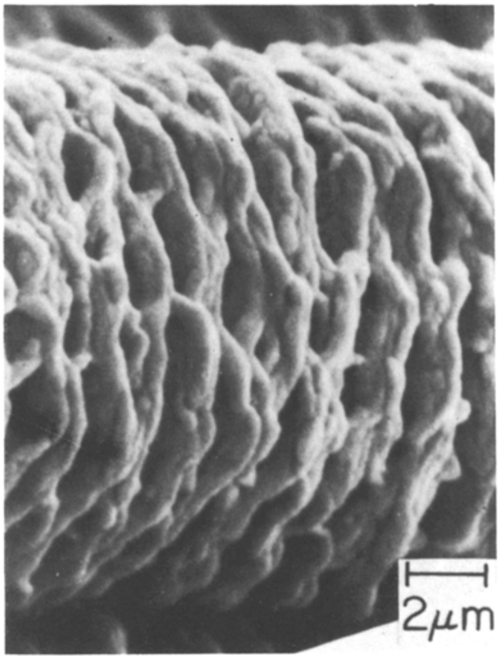

Figure 4 Fibre CC held at constant strain in boiling hypochlorite solution for 70 min.

surface regions is responsible for the serpentine appearance of the cracks and the rounded aspect of the crack edges. In contrast, unplasticized fibres, as illustrated by PET in amines, invariably develop sharp-edged cracks with no rounding or softening. After 80 min under tension, the CC fibres usually fail and break apart. After about 200 min, the separate filaments disintegrate into a fine chaff.

When a long crack opens up (widens), it relieves the tensile stresses in the (axially) adjacent regions and stops both the initiation of cracks in these regions and the circumferential propagation of existing cracks in these regions. This is shown in Fig. 5.

CH fibres are somewhat more resistant to hypochlorite stress-cracking than CC fibres. Scattered pitting occurs after 35 to 45 min under constant strain. Transverse seams (fine superficial crack lines) then grow circumferentially upward from each etch pit. Similar transverse seams also develop in regions of the fibre surface which are free of etch pits. Analogous developments occur in the ozone cracking of rubbers. Eventually a network of short, shallow cracks covers the entire fibre surface (see Fig. 6). This process requires 50 to 70 min. Compared to CC fibres at these etching times, the cracks in CH fibres are short and shallow.

During the next hour of etching time, the largest cracks grow circumferentially and open up axially, while the numerous minor cracks disappear. The latter may represent either an undifferentiated etching away of the entire fibre surface or stress relief allowing physical crack closure. As a result of this process, the CH fibre after 150 min (Fig. 7) resembles the CC fibre after 70 min (Fig. 4). The larger cracks continue to grow and deepen with time. After 210 min of boiling, the fibres appear severely stress-cracked.

The time dependence of stress cracking varies considerably from run to run. Nominally identical experimental conditions give variations of up to 40% in time-to-pit, time-to-crack, etc. Part of this variation results from imperfect control of the effective applied tensile stress, due to knot-slipping, frame-bending, etc. Part results from imperfect control of fibre manufacturing; variations in residual stresses, effective draw ratio, fibre diameter, etc. As an example of the latter, the variation in cross-sectional diameter of CH fibres is ± 22% ($= \pm 2\sigma$). The variation in orientation was not measured but is likely considerable.

Figure 6 Fibre CH held at constant strain in boiling hypochlorite solution for 51 min.

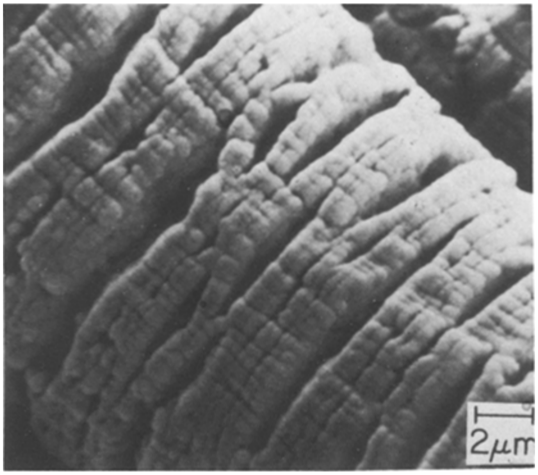

Figure 5 Fibre CC held at constant stress in boiling hypochlorite solution for 27 min.

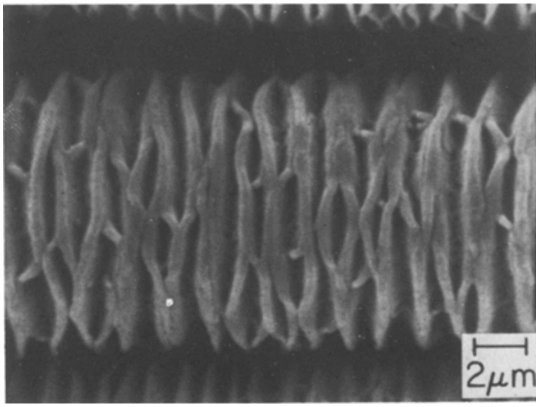

Figure 7 Fibre CH held at constant strain in boiling hypochlorite solution for 150 min.

3.2. Unstressed CC and CH fibres

Fibre samples were tied at one end to a short piece of glass rod, then immersed in 400 ml of gently boiling hypochlorite solution. The weight simply held the fibres in place; the free end of each sample floated unrestrained.

Compared to externally stressed samples, unstressed samples of CC and CH fibres show remarkable resistance to hypochlorite attack. Both types of fibres are unmarked after 50 min. Sharp, narrow cracks appear after 185 min (see Fig. 8). Similar results were obtained for both CC and CH fibres. The major difference is a higher crack density for CH fibres: 14 cracks per 10^{-5} m for CH fibres, as compared with 7 for CC fibres.

The differences in rate of cracking between stressed and unstressed fibres can be explained on the basis of internal and external retractile forces, radial permeability, and chain-packing density. When held under external tension, both CC and CH fibres are subject to a high retractile force. The CC fibres crack faster because their lower orientation allows for more rapid diffusion of hypochlorite solution. Also, the more highly oriented CH fibres have a higher number of load-bearing chains per unit volume, which require more time for cleaving before the crack can grow. Crack initiation and propagation are thus faster in the CC fibres.

In the absence of external tension, the presence of low-level internal retractile forces becomes critical for crack development. These internal retractile forces are higher in CH fibres because of their higher degree of orientation. This compensates for their lower permeability and higher density of stress-bearing chains.

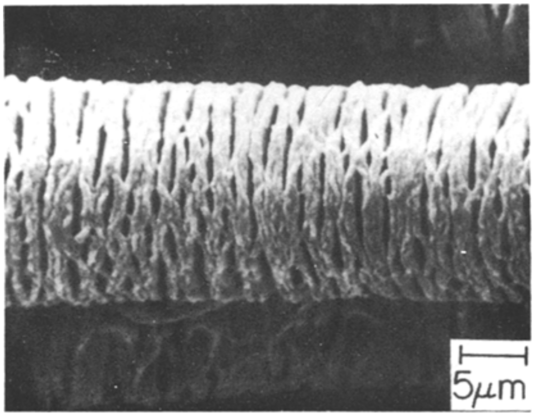

Figure 8 Fibre CC immersed unconstrained in boiling hypochlorite solution for 185 min.

3.3. Stressed DT fibres

Samples of drawn (x 2.5), slightly drawn (x 1.5), and undrawn (x 1) DT fibres were loaded at one end with a 40 g weight; the other end was tied to a horizontal support [calculated stress about 3.2 MPa (470 psi)]. The samples were then immersed in boiling hypochlorite solution for 265 min. A second set of experiments used a 55 g weight (4.4 MPa) for 143 min, at which time the yarns broke.

Undrawn (x 1) and slightly drawn (x 1.5) DT fibres showed no stress-cracking under the experimental conditions. After 265 min boiling in hypochlorite under 3.2 MPa tension, only minor roughening of the surface occurred. After identical treatment, drawn (x 2.5) DT fibres show a network of short, transverse, fine crack lines or seams. Some of the seams have begun to open up slightly. The mean axial separation of the seams was about 0.3 μm.

Drawn DT fibres shows more restistance to stress-cracking, pitting, and surface erosion than do similar M, N, CC, CH or 043 fibres. Since DT is a homopolymer, it has higher degree of local order, denser chain packing, a higher glass transition temperature, and a much lower permeability to aqueous solutions than the copolymer yarns. Hence its greater resistance to attack. The absence of stress cracking in the lightly loaded undrawn samples suggests again that crack initiation is a result of external stresses, internal stresses and time in the etching solution, as well as local order.

3.4. Unstressed N fibres

Samples of N fibres (N1–N6) were boiled without load (one end of the yarns floating free) in hypochlorite solution for 200 min. An additional 180 min of treatment time was imposed on a sample of N1 fibre.

Fibre N1 was unchanged after the 200 min treatment. Short, superficial cracks developed after 380 min (see Fig. 9). The orientation of the cracks is low, and the crack spacing is random (up to 400 nm). Some of the short cracks in Fig. 9 are beginning to link up to form serrated lines oriented at angles of 65 to 90° to the fibre axis (i.e. more or less transverse to the fibre axis). This specimen has the most irregular structure of any of the stress-cracked fibres in the present study.

Results for fibres N1 through N6 after boiling in hypochlorite for 200 min (unloaded) are shown

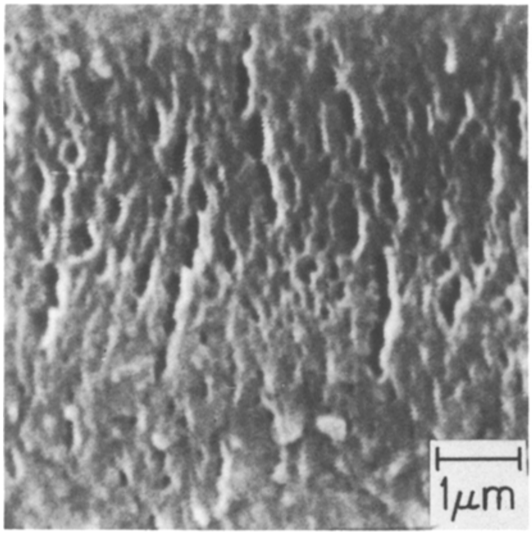

Figure 9 Fibre N1, nominal draw ratio of 1, held at constant strain in boiling hypochlorite solution for 380 min.

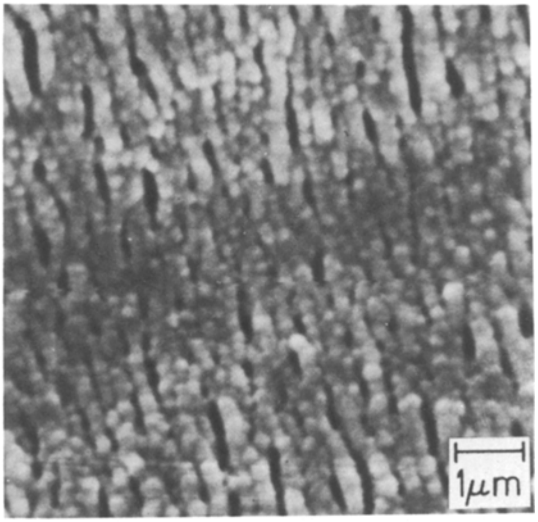

Figure 10 Fibre N6, nominal draw ratio of 6, immersed unconstrained in boiling hypochlorite solution for 200 min.

in Table III. A representative micrograph for the N6 fibre is shown in Fig. 10. The most highly oriented fibre (N6) shows the least crack-opening (i.e. the narrowest crack width) of any of the oriented fibres. It appears to be at a less advanced stage of stress-cracking than the other oriented fibres, presumably because of its lower permeability, higher degree of order, etc. It shows, however, a higher density of cracks and a more regular crack pattern than the other fibres.

When the data in Table III on unstressed acrylic fibres treated in boiling hypochlorite are compared with those in Table I for PET fibres treated with amines, notable similarity in crack spacing as a function of draw ratio is observed. The principal difference between the behaviours of the two types of fibre lies in the more extensive weight loss for undrawn PET fibres. Unstressed acrylic fibres undergo little or no chemical degradation from hypochlorite ion due to the relative inertness of the carbon–carbon backbone. Unstressed PET fibres, on the other hand, undergo rapid chemical degradation by amines due to the susceptibility of the backbone ester linkage to aminolysis.

3.5. Stressed and unstressed O43 fibres

A tow of O43 fibres was stretched over a glass frame and immersed in boiling hypochlorite for various times. After 45 to 55 min faint pinpricks appear over the fibre surface. After 110 min, transverse seams (superficial crack lines) cover the surface; the original pinpricks are still visible

TABLE III Cracking data for N fibres boiled 200 min in hypochlorite (unloaded)

Fibre	Estimated permeability	Overall weight loss (surface corrosion and erosion)	Crack density: Number of transverse cracks per 10^{-5} m	Regularity of spacing; (degree of transverse orientation)	Width of transverse cracks (µm)	Mean number of transverse seams per 10^{-5} m
N1	High	None	0	–	–	0
N2	Moderate	serious pitting	7	Low (distorted, irregular)	0.27	28
N3	Low	None	12	Moderate (fairly regular)	0.22	27
N4	Low	None	14	Moderate (fairly regular)	0.20	29
N6	Low	None	15	High (very regular)	0.12	37

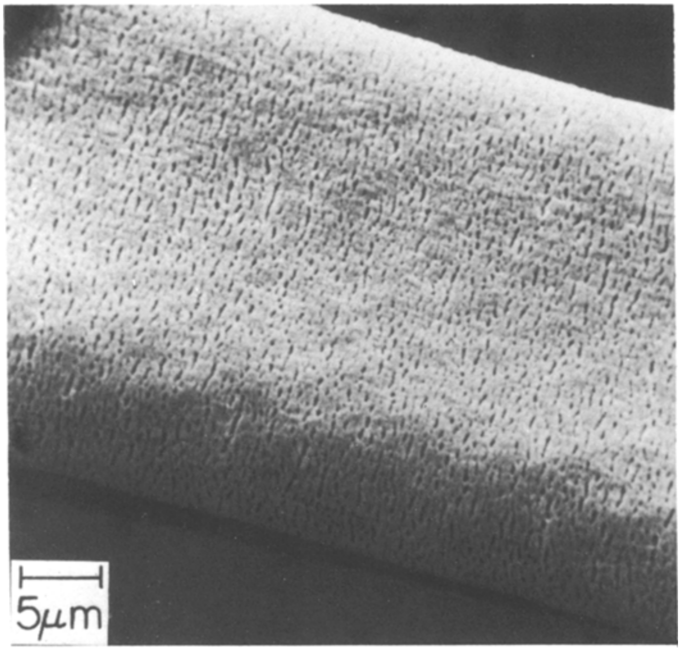

Figure 11 Fibre O43 held at constant strain in boiling hypochlorite solution for 240 min.

as small etch pits, from which seams propagate transversely. After 240 min, short, superficial cracks are scattered over the surface (see Fig. 11). The fibre appears otherwise unaffected with regard to swelling, plasticization, generalized corrosion, etc.

Unstressed fibres are even more resistant to hypochlorite attack. Tiny pits, not much more than simple surface roughening, appear only after 120 min. Cracking appears after 300 min.

3.6. Split fibres

Individual filaments of CC tow and O43 tow were glued onto microscope slides using RTV 108 silicone rubber adhesive. Each filament was split in half lengthwise with a scalpel. The low transverse tenacity of the oriented filaments allowed them to be split easily. The exposed longitudinal cross-section of the filament was somewhat roughened and irregular as a result of this tearing action. A slight fibrillation of the tear surface occurred in some regions. All these surface features were longitudinal in orientation; no transverse cracks, wrinkles, or other irregularities were produced.

The split-fibre mounts were immersed in boiling hypochlorite solution for various times. The external tension on the fibres was very low (just enough to keep them from curling).

The exposed longitudinal cross-section of the split CC fibre was highly susceptible to stress-cracking. After 42 min boiling in hypochlorite, under negligible external tension, the exposed section was covered with fine transverse crack lines (seams) and wide, deep transverse cracks (see Fig. 12). This contrasts with the fibre skin on unsplit fibres, which showed only a few short cracks after the same treatment time. Similarly effects were observed with split O43 fibres. The

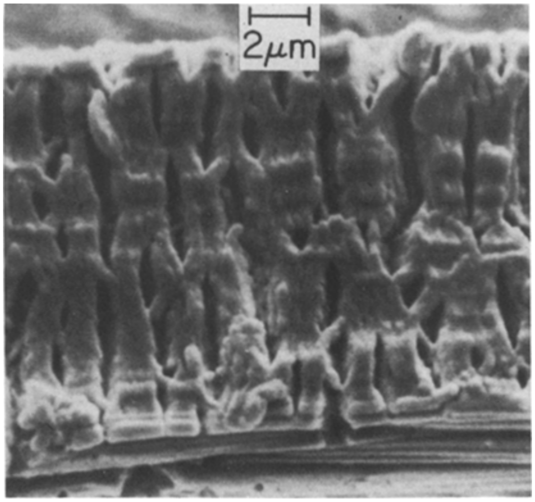

Figure 12 Fibre CC, split to expose fibre core, immersed loosely constrained in 100° C hypochlorite solution for 42 min. The essentially unetched fibre skin is shown at the bottom of the photograph.

exposed surface etched rapidly, with a similar level of cracking being observed after 45 min as seen after 240 min for the unsplit fibres held under external tension.

The split-fibre experiments emphasize the importance of permeability in chemical stress-cracking. The major structural difference between the skin and the core is the higher permeability of the core. (The lower permeability of the skin is a result of: (a) its higher orientation, due to shear during fibre spinning; and (b) its lower porosity, due to more complete mass exchange (solvent removal) during coagulation.) Its higher permeability allows the core of the split fibres to stress-crack rapidly, while the skin remains resistant. Although the core comprises most of the fibre cross-section, the observed resistance of an intact acrylic fibre to chemical stress cracking will be determined by its skin.

3.7. Fibre shrinkage

15 cm lengths of various acrylic fibres were immersed, anchored at one end, in large test tubes filled with boiling hypochlorite solution. Lengths were remeasured after various times, and net shrinkage was calculated. The precision of the shrinkage measurements was about ± 0.4%. The results are plotted in Fig. 13. It is seen that fibre M shows the greatest shrinkage: 10.8%, compared to 6.3% for CH fibres. Despite the high shrinkage, fibre M has a very slow rate of stress cracking. Thus, the amount of fibre shrinkage does not itself determine the rate of chemical stress cracking.

3.8. Annealed fibres

In an attempt to remove latent or residual stresses due to fibre orientation, loose CC yarn and loose 043 tow were annealed in argon for 30 min at 150° C. The annealed fibres plus untreated controls were etched unrestrained in boiling hypochlorite for 120 min.

Annealing at 150° C has no effect on the rate or appearance of stress cracking in CC or 043 fibres. The annealing temperature is about 50° C higher than the suggested glass transition of PAN (polyacrylonitrile) [16]. It is about 10° C higher than the suggested second-order transition for acrylic copolymers [17]. Thus, the strain which can be annealed out is small compared with the residual or latent strain which is locked into the amorphous regions by the cross-linking effect of the ordered regions. Recall that fibres drawn x 6 or more recover only a few per cent. Apparently this residual strain can be activated only by chain

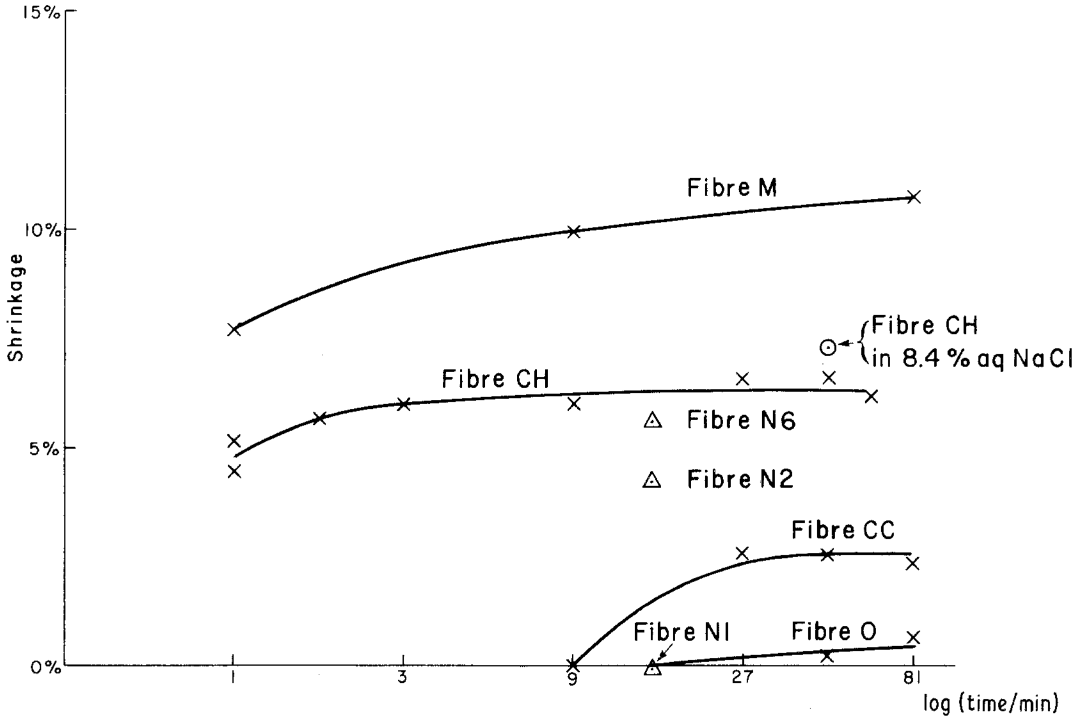

Figure 13 Per cent shrinkage of drawn acrylic fibres upon immersion in boiling water as a function of log time.

cleavage or otherwise disrupting the ordered regions.

In an attempt to remove this refractory residual strain by thermally altering the ordered regions, type M fibres were annealed in the flowing argon at 300° C for 5 sec, and then etched in boiling hypochlorite for 120 min. Unfortunately this high temperature also initiates thermal degradation of the polymer, manifested as a faint yellow tint. The net result is a modest increase in the rate and severity of stress cracking.

3.9. Pyrolysed fibres

Various acrylic fibres were heat treated for 60 min at 225° C in air. Such fibres are considered pyrolysed rather than annealed. They are deeply coloured due to cyclization and oxidation. After 3 min immersion in boiling hypochlorite, they show catastrophic brittle cracking, both axially and circumferentially.

This is a form of brittle mud-cracking: the axial and circumferential stresses are analogous to the in-plane stresses in mud as it dries and shrinks. The observed behaviour is qualitatively different from the CSC observed for unpyrolysed acrylic fibres.

3.10. Plasticized fibres

CH fibres were boiled unrestrained for various times in a 1.5 M NaCl solution. This solution resembles commercial hypochlorite in ionic strength and chemical composition, but it is non-oxidizing, non-nucleophilic, and non-basic. Such fibres are designated CH-S. Other CH fibres were boiled unrestrained for various times in a 1.5 M NaCl solution containing sufficient KOH to provide a pH of 11.2. This solution provides hydroxide ion at a concentration which is double that of commercial hypochlorite solution (pH 10.9). Such fibres are designated CH-K. The resulting fibres were carefully removed from their respective solutions and immediately immersed, unrestrained, in boiling hypochlorite.

The CH-S fibres were quite susceptible to chemical stress cracking. While there was no reaction after 14 min in boiling hypochlorite, long, sharp, narrow cracks develop after just 31 min. This should be compared with 185 min for virgin CH fibres.

The CH-K fibres were reddish in colour, but bleached immediately upon immersion in boiling hypochlorite. Short but well-opened cracks developed after just 14 min. The cracks deepened and widened rapidly so that the fibres showed extensive cracking after 31 min. For comparison, even stressed CH virgin fibres required about 150 min to reach a comparable level of cracking.

The results indicate that boiling water plasticization and nucleophilic hydrolysis each facilitate chemical stress cracking, causing a dramatic (5 to 15 fold) acceleration in the rate of CSC. It seems, therefore, possible that plasticization or preliminary hydrolysis of the fibres is an important first step in CSC by hypochlorite solutions.

Plasticization of the amorphous regions of the fibre would increase permeability and also facilitate chain retraction after scission by hypochlorite. As discussed in Section 1, plasticization accelerates CSC by increasing the molecular mobility.

The results on both annealed and plasticized fibres illustrate the refractory nature of the chain orientation in acrylic fibres. This orientation remains substantially unaltered by plasticizing agents or temperatures above the glass transition. The liquid crystalline regions in acrylic fibres act as giant cross-links and prevent chain retraction. Before chains can retract more than a few per cent, chemical bonds must be cleaved. In CC and CH fibres, it appears impossible to destroy the chain orientation by any simple thermal treatment, since the nitrile units begin to cyclize well before the liquid crystal domains melt or lose their *c*-axis rigidity. This refractory orientation is critical for the production of high-tenacity carbon fibres, since disruption of orientation degrades the mechanical properties of the final product.

4. Concluding discussion

The specific chemical processes involved in the reaction between alkaline hypochlorite and acrylic fibres remains obscure. Aliphatic nitriles are resistant to hot alkaline hypochlorite; and indeed acetonitrile can be used as an inert solvent. There may be a small amount of hydrolysis to aliphatic carboxylate; but the latter is inert to hypochlorite oxidation. If the amide is formed by hydrolysis, it would probably undergo the Hofmann reaction to form the amine.

The probable mechanism involves base attack on the nitrile group, causing a small amount of nitrile polymerization, followed by hypochlorite attack on the polymerized nitrile groups which then leads to chain scission. Acrylic polymers in solution are readily attacked by base to form reddish to blackish solutions, depending upon the polymer and base concentrations [18]. The polymerized nitrile groups formed by base attack are then readily decoloured by the hypochlorite ion. The action of base on acrylic fibres produces a reddish colour which disappears immediately upon immersion in hot hypochlorite.

A mechanism of hypochlorite attack can be written similar to that used to describe the decolouration reaction in stabilized acrylic fibres [2]. The stabilized fibres have also undergone some hydrogen elimination to form an aromatic heterocyclic. To adapt that mechanism to the present case requires an additional mechanism for aromatization prior to chain scission. In view of the complexity of reactions involved, it seems preferable to suggest simply a concerted base and hypochlorite differs from CSC of PET fibres by amines in that unoriented (x 1) or negligibly oriented (x 1.5) acrylic fibres seems immune to stress cracking. Even after long immersion under external tension, the homopolymer DT fibre is unaffected. Fibre N1, a copolymer, is only slightly more susceptible. In contrast, unoriented PET homopolymer rapidly stress cracks when placed under modest external tension. The difference is not due to any chemical inertness of acrylic polymers, because oriented fibre DT (x 2.5) and fibre N (x 2) develop distinct stress-cracks under similar conditions.

The differences in susceptibility to stress-cracking between oriented and unoriented acrylic fibres may be understood in terms of the surface reactions which any polymer will undergo when exposed to a stress-cracking reagent:

Stage	Surface material	Molecular weight of surface material
I	Intact polymer–strong, elastic	High
II	Partially cleaved polymer–still somewhat elastic	Moderately high
III	Extensively cleaved–tacky viscous fluid	Moderate

Only Stage II is conducive to crack formation and growth. Once molecular weight degradation has proceeded to Stage III, the tacky sludge surrounding a nascent etch pit or crack seam will act as a protective layer, retarding further attack. The characteristic morphological change will no longer be elastic retraction of the cleaved chains to form the growing crack, but rather viscous flow and relaxation which fill in and blunt the crack tips.

A similar effect occurs with ozone/rubber stress cracking. Unstressed rubber is immune to ozone cracking because of the formation of a protective viscous surface layer composed of degraded rubber molecules. In ozone/rubber or hypochlorite/acrylic stress cracking, a key function of the nascent etch pit or crack seam is to give the reagent access to fresh, undegraded substrate at the crack tip. But an opposite effect also occurs as a degraded surface layer forms within the crack itself. This degraded material restricts the rate of arrival of the reagent, in contrast to its unrestricted access to the original polymer surface. Chain cleavage then tends to occur outside the original nascent crack; unless chain-retractile forces manage to pull the crack open and expose more fresh surface area.

In the case of PET, the amine stress-cracking reagent can diffuse though the bulk polymer at a fairly rapid rate, as indicated by morphological changes observed in transmission electron microscopy. In contrast, the penetration of acrylic fibres by hypochlorite is a very slow process [3].

In summary, chemical stress cracking is defined and characterized by the combination of chemical chain scission with subsequent mechanical chain retraction. Oriented acrylic fibres exhibit a regular transverse crack pattern after boiling for periods in the range of 2 h in alkaline sodium hypochlorite solutions. Such chemical stress cracking of acrylic fibres in boiling hypochlorite is shown to be accelerated by:

(a) External tensile stress. A constant stress of a few MPa causes extensive cracking after just 27 min.

(b) Plasticization. Oriented fibres plasticized by boiling in water for 3.5 h exhibit deep, extensive stress-cracking after just 31 min in hypochlorite (unloaded).

Plasticization by water increases both the polymer chain mobility and the permeability to hypochlorite ions. The increase in chain mobility can activate entropic retraction forces in the oriented molecules. These retraction forces can also be activated by a small amount of chain-backbone cleavage. Too much cleavage reduces or eliminates, however, the entropic retraction forces, as the viscous degradation product cannot support a stress and flows rather than cracks.

Boiling water or salt solutions (isotonic with the hypochlorite solution) cause less than 7% shrinkage even in highly oriented acrylic fibres. This leaves most of the original fibre orientation intact. In boiling hypochlorite solution, the combination of water plasticization and localized chain scission apparently activates this residual orientation, causing chain retraction at each point of attack. Crack initiation and growth ensue,

(c) Moderate orientation. Fibres with moderate orientation ($DR \approx 6.5$) suffer the most rapid and extensive stress-cracking. Highly oriented ($DR \approx 11$) acrylic fibres stress-crack more slowly and less deeply, This is due to their lower solute permeability and their higher density of load-bearing chains (which must all be cleaved). These two factors outweigh the higher latent retractile forces in the highly oriented fibres.

(d) High permeability. The effects of permeability on stress-cracking appear graphically in the photographs of split fibres. In split Orlon fibres, e.g. the exposed permeable core is rapidly covered with a network of fine cracks, while the dense skin is almost unaffected. For intact acrylic fibres, the resistance to stress-cracking is determined largely by the properties of the thin, dense, protective skin.

Acknowledgements

The impetus for this work arose from an extended discussion with Dr William Watt who first observed hypochlorite chemical stress cracking, explored this reaction as a possible method of enhancing the surface area of carbon fibres, and drew our attention to the similarity of the patterns produced by cryogenic ion etching and by chemical stress cracking.

Financial support was provided by the Office of Naval Research. This support is gratefully acknowledged, as are stimulating discussion with Professor A. Argon of MIT. Also acknowledged is the support of the John Simon Guggenheim Foundation, who provided one ot the authors (DRU) with a Fellowship for the 1981–82 year.

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Received 14 May
and accepted 14 September 1982