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CHEMICAL STRESS CRACKING OF ACRYLIC FIBERS

by

J. Herms, L.H. Peebles, Jr. and D.R. Uhlmann

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ABSTRACT

The generation of periodic microscopic transverse cracks in oriented acrylic fibers 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 fiber permeability, moderate fiber orientation, and water-plasticization. The proposed mechanism for bond cleavage involves cyclization of nitrile groups (similar to the "prefatory reaction" in pyrolysis of acrylic fibers), 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 fiber morphology. The cracking process does, however, appear to be a sensitive indicator of residual latent strain in the fiber, which may persist even after high-temperature annealing.

I. INTRODUCTION

An earlier study by Warner et al. (1) on the cryogenic ion etching of oriented acrylic fibers, stabilized acrylic fibers, and carbon fibers made from acrylic fibers reported the observation of periodic transverse striations on a sub-micron 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 fiber axis and the periodicity of the striations led to the proposal that the original acrylic fibers were hetero-geneous and that heterogeneities persisted throughout the process as the acrylic fiber was converted to carbon fiber.

Dr. William Watt (private communication) drew our attention to the similarity in scanning electron micrographs between acrylic fibers subjected to the cryogenic ion etching and acrylic fibers 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 fiber. The present paper reports on the chemical etching of acrylic fibers by hot hypochlorite solutions in relation to fiber orientation, tensile stress, chemical composition, plasticization, and other factors. It will be shown that the etching behavior does not reflect underlying hetero-geneities in the fibers, as originally thought, but represents a form of chemical stress cracking.

The present work differs from that previously reported on the decoloration of stabilized acrylic fibers (2) in two important aspects. The material under investigation in the present study is as-received acrylic fiber exposed

to alkaline hypochlorite at the boil. The material used in the decoloration study had undergone partial stabilization reactions by heating the as-received fibers at about 230 C in air for various periods of time. The stabilization process causes both chemical and color changes in the fibers. The partially stabilized fibers 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 decades (3-6, e.g.); and the interested reader is referred to them for extensive bibliographies as well as insightful 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.

A. 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--viz. 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.

B. Chemical Stress Cracking (CSC)

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

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. In contrast to simple tensile cracking in the absence of a CSC agent, the total strain at the crack tip in ozone cracking of rubber is low--about 30% for ozone cracking vs. 700% for ordinary tensile cracking (8). In this form of CSC, as in others, 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 restricted 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 500 $\overset{\circ}{A}$ or less in width (Stage II). Still later in the reaction, 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 further impedes attack by the chemical agent (Stage III).

The initial microcracks of Stage I are typically spaced less than 1 μm apart. As the more rapidly growing microcracks open up, they relieve much of the longitudinal stress in the adjoining surface regions. The smaller microcracks in these regions stop growing as the stress is relieved. They are subsequently obliterated by the gradual progression of undifferentiated uniform surface degradation, by dissolution, or by stress relaxation. Only a small percentage of the original microcracks attain macroscopic dimensions; the rest disappear.

In ozone cracking of rubber, the crack initiation rate, the circumferential propagation rate, and the crack density all increase with strain up to 70% strain. The radial penetration rate for an existing crack is, however, independent of strain, once the critical strain energy density has been achieved--typically at 3-5% strain for most rubbers. Radial crack propagation is limited by the rate of ozone diffusion, which in turn is independent of strain. In contrast, circumferential propagation is not limited by ozone diffusion, since the surface of the fiber suffers a substantially uniform extent of bond scission by ozone.

2. Amine Cracking of PET

Amine stress-cracking of PET fibers is similar in many respects of ozone/ rubber cracking; but the appearance of the affected polymer surface is markedly different. Sweet & 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 minutes.

Undrawn filaments which were not loaded showed much greater resistance to cracking. After 4 hr 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 fiber orientation on the development of stress cracks in methylamine-treated PET are summarized in Table I. 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 2X to 4X. This very likely reflects a decreased permeability of the fibers and an increased concentration of load-bearing chains with increasing DR.

Increasing the fiber 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 behavior 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 fiber. This likely corresponds to variations in the fiber spinning or drawing processes. Sweet and Bell found a 20% variation in birefringence for different regions of a single PET filament, and an additional 20% variation for PET filaments with nominally identical draw ratios.

A major difference between ozone/rubber cracking and amine/PET cracking lies in the overall appearance of the etched surface. The rigid semi-crystalline PET fibers do not show the initial etch pits and the fine seams

that occur in the elastomeric, amorphous rubber. PET fibers simply show an incubation period of 0-2 hours with no surface alterations, followed by the appearance of short, distinct, sharp-edged cracks which rapidly deepen and widen.

3. Other Types of Chemical Stress Cracking

Hinton and Keller (11) made a definitive study of the CSC of compression-molded HDPE 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 hours. Oriented material held under 25% of the yield stress reacted more slowly, with a time-to-failure of 20 hours. 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 hours. Oriented unstressed material developed cracks parallel to the direction of orientation. This is not CSC (by definition), but rather a "structural etch." Polythylene 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 total absence of plasticization in the HDPE/HNO$_2$ system.

E. 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" fibers is sufficient to cause chain retraction and stress-cracking. In contrast, ESC 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.

With this background, let us consider the effect of hypochlorite solutions on acrylic fibers.

II. EXPERIMENTAL PROCEDURES

A. Hypochlorite Reagent

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

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

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

$$NaOCl + NaClO_2 \xrightarrow{fast} NaClO_3 + NaCl \qquad (1b)$$
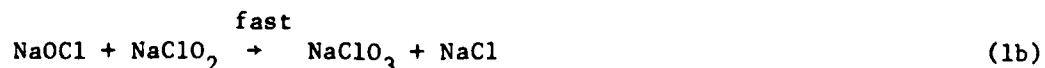
The rate of disproportionation increases with increased hypochlorite concentration, increased acidity, and increased temperature. Extrapolation of Lister's (13) results gives the following relation:

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

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

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 resistant 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 ($\sim$ 1 hr) and Hysol oven-cured "Epoxi-Patch" ($\sim$3 hr).

Standard etching conditions involved roughly 1/2 gram of acrylic fiber 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 fiber. With such an excess of hypochlorite, the effective concentration should not be diminished by reaction with the fiber 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 products--presumably oxygen or chloramine-- from the hot solution and their entrapment in the loose fibers caused the fibers to float on the top of the hot solution. To keep the fibers 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 fibers in the alkaline solutions. To verify this suggestion, CH-type fibers (see Table II below for identification) and heat-treated stabilized acrylic fibers 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 fibers.

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 thirty minutes. No observable effects resulted from exposure of the fibers to HOCl solutions for 130 min. at 98 C.

Fibers were also boiled for 210 min. in 1.5 M NaCl without observable etching, although the fibers were definitely plasticized by this treatment. Other fibers were boiled in 1.5 M NaCl containing sufficient KOH to give

a solution with pH $\sim$ 11.2, or roughly double the hydroxide concentration of commercial hypochlorite solution (pH $\sim$ 10.9). These fibers become reddish in color 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.

B. Fiber Samples

The acrylic fiber samples are described in Table II. The nominally undrawn N1 fiber 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 Fiber D was prepared by extending the fiber while submerged in hot (155 C) glycerol. Control samples were subjected to hot glycerol treatment for two minutes without tension.

C. Scanning Electron Microscopy (SEM)

After immersion in not 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 fibers. A small section was then mounted with silver paint onto an aluminum SEM tab. The mounted fibers were dried overnight in a desiccator then coated at two different angles to give a gold layer several hundred $\overset{\circ}{A}$ thick.

To ensure that the cracks were not caused by the drying process (i.e., mud cracking), a sample of CC fiber was carefully freeze-dried after 60 min. etching at 100 C, then gold coated. The fiber appearance was indistinguishable from a similarity etched fiber dried at room temperature.

III. RESULTS AND DISCUSSION

Etching of oriented acrylic fibers by boiling alkaline hypochlorite solution appears to be a classical example of chemical 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.

A. Stressed CC and CH Fibers

The initial stages of hypochlorite cracking are very similar to those observed in ozone/rubber cracking. CC fibers (DR $\sim$ 6.5) and CH fibers (DR $\sim$ 11) were stretched tightly over a glass frame (effective strain 0.7-0.8%) and subjected to boiling hypochlorite solution. Under such constant-strain conditions, both types of fiber have an induction period for stress-cracking of about 35 min. The appearance of the fibers remains unchanged throughout this period, except for a barely-discernible surface roughening.

In CC fibers, 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 fiber in Fig. 1). The cracks then deepen and widen.

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 $\sim$5.5 MPa. These pinhole pits and short seams rapidly deepen, widen and lengthen to give an interleaving network of sharp cracks (see the fibers

on the left side of Fig. 3). Note the difference in appearance between the fiber furthest to the left and the fibers on the right. The last are more extensively degraded, resembling water-plasticized fibers (see below).

After 70 min. under tension in boiling hypochlorite, CC fibers are covered with deep stress cracks, as in Fig. 4. Extensive plasticization of the surface regions of the fiber is responsible for the serpentine appearance of the cracks and the rounded aspect of the crack edges. In contrast, unplasticized fibers, as illustrated by PET in amines, invariably develop sharp-edged cracks with no rounding or softening. After 80 min. under tension, the CC fibers 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 into these regions. This is shown in Fig. 5.

CH fibers are somewhat more resistant to hypochlorite stress-cracking than CC fibers. Scattered pitting occurs after 35-45 min. under constant strain. Transverse seams (fine superficial crack lines) then grow circumferentially outward from each etch pit. Similar transverse seams also develop in regions of the fiber 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 fiber surface (see Fig. 6). This process requires 50-70 min. Compared to CC fibers at these etching times, the cracks in CH fibers are quite 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 does not represent crack healing, bur rather either an undifferentiated etching away of the entire fiber surface or stress relief which allows crack closure. As a result of this process, the CH fiber after 150 min. (Fig. 7) resembles the CC fiber after 70 min. (Fig. 4). The larger cracks continue to grow and deepen with time. After 210 min. of boiling, the fibers 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 of it results from imperfect control of fiber manufacturing--variations in residual stresses, effective draw ratio, fiber diameter, etc. As an example, the variation in cross-sectional diameter for CH fibers is $\pm$ 22% ($= \pm$ 2σ). The variation in orientation was not measured but is likely considerable.

B. Unstressed CC and CH Fibers

Fiber 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 served simply to "anchor" the fibers in place; the free end of each sample floated unrestrained.

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

These phenomena may 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 fibers are subject to a high retractile force. The CC fibers crack faster because their lower orientation allows for more rapid diffusion of hypochlorite solution. Also, the more highly oriented CH fibers 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 fibers.

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 fibers because of their higher degree of orientation. This compensates for their lower permeability and higher density of stress-bearing chains.

C. Stressed DT Fibers

Samples of drawn (2.5X), slightly drawn (1.5X), and undrawn (1X) DT fibers were loaded at one end with a 40g weight; the other end was tied to a horizontal support (calculated stress ∿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 weight (4.4 MPa) for 143 min., at which time the yarns broke.

Undrawn (1X) and slightly drawn (1.5X) DT fibers 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 (2.5X) DT fibers shows 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 fibers shows more resistance to stress-cracking, pitting, and surface erosion than do similar M, N, CC, CH or 043 fibers. 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.

D. Unstressed N Fibers

Samples of N fibers (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 fiber.

Fiber 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 4000 $\overset{o}{A}$). Some of the short cracks in Fig. 9 are beginning to link up to form serrated lines oriented at angles of 65-90° to the fiber axis (i.e., more or less transverse to the fiber axis). This specimen has the most irregular structure of any of the stress-cracked fibers in the present study.

Results for fibers N1 through N6 after boiling in hypochlorite for 200 min. (unloaded) are shown in Table III. A representative micrograph for the N6 fiber is shown in Fig. 10. The most highly oriented fiber (N6) shows the least crack-opening (i.e., the narrowest crack width) of any of the oriented fibers. It appears to be at a less advanced stage of stress-cracking than the other oriented fibers, 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 fibers.

When the data in Table III on unstressed acrylic fibers treated in boiling hypochlorite are compared with those in Table I for PET fibers

treated with amines, notable similarity in crack spacing as a function of draw ratio is observed. The principal difference between the behaviors of the two types of fiber lies in the extent of overall weight loss for undrawn fibers. Unstressed acrylic fibers undergo little or no chemical degradation from hypochlorite ion due to the relative inertness of the carbon-carbon backbone. Unstressed PET fibers, on the other hand, undergo rapid chemical degradation by amines due to the susceptibility of the backbone ester linkage to aminolysis.

E. Stressed and Unstressed 043 Fibers

A tow of 043 fibers was stretched over a glass frame and immersed in boiling hypochlorite solutions for various times. After 45-55 min. faint pinpricks appear over the fiber surface. After 110 min., transverse seams (superficial crack lines) cover the surface; the original pinpricks are still visible as small etch pits, from which seams propagate transversely. After 240 min., short, superficial cracks are scattered over the surface (see Fig. 11). The fiber appears otherwise unaffected with regard to swelling, plasticization, generalized corrosion, etc.

Unstressed fibers 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.

F. Split Fibers

Individual filaments of CC tow and 043 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 <u>longitudinal</u> in orientation; no transverse cracks, wrinkles, or other irregularities were produced.

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

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

Similar effects are observed with split 043 fibers. The exposed surface etches rapidly with a similar level of cracking being observed after 45 min., as seen after 240 min. for the unsplit fibers held under external tension.

The split-fiber 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: (1) its higher orientation, due to shear during fiber spinning; and (2) its lower porosity (higher density), due to more complete mass exchange (solvent removal) during coagulation.] Its higher permeability allows the core of the split fibers to stress-crack rapidly, while the skin remains resistant. Although the core comprises most of the fiber cross-section, the observed resistance of an intact acrylic fiber to chemical stress cracking will be determined by its skin. The comparatively dense, impermeable skin protects the core from rapid attack.

G. Fiber Shrinkage

15-cm lengths of various acrylic fibers were immersed in large test tubes filled with boiling hypochlorite solution. The fibers were anchored at one end. Lengths were re-measured after various boiling times, and net shrinkage was calculated. The precision of the shrinkage measurements was about $\pm$ 0.4%.

The results are plotted in Fig. 13. It is seen that Fiber M shows the greatest shrinkage: 10.8%, vs. 6.3% for CH fibers. Despite the high shrinkage, Fiber M has a very slow rate of stress cracking. Thus, the amount of fiber shrinkage does not itself determine the rate of chemical stress cracking.

H. Annealed Fibers

In an attempt to remove latent or residual stresses due to fiber orientation, loose CC yarn and loose 0.43 tow were annealed in argon for 30 min. at 150 C. The annealed fibers plus untreated controls were etched unrestrained in boiling hypochlorite for 120 min. In a similar test, loose Fiber M yarn was annealed in flowing argon for 5 sec at 300 C. The annealed fibers were then etched in boiling hypochlorite for 210 min.

Annealing at 150 C has no effect on the rate or appearance of stress cracking in CC or 043 fibers. The annealing temperature is about 50 C higher than the suggested glass transition of PAN (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 fibers drawn 6X or more recover only a few percent. Apparently this residual

strain can be activated only by chain cleavage or otherwise disrupting the ordered regions.

In an attempt to remove this refractory residual strain by thermally altering the ordered regions, type M fibers were annealed at 300 C for 5 sec. 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.

I. Pyrolyzed Fibers

Various acrylic fibers were heat treated for 60 min. at 225 C in air. Such fibers are considered pyrolyzed rather than annealed. They are deeply colored 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 those in mud as it dies and shrinks. The observed behavior is qualitatively different from the CSC observed for unpyrolyzed acrylic fibers.

J. Plasticized Fibers

CH fibers 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 fibers are designated CH-S. Other CH fibers 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 fibers are designated CH-K. The resulting fibers were carefully removed from their respective solutions and immediately immersed, unrestrained, in boiling hypochlorite.

The CH-S fibers 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 fibers.

The CH-K fibers were reddish in color, 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 fibers showed extensive cracking after 31 min. For comparison, even stressed CH virgin fibers 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 fibers is an important first step in CSC by hypochlorite solutions.

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

The results on both annealed and plasticized fibers illustrate the refractory nature of the chain orientation in acrylic fibers. This orientation remains substantially unaltered by plasticizing agents or temperatures above the glass transition. The liquid crystalline regions

in acrylic fibers act as giant cross-links and prevent chain retraction.
Before chains can retract more than a few percent, chemical bonds must be
cleaved. In CC and CH fibers, 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 fibers, since disruption of orientation degrades the
mechanical properties of the final product.

Determination of the structural changes produced by very long etching
times is precluded by the tendency of acrylic fibers to disintegrate after
boiling in hypochlorite for several hours. For example, CH fibers which
have been boiled for 155 min. disintegrate into fine chaff during attempts
to remove them from the hypochlorite bath, and such fibers spontaneously
disintegrate into fine chaff after about 180 min. boiling. In the latter
case, mechanical stresses due to gentle flexing in thermal eddy currents
are sufficient to break up the weakened fibers.

The resulting chaff consists of tiny pieces of fiber up to ~ 0.2 mm
in length. The diameter remains approximately constant; and the original
cylindrical appearance is unchanged; hence no gross swelling, congealing,
or fibrillation seems to occur.

If special care is taken to minimize thermal eddy currents (bath
temperature maintained at 98-99 C to reduce bubble formation, etc.), CH
fibers can be treated in hypochlorite solution for 420 min. without
disintegrating. After 315 min., a few of the larger cracks have grown
considerably and now cover one or more radians of arc. The smaller cracks
have partially disappeared--the result of generalized surface degradation/
dissolution in the presence of overall stress relief. The remnants of these

cracks appear only as faint lines in the regions midway between the large cracks (see Fig. 14).

After 420 min., the smaller cracks have completely disappeared. The overall fiber diameter may have decreased slightly. The fibers are quite soft and weak (the result of extensive plasticization and degradation). Even more dramatic is the distorted, irregular crack pattern (see Fig. 15). The skewed alignment of the cracks is likely the result of decreased orientation of the plasticized polymer chains in the surface regions.

Note that crack propagation is no longer limited to the circumferential direction. Cracks link up with each other diagonally or even axially. The occurrence of diagonal, and even axial, cracking in these fibers suggests that the orientation in the surface layer has decreased markedly from its original value. An illusory healing of the smaller cracks also appears to occur in these softened fibers, due to generalized etching away of the fiber surface. A similar phenomenon has been reported for ozone/ rubber CSC (see Ref. 8). Crack closing but not healing can also occur from stress relaxation.

IV. CONCLUDING DISCUSSION

The specific chemical processes involved in the reaction between alkaline hypochlorite and acrylic fibers 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. Acrylic powders in strong base turn bright red during the conversion to colorless carboxylate salts. Once a small amount of polymerized nitrile groups is formed by base, these groups are then readily decolored by the hypochlorite ion. The action of base on acrylic fibers produces a reddish color which disappears immediately upon immersion in hot hypochlorite.

A mechanism of hypochlorite attack can be written similar to that used to describe the decoloration reaction in stabilized acrylic fibers. The stabilized fibers 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 effect leading to chain scission.

CSC of acrylic fibers by hypochlorite differs from CSC of PET fibers by amines in that unoriented (1X) or negligibly oriented (1.5X) acrylic fibers seems immune to stress cracking. Even after long immersion under high external tension, the homopolymer DT fiber is completely unaffected. Fiber 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 fiber DT (2.5X) and fiber N (2X) develop distinct stress-cracks under similar conditions.

The differences in susceptibility to stress-cracking between oriented and unoriented acrylic fibers may be understood on the following basis: Any polymer will undergo the following surface reactions when exposed to a reagent appropriate for stress-cracking:

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 driven by surface tension to 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 oily 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 <u>outside</u> 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 through the bulk polymer at a fairly rapid rate, as indicated by morphological changes observed in transmission electron microscopy. In contrast, the penetration of acrylic fibers 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 fibers exhibit a regular transverse crack pattern after boiling for periods in the range of 2 hours in alkaline sodium hypochlorite solutions. Such chemical stress cracking of acrylic fibers in boiling hypochlorite is shown to be accelerated by:

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

(b) <u>Plasticization</u>. Oriented fibers plasticized by boiling in water for 3.5 hrs. 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 fibers. This

leaves most of the original fiber 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) <u>Moderate orientation</u>. Fibers with moderate orientation (D.R.$\sim$ 6.5) suffer the most rapid and extensive stress-cracking. Highly oriented (D.R. $\sim$ 11) acrylic fibers 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 fibers.

Solute permeability and density of load-bearing chains seem to be the key factors in determining the rate of crack growth. The latent retractile force, assuming it is greater than zero, has little effect on the rate of crack growth.

Acrylic fibers which have <u>zero</u> latent retractile force (i.e., D.R.=1) show no stress-cracking at all (even when externally stressed). This is significant and indicates that a protective layer of degraded polymer "sludge" may be forming on the fiber surface before cracking can initiate.

(d) <u>High permeability</u>. The effect of permeability on stress-cracking appear graphically in the photographs of split fibers. In split Orlon fibers, 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 fibers, the resistance to stress-cracking is determined largely by the properties of the thin, dense, protective skin.

ACKNOWLEDGEMENTS

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Cleveland, 1971).

Table I

Cracking Data for PET Fibers in 40% Methylamine
(No External Stress), after Ref. 10

Fiber draw ratio	Estimated permeability	Rate of overall weight loss	Rate of stress-crack development	Ultimate crack density	Regularity of Spacing Degree of transverse orientation
1X	High	Moderate	Zero	-	-
2X	High	High	High	Low	Low
3X	Moderate	Moderate	Moderate	Moderate	Moderate
4X	Low	Low	Low	High	High

33.

Table II

Acrylic Fibers 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 approx. 11. ~1.5 dpf.
043	Orlon 43	Du Pont	6% methul acrylate 1% sodium styrene p-sulfonate	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.

Table III

Cracking Data for N Fibers Boiled 200 min in Hypochlorite (Unloaded)

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

FIGURE CAPTIONS

Fig. 1 - Fiber CC held at constant strain in boiling hypochlorite solution
for 45 min.

Fig. 2 - Fiber CC held at constant stress in boiling hypochlorite solution
for 27 min.

Fig. 3 - Fiber CC held at constant stress in boiling hypochlorite solution
for 40 min.

Fig. 4 - Fiber CC held at constant strain in boiling hypochlorite solution
for 70 min.

Fig. 5 - Fiber CC held at constant stress in boiling hypochlorite solution
for 27 min.

Fig. 6 - Fiber CH held at constant strain in boiling hypochlorite solution
for 51 min.

Fig. 7 - Fiber CH held at constant strain in boiling hypochlorite solution
for 150 min.

Fig. 8 - Fiber CC immersed unconstrained in boiling hypochlorite solution
for 185 min.

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

Fig.10 - Fiber N6, nominal draw ratio of 6, immersed unconstrained in
boiling hypochlorite solution for 200 min.

Fig.11 - Fiber 043 held at constant strain in boiling hypochlorite solution
for 240 min.

Fig. 12 – Fiber CC, split to expose fiber core, immersed loosely constrained in 100 C hypochlorite solution for 42 min. The essentially unetched fiber skin is shown at the bottom of the photograph.

Fig. 13 – Percent shrinkage of drawn acrylic fibers upon immersion in boiling water as a function of log time.
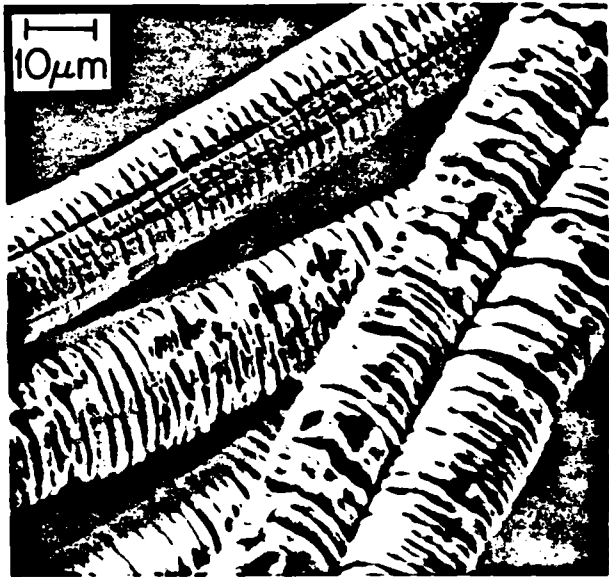
Fig. 14 – Fiber CH immersed unconstrained in boiling hypochlorite solution for 315 min.
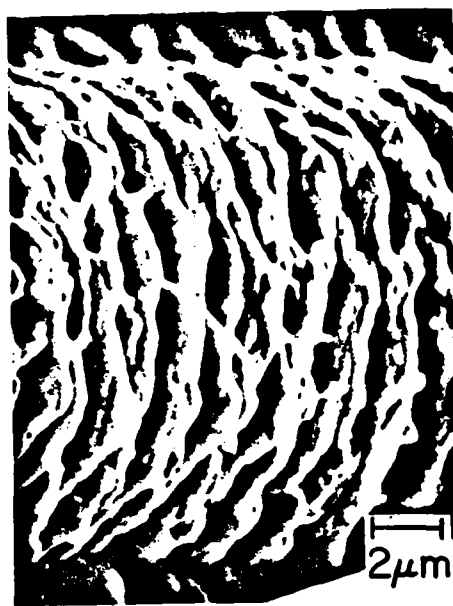
Fig. 15 – Fiber CH immersed unconstrained in boiling hypochlorite solution for 420 min.
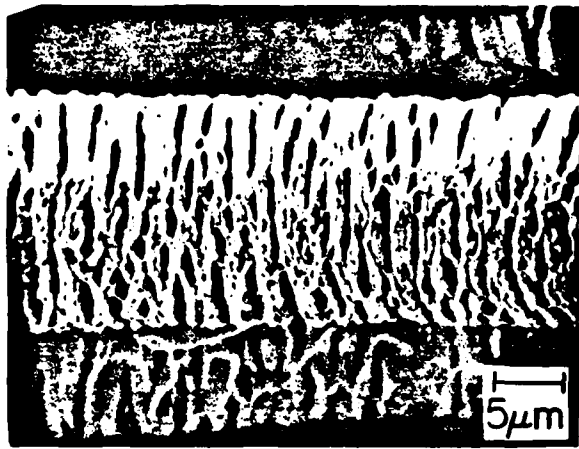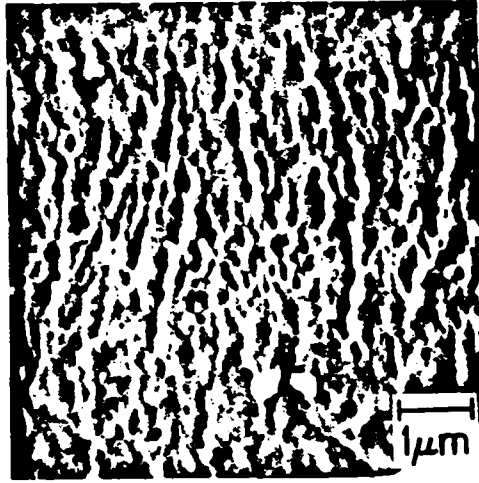
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0.5μm

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2μm

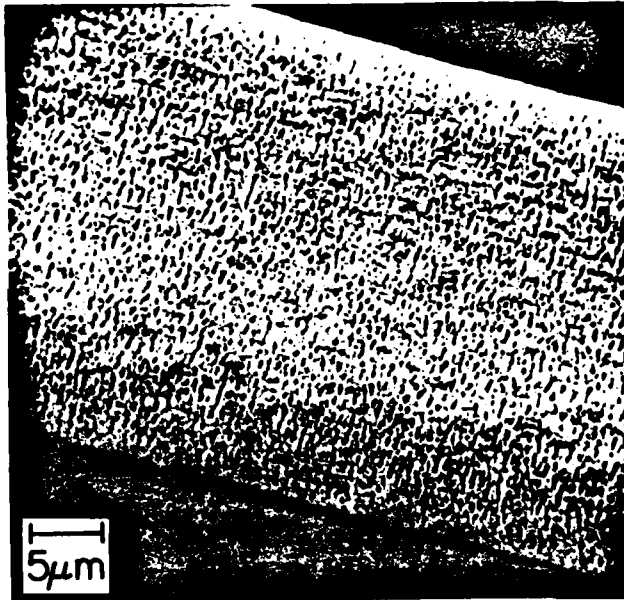2μm

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