

The Crosslinking of Chitosan Fibers

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SYNOPSIS

A need exists for the development of totally biodegradable packaging materials. Chitosan is an under-utilized polymer which possesses many of the desired characteristics for this application. This article describes the crosslinking of chitosan fibers. Epichlorohydrin (ECH) was selected as a convenient base catalyzed crosslinking agent. The strength of chitosan fibers, especially wet tenacity, is improved by crosslinking. © 1992 John Wiley & Sons, Inc.

Keywords: chitin • chitosan • fibers • crosslinking • epichlorohydrin • film

INTRODUCTION

A need exists for the development of biodegradable packaging materials. Chitosan is an under-utilized polymer which possesses many of the desired characteristics for this application, i.e., it is readily mineralized in the environment, by the action of microbes and weathering. It is already known to be suitable for biomedical implants, degradable sutures, slow release delivery of drugs, etc. In earlier work, Kaplan et al.¹ and Arcidancono et al.² described the biosynthesis of chitosan and how it could be controlled in a fungus to yield chitosan polymers of controlled molecular weight distributions. The subsequent functional properties of the films cast from these polymers can thus be tailored to the application desired.

This article describes our work to crosslink chitosan fibers. It is our objective to improve the functional properties of this material. Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose. Chitosan, however, is less easily defined as it is difficult to fully deacetylate chitin. Chitosan is a preferred form of the polymer though, as it is a more tractable form to process into fibers or films than chitin. A drawback of chitosan is its enhanced hydrophilicity compared to chitin,

which results in a considerable loss of tensile strength when wet.

Epichlorohydrin (ECH) was selected as a convenient base catalyzed crosslinking agent. An advantage of ECH is that it does not eliminate the cationic amine function of chitosan. Most notably, the crosslinking by ECH considerably improves the wet strength of the chitosan films.³ A similar effect is also described here, for the crosslinked fibers.

EXPERIMENTAL

Materials

Powdered crab shell chitin was obtained from Sigma Chemical Co. The chitosan used for fiber preparation was obtained by the hydrolysis of chitin. Two hundred grams of chitin powder was added to 50% NaOH (2000 mL) in a 3 L flask. The mixture was purged with nitrogen and stirred for 2 h at 100°C. The reactor was then placed in an ice bath and cooled to room temperature. The chitosan was filtered off, repeatedly washed until the filtrate was neutral at pH 7, then washed with ether, and air-dried. The process was repeated to increase the degree of deacetylation.

Analytical Methods

Percent N-Acetyl

The percent *N*-acetyl groups were determined by infrared (IR) spectroscopy and by titration of the

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hydrobromide salt of chitosan. IR spectroscopy was performed on chitosan in film form. Films were cast from solution in 5% aq. formic acid and steeped in 0.05 M sodium methoxide/methanol solution to deprotonate the amine group. The films were finally washed in water to remove any salts. The amide I band at 1655 cm^{-1} is used for determination of the residual $-\text{CO}-\text{NH}-$ groups. The $-\text{CH}$ stretching band at 2867 cm^{-1} is used as an internal standard, according to the method of Domszy and Roberts.⁴

The chitosan was also converted to the water-soluble hydrobromide salt and titrated with standardized NaOH solution using phenolphthalein to determine the end point.⁴ To obtain this salt, 0.5 g of chitosan was dissolved in 0.2 M HBr (100 mL); to this, 9 M HBr (50 mL) was added to precipitate the hydrobromide salt. The hydrobromide salt was then filtered off, washed with methanol till neutral, then washed with several portions of ether, and air-dried. The washing process was repeated three times. The dried salt was then titrated and results correlated well with the IR method. The values of the percent *N*-acetyl determined are found in Table I.

Molecular Weight

Molecular weight and its distribution, of the polymer was obtained by gel permeation chromatography (GPC). The chromatographs were performed on a Waters (Waters Chromatography Division, Millipore Corporation) 150C ALC/GPC using three Bio-Gel columns (Bio-Rad Laboratories, Richmond, CA). The solvent used was 2% acetic acid with 0.1 M sodium acetate and 0.008 M sodium azide. The molecular weight and polydispersity values are summarized in Table II.

Chitosan Fiber Spinning

Chitosan filament was wet spun by generally following the methods described by G. C. West and the

Table I. *N*-Acetyl Content of Chitosan

Sample (Hydrolysis Cycles)	<i>N</i> -Acetyl Content ^a (%)	
	IR Spectroscopy	Titration of Chitosan Salt
1	23.5	21.0
2	11.0	9.5

^a *N*-acetyl content (%) expressed as the ratio of the number of *N*-acetylated residues over the number of monomer unit $\times 100$.

Table II. Molecular Weight Values for Chitosan by GPC

Sample (Hydrolysis Cycles)	Molecular Weight		
	$M_w \times 10^{+5}$	$M_n \times 10^{+5}$	M_w/M_n
1	4.0	3.1	1.3
2	1.9	0.89	2.1
Wet-spun	1.4	0.87	1.6

Fuji Spinning Co.^{5,6} A spin dope was prepared by dissolving 5% w/v chitosan in 5% v/v aq acetic acid. The coagulating bath was 1 M NaOH. Spinnerette dimensions were 0.25 mm diameter and a capillary length to diameter ratio of 2. A piston/ram device was employed to extrude the fibers, at room temperature. Tensile properties of the fibers were determined on an Instron Tensiometer, Canton, MA, by ASTM method D2101-82 (1988).

Crosslinked Fibers

The use of ECH to crosslink amylose was reported by Luby.⁷ This methodology was adapted to crosslink chitosan films³ and in this work, fibers. Fibers were crosslinked in the wet state only. A 38 cm length of fiber was tied as a single loop and placed in a large tube containing the ECH solution, purged with N_2 and sealed. Tension on the filament was varied by hanging different steel weights on it. The standard conditions employed used 0.067 M NaOH (pH 10) and a reaction temperature of 40°C . The reaction time, tension, and ECH concentration were varied.

RESULTS AND DISCUSSION

The relationship of the tenacity of the crosslinked fiber to the ECH concentration used, is shown in Figure 1, for fibers tested dry and Figure 2 for fibers tested wet. It is evident that the strength of the chitosan fiber, especially wet tenacity, is improved by crosslinking. The data in Figure 1 for the dry tensile strengths indicate that crosslinking the chitosan fiber in the wet, swollen state does not reduce or degrade the strength of the fibers. Typically, during the "pad bake" crosslinking of cellulose fibers, there is considerable degradation of the tensile properties through the process.⁸

Table III shows the effects of ECH concentration during crosslinking on the tensile properties. As the

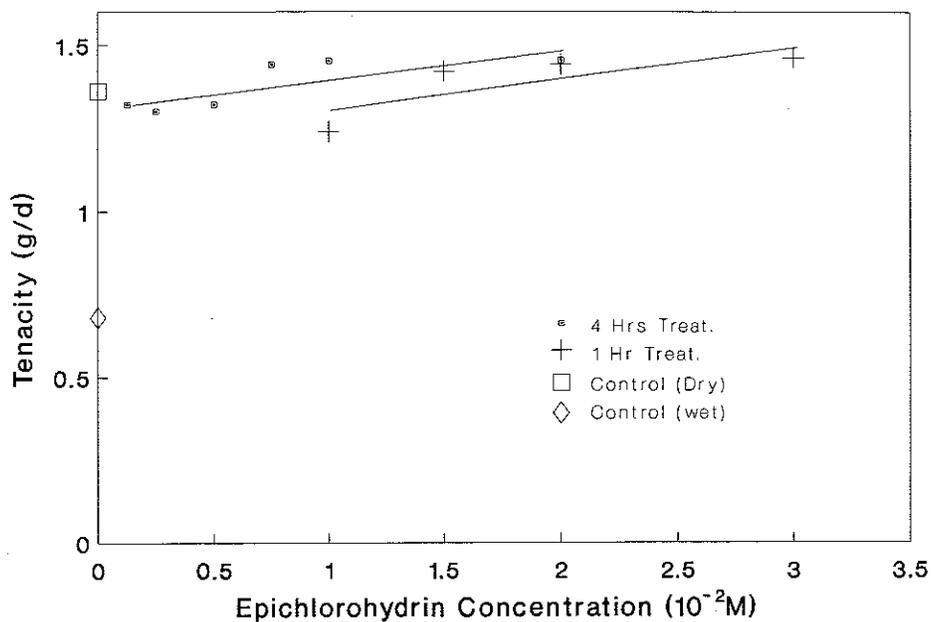


Figure 1. The effect of epichlorohydrin concentration on dry fiber tenacity. The dry control fiber (\square) had a tenacity of 1.36 g/den.

ECH concentration is increased, the tenacity increased for each of the two series of treatments. However, increasing the concentrations above $1.0 \times 10^{-2}M$ did not produce a further increase in tenacity in the case of 4 h of crosslinking. The change

in elongation to failure with crosslinking, as determined for dry fibers and for wet fibers, is presented in Figures 3 and 4. For the wet fibers, it is evident that a significant increase in toughness of the fibers is observed by the large increase in the elongation

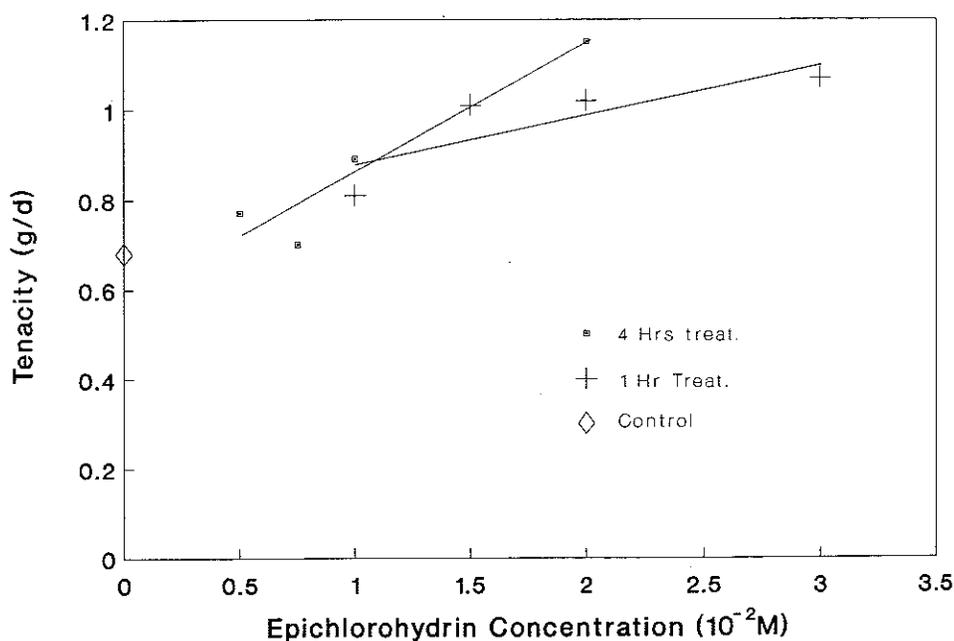


Figure 2. The effect of epichlorohydrin concentration on wet fiber tenacity. The wet control fiber (\diamond) had a tenacity of 0.68 g/den.

Table III. The Effect of ECH Concentration on Fiber Tensile Properties^a

[ECH] × 10 ² M	Reaction Time (h)	Swelling Ratio	Tensile Properties (Dry/Wet)		
			Tenacity (g/den)	Elongation (%)	Modulus (g/den)
0.125	4	soluble	1.32/ND	9.9/ND	73.4/ND
0.25	4	81.0	1.30/0.36	9.4/42.4	61.2/0.8
0.50	4	25.0	1.32/0.77	8.7/33.5	48.1/1.9
0.75	4	17.4	1.44/0.70	10.2/30.7	55.9/2.0
1.00	4	11.1	1.45/0.89	10.6/22.0	61.0/4.5
1.00	1	24.4	1.24/0.81	9.1/38.1	52.6/2.2
1.50	1	21.4	1.42/1.01	9.6/25.2	58.6/5.9
2.00	4	8.5	1.45/1.15	8.9/22.4	59.1/11
2.00	1	18.4	1.44/1.02	8.9/22.8	59.1/5.3
3.00	1	5.6	1.46/1.07	9.2/22.0	53.4/11
Control Fiber			1.36/0.68	10.4/15.0	66.5/7.3

^a The chitosan fiber was crosslinked with ECH in 0.067M NaOH under no tension at 40°C.

to failure. Again, it is noted that there is not a deleterious effect on the dry fiber properties as a result of the crosslinking.

A convenient proof of crosslinking is the swelling behavior of the crosslinked fiber in 5% aq. acetic acid. Simple swelling measurements were employed to estimate the extent of crosslinking. A swelling ratio (the ratio of volumes between swollen and unswollen fibers) was determined by examining the

diameters of the fibers using optical microscopy. The swelling ratios are also reported in Table III. Figure 5 shows that there is also a correlation between the swelling ratio and the log of the crosslinking time.

The effect of reaction temperature on tenacity is shown in Table IV. Additional crosslinking can be achieved by increasing reaction temperature. When higher than 40°C, it causes severe reduction of tenacity, probably because the polymer chains are de-

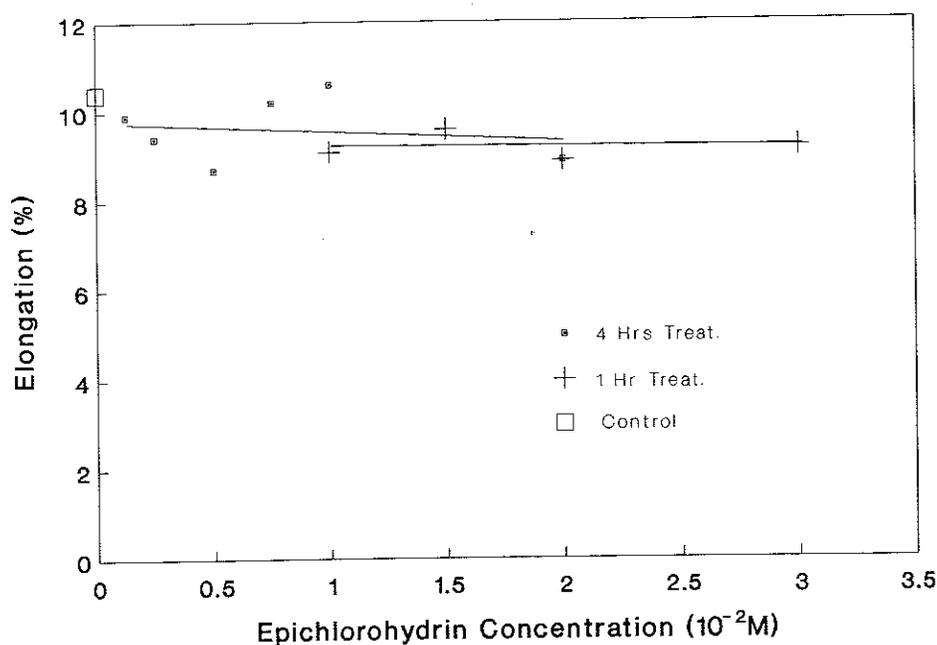


Figure 3. The effect of epichlorohydrin concentration on dry fiber elongation to failure. The dry control fiber (□) had an elongation of 10.4%.

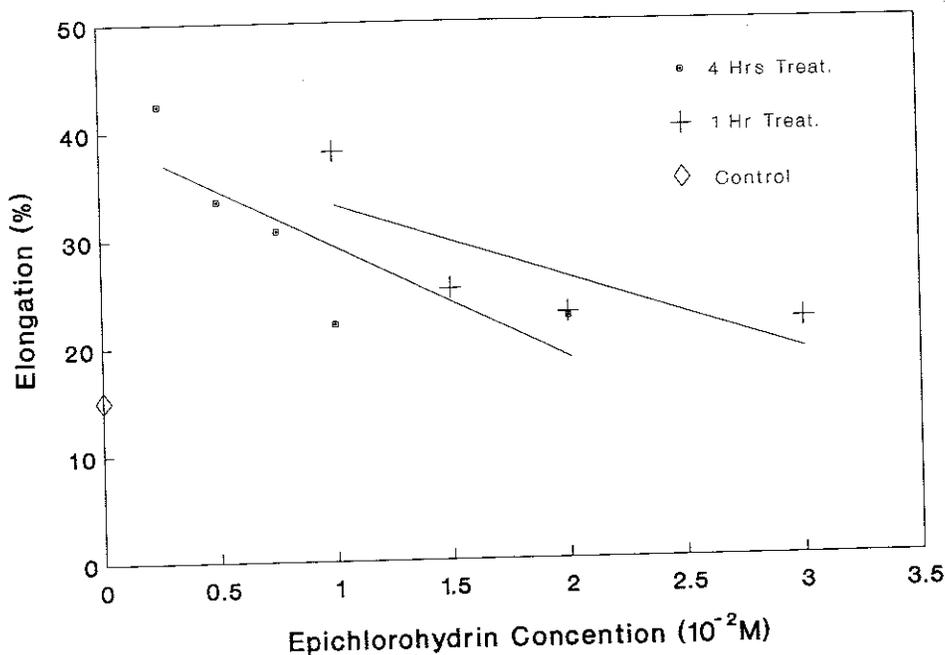


Figure 4. The effect of epichlorohydrin concentration on wet fiber elongation. The wet control fiber (\diamond) had an elongation of 15.0%.

graded, and also as the crosslink density increases, load distribution during tensile testing is not as efficient, leading to brittleness.

The effect of reaction time at 40°C on the tensile properties of the crosslinked fiber is presented in

Table V. The strength and swelling ratio rise rapidly at first and then drop off. When the crosslinking is applied under tension, however, no significant change in tensile properties is observed, as seen in Table VI.

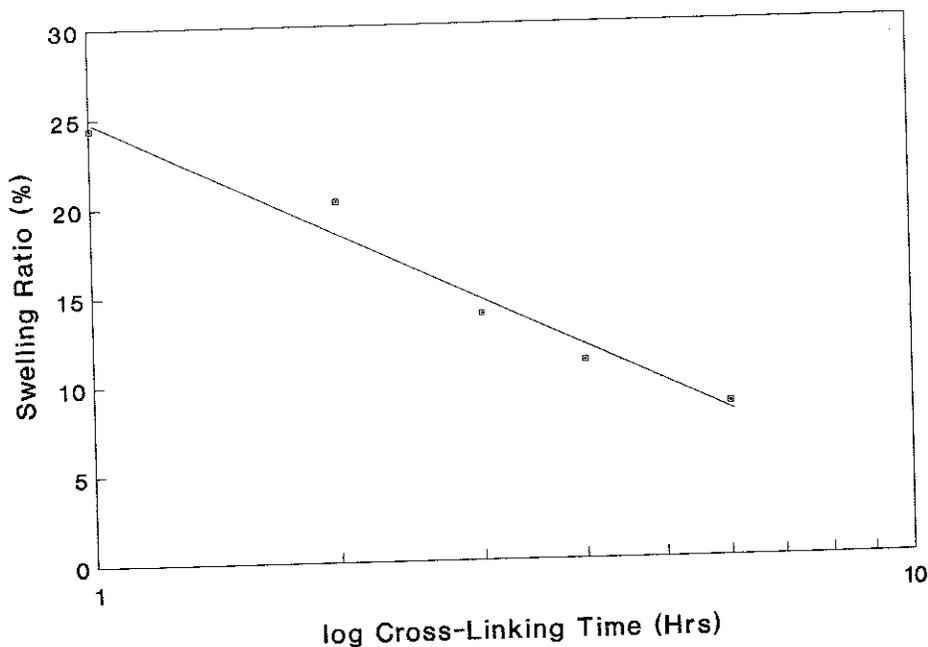


Figure 5. The swelling ratio of the crosslinked fibers as a function of the log of the crosslinking time.

Table IV. The Effect of Reaction Temperature on the Fiber Tensile Properties^a

Reaction Temperature (°C)	Swelling Ratio	Tensile Properties (Dry/Wet)		
		Tenacity (g/den)	Elongation (%)	Modulus (g/den)
22	soluble	1.42/ND	8.9/ND	61.5/ND
40	11.1	1.45/0.89	10.6/22.0	61.0/4.5
50	9.5	1.23/0.98	7.6/22.6	59.4/5.3
60	9.2	1.19/0.92	7.9/12.6	48.5/6.7

^a The chitosan fiber was crosslinked with $1 \times 10^{-2}M$ ECH in 0.067M NaOH under no tension.

The fracture surface of the crosslinked fibers after tensile failure in the dry state were observed by scanning electron microscopy (SEM). Figure 6 is that of a fiber, fractured under tension in the dry state. It had been crosslinked with an [ECH] of $2 \times 10^{-2}M$, for 4 h at 40°C. The fibrillar fine structure of these chitosan fibers is readily seen in the SEM. A ductile failure mode is indicated. As the fiber stretched before breaking, elastic recoil after breaking caused the fiber end to split back. This also in-

dicates that the lateral strength of the fiber may not be high, which is in agreement with the observation of the fibrillar morphology.

In summary, chitosan fibers and films are readily crosslinked by ECH which results in changes in the mechanical properties of these materials. There is a considerable relative improvement in the tensile strength of the films compared to the fibers. This is interpreted to reflect the differing morphology of the film compared to the fiber. It is expected that the

Table V. The Effect of Reaction Time on Fiber Tensile Properties^a

Reaction Time (h)	Swelling Ratio	Tensile Properties (Dry/Wet)		
		Tenacity (g/den)	Elongation (%)	Modulus (g/den)
1	24.4	1.24/0.81	9.1/38.1	52.6/2.2
2	20.2	1.27/0.88	7.9/23.6	61.4/4.7
3	13.8	1.28/0.88	7.5/26.8	59.6/5.3
4	11.1	1.45/0.89	10.6/22.0	61.0/4.5
6	8.6	1.35/1.05	8.1/27.1	54.8/3.0

^a The chitosan fiber was crosslinked with $1 \times 10^{-2}M$ ECH in 0.067M NaOH under no tension.

Table VI. The Effect of Tension on the Tensile Properties of the Crosslinked Chitosan Fibers^a

Tension (mg)	Swelling Ratio	Tensile Properties (Dry/Wet)		
		Tenacity (g/den)	Elongation (%)	Modulus (g/den)
30	12.1	1.44/0.97	10.4/19.7	60.3/5.0
90	11.9	1.56/0.88	11.2/25.2	64.8/4.5
120	11.7	1.45/0.98	9.8/23.6	49.7/4.5
230	13.4	1.43/0.96	8.4/24.1	48.3/4.6
520	12.5	1.46/0.93	8.4/28.7	60.7/8.5
980	10.9	1.40/0.86	8.3/35.4	55.3/8.4

^a The chitosan fiber was treated with $1 \times 10^{-2}M$ ECH in 0.067M NaOH solution at 40°C.

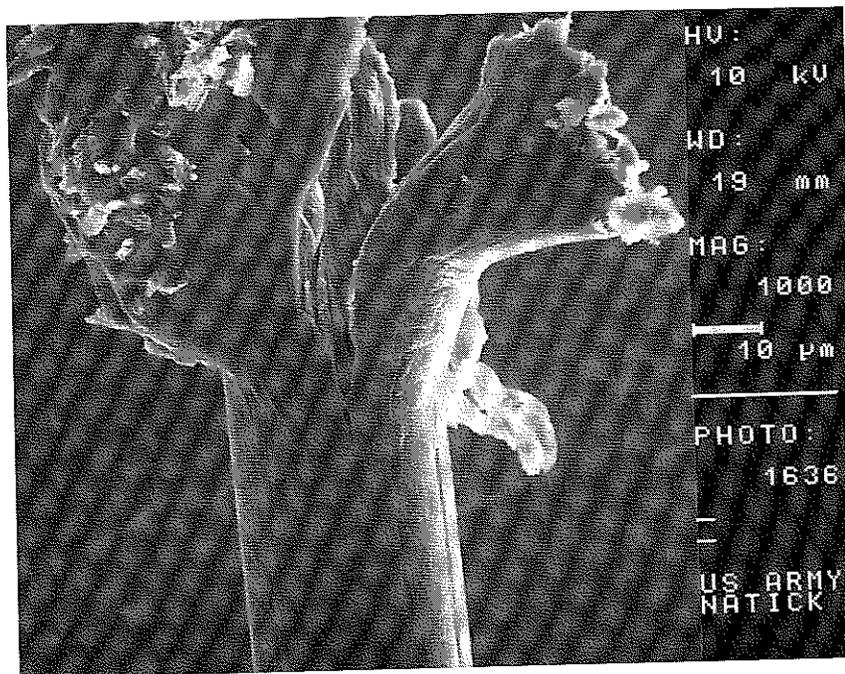


Figure 6 A. scanning electron micrograph of the fracture surface of a fiber that failed while under tensile loading. The fiber was tested in the dry state.

fiber will have a more oriented fibrous structure than the films. Thus, it is observed that cross-linking the films has a more profound effect on the tenacity of the poorly-oriented film, than for the fibers. The wet strength of the fibers is considerably improved, whereas crosslinking has a negligible effect on the dry fiber properties.

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