

## Rheological Properties of Elastomers Based on Cellulose Fibers\*

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### Synopsis

Elastomers, based on cellulose fibers, were synthesized by grafting ethyl acrylate onto fibers preirradiated by a high-energy electron beam. The rheological properties and fine structure of the elastomers were investigated in order to determine factors in development of rubber-like elastomeric behavior. Mechanical properties of the elastomers depended on (1) degree of polymerization of irradiated cellulose molecules, (2) extent of grafting, and (3) experimental methods of evaluation, particularly in varying environmental conditions, for example, in making measurements in air, water, or ethyl acetate. Glass transition temperatures of the elastomers were dependent on the environmental conditions of evaluation; stiffnesses of the elastomers levelled off at about 0°C; and in all environments, a rubber-like plateau was observed. Poly(ethyl acrylate) separated from the elastomers was not soluble in acetone. The mean molecular weight of the separated poly(ethyl acrylate) of the elastomer was determined in ethyl acetate by the equilibrium swelling method. It was concluded that crosslinks existed in the elastomers. Electron microphotographs of cross sections of the elastomers, which exhibited rubber-like behavior, indicated that the fibrillar structure of the irradiated cellulose fibers formed a uniform network and that poly(ethyl acrylate) was uniformly distributed among the fibrils.

### INTRODUCTION

In previous papers, it was reported that viscose rayon fibers grafted with ethyl acrylate by the ceric ion method had rubber-like elastomeric behavior above 1000% extent of grafting. The combined effects of the flexible grafted polymer corresponded to soft, amorphous segments, having glass transition temperatures below room temperature; the rigid cellulose trunk polymer determined this behavior.<sup>1,2</sup> Syntheses of elastomers, based on preirradiated cellulose fibers, have been accomplished by grafting ethyl acrylate onto the fibers. Rheological properties and fine structures of these elastomers have been investigated in order to determine factors in

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development of rubber-like elastomeric behavior. These syntheses and properties of the elastomers are given in this report.

### EXPERIMENTAL

Ordinary type rayon yarns (bright, 120 denier, 50 filaments) were preirradiated in air at room temperature by a 2 MeV EBG generator with a dose rate of  $9.18 \times 10^4$  rad/sec to total dosages ranging from 6 to 50 megarads (Mrad). The preirradiated fibers were placed in a reaction vessel which was evacuated to 3 torr. A monomer mixture, containing 5–10 vol-% ethyl acrylate, 10 vol-% acetone, and 80–85 vol-% distilled water, was aerated by high-purity nitrogen to remove the dissolved oxygen. The amount of this monomer mixture used in the reaction vessel was 300 ml/g fiber. The graft copolymerization reaction was conducted at  $25 \pm 2^\circ\text{C}$  for periods of time ranging from 1 to 6 hr. The grafted products were extracted at reflux for 72 hr in a Soxhlet with acetone and then dried under reduced pressure at  $50^\circ\text{C}$ . The extent of grafting was expressed as a wt-% increase, based on the original weight of the fiber. The extent of grafting was controlled by the concentration of monomer in the mixture and the time of reaction.

**Degree of Polymerization of Cellulose.** The preirradiated cellulose fibers were nitrated with Mitchell's mixed acids (fuming nitric acid, phosphoric acid, and phosphorus pentoxide). The degree of polymerization of the products was determined in ethyl acetate by viscometry.<sup>3,4</sup>

**Separation of Grafted Poly(Ethyl Acrylate).** The grafted fibers were swollen by acetone and then water washed. Excess water contained in the fibers was removed by padding with filter paper. The cellulose fibers were hydrolyzed with 72% sulfuric acid (fiber-to-liquor ratio 1:100) at  $20^\circ\text{C}$  for 15 hr, followed by diluting the solution with a large amount of water in order to precipitate the poly(ethyl acrylate). The separated polymer was rinsed with water until acid was removed; then the polymer was dried under reduced pressure at  $50^\circ\text{C}$ . Under the conditions of hydrolysis, the poly(ethyl acrylate) was also partially saponified with acid; that is, a copolymer of ethyl acrylate and acrylic acid was produced, which was not soluble in the solvent used for poly(ethyl acrylate). In order to obtain pure poly(ethyl acrylate), the separated polymer was again swollen with acetone; the excess acetone was removed. Then the sample was esterified with ethanol in the presence of sulfuric acid (fiber-to-liquor ratio 1:100) at  $78^\circ\text{C}$  for 40 hr. The product was water washed until acid was removed; then it was dried under reduced pressure at  $50^\circ\text{C}$ .<sup>5</sup>

**Crystallinity and Orientation of Cellulose.** The degree of crystallinity of untreated and irradiated fibers and of cellulose in the grafted fibers was determined using an x-ray diffractometer with Cu  $K_\alpha$  radiation which was operated at 30 kV and 15 ma. The integral method over an angular range of  $2\theta = 5^\circ\text{--}42^\circ$ , with the bundle of fibers rotated in the plane vertical to the x-ray beam (80 rpm), was used.<sup>1,6,7</sup> In order to determine the degree of orientation of cellulose in the grafted fibers, the intensity of the (002) re-

flection of the cellulose was measured along the Debye ring; then the half-width value was determined.<sup>8</sup>

**Mechanical Testing.** Tensile strength, breaking elongation, initial modulus of elasticity, elastic recovery, and stress-strain curves of the grafted fibers were measured using a Tensilon UTM-III tester in air (65% RH and 20°C), water (20°C), and ethyl acetate (20°C), respectively. The testing machine was set to extend and return the fiber at a rate of 20 mm/min in all cases. The elastic recovery and the hysteresis curves of the grafted fibers were measured by allowing the fibers to recover immediately after extension.

**Glass Transition Temperature.** In order to determine glass transition temperature of the grafted fibers in dry air, water, and ethyl acetate, the effect of temperature on the stiffness and resiliency of the fiber was determined by the above described testing machine. The stiffness was defined as the slope at the origin of the load-elongation curve. Resiliency was calculated from the linear recovery of the grafted fiber after 10% elongation.<sup>9,10</sup>

**Equilibrium Degree of Swelling.** Equilibrium degree of swelling of the grafted fibers, swollen with ethyl acetate, was determined at 25°C by means of a torsion balance.<sup>11</sup>

**Electron Microscopy.** Untreated fiber was stained with an aqueous solution containing 1% direct dye (Coprantine Rubine RLL) and 10% Na<sub>2</sub>SO<sub>4</sub> at 90°C for 2 hr, and then water washed. The fiber was treated with an aqueous solution of CuSO<sub>4</sub> at room temperature for 24 hr to chelate the cupric ions to the direct dye, then water washed and dried. The specimen obtained was embedded in prepolymer of epoxy resins under reduced pressure, then heat treated at 35°, 45°, and 60°C for 24 hr, respectively. The embedded sample was ultrathin sectioned on an ultramicrotome equipped with a glass knife. The thickness of the ultrathin section was about 200–500 Å. The sectioned specimen was floated on a water surface from which it was picked up on a copper grid and then dried at room temperature.

The ethyl acrylate-grafted fibers were swollen with acetone, rinsed in water, and then treated at 80°C for 60 min in the presence of 5% NaOH in order to hydrolyze the grafted poly(ethyl acrylate) partially. Afterwards the water-washed specimens were immersed in an aqueous solution of 3% CuSO<sub>4</sub> to react cupric ions with the carboxyl groups formed during the hydrolysis, water washed, and then dried under reduced pressure. Later these samples were ultrathin sectioned and treated in the same manner as described for untreated fiber.

## RESULTS AND DISCUSSION

### Degree of Polymerization of Cellulose

The effect of total dosage on the degree of polymerization of cellulose fibers is shown in Table I. The degree of polymerization of cellulose was

TABLE I  
Effect of Dosage on Degree of Polymerization of Cellulose Fibers

Dosage, Mrad	Degree of polymerization
0	210
6	120
10	100
20	75
50	40

decreased with increasing dosage, similar to that observed in the case of cotton cellulose irradiated by  $\gamma$ -radiation.<sup>12</sup>

### Separation of Grafted Poly(Ethyl Acrylate)

Previously it was reported that when viscose rayon fibers, grafted with ethyl acrylate from aqueous emulsion systems by the ceric ion method at 0°C, were treated with acetone, the poly(ethyl acrylate), separated from the grafted fibers below 1000% extent of grafting, was soluble in acetone.<sup>1,2</sup> However, when viscose rayon fibers were grafted with ethyl acrylate from aqueous emulsion systems by the preirradiation method, the separated poly(ethyl acrylate) was only swollen when immersed in acetone. The existence of crosslinks in the grafted poly(ethyl acrylate), which was isolated after hydrolytic degradation of the cellulose, was suggested for all of the grafted fibers (total dosage 6 to 50 Mrad; extent of grafting 150 to 1000%). Poly(ethyl acrylate), crosslinked or entangled, is not soluble in acetone. The preparation of this type of polymer is dependent on polymerization conditions.

### Degree of Crystallinity and Orientation of Cellulose

The degree of crystallinity and the orientation of cellulose in the grafted fibers are shown in Table II. The degree of crystallinity of cellulose fractions in the grafted fibers was hardly changed with increasing extent of grafting and dosage. However, the degree of orientation of the cellulose was somewhat decreased with increase in the extent of grafting. It is suggested that the grafting reactions mainly occurred in the amorphous regions of the cellulose fiber. Similar results were observed in the case of elastomer, based on the cellulose fiber with ethyl acrylate grafting by the ceric ion method.<sup>1</sup>

### Mechanical Properties

Mechanical properties of the grafted fibers in air are shown in Table II. The tensile strength of the irradiated cellulose fibers decreased with increasing dosage. The tensile strength of the grafted fibers also decreased with increasing dosage, especially at the lower extent of grafting. It is suggested that these relationships resulted from the fact that the degree of polymerization of the cellulose molecule decreased with increasing dosage

and that the grafted amorphous polymer did not contribute to the tensile strength of the fiber. The initial modulus of elasticity of the irradiated fibers was not changed with increase in dosage; however, this property of the grafted fibers decreased with increase in dosage, especially at the lower extent of grafting. It is suggested that such a result is caused by the amorphous, grafted poly(ethyl acrylate). If crosslinking is introduced into the grafted poly(ethyl acrylate), the initial modulus of elasticity should be increased, as shown for a copolymer of ethyl acrylate and tetraethylene glycol dimethacrylate.<sup>13-16</sup> However, from the insolubility of the poly(ethyl acrylate), separated from the grafted fibers, in acetone, it is suggested that crosslinks were introduced into the structure of the grafted polymer. The breaking elongation of the grafted fibers was about the same at about 150% extent of grafting and was not dependent on dosage. In the case of higher extent of grafting, breaking elongation increased with increase in dosage and the extent of grafting. The large increase in breaking elongation with increase at the higher dosage could be due to the depolymerization of the cellulose molecule and homogeneous grafting within the fibrous structure. The degree of elastic recovery of the grafted fibers was distinctly increased with increase in dosage and the extent of grafting. In the case of grafted fibers at a dosage of less than 20 Mrad, the minimum region of degree of elastic recovery was observed at about 50% extension. However, for the grafted fiber irradiated to 50-Mrad dosage, the minimum

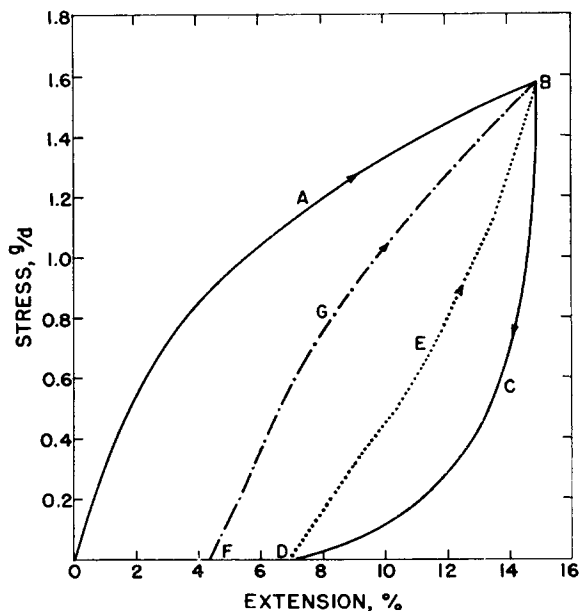


Fig. 1. Hysteresis curve of control fiber. Measuring conditions 15% extension, 65% RH, 20°C: (OABCD) 1st cycle; (DEBCD) 2nd or 3rd cycles; (FGBCD), 1st cycle after allowing the fiber, which had been cycled 3 times, to relax for 24 hr in air at 65% RH, 20°C.

TABLE II  
Mechanical Properties, Degree of Crystallinity, and Orientation of Grafted Fibers<sup>a</sup>

<i>Part A</i>				
Extent of grafting, <sup>b</sup> %	Fineness, d	Tensile strength, g/d	Breaking elongation, %	Initial modulus of elasticity, g/d
0 Mrad				
—	2.5	2.1	32	28.8
6 Mrad				
—	2.5	1.8	32	28.0
148	5.8	0.96	43	7.80
291	9.0	0.62	62	2.31
501	14	0.37	91	1.34
691	18	0.26	110	1.06
987	25	0.22	119	0.83
10 Mrad				
—	2.5	1.5	31	28.5
134	5.4	0.84	42	9.01
286	8.9	0.50	100	2.70
499	14	0.27	330	1.03
716	19	0.19	425	1.10
979	25	0.16	465	0.81
20 Mrad				
—	2.5	1.25	32	28.6
154	5.9	0.60	42	5.66
302	9.3	0.36	523	1.46
508	14	0.23	635	1.04
719	19	0.17	680	0.82
900	25	0.15	700	0.63
50 Mrad				
—	2.5	0.62	31	28.5
136	5.4	0.40	41	5.02
302	9.3	0.21	630	0.40
549	15	0.15	770	0.13
987	25	0.11	820	0.02

region disappeared, and the degree of elastic recovery was increased over the whole range of grafting. It is suggested that the minimum region resulted mainly from the chain scission of the cellulose molecule by the extension and that its disappearance in the case of 50-Mrad dosage arose from the depolymerization of the cellulose molecule at the highest dosage.

Hysteresis curves of untreated and grafted fibers, measured at 65% RH and 20°C, are shown in Figures 1, 2, 3, and 4. The initial modulus of elasticity and energy loss, calculated from the hysteresis curves, are shown in Table III. The energy loss of untreated fiber was greater than that of grafted fiber (20 Mrad, 302% extent of grafting) on each cycle at 15%

Table II (continued)

Extent of grafting, %	Degree of elastic recovery, <sup>c</sup> %					Degree of crystallinity, %	Degree of orientation, %
	10%	50%	100%	300%	500%		
	<i>Part B</i>						
0 Mrad							
—	50	—	—	—	—	40	83
6 Mrad							
—	51	—	—	—	—	40	80
291	55	—	—	—	—	38	78
501	60	55	—	—	—	—	—
10 Mrad							
—	52	—	—	—	—	—	—
286	63	57	—	—	—	—	—
499	71	62	66	—	—	—	—
20 Mrad							
—	50	—	—	—	—	42	81
154	57	—	—	—	—	39	80
302	80	75	80	89	89	39	77
508	81	76	80	89	89	38	65
719	84	81	88	95	95	37	62
900	87	82	87	94	95	—	—
50 Mrad							
—	49	—	—	—	—	39	82
302	100	97	94	90	88	39	78
549	100	98	95	90	89	—	—
987	100	98	97	93	90	—	—

<sup>a</sup> Measuring conditions: 65% RH, 20°C; irradiation doses as indicated.

<sup>b</sup> Grafted poly(ethyl acrylate) = all polymer insoluble in acetone, which may result from grafting and/or crosslinking.

<sup>c</sup> At indicated extensions.

extension. The initial modulus of elasticity in the second and third cycles of these fibers was lower than in the first cycle. After allowing the fibers, which had been cycled 3 times at 15% extension, to relax for 24 hr in air, the hysteresis curve of the untreated fiber was not the same as the original cycle; however, the grafted fibers recovered to the original state. The former result is considered to be due to the existence of irreversible hydrogen bonds in cellulose which are broken during 15% extension; the latter is probably due to the elastomeric property of the grafted fiber which complemented the irreversibility of the cellulose polymer. In the case of 200% extension of the grafted fiber (302% extent of grafting) irradiated to 20 Mrad, as shown in Figure 3 and Table III, the first cycle of the hysteresis curves showed the maximum point of the stress at about 30% extension which corresponded to the breaking elongation of the ungrafted fiber.

TABLE III  
Energy Loss and Initial Modulus of Elasticity from Hysteresis Curves of Grafted Fibers<sup>a</sup>

Dosage, Mrad	Extent of grafting, %	Extension, %	Cycle									
			1st			2nd			3rd			Relaxed fibers <sup>b</sup>
			E.L., %	I.M., g/d	E.L., %	I.M., g/d	E.L., %	I.M., g/d	E.L., %	I.M., g/d	E.L., %	I.M., g/d
---	---	15	83	28.8	50	16.5	50	16.5	50	16.5	65	24.4
20	302	15	70	1.46	31	0.30	31	0.30	31	0.30	70	1.46
20	302	200	88	1.40	38	0.01	38	0.01	25	0.01	40	0.02
50	302	200	75	0.40	35	0.01	35	0.01	24	0.01	42	0.03

<sup>a</sup> Measured at 65% RH, 20°C. E.L. = Energy loss; I.M. = initial modulus of elasticity based on denier of grafted fibers.

<sup>b</sup> First cycle after allowing fiber, which had been cycled 3 times, to relax for 24 hr in air at 65% RH and 20°C.



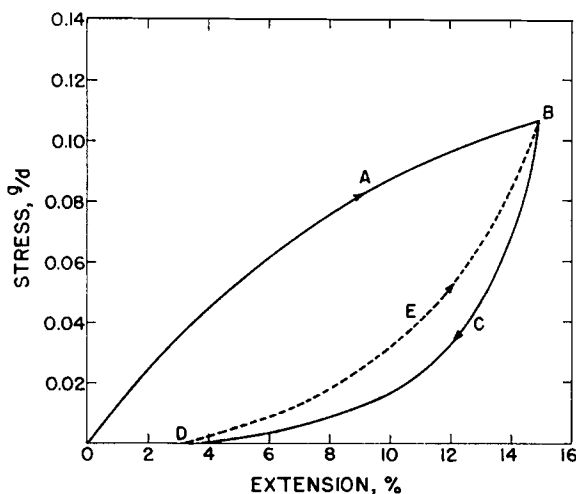


Fig. 2. Hysteresis curve of grafted fiber. Dosage 20 Mrad; extent of grafting 302%; measuring conditions 15% extension, 65% RH, 20°C: (OABCD) 1st cycle or 1st cycle after allowing the fiber, which had been cycled 3 times, to relax for 24 hr in air at 65% RH, 20°C: (DEBCD) 2nd or 3rd cycle.

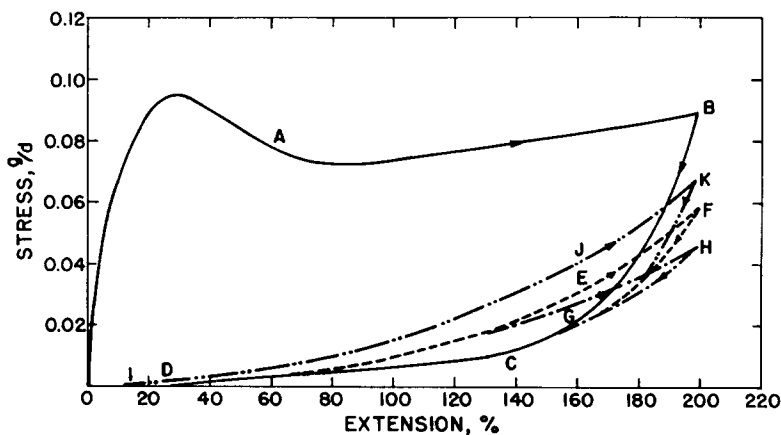


Fig. 3. Hysteresis curve of grafted fiber. Dosage 20 Mrad; extent of grafting 302%; measuring conditions 200% extension, 65% RH, 20°C: (OABCD) 1st cycle; (DEFCD) 2nd cycle; (DGHCD) 3rd cycle; (IJKCD) 1st cycle after allowing the fiber, which had been cycled 3 times, to relax for 24 hr in air at 65% RH, 20°C.

However, such a point of stress disappeared in the second and third cycles. As compared with the case of 15% extension, the energy loss was increased, especially in the first cycle, and the initial modulus of elasticity of the second and third cycles was decreased. The first cycle after allowing the fiber, which had been cycled 3 times to 200% extension, to relax for 24 hr in air was not the same as the original cycle. Chain scission of the cellulose and unravelling of the entanglement of the grafted polymer with itself and

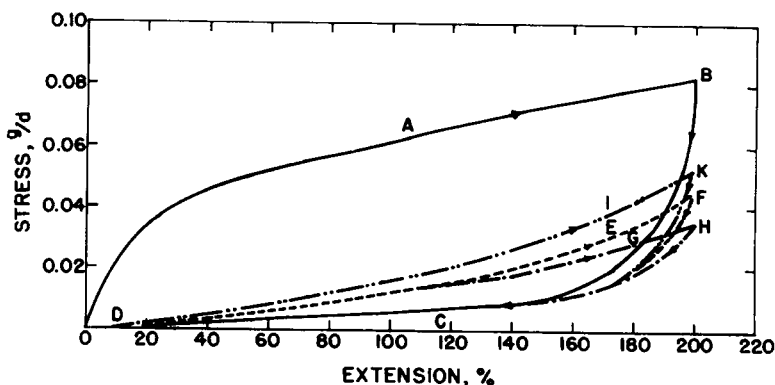


Fig. 4. Hysteresis curve of grafted fiber. Dosage 50 Mrad; extent of grafting 302%; measuring conditions, 200% extension, 65% RH, 20°C: (OABCD) 1st cycle; (DEFGD) 2nd cycle; (DGHCD) 3rd cycle; (DIKCD) 1st cycle after allowing the fiber, which had been cycled 3 times, to relax for 24 hr in air at 65% RH, 20°C.

between the grafted polymer and the cellulose during the greater extension probably accounted for this behavior.

However, the fiber grafted at 50 Mrad, as shown in Figure 4 and Table III, did not show the maximum point of stress in the hysteresis curve in each cycle, in contrast to the fiber grafted at 20 Mrad to the same extent of grafting and extension which showed a maximum point of stress in the curve. Although the energy loss and the initial modulus of elasticity of second and third cycles were similar to those for the fiber grafted at 20 Mrad, the values for the first cycle were decreased. It is suggested that these results are due to the depolymerization of the cellulose molecule at the highest dosage and subsequently to the more homogeneous grafting of the poly(ethyl acrylate). The first cycle after allowing the fiber, which had been cycled 3 times at 200% extension, to relax for 24 hr in air was not recovered to the original cycle; therefore, it is suggested that the irreversible unravelling of the entanglement in the grafted polymer and between the grafted polymer and the cellulose molecule may have occurred during the large extension.

### Mechanical Properties in Water and Ethyl Acetate

For purposes of investigating the influence of the grafted poly(ethyl acrylate) and the trunk polymer cellulose on the mechanical properties of the grafted fibers, the physical properties of the grafted fibers were measured in water, which is a swelling agent for the cellulose, and in ethyl acetate, which is a solvent for the grafted poly(ethyl acrylate). Relations between stress and strain of the grafted fibers, measured in air, water, and ethyl acetate, are shown in Figure 5. In water, the initial modulus of elasticity of the grafted fiber was lower than in ethyl acetate; the breaking elongations were higher in water than in ethyl acetate. Moreover, the maximum point of stress, which appeared in air, disappeared in water, even in the

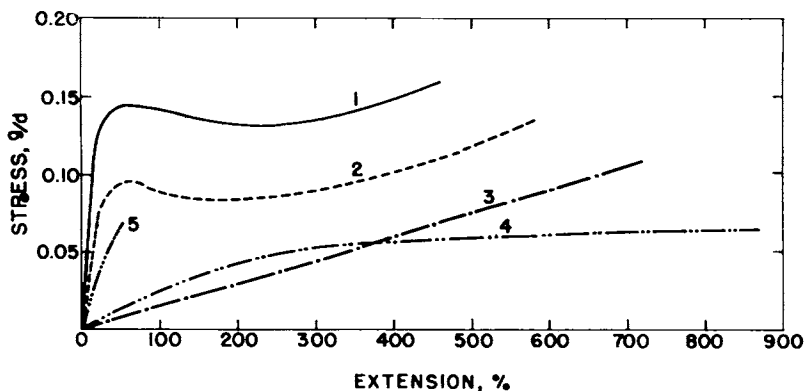


Fig. 5. Stress versus extension of grafted fibers in air, water, and ethyl acetate: (1) 10 Mrad, 979% extent of grafting, in air at 65% RH, 20°C; (2) 20 Mrad, 900% extent of grafting, in air at 65% RH, 20°C; (3) 50 Mrad, 987% extent of grafting, in air at 65% RH, 20°C; (4) 20 Mrad, 900% extent of grafting, in water at 20°C; (5) 50 Mrad, 900% extent of grafting, in ethyl acetate, 20°C.

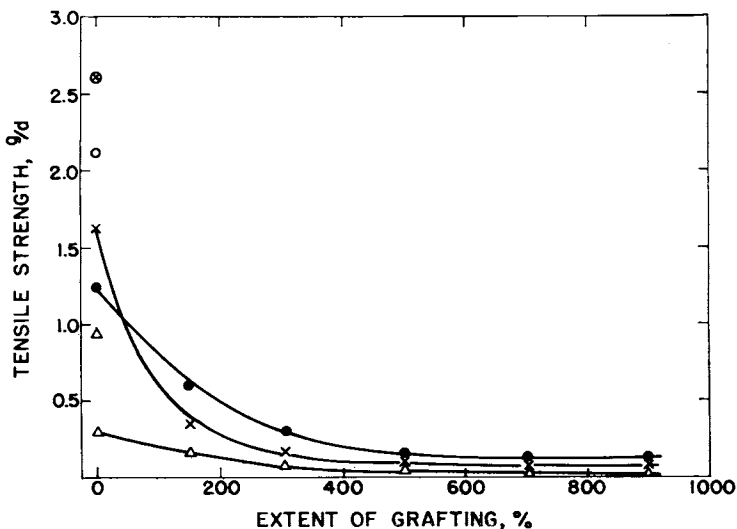


Fig. 6. Tensile strength versus extent of grafting of fibers in air, water, and ethyl acetate. Dosage 20 Mrad: (●) in air at 65% RH, 20°C; (Δ) in water at 20°C; (×) in ethyl acetate at 20°C. At zero grafting symbols indicate untreated, irradiated fibers in respective environments.

grafted fiber irradiated to 20 Mrad. On the other hand, in ethyl acetate, the initial modulus of elasticity was higher than in water, and the breaking elongation was lower than in water.

Relations between tensile strength of the grafted fibers, measured in air, water, and ethyl acetate, and extent of grafting are shown in Figure 6. The tensile strength of the grafted fibers was decreased with increase in the

extent of grafting in all cases, especially at the lower extent of grafting. The differences in the tensile strengths of the fibers were dependent on the experimental conditions of measurement. The tensile strength of untreated and irradiated fibers ranked in the following order: in ethyl acetate > in air > in water. The order was reversed for the grafted fibers in air and ethyl acetate.

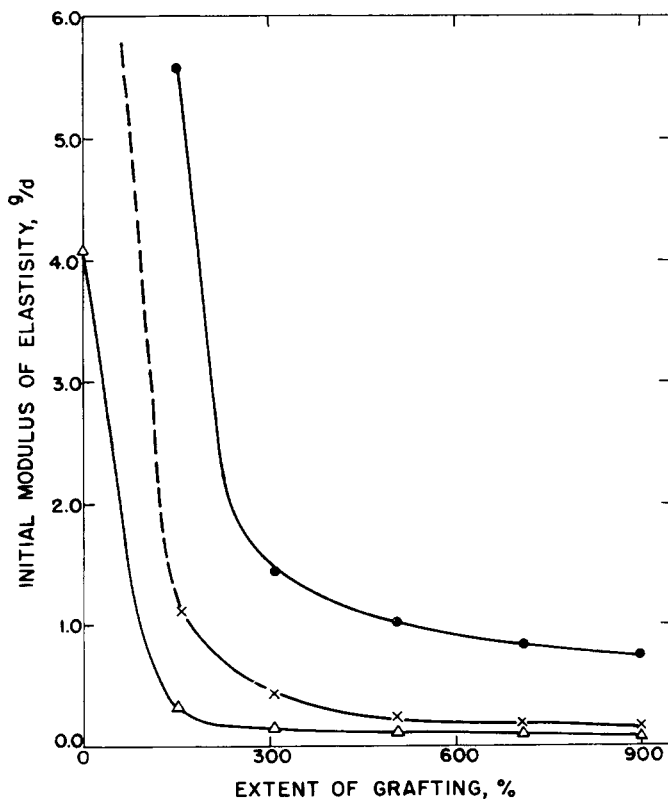


Fig. 7. Initial modulus of elasticity versus extent of grafting of fibers in air, water, and ethyl acetate. Dosage 20 Mrad: (●) in air at 65% RH, 20°C; (Δ) in water at 20°C; (×) in ethyl acetate at 20°C.

Similar effects of experimental conditions of measurement on the initial modulus of elasticity of the fibers are shown in Figure 7. Relations between breaking elongation of the grafted fibers in air, water, and ethyl acetate and extent of grafting are shown in Figure 8. The breaking elongation of the grafted fibers, measured in water, was dependent on the extent of grafting, as it was in the case of measurement in air. The breaking elongation, measured in water, was higher than that measured in air, especially at about 150% extent of grafting. However, in ethyl acetate the breaking elongations of the grafted fibers did not change with increase in extent of grafting and were lower than those measured in air and water.

Relations between elastic recovery at 10% extension in air, water, and ethyl acetate and extent of grafting of the grafted fibers are shown in Figure 9. The elastic recovery of the grafted fibers was generally in-

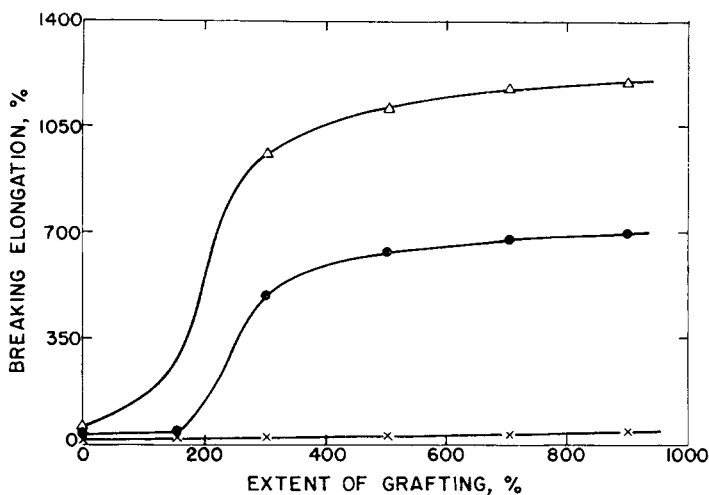


Fig. 8. Breaking elongation versus extent of grafting of fibers in air, water, and ethyl acetate. Dosage 20 Mrad: (●) in air at 65% RH, 20°C; (Δ) in water at 20°C; (X) in ethyl acetate at 20°C.

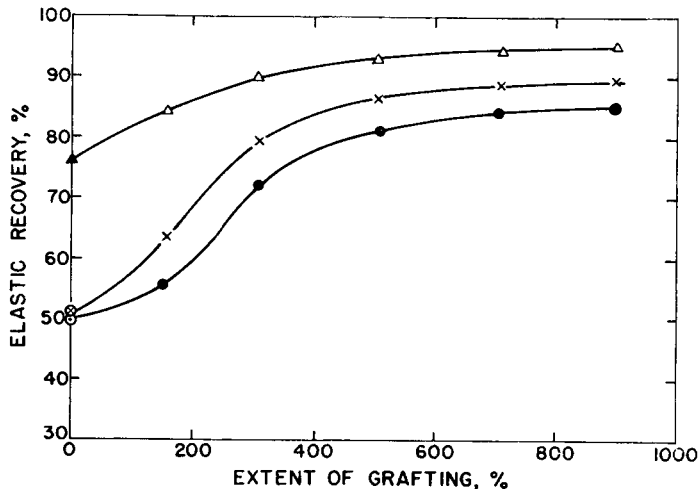


Fig. 9. Elastic recovery versus extent of grafting of fibers in air, water, and ethyl acetate. Dosage 20 Mrad: (●) in air at 65% RH, 20°C; (Δ) in water at 20°C; (X) in ethyl acetate at 20°C.

creased with increased extent of grafting and gave the highest value when measured in water and the lowest value when measured in air. Similar results were previously reported for cotton grafted with ethyl acrylate.<sup>17</sup>

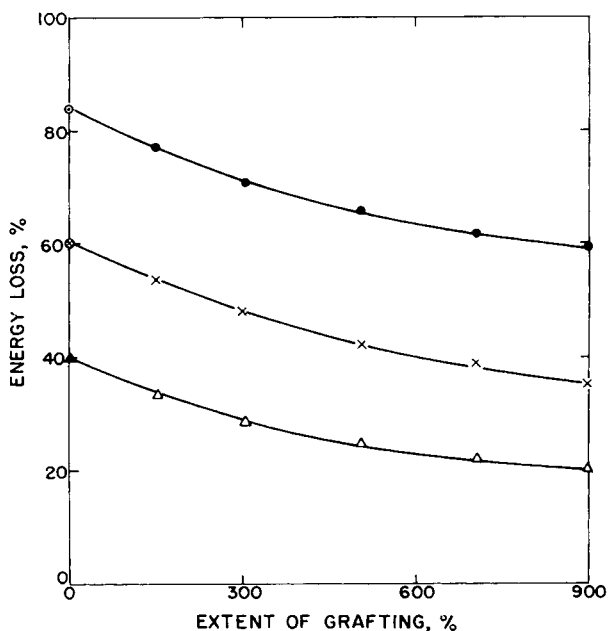


Fig. 10. Energy loss versus extent of grafting of fibers in air, water and ethyl acetate. Dosage 20 Mrad; extension 10%: (●) in air at 65% RH, 20°C; (△) in water at 20°C; (×) in ethyl acetate at 20°C.

Relations between energy loss in hysteresis curves for the grafted fibers at 10% extension, measured in air, water, and ethyl acetate, and extent of grafting are shown in Figure 10. The energy loss was decreased with increased extent of grafting. Energy loss was lowest when measured in water and was highest when measured in air.

### Influence of Temperature on Stiffness and Resiliency

In order to investigate the mechanical properties of the grafted fibers in air, water, and ethyl acetate in more detail, the glass transition temperatures of the grafted fibers were determined by measuring the stiffness and resiliency of the fibers at various temperatures. The influence of temperature on the stiffness of the untreated and grafted fibers in air, water, and ethyl acetate is shown in Figures 11 and 12. The stiffness of the untreated fiber decreased linearly with increase in temperature in air and ethyl acetate. Stiffness of the untreated fiber was lower when measured in air than when measured in ethyl acetate. The stiffness of the untreated fiber, measured in water, was lower than that measured in air or in ethyl acetate; in water the stiffness did not change with increase in temperature of measurement. The stiffness of grafted fiber in air, as seen in Figure 12, decreased sharply at about  $-20^{\circ}\text{C}$  and levelled off above  $0^{\circ}\text{C}$  as the temperature of measurement was increased. This effect was not dependent on the extent of grafting. The stiffness of the fibers in water and ethyl acetate

was not changed over the range of temperature of measurement. The stiffness of the fibers, when measured in the plateau region, decreased with increase in extent of grafting and was ranked in the following order: in air > in ethyl acetate > in water.

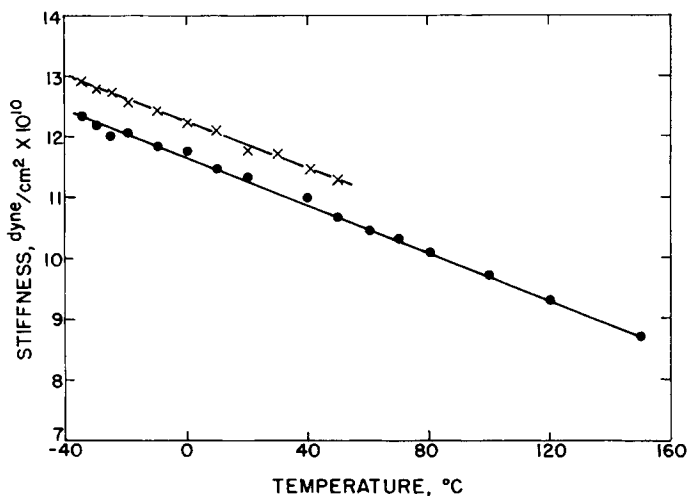


Fig. 11. Effect of temperature on stiffness of control fiber in air and ethyl acetate: (●) in dry air; (×) in ethyl acetate.

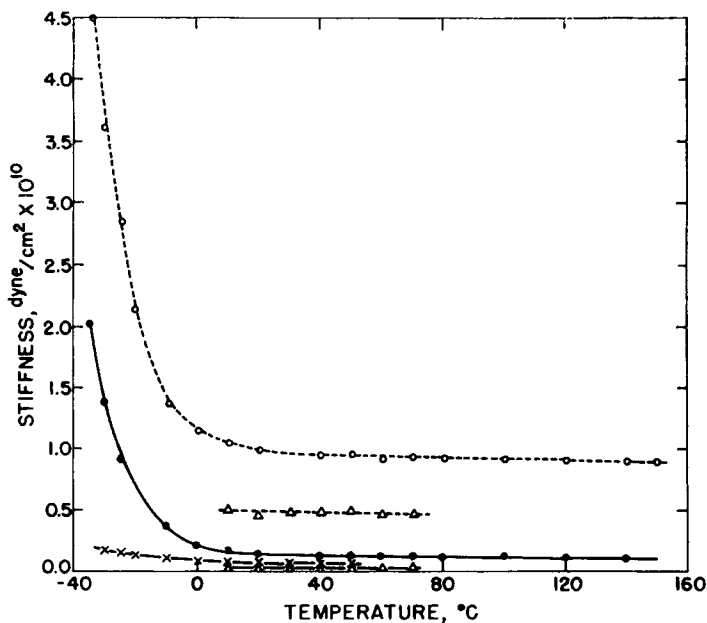


Fig. 12. Effect of temperature on stiffness of grafted fibers in air, water, and ethyl acetate. Dosage 20 Mrad. 900% Extent of grafting: (—●—) in air; (—△—) in water; (—×—) in ethyl acetate. (—○—) 154% Extent of grafting: in air. (—△—) zero grafting in water.

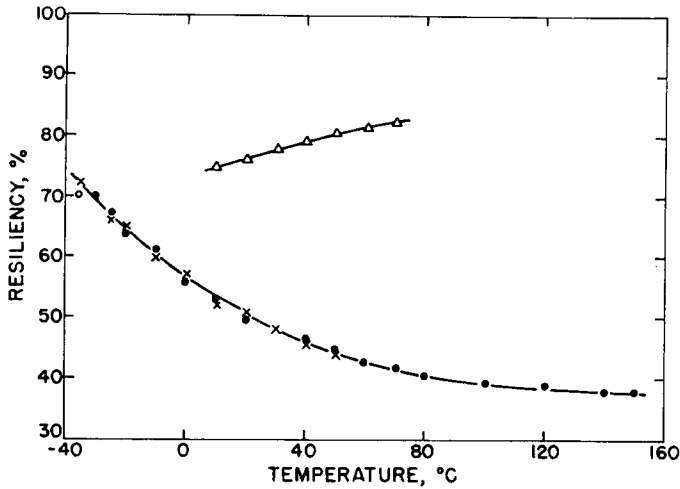


Fig. 13. Effect of temperature on resiliency of control fiber in air, water, and ethyl acetate. Extension 10%: (●) in air; (Δ) in water; (X) in ethyl acetate.

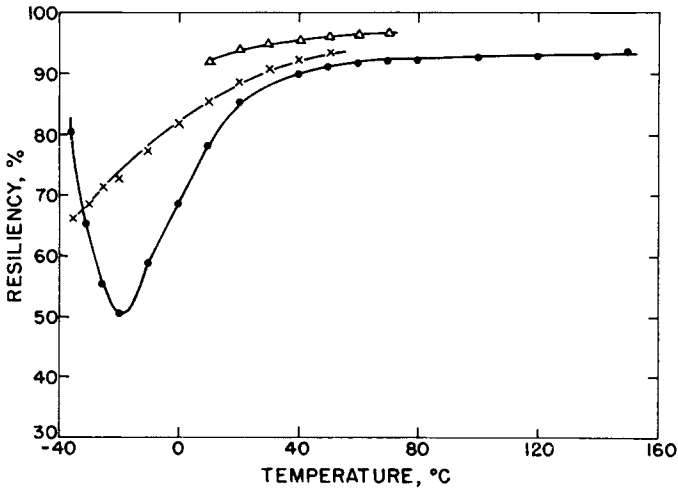


Fig. 14. Effect of temperature on resiliency of grafted fiber in air, water, and ethyl acetate. Dosage 20 Mrad; extent of grafting 900%; extension 10%: (●) in air; (Δ) in water; (X) in ethyl acetate.

The influence of temperature on the resiliency of the fibers, measured in air, water, and ethyl acetate, is shown in Figures 13 and 14. The resiliency of the untreated fibers, when measured in air and ethyl acetate, decreased to the same degree as the temperature of measurement was increased. The resiliency of the fibers in water increased with increase in temperature. The resiliency of the grafted fiber, as shown in Figure 14, increased with increase in temperature when measured in water and ethyl acetate. On the other hand, when measured in air, the minimum point of resiliency of the grafted fiber was at about  $-20^{\circ}\text{C}$ . The resiliency of the fibers in the



plateau region was highest when measured in water and lowest when measured in air. Generally, the temperature where the minimum region of the resiliency of the fibers was recorded coincided with the temperature where the stiffness of the fibers changed sharply and corresponded to the glass transition temperature.<sup>9,10</sup> It has been reported that the general characteristics of the stiffness-versus-temperature curve for the graft copolymer are similar to those observed for physical mixtures of homopolymers.<sup>18,19</sup> Also, it has been reported that the glass transition temperature of poly(ethyl acrylate) is  $-23^{\circ}$  to  $-29^{\circ}\text{C}$ .<sup>20</sup> The glass transition temperatures of the ungrafted fibers were above  $50^{\circ}\text{C}$ ,  $160^{\circ}\text{C}$ , and below  $5^{\circ}\text{C}$  when measured in ethyl acetate, dry air, and water, respectively. The transition temperatures of grafted fibers were below  $-35^{\circ}\text{C}$ , about  $-20^{\circ}\text{C}$ , and below  $5^{\circ}\text{C}$  when measured in ethyl acetate, dry air, and water, respectively. Also, it is suggested that the glass transition temperatures measured in ethyl acetate and air for the grafted fibers resulted from the grafted poly(ethyl acrylate). The glass transition temperature measured in water is attributed to both the trunk cellulose and grafted poly(ethyl acrylate), as related to the mechanical properties of the fibers in water. Consequently, it is considered that the grafted fiber is made up of the two separated phases which independently contributed to the mechanical properties. As seen in Figure 12, the rubbery plateau region was observed in all experimental environments above  $0^{\circ}\text{C}$ . Since similar behavior is generally recognized in block polymers and crosslinked polymers,<sup>21-26</sup> the results are considered to be due to the contribution of the rigid crystalline parts of the cellulose fiber stabilizing the amorphous, grafted poly(ethyl acrylate). Above the glass transition temperature, crosslinking and entanglement of the poly(ethyl acrylate) molecules with themselves and entanglement between the cellulose molecule and the poly(ethyl acrylate) molecule probably occurred.

The mechanical properties of the grafted fibers are also dependent on the differences in the glass transition temperatures of the trunk polymer cellulose and the grafted poly(ethyl acrylate) and on the differences in the configurations of the grafted polymer and the trunk polymer cellulose under the different experimental conditions. The elastic recovery, the breaking elongation, and the decrease in energy loss were increased in water, which is a swelling agent for cellulose but a poor solvent for the grafted poly(ethyl acrylate). Also, the tensile strength and the initial modulus of elasticity of the grafted fibers were highest in air, which is probably a poor environment for both cellulose and grafted poly(ethyl acrylate).<sup>17</sup> Generally, polymer in a poor environment has a curled-up configuration and increased inter- and intramolecular bonding which leads to increased tensile strength and initial modulus of elasticity.

### Equilibrium Degree of Swelling

As reported earlier, crosslinked poly(ethyl acrylate) which was separated from the grafted fibers after hydrolytic degradation of the cellulose was

not soluble in acetone. The average molecular weight per crosslinked poly-(ethyl acrylate) chain segment ( $M_c$ ) was determined in ethyl acetate by means of the equilibrium swelling method. The relation between the equilibrium degree of swelling in a liquid and the network structure has been reported by Flory<sup>27</sup> to be

$$-\ln(1 - V_2) - V_2 - \mu V_2^2 = \rho V_s M_c^{-1} [V_2^{1/3} - (V_2/2)] \quad (1)$$

where  $V_2$  is the volume fraction of the dried poly(ethyl acrylate) to the grafted poly(ethyl acrylate) swollen with ethyl acetate when the grafted fibers are immersed in ethyl acetate;  $V_s$  is the molar volume of ethyl acetate;  $\mu$  is a characteristic interaction constant between the poly(ethyl acrylate) and ethyl acetate (0.42 at 25°C)<sup>28</sup>; and  $\rho$  is the density of poly-(ethyl acrylate) (1.115 at 25°C). The volume fraction  $V_2$  is calculated from the following equation:

$$V_2 = \frac{\text{vol of dried grafted poly(ethyl acrylate)}}{\text{vol of dried grafted poly(ethyl acrylate)} + \text{vol of swelling medium taken up}} \quad (2)$$

Then if  $\bar{W}_0$  = weight of dried grafted fiber,  $\bar{W}$  = weight of wet grafted fiber,  $G$  = extent of grafting, and  $\phi$  = density of ethyl acetate (0.8980 at 25°C.),

$$V_2 = \frac{\bar{W}_0 G \phi}{\bar{W}_0 G \phi + (100 + G)(\bar{W} - \bar{W}_0)} \quad (3)$$

Effects of dosage, extent of grafting, and extension ratio in air before swelling on  $M_c$  or number of crosslinks per gram of grafted poly(ethyl

TABLE IV  
Equilibrium Swelling of Grafted Fibers in Ethyl Acetate at 25°C

Dosage, Mrad	Extent of grafting, %	Extension ratio in air before swelling, %	$V_2$	$M_c$	No. of crosslinks per g grafted poly- (ethyl acrylate), $\times 10^4$
6	291	0	0.3152	2653	1.88
6	987	0	0.2943	3840	1.30
6	987	30	0.2692	3984	1.25
6	987	100	0.2527	4633	1.07
20	154	0	0.2558	4231	1.18
20	900	0	0.2267	6100	0.81
20	900	100	0.1572	14124	0.35
20	900	400	0.1410	17751	0.28
50	302	0	0.1569	20968	0.23
50	989	0	0.1272	22889	0.21
50	989	30	0.1066	32944	0.15
50	989	100	0.0834	49683	0.10
50	989	400	0.0800	62950	0.07
50	989	600	0.0800	62950	0.07

acrylate) calculated by the above equations are shown in Table IV.  $M_c$  increased with increased dosage, extent of grafting, and extension ratio. That is, the number of crosslinks per gram of grafted poly(ethyl acrylate) decreased in all cases. The decrease of  $V_2$  with increase in depolymerization of the cellulose molecule, the more homogeneous grafting in the structure of the cellulose fiber with increase in extent of grafting, the chain scission of the cellulose molecule, the unravelling of entanglement of the grafted polymer with itself, and the untying of entanglement between the grafted polymer and the cellulose molecule based on the increase of extension ratio all contributed to these effects.

When  $M_c$  is calculated by Flory's equation for the swelling equilibrium of the crosslinked rubber-elastomeric polymer, it must, strictly speaking, be considered that the degree of swelling of the grafted poly(ethyl acrylate) is restricted by the energetic contribution of the trunk cellulose molecule. That is, Flory's equation for the swelling equilibrium would be more effectively applied to the grafted fibers irradiated to the highest dosage, 50 Mrad. The  $M_c$  calculated for grafted fibers irradiated below 20 Mrad would probably contain a large deviation, because the energetic effect of the cellulose molecule controlling the degree of swelling of the grafted poly-

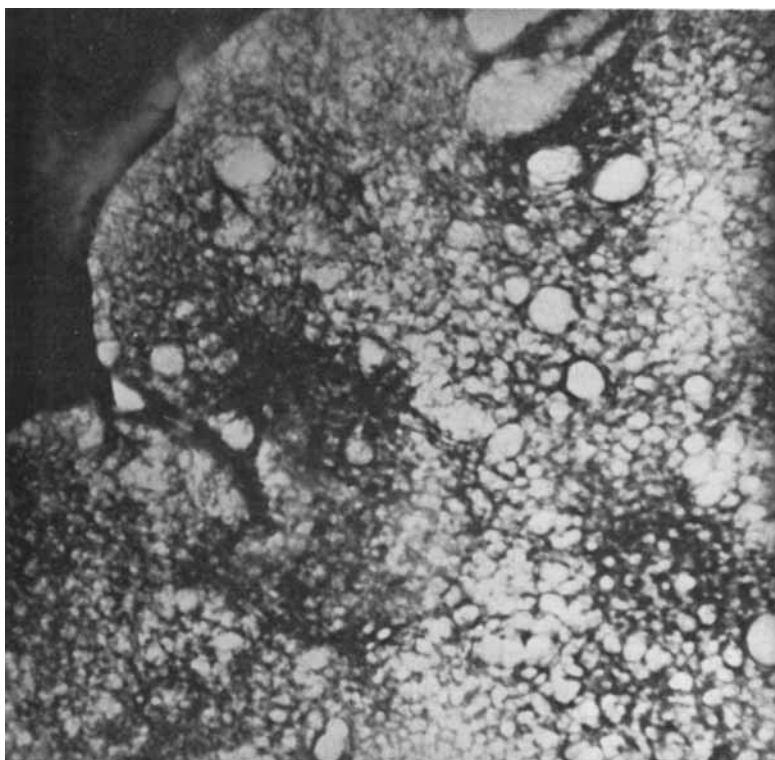


Fig. 15. Control fiber,  $\times 8800$ .

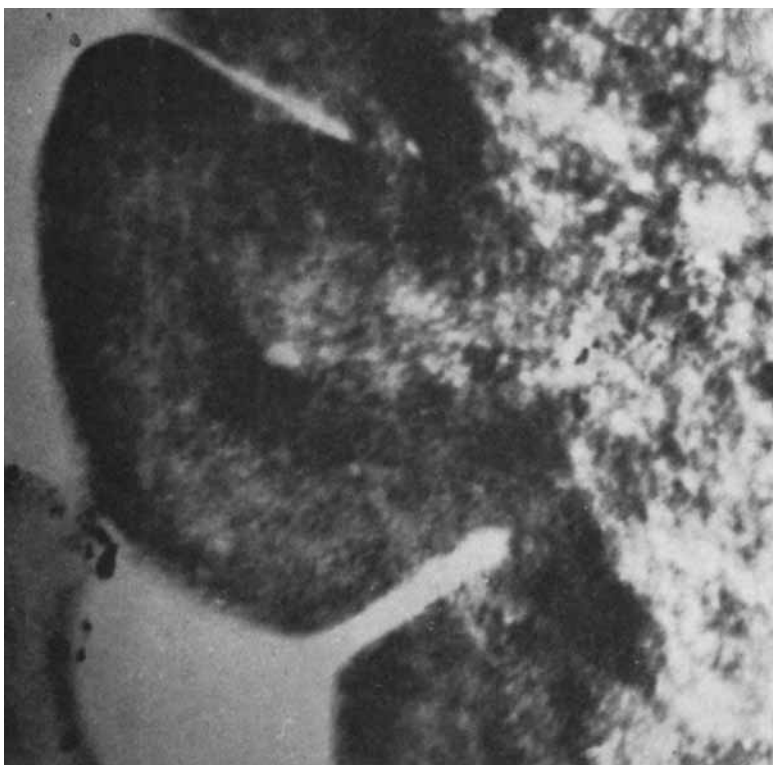


Fig. 16. Poly(ethyl acrylate)-grafted fiber. 20 Mrad; 154% extent of grafting;  $\times 12,320$ .

(ethyl acrylate) would be greater at the lower dosages due to less depolymerization of the cellulose molecule. However, the untying of entanglement of the grafted polymer with itself or between the grafted polymer and the cellulose molecule and the extension ratio in air before swelling the grafted fiber irradiated to 50 Mrad probably had a greater effect on  $M_c$  than the energetic contribution of the cellulose.

### Electron Microscopy

As describe above, the mechanical properties of the grafted fibers depended on the extent of grafting, so these fibers were examined by electron microscopy to determine their morphology, fine structure, and the location and distribution of poly(ethyl acrylate) in the structure of the fibers. Electron microphotographs of cross sections of the untreated and the grafted fibers, preirradiated to 20 Mrad, are shown in Figures 15, 16, 17, 18, and 19. There were many round voids in the cross section of the untreated fiber, as shown in Figure 15; the white regions in the microphotographs were voids or undyed cellulose. However, as shown in Figure 16 in the section of fiber grafted to 154%, few voids were due to filling of the structure with homopolymer of poly(ethyl acrylate); black portions in

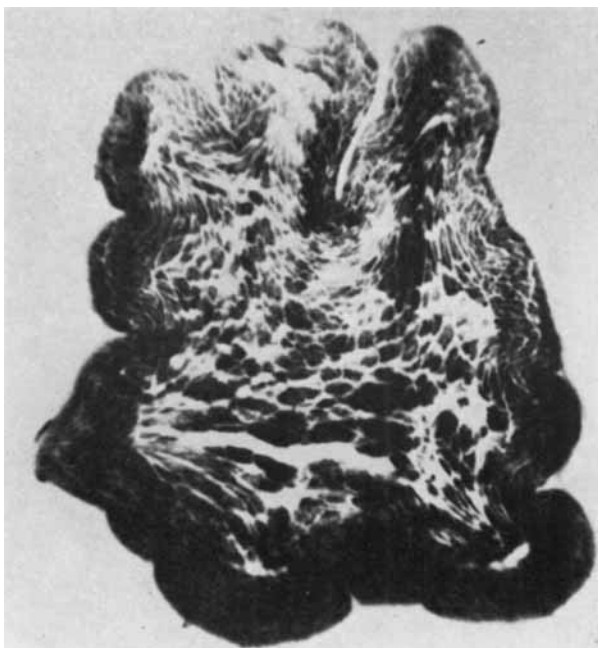


Fig. 17. Poly(ethyl acrylate)-grafted fiber. 20 Mrad; 302% extent of grafting;  $\times 2600$ .

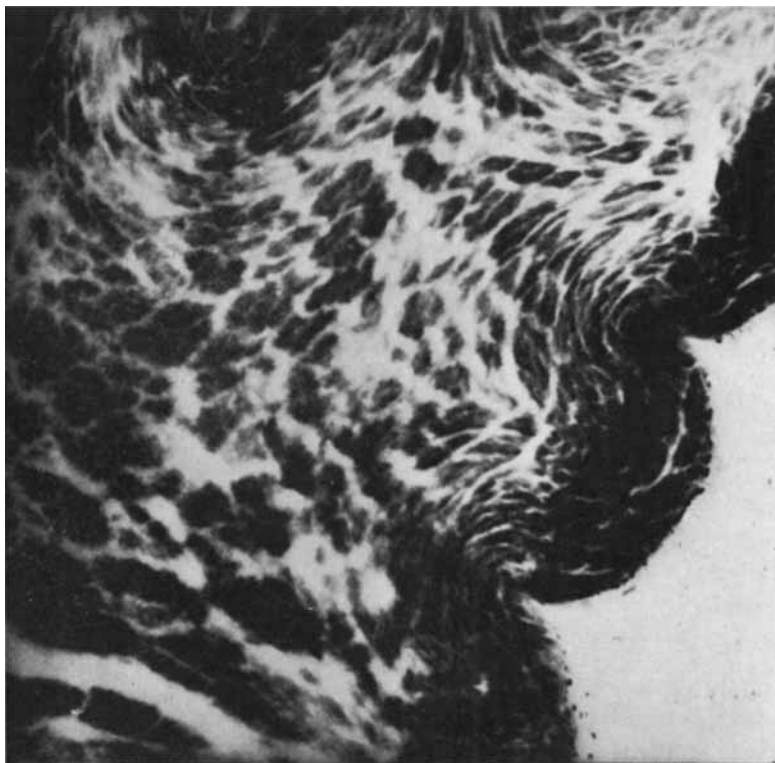


Fig. 18. Poly(ethyl acrylate)-grafted fiber. 20 Mrad; 302% extent of grafting;  $\times 7000$ .

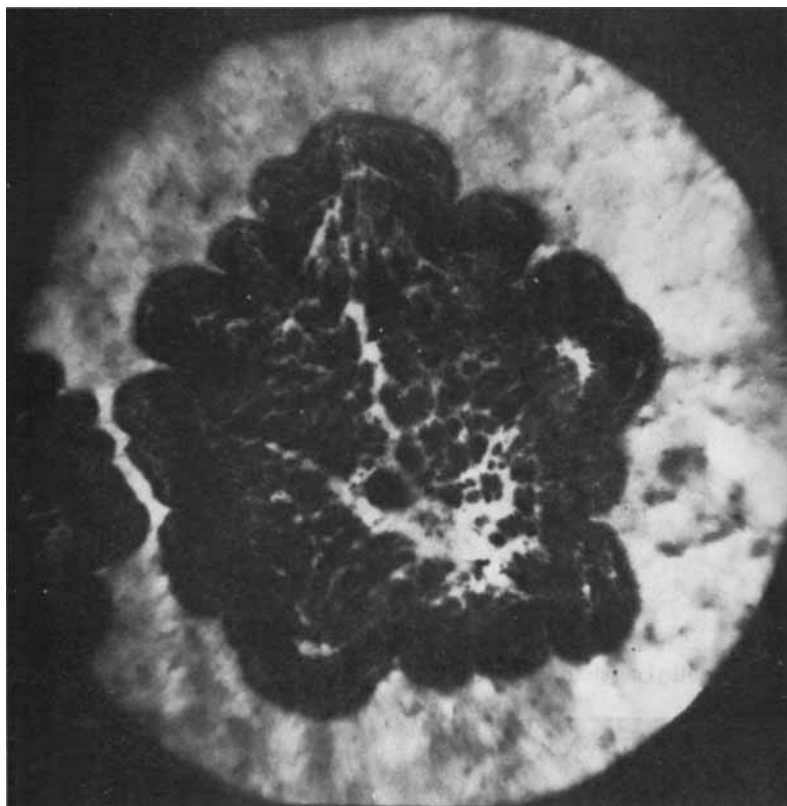


Fig. 19. Poly(ethyl acrylate)-grafted fiber. 20 Mrad; 900% extent of grafting;  $\times 1600$

the microphotographs were caused by poly(ethyl acrylate). Also, this sample had a dense band of grafted poly(ethyl acrylate) located in the outer layers of the fiber. These results are similar to electron microphotographs of cross sections of grafted cellulose fibers reported previously.<sup>28-31</sup> As the extent of grafting was increased, the cellulose fiber was separated into fibrillar structure, forming a uniform network which was not visible in the untreated fibers, as shown in Figures 17 and 18. Also, as the extent of grafting increased, the grafted and homopolymer poly(ethyl acrylate) which was not removed by extraction with acetone was uniformly distributed within the fibrous structure. As the extent of grafting was increased to 900%, as shown in Figure 19, portions of the grafted and homopolymer poly(ethyl acrylate) became more dense, especially in the outer layers. It is interesting that the fibers grafted to extents greater than 300% with poly(ethyl acrylate), which gave the singular fine structure, developed rubber-like elastomeric behavior.

Experimental work was conducted in the Japanese institutions. Yoshio Nakamura is presently on leave from Gunma University and is an NAS-NRC postdoctoral research associate at SRRL.

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