

Elastomers Based on Cellulose Fibers.

II. Ethyl Acrylate Grafting onto Disulfide-Crosslinked Cellulose

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Synopsis

Partially disulfide-crosslinked viscose rayon fibers ($-\text{S}-\text{S}-$ 2.3 mole/10⁴ g. cellulose) were prepared by means of mercaptoethylation and successive oxidation and then grafted to the extent of 200-1200% graft-on of ethyl acrylate with or without preswelling by zinc chloride, by using the ceric ion method. The tensile strength, breaking elongation, initial modulus, elastic recovery, and extension energy loss of the modified fibers were measured. In the disulfide-crosslinked, about 1000% ethyl acrylate-grafted fibers with preswelling, typical rubber elasticity was found. The disulfide crosslinkage in the grafted fibers was found generally to be capable of cleaving and re-forming by the reduction and successive oxidation treatments, and the properties were also well reversible. Therefrom, it was confirmed that intermolecular crosslinking between cellulose molecules plays an important role for developing of elastomeric properties, as was found for the methylene-crosslinked and grafted fiber reported previously. Most of elastomeric properties in our grafted fibers seem to be essentially attributable to the random conformation of the decrystallized, disoriented, and weakly crosslinked cellulose chains which are embedded in a matrix of flexible graft polymers.

INTRODUCTION

In a previous report from our laboratory, it was reported that a viscose fiber highly grafted with ethyl acrylate showed the rubber elastic behavior, especially on being grafted onto crosslinked cellulose with formaldehyde.¹

In the present paper, in order to elucidate the role of crosslinking, the introduction of disulfide crosslinks into cellulose by means of mercaptoethylation with ethylene sulfide followed by oxidation with hydrogen peroxide was attempted, and then grafting with ethyl acrylate with or without preswelling by a concentrated aqueous solution of zinc chloride was carried out. The physical properties of the products were measured, special attention being paid to the effect of crosslinking. It is well known that disulfide crosslinks can easily be cleaved and rebuilt by the reduction and oxidation reactions. This unique capability is deemed to be of interest in our investigation.

EXPERIMENTAL

Materials

The viscose fibers used were of bright regular type having a degree of polymerization of 210 (120 den., 25 filaments).

Ethylene sulfide was synthesized by blowing ethylene oxide into 50% aqueous KSCN solution according to the method described by Furukawa et al.² and purified by distillation, b.p. 55–56°C.

Ethyl acrylate was commercial material purified by the usual method.

Mercaptoethylation of Cellulose and Its Crosslinking

Mercaptoethylation of cellulose fibers was carried out by the method of Chaudhuri and Hermans.³ First, the water in the water-swollen cellulose fibers was displaced by treatment three times with absolute ethanol, and then the alcohol was replaced by treatment three times with dry benzene. The cellulose fibers, about 5 g., were reacted in 300 ml. benzene by dropwise addition of a benzene solution of ethylene sulfide (5 g./100 ml.), after which the reaction vessel was heated for 8 hr. at 75–80°C. with bubbling in of dry nitrogen gas throughout the duration of reaction. After mercaptoethylation of cellulose, the fibers were washed thoroughly with benzene, ethanol, and finally water freed of air by bubbling in of nitrogen gas. The partially mercaptoethylated cellulose obtained thus was crosslinked by soaking in 3% aqueous hydrogen peroxide solution (pH 8) for 20 hr. at room temperature.

The content of —SH groups before and after oxidation with hydrogen peroxide was determined by polarographic analysis according to the method of Leach⁴ applied in the fibrous keratin, and therefrom the —S—S— content of the crosslinked product was estimated. The content of —SH groups in the partially mercaptoethylated cellulose was found to be 4.6 mole/10⁴ g. cellulose and disappeared almost entirely on the successive oxidation. In addition, the oxidized sample was reduced with 0.5*N* thioglycolic acid solution of pH 4.7 for 12 hr. at 30°C. and washed well with water freed of air; the oxidation was reversible, i.e., the reduced sample was found to have almost the same content of —SH groups as before oxidation. From these facts, the oxidation product of partially mercaptoethylated cellulose was estimated to have a —S—S— crosslinks content of 2.3 mole/10⁴ g. cellulose.

Swelling Treatment

Disulfide crosslinked and untreated fibers were swollen with 10–60% aqueous zinc chloride solution for 24 hr. at 20 or 50°C. (liquor ratio, 300:1). After the swelling treatment, the fibers were washed well with water, then 0.1% acetic acid, and again with water. The swollen fibers obtained thus were subjected to graft copolymerization in the wet state.

To determine the extent of the opening of fiber structure by the swelling treatment, the water imbibition and the crystallinity of the fibers in the wet state after swelling with zinc chloride solution and washing well were determined by the same method as in the previous report.¹

Grafting Procedure

Graft copolymerization was carried out by the ceric ion method. The reaction system contained 2–15% ethyl acrylate, 0.02 mole/l. ceric ion ammonium nitrate, 0.01 mole/l. nitric acid, and 0.5% cationic detergent (lauryl pyridinium chloride). The reaction of grafting was performed for 24 hr. at 0°C. with bubbling in of nitrogen gas (liquor ratio, 300:1). After reaction, the fibers were washed with acetone, then water, and finally Soxhlet-extracted with acetone for 30 hr. to remove the homopolymer.

Reduction and Oxidation Treatment of Disulfide-Crosslinked and Grafted Fibers

The disulfide-crosslinked and grafted fibers were soaked in ethanol as the wetting agent for 3 hr. at room temperature, then washed with water several times, the excess water being removed with filter paper. The fibers in the wet state were reduced with 0.5*N* thioglycolic acid solution of pH 4.7 for 12 hr. at 30°C. (liquor ratio, 300:1), then washed well with water freed of air, and dried.

The reduced and water-washed fibers were immediately oxidized in 3% aqueous hydrogen peroxide solution of pH 8.0 (liquor ratio, 300:1) for 20 hr. at room temperature, then washed with water and dried.

The reduced or successively oxidized samples were soaked in ethanol free of air for 3 hr. at room temperature, then washed well with water free of air, and the excess water removed with filter paper. These samples in the wet state were immediately subjected to the quantitative analysis for —SH groups by the polarographic method.

Physical Testing

The tensile strength, breaking elongation, initial modulus of elasticity, instantaneous elastic recovery, and energy loss in hysteresis of the modified fibers were measured at 65% R.H. and 20°C. by using a Tensilon UTM-11 instrument. The cellulose crystallinity of the grafted fibers in the dry state was determined by the same method as mentioned in previous report.¹

Furthermore, the heat resistance was measured as the extent of shrinkage of fibers under a load of 0.2 mg./den. in an air oven for 10 min. at 100–250°C. or in boiling water for 30 min.

Also, the change of the viscosity-average degree of polymerization of cellulose in a series of reaction processes was measured for the untreated fibers.

RESULTS AND DISCUSSION

Water Imbibition and Crystallinity of ZnCl₂-Swollen Fibers

The effect of concentration of zinc chloride as the swelling agent on the water imbibition for untreated and disulfide-crosslinked fibers is shown in Figure 1. Though the water imbibition is hardly changed up to 40% zinc chloride solution, it suddenly increases over the concentration independent

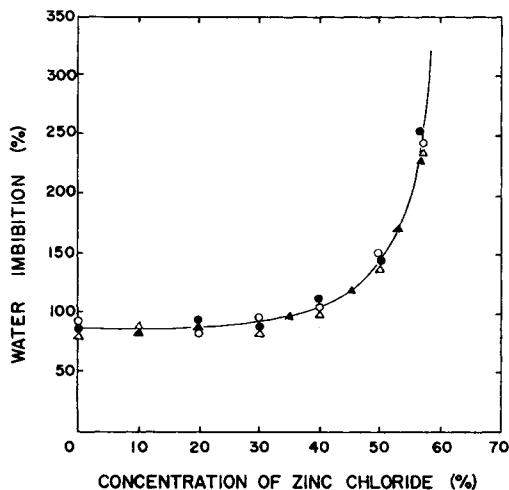


Fig. 1. Effect of concentration of zinc chloride as swelling agent on the water imbibition of rayon fibers: (○) untreated fibers swollen at 20°C.; (●) untreated fibers swollen at 50°C.; (△) disulfide-crosslinked fibers swollen at 20°C.; (▲) disulfide-crosslinked fibers swollen 50°C.

of the introduction of disulfide crosslinks and the temperature of swelling (20, 50°C.). Such behavior is the same as that in the methylene-crosslinked fiber reported previously.¹

The crystallinity of the fibers in the wet state after the swelling treatment by zinc chloride is shown in Table I. The decreasing crystallinity with increasing zinc chloride concentration is similar to that reported previously,¹ being almost unaffected by the amount of crosslinks. The fact that the crosslinked fibers are insoluble in concentrated (60%) zinc chloride solution

TABLE I
Changes of Cellulose Crystallinity in Wet State by ZnCl₂ Swelling Treatment for Untreated and Disulfide-Crosslinked Rayon Fibers

Concentration of zinc chloride, %	Temperature of treatment, °C. ^a	Cellulose crystallinity in wet state, % ^b	
		Untreated	Disulfide-crosslinked
Untreated	—	41	40
40	20	35	33
50	20	29	28
56	20	26	25
60	20	Soluble	23 ^c
50	50	27	26
56	50	24	24
60	50	Soluble	20 ^c

^a Swollen for 24 hr.

^b By x-ray diffraction method.

^c Agglutinated to some extent.

appears to be evidence for the presence of intermolecular disulfide crosslinks between cellulose chains.

Effect of Monomer Concentration on Graft-On

The graft-on of ethyl acrylate onto rayon fibers at varying concentration of monomer is shown in Figure 2. It is seen that the extent of grafting increases with increasing concentration of monomer, is almost unaffected by the presence of crosslinks and considerably increased by the swelling treatment, which shows the effect of opening of fiber structure. These results also coincide well with those for the methylene-crosslinked fibers.¹

Tensile Strength, Breaking Elongation, Initial Modulus, and Crystallinity of Grafted Fibers

Tensile strength, breaking elongation, initial modulus of elasticity, and cellulose crystallinity of the grafted fibers are shown in Table II. General-

TABLE II
Physical Properties of Disulfide Crosslinked and
EA-Grafted Rayon Fibers

Sample	Extent of grafting, %	Tensile strength, g./den. ^a	Breaking elongation, %	Initial modulus, g./den. ^a	Cellulose crystallinity in dry state, % ^b
Untreated rayon	—	1.60	28.8	22.0	42
Disulfide-crosslinked	—	1.53	25.0	28.0	41
EA-grafted	200	0.90	40.0	5.5	38
	510	0.47	53.5	1.2	37
	850	0.28	110	0.5	35
	1250	0.20	320	0.3	—
EA-grafted, after swelling ^c	220	0.88	55.0	2.0	24
	650	0.43	110	0.4	22
	800	0.32	161	0.3	22
	1200	0.21	380	0.2	—
EA-grafted after crosslinking	230	0.85	57.0	1.8	37
	550	0.43	120	0.5	36
	850	0.31	225	0.4	36
	1240	0.23	420	0.1	—
EA-grafted after crosslinking and swelling ^c	230	0.60	77.0	1.9	23
	490	0.33	170	0.6	23
	790	0.18	280	0.2	22
	1180	0.12	530	0.1	—

^a Based on grafted fibers.

^b By x-ray diffraction method.

^c Swollen in 56% ZnCl₂ at 20°C. for 24 hr.

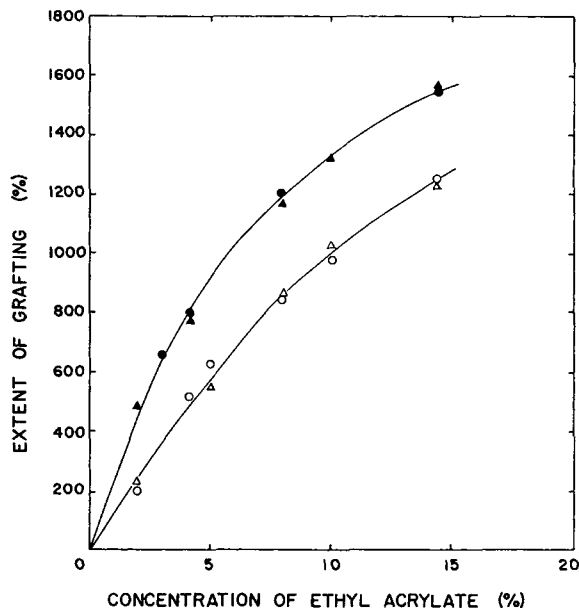


Fig. 2. Effect of concentration of ethyl acrylate on the graft-on for rayon fibers: (○) untreated unswollen fibers; (●) fibers preswollen in 56% $ZnCl_2$ at 20°C. for 24 hr.; (Δ) disulfide-crosslinked fibers, unswollen; (▲) disulfide- and crosslinked fibers preswollen as above.

ly, for the fibers highly grafted with ethyl acrylate, the tensile strength and initial modulus decrease and the breaking elongation increases with increasing graft-on. A marked decrease of tensile strength and an increase of elongation are brought about by the preswelling treatment of the disulfide-crosslinked fibers.

The effect of preswelling on the cellulose crystallinity in the dry state seems to be retained after grafting, being almost unaffected by the graft-on.

Elastic Recovery

The instantaneous elastic recovery of the grafted fibers was measured in the range of 20–200% extension. These results are shown in Table III. It is found that the elastic recovery is increased with the graft-on, and the fiber with about 1000% graft-on and containing disulfide crosslinks shows the most improvement in elastomeric properties. Though the preswelling treatment seems to decrease the elastic recovery, the disulfide-crosslinked and grafted fibers do not show the same effect as the graft product of methylene-crosslinked fibers.¹

The change of degree of polymerization of cellulose was measured in the untreated fibers in a series of reaction processes involving the treatments by hydrogen peroxide, zinc chloride, and ceric ion in that order, in which the depolymerization of cellulose chains is considered to occur to some

TABLE III
Elastic Recovery of Disulfide-Crosslinked and EA-Grafted Rayon Fibers

Sample	Extent of grafting, %	Elastic recovery, %			
		20% extension	50% extension	100% extension	200% extension
Untreated rayon	—	44	—	—	—
Disulfide-crosslinked	—	47	—	—	—
EA-grafted	200	75	—	—	—
	510	83	71	—	—
	850	88	77	65	—
	1250	95	88	80	75
EA-grafted after swelling ^a	220	60	40	—	—
	650	68	47	33	—
	800	79	59	42	—
	1200	83	70	59	51
EA-grafted after crosslinking	230	80	58	—	—
	550	89	80	70	—
	850	93	88	79	70
	1240	97	95	93	91
EA-grafted after crosslinking and swelling ^a	230	81	60	—	—
	490	89	80	71	—
	790	94	91	77	71
	1180	97	95	93	92

^a Swollen in 56% ZnCl₂ at 20°C. for 24 hr.

extent. The change was not very great, however, giving a decrease to 150 from 210 for the average degree of polymerization of cellulose.

Rayon fibers' relatively low degrees of grafting with acrylate have been reported to become elastomeric on being subjected to drastic acid hydrolysis of cellulose trunk chains;⁵ our measurements, however, indicate that a product of this kind appears to be more plastomeric, if anything.

Most of the elastomeric properties in our highly grafted fibers at least may be presumed to be essentially attributable to the random conformation of the considerably decrystallized, disoriented, and weakly crosslinked cellulose chains which are embedded in the matrix of flexible graft polymer, though the randomization of cellulose chains may be facilitated to some extent by the depolymerization of cellulose.¹

Extension Energy Loss

The energy loss of the fibers with about 1200% grafting was measured at 300% extension. The results obtained are shown in Table IV. In general, the energy loss is the greatest in the first cycle and decreased remarkably to almost the same extent in the second and third cycles. Also, it is found that the energy loss is decreased distinctly by the introduction of disulfide crosslinks and increased somewhat by preswelling

TABLE IV
Energy Loss at 300% Extension of Disulfide-Crosslinked and
EA-Grafted Rayon Fibers

Sample	Extent of grafting, %	Relaxation condition after 3rd cycle of 300% extension in air 65% R.H., 20°C.	Energy loss, ^a %		
			1st cycle	2nd cycle	3rd cycle
EA-grafted	1250	—	82	22	19
		In air, 65% R.H., 20°C., 24 hr.	41	23	20
		In water containing 0.1% non-ionic detergent, 20°C., 24 hr. ^b	38	22	20
		In acetone, 20°C., 24 hr. ^b	65	26	22
EA-grafted after crosslinking	1240	—	40	15	10
		In air, 65% R.H., 20°C., 24 hr.	27	12	7
		In water containing 0.1% non-ionic detergent, 20°C., 24 hr. ^b	25	10	7
		In acetone, 20°C., 24 hr. ^b	34	13	9
EA-grafted after crosslinking and swelling	1180	—	45	16	11

^a Measured at 65% R.H., 20°C.

^b Air-dried, then vacuum-dried before conditioning.

before grafting. These results correspond well to those for the methylene-crosslinked fibers.¹

After the three cycles of 300% extension and release at 65% R.H. and 20°C., the fibers were allowed to relax for 24 hr. in air or water containing 0.1% non-ionic detergent at 20°C. and the 300% extension-release cycle again repeated three times. The energy loss of the first cycle showed incomplete restoration to the original state; but, when the relaxation was carried out in a good solvent for the graft polymers (acetone) for 24 hr. at 20°C., the extent of the restoration of energy loss was found to be considerable. These facts appear to suggest that the deformation mechanism in the first extension cycle involves much release of the loosely entangled crosslinks between the graft polymers or the cellulose chains and graft polymers.

Effects of Cleaving and Re-forming of Disulfide Crosslinks

The disulfide-crosslinked and 1240% grafted fiber was subjected to the reduction and successive oxidation which appeared capable of cleaving or

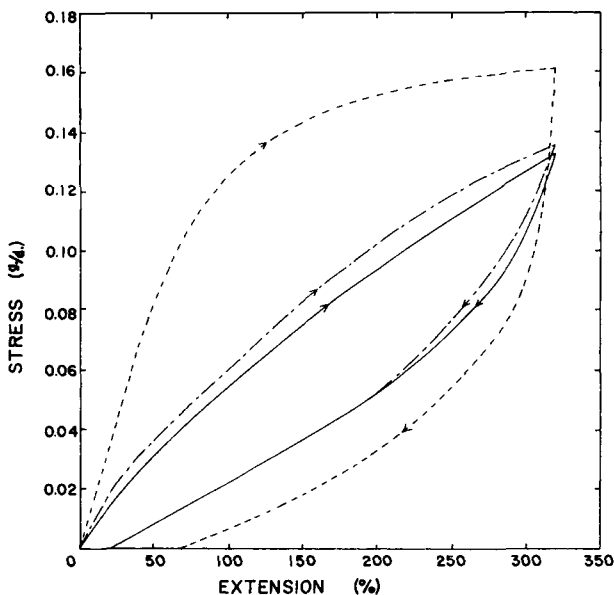


Fig. 3. Effects of reduction and oxidation treatments on the hysteresis curve at 300% extension for the disulfide-crosslinked and 1240% EA-grafted rayon fibers: (—) crosslinked and grafted; (--) after reduction; (- · -) after reduction and successive oxidation.

re-forming most of the crosslinks as shown in Table V. The elastic properties were measured at 65% R.H. and 20°C. after each treatment. The results obtained are given in Table V and Figure 3. It is obvious that the initial modulus, elastic recovery, and energy loss of the reduced fibers reach the same level observed in the grafted fiber without crosslinks and the most of changes by reduction are again restored by the successive oxidation.

TABLE V
Changes of Elastic Properties at 300% Extension by Reduction and Oxidation Treatments for Disulfide-Crosslinked and 1240% EA-Grafted Rayon Fibers

Sample	Content —S—S— group, mole/10 ⁴ g. cellulose	Reduction or oxidation treatment	Initial modulus of elasticity, g./den.	Elastic re- covery, %	Energy loss, %		
					1st cycle	2nd cycle	3rd cycle
EA-grafted	0	None	0.20	75	82	22	19
EA-grafted	2.3	None	0.09	93	40	15	10
after	0.0	Reduction	0.20	80	83	26	21
cross- linking	2.2	Oxidation	0.12	93	45	16	12
		after reduction					

As expected, it was confirmed that the intermolecular crosslinking between cellulose molecules plays an important role in elastomer based on the grafted cellulose fibers. Thus, the lower initial modulus and energy loss and the higher elastic recovery developed in the crosslinked and grafted fibers might be considered to be the prominent proof of the typical rubber elasticity.

Heat Resistance

The heat shrinkage of the grafted fibers was measured in the dry or wet state. The effect of disulfide crosslinking on the heat resistance is clear, Table VI.

TABLE VI
Heat Resistance of Disulfide-Crosslinked and EA-Grafted Rayon Fibers

Sample	Extent of grafting, %	Shrinkage, %				Boiling water ^b
		Dry air ^a				
		100°C.	150°C.	200°C.	250°C.	
Untreated rayon	—	1.0	2.1	4.8	Brittle	1.45
Disulfide-crosslinked	—	0.2	0.3	0.4	Brittle	0.21
EA-grafted	1250	1.2	2.3	5.2	Melt	2.55
EA-grafted after crosslinking	1240	0.20	0.21	0.9	Melt	0.32
EA-grafted after crosslinking and swelling	1180	0.20	0.30	0.8	Melt	0.33

^a After 10 min. under load of 0.2 mg./den.

^b After 30 min. under load of 0.2 mg./den.

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Received September, 6, 1967