

Crosslinking of Cyanoethylated Cotton

In previous work at this Laboratory, described in earlier publications,¹⁻³ cotton fabric was modified with a variety of substituents introduced under different conditions and was then crosslinked with methylol amide agents. This work has now been extended to the crosslinking of a cyanoethylated cotton with the subsequent removal of the cyanoethyl groups after crosslinking.

With alkali-stable crosslinks such as produced by dimethylol ethyleneurea, hydrolytic cleavage of the alkali-sensitive cyanoethyl groups was planned to regenerate the cellulose with crosslinks intact. The crosslink distribution of fabric treated by this scheme should be considerably different than that of cotton crosslinked conventionally. The cyanoethyl groups, if inert to the crosslinking agent, will block reaction at many of the cellulosic hydroxyl groups that would ordinarily react. It was believed that cotton with this unusual distribution of cellulose crosslinks could have novel properties.

Results from the described experiment are shown in the accompanying table. The

TABLE I
Crosslinking and Hydrolysis of Cyanoethylated Cotton

Properties of cyanoethylated cotton ^a						
Cyanoethyl D.S.	Before crosslinking ^b		After crosslinking		After crosslinking and hydrolysis ^c	
	Nitrogen, %	Wrinkle-recovery angle, ^d deg., $w + f$	Nitrogen, %	Wrinkle-recovery angle, deg., $w + f$	Nitrogen, %	Wrinkle-recovery angle, deg., $w + f$
0.0 ^e	—	206	1.18	276	1.19	261
0.52	3.69	—	^f	—	0.06	—
0.26	2.04	182	2.92	273	1.30	205
0.41	3.13	169	4.12	245	1.16	181
0.68	4.81	168	5.01	200	0.83	159

^a Cyanoethylated using different reaction times and the method of Kullman, Frick, Reinhardt, and Reid.¹

^b Crosslinked by application of 8% dimethylol ethyleneurea with 0.5% zinc nitrate hexahydrate, drying, and curing at 160°C.

^c Hydrolyzed in 0.05*N* ethanolic KOH, 60 min at 75–80°C.

^d Determined by the AATCC method, Technical Manual of the Amer. Assoc. of Textile Chemists and Colorists, 1966, Vol. 42, p. B155.

^e Unmodified control.

^f Not crosslinked.

hydrolytic conditions employed were sufficiently strong to completely remove cyanoethyl groups. The conditions did not affect the dimethylol ethyleneurea crosslinks although a small drop in wrinkle recovery did occur in the same that was crosslinked but not cyanoethylated. Hydrolysis of cyanoethylated cotton after crosslinking showed a loss of nitrogen content that was less than expected because it was less than the nitrogen introduced by cyanoethylation. The difference between the nitrogen lost on hydrolysis and the nitrogen introduced by cyanoethylation is probably due to loss of cyanoethyl groups during crosslinking. Trial treatments of cyanoethylated cotton with crosslinking catalyst alone under the reaction conditions produced a small loss of nitrogen.

During hydrolysis of the cyanoethylated and crosslinked cotton, an unexpectedly large drop in wrinkle-recovery angles occurs. Two hypotheses are offered to explain this phenomenon.

When cyanoethylated cotton is crosslinked, reactive sites may consist of those remaining unreacted after cyanoethylation, or those made by cleavage of cyanoethyl groups during crosslinking, or both. Unreacted hydroxyl groups may remain even in very accessible regions because of the reversibility of the cyanoethylation reaction. If the crosslinking reaction cannot reach all groups accessible to cyanoethylation, hydrolysis of cyanoethyl groups will leave regions of regenerated cellulose without crosslinks. These regions may have a low degree of lateral order because the tendency to return to a more ordered structure will be restrained by crosslinks in adjacent regions on cellulose chains common to both regions. These regions, without crosslinks and with little interchain attraction, will cause loss of resiliency and consequently a decrease in wrinkle-recovery angle. They will be weak links in the chain of resiliency.

An alternative explanation is that part of the crosslinking on cyanoethylated cotton occurs on a substituent group rather than on an unsubstituted hydroxyl group of the cellulose. This substituent group could be the group originally introduced or one that was modified by the crosslinking treatment. Hydrolytic cleavage of the substituent group then would cause loss of the crosslink.

The latter hypothesis is simpler but has the disadvantage that no such reaction is known. Reaction directly with cyanoethyl groups under acidic conditions seems unlikely. Reaction with carbamoylethyl groups, from the hydrolysis of cyanoethyl groups under reaction conditions, gives a product that was experimentally determined to be less susceptible to alkaline hydrolysis than the product from dimethylol ethyleneurea and cyanoethylated cotton.

Grafting of monomers to cotton, including acrylonitrile under ionic conditions, is becoming a widely used experimental procedure for modifying cotton.⁴ The phenomenon encountered in the present work may occur in the use of such modified cotton as substrates in sequential reactions.

References

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