Crease Recovery and Cuprammonium Solubility of Some Crosslinked Cotton Fabrics

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Synopsis

Cotton fabrics crosslinked with the pyridinium salts of three di(chloromethyl) ethrse become largely insoluble in cuprammonium hydroxide solution and their wet and dry crease recovery increases. The solubility falls to below 40% under all the conditions studied. Good improvements in crease recovery are observed only when solubility is below 4%, but the reverse does not hold; some fabrics of poor crease recovery may also have low solubility.

INTRODUCTION

The insolubility in cuprammonium hydroxide solution of a cellulose derivative of fairly low degree of substitution provides a strong indication that it is crosslinked, but the evidence is not conclusive, since at high degrees of substitution some monofunctional derivatives, e.g., methyl celluloses, are also insoluble.[1]

Mehta and co-workers[2-4] found no definite relation between cuprammonium solubility and crease recovery for cotton fabrics crosslinked with dimethylolurea (DMU) and dimethylolethyleneurea (DMEU). The treated fabrics were largely insoluble even after very mild treatments, and the insolubility persisted after removal of the resins by mild acid hydrolysis. The authors concluded that insolubilization was caused by formation of a relatively small number of methylene ether bridges. Small amounts of formaldehyde were found in all the samples after removal of the resins and the cuprammonium solubility was related to the amount present.

In the course of the present study of the crosslinking of cotton cellulose with several difunctional chloromethyl ethers, a considerable number of results linking crease recovery and solubility in cuprammonium hydroxide solution was obtained some time ago. Very little quantitative evidence on these lines seems to have been published.

The crosslinking agents used were di(chloromethyl) ether, di(chloromethoxy)methane and ethylene glycol di(chloromethyl) ether, all of which should give links chemically similar to methylene ether bridges and therefore stable to cuprammonium hydroxide. They were applied to cotton fabric as aqueous solutions of their pyridinium or N,N-dimethylanilinium

salts, in the presence of various concentrations of sodium acetate, and cured. The treated fabrics were tested for change in weight, wet and dry crease recovery, and cuprammonium solubility. The crosslinking mechanism is illustrated by the following equation for the reaction between cellulose and the pyridinium salt of di(chloromethyl) ether.

$$ClN(C_5H_5)CH_2OCH_2(C_5H_5)NCl + 2\,Cell.OH = Cell.OCH_2OCH_2OCell$$

$$+ \;\; 2C_5H_5N \;\; + \;\; 2HCl$$
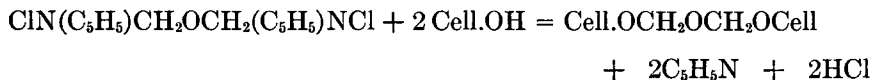
where Cell.OH represents cellulose.

EXPERIMENTAL

Materials

A scoured and bleached cotton poplin (4 oz/yd^2) was used. Di(chloromethyl) ether and di(chloromethoxy)methane were prepared as described by Head.[5] Ethylene glycol di(chloromethyl) ether was made by adding thionyl chloride (80 cc) gradually to a mixture of ethylene glycol (31 g) and paraformaldehyde (31 g). When the vigorous reaction had subsided,
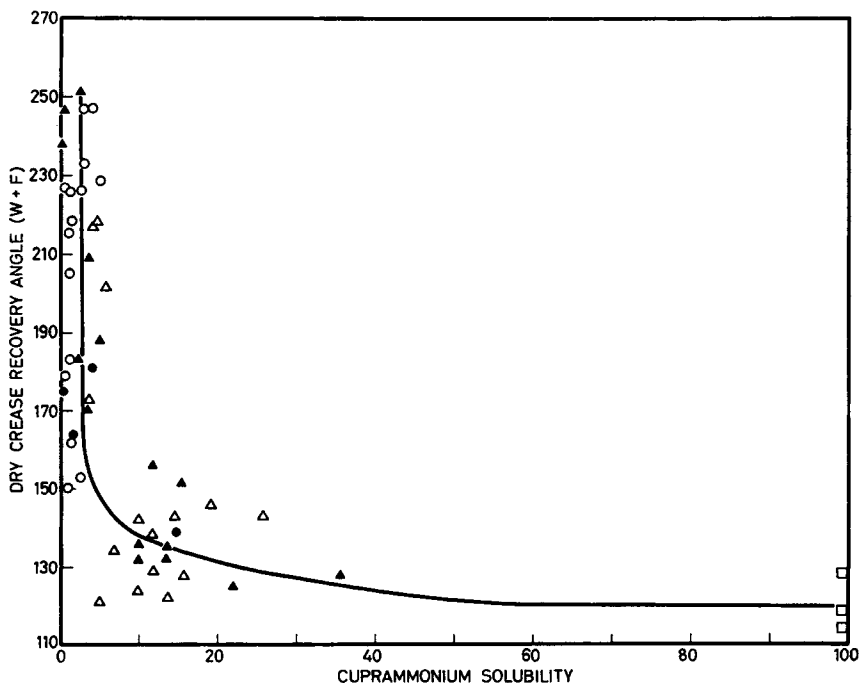

Fig. 1. Dry crease recovery and cuprammonium solubility of cotton fabrics, untreated (□) or treated with ethylene glycol di(chloromethyl) ether [pyridinium salt (O) or dimethylanilinium salt (●)], or with the pyridinium salts of di(chloromethyl) ether (△) or di(chloromethoxy)methane (▲).

the mixture was heated cautiously for a short time until it became homogeneous and then was fractionally distilled under reduced pressure. The compound (66.7 g) boiled at 86°–88°C/8 mm (literature[6] 95°C/13 mm).

The pyridinium salts of di(chloromethyl) ether and di(chloromethoxy) methane were made by mixing solutions of the dichloro compounds in ether with the theoretical amounts of pyridine and leaving the mixtures for several days at room temperature. The solids which separated were washed with ether and dried in vacuo over phosphorus pentoxide. The pyridinium and dimethylanilinium (DMA) salts of ethylene glycol di(chloromethyl) ether were made similarly, but with acetone as the solvent. Before use, aqueous solutions of the DMA salt were freed from dimethylaniline (present as the hydrochloride) by neutralization to pH ca. 7 and extraction with ether.

Application

Strips of cloth were soaked in aqueous solutions of the pyridinium or DMA salts and mangled so that the uptake of the salt was 5% or 10% on the weight of the cloth. The salt solutions were first adjusted to pH 6 by addition of sodium bicarbonate and then treated with quantities of sodium acetate ranging from 0 to 100% of the equivalent of the chlorine present.
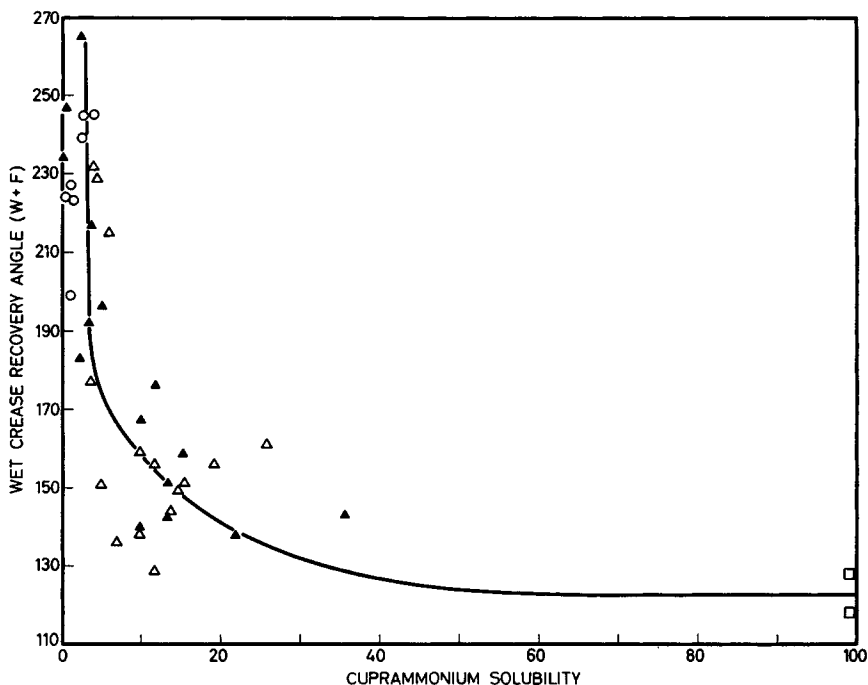

Fig. 2. Wet crease recovery and cuprammonium solubility of cotton fabrics, untreated (□) or treated with the pyridinium salts of ethylene glycol di(chloromethyl) ether (O), di(chloromethyl) ether (△), or di(chloromethoxy)methane (▲).

TABLE I
Treatment of Cotton Fabric with Pyridinium Salt (A) and
Dimethylanilinium Salt (B) of Ethylene Glycol
Di(chloromethyl) Ether

| Treat-ment | Amount of reagent on cloth, % | Initial pH of bath | Sodium acetate added,[a] % | Solubility in cupram-monium Hy-droxide % | Crease recovery angles | | | |
| | | | | | Dry | | Wet | |
					W	F	W	F
A	0	—	0	99.3	62	66	—	—
	10	6	0	2.8	125	122	—	—
	5	6	0	4.9	117	112	—	—
	10	6	50	0.5	115	112	—	—
	5	6	50	1.2	91	92	—	—
	10	6	100	2.5	76	77	—	—
	5	6	100	1.3	82	80	—	—
	10	9	0	1.1	116	110	—	—
	5	9	0	1.1	102	103	—	—
A	0	—	0	99.2	56	58	68	60
	10	6	0	4.0	123	124	130	115
	10	6	10	2.9	119	114	126	119
	10	6	20	2.7	112	114	125	114
	10	6	40	1.5	112	106	114	109
	10	6	60	1.1	109	106	117	110
	10	6	80	0.5	92	87	110	114
	10	6	100	1.0	78	72	104	95
B	10	7	50	0.4	90	85	—	—
	10	7	100	14.7	71	68	—	—
	10	9	0	4.0	90	91	—	—
	10	6	50	1.8	85	79	—	—

[a] Percentage of amount equivalent to available acid present in A or B.

Alternatively they were adjusted to ca. pH 9 by addition of sodium carbonate. The dried cloth samples were baked in an oven at 120°C for 1 hr, extracted twice with acetone, washed thoroughly with water, heated for 0.5 hr at 95°C in a solution containing 0.5% soap and 0.2% sodium carbonate, washed again, and dried.

Test Procedures

Dry crease recovery angles were measured by the British Standards method[7] except that times of loading and recovery were each 1 min instead of 3 min. Wet crease recovery angles were determined on specimens soaked for 2 hr in distilled water at 20°C and folded between filter papers.

Solubility in cuprammonium hydroxide solution was determined by a modification of Krässig's method.[8] The solutions were made up as for the determination of cuprammonium fluidity by the British Standards method,[9] but two small steel ball bearings were used for mixing instead of the mercury. The undissolved portion, washed with (a) cuprammonium hydroxide

TABLE II. Treatment of Cotton Fabric with Pyridinium Salts of Di(chloromethyl) Ether (C) and Di(chloromethoxy)methane (D)

Treat-ment	Amount of reagent on cloth, %	Initial pH of bath	Sodium acetate added, %	Solubility in cuprammonium hydroxide, %	Crease recovery angles			
					Dry		Wet	
					W	F	W	F
C	0	—	0	99.2	60	59	61	57
	10	6	0	4.5	106	112	116	113
	10	6	50	13.8	60	62	72	72
	10	6	100	5.0	61	60	79	72
	10	9	0	15.5	63	65	77	74
C	10	6	0	3.9	108	109	116	116
	10	6	10	5.9	102	100	110	105
	10	6	40	19.2	74	72	83	73
	10	6	80	11.6	67	71	83	73
	10	6	100	9.9	68	74	80	79
	10	9	0	23.8	72	71	82	79
	10	—	50 (Na₂CO₃)	14.5	72	71	77	72
C	10	6	0	3.6	91	82	95	82
	10	6	5	6.9	67	67	70	66
	10	6	10	9.9	61	63	67	71
	10	6	15	11.8	65	64	67	62
D	11	6	0	2.4	128	123	134	131
	11	6	50	13.3	65	67	83	68
	11	6	100	35.6	66	62	74	69
	11	9	—	11.8	78	78	94	82
D	11	6	0	0.5	126	120	130	117
	11	6	10	3.3	88	82	106	86
	11	6	20	10.0	72	64	81	86
	11	6	40	10.0	66	66	78	62
	11	6	100	21.9	63	62	72	66
	11	9	0	15.3	79	72	82	77
	11	—	50 (Na₂CO₃)	13.4	69	66	74	69
D	11	6	0	0.1	119	119	120	114
	11	6	5	3.6	105	104	111	106
	11	6	10	2.2	93	90	96	87
	11	6	15	5.0	95	93	101	95

solution, (b) 10% Rochelle salt solution, and (c) water, was dried for 2 hr at 120°C.   Means of two determinations are quoted.

RESULTS AND DISCUSSION

The treatments occasioned small increases in weight (not more than 3%), but losses in tensile strength were in some cases considerable.   The results given in Tables I and II and plotted in Figures 1 and 2 link the dry and wet recovery angles (sums of warp and fill, $W + F$) with cuprammonium solubility.

High values of dry crease recovery (Fig. 1) were invariably associated with very low solubilities—less than 4%—but the reverse did not hold. Several treated fabrics less than 4% soluble had ($W + F$) values between 150° and 190°.   Only four fabrics with a ($W + F$) value above 150° were more than 4% soluble, but below this level solubilities ranged from 5% to 35%, and there was considerable scatter of the points.   All the treatments, therefore, led to a great reduction in solubility.   Of the crosslinking agents used, the pyridinium salt of ethylene glycol di(chloromethyl) ether gave the best results, and di(chloromethoxy)methane was better than di(chloromethyl) ether.   Wet crease recoveries were of the same order as the dry recoveries, and the conclusions to be drawn from Figure 2 are very similar to those from Figure 1.

The ($W + F$) values exceeded 240° only for fabrics treated in the absence of sodium acetate buffer, but considerable weakening of the fabric then occurred.   Addition of sodium acetate reduced both the weakening and the improvement in crease recovery, though many of the products were of low cuprammonium solubility.

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