

Studies on Chemically Modified Cotton Fabrics: Part III—Chemical Properties of DMEU Stripped Hydrocellulose and Hypochlorite Oxycellulose

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Two chemically modified cotton fabrics, viz. (1) hydrocellulose and (2) hypochlorite oxycellulose of degrees of polymerization (DPn) varying from 2300 to 350 were subjected to (i) catalyst treatment using 20 g/litre $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, (ii) DMEU finishing, (iii) urea-phosphoric acid (UPac) hydrolysis, and (iv) DMEU stripping. Evaluation of changes in functional groups and DPn has shown that catalyst treatment and UPac hydrolysis do not alter either the DPn or the contents of various functional groups of the two chemically modified fabrics. DMEU finishing introduces DMEU crosslinks. DMEU stripping by UPac hydrolysis causes a slight increase in DPn values, but there is no change in the contents of functional groups of hydrocellulose. Similar treatment of hypochlorite oxycellulose causes reduction in DPn values and significant increase in aldehyde and carboxyl group contents.

In the authors' earlier studies in this series^{1,2}, it was found that chemical modifications of cotton fabric through either acid hydrolysis or alkaline hypochlorite oxidation produce in the case of acid hydrolysis, hydrocelluloses which are characterized by high aldehyde group content of reducing type with low carboxyl and moderately high carbonyl groups, and in the case of alkaline hypochlorite oxidation, hypochlorite oxycelluloses possessing high content of carboxyl groups along with high non-reducing type of aldehyde groups and slightly low level of carbonyl groups. Study of the strength-abrasion properties of these two types of fabrics showed that the latter give better performance compared to the former, both before and after DMEU finishing. With a view to studying the factors contributing to this varied behaviour of these two chemically modified cotton fabrics, it was thought worthwhile to assess the changes in the chemical and physical properties of these two celluloses after the removal of DMEU crosslinks introduced during the pad-dry-cure treatment with DMEU-catalyst system. A pad-dry-cure treatment with catalyst alone was also given to assess the contribution of catalyst and thermal treatment on the molecular degradation of these two fabrics.

Materials and Methods

Poplin fabric of the same construction and subjected to the same pretreatments as described earlier¹ was employed in the present study. The two modified

cotton fabrics, viz. hydrocellulose and hypochlorite oxycellulose with levels of DPn varying from 1400 to 350 were prepared employing the conditions reported earlier¹, except that the duration of treatment ranged from 65 min for DPn 1400 to 375 min for DPn 350 for hydrocellulose and 10 min for DPn 1400 to 210 min for DPn 350 for hypochlorite oxycellulose.

Treatments

DMEU and catalyst treatment—For thermal treatment in the presence of catalyst, the two modified cotton fabrics were padded through 20 g/litre magnesium chloride hexahydrate solution at 80% pick-up followed by drying at 80°C for 5 min and curing at 150°C for 5 min. DMEU finishing of these two modified cotton fabrics was also carried out using a solution of 150 g/litre DMEU and 20 g/litre magnesium chloride hexahydrate under the above-mentioned conditions for pad-dry and cure steps. In both the cases, a thorough afterwash was carried out using 5 g/litre soap and 2 g/litre soda ash at 95°C for 30 min followed by hot and cold water rinses. The samples were then line dried.

Urea-phosphoric acid (UPac) hydrolysis—To remove the DMEU crosslinks from the finished samples, UPac hydrolysis was carried out as per the method employed by Jung *et al.*³ using a solution of 5% by weight of urea and 1.5% by weight of phosphoric acid at 80°C for 30 min with material-liquor ratio 1:25. The samples were then washed with hot water for 15

min followed by air drying. Similar treatments were given to unfinished modified fabrics also.

Methods

Chemical test methods for the determination of cuprammonium fluidity, copper number, carboxyl content, etc. employed in the present study were the same as reported earlier¹, except that for the aldehyde content determination, chlorous acid treatment was carried out at room temperature (28-30°C) and not at 20°C as in the earlier study, since it was found that although increase in temperature causes increase in aldehyde content, it gives more uniform and reproducible results. In addition to the above chemical tests, combined formaldehyde of DMEU finished fabrics was determined by the colorimetric method using chromotropic acid, as suggested by Roff⁴. Infrared absorption spectra were recorded with Perkin-Elmer double beam spectrophotometer type 377 using KBr disc technique of O'Connor *et al.*⁵. The accessibility index was determined by a modified version of the iodine absorption technique of Nelson *et al.*⁶.

Results and Discussion

Unfinished hydrocelluloses and hypochlorite oxycelluloses—As in the earlier study¹, the two modified celluloses, viz. hydrocellulose and hypochlorite oxycellulose, show wide differences in their values for various functional groups (Table 1). Thus, for a given degree of polymerization (DPn), the copper numbers of hydrocellulose samples are considerably higher than those for hypochlorite oxycellulose, especially as the DPn decreases. The carboxyl content of hydrocellulose sample is unchanged with change in DPn, whereas hypochlorite oxycellulose samples show considerable increase in carboxyl content as the DPn decreases. The aldehyde and carbonyl contents of both these modified celluloses increase with decreasing DPn, more so in the case of hydrocellulose samples. The accessibility index shows a decreasing trend with decrease in DPn on both these modified celluloses, probably due to the dissolution of highly degraded accessible portions of the two modified celluloses. However, moisture regain data do not show any such trend.

Effect of thermal treatment in the presence of catalyst—The effect of thermal treatment (pad-dry-cure treatment) in the presence of magnesium chloride hexahydrate as catalyst on the above properties/functional groups was studied. The data obtained are given in Table 1. Thermal treatment causes reduction in the chain length of the cellulose molecules of both the modified celluloses, as seen from the decrease in their DPn values. However, the extent of reduction is

not uniform with either of the modified celluloses. The copper number of hydrocellulose samples decreases on catalyst treatment, especially for those having lower DPn values, whereas in the case of hypochlorite oxycellulose, there is a slight increasing trend in this property for all the samples. The carboxyl content of hydrocellulose samples remains unchanged, but the values for hypochlorite oxycellulose show an increase over values for the respective untreated samples. The aldehyde content of hydrocellulose samples decreases on catalyst treatment, whereas the values for hypochlorite oxycellulose show a slight increase. The carbonyl content, moisture regain and accessibility index of both the modified celluloses show hardly any change on catalyst treatment.

From the decrease in copper number and aldehyde content on catalyst treatment of hydrocellulose samples, it can be inferred that some of the reducing ends of hydrocellulose are converted into 1,6-anhydro derivative during the pad-dry-cure treatment with magnesium chloride hexahydrate. Similar treatment on hypochlorite oxycellulose leads to an increase in aldehyde and carboxyl groups, which may be due to the oxidation of some of the alcoholic groups to aldehyde groups and subsequently to carboxyl groups. However, it is to be noted that these changes in the contents of functional groups of both modified celluloses are of a low order.

In a recent study by Koudelka⁷ on periodate oxycellulose it was found that there is a significant reduction in DPn, copper number, carboxyl content and carbonyl content on thermal treatment in the presence of magnesium chloride hexahydrate as catalyst. Periodate oxycellulose is known to possess aldehyde groups of reducing type characterized by high copper number at C₂ and C₃ positions in the anhydroglucose unit of the cellulose molecule, whereas in the case of hydrocellulose, such reducing type of aldehyde groups are present at C₁ position. In the case of hypochlorite oxycellulose, the pseudo-aldehyde groups of non-reducing type are present at C₆ position. Thus, hydrocellulose follows a slight decreasing trend in functional groups similar to that observed by Koudelka in periodate oxycellulose. In contrast to this, a slight increasing trend in the case of hypochlorite oxycellulose is seen, probably due to the nature and position of aldehyde group in the anhydroglucose unit of this oxycellulose.

Effect of DMEU crosslinking—The crosslinking reaction of DMEU with two chemically modified fabrics introduces additional groups, such as amido, N-methylol, carbonyl, etc. and thus the evaluation of the various functional groups will be interfered by the presence of these groups. Hence, no attempt has been made to assess the various functional groups, as

Table 1—Chemical Test Results on Hydrocellulose and Hypochlorite Oxycellulose After Catalyst Treatment and DMEU Stripping

Sample	Treatment condition min./°C	DPn			Copper number			Carboxyl content meq/100 g			Aldehyde content meq/100 g			Carbonyl content meq/100 g			Accessibility index, %			Nitrogen % owf			Moisture regain % owf						
		A	B	E	A	B	E	A	B	E	A	B	E	A	B	E	A	B	E	A	B	E	A	B	E	C			
Hydrocellulose																													
MSB	—	2360	1979	2520	—	—	—	—	—	—	0.63	0.65	0.61	0.48	0.49	0.53	0.12	0.07	0.10	13.0	7.0	7.0	0.03	0.05	0.05	6.83	6.79	6.85	6.26
(Control)			(-16.2)*	(+6.7)																									
H ₁	65/40	1400	1303	1437	0.08	0.13	0.05	0.65	0.78	0.65	0.78	0.69	0.68	0.21	0.23	0.19	6.9	7.0	4.7	0.03	0.03	0.03	0.03	0.03	0.03	6.66	6.50	6.54	5.92
			(-6.9)	(+6.4)																									
H ₂	350/40	750	658	820	0.99	0.66	0.57	0.69	0.70	0.71	0.90	0.82	0.80	0.45	0.52	0.47	4.2	4.2	5.4	0.03	0.02	0.03	0.03	0.02	0.03	6.45	6.29	6.35	5.98
			(-11.3)	(+9.0)																									
H ₃	170/50	560	582	585	1.40	1.35	1.60	0.62	0.64	0.73	1.75	1.50	1.68	0.73	0.65	0.76	6.8	3.1	3.3	0.04	0.03	0.04	0.03	0.04	0.03	6.62	6.70	6.74	6.08
			(+4.6)	(+2.5)																									
H ₄	375/50	380	379	434	3.03	2.69	2.75	0.57	0.65	0.66	2.13	2.74	2.78	1.39	1.12	1.10	4.5	5.0	5.8	0.02	0.03	0.03	0.03	0.03	0.03	6.50	6.29	6.57	5.67
			(-0.8)	(+15.4)																									
Hypochlorite oxycellulose																													
MSS	—	2360	2253	—	—	—	—	0.57	0.57	0.57	0.55	0.59	0.59	0.07	0.10	0.12	7.7	7.0	9.2	0.03	0.03	0.03	0.05	0.03	0.05	6.95	6.77	6.79	6.02
(Control)			(-4.6)																										
HC ₁	10/50	1490	1326	1266	—	0.01	0.02	0.94	0.96	1.11	0.43	0.52	0.67	0.15	0.18	0.25	10.4	9.7	8.1	0.03	0.02	0.03	0.03	0.02	0.03	6.58	6.56	6.60	5.92
			(-11.2)	(-15.8)																									
HC ₂	40/50	740	625	601	0.13	0.24	0.58	1.85	2.00	2.38	0.59	0.65	0.81	0.31	0.30	0.47	7.7	9.4	6.7	0.03	0.03	0.03	0.03	0.03	0.03	6.48	6.35	6.36	5.79
			(-16.6)	(-18.6)																									
HC ₃	75/50	570	566	492	0.33	0.34	1.04	2.73	3.13	3.88	1.27	1.22	1.74	0.48	0.48	0.79	7.3	3.5	4.5	0.03	0.03	0.03	0.04	0.03	0.04	6.79	6.77	6.64	6.15
			(-3.3)	(-12.1)																									
HC ₄	210/50	360	312	290	0.53	0.57	0.92	5.44	5.26	5.56	1.41	1.68	1.20	0.64	0.71	0.35	5.2	4.1	6.7	0.03	0.03	0.03	0.04	0.03	0.04	6.52	6.31	6.41	5.79
			(-14.5)	(-17.6)																									

A, Unfinished; B, Catalyst treated; C, DMEU finished; and E, DMEU stripped samples.
*Figures given within parentheses represent % change based on values in column A.

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mentioned above, on DMEU finished fabrics. However, chemical analysis data for fixed nitrogen and bound formaldehyde (Table 3) and IR spectra of DMEU finished samples (Figs. 1-3) confirm the presence of these crosslinks on DMEU finished fabrics. Moisture regain by DMEU finished samples of both the modified fabrics (Table 1) shows a marked decrease, suggesting reduced accessibility of cellulosic hydroxyl groups to water vapour which has been brought about by DMEU crosslinks of cellulose molecules in the collapsed state.

Effect of urea-phosphoric acid hydrolysis—Urea-phosphoric acid (UPac) hydrolysis is used widely for the removal of DMEU crosslinks from the finished fabrics^{3,8}. In this study, DMEU stripping by UPac hydrolysis was attempted to find out the chemical and physical changes taking place on hydrocelluloses and

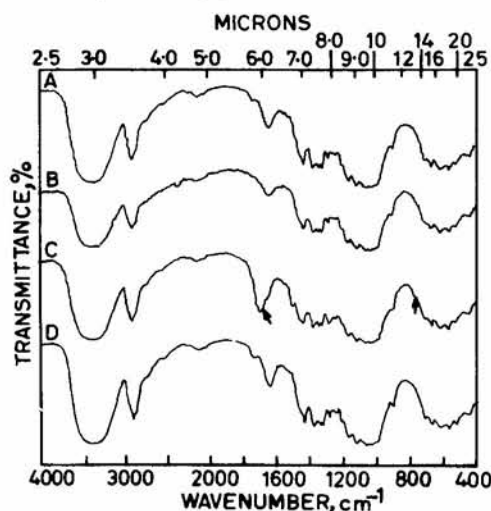


Fig. 1—Infrared spectra of mercerized-scoured-bleached (MSB) poplin [(A) control, (B) catalyst treated, (C) DMEU finished, and (D) DMEU stripped]

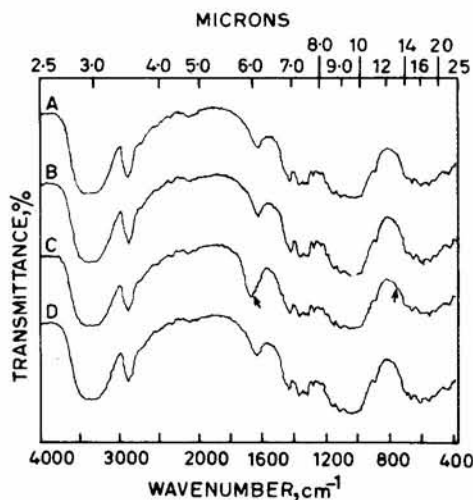


Fig. 2—Infrared spectra of hydrocellulose of around 350 DPn (H₄) [(A) unfinished, (B) catalyst treated, (C) DMEU finished, and (D) DMEU stripped]

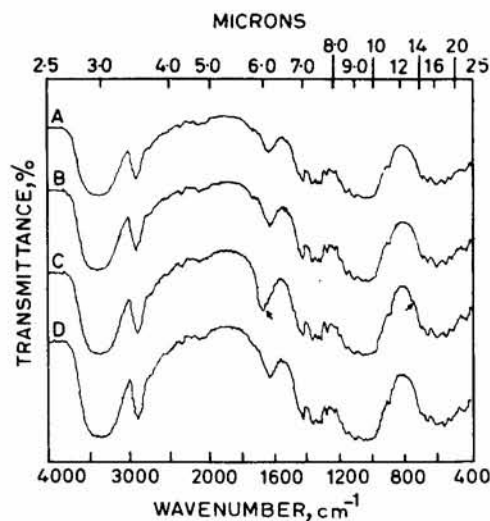


Fig. 3—Infrared spectra of hypochlorite oxycellulose of around 350 DPn (HC₄) [(A) unfinished, (B) catalyst treated, (C) DMEU finished, and (D) DMEU stripped]

hypochlorite oxycelluloses during DMEU finishing. The conditions of UPac hydrolysis are such that they do not affect the functional groups and DPn of the modified celluloses. This was confirmed in the present study by measuring these properties before and after UPac hydrolysis of unfinished samples. These data are given in Table 2. Three DPn levels of both hydrocellulose and hypochlorite oxycellulose were studied for copper number, carboxyl, aldehyde and carbonyl group contents before and after UPac hydrolysis. No significant change in any of these functional groups is seen on UPac hydrolysis. Therefore, when UPac hydrolysis is carried out on DMEU finished samples, the estimation of various functional groups on DMEU stripped samples will indicate the changes taking place during DMEU finishing. In the present study, some interesting observations have been made on hydrocellulose and hypochlorite oxycellulose after DMEU stripping. The values for various functional groups and DPn of DMEU stripped hydrocellulose and hypochlorite oxycellulose are given in Table 1.

Effect of DMEU stripping—The removal of DMEU crosslinks is complete during UPac hydrolysis, as seen from the residual nitrogen values which are similar to those for untreated samples (Table 1) and also from infrared spectra (Figs. 1-3). This is also in conformity with the findings of Jung *et al.*³. Also, the moisture regain by these samples (Table 1) is close to that for unfinished samples. This confirms the removal of DMEU crosslinks. In the case of hydrocellulose, there is a slight increase in DPn values. This can be attributed to either the presence of a few methylene linkages or 1-4 or 4-4 linkages of terminal aldehyde

Table 2—Chemical Test Results on Hydrocelluloses and Hypochlorite Oxycelluloses Before and After Urea Phosphoric Acid Treatment

Sample	DPn		Copper number		Carboxyl content m eq/100 g		Aldehyde content m eq/100 g		Carbonyl content m eq/100 g	
	Before	After	Before	After	Before	After	Before	After	Before	After
	A	D	A	D	A	D	A	D	A	D
Hydrocellulose										
H ₁	1342	1288	0.07	0.09	0.65	0.68	0.60	0.53	0.22	0.22
H ₂	655	630	1.00	1.16	0.56	0.56	1.19	1.16	0.69	0.68
H ₃	376	365	3.03	3.05	0.57	0.68	2.13	2.19	1.39	1.10
Hypochlorite oxycellulose										
HC ₁	1280	1318	0.02	0.03	0.97	0.89	0.50	0.53	0.21	0.19
HC ₂	661	620	0.35	0.36	2.00	2.23	0.74	0.80	0.33	0.38
HC ₃	369	344	0.53	0.71	5.30	5.40	1.41	1.88	0.64	0.55

A, Unfinished, and D, UPac hydrolysed samples

groups of hydrocellulose, as suggested by Koudelka⁷, who also observed an increasing trend in DPn values of hydrocellulose on crosslinking with either formaldehyde or DMDHEU. In functional groups, such as copper number, carboxyl, aldehyde and carbonyl contents, there is hardly any change. Thus, it is evident that in the case of hydrocellulose, DMEU finishing does not change the content or nature of various functional groups. In the case of hypochlorite oxycellulose, there is a significant reduction (12-18%) in DPn. This oxycellulose is known to possess aldehyde group at C₆ position and keto groups at C₂ and C₃ positions⁹. The presence of keto groups at C₂ and C₃ positions would have contributed to inductive cleavage of 1-4 glucosidic linkage in cellulose molecule, leading to a decrease in DPn during DMEU finishing. A similar higher order of decrease in DPn on DMDHEU and formaldehyde finishing of periodate oxycellulose was reported by Koudelka⁷. The aldehyde and carboxyl group contents of hypochlorite oxycellulose also increase, suggesting that oxidation of the primary hydroxyl group at C₆ position to aldehyde and further to carboxyl group may be taking place during DMEU finishing of this oxycellulose. Also, the side reaction of the formation of reducing groups due to the presence of C₂ and C₃ carbonyl groups and the subsequent conversion of these groups to carboxyl groups might be taking place. However, none of the above changes take place in the absence of DMEU, as is seen from the values of these functional groups for catalyst treated samples.

Table 3—Nitrogen and Bound Formaldehyde Contents of DMEU Finished Samples

Sample	Nitrogen % owf	Bound HCHO % owf	HCHO/N
C			
MSB	1.07	1.47	0.64
H ₄	1.10	1.71	0.73
HC ₄	1.10	1.51	0.64

C, DMEU finished.

Infrared spectroscopic studies—Preliminary studies using infrared (IR) absorption spectroscopic technique were carried out on control and two unfinished chemically modified celluloses (DPn 360) as well as after catalyst treatment, DMEU finishing and DMEU stripping. The spectra obtained for a mercerized-scoured-bleached (MSB) control, hydrocellulose and hypochlorite oxycellulose are shown in Figs. 1-3.

Spectra A for unfinished samples in Figs. 1-3 are similar, showing that reduction in DPn and increase in functional groups by either hydrolysis or oxidation are not discernible by the IR absorption technique¹⁰. Spectra B in Figs. 1-3 correspond to the catalyst treated samples and they are identical with spectra A in all the three cases. This confirms the chemical test results that no significant change in functional groups occurs during catalyst treatment. Spectra C are for DMEU finished samples. It is significant that the peaks for amide linkages at 5.9 μ and 13.2 μ bands are observed in all the three cases. This has been confirmed by chemical analysis data given in Table 3, where fixed

nitrogen and bound formaldehyde values for all the DMEU finished samples are given. Spectra D for DMEU stripped samples show that the above amide bands disappear in all the three cases and these spectra revert back to those for untreated samples (Spectra A), confirming complete removal of DMEU crosslinks. A similar observation was made by Jung *et al.*³.

Conclusions

(1) Thermal treatment in the presence of magnesium chloride hexahydrate as catalyst and urea-phosphoric acid hydrolysis of unfinished samples of both hydrocellulose and hypochlorite oxycellulose with varying DPn levels do not bring about any significant change either in the degree of polymerization (DPn) or nature and quantity of various functional groups of either hydrocellulose or hypochlorite oxycellulose.

(2) DMEU finishing introduces DMEU crosslinks, as shown by nitrogen and formaldehyde analyses and IR spectra.

(3) DMEU stripping by UPac hydrolysis of DMEU finished hydrocellulose shows slight increase in DPn values and hardly any change in the functional groups; a similar treatment on hypochlorite oxycellulose causes reduction in DPn values and significant increase in the contents of aldehyde and carboxyl groups.

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