

X-ray Diffraction of Cotton Treated with Neutralized Vegetable Oil-based Macromolecular Crosslinkers

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ABSTRACT

Maleinized soybean oil (MSO) has been investigated as a flexible, macromolecular crosslinker for cotton fabrics. The ability of MSO to penetrate crystalline cellulose and crosslink aligned cellulose chains upon cure has been in question. This study compares the penetration capability of MSO to dimethyloldihydroxyethyleneurea (DMDHEU), which is the commercial standard for durable press finishing and is an efficient cellulose crosslinker. X-ray diffraction was employed to characterize changes in the crystalline morphology upon heating unmercerized cotton fabrics treated with aqueous DMDHEU and soybean oil derivatives. Displacement of characteristic interplanar spacings and the genesis/elimination of diffraction intensities from quintessential planes were evidence of structural modification. The penetration of ammonia neutralized MSO (acid value 230.00 mg KOH/g) into the microstructure of cotton cellulose is similar to that of DMDHEU in terms of expanding the interplanar spacings of characteristic planes. Moreover, polymorphism of cotton and mercerized cotton occurred upon treatment with aqueous solutions of MSO. These findings suggest that macromolecular reagents can diffuse into cellulose fibrils if they are sufficiently hydrated or enshrouded by more favored penetrants.

KEYWORDS

Maleinized soybean oil (MSO), X-ray diffraction, dimethyloldihydroxyethyleneurea (DMDHEU) cellulose, cotton

INTRODUCTION

Commercial wrinkle-free finishes employ *N*-methylol derivatives such as dimethyloldihydroxyethyleneurea (DMDHEU) to crosslink cellulosic fabrics and facilitate bulk recovery from wrinkles induced by wear and laundering. Maleinized soybean oil (MSO) was investigated as a formaldehyde-free alternative to DMDHEU for wrinkle-prone cellulosic fabrics [1]. 1,2,3,4-Butanetetracarboxylic acid (BTCA) [1-3] has been suggested as an alternative to DMDHEU, but its

high cost precludes its commercial viability [2]. Yang *et al.* synthesized macromolecular crosslinkers from maleic anhydride that were structurally similar to BTCA; however, they did not impart the similar level of wrinkle resistance [4,5]. The molecular weight of the maleic anhydride derivatives was assumed to have restricted reaction with cellulose hydroxyls [4,5]. Although MSO is of similar molecular weight as the crosslinkers synthesized by Yang *et al.* [4,5], our studies have demonstrated its ability to impart high wrinkle resistance in the dry state [1].

Aqueous ammonia finishes of MSO improved the wrinkle resistance of dry cotton fabrics. Yet to date, the fabric smoothness upon laundering has not been competitive with commercial finishes. MSO cotton finishing has marked improved strength retentions among fabrics having wrinkle recovery on par with DMDHEU [1]. These findings led to the investigation of the mechanism by which MSO penetrates the cotton microstructure and reacts with anhydroglucose hydroxyls.

Cellulose Microstructure and Susceptibilities

Cellulosic fibers are constituted of microfibrils (3-15 nm in thickness and 10-30 nm in width [6,7]) that contain semi-crystalline bundles of finer, nanoscale threads termed fibrils (2-6 nm in width) [6,7]. These microfibrils organize helically along the fiber axis and ultimately form annular layers within the fiber cross section [8,9].

X-ray diffraction studies and molecular modeling have aided the construction of the Meyer and Misch unit cell model of native cellulose (also known as cellulose I) and its intra/intermolecular bonding [10-13]. The monoclinic unit cell for native cellulose contains two parallel *D*-glucose dimers at its corners and a central dimer [10-13]. The 1926 Spenser and Dore unit cell (*Figure 1*) illustrates the sheet arrangement of cellulose molecules along the 002 plane and parallel to the *b*-molecular axis [9,10,14]. This collection of molecularly aligned, sheets of

cellulose molecules precedes the solid-state, fibrillar structure [7]. The sheet arrangement of cellulose molecules produces distinct polar and nonpolar surfaces [7]. Dispersive, intermolecular forces maintain the parallel sheets configuration [7]. Within these sheets, aligned cellulose chains intermolecularly hydrogen bond between adjacent O6-H.....3-O' sites [7,15,16]. Intramolecular hydrogen bonding occurs between the O3-H...O5 ring oxygen and between the O2-H....O6' [7,15,16]. Adaptations to the hydrophilic domains will

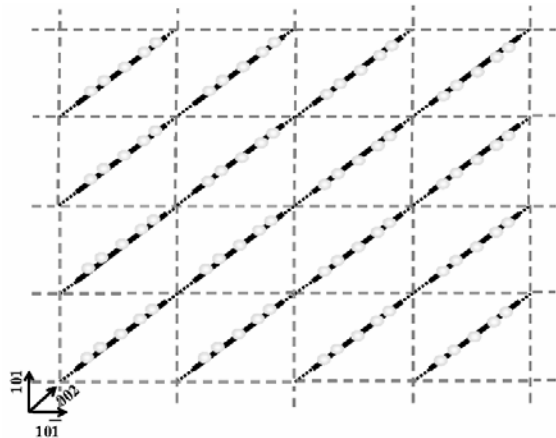


FIGURE 1. Sponser and Dore Unit Cell of Native Cellulose

influence diffraction from the 101 and $10\bar{1}$ planes [7,11]. Diffuse scattering among X-ray patterns suggest the presence of amorphous domains within cellulose. The nature of the amorphous domain has been likened to the randomness associated within the Fringe-Micelle model or as regions of imperfect chain alignment [7,17,18].

Electron and X-ray diffraction studies have identified four types of cellulose polymorphs (I, II, III, and IV) that can coexist simultaneously [10,11,13,19-22]. Native cellulose, e.g., cotton, is termed cellulose I, whereas modified cellulose, e.g., rayon and mercerized cotton, is classified as cellulose II [7,11,13,17-19]. Aqueous sodium hydroxide treatment of cotton fabrics (called mercerization)

results in the transition from cellulose I to cellulose II [11,13-15]. Mercerization reduces the crystallinity of cotton by 7 - 11% [7,17], and is of commercial importance due to the resulting improvement in strength, reagent uptake, and fiber luster [7,11,13]. Polymer chains within cellulose II are organized in an anti-parallel configuration, which allows for intersheet hydrogen bonding and a more stable morphology [10,11,13,17,19,21]. Other morphologies derived from cellulose I depend upon the type of swelling agents, temperature, and time [9,11,18-23].

Cellulose III is derived from the liquid ammonia finishing of cellulose I [11,13,16-22]. Transformation from cellulose III back to cellulose I may occur upon laundering or with additional heat treatment [19]. Treatment of cellulose I with ethylene diamine and subsequent boiling in formamide yields cellulose IV [11,17,19]. Hot glycerol is known to convert cellulose II and III to cellulose IV [11,17,19]. Unit cell similarities between cellulose I and IV, and cellulose II and III have led to the characterization of cellulose III and IV as disordered phases of their respective pair [13,19].

The crystalline structure of cellulose and the accessibility of its hydroxyls are limitations to its reactivity with reagents [13,18]. The property of accessibility takes into account the acidity of cellulose hydroxyls on the anhydroglucose monomer, the hydrophilic edges of crystalline regions, the cellulose amorphous domains, and porosity [7,8,18,25]. Although the OH-2 hydroxyl is the most reactive functional group, the reactivity of OH-6 becomes greatly enhanced upon reaction of the OH-2 [25]. Strong acids and base metal hydroxides can swell cellulose, thereby facilitating greater penetration of reagent chemistries into the microstructure of cellulose [7,8]. Ekman *et al.* demonstrated that the use of urea dissolved in liquid ammonia improved the yield of cellulose carbamate in comparison to systems without ammonia [25].

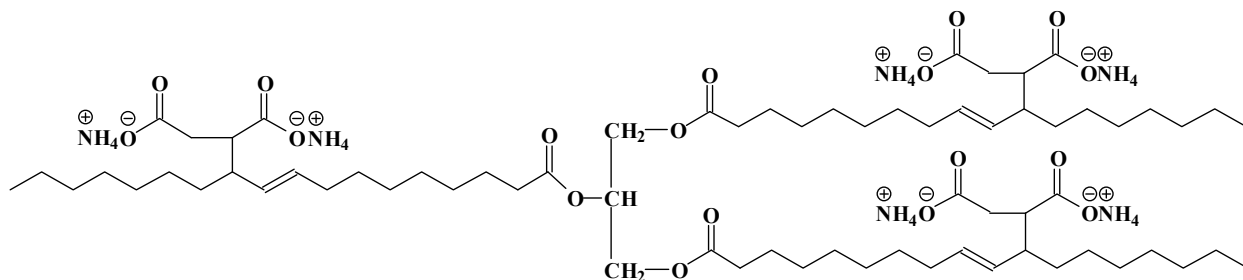


FIGURE 2. Ideal Structure of Ammonium Hydroxide Neutralized MSO-3.

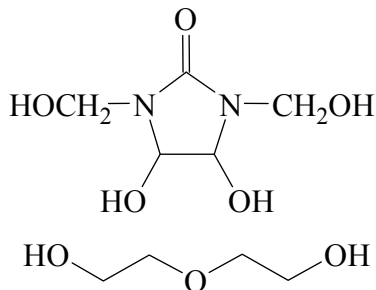


FIGURE 3. Glycolated DMDHEU.

EXPERIMENTAL

MSO Synthesis

500 g (0.56 mole) of soybean oil (Alnor Oil Company, Inc.) and 83.5 mg of 2-mercaptobenzothiazole (Fluka & Riedel-de Haën) were charged into a 1000 mL, three-neck flask equipped with condenser, stirrer, and nitrogen inlet. The reactants were heated to 100°C and purged with nitrogen for an hour to remove the oxygen existing in the system. 111.8 g (1.12 moles) of maleic anhydride (Acros Organics) was added to the flask, and the temperature was increased to 215°C and maintained for 2.5 hours to yield MSO-2. MSO-3 was prepared using a similar method to add approximately three moles of maleic anhydride per mole of soybean oil. MSO-2 and MSO-3 are viscous fluids with acid values (determined via ASTM D 1980) of 155.57 mg KOH/g and 230.00 mg KOH/g, respectively. Neutralized maleinized soybean oil NMSO were prepared from 53 weight percent (wt %) MSO blended with ammonium hydroxide (Fisher Scientific) and further diluted with deionized to prepare different concentrations.

Cotton Fabric Finishing

Bleached, desized (un-mercerized) cotton print cloth item #400 from Testfabrics Inc. and bleached, desized mercerized cotton fabric item #400M from Testfabrics Inc. were treated with aqueous finishes of ammonium hydroxide neutralized MSO (NMSO, Figure 2), dried at 80°C for 6 minutes, and heated at elevated temperatures. Solutions of various wt% MSO had pH values ranging from 9-10. MSO-2 treated fabrics were heated at 170°C for 4 minutes, while MSO-3 treated fabrics were heated at 160°C for 4 minutes after drying.

Reaction between MSO-2, MSO-3, and DMDHEU (from aqueous solutions) with cotton cellulose was supported by their durable press performance as reported in Johnson *et al.* [1].

Un-mercerized cotton fabrics were bathed in 3.6 wt% (i.e. percent solids) of soybean oil dissolved in hexanes (Acros Organics) and 10 wt% (un-neutralized) MSO-2 dissolved in tetrahydrofuran (THF, Acros Organics). Fabrics treated with organic solvents were initially dried in ambient temperature fume hoods for 24 hours prior to 160°C heating for 10 minutes.

Finishes based on glycolated DMDHEU (i.e. 42% active Permafresh® EFC, Figure 3), were formulated with 0.2% Sequawet® 16, 3% Sequasoft® 69 (siloxane) softener, and 1% Mykon® HD (high density polyethylene) softener, all of which were acquired from Omnova Solutions, Inc. (all percentages expressed on weight of bath), and the treated fabrics were cured at 150°C for 10 minutes.

X-ray Diffraction

X-ray diffraction plots were acquired from stacked sheets of cotton fabrics treated with aqueous DMDHEU and NMSO-2, MSO/THF, and soybean oil/hexanes solutions. The diffraction peak intensities from ground samples of MSO-3 treated (un-mercerized and mercerized) cotton fabrics were more distinct and clear than from samples prepared as layered fabric. Therefore, MSO-3 treated cotton and mercerized cotton fabrics were ground using a Wiley Mill (Model ED-85, Arthur H. Thomas Co.) with a 200 steel mesh screen prior to testing. Equatorial scans were performed on the X-ray Rigaku Ultima III diffractometer at 40 kV and 44 mA with copper radiation of 1.54 Å.

The raw diffractometer data was smoothed (using JADE software, version 7) and normalized according to Equation 1. The normalized intensity (I) is the ratio of the intensity, i_n , at 2θ divided by the sum of intensities over the entire 2θ range. Gaussian fits (having $r^2 \geq 0.99$) of diffraction spectra and their deconvoluted peaks were prepared in OriginPro 8. Percent crystallinity, interplanar distances between lattice planes, and crystal sizes were of interest for this study. The percent crystallinity [26] was determined from the integrated peak intensities of the 101, $10\bar{1}$, 002, 021 (when present), and 040 diffraction planes.

$$\text{Normalized Intensity (I)} = \frac{i_n}{\sum_n i} \times 10^6 \quad (1)$$

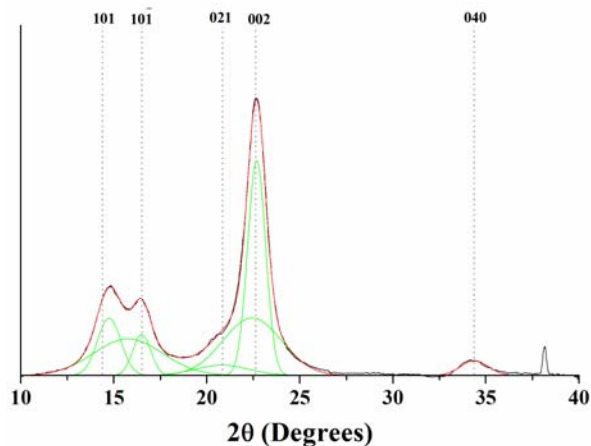


FIGURE 4. X-ray diffraction patterns
 — smoothed raw data, — fitted curve, and
 — deconvoluted crystalline peaks of un-mercerized cotton fabric

RESULTS AND DISCUSSION

Mercerized and Un-mercerized Cotton

Plots of diffraction intensities from un-mercerized cotton and mercerized cotton are shown in *Figures 4* and *5*, respectively. Diffraction peaks in *Figure 4* are characteristic of cellulose I (*Table I*) [11]. Interplanar spacings, crystal sizes, and percent crystallinity (% Xc) are located in *Tables II-V*. As observed in *Figure 4* and *Table I*, the morphology of the fabric termed ‘mercerized cotton’ has not fully converted to cellulose II. However, the diffraction intensities of *Figure 5* are common among fabrics treated commercially with sodium hydroxide versus unconstrained yarns that have converted from cellulose I to II [11]. In this paper, ‘mercerized’ signifies the preparation of cotton fabric with sodium hydroxide rather than a morphology consisting wholly of cellulose II.

Relative to un-mercerized cotton, diffractometer angles of the mercerized cotton have shifted toward lower 2θ values (*Figures 4-5*), and the interplanar spacings of characteristic planes expanded upon mercerization (*Table II, IV*). Mild shoulders were observed at diffractometer angles of 20.8 and 20.1 (*Table IV*) for un-mercerized cotton and mercerized cotton, respectively. These shoulders were fitted with broad, low intensity peaks (*Figures 4-5*). The shoulder represents diffraction from the 021 planes in the case of un-mercerized cotton and the existence of cellulose II- $10\bar{1}$ diffraction (*Table I*) among mercerized cotton.

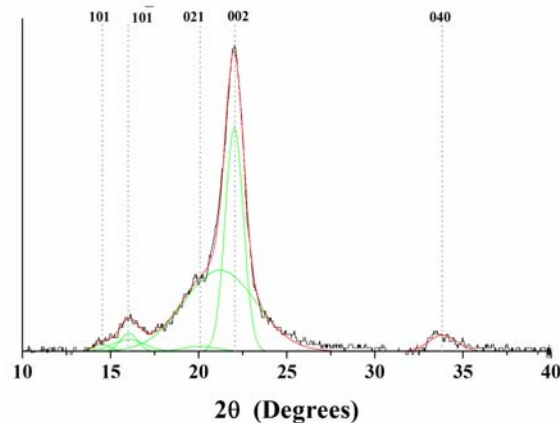


FIGURE 5. X-ray diffraction patterns
 — smoothed raw data, — fitted curve, and
 — deconvoluted crystalline peaks of mercerized cotton fabric.

Two main peaks from amorphous scattering occurred between the diffractometer angles for the 1) $10\bar{1}$ and $10\bar{1}$ planes and 2) the 002 and 021 planes. From these results, the percent crystallinity of cotton was determined to be 11% more than mercerized cotton (*Table V*). As is common among mercerized fabrics, their crystallinity is less than cotton fabrics of cellulose I [17]. Conversion from cellulose I to cellulose II takes place in the amorphous regions and gradually converts crystals of increasingly larger dimensions [22]. Thus, this process yields a more amorphous microstructure. The relative 101 to 002 plane peak intensity for mercerized fabric sample is less than for un-mercerized cotton fabric (*Figures 4-5*) and is an indication of cellulose I to II conversion [11,13]. The reported crystal sizes, obtained from mercerized cotton fabrics, were either larger than (see the crystal size of the 101 and 021 peaks in *Table III, IV*) or within a few nanometers of (see the crystal size of the 002 planes of *Table III*) un-mercerized cotton. The presence of large crystals is therefore attributed to less immediate conversion of larger crystals. The 002 plane, which consists of layered sheets of parallel chains [7], produces the greatest intensity among these cellulose polymorphs [18].

TABLE I. X-ray Diffractometer Parameters from Cellulose Polymorphs

	Lattice Plane									
	101		10 $\bar{1}$		021		002		040	
	2 θ (°)	(Å)	2 θ (°)	(Å)	2 θ (°)	(Å)	2 θ (°)	(Å)	2 θ (°)	(Å)
Cellulose I ^a	14.7	6.01	16.6	5.35	20.6	4.31	22.5	3.94	34.7	2.58
Cellulose II ^a	12.3	7.19	20.1	4.42	-	-	21.9	4.06	34.7	2.58
Cellulose III _I ^b	11.7	7.55	20.7	4.29	-	-	20.7	4.29	-	-
Cellulose III _{II} ^b	12.1	7.31	20.6	4.31	-	-	20.6	4.31	-	-
Cellulose IV _I ^b	15.6	5.67	15.6	5.67	-	-	22.2	4.00	-	-
Cellulose IV _{II} ^b	15.6	5.67	15.6	5.67	20.2	4.39	22.5	3.95	-	-

a) Diffractometer angles for cellulose I and II [15]. b) Diffractometer angles and interplanar distances for cellulose III and IV [11].

TABLE II. Interplanar Spacings of Crystalline Planes From DMDHEU, NMSO-2, and NMSO-3 Treated Un-mercerized and Mercerized Cotton Fabrics

Un-mercerized Cotton Fabric												Mercerized Cotton Fabric			
DMDHEU				MSO-2				MSO-3				MSO-3			
% Solids	d-spacing (Å)			% Solids	d-spacing (Å)			% Solids	d-spacing (Å)			% Solids	d-spacing (Å)		
	101	10 $\bar{1}$	002		101	10 $\bar{1}$	002		101	10 $\bar{1}$	002		101	10 $\bar{1}$	002
0	6.00	5.37	3.92	0	6.00	5.37	3.92	0	6.00	5.37	3.92	0	6.10	5.52	4.03
3.6	6.16	5.50	3.99	1.6	6.07	5.43	3.95	3.4	6.10	5.53	4.02	3.5	6.14	5.50	4.01
4.5	6.16	5.50	3.99	1.7	6.06	5.43	3.93	4.3	-	-	4.04	4.3	-	5.58	4.03
6.0	6.13	5.52	3.99	3.6	6.03	5.40	3.93	6.2	6.13	5.54	4.01	6.5	6.08	5.49	3.99
7.0	6.17	5.52	3.99	3.9	6.00	5.38	3.92	8.2	6.13	5.54	4.01	8.3	6.08	5.49	3.99
9.6	6.18	5.48	3.98	6.2	6.01	5.38	3.93	9.5	6.09	5.54	4.04	9.8	6.10	5.49	3.99
				7.7	6.01	5.43	3.93	11.6	6.16	5.54	4.03	12.1	6.03	5.55	4.03
				8.4	6.08	5.43	3.95	18.4	6.25	5.50	4.01	18.4	6.15	5.55	4.03
				9.2	6.01	5.38	3.92	24.5	6.16	5.52	4.00	24.5	6.14	5.56	4.02
				10.1	6.07	5.44	3.95	32.1	6.12	5.51	4.00	32.1	6.23	5.53	4.02
				11.8	6.05	5.40	3.94								

d-spacing = interplanar distance

TABLE III. Crystal Size Comparison of DMDHEU, NMSO-2, and NMSO-3 Treated Un-mercerized and Mercerized Cotton Fabrics

Un-mercerized Cotton Fabric												Mercerized Cotton Fabric			
DMDHEU				MSO-2				MSO-3				MSO-3			
% wt	Crystal Size (nm)			% wt	Crystal Size (nm)			% wt	Crystal Size (nm)			% wt	Crystal Size (nm)		
	101	10 $\bar{1}$	002		101	10 $\bar{1}$	002		101	10 $\bar{1}$	002		101	10 $\bar{1}$	002
0	5.4	7.0	7.1	0	5.4	7.0	7.1	0	5.5	7.0	7.1	0	7.1	7.0	6.7
3.6	5.6	7.2	7.2	1.6	5.2	6.8	7.3	3.4	6.4	8.3	6.7	3.5	6.7	7.5	6.4
4.5	6.7	7.6	6.8	1.7	5.3	6.7	7.0	4.3	-	-	6.5	4.3	5.8	4.5	6.2
6.0	5.2	7.0	7.0	3.6	5.2	6.9	7.0	6.2	6.3	5.2	6.7	6.5	5.8	6.3	6.1
7.0	5.6	6.8	7.0	3.9	5.3	6.8	7.0	8.2	6.3	5.2	6.7	8.3	6.5	6.3	6.1
9.6	7.7	8.7	6.9	6.2	5.1	6.8	6.9	9.5	6.3	7.3	6.0	9.8	9.1	6.0	6.4
				7.7	5.1	6.9	6.9	11.6	6.9	4.6	6.5	12.1	10.3	5.7	6.4
				8.4	5.2	6.8	7.2	18.4	8.3	9.6	6.8	18.4	5.8	4.7	6.5
				9.2	5.2	6.8	6.8	24.5	5.6	7.3	7.0	24.5	4.8	3.1	6.3
				10.1	5.5	6.6	7.0	32.1	6.2	6.0	6.7	32.1		7.2	6.3
				11.8	5.9	7.2	6.8								

TABLE IV. DMDHEU, NMSO-2, and NMSO-3 Treated Un-mercerized and Mercerized Cotton Fabrics Interplanar Spacings and Crystal Sizes from Shoulders Along the 002 Plane

Un-mercerized Cotton Fabric						Mercerized Cotton Fabric					
DMDHEU			MSO-2			MSO-3			MSO-3		
% wt	d-spacing (Å)	Crystal Size (nm)	% wt	d-spacing (Å)	Crystal Size (nm)	% wt	d-spacing (Å)	Crystal Size (nm)	% wt	d-spacing (Å)	Crystal Size (nm)
0	4.26	2.4	0	4.26	2.4	0	4.26	2.4	0	4.41	3.6
3.6	4.27	3.4	1.6	-	-	3.4	4.33	2.7	3.4	4.32	2.9
4.5	4.28	5.2	1.7	-	-	4.2	4.39	3.8	4.3	4.37	2.7
6.0	-	-	3.6	-	-	6.2	4.28	3.2	6.5	4.34	3.3
7.0	4.3	2.8	6.2	-	-	8.2	4.28	3.2	8.3	4.34	3.3
9.6	4.2	2.6	6.2	-	-	9.5	4.43	3.2	12.1	4.31	2.8
			7.7	-	-	11.6	4.35	2.4		4.30	2.4
			8.4	-	-	18.4	4.30	5.0		4.39	2.6
			9.2	-	-		4.32	3.3		4.36	2.6
			10.1	-	-		4.33	2.2		4.34	3.3
			11.8	4.2	4.3						

d-spacing = interplanar distance

TABLE V. Percent Crystallinity of Aqueous DMDHEU, NMSO-2, NMSO-3 Treated Mercerized and Un-mercerized Cotton Fabrics

Un-mercerized Cotton Fabric						Mercerized Cotton Fabric	
DMDHEU		MSO-2		MSO-3		MSO-3	
wt (%)	Xc (%)	wt (%)	Xc (%)	wt (%)	Xc (%)	wt (%)	Xc (%)
0	54	0	54	0	54	0	45
3.6	49	1.6	51	3.4	55	3.4	58
4.5	45	1.7	50	4.2	54	4.3	65
6.0	51	3.6	49	6.2	53	6.5	68
7.0	56	3.9	43	8.2	53	8.3	63
9.6	48	6.2	48	9.5	61	9.8	62
		7.7	45	11.6	58	12.1	65
		8.4	47	18.4	42	18.4	54
		9.2	49	24.5	42	24.5	58
		10.1	47	32.1	52	32.1	56
		11.8	45				

% wt: weight percent, % Xc: percent crystallinity

DMDHEU Treated Un-mercerized Cotton

DMDHEU crosslinking on the microstructure of cotton cellulose was examined using X-ray diffraction. Diffraction results at 0 wt % DMDHEU represent untreated, un-mercerized cotton. The results (Figure 6, Tables II-IV) suggest that the crystalline structure of cotton cellulose was modified with upon reaction with DMDHEU.

Penetration of DMDHEU molecules into the microstructure of cotton cellulose was observed as wider 101, 10 $\bar{1}$, and 002 interplanar spacings than untreated cotton (Table II). The widening of these

interplanar spacings is observed as shifts of the diffraction peaks toward lower 2 θ values (Figure 6).

DMDHEU intercepts the hydrogen bonding domains between adjacent cellulose molecules that in turn expand the 101 and 10 $\bar{1}$ planar spacings. The crystal sizes of some of the aforementioned planes grew upon DMDHEU incorporation, but their growth was not in direct proportion to DMDHEU concentration. According to Tables III-V, neither positive nor negative increases in percent crystallinity are associated with the DMDHEU concentration in the chemical bath. Intramolecular crosslinking along the

same cellulose molecule, competition between cellulose hydroxyls and glycols (Figure 3) at elevated temperatures, and the accessibility of cellulose hydroxyls are factors that would affect the non-linear expansions in crystal size and interplanar distances (11). These competing variables would also affect the resulting percent crystallinity.

A significant increase in the intensities of the 002 diffraction peak is observed for all concentrations of applied DMDHEU (Figure 6). The integrated intensities from 002 planes (relative to the entire intensity plot) were greater for the DMDHEU treated fabrics (ranging 32 to 37%) than untreated cotton (30%). The integrated diffraction peaks are proportional to the crystalline phase [13], which would suggest an increase in the crystallinity represented by the 002 planes. The full-width at half maximums (FWHMs) of the Gaussian fits were indicative of crystal sizes ranging from 6.8 to 7.2 nm for DMDHEU treated fabrics in comparison to 7.1 nm for 002 planes within untreated cotton (Table IV). Expansion of the interplanar distances between 002 planes from 3.92 for untreated cotton to 3.98-3.99 Å (Table II) suggests the inclusion of DMDHEU between sheets of cellulose chains. The presence of DMDHEU between cellulose sheets may have contributed to the 002 intensity (Figure 6). The

hydrophilic nature of DMDHEU and/or glycol species may disrupt hydrophobic, intersheet attractions which yield the 002 diffraction. Shoulders, indicative of diffraction from the 021 planes, are observed among DMDHEU treated cotton except for fabric treated with 6 wt% DMDEHU (Table IV). The crystal sizes of the 021 planes among DMDHEU treated cotton were larger than that for untreated cotton (Table IV). The inclusion of DMDHEU between molecular sheets appears to skew some cellulose chains out of their parallel alignment [27], thus resulting in diffraction by 021 planes (Table IV).

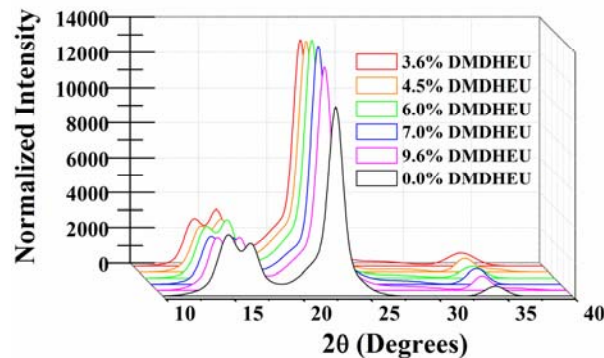


FIGURE 6. X-ray diffraction of DMDHEU treated cotton fabric.

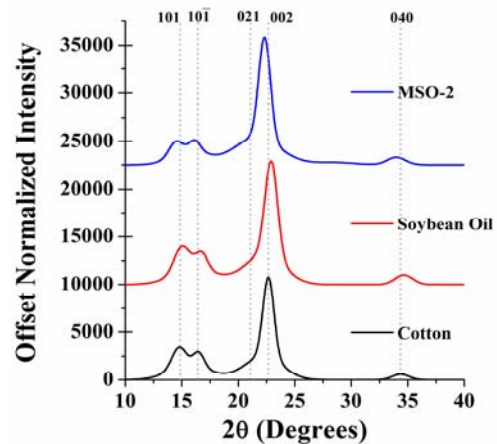


FIGURE 7. X-ray Diffraction of Soybean oil, MSO-2, and Untreated (Un-mercerized) Cotton Fabrics.

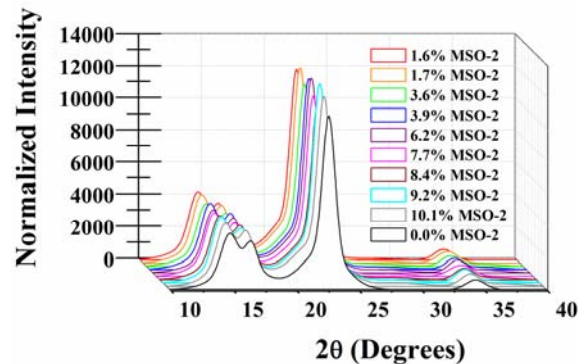


FIGURE 8. X-ray diffraction patterns of NMSO-2 treated cotton fabric.

TABLE VI. X-ray Diffraction of Cotton Bathed in Soybean Oil/Hexanes and MSO-2/THF

		Cotton Fabric	Soybean Oil	MSO-2
% Xc		54	52	46
Crystal Size (Å)	101	5.4	4.8	5.9
	101̄	7.0	6.3	7.3
	021	2.4	-	4.4
	002	7.1	6.2	6.7
d-spacing (nm)	101	6.00	5.89	6.14
	101̄	5.37	5.28	5.48
	021	4.26	-	4.27
	002	3.92	3.98	3.98

%Xc: percent crystallinity

Un-mercerized Cotton Treated with Organic Soybean Oil and MSO-2 Solutions

The treatment of cotton with solutions of soybean oil and MSO-2 dissolved in organic and aqueous solvents was studied to compare the effects of the solvent polarity on the crystalline morphology of cellulose. Intensity plots of cellulose diffraction are shown in *Figure 7*. Diffraction peaks from 101, $10\bar{1}$, and 002 planes were observed for cotton treated with soybean oil and un-neutralized MSO-2/THF (*Figure 7*). Excluding the 021 peak, the most intense diffraction peaks were observed for unfunctionalized soybean oil treated fabrics.

The overall percent crystallinities of soybean oil (52%) and MSO-2 (46%) treated fabrics were less than untreated cotton fabrics (54%) (*Table VI*). Crystal sizes were smaller among the soybean oil treated cotton than among untreated cotton (*Table VI*). The interplanar spacings of the 101 and $10\bar{1}$ planes contracted in the presence of soybean oil. The narrowing of 101 and $10\bar{1}$ interplanar distances and reduced crystal sizes are attributed to repulsion between the cellulose hydroxyls and the hydrophobic soybean oil molecules. The interplanar spacings between 002 planes widened from 3.92 to 3.98 Å in the soybean oil/hexanes bath. Expansion of the 002 planes suggests the inclusion of soybean oil molecules between the hydrophobic surfaces of molecular sheets. Similar 002 inter-spatial distances were observed among DMDHEU treated fabrics and MSO-2/THF treated fabrics. The loci of foreign molecules between 002 planes appear to re-crystallization upon solvent removal.

The crystal sizes of all diffracting planes except 002 planes, enlarged upon treatment with MSO-2/THF solution (*Table VI*). The interplanar distances of the 101 and $10\bar{1}$ planes expanded from 6.00 Å for untreated cotton to 6.14 and 5.48 Å, respectively (*Table VI*). Similar expansions were observed among DMDHEU treated cotton fabrics. MSO-2 is water insoluble unless neutralized with a base. However, the 101 and $10\bar{1}$ planes were observed to expand rather than contract as recorded for soybean oil treated cotton. Unlike hexanes, THF is capable of accepting hydrogen bonding, which would allow it to penetrate the polar surfaces of the cellulose crystal. Therefore, the use of THF is believed to have aided

the transport of MSO-2 into the crystalline microstructure of cellulose. The inclusion of MSO-2 in the 101 and $10\bar{1}$ appears to have increased their crystal size.

Ammonia Neutralized MSO-2 Treatment of Un-mercerized Cotton

X-ray diffractometer patterns of cotton treated with aqueous solutions of NMSO-2 are shown in *Figure 8*. In spite of its aqueous base, NMSO did not have the penetrating effects observed for DMDHEU and MSO-THF solutions. Relative to DMDHEU, mild to non-existent changes in the interplanar spacings of the 101 and $10\bar{1}$ planes (6.00-6.08 Å and 5.38-5.44 Å, respectively) were observed among the NMSO-2 treated cotton (*Table II*). Only in the case of 11.8 wt% MSO-2, were the crystal sizes of the 101 and $10\bar{1}$ planes (5.9 and 7.2 nm, respectively) reportedly larger than untreated cotton (5.4 and 7.0 nm, respectively) (*Table II*).

The interspatial distances between the 002 planes ranged from 3.92-3.95 Å in comparison to 3.92 Å for untreated cotton (*Table II*). The only increase in crystal size was observed for cotton treated with 1.6% MSO-2, otherwise the crystal sizes of the 002 planes ranged from 6.6 to 7.0 nm. Diffraction from 021 planes was only observed for fabric treated with 11.8 wt% MSO-2, and the crystal size calculated from the 021 diffraction intensity was larger than for untreated cotton (*Table IV*).

Neutralized MSO-3 Treated Un-mercerized Cotton Fabrics

Aqueous solutions of NMSO-3 showed ample ability to penetrate cellulose crystals. The expansion of interplanar distances was similar to DMDHEU treatments rather than NMSO-2 (*Table II*). NMSO-3 appears to reside in the 101 and $10\bar{1}$ planes of cotton cellulose, where the interplanar spacing ranged from 6.09-6.25 Å and 5.50 to 5.54 Å, respectively. On average, the hydration of NMSO-3 would be higher than that of NMSO-2 due to the increase in ammonium carboxylated anions per triglyceride. The increased hydration from the additional ammonium carboxylates is believed to have aided the transport of NMSO-3 into the crystalline microstructure.

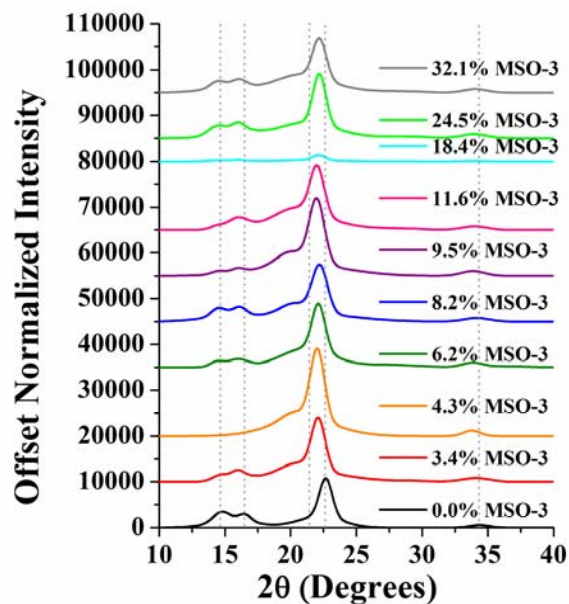


FIGURE 9. X-ray diffraction of NMSO-3 treated un-mercerized cotton.

NMSO-3 was also shown to locate between the sheets of cellulose molecules. The interplanar distances of the 002 planes expanded to 4.00-4.04 Å in comparison to 3.92 Å for untreated cotton (Table II), and were even wider than the 002 interplanar distances observed for DMDHEU (Table II). The differences in 002 spacing from 1) untreated cotton and 2) MSO-2 is attributed more to the cationic functionalization of MSO-3 than its molecular weight because 1) cationic species are known to swell and delaminate cellulose crystals [7,11] and 2) MSO-3 has flexible fatty acid chains. The crystal sizes of the 002 planes were ranged from 6.0 to 7.0 nm, i.e., less than that of untreated cotton. The inclusion of MSO-3 between the planes of cellulose molecules is believed to have reduced the re-crystallization of some 002 planes.

The diffraction pattern of un-mercerized cotton fabric treated with NMSO-3 (Figure 9) reveals morphology changes distinct from those obtained from NMSO-2 treated fabrics (Figure 8). At similar concentrations of MSO, both NMSO-2 and NMSO-3 finishes contain similar weight percents of aqueous ammonia. However, NMSO-3 has more ammonium carboxylates than NMSO-2. Therefore, NMSO-3 is more adept in swelling the crystalline morphology of cellulose. The amorphous content of the NMSO-2 treated fabrics (for less than 12 wt% MSO) is higher than for NMSO-3 (Table V), MSO2-/THF (Table VI), and soybean oil treatments (Table VI). This study

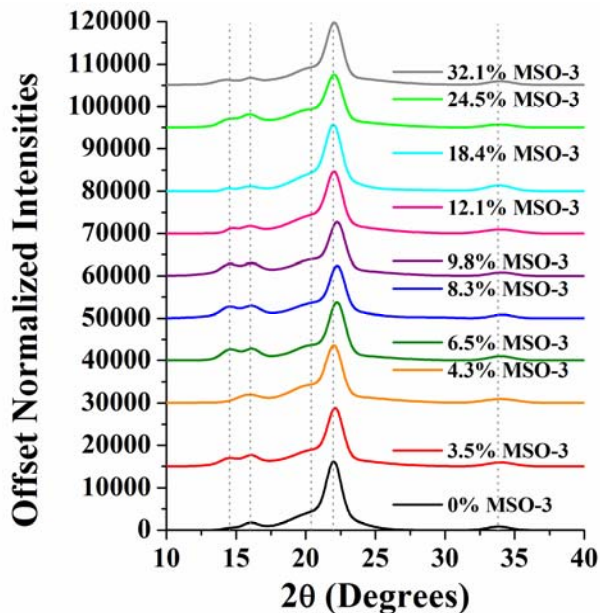


FIGURE 10. X-ray diffraction of NMSO-3 treated mercerized cotton.

suggests that NMSO-2 more readily resides in amorphous cellulose and that swelling of the amorphous and/or pores leads to reductions in the overall crystallinity.

Polymorphism would help explain the sporadic changes in the normalized intensities of the 101 and $10\bar{1}$ diffraction peak intensities and crystal sizes of NMSO-3 treated fabrics (Figure 9, Table III). At 4.2 wt% MSO-3, diffraction from 101 and $10\bar{1}$ was not observed. Literature references indicate that swelling of cellulose crystals can change cellulose I into another polymorph [13,17-19, 22-25]. For most treatments with NMSO-3, the crystal sizes of the 101 diffraction peaks were larger than that for untreated cotton. The crystal sizes of the $10\bar{1}$ planes varied irregularly with wt% NMSO-3. Shoulders along the 002 peak have been deconvoluted from intensity plots of diffraction from MSO-3 treated cotton. Some shoulders (Table IV) are speculated as being from 021 diffraction or from a minor phase of other cellulose polymorphs (Table I), especially in the case of 4.2, 9.5 and 11.6% NMSO-2. The transformation of cellulose I with NMSO-3 is similar to the conversion of cellulose I to II (as discussed in “Mergerized and Un-mergerized Cotton”). In other cases, NMSO-3 treatment has expanded the interspatial distance between the 021 planes. The permeability of NMSO-3 into the cellulose crystal appears to skew the alignment of

some cellulose chains into the 021 planes. Growth of the 021 crystal size was observed for most treatments with NMSO-3; same or smaller 021 crystal sizes were observed with 11.6 and 32.1 wt% MSO-3.

Neutralized MSO-3 Treated Mercerized Cotton Fabrics

Changes in the diffractometer curves of mercerized cotton were observed upon treatment with neutralized NMSO-3 (*Figure 10*). The increase in intensity of the 101 plane for more than 3.4 wt% MSO-3 implies a change towards increasing fractions of cellulose I (*Figure 10, Table I*). Since mercerized fabric has not been fully converted to cellulose II, the residual cellulose I can participate as nuclei for larger crystallites [11]. Furthermore, the interplanar spacing of untreated mercerized cotton contracts for most (but not all) treatments with NMSO-3 (*Table II*). Additionally, the percent crystallinity of NMSO-3 treated mercerized cotton increased over all concentrations of NMSO-3. These behaviors indicate coexisting polymorphs (according to 2θ angles given in *Tables I*) as was observed for NMSO-3 treated cotton.

NMSO-3 treated mercerized cotton revealed 101, $10\bar{1}$, and 002 interplanar spacings similar to NMSO-3 treated cotton. Non-linear variations in the crystal sizes and integrated areas of the 101 and $10\bar{1}$ planes were attributed to MSO-3 penetration of those planes and polymorphism. The 002 planes of un-mercerized and mercerized cotton exhibited similar interspatial distances, i.e., 4.32 to 4.43 Å (*Table II*). According to *Table V*, MSO-3 increased the overall crystallinity of treated mercerized cotton. These cases of NMSO-3 treatments of mercerized and un-mercerized cotton suggest that the permeability of maleinized triglycerides into crystalline cellulose was made possible via ample cationic functionalization.

CONCLUSIONS

Modification of Cellulose Crystals

The modification of cellulose with reactive vegetable oil macromonomers and DMDHEU was elucidated using X-ray diffraction. The role of the solvent is very important in enabling the entry of macromolecules into cotton's crystalline and amorphous phases. For instance, THF enabled water insoluble MSO-2 to penetrate cellulose crystals, but hexane could not enable soybean oil to do so.

Ammonia neutralization enabled MSO-3's penetration into crystalline cellulose, unlike NMSO-

2. Neither did NMSO-2 result in the polymorphism which MSO-3 treatments promoted. It is known that monovalent cations aid the retention of softeners on cotton fabrics [28] and that they may induce pore openings [7,11]. The physical differences between cellulose treated with MSO-2 and MSO-3 are therefore attributed to the higher acid value of MSO-3 and its greater hydration upon neutralization. Observation of higher percent crystallinities for NMSO-3 treated cotton and mercerized cotton than among DMDHEU and NMSO-2 treated fabrics has been attributed to the cationic swelling of cotton provided by NMSO-3, which results in the expansion of 101, $10\bar{1}$, and 002 interplanar distances. Swelling also affords the opportunity for amorphous chains to form crystallites around existing nuclei of cellulose I and II at elevated temperatures and increase the overall percent crystallinity [11] as was observed in NMSO-3 treated cotton and mercerized cotton.

Implication for Durable Press Finishing

X-ray diffraction of DMDHEU-treated fabrics supports the washing of excess, unreacted DMDHEU from durable pressed fabrics. This study has shown that reagent impurities can remain between the collapsed lamellar sheets (molecular planes of aligned cellulose [11]) upon heating [11] and reduce the crystal size of the 002 phase. Water rinsing may aid removal of these impurities and re-crystallization of cellulose [27].

Insight from this study is applicable to our previous study of NMSO finishing of cotton and mercerized cotton fabrics [1]. An acid value greater than 156 mg KOH/g is required for MSO to penetrate cellulose crystals, however NMSO-2 is able to penetrate as suggested by relative amorphous contents shown in this study and our FTIR study on MSO-2 retention [1]. Research on durable press finishing suggests reagent modification of cellulose crystals is crucial to achieving high wrinkle recovery angles (WRAs) in the dry state and smoothness upon laundering. This study of NMSO-3 supports its penetration into the crystalline phase and our previous study cites high accompanying WRAs. Expansion of the 101 and $10\bar{1}$ planar spacings to distances comparable to DMDHEU finishing suggests that MSO-3 chemistries enable esterification with cellulose hydroxyls. However, the laundered smoothness was lower than those obtained with DMDHEU treated fabrics having similar WRA. Molecular weight and flexibility are believed contributing factors to the laundered performance and mechanical deformation of treated cotton.

The low glass transition temperature of these flexible MSO-3 triglycerides helps explain this behavior. It is also important to note the increase of cotton WRA upon NMSO-2 treatment (although lower than NMSO-3 and DMDHEU) since the majority of MSO-2 resides in the amorphous regions.

This X-ray diffraction study aided knowledge of the loci of soybean bean oil derivatives in cotton cellulose in comparison to DMDHEU. Its finding has applicability to the research of aqueous, non-formaldehyde based crosslinkers of varied molecular weights.

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