

Degree of Crosslinked Cotton Cellulose with Prereacted DMDHEU-AA

JUI-CHIN CHEN, WEI-HUA YAO, CHIEN-HSIN CHEN, CHENG-CHI CHEN

Department of Materials and Textiles, Oriental Institute of Technology, Pan-Chiao, 22064 Taiwan, Republic of China

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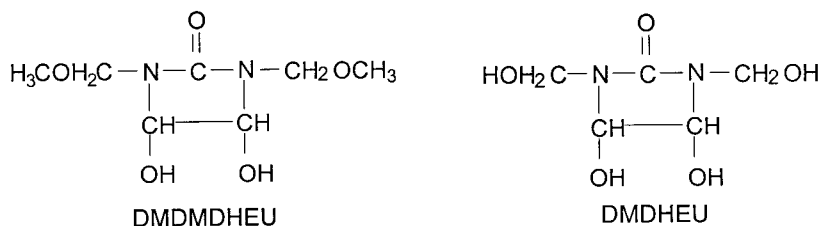
ABSTRACT: Dimethyloldihydroxyethyleneurea (DMDHEU) and acrylic acid (AA) were used to synthesize the dimethyloldihydroxyethyleneurea-acrylic acid product (DMDHEU-AA, mole ratios of DMDHEU/AA = 1/0, 1/1, and 1/2, respectively). Cotton fabrics were treated with the various prereacted DMDHEU-AA products by changing resin concentrations in the bath. We found that the dry crease recovery angle (DCRA) and wet crease recovery angle (WCRA) of the treated fabrics increased with the increase of acrylic acid in the prereacted DMDHEU-AA at the same value of resin concentration in the bath, whereas the tensile strength retention (TSR) showed the inverse tendency. For a given value of number of crosslinks per anhydroglucose unit (CL/AGU), the DCRA and WCRA values of the DMDHEU-AA-treated fabrics were higher than those for DMDHEU-treated fabrics. Additionally, agent distribution and the reaction between -COOH of the crosslinking agent and cellulose molecule were also investigated in this study. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1580-1586, 2001

Key words: cotton; crosslinking; finishing; number of crosslinks per anhydroglucose unit; length of crosslinks; crease recovery angle; tensile strength retention; agent distribution; acrylic acid; dimethyloldihydroxyethyleneurea

INTRODUCTION

It is well known that the wet crease recovery angle of finished cotton fabrics is affected by the fiber state of the fabrics.¹⁻³ Previous work revealed that the physical properties of the finished fabrics are affected by the crosslinking structure.⁴⁻⁶ Steven et al.⁷ pointed out that hydrogen

bonds in the finished fibers could affect the physical properties of the treated fabrics. Additionally, our previous study^{8,9} showed that the physical properties, reaction rate constants, and the reaction energy consumption of the treated fabrics were affected by the introduction of the carboxyl group to the crosslinking agent of dimethyloldihydroxy-ethyleneurea (DMDHEU).



Scheme 1

Correspondence to: C.-C. Chen (fc002@ica.oit.edu.tw).

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In this study, dimethyloldihydroxyethyleneurea (DMDHEU) and acrylic acid (AA) were used to synthesize the various prereacted DMD-

HEU-AA of crosslinking agents to treat the cotton fabrics. We expect that the physical properties and crosslinks of the finished fabrics may be affected by the carboxyl group of the prereacted DMDHEU-AA. However, detailed information is lacking on the degree of crosslinking and structure of the crosslinks formed in the treated cotton fabrics with the prereacted DMDHEU-AA. We examine the crosslinking of cotton fabrics with various prereacted DMDHEU-AA (DMDHEU/AA = 1/0, 1/1, and 1/2, respectively) products (using ammonium sulfate as catalyst) with respect to nitrogen and formaldehyde content, distribution of crosslinks per anhydroglucose unit (CL/AGU), length of crosslinks, and various physical properties of the treated fabrics.

EXPERIMENTAL

In this study, we used desized, scoured, and bleached cotton fabric, 20s × 20s ends (60) and picks (60) (Far Eastern Textile Co. Ltd.).

The crosslinking agents were the prereacted DMDHEU-AA products (Cyanamid Corp. and Ferak Laboratories, GmbH, Berlin).^{8,9} Methylcellulose was obtained from the Dow Chemical Company (Midland, MI). Ammonium sulfate (Nihon Shizaku Industries, Ltd.) and methylcellulose

were reagent grade, as were the other chemicals. The dye was C. I. Direct Red 81.

Two cotton samples were used in this study. One set of samples were padded twice to about 90% wet pickup with freshly prepared aqueous solutions of DMDHEU (2, 4, 6, and 8%) in the presence of ammonium sulfate catalyst. Another set of samples were padded twice to about 90% wet pickup with freshly prepared aqueous solutions of the prereacted DMDHEU-AA products in the presence of ammonium sulfate catalyst. The catalyst concentration was 0.10 times the used amounts of DMDHEU. Padded fabrics were dried at 80°C for 5 min, cured at 160°C for 3 min, soaped with 1.0 g/L soap at 40°C for 5 min, washed with tap water at room temperature for 5 min, and dried at 60°C.

DMDHEU-AA products were obtained by using 2, 4, 6, and 8% of DMDHEU to be prereacted with acrylic acid (there are two sets of the mole ratios of DMDHEU/AA = 1/1 and 1/2) in the presence of H₂O₂ initiator [0.017, 0.033, 0.050, and 0.067% H₂O₂ (35% v/v), respectively] at 40°C for 10 min.⁹

Tensile strengths of the warp yarns were measured on an Instron tensile tester. ASTM standard D 1295-67 was used to determine dry and wet crease recovery angles. Formaldehyde and nitrogen determinations were made using the

Table I Physical Properties of Cotton Fabrics Finished with Various Prereacted DMDHEU-AA Products

DMDHEU/AA (mole ratio)	DMDHEU Concentration (%)	Properties of Finished Fabrics				
		Dry Crease Recovery Angle [(W + F)°]	Wet Crease Recovery Angle [(W + F)°]	Tensile Strength Retention (%)	[D]f (g dye/kg cotton)	K/S
—	—	201	181	100	13.873	7.81
1/0	2	233	231	91.4	2.609	0.933
1/0	4	263	258	78.3	0.699	0.396
1/0	6	286	278	67.1	0.274	0.190
1/0	8	295	285	60.9	0.184	0.147
1/1	2	251	243	85.9	2.737	1.079
1/1	4	275	280	72.1	0.760	0.417
1/1	6	289	294	61.7	0.392	0.241
1/1	8	293	302	60.6	0.243	0.187
1/2	2	258	246	82.4	3.228	1.200
1/2	4	279	283	67.4	1.005	0.520
1/2	6	292	295	61.1	0.321	0.270
1/2	8	297	304	57.5	0.255	0.193

chromatropic acid¹⁰ and Kjeldahl methods, respectively. A CS-5 Chroma-Sensor (a product of Applied Color System, Inc.) was used to measure the depth of color of the various treated fabrics dyed with C. I. Direct Red 81.

Infrared spectra of the samples were obtained using a KBr disk technique.¹¹ Samples were prepared to give a dry weight of 1.8 mg after storage in 1-dram vials over P_2O_5 for 3 days. Spectral-grade KBr (250–300 mg) was ground, transferred to individual sample vials, dried in an oven at approximately 200°C for several hours, and stored in an oven at 110°C. Samples were ground and mixed with the KBr and pressed in an evacuated die under suitable pressure. The (a) methylcellulose (because cellulose powder is not soluble in water, methylcellulose was selected as a model of cotton cellulose), (b) mixture of methylcellulose and acrylic acid, and (c) cured methylcellulose–acrylic acid (coated on a piece of glass, dried at 80°C for 5 min, cured at 160°C for 3 min) and KBr were mixed, ground, and dried in 1-dram vials over P_2O_5 for 3 days. The samples were then pressed in an evacuated die under suitable pressure. To confirm the reaction between $-CH-OH$ of methylcellulose and $-COOH$ of acrylic acid under the pad-dry-cure process, 1/3 mole ratio of methylcellulose repeat unit/acrylic acid were mixed with 10% (w/w) of ammonium sulfate (cat-

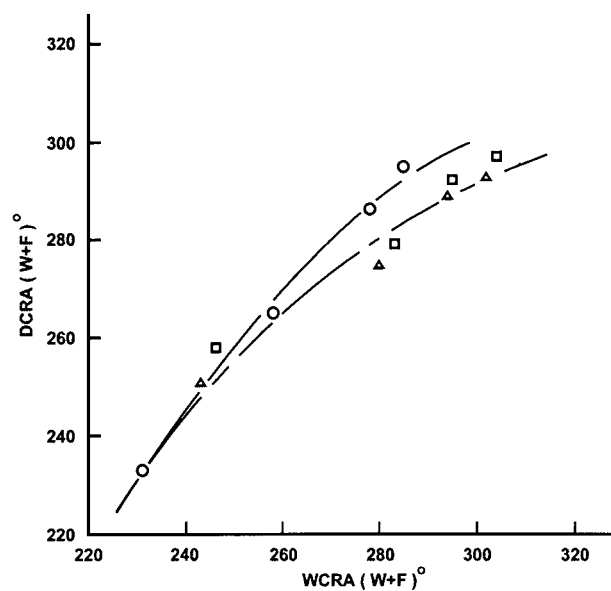


Figure 1 Relationship between DCRA and WCRA of the fabric samples treated with various prereacted DMDHEU–AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

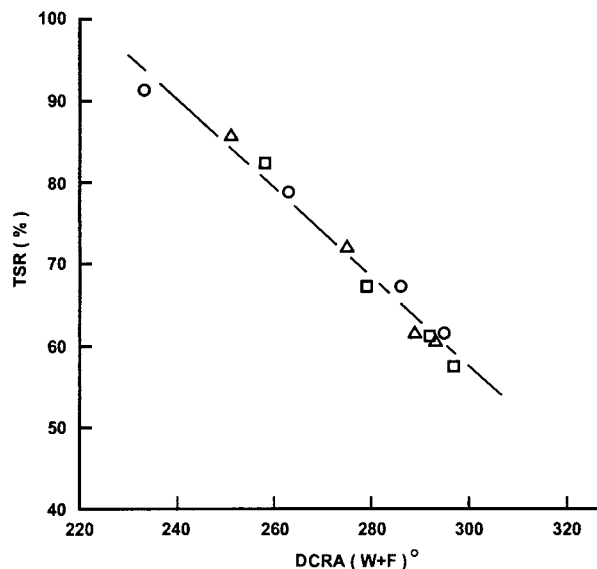


Figure 2 Relationship between DCRA and TSR of the fabric samples treated with various prereacted DMDHEU–AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

alyst), on the total weight of methylcellulose and acrylic acid. A Fourier transform infrared spectrophotometer (Jasco model FT/IR-3) was used to obtain spectra.

RESULTS AND DISCUSSION

Relationships Between Physical Properties

Table I shows the dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and the tensile strength retention (TSR) of the finished fabrics with various crosslinking agents. The table shows that DCRA and WCRA increase with increased resin concentration in the bath, whereas TSR decreases in all cases. The DCRA and WCRA values of the fabrics finished with DMDHEU are lower than those for the DMDHEU–AA-treated fabrics; however, the TSR values of the finished fabrics are higher than those for the DMDHEU–AA-treated fabrics. Additionally, the higher AA contained in the prereacted DMDHEU–AA will result in higher DCRA and WCRA and the lower TSR at the same resin concentration in the bath. The higher DCRA and WCRA of the treated fabrics with prereacted DMDHEU–AA may be caused by the formation of hydrogen bonds and/or the covalent bond between the hydroxyl group ($-OH$) of the cellulose and the

carboxyl group ($-\text{COOH}$) of the prereacted DMDHEU-AA. Steven et al.⁷ pointed out that hydrogen bonds in the finished fibers could affect the physical properties of the treated fabrics. Some previous studies^{7,8} pointed out that the carboxyl acid group of the polycarboxylic acid could react with the cellulose molecule. The lower strength in the cotton fabrics crosslinked with formulations containing higher quantities of AA in the DMDHEU-AA products (Table I) may be caused by crosslinking and/or the crosslink distribution in the fabric. Previous works^{1,4} revealed that the distribution of crosslinking agent on the surface of the treated fabrics would decrease the strength of the treated fabrics.

The relationships between DCRA, WCRA, and TSR of the finished fabrics with various crosslinking agents are shown in Figures 1, 2, and 3, respectively. From the relationships between DCRA and WCRA of the finished fabrics (Fig. 1), we found that the WCRA of the DMDHEU-AA-treated fabrics were higher than those of the DM-DHEU-treated fabrics at a given DCRA. Figure 2 shows the plots of DCRA versus TSR of the finished fabrics. For given values of TSR, the DCRA values are the same in all cases. The plots of WCRA versus TSR of the finished fabrics shown in Figure 3 reveal that the WCRA values of the DMDHEU-AA-treated fabrics are higher than those of the DMDHEU-treated fabrics.

Degree of Crosslinking and Physical Properties

The nitrogen and formaldehyde contents and number and length of crosslinks for the cotton fabrics crosslinked with varying resin concentrations are presented in Table II. As expected, nitrogen and formaldehyde contents show a gradual increase with increasing resin content in the bath in all cases. The nitrogen content of the finished sample increases with increasing AA in the prereacted DMDHEU-AA at a given resin concentration in the bath, whereas its formaldehyde content is almost the same in all cases. These results reveal that the crosslinks are affected by the degree of AA content in DMDHEU-AA.

The number of crosslinks per anhydroglucose unit (CL/AGU) and length of crosslinks (CL length) of the finished fabrics listed in Table II, obtained using the methods of Frick et al.,^{14,15} indicate that both increase as the concentration of the resin in the bath increases. The curvilinear relationship between the length of crosslinks and CL/AGU for samples treated with DMDHEU (Fig.

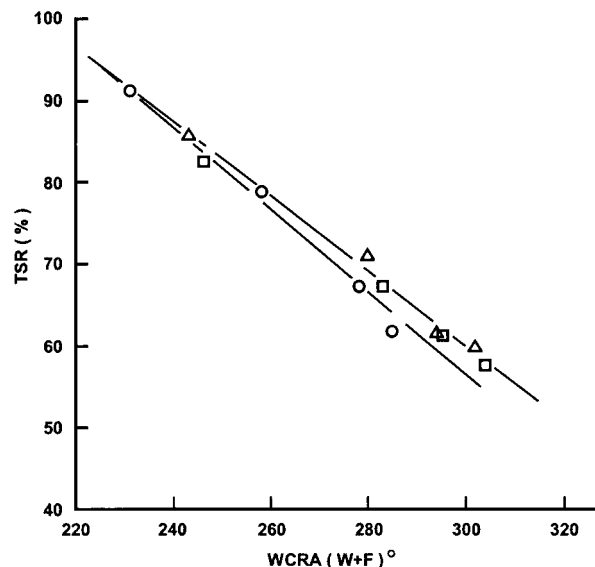


Figure 3 Relationship between WCRA and TSR of the fabric samples treated with various prereacted DMDHEU-AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

4) is similar to that reported in our previous study.¹⁶ The relationship between the two parameters is also curvilinear for cotton fabrics treated with the prereacted DMDHEU-AA. For a given number of CL/AGU, the CL length increases with the amount of AA in the prereacted DMDHEU-AA. This may be attributed to self-condensation of the crosslinking agent. A previous study³ showed that the acidity of the bath would affect the CL length of the treated fabrics.

To confirm the effects of crosslinkage on the physical properties, the physical properties are plotted versus CL/AGU for the finished fabrics in Figure 5(a), (b), and (c), respectively. For a given CL/AGU, DCRA and WCRA values of the finished fabrics are increased with the increase of AA in the prereacted DMDHEU-AA [Fig. 5(a), (b)], whereas TSR values are decreased with increasing AA in the prereacted DMDHEU-AA [Fig. 5(c)]. Previous studies^{1,4} revealed that the longer the crosslinking length, the higher the WCRA of the treated fabric. The result of Figure 5(b) is consistent with that of Figure 4. The higher DCRA of the prereacted DMDHEU-AA may be caused by the hydrogen bond formed and the reaction between the carboxyl group of the prereacted DMDHEU-AA and cellulose molecule.

The K/S and $[D]f$ values of the finished fabrics listed in Table I are plotted in Figure 6 according to the method described by Rowland et al.,^{17,18}

Table II Structural Characteristics of Cotton Cellulose Treated with Various Prereacted DMDHEU-AA Products

DMDHEU/AA (mole ratio)	DMDHEU Concentration (%)	Formaldehyde (%)	Nitrogen (%)	Moles/AGU			CL Length
				Nitrogen	Formaldehyde	CL/AGU	
1/0	2	0.56	0.28	0.0329	0.0307	0.0142	1.15
1/0	4	1.02	0.52	0.0618	0.0566	0.0257	1.20
1/0	6	1.42	0.77	0.0927	0.0798	0.0334	1.39
1/0	8	1.74	0.99	0.1205	0.0988	0.0386	1.56
1/1	2	0.56	0.28	0.0329	0.0307	0.0142	1.15
1/1	4	1.01	0.52	0.0618	0.0560	0.0251	1.23
1/1	6	1.43	0.79	0.0952	0.0804	0.0328	1.45
1/1	8	1.74	1.03	0.1256	0.0990	0.0362	1.73
1/2	2	0.58	0.30	0.0352	0.0318	0.0142	1.24
1/2	4	1.00	0.53	0.0630	0.0555	0.0240	1.31
1/2	6	1.42	0.79	0.0952	0.0798	0.0322	1.48
1/2	8	1.72	1.06	0.1294	0.0980	0.0333	1.94

and the linear relationships are similar to their results.¹⁸ K is the coefficient of absorption, S is the coefficient of scattering, K/S is the color intensity calculated from the equation $K/S = (K/S)_{\text{dye}} - (K/S)_{\text{white}}$, and $[D]f$ (g dye/kg cotton) is the dye content of the finished fabric, determined spectrophotometrically after extraction with pyridine/water (1/3) at 60°C. Color intensity is an inverse measure of crosslinking on fabric surfaces, and dye content is an inverse measure of total crosslinking content through fabric thickness. K/S results are the averages for the two sides of the fabric samples. Agent distribution follows the rule that the lower the value of K/S at a specific level of dye content and the lower the dye fixation on the surface of the fabric, the higher the concentration of crosslinks on the surface of the fabric and the greater the agent distribution on the fabric. Figure 6 shows the similar values of $\log(K/S)$ for finished fabrics in all cases at the same value of $\log[D]f$, that is, the surface distribution of the crosslinking agent on the finished fabrics is similar for all cases. This result strongly supports the conclusion that the lower TSR of the DMDHEU-AA-crosslinked cotton fabrics may be caused mainly by the crosslinking reaction between the cellulose and the -COOH of the prereacted DMDHEU-AA.

To confirm the crosslinking between cellulose and the -COOH of the prereacted DMDHEU-AA, methycellulose was selected as a model molecule of cotton cellulose (because cellulose powder is not soluble in water, we selected methycellulose as a

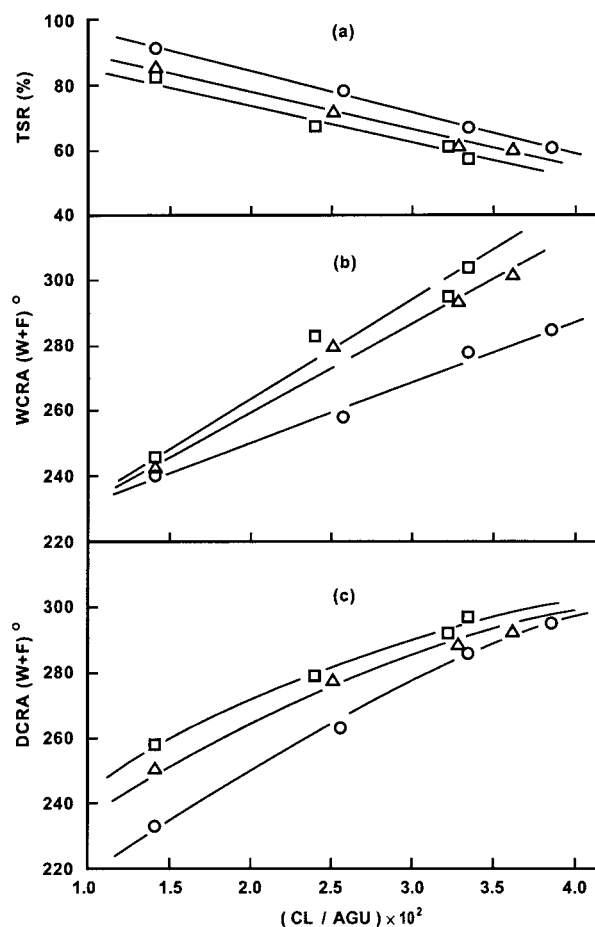


Figure 4 Plots of CL length versus CL/AGU of fabric samples treated with various prereacted DMDHEU-AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

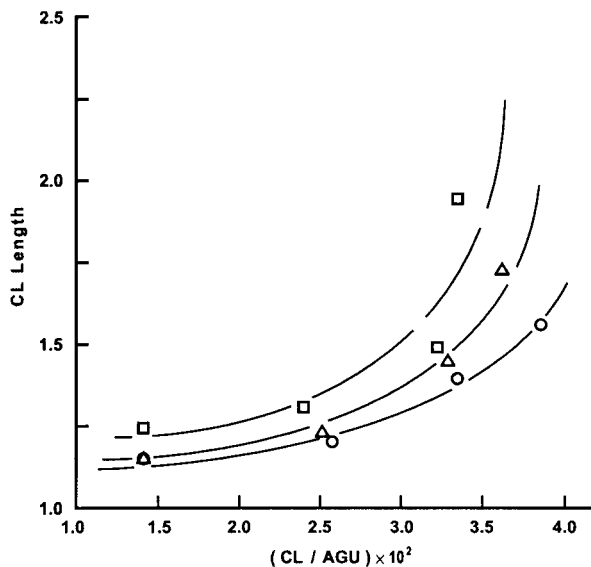


Figure 5 Plots of (a) DCRA versus CL/AGU, (b) WCRA versus CL/AGU, and (c) TSR versus CL/AGU of fabric samples treated with various prereacted DMDHEU-AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

model of cotton cellulose) to react with acrylic acid under the pad-dry-cure process in the presence of ammonium sulfate as catalyst. The IR spectra of (a) methylcellulose, (b) mixture of methylcellulose and acrylic acid, and (c) cured methylcellulose-acrylic acid, and (c) cured methylcellu-

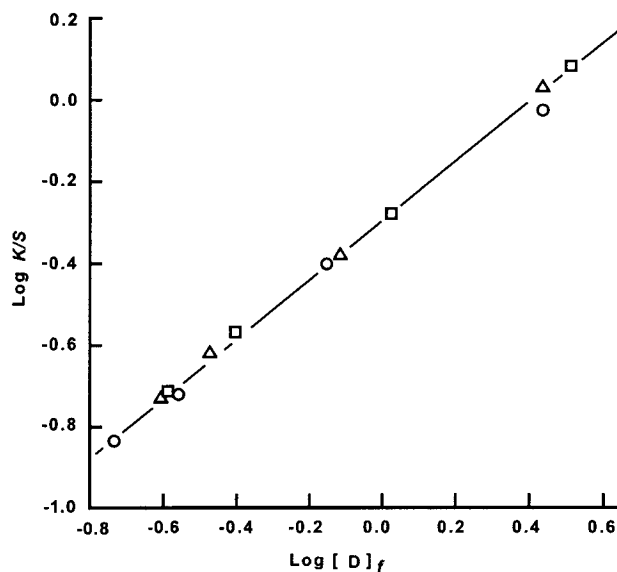


Figure 6 Plots of $\log(K/S)$ versus $\log[D]f$ of fabric samples treated with various prereacted DMDHEU-AA products: \circ = DMDHEU/AA = 1/0; \triangle = DMDHEU/AA = 1/1; \square = DMDHEU/AA = 1/2.

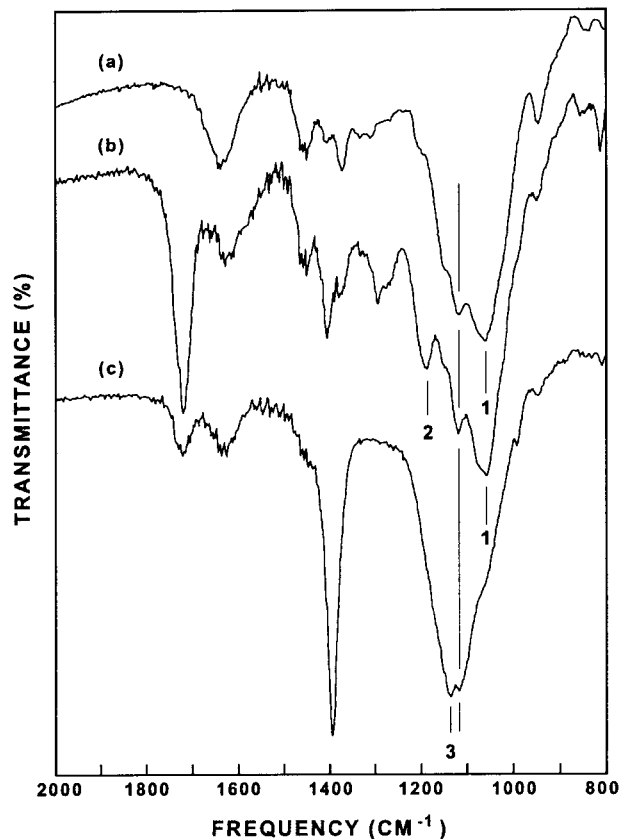


Figure 7 IR spectra of (a) methylcellulose, (b) mixture of methylcellulose and acrylic acid, and (c) cured methylcellulose-acrylic acid. 1 = 1060 cm^{-1} ; 2 = 1190 cm^{-1} ; 3 = 1140 cm^{-1} .

lose-acrylic acid are shown in Figure 7(a), (b), and (c), respectively. The interesting and important absorbing bands are those of $-\text{CHOH}$ (1060 cm^{-1})¹⁹ for methylcellulose [Fig. 7(a)]. As the methylcellulose and acrylic acid were mixed together, the IR spectrum [Fig. 7(b)] was changed. Figure 7(b) shows a new important absorbing band at $-\text{COOH}$ (1190 cm^{-1}). However, we can find that the IR spectrum for cured methylcellulose-acrylic acid [Fig. 7(c)] disappears at 1190 cm^{-1} ($-\text{COOH}$) and 1060 cm^{-1} ($-\text{CHOH}$), but generates a new absorbing band of 1140 cm^{-1} . From the description of Silverstein et al.,²⁰ we can find that the new absorbing band of 1140 cm^{-1} in Figure 7(c) is a conjugated ester group. This result strongly supports the observation that the crosslinking reaction between the $-\text{OH}$ of cellulose and the $-\text{COOH}$ of the prereacted DMDHEU-AA can be formed in the pad-dry-cure process.

CONCLUSIONS

We used the prereacted DMDHEU-AA products (mole ratios of DMDHEU/AA = 1/0, 1/1, and 1/2, respectively) to finished cotton fabrics by changing concentrations in the bath. It can be found that the WCRA values of the DMDHEU-AA-treated fabrics were higher than those of the DM-DHEU-treated fabrics for the given value of DCRA and TSR. At a same CL/AGU value, the DCRA and WCRA values of the DMDHEU-AA-treated fabrics were higher than those for the DMDHEU-treated fabrics. The distribution of crosslinking agent on the surface of the treated fabrics showed the same degree in all cases. The crosslinking reaction between the -OH of cellulose and the -COOH of the prereacted DMDHEU-AA under the pad-dry-cure process was improved.

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