

# Pore and Crosslinking Structures of Cotton Cellulose Crosslinked with DMDHEU-Maleic Acid

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**ABSTRACT:** Two dicarboxylic acids (maleic acid and tartaric acid) were used in conjunction with DMDHEU as the crosslinking agents to treat cotton fabric samples. The treated fabrics then were dyed with direct red 81. The results show that the values of the dye absorption, equilibrium absorption, rate constants, and the pore index of structural diffusion resistance constant for the various crosslinking agents are ranked as DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU alone at the same dyeing temperature. The activation energies for the three crosslinked fabrics are in the rank of DMDHEU > DMDHEU-maleic acid

> DMDHEU-tartaric acid. The CL length values for the various crosslinking agent systems are in the series of DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU alone for a given number of CL/AGU. The values of the pore index of structural diffusion resistance constant and dyeing rate constant are increased with the increase of CL length. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 143–148, 2005

**Key words:** crosslinking; activation energy; catalysts; UV-vis spectroscopy

## INTRODUCTION

Some previous studies have shown that the carboxylic acid group of a polycarboxylic acid<sup>1–3</sup> or acrylic acid<sup>4</sup> can react with cellulose to improve the crease recovery property of the finished fabrics. Our recent study<sup>5,6</sup> showed that the carboxylic acid of the  $\alpha$ -amino acids used as coreactants of crosslinking reagents can react with the hydroxyl group of the *N*-methylol crosslinking agent (DMDHEU) to affect the physical properties of the treated fabrics. Such an additional reaction should affect the crosslinking structures and pore structures of the treated fabrics.

In this study, we are interested in the effects of the vinyl group of the dicarboxylic acid that was joined with the *N*-methylol compound together to treat the cotton fabric samples on the crosslinking structures and pore structures of the treated fabrics. Dimethyloldihydroxyethyleneurea (DMDHEU) and two dicarboxylic acid compounds (one is vinyl group contained maleic acid, and the other is nonvinyl group contained tartaric acid) were used as the crosslinking agent and coreactants, respectively. Here, we expect the reaction between the vinyl group of dicarboxylic acid and the cellulose and/or DMDHEU under a pad-dry-cure

process to change the pore structures and the crosslinking structures of those finished cotton fabrics.

Also, C I Direct Red 81 having a molecular weight of 767 g/mol will be used to study the pore structures of the DMDHEU-dicarboxylic acids treated fabrics. We studied the pore structure by using the following diffusion equation<sup>7,8</sup>:

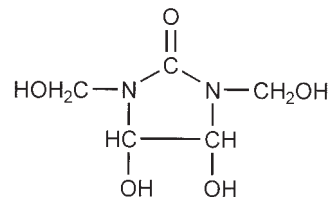
$$a = a_e [1 - \exp(-kC_0t)]^n \quad (1)$$
$$= a_e [1 - \exp(-k't)]^n,$$

where  $a$  is the absorption of the dye on cotton in time  $t$ ,  $a_e$  is the equilibrium absorption at  $t \rightarrow \infty$ ,  $k$  is the specific rate constant,  $k'$  is the rate constant,  $C_0$  is the concentration of cotton in a finite bath, and  $n$  is the structural diffusion resistance constant. The higher the value of  $n$ , the larger the pore size of the treated fabric.

## EXPERIMENTAL

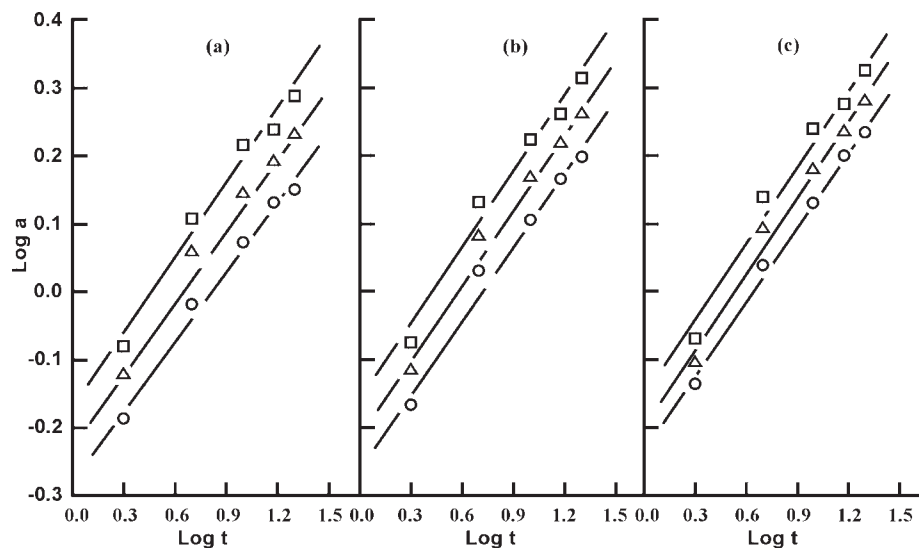
In this study, we used desized, scoured, and bleached cotton fabric 32s  $\times$  32s end (60) and picks (60).

The crosslinking agent used was DMDHEU (dimethyloldihydroxyethyleneurea).



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**Figure 2** Plots of  $\log a$  versus  $\log t$  for (a) DMDHEU, (b) DMDHEU-maleic acid, and (c) DMDHEU-tartaric acid crosslinked fabrics (dyed with C I Direct Red 81) ( $\square$  - 70°C,  $\triangle$  - 60°C,  $\circ$  - 50°C).

DMDHEU at a given temperature. This phenomenon may be caused by the condensation reaction between DMDHEU and dicarboxylic acids being significantly higher than that between DMDHEU and DMDHEU to form a loose crosslink. Our previous study<sup>10</sup> revealed the reaction between DMDHEU and dicarboxylic acids. Additionally, the equilibrium absorption value for DMDHEU-tartaric acid crosslinked cellulose is higher than that for DMDHEU-maleic acid. This result may be caused by: (1) the bonding between the two dicarboxylic acids and direct dye, and (2) the crosslinking structures of the treated fabrics for the two dicarboxylic acids are different from each other.

For all cases, the rate constants are increased with the rise of dyeing temperature. Rate constants for the three crosslinked fabrics that were dyed with the same direct dye and at the same dyeing temperature show the rank of DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU. Those results may be caused by the pore structure and/or bonding dependence of the dye absorption.<sup>11,12</sup>

Structural diffusion resistance constants are only slightly changed with increasing the dyeing temperature (Table I). Table I also shows that the structural diffusion resistance constants for the three crosslinked fabrics reveal the following rank: DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU. Several reports<sup>13-15</sup> revealed that the crosslinks decrease the structural diffusion resistance constant. Those results agree with the results of the expansion patterns of SEM in another report,<sup>10</sup> and indicate that the pore structure of the crosslinked cotton is changed with the addition of different dicarboxylic acids to DMDHEU and the functional groups of dicarboxylic acids. We reported that the coreactant dicarboxylic acids will

react with crosslinking agent (DMDHEU)<sup>10</sup> to create a loose crosslink that is a larger pore structure.

Arrhenius plots (three crosslinked fabrics) for the C I Direct Red 81 are shown in Figure 3. The activation energies ( $\Delta E^*$ ) from the figures are also listed in Table I. The activation energies for the three crosslinked fabrics are ranked as follows: DMDHEU > DMDHEU-maleic acid > DMDHEU-tartaric acid. This ranking also agrees with the pore structure of the crosslinked fabrics that is the structural diffusion resistance constant. Crosslinking length is a powerful factor for the estimation of pore size.

### Degree of crosslinking

The nitrogen and formaldehyde contents and number and length of crosslinks for the cotton fabric crosslinked with varying resin concentrations for DMDHEU alone, DMDHEU-maleic acid, and DMDHEU-tartaric acid are presented in Table II. As expected, the values of nitrogen and formaldehyde contents and mole/AGU of nitrogen and formaldehyde show a gradual increase with increasing resin content in the bath in all cases. The nitrogen and formaldehyde contents of the finished samples for DMDHEU-dicarboxylic acids are significantly lower than those for DMDHEU alone for a given resin concentration in pad bath and are shown in Figures 4(a) and (b), respectively. Those results are mainly caused by the use of dicarboxylic acid crosslinking agents, which have no nitrogen and formaldehyde contained in molecules. On the other hand, the nitrogen and formaldehyde contents of the finished samples for DMDHEU-maleic acid are slightly lower than those for DMDHEU-tartaric acid at a given resin concentration. Clearly, the difference



TABLE II  
Structural Characteristics of Cotton Cellulose Fabrics Treated with DMDHEU Alone, DMDHEU-Maleic Acid, and DMDHEU-Tartaric Acid

Di-carboxylic acids	Di-carboxylic acids conc., (%)	DMDHEU conc., (%)	Nitrogen (%)	Formaldehyde (%)	Moles/AGU		CL/AGU ( $\times 10^2$ )	CL length
					Nitrogen	Formaldehyde		
-		2	0.180	0.326	0.0210	0.0177	0.724	1.448
		4	0.360	0.635	0.0422	0.0348	1.365	1.547
		6	0.513	0.890	0.0605	0.0490	1.875	1.614
		8	0.706	1.118	0.0839	0.0620	2.006	2.091
Maleic acid	1.5/3	4.5/3	0.152	0.267	0.0177	0.0145	0.567	1.563
	3.0/3	9.0/3	0.275	0.466	0.0323	0.0255	0.938	1.719
	4.5/3	13.5/3	0.403	0.643	0.0476	0.0354	1.164	2.044
	6.0/3	18.0/3	0.535	0.818	0.0636	0.0454	1.357	2.341
Tartaric acid	1.5/3	4.5/3	0.148	0.257	0.0173	0.0140	0.536	1.611
	3.0/3	9.0/3	0.259	0.437	0.0304	0.0239	0.873	1.739
	4.5/3	13.5/3	0.398	0.634	0.0470	0.0349	1.143	2.054
	6.0/3	18.0/3	0.527	0.803	0.0626	0.0445	1.321	2.368

(Fig. 5) is similar to that reported in our previous study.<sup>18</sup> For a given number of CL/AGU, the CL length values for the various crosslinking agent systems are in the rank of DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU alone. The longer CL length for DMDHEU-dicarboxylic acids may be caused by the higher aggregation of the crosslinking agents in pad bath by Scheme 4 to enlarge the pore size.

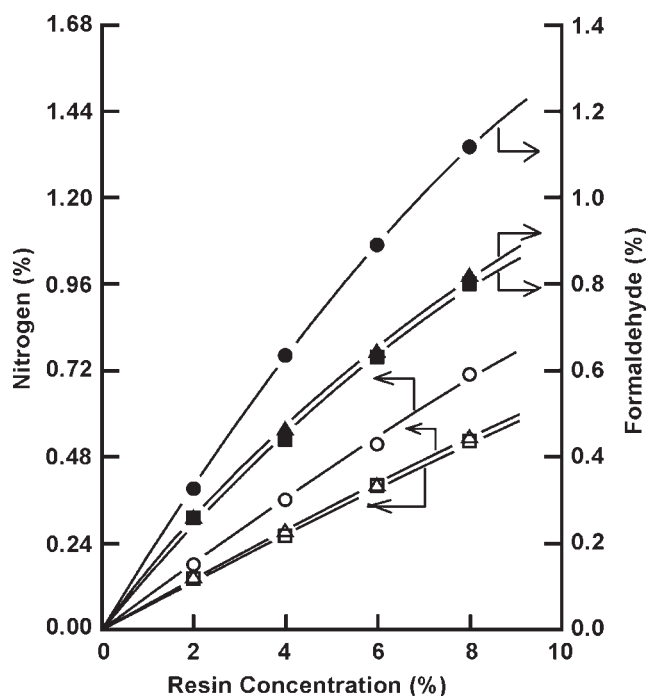


Figure 4 The nitrogen and formaldehyde contents of the crosslinked fabrics for the different resin concentrations. DMDHEU: nitrogen content (○), formaldehyde (●); DMDHEU-maleic acid: nitrogen content (△), formaldehyde (▲); and DMDHEU-tartaric acid: nitrogen content (□), formaldehyde (■).

Figure 6 reveals the relationships between the values of  $n$  (structural diffusion resistance constant) and  $k'$  (rate constant) and the CL length of the various treated fabrics, which shows that the values of  $n$  and  $k'$  are increased with the increase of CL length. Those results clearly show that the pore sizes are dependent on the length of crosslink.

## CONCLUSION

In this study, we used two dicarboxylic acids (maleic acid and tartaric acid) to join with DMDHEU as the

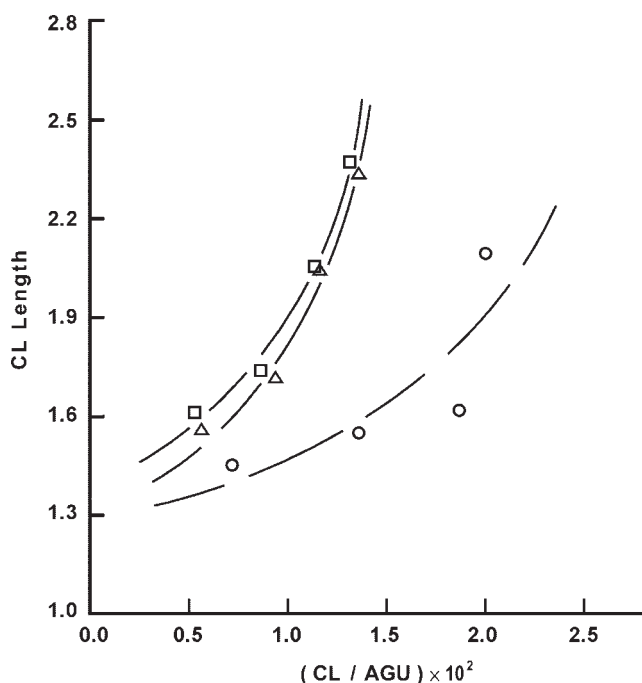
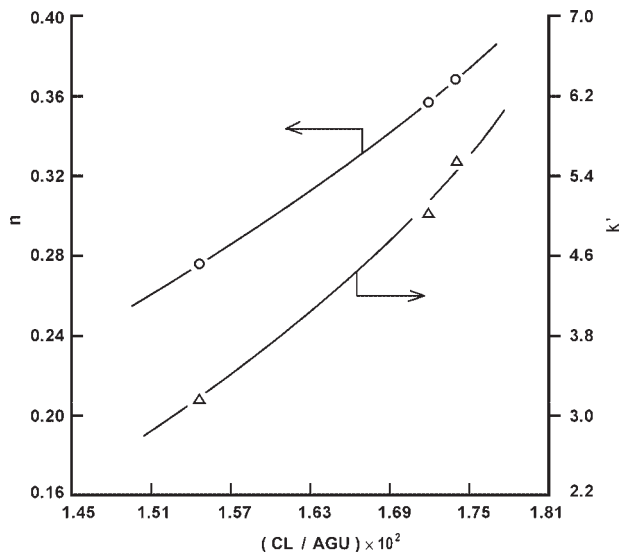


Figure 5 Plots of CL length versus CL/AGU for DMDHEU (○), DMDHEU-maleic acid (△), and DMDHEU-tartaric acid (□) crosslinked fabrics, respectively.



**Figure 6** The relationships between CL length and the rate constant ( $k'$ ,  $\Delta$ ) and structural diffusion resistance constant ( $n$ ,  $\circ$ ) for the various crosslinked fabrics.

crosslinking agents to treat cotton fabric samples. The treated fabrics then were dyed with C I Direct Red 81 to study the crosslinking structures and pore structures. The values of the dye absorption, equilibrium absorption, rate constants, and structural diffusion resistance constant for the various crosslinking agents are in the rank of DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU alone at the same dyeing temperature. The activation energies for the three crosslinked fabrics are ranked as follows: DMDHEU > DMDHEU-maleic acid > DMDHEU-tartaric acid. For a given number of CL/AGU, the CL length values

for the various crosslinking agent systems are in the rank of DMDHEU-tartaric acid > DMDHEU-maleic acid > DMDHEU alone. The relationships between the values of  $n$  (structural diffusion resistance constant) and  $k'$  (rate constant) and the CL length of the various treated fabrics show that the values of  $n$  and  $k'$  are increased with the increase of CL length.

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