

Crosslinking of Cotton Cellulose in the Presence of Serine and Glycine. I. Physical Properties and Reaction Kinetics

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ABSTRACT: Serine and glycine were used to combine with dimethyloldihydroxyethyleneurea (DMDHEU) as crosslinking agents to study the physical properties of the crosslinked fabrics and the reaction kinetics, and find that the bound nitrogen is in the series of DMDHEU \gg DMDHEU-serine $>$ DMDHEU-glycine at the same resin concentration. The results also show that the wet crease recovery angle (WCRA) value of the treated fabrics for the three crosslinking agent systems is in the series of DMDHEU-serine $>$ DMDHEU-glycine $>$ DMDHEU alone at a given dry crease recovery angle (DCRA). The DCRA values of the treated fabrics for DMDHEU alone are higher than those for DMDHEU- α -amino acids for a given value of tensile strength retention (TSR). WCRA values for the various treated fabrics is in the rank of DMDHEU-serine $>$ DMDHEU alone $>$ DMDHEU-glycine at the same TSR. Rate

constants for the various crosslinking agents are in the series of DMDHEU-glycine $>$ DMDHEU-serine $>$ DMDHEU alone at the given heated temperatures. Energies needed to crosslink and the values of enthalpies and entropies of activation are all DMDHEU-glycine $>$ DMDHEU-serine $>$ DMDHEU alone. Infrared ray (IR) spectra strongly suggest the reaction between DMDHEU and serine and the reaction between the hydroxyl group (cellulose) and serine can occur in the pad-dry-cure process, but only a little for the latter. The reaction between the functional groups of serine and the aluminum ion to form a complex also confirm with IR spectrum. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 595–603, 2005

Key words: crosslinking; kinetics; activation energy; catalysts; resins

INTRODUCTION

Some previous studies showed that the carboxylic acid and amino groups of α -amino acid^{1,2} could react with the *N*-methylol group of a crosslinking agent to improve the wet crease recovery and tensile strength retention property of the finished fabrics, and alter the reaction state of the crosslinking reaction. Amino acids were also used for the improvement of finishing and dyeing, antibacterial, and antisoiling properties.^{3–5} Other recent studies^{6,7} revealed that the addition of a reactive vinyl group containing compounds could also modify the physical properties and the crosslinking reaction. It is well known that the physical properties can be affected by varying the functional groups on crosslinking agents.^{8–11}

Aspartic acid and glutamic acid all have two carboxylic acid groups and one amino group. Our previous study² showed that the carboxylic acid could react

with the aluminum ion to buffer the crosslinking reaction. In this study, we are interested in the effects of the α -amino acids of relative low molecular weight, such as serine and glycine, who have one carboxylic acid and one amino group, on the physical and agent distribution properties. The dimethyloldihydroxyethyleneurea (DMDHEU) and two α -amino acids (serine and glycine) will be combined as the crosslinking agent. Here, we expect that the reaction between the α -amino acid and the DMDHEU under a pad-dry-cure process will change the physical properties and the reaction kinetics of those finished cotton fabrics, and the same for the hydroxyl group of serine.

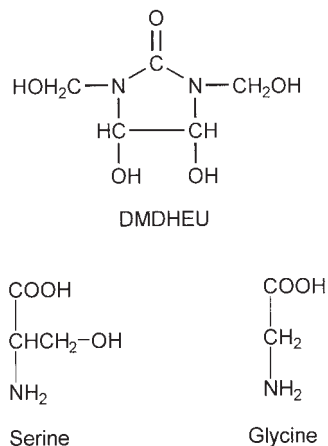
EXPERIMENTAL

In this study, we used desized, scoured, and bleached cotton fabric with 60 ends (20s) and 60 picks (20s).

The crosslinking agents used were dimethyloldihydroxyethyleneurea (DMDHEU) and α -amino acids (glycine acid and serine), respectively.

Aluminum sulfate was reagent grade, as were the other chemicals.

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Scheme 1

The cotton fabric samples were padded twice to about 80% wet pickup with freshly prepared (2 ~ 8% w/w) aqueous solution of DMDHEU alone or in the presence of α -amino acids (the mole ratio of DMDHEU to α -amino acids was 3 to 1) and the ammonium sulfate catalyst. The catalyst concentration was 0.10 times the crosslinking agent solid concentration. Padded fabrics were dried at 80°C for 5 min, cured at 160°C for 3 min, soaped, washed, and dried.

For reaction kinetic studies, the cotton fabric samples were padded twice to about 90% wet pickup with freshly prepared DMDHEU and DMDHEU- α -amino acids solutions (0.36M, the mole ratio of DMDHEU to α -amino acid was 3 to 1) in the presence of the aluminum sulfate catalyst (0.036M). To obtain the bound nitrogen contents of the heated fabrics with different heating temperatures, padded fabric samples were heated at 80, 90, and 100°C for different time intervals, then soaped, washed, and dried.

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

Infrared spectra of the samples were obtained using a KBr disk technique.¹² Samples were prepared to give a dry weight of 1.8 mg after storage in 1-dram vials over P₂O₅ 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. One set is (a) DMDHEU (b) serine, and (c) cured DMDHEU-serine. (One to one mole ratio of DMDHEU to serine was mixed with 10% (w/w) of aluminum sulfate, then coated on a piece of glass, dried at 80°C for 5 min, and cured at 160°C for 3 min.) The second set is (a) polyvinyl alcohol (because cellulose powder is not soluble

in water, polyvinyl alcohol is selected as a model of cotton cellulose), (b) serine, and (c) cured polyvinyl alcohol-serine. (One to one mole ratio of polyvinyl alcohol repeat unit to serine was mixed with 10% (w/w) of aluminum sulfate, then coated on a piece of glass, dried at 80°C for 5 min, and cured at 160°C for 3 min.) The third set is (a) serine, (b) aluminum sulfate, and (c) cured serine-aluminum sulfate. (One to 0.5 mol ratio of serine to aluminum sulfate was mixed, solved, then coated on a piece of glass, dried at 80°C for 5 min, and cured at 160°C for 3 min.) Each of the samples and KBr was mixed, ground, and dried in 1-dram vials over P₂O₅ for 3 days. The samples were then pressed in an evacuated die under suitable pressure. A Fourier transform infrared spectrophotometer (Jasco model FT/IR-3) was used to obtain spectra.

RESULTS AND DISCUSSION

Physical properties

The nitrogen content (N content), dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile strength retention (TSR) of the DMDHEU, DMDHEU-glycine, and DMDHEU-serine finished fabrics are listed in Table I. Nitrogen contents for DMDHEU, serine, and glycine molecules are 15.73%, 13.33%, and 18.67%, respectively; however, the calculated N contents in the same total padding solution (10% as an example, the ratio of DMDHEU to α -amino acid is 3 to 1) are 0.157%, 0.151%, and 0.165%, respectively, for DMDHEU, DMDHEU-serine, and DMDHEU-glycine. From Table I and Figure 1, which shows the plots of nitrogen contents (N contents) of the finished fabrics versus the resin concentrations, it is interesting to note that the bound nitrogen for the various treated fabrics is in the series of DMDHEU \gg DMDHEU-serine > DMDHEU-glycine at the same resin concentration in padding solution. This series does not fit the calculated nitrogen contents above, which may be caused by the different reaction properties among the cellulose, DMDHEU, and amino acids.

The relationships between the N content and dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile strength retention (TSR) are plotted in Figures 2(a), 2(b), and 2(c), respectively. We can find that the values of DCRA of the finished fabrics are ranked in the series of DMDHEU \gg DMDHEU-glycine > DMDHEU-serine for a given N content in Figure 1(a); however, the values of TSR are ranked inversely in Figure 1(c). Additionally, the values of WCRA of the finished fabrics are ranked in the series of DMDHEU > DMDHEU-serine > DMDHEU-glycine for a given N content in Figure 1(b). Those results may be caused by the different crosslinking reactions among the crosslinking agent systems.

TABLE I
Physical Properties of Cotton Fabrics Treated with DMDHEU, MDHEU-serine, and DMDHEU-glycine

Crosslinking agents	Total conc. (%)	Properties of finished fabrics			
		Nitrogen, %	Dry crease recovery angle (W+F) ^o	Wet crease recovery angle (W+F) ^o	Tensile strength retention, %
-	-	0	182	160	100
DMDHEU	2	0.185	261	216	81.1
	4	0.398	281	240	70.1
	6	0.611	295	260	56.9
	8	0.779	301	281	48.4
DMDHEU-serine	2	0.135	230	194	90.1
	4	0.284	245	220	81.7
	6	0.412	251	231	76.1
	8	0.554	256	244	72.8
DMDHEU-glycine	2	0.135	232	182	88.4
	4	0.291	251	204	78.7
	6	0.415	255	223	73.5
	8	0.561	263	242	68.3

The relationships between DCRA, WCRA, and TSR of the finished fabrics with the three crosslinking agent systems are plotted in Figures 3, 4, and 5, respectively. From the relationships between DCRA and WCRA of the finished fabrics (Fig. 3), we find that the WCRA values of the treated fabrics for DMDHEU alone are lower than those for DMDHEU-serine and DMDHEU-glycine at a given DCRA, but the WCRA values for DMDHEU-glycine are lower than those for DMDHEU-serine. Figure 4 shows the plots of DCRA versus TSR of the various finished fabrics. For a given value of TSR, the DCRA values of the treated fabrics for DMDHEU alone are higher than those for DMD-

HEU- α -amino acids, but the DCRA values are the same for DMDHEU-serine and DMDHEU-glycine. The plot of WCRA against TSR of the finished fabrics shown in Figure 5 reveals that the series of the WCRA values for the various treated fabrics is in the rank of DMDHEU-serine > DMDHEU alone > DMDHEU-glycine at the same TSR. The higher WCRA of the DMDHEU-serine treated fabrics may be caused by the higher condensation reaction between the *N*-methylol

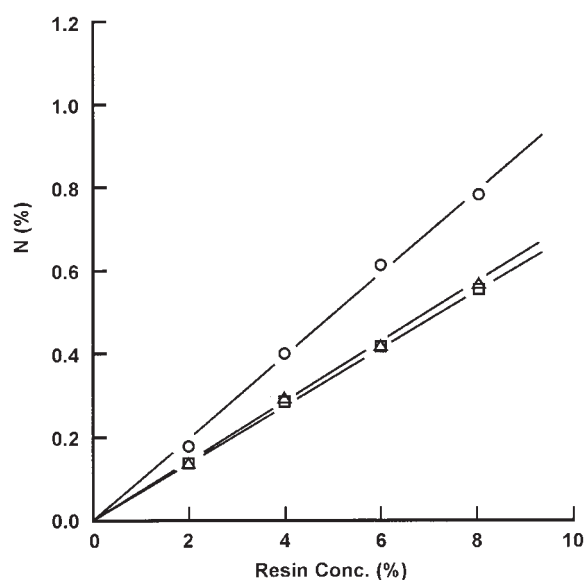


Figure 1 The nitrogen contents of the DMDHEU, DMDHEU-serine, and DMDHEU-glycine treated fabrics for different resin concentrations: \circ = DMDHEU, Δ = DMDHEU-glycine, \square = DMDHEU-serine.

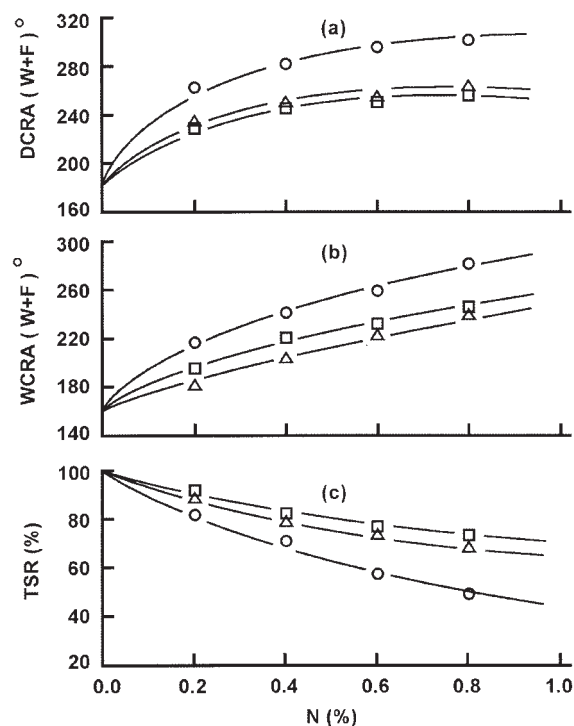


Figure 2 Plots of DCRA (a), WCRA (b), and TSR (c) values of the DMDHEU, DMDHEU-serine, and DMDHEU-glycine treated fabrics versus nitrogen contents, respectively: \circ = DMDHEU, Δ = DMDHEU-glycine, \square = DMDHEU-serine.

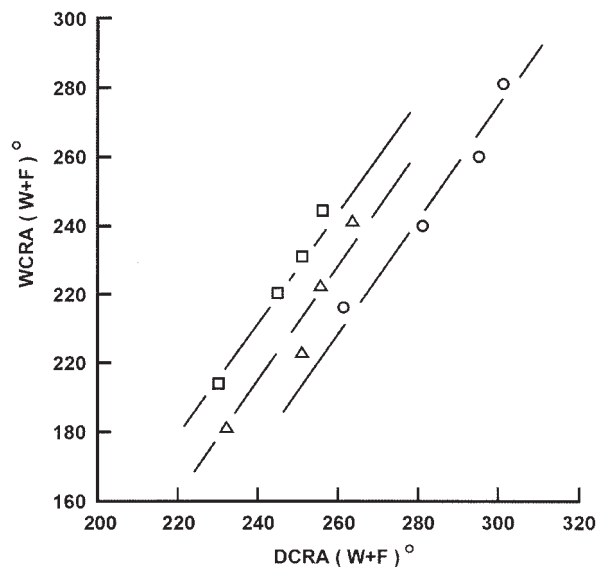


Figure 3 Relationship between DCRA and WCRA of the DMDHEU, DMDHEU-serine, and DMDHEU-glycine treated fabrics: \circ = DMDHEU, \triangle = DMDHEU-glycine, \square = DMDHEU-serine.

group of DMDHEU and the reactive groups of the serine, especially the hydroxyl group. Some studies¹³⁻¹⁵ showed that the condensation between crosslinking agents in the treated fabrics would raise the wet crease recovery angles.

Interaction between the components

To clarify the crosslinking reaction among DMDHEU, cellulose, and the functional groups of the α -amino

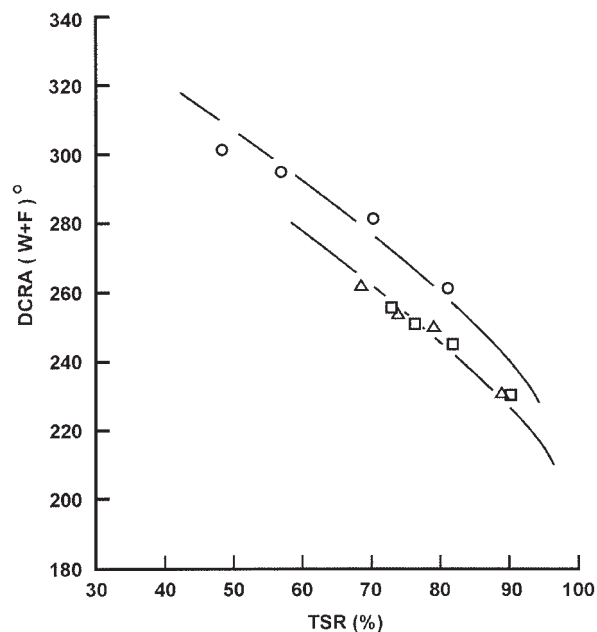


Figure 4 Relationship between DCRA and TSR of the DMDHEU, DMDHEU-serine, and DMDHEU-glycine treated fabrics: \circ = DMDHEU, \triangle = DMDHEU-glycine, \square = DMDHEU-serine.

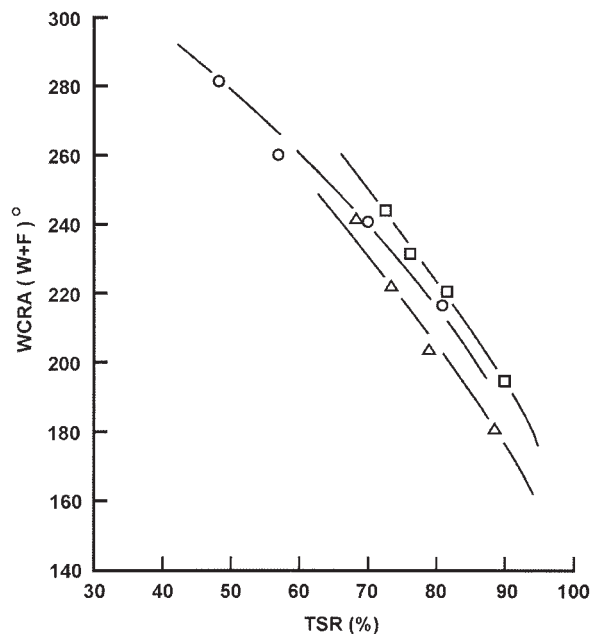


Figure 5 Relationship between WCRA and TSR of the DMDHEU, DMDHEU-serine, and DMDHEU-glycine treated fabrics: \circ = DMDHEU, \triangle = DMDHEU-glycine, \square = DMDHEU-serine.

acids, DMDHEU was used to react with serine under the pad-dry-cure process in the presence of aluminum sulfate as catalyst. The IR spectra of DMDHEU, serine, and cured DMDHEU-serine are shown in Figures 6(a), 6(b), and 6(c), respectively. The interesting and important absorbing bands are those of $-CH_2OH$ (1027cm^{-1} , 1077cm^{-1}) and the carbonyl group (1702cm^{-1})¹⁶ for DMDHEU (Fig. 6(a)), and the hydroxyl group (1013 and 1082cm^{-1}), amino group (1598cm^{-1}), and carboxylic acid group (1408cm^{-1}) of serine (Fig. 6(b)). We find that the IR spectrum for cured DMDHEU-serine (Fig. 6(c)) disappears at 1013 , 1082cm^{-1} (hydroxyl group of serine), and 1598cm^{-1} (amino group of serine), but generates a new absorbing band around 1630cm^{-1} and the new absorbing band around 1108cm^{-1} . Additionally, 1702cm^{-1} (the carbonyl group of DMDHEU) is shifted to 1712cm^{-1} , and 1408cm^{-1} (the carboxylic acid group of serine) is shifted to 1398cm^{-1} . From the description of Silverstein et al.,¹⁷ we find that the new absorbing bands of 1630cm^{-1} are the amide group, and 1108cm^{-1} is the ether group. The formations of the new ether group at 1108cm^{-1} and the amide group at 1630cm^{-1} strongly suggest that the reaction between DMDHEU and serine can occur in the pad-dry-cure process by the functional groups of hydroxyl, carboxylic acid, and amine.

The IR spectra of PVA, serine, and cured PVA-serine are shown in Figures 7(a), 7(b), and 7(c), respectively. The interesting and important absorbing bands are those of $-CHOH$ (1092cm^{-1})¹⁷ for PVA (Fig. 7(a)),

and the hydroxyl group (1013 and 1082cm^{-1}), amino group (1598cm^{-1}), and carboxylic acid group (1408cm^{-1}) for serine (Fig. 7(b)). We find that the IR spectrum for cured PVA-serine (Fig. 7(c)) disappears at 1092cm^{-1} (the hydroxyl group of PVA), but gener-

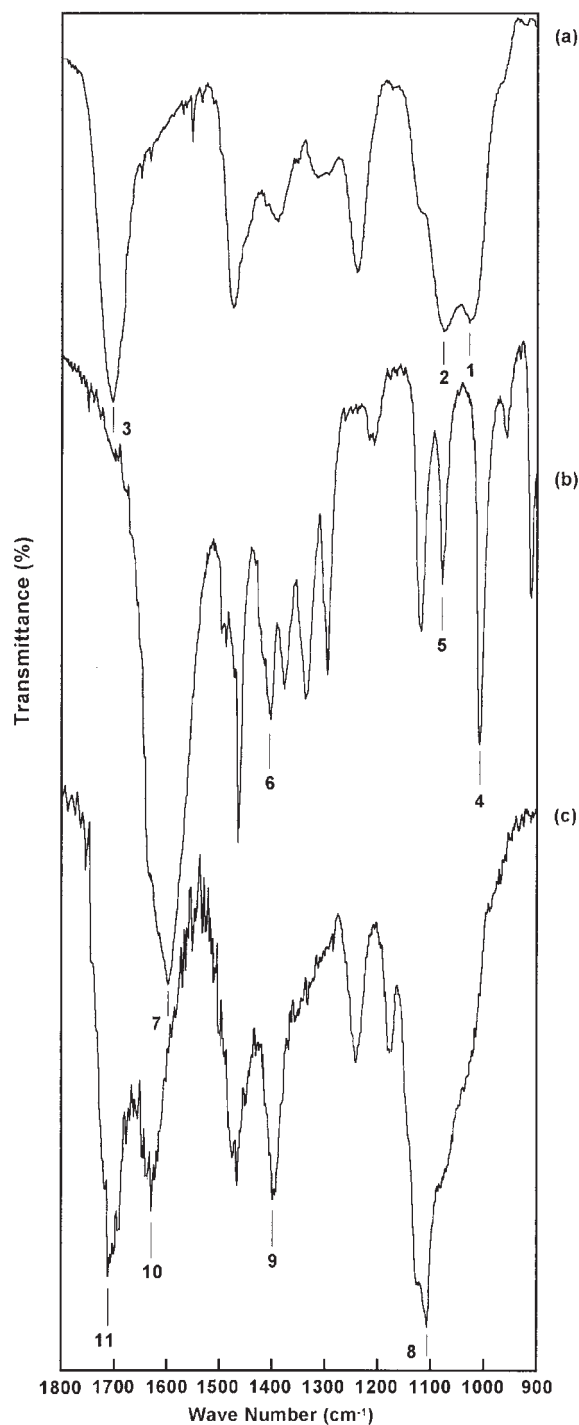


Figure 6 IR spectra of (a) DMDHEU, (b) serine, and (c) DMDHEU/serine. (1) 1027 cm^{-1} ; (2) 1077 cm^{-1} ; (3) 1702 cm^{-1} ; (4) 1013 cm^{-1} ; (5) 1082 cm^{-1} ; (6) 1408 cm^{-1} ; (7) 1598 cm^{-1} ; (8) 1108 cm^{-1} ; (9) 1398 cm^{-1} ; (10) 1630 cm^{-1} ; (11) 1712 cm^{-1} .

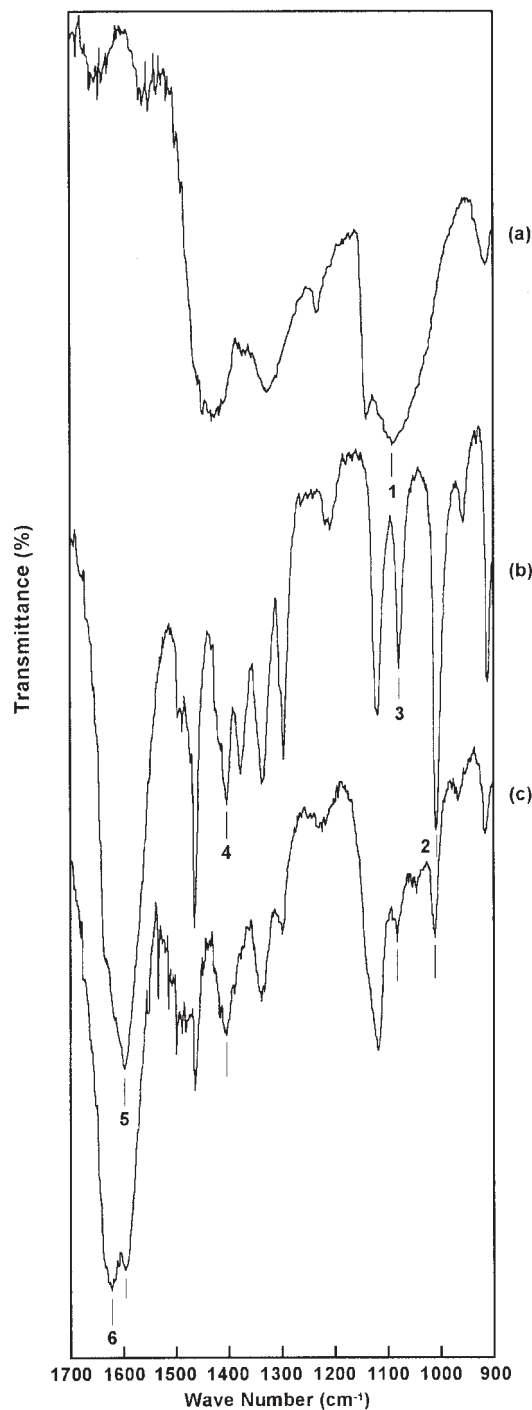


Figure 7 IR spectra of (a) PVA, (b) serine, and (c) PVA/serine. (1) 1092 cm^{-1} ; (2) 1013 cm^{-1} ; (3) 1082 cm^{-1} ; (4) 1408 cm^{-1} ; (5) 1598 cm^{-1} ; (6) 1622 cm^{-1} .

ates a new absorbing band around 1622cm^{-1} ; however, the hydroxyl group, amino group, and carboxylic acid group for serine are only slightly decreased. We account the new absorbing band around 1622cm^{-1} is a secondary imine group.¹⁷ The formations of the new secondary imine group at 1622cm^{-1} strongly suggest that the reaction between PVA and serine can occur in the pad-dry-cure process, but only a little.

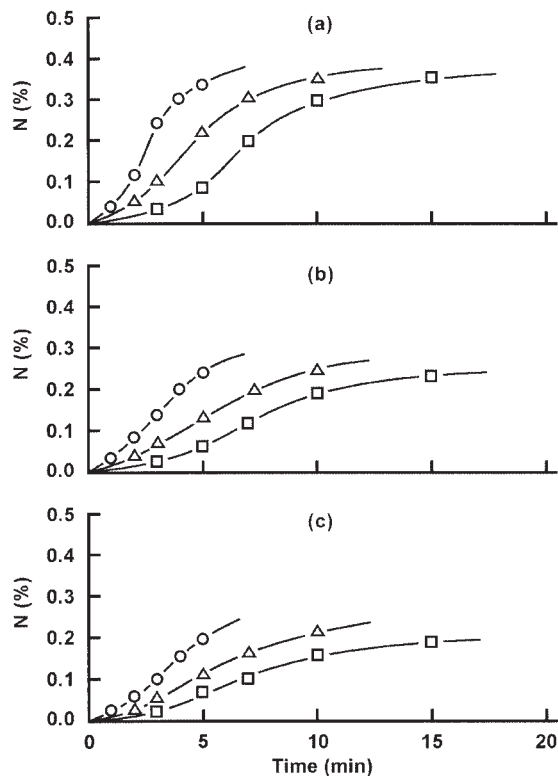


Figure 8 Changes in nitrogen content for the fabrics treated with (a) 0.36M DMDHEU, (b) 0.27M DMDHEU + 0.09M serine, and (c) 0.27M DMDHEU + 0.09M glycine versus heating time: \circ = 100°C, \triangle = 90°C, \square = 80°C.

The above results clearly indicate that serine and glycine can mainly react with DMDHEU (condensation) to affect the physical properties of the treated fabrics, but the crosslinking reaction between serine/glycine and cellulose can only affect the physical properties a little. Additionally, the condensation reaction between DMDHEU-serine and DMDHEU-glycine are different from each other due to containing the hydroxyl group or not.

Reaction kinetics

The data in Figures 8(a), 8(b), and 8(c) show the changes in nitrogen content of cotton fabrics treated with the DMDHEU alone, DMDHEU-serine, and DMDHEU-glycine, respectively. All samples were catalyzed by aluminum sulfate with heated time (minutes). The figures reveal that the nitrogen contents of the treated fabrics increase with the increase of heated time for all cases. Here, we can see the initial slightly concave upward shape of the relationships between nitrogen content and the initial curing time in all cases, which we attribute to the time needed to raise the temperature of the fabric in the oven.^{9,16} The lower nitrogen reacted on cotton cellulose in Figures 8(b)

and 8(c) again confirms the lower crosslinking reactivity of the two α -amino acids.

Semi logarithmic plots of $(\%N - \%N_0)/\%N_0$ against heated time in minutes are shown in Figures 9(a), 9(b), and 9(c) for DMDHEU alone, DMDHEU-serine, and DMDHEU-glycine, respectively. $\%N_0$ is the nitrogen content of the treated fabric after a pad-dry-cure process (i.e., 90% wet pick-up, dried at 80°C for 5 min, cured at 160°C for 3 min; the samples are thought to be fully cured at this condition).^{15,17} $\%N$ is the bound nitrogen after a given time interval at the temperature indicated (80°C, 90°C, and 100°C). We obtained straight lines for all cases, the linearity indicating that the reaction is pseudofirst-order for the time shown.

Table II contains data calculated from the semi logarithmic plots using least square analysis for each data set at 80, 90, and 100°C. Based on pseudofirst-order reaction kinetics, the specific reaction rate constants (k') were calculated from the slopes of lines. The k' values shown in Table II reveal that the rate constants for DMDHEU alone are higher than those for the two DMDHEU- α -amino acids, and the rate constants for DMDHEU-serine are higher than those for DMDHEU-glycine at the same heated temperatures. The lower specific reaction rate constant for DMDHEU-amino

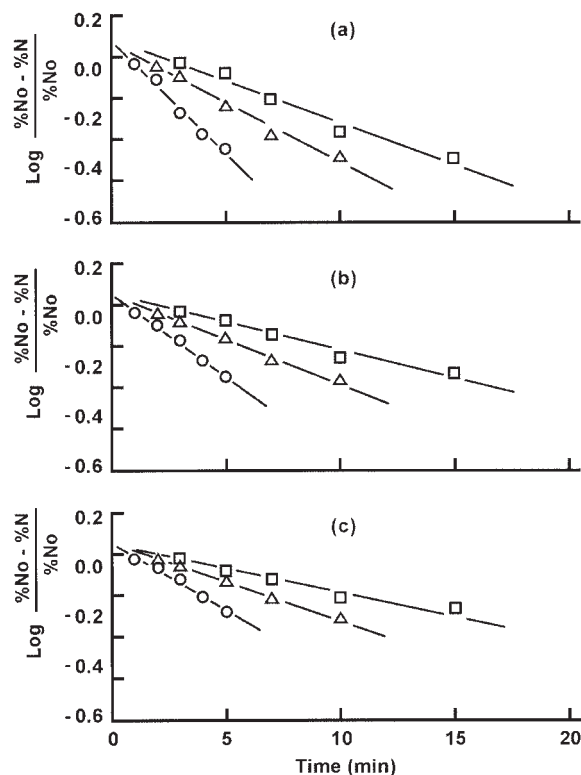


Figure 9 Semilogarithmic graphs of $(\%N - \%N_0)/\%N_0$ versus heating time for fabrics treated with (a) 0.36M DMDHEU, (b) 0.27M DMDHEU + 0.09M serine, and (c) 0.27M DMDHEU + 0.09M glycine: \square = 100°C, \triangle = 90°C, \circ = 80°C.

TABLE II
Reaction Rate Constants (k') and Activation Parameters of Cotton Treated with DMDHEU, DMDHEU-serine, and DMDHEU-glycine at Different Heating Conditions

Crosslinking agents	Heating temp. (°C)	$k' \times 10$ (min ⁻¹)	ΔH^* (Kcal/mole)	$\Delta S^* \times 10^2$ (Kcal/°K-mole)	ΔG^* (Kcal/mole)
DMDHEU	80	0.935	12.115	-2.112	19.570
	90	1.312	12.095	-2.150	19.900
	100	2.498	12.075	-2.122	19.991
DMDHEU-serine	80	0.612	13.693	-1.749	19.867
	90	0.948	13.673	-1.780	20.135
	100	1.844	13.653	-1.760	20.216
DMDHEU-glycine	80	0.461	14.533	-1.567	20.066
	90	0.830	14.513	-1.575	20.231
	100	1.477	14.493	-1.578	20.381

acids may be attributed to the lower crosslinking reaction ability for the two α -amino acids and the buffer effect caused by the complex formation between amino acids and aluminum ion, and the higher k' for DMDHEU-serine than for DMDHEU-glycine may be caused by the higher buffer property of glycine in this system and/or the additional reaction between the hydroxyl group of serine and the *N*-methylol group of DMDHEU. Our previous study² has revealed the buffer effect of α -amino acids (glutamic acid and aspartic acid) as they were used in the crosslinking process.

Figure 10 shows the semi logarithmic Arrhenius plots of the specific reaction rate constants. Lines were determined using the least square method, and activation parameters for the various crosslinking agent systems are recorded in Table II, using the method of Ziiffler et al.¹⁸ Free energies of activation (ΔG^*) based on nitrogen for each fabric were positive. The energies needed for the crosslinking for the various crosslinking agents are DMDHEU-glycine > DMDHEU-serine > DMDHEU alone. The positive enthalpies (ΔH^*) of activation for each treated fabric indicate that the transition state complex is endothermic. The series of the enthalpies of activation for the various crosslinking agents is DMDHEU-glycine > DMDHEU-serine > DMDHEU alone, that is, the transition state complex is different from each other. Entropies (ΔS^*) of activation for both samples are positive, and are in the rank of DMDHEU-glycine > DMDHEU-serine > DMDHEU alone. The entropies of activation are affected by the existence of amino acid in the crosslinking agent systems. Those data again support that the crosslinking between DMDHEU-amino acids and cellulose molecules is different from that between DMDHEU and cellulose molecules, and also between DMDHEU-serine and DMDHEU-glycine, which indicates the amino acids can participate in the crosslinking reaction, but not obviously. The latter may be attributed to the presence of the hydroxyl group in the serine molecule, which can react with DMDHEU and

the aluminum ion, respectively, for reaction and buffer effects.

IR spectra for serine, aluminum sulfate, and cured serine-aluminum sulfate are shown in Figures 11(a), 11(b), and 11(c), respectively. The interesting and important absorbing bands are those of the hydroxyl group (1013 and 1082cm⁻¹), the amino group (1598cm⁻¹), and the carboxylic acid group (1408cm⁻¹) of serine¹⁷ (Fig. 11(a)). We find that the IR spectrum for cured serine-aluminum sulfate (Fig. 11(c)) disappears at 1013 and 1082cm⁻¹ (the hydroxyl group of serine), but generates a small but new absorbing band of 1060cm⁻¹. Additionally, the amino group of serine at 1598cm⁻¹ shifts to 1627cm⁻¹, and the carboxylic acid group at 1408cm⁻¹ of serine shifts to 1403cm⁻¹.

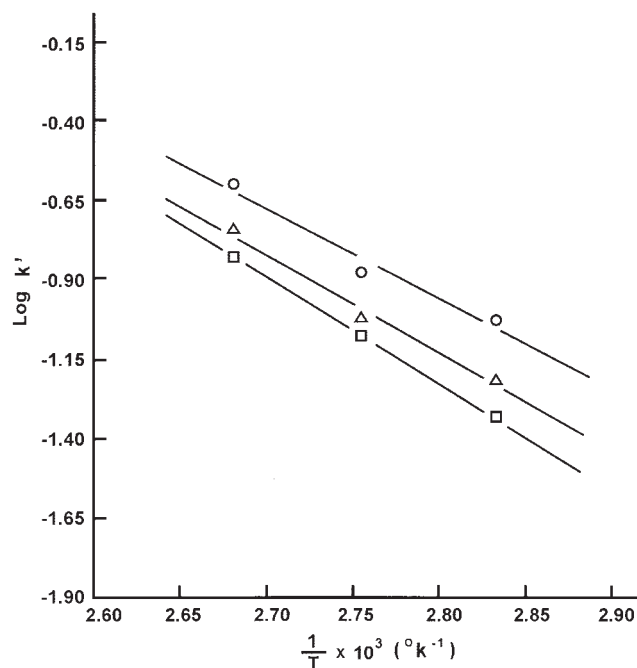


Figure 10 Plots of $\log k'$ based on nitrogen content versus reciprocal of absolute temperature: \circ = DMDHEU, Δ = DMDHEU-glycine, \square = DMDHEU-serine.

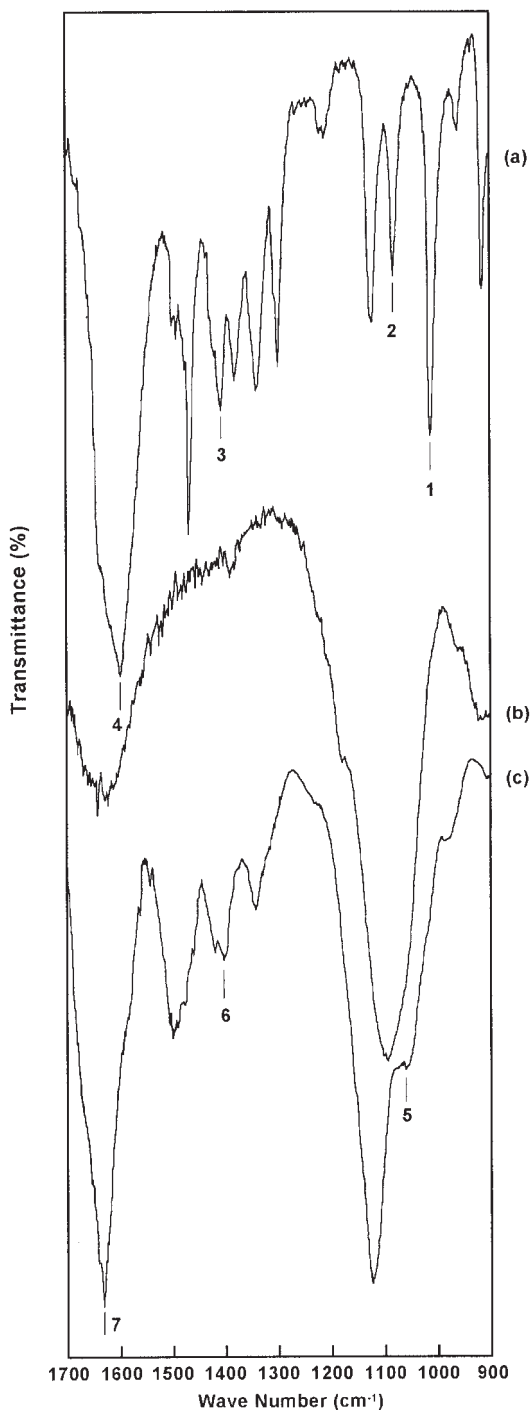


Figure 11 IR spectra of (a) serine, (b) $\text{Al}_2(\text{SO}_4)_3$, and (c) serine/ $\text{Al}_2(\text{SO}_4)_3$. (1) 1013 cm^{-1} ; (2) 1082 cm^{-1} ; (3) 1408 cm^{-1} ; (4) 1598 cm^{-1} ; (5) 1060 cm^{-1} ; (6) 1403 cm^{-1} ; (7) 1627 cm^{-1} .

These results support the reaction between the functional groups of serine and the aluminum ion to form a complex to buffer the crosslinking reaction to decrease the reaction kinetics and raise the energies needed to crosslink. Our previous studies^{2,19} revealed the formation of a complex between the organic mol-

ecules that contain the carboxylic acid and/or other functional groups and the aluminum ion to buffer the crosslinking reaction.

CONCLUSIONS

In this study, serine and glycine were used to combine with DMDHEU as crosslinking agents to study the physical properties of the crosslinked fabrics and the reaction kinetics. We found that the bound nitrogen is in the series of $\text{DMDHEU} \gg \text{DMDHEU-serine} > \text{DMDHEU-glycine}$ at the same resin concentration in a padding solution. We also found that the WCRA values of the treated fabrics for DMDHEU alone are lower than those for DMDHEU-serine and DMDHEU-glycine at a given DCRA, but the WCRA values for DMDHEU-glycine are lower than those for DMDHEU-serine. For a given value of TSR, the DCRA values of the treated fabrics for DMDHEU alone are higher than those for DMDHEU- α -amino acids, but the DCRA values are the same for DMDHEU-serine and DMDHEU-glycine. The series of the WCRA values for the various treated fabrics is in the rank of $\text{DMDHEU-serine} > \text{DMDHEU alone} > \text{DMDHEU-glycine}$ at the same TSR. IR spectra strongly suggest the reaction between DMDHEU and serine can occur in the pad-dry-cure process, and the reaction between the hydroxyl group (cellulose) and serine can also occur in the pad-dry-cure process, but only a little. The rate constants for DMDHEU alone are higher than those for the two DMDHEU- α -amino acids, and the rate constants for DMDHEU-serine are higher than those for DMDHEU-glycine at given heated temperatures. The energies needed for the crosslinking and the values of enthalpies and entropies of activation are all ranked as: $\text{DMDHEU-glycine} > \text{DMDHEU-serine} > \text{DMDHEU alone}$. IR spectra also support the reaction between the functional groups of serine and the aluminum ion to form a complex to buffer the crosslinking reaction.

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