Crosslinking of Cotton Cellulose in the Presence of Alkyl Diallyl Ammonium Salts. I. Physical Properties and Agent Distribution

Jui-Chin Chen,[1] Jen-Taut Yeh,[2] Cheng-Chi Chen[1]

[1]*Department of Materials and Textiles, Oriental Institute of Technology, Pan-Chiao, Taiwan 22064, Republic of China*
[2]*Department and Graduate School of Fiber and Polymer Engineering, National Taiwan University of Science Technology, Taipei, Taiwan 10673, Republic of China*

ABSTRACT: We used three kinds of alkyl diallyl ammonium salts (methyl, ethyl, and propyl) in combination with dimethyloldihydroxyethyleneurea (DMDHEU) as crosslinking agents. The nitrogen content, dry crease recovery angle (DCRA), moisture regain, and wicking height for the DMDHEU/alkyl diallyl ammonium salts were in the order of $-CH_3 > -C_2H_5 > -C_3H_7$, but the wet crease recovery angle (WCRA) and tensile strength retention (TSR) were in the opposite order at the same resin concentration. For the same DCRA and TSR, the WCRA values for only DMDHEU were lower than those for DMDHEU/alkyl diallyl ammonium salts, and the WCRA values for DMDHEU/alkyl di- allyl ammonium salts were in the order of $-C_3H_7 > -C_2H_5 > -CH_3$. Both the $-OH$ group of the cellulose and DMDHEU could react with the vinyl or epoxy groups of the alkyl diallyl ammonium salts during the pad–dry–cure process. The surface migration for DMDHEU/alkyl diallyl ammonium salts was in the order of $-CH_3 > -C_2H_5 > -C_3H_7$. Fabrics treated with DMDHEU/alkyl diallyl ammonium salts showed good antibacterial properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1662–1669, 2003

Key words: crosslinking; resin; structure-property relations

INTRODUCTION

Previous studies[1–3] have shown that agents containing vinyl groups can act as crosslinking agents to improve the crease recovery angles of finished fabrics in a base condition. At the same time, Sumrell et al.[1] mentioned that the vinyl groups of *N*-vinyl amide, *N*-vinyl sulfonamide, and vinyl ethers reacted with cotton cellulose in the presence of an acid catalyst, but little crosslinking was obtained. Töpfl[4] pointed out that alkyl diallyl ammonium salts could improve the fastness of colored cotton fabrics. Tesoro[5] used quaternary ammonium derivatives of bischloromethyl ethers as crosslinking agents for reactions with cellulose. Additionally, it is well known that cationic reagents can have an antibacterial function.

In this study, we expected that the reactions of alkyl diallyl ammonium salts, crosslinking agents, and cellulose molecules would improve the crease recovery and antibacterial properties simultaneously. We also expected the distribution of crosslinking agents on finished fabrics to be affected by the presence of alkyl diallyl ammonium salts, and the distribution was de- tected and measured by negative staining with a direct dye, as described by De Boer.[6]

We used dimethyloldihydroxyethyleneurea (DMDHEU) in combination with three kinds of alkyl diallyl ammonium salts (methyl, ethyl, and propyl) as crosslinking agents in this study. We examined some physical properties, antibacterial properties, and agent distributions of finished cotton fabrics.

EXPERIMENTAL

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

The crosslinking agent was DMDHEU:
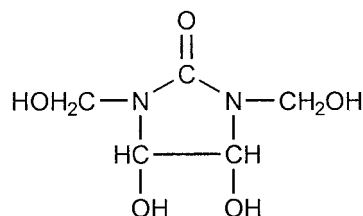
Alkyl diallyl ammonium salts were synthesized with the method described by Töpfl.[4] The alkyl groups were $-CH_3$, $-C_2H_5$, and $-C_3H_7$:

TABLE I
Physical Properties of Cotton Fabrics Finished with DMDHEU Containing Various Alkyl Diallyl Ammonium Salts

Alkyl group	Alkyl diallyl ammonium salts (%)	DMDHEU (%)	Properties of finished fabrics					
			Nitrogen (%)	DRCA, (W + F)*	WCRA, (W + F)*	TSR, (%)	MR (%)	WH (cm)
—	—	—	—	189	170	100	8.6	8.9
	—	1.0	0.20	210	191	90.5	—	—
	—	2.0	0.32	227	211	81.6	—	—
—	—	4.0	0.56	262	232	61.7	—	—
	—	6.0	0.77	281	249	58.7	5.8	8.2
	0.5	1.0	0.32	230	210	80.7	—	—
	1.0	2.0	0.48	252	223	70.7	—	—
—CH₃	2.0	4.0	0.88	274	252	56.5	—	—
	3.0	6.0	1.08	290	260	52.0	7.8	10.5
	0.5	1.0	0.24	225	221	86.3	—	—
	1.0	2.0	0.43	247	240	72.5	—	—
—C₂H₅	2.0	4.0	0.76	273	260	57.6	—	—
	3.0	6.0	0.98	290	274	53.4	7.4	10.4
	0.5	1.0	0.21	215	223	89.4	—	—
	1.0	2.0	0.38	235	243	75.7	—	—
—C₃H₂	2.0	4.0	0.68	272	263	59.4	—	—
	3.0	6.0	0.91	289	276	54.5	7.3	10.2

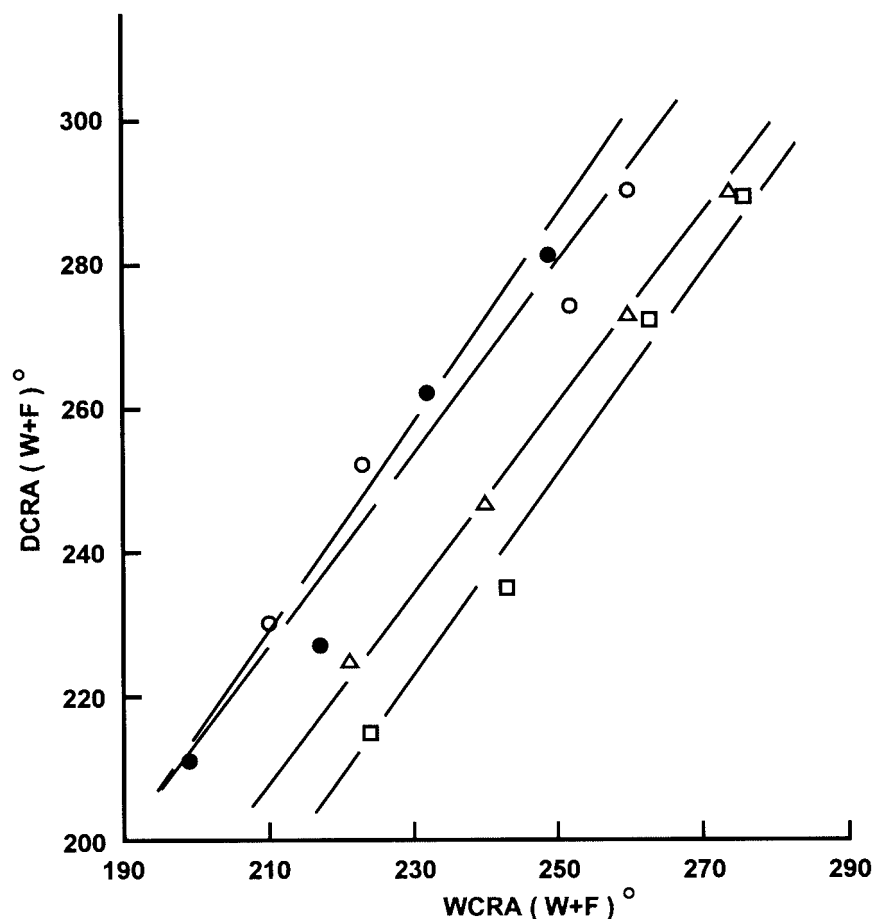* The sum of warp (W) and filling (F) directions.

Figure 1 Relationship between DCRA and WCRA of the fabric samples treated with DMDHEU/alkyl diallyl ammonium salts: (●) DMDHEU, (○) DMDHEU/methyl diallyl ammonium salt, (△) DMDHEU/ethyl diallyl ammonium salt, and (□) DMDHEU/propyl diallyl ammonium salt.
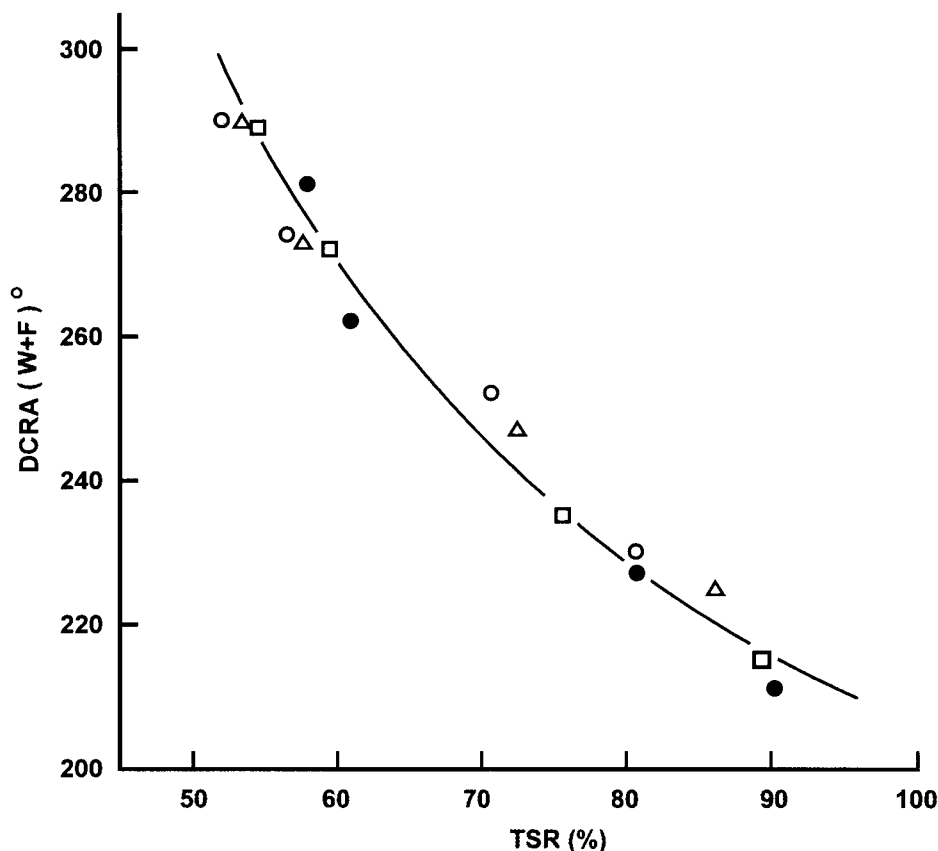
Figure 2 Relationship between DCRA and TSR of the fabric samples treated with DMDHEU/alkyl diallyl ammonium salts: (●) DMDHEU, (○) DMDHEU/methyl diallyl ammonium salt, (△) DMDHEU/ethyl diallyl ammonium salt, and (□) DMD-HEU/propyl diallyl ammonium salt.
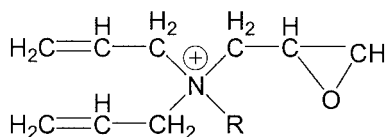

Ammonium sulfate was reagent-grade, as were the other chemicals. The dye was C I Direct Red 81.

The cotton fabric samples were padded twice to about 90% wet pickup with freshly prepared (1, 2, 4, and 6% w/w) aqueous solutions of DMDHEU in the presence of alkyl diallyl ammonium salts and the ammonium sulfate catalyst. The alkyl diallyl ammonium salt and catalyst concentrations were 0.50 and 0.10 times the crosslinking agent solid concentration, respectively. The padded fabrics were dried at 80 °C for 5 min, cured at 160°C for 3 min, soaped, washed, and dried.

The tensile strength of the warp yarns was measured on an Instron tensile tester. ASTM standard method D 1295-67 was used to determine the dry crease recovery angle (DCRA) and wet crease recovery angle (WCRA). The wicking behavior was evaluated by the wicking height (WH) with the JIS L 190 method. ASTM method D629-59T was used for the weighting procedure. Nitrogen determinations were made with the Kjeldahl methods. The reagent distribution was detected and measured by negative staining with Direct Red 81 as described by De Boer.[6] A CS-5 Chroma-Sensor applied color system was used to measure the depth of color of the various finished and dyed fabrics. The antibacterial properties (bacterial inhibition values) of the treated cotton fabrics were tested with AATCC test method 100-1998, and *staphylococcus aureus* was used.

IR spectra of the samples were obtained with a KBr disk technique.[7] 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 KBr and pressed in an evacuated die under suitable pressure. One set was DMDHEU, alkyl diallyl ammonium salts, and cured DMDHEU/alkyl diallyl ammonium salts [1:1 molar ratios of DMDHEU to alkyl diallyl ammonium salts were mixed with 10% (w/w) ammonium sulfate, dried at 80°C for 5 min, and cured at 160°C for 3 min]. Another set was methylcellulose (because cellulose powder is not soluble in water, methylcellulose was selected as a model for
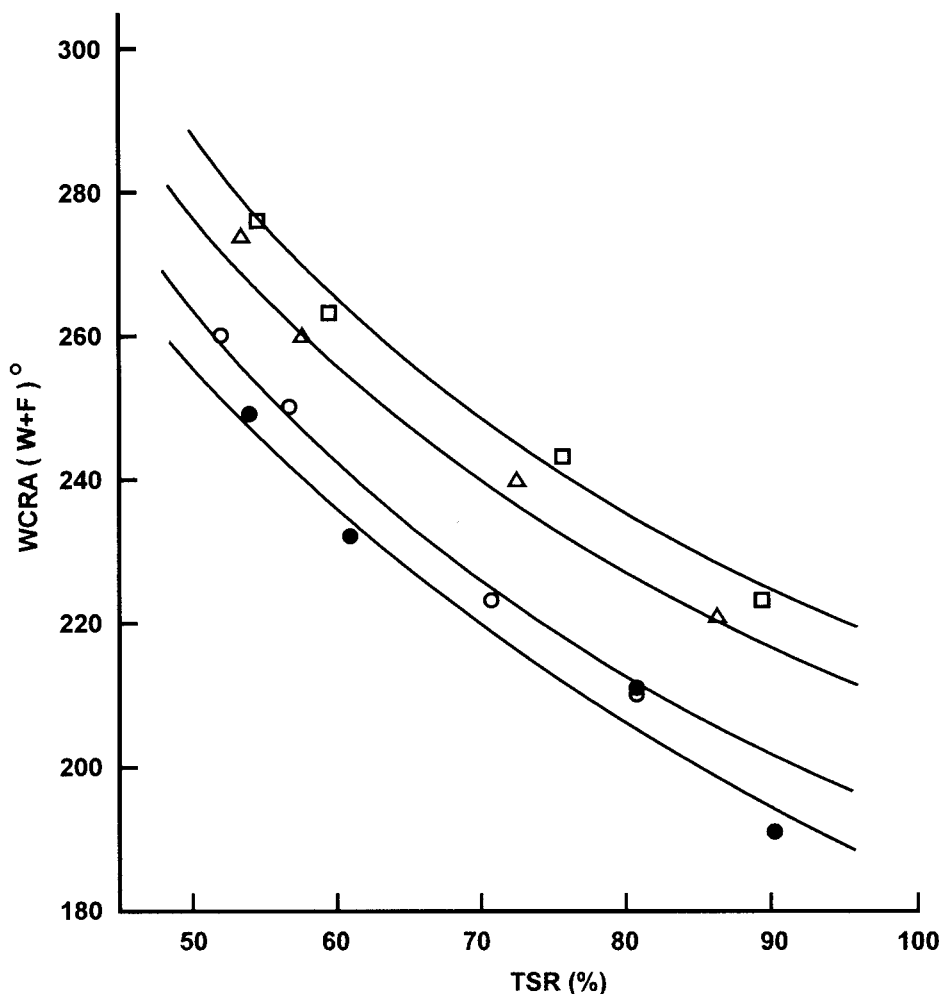
Figure 3 Relationship between WCRA and TSR of the fabric samples treated with DMDHEU/alkyl diallyl ammonium salts: (●) DMDHEU, (○) DMDHEU/methyl diallyl ammonium salt, (△) DMDHEU/ethyl diallyl ammonium salt, and (□) DMD-HEU/propyl diallyl ammonium salt.

cotton cellulose), alkyl diallyl ammonium salts, and cured methylcellulose/alkyl diallyl ammonium salts [1:2 molar ratios of methylcellulose repeat units to alkyl diallyl ammonium salts were mixed with 10% (w/w) ammonium sulfate, dried at 80°C for 5 min, and cured at 160°C for 3 min]. All the samples and KBr were mixed, ground, and dried in 1-dram vials over P_2O_5 for 3 days, and the samples were then pressed in an evacuated die under suitable pressure. A Fourier transform infrared spectrophotometer (FT/IR-3, Jasco) was used to obtain the spectra.

RESULTS AND DISCUSSION

Physical properties

The nitrogen content, DCRA, WCRA, tensile strength retention (TSR), moisture regain (MR), and WH of the finished fabrics are given in Table I. The nitrogen content, DCRA, and WCRA values for the various fabric samples gradually increase with an increasing amount of the crosslinking agent, but TSR decreases in all cases. At a given resin concentration, the nitrogen content, DCRA, and WCRA for alkyl diallyl ammonium salts containing the crosslinking agent are higher than those for DMDHEU, but the TSR values are lower. Additionally, the nitrogen content, DCRA, MR, and WH values for the alkyl diallyl ammonium salts containing the crosslinking agent are in the order of —CH_3 > —C_2H_5 > —C_3H_7; however, the order of WCRA and TSR values are the opposite at the same resin concentration.

The relationships between DCRA, WCRA, and TSR of the finished fabrics with various crosslinking agent systems are shown in Figures 1–3, respectively. From the relationships between DCRA and WCRA of the finished fabrics (Fig. 1), we find that the WCRA of the DMDHEU-treated fabrics are lower than those of the fabrics treated with DMDHEU/alkyl diallyl ammonium salts, and the order of the WCRA for the various fabrics treated with DMDHEU/alkyl diallyl ammo-

TABLE II
K/S and [D]*f* Values of Cotton Fabrics Finished with DMDHEU Containing Various Alkyl Diallyl Ammonium Salts

Alkyl group	Alkyl diallyl ammonium salts (%)	DMDHEU (%)	*K/S* values	[D]*f* (mg of Dye/kg of cotton)	*K/S* values after extraction	Bacteria inhibition (%)	
						3 h	6 h
—	—	—	4.68	8.23	—	0	0
	—	1.0	0.92	3.47	—	—	—
	—	2.0	0.70	2.60	0.18	—	—
—	—	4.0	0.45	1.60	0.09	—	—
	—	6.0	0.31	0.91	0.01	—	—
	0.5	1.0	1.66	3.86	—	—	—
	1.0	2.0	1.30	3.01	0.41	—	—
—CH₃	2.0	4.0	0.70	1.85	0.37	78	>99
	3.0	6.0	0.50	1.15	0.29	—	—
	0.5	1.0	1.50	4.22	—	—	—
	1.0	2.0	1.11	3.42	0.33	—	—
—C₂H₅	2.0	4.0	0.65	2.02	0.25	—	—
	3.0	6.0	0.46	1.29	0.19	—	—
	0.5	1.0	1.42	4.75	—	—	—
	1.0	2.0	1.02	3.98	0.28	—	—
—C₃H₇	2.0	4.0	0.63	2.20	0.12	72	>99
	3.0	6.0	0.38	1.35	0.09	—	—

nium salts is —C_3H_7 > —C_2H_5 > —CH_3 at a given DCRA. Figure 2 shows plots of DCRA versus TSR for the finished fabrics. For a given value 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 various fabrics treated with DMDHEU/alkyl diallyl ammonium salts are higher than those of the DMDHEU-treated fabrics, and the order of the WCRAs for the various fabrics treated with DMDHEU/alkyl diallyl ammonium salts is —C_3H_7 > —C_2H_5 > —CH_3 at a given TSR. For DMDHEU/alkyl diallyl ammonium salts, the higher WCRA may be caused by the reaction between DMDHEU and alkyl diallyl ammonium salts. Previous studies[8,9] have revealed that the higher the condensation degree is of the crosslinking agent, the higher the WCRA is of the treated fabric.

Antibacterial properties

The bacterial inhibition values are defined as $(M_b - M_a)/M_b \times 100\%$, where M_b and M_a are the numbers of bacteria of the finished fabrics for 0 h of nourishment and the specific hours of nourishment, respectively. The higher the values are of bacterial inhibition, the higher the effect is of the antibacterial properties. Table II shows the bacterial inhibition values for the control fabric and fabrics treated with DMDHEU/ alkyl diallyl ammonium salts, and it reveals that the bacterial inhibition values increase with an increase in the testing time period. The control fabric has no antibacterial properties, and fabrics treated with DMD-HEU/alkyl diallyl ammonium salts have significant antibacterial properties. This may be caused by the

cationic ion of ammonium. Kanazawa et al.[10] showed that tributyl-3-[(and 4-) vinyl-benzyl]ammonium chloride could provide antibacterial properties.

Interaction between the components

To confirm the crosslinking between the cellulose and the vinyl and epoxy groups of the alkyl diallyl ammonium salts, we selected methylcellulose as a model molecule of cotton cellulose (because cellulose powder is not soluble in water, we selected methylcellulose as a model of cotton cellulose) to react with *N*-epoxy-2,3-propyl-*N*-propyl-*N,N*-diallyl-ammonium propyl sulfate in a pad–dry–cure process in the presence of ammonium sulfate as a catalyst. The IR spectra of methylcellulose, *N*-epoxy-2,3-propyl-*N*-propyl-*N,N*-diallyl ammonium propyl sulfate, and cured methylcellulose/*N*-epoxy-2,3-propyl-*N*-propyl-*N,N*-diallyl ammonium propyl sulfate are shown in Figure 4(a–c), respectively. The interesting and important absorbing bands are those of —$CHOH$ (1060 cm^{-1})[11] for methylcellulose [Fig. 4(a)] and those of —CH=CH_2 (995 cm^{-1}) and epoxy groups (1218 cm^{-1}) for *N*-epoxy-2,3-propyl-*N*-propyl-*N,N*-diallyl ammonium propyl sulfate [Fig. 4(b)]. The IR spectrum disappears at 995 cm^{-1} (α-unsaturated bond—CH=CH_2) and decreases at 1218 cm^{-1} (epoxy group) for cured methylcellulose/*N*-epoxy-2,3-propyl-*N*-propyl-*N,N*-diallyl ammonium propyl sulfate but generates two new absorbing bands at 1103 and 1130 cm^{-1} [Fig. 4(c)]. From the description of Silverstein et al.,[12] we find that the new absorbing bands at 1103 and 1130 cm^{-1} in Figure 4(c) are for ether groups. This result strongly supports the idea that the crosslinking reaction between —OH of

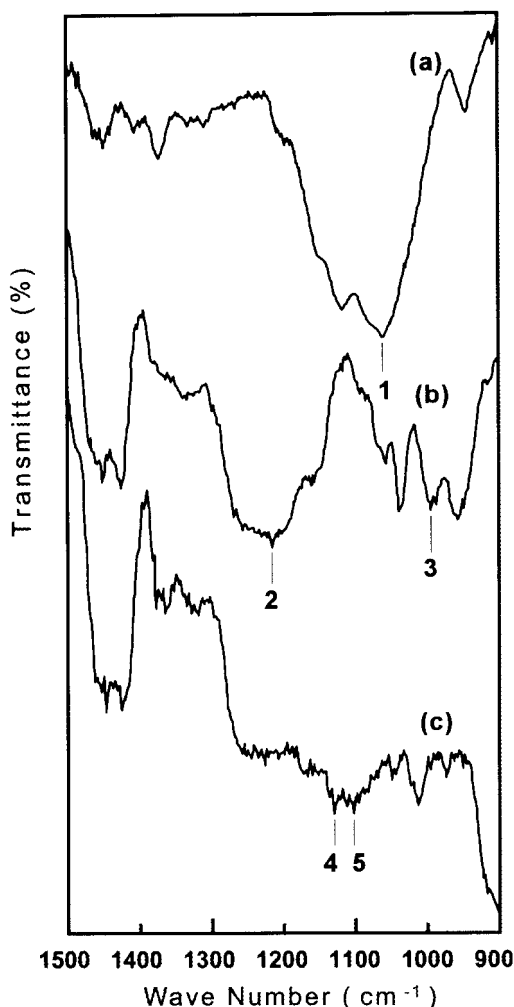**Figure 4** IR spectra of (a) methylcellulose, (b) N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate, and (c) cured methylcellulose/N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate: (1) 1060, (2) 1218, (3) 995, (4) 1130, and (5) 1103 cm^{-1}.

cellulose and the vinyl and epoxy groups of N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate can be formed in a pad–dry–cure process to reduce the TSR and increase the nitrogen content (Table I).

The IR spectra of DMDHEU, N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate, and cured DMDHEU/N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate are shown in Figure 5(a–c), respectively. The interesting and important absorbing bands are those of —CH$_2$OH (1080 and 1030 cm^{-1}) and —CH—OH (1240 cm^{-1})[9] for DMDHEU [Fig. 5(a)] and those of the α-unsaturated bond —CH=CH$_2$ (995 cm^{-1}) and the epoxy group (1218 cm^{-1}) for N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate [Fig. 5(b)]. For cured DMDHEU/N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate, the IR spectrum [Fig. 5(c)] shows changes. The peaks disappear at 1240

(—CHOH), 1080 and 1030 (—CH$_2$OH), and 995 cm^{-1} (—CH=CH$_2$) and decrease at 1218 cm^{-1} (epoxy group), but a new absorbing band is generated at 1235 cm^{-1}. From the description of Silverstein et al.,[12] we find that the new absorbing band at 1235 cm^{-1} in Figure 5(c) is for an ethyleneurea ether group. This result strongly supports the idea that the condensation reaction between —OH of DMDHEU and the vinyl and epoxy groups of N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate can occur in a pad–dry–cure process. Sumrell et al.[1] revealed that the vinyl group of divinyl sulfone could react with cotton cellulose in the presence of zinc nitrate as a catalyst.

Distribution of the crosslinking agent

The K/S and [D]$_f$ values of the finished fabrics listed in Table II are plotted in Figure 6 according to the method described by Rowland et al.,[13,14] and the linear relationships are similar to their results.[14] K is the
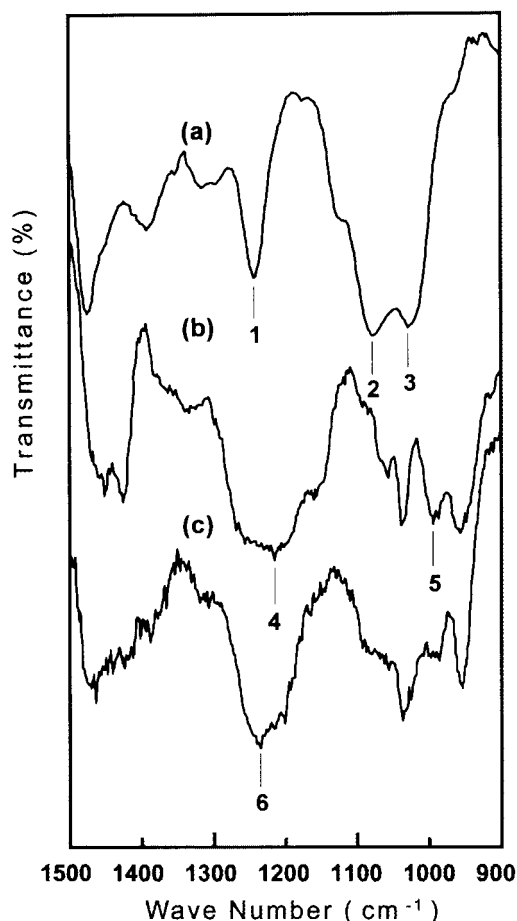

Figure 5 IR spectra of (a) DMDHEU, (b) N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate, and (c) cured DMDHEU/N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate: (1) 1240, (2) 1080, (3) 1030, (4) 1218, (5) 995, and (6) 1235 cm^{-1}.
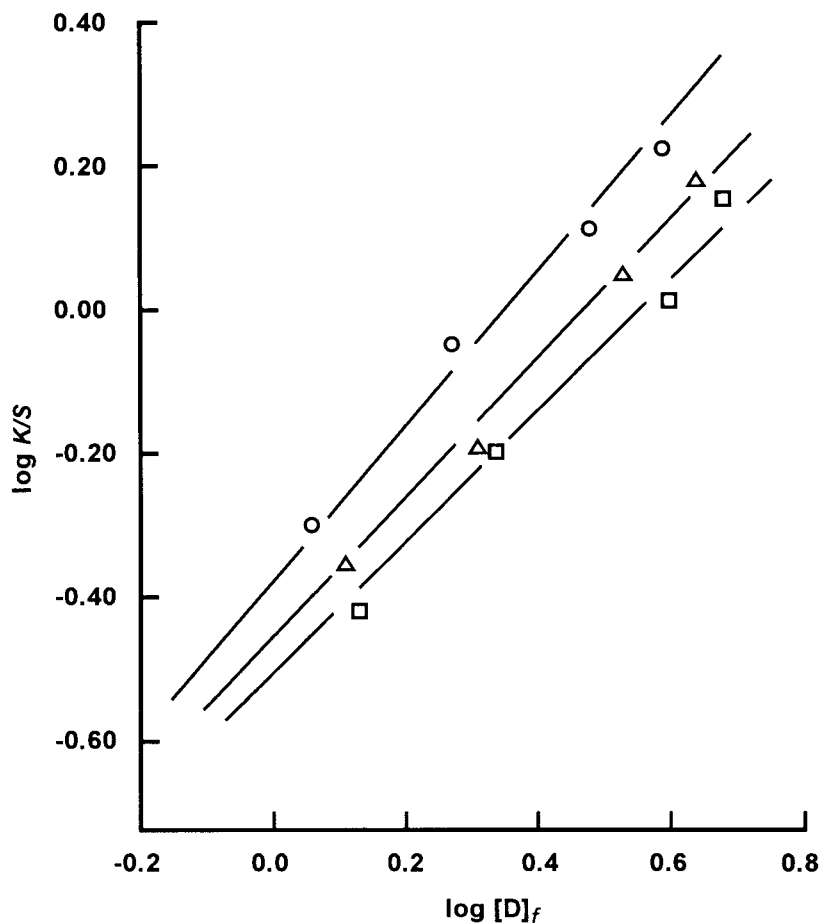
Figure 6 Log K/S versus log $[D]_f$ for fabric samples treated with DMDHEU/alkyl diallyl ammonium salts: (○) DMDHEU/methyl diallyl ammonium salt, (△) DMDHEU/ethyl diallyl ammonium salt, and (□) DMDHEU/propyl diallyl ammonium salt.

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 of dye/kg of cotton) is the dye content of the finished fabric, determined spectrophotometrically after extraction with pyridine/water (1/3) at 60°C. K/S is an inverse measure of crosslinking on fabric surfaces, and $[D]_f$ is an inverse measure of the total crosslinking content through the fabric thickness. The K/S results are average for the two sides of the fabric samples.

For a negative staining condition, the agent distribution follows the rule that the lower K/S is at a specific level of the dye content and the lower the dye fixation is on the surface of the fabric, the higher the crosslink concentration is on the surface of the fabric and the greater the agent distribution is on the fabric. However, the cationic ammonium ion of alkyl diallyl ammonium salts will highly adsorb the direct dye molecule (anionic), raising the K/S values in this study. Inversely, the higher log K/S is, the higher the surface distribution is of the crosslinking agent. Therefore, the agent distribution can only be compared among the DMDHEU/alkyl diallyl ammonium salts. Figure 6 reveals higher values of log K/S for shorter

alkyl groups of diallyl ammonium salts at the same value of log $[D]_f$; that is, the surface distribution of the crosslinking agent on the finished fabrics is significant for shorter alkyl diallyl ammonium salts, and the surface distribution follows the order of —CH_3 > —C_2H_5 > —C_3H_7. It may be caused by the hindrance of longer alkyl groups in the reaction between alkyl diallyl ammonium salts and DMDHEU and/or cellulose.

The K/S values of the various finished, dyed, and extracted (with pyridine/water) fabric samples are shown in Figure 7 (the data are also listed in Table II). The K/S values for the various finished fabrics before and after extraction at the same resin concentration are also ordered as follows: —CH_3 > —C_2H_5 > —C_3H_7. This result strongly agrees with the results shown in Figure 6.

CONCLUSIONS

In this study, three kinds of alkyl diallyl ammonium salts (methyl, ethyl, and propyl, respectively) have been used in combination with DMDHEU as crosslinking agents. The nitrogen content, DCRA, MR,
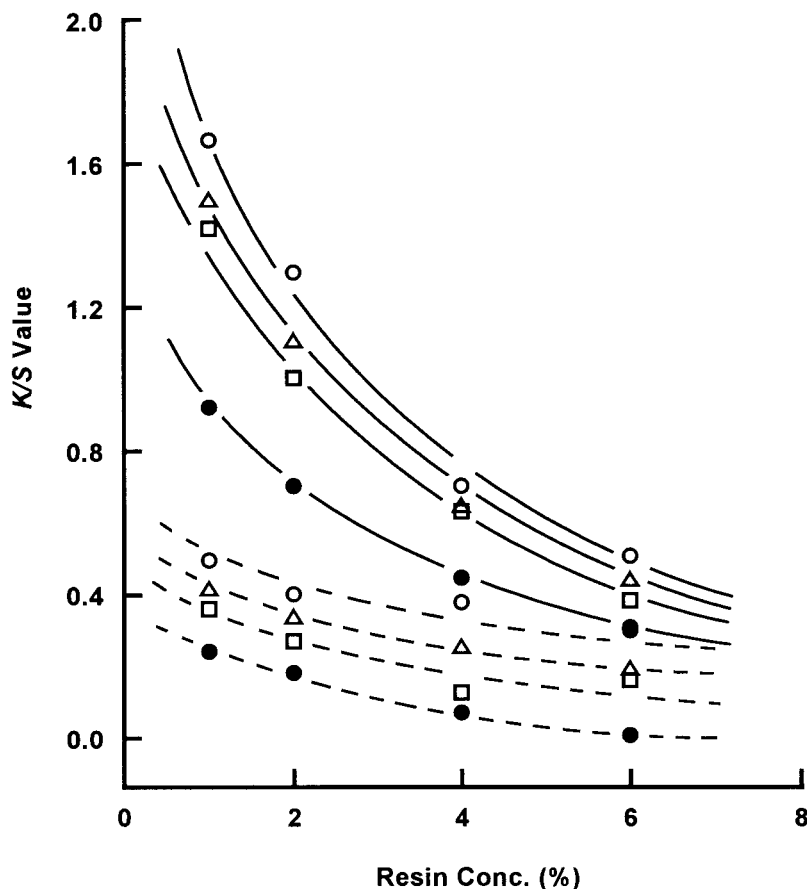
Figure 7 K/S versus the resin concentration for fabric samples treated with DMDHEU/alkyl diallyl ammonium salts (—) before and (–) after extraction: (●) DMDHEU, (○) DMDHEU/methyl diallyl ammonium salt, (△) DMDHEU/ethyl diallyl ammonium salt, and (□) DMDHEU/propyl diallyl ammonium salt.

and WH values for the DMDHEU/alkyl diallyl ammonium salts are in the order of —CH_3 > —C_2H_5 > —C_3H_7; however, the WCRA and TSR values are in the order of —C_3H_7 > —C_2H_5 > —CH_3 at the same resin concentration. The WCRAs of the DMDHEU-treated fabrics are lower than those of the fabrics treated with DMDHEU/alkyl diallyl ammonium salts at a given DCRA and TSR, and the order of the WCRAs for the various fabrics treated with DMD-HEU/alkyl diallyl ammonium salts is —C_3H_7 > —C_2H_5 > —CH_3. Fabrics treated with DMDHEU/alkyl diallyl ammonium salts have significant antibacterial properties. The reaction between —OH of cellulose and DMDHEU and the vinyl and epoxy groups of N-epoxy-2,3-propyl-N-propyl-N,N-diallyl ammonium propyl sulfate can occur in a pad–dry–cure process. The surface distribution for the fabrics finished with DMDHEU/alkyl diallyl ammonium salts follows the order of —CH_3 > —C_2H_5 > —C_3H_7.

References

1. Sumrell, G.; Margavio, M. F.; Welch, C. M. Text Res J 1969, 39, 78.
2. Tesoro, G. C. Text Res J 1962, 32, 189.
3. Tesoro, G. C.; Linden, P.; Sello, S. B. Text Res J 1961, 31, 283.
4. Töpfl, R. U.S. Pat. 5,147,411 (1992).
5. Tesoro, G. C. Text Res J 1960, 30, 192.
6. De Boer, J. J. Text Res J 1980, 50, 648.
7. O'Connor, R. T.; Du Pre, E. F.; McCall, E. R. Anal Chem 1957, 29, 998.
8. Chang, H. L.; Chen, C. C. Text Res J 1996, 66, 803.
9. Jang, T. R.; Sheu, T. C.; Sheu, J. J.; Chen, C. C. Text Res J 1993, 63, 679.
10. Kanazawa, A.; Ikeda, T.; Endo, T. J Polym Sci Part A: Polym Chem 1993, 31, 335.
11. Japan Science Promoting Committee. New Dyeing and Finishing Lecture (in Japanese); Konlee: Tokyo, 1972; Vol. 12, p 202.
12. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectrometric Identification of Organic Compounds, 3rd ed.; Wiley: New York, 1974; pp 136.
13. Bertoniere, N. R.; King, W. D.; Rowland, S. P. Text Res J 1981, 51, 242.
14. Rowland, S. P.; Bertoniere, N. R.; King, W. D. Text Res J 1984, 54, 318.