Studies of Crosslink Structures in Cotton Fabrics Treated with Dimethylol Ethylene Urea and Monomethylol Ethylene Urea Prepolymer Mixture for Wrinkle-Resistant Finish

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ABSTRACT: Ethylene urea and paraformaldehyde with different mole ratios are used as source materials to synthesize dimethylol ethylene urea/monomethylol ethylene urea (DMEU/MMEU) prepolymer resin. The DMEU/MMEU prepolymer resin is then applied to cotton fabrics for wrinkle-resistant finishing. The influence of DMEU/MMEU prepolymer resin on crosslink structures in the treated fabrics is studied. The results show that the formaldehyde content in the treated cotton fabrics with various crosslink structures is determined by the mole ratio of paraformaldehyde in the source mixture and the curing temperature in the finishing process. The crosslink integrity shows various effects on the physical properties of the treated fabrics. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 489–493, 2000

Key words: crosslink structures; cotton fabrics; prepolymer mixture; wrinkle-resistant finish

INTRODUCTION

In general, seven crosslink structures can be derived from the reactions between a crosslink agent and cellulose or the crosslink agent itself after cotton fabrics are treated with resin.[1–3] Four of the structures dominate: cellulose ether binding cell—O—CH_2—N< (F_c), methyl ether binding >N—CH_2—O—CH_2—N< (F_e), methyl binding >N—CH_2—N< (F_m), and unreacted end radical >N—CH_2—OH (F_1). Yen and Tomami[4] showed that the various crosslink structures in the treated fabrics can be affected by the types of catalysts, the concentration of the catalysts, and curing conditions. In addition, crosslink structures can also be affected by the types of fabrics and pretreatment. Changes in crosslink structures will affect the physical and chemical properties of the treated fabrics.[4,5] Therefore, the influence of various finishing conditions on crosslink structures in the treated fabrics is studied in the present experiment.

EXPERIMENTAL

Materials

Cotton fabric, 40s × 40s ends (100) and picks (80), was desized, scoured, and bleached. Sodium hydroxide, sulfuric acid, selenium mixture catalyst, boric acid, pyridine, magnesium chloride, ethylene urea (EU), paraformaldehyde (PF), and methanol were reagent grade.

Methods

Process

The cotton fabrics were first impregnated for 10 min at room temperature in a solution containing

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Table I Contents in CH_2O of Various Forms and Crosslink Structures in Various Resin Treated Fabrics

EU : PF[a]	Curing Temp. (°C)	Combined CH_2O (%) in F_1	F_c	F_e	F_m	Total CH_2O (μ mol/g)	α	n	γ
1 : 1.0	110	5.4	25.8	35.4	31.6	354	0.82	4.16	63
	130	3.6	29.0	34.1	30.2	380	0.89	3.99	69
	140	2.5	30.2	31.6	31.7	408	0.92	3.91	75
	150	1.1	33.4	28.5	32.1	437	0.96	3.61	86
1 : 1.3	110	6.7	29.7	31.6	26.2	428	0.81	3.30	95
	130	4.0	33.1	28.8	26.9	446	0.89	3.23	101
	140	3.0	34.2	26.2	27.9	485	0.91	3.20	109
	150	1.3	36.7	23.4	28.5	506	0.96	3.13	114
1 : 1.5	110	7.9	30.4	28.0	24.6	479	0.80	3.01	113
	130	4.5	34.2	25.7	25.3	498	0.88	2.97	118
	140	3.6	35.5	23.6	26.4	516	0.90	2.95	125
	150	1.5	37.4	22.2	27.0	524	0.96	2.94	128
1 : 1.7	110	8.3	30.6	27.6	23.2	490	0.79	2.90	120
	130	4.8	34.3	25.1	24.3	504	0.88	2.88	125
	140	3.7	35.6	22.4	25.1	518	0.90	2.84	131
	150	1.7	38.1	19.5	26.0	531	0.96	2.79	138
1 : 1.9	110	8.0	31.2	26.4	22.2	503	0.80	2.80	125
	130	5.2	34.6	23.4	23.5	536	0.87	2.76	131
	140	3.9	36.4	20.8	24.2	551	0.90	2.71	140
	150	2.0	38.9	17.2	25.3	570	0.95	2.66	149
1 : 2.0	110	7.8	32.7	24.2	21.5	537	0.80	2.66	134
	130	5.0	35.8	22.3	22.4	564	0.88	2.64	141
	140	3.6	37.2	18.5	23.3	583	0.91	2.60	148
	150	1.9	39.4	15.3	24.9	594	0.95	2.58	156

The resin concn was 8%; $MgCl_2$ was 0.8%; drying was at 80°C for 5 min; curing time was 3 min.
[a] The mole ratio of ethylene urea : paraformaldehyde.

finishing agent (8% prepolymer) and magnesium chloride (10% of the weight of the prepolymer). This was followed by squeezing to a wet pick up of 80%, pinning on a frame without tension, drying at 80°C for 5 min, and then curing at different temperatures (110–150°C). After curing the samples were throughly washed in a solution containing 2 g/L soap and dried in ambient conditions.

Analysis and Calculations

Nitrogen content and total formaldehyde content in the treated fabrics was measured by the Kjeldahl method and chromotropic acid method, respectively. The amount of formaldehyde connected to various crosslink structures was measured according to the method developed by Yen[5] in which samples are hydrolyzed by an interfacial activation agent and acetic acid, then reverse titrated by KCN-$Hg(NO_3)_2$. The types of bindings include cellulose ether binding cell—O—CH_2—N< (F_c), methyl ether binding >N—CH_2—O—CH_2—N< (F_e), methyl binding >N—CH_2—N< (F_m), and unreacted end radical >N—CH_2—OH (F_1). The average crosslink length (n), average crosslink number (γ), and average crosslink integrity (α) can be calculated by

$$n = [(F_e/2 + F_m)/(F_c + F_1)/2] + 1 \quad (1)$$

$$\gamma = (N/2)/n \quad (2)$$

$$\alpha = (F_c)/(F_c + F_1) \quad (3)$$

where N is the nitrogen content in the treated fabrics. The crosslink integrity is judged as an index to the amount of the ether combined in the fiber and resin. If the large index value of the ether combined in the fiber and resin is sufficient, the more the affect of the material characteristics

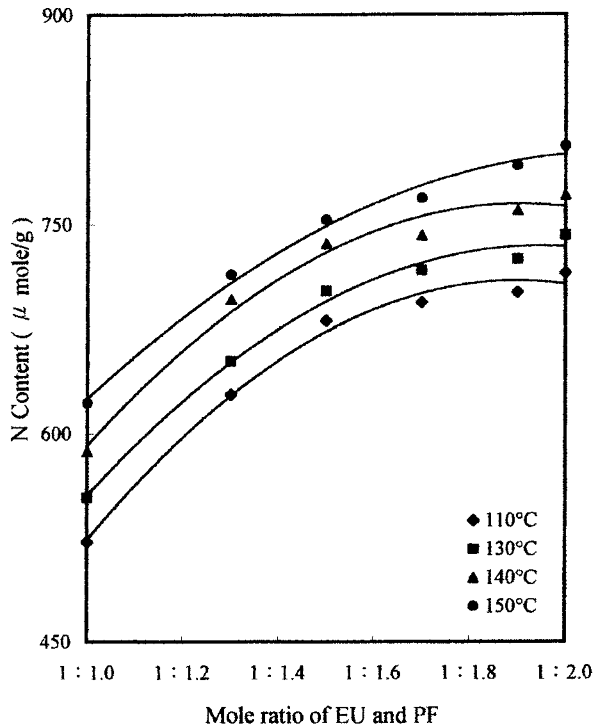

Figure 1 The change of the total CH_2O against the mole ratio of EU and PF for mixed prepolymer treated fabrics under different curing temperatures.

is obvious. For example, the higher the dry crease angle is, the more crosslinks there are.

RESULTS AND DISCUSSION

Influences on Crosslink Structures in Treated Fabrics

According to the previous report, finishing conditions affect crosslink structures in the fabrics.[4,5] Table I shows the percentage bound to CH_2O for unreacted end radical (F_1), cellulose ether binding (F_c), methyl ether binding (F_e), and methyl binding (F_m). This table indicates that F_1 and F_c increase with an increasing PF mole ratio in the source material, while F_e and F_m both decrease. This is because the amount of dimethylol EU (DMEU) in the prepolymer increases with increasing PF mole ratio in the source material. Therefore, more crosslink reactions take place on cellulose so that the amount of F_1 and F_c increase. In addition, F_1 and F_e decrease with increasing curing temperature, while F_c and F_m increase. This is because a high curing temperature promotes reactions between the cellulose and crosslink agent. Hence, the amount of cellulose ether binding increases. The amount of methyl binding (F_m) also increases due to the decomposition of the self-polymerized resin at a high temperature.

The calculation results for n, γ, and α are also shown in the table. The γ in the treated fabrics increases with increasing curing temperature and PF content in the source material, while the n decreases. This is because the reaction between the finishing agent and cellulose is complete in the above-mentioned conditions. Although it increases with curing temperature, the crosslink integrity is less related to the source mole ratio. The total formaldehyde (F_o) and nitrogen content in the treated fabrics also shows the same trend as shown in Figures 1 and 2.

Relations Between Physical Properties of Treated Fabrics and Crosslink Structure

The relations between physical properties of the treated fabrics and crosslink structures were studied by Yen and Chen[5,6] with the Pad–Dry–Cure method to provide wrinkle resistancy for cotton fabrics. The results show a linear relation

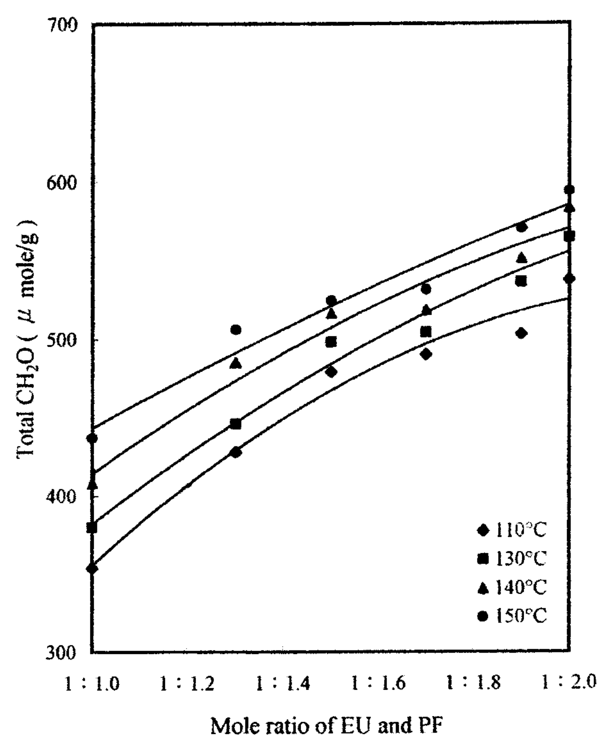

Figure 2 The change of the total N content against the mole ratio of EU and PF for mixed prepolymer treated fabrics under different curing temperatures.

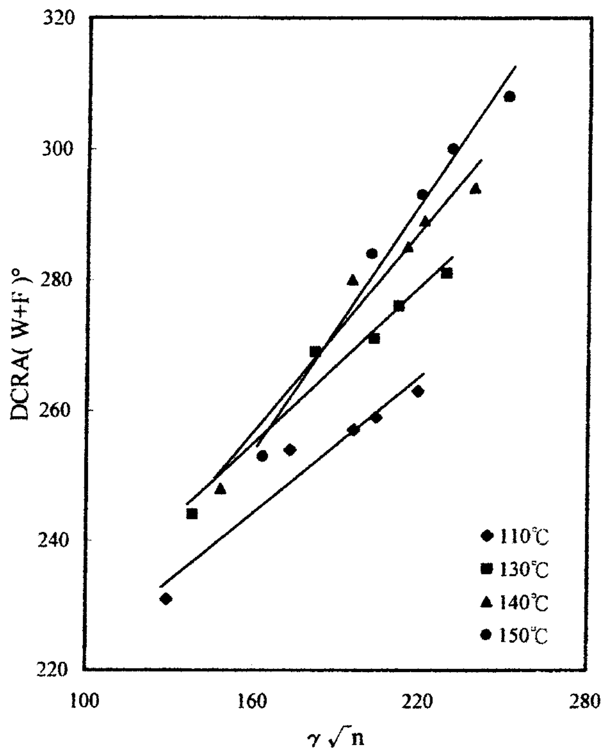

Figure 3 The relationship between the DCRA and the $\gamma\sqrt{n}$ of DMEU treated fabrics at different curing conditions.

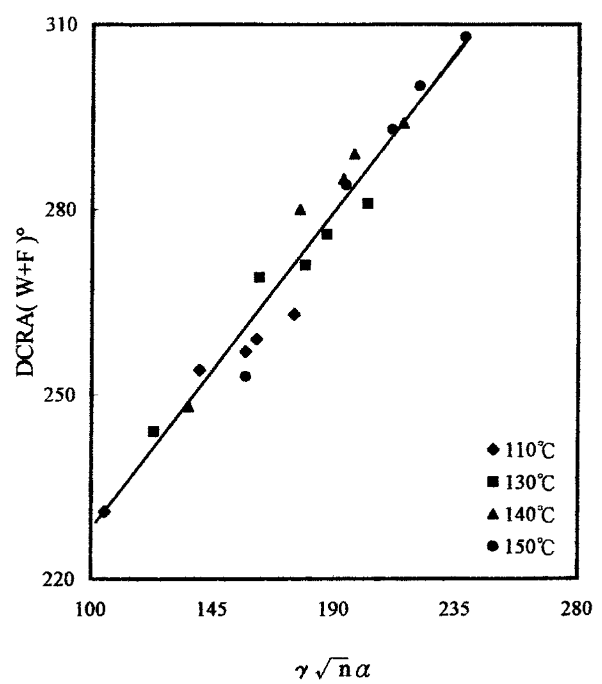

Figure 4 The relationship between the DCRA and the $\gamma\sqrt{n}\alpha$ of DMEU treated fabrics at different curing conditions.

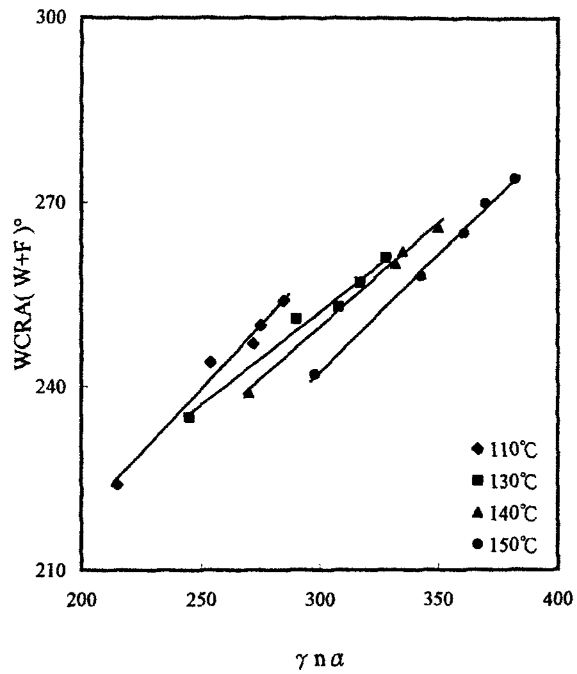

Figure 5 The relationship between the WCRA and the $\gamma n \alpha$ of DMEU treated fabrics at different curing conditions.

between DCRA (Dry Crease Recovery Angle) and $\gamma\sqrt{n}$. The DCRA obtained in the present study was plotted against $\gamma\sqrt{n}$ for various curing tem-

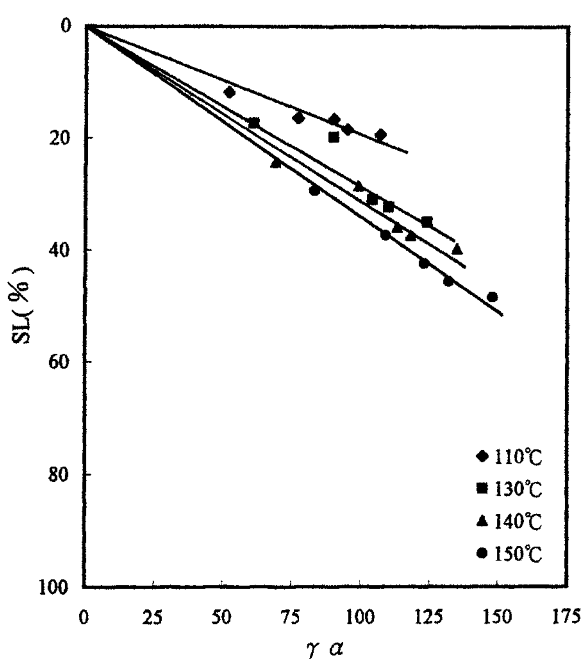

Figure 6 The relationship between the SL and the $\gamma\alpha$ of DMEU treated fabrics at different curing conditions.

peratures as shown in Figure 3. The results show that the DCRA of the treated fabrics is linear to $\gamma\sqrt{n}$ but with different slopes. This result suggests that there might be other factors affecting physical properties of the treated fabrics besides the crosslink length and crosslink number. In the present study we include crosslink integrity as a factor. Figure 4 shows the plot of DCRA against $\gamma\sqrt{n}\alpha$ in which linear relations are obtained. Moreover, each line shares a similar slope except for a small $\gamma\sqrt{n}\alpha$ value, which corresponds to a source mole ratio of 1 : 1–1 : 1.3. In addition, the reaction between the finishing agent and fabrics is less active, and the inconsistant slope is also due to different types of crosslink binding between the synthesized finishing agent and the fabrics when the source mole ratio is varied. Under such conditions weak bonding dominates. Therefore, α shows different effects in both conditions. Figure 5 shows a linear relation between WCRA (Wet Crease Recovery Angle) and $\gamma n\alpha$ with a similar slope. Figure 6 also shows a linear relation between SL (Strength Lost) and $\alpha\gamma$. Both results are consistent with the previous report by Yen.[5]

CONCLUSION

The following conclusions were obtained from the studies of cotton fabrics treated with a DMEU/monomethylol EU(MMEU) prepolymer mixture in a wrinkle-resistant finish:

1. Crosslink number, cellulose ether binding, and unreacted end radical content increase with the PF mole ratio in the source mixture.
2. Crosslink length, unreacted end radical content, and methyl ether links decrease with increasing curing temperature.
3. Linear relations of DCRA, WCRA, and SL against $\gamma\sqrt{n}\alpha$, $\sqrt{n}\alpha$ and $\gamma\alpha$ are obtained for finishing agent synthesized from a high PF mole ratio in the source mixture.
4. Crosslink integrity shows varied effects on the treated fabrics.

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