

Physical Properties of Cotton Fabrics and Free CH₂O Content in Crease-Resistant Finish with DMEU/MMEU Prepolymer Mixture

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Received 11 January 1999; accepted 7 June 1999

ABSTRACT: Combinations of ethylene urea and paraformaldehyde with different mol ratios are used as source materials to synthesize a DMEU/MMEU resin prepolymer in various mixing ratios. The DMEU/MMEU resin prepolymer is then applied to the crease-resistant finish of cotton fabrics. The results show that the dry and wet crease-recovery angles and nitrogen and free formaldehyde contents increase with increasing curing time, curing temperature, and mol ratio of paraformaldehyde, while the tensile strength retention decreases. Optimized relations between both physical and chemical properties can be obtained by mixing the source materials in a 1 : 1.5–1 : 1.7 ratio, drying at 80°C for 5 min, and curing at 150°C for 3 min. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 390–395, 2000

Key words: prepolymer; cotton fabrics; curing; molratio

INTRODUCTION

Cotton fabrics which are often loosely crystallized contain a large amount of hydrophobic —OH groups. Therefore, when cotton fabrics absorb moisture, the bonding strength between the cellulose molecules decreases dramatically. This results in the translation of the cellulose molecule inelastic deformation, and, hence, the cotton fabrics retrack and wrinkle. To reduce wrinkling due to wearing or washing, an appropriate cross-linked agent is applied to the fabrics to crosslink cellulose molecules and prevent them from translation. The elasticity of the fabrics is thus enhanced and crease resistance is guaranteed. Crease-resistant finishes for cotton fabrics was first developed over 60 years ago. The first application was the patent announced by an Italian company, Tootal Broadhurs & Lee, in 1926.¹ A prepolymer of urea and formaldehyde was used as the crease-resistant finishing agent. Since then,

development of the finishing agent has been the key research. In general, a crease-resistant finishing agent consists mainly of *N*-methylol (—N—CH₂OH) compounds, such as compounds of dimethylol and urea derivatives like ethylene urea, propylene urea, and bihydroxyl ethylene urea or as compounds of methylol and tripolyamide.² But *N*-methylol compounds are preferred in the finishing process.

Reactions of the agent in the finishing process are quite complicated. They can be divided into three types: crosslinked reactions between the finishing agent molecules and the cellulose molecules, polycondensation among the finishing agent molecules, and various side reactions, such as the release of formaldehyde.^{3,4} Nevertheless, formaldehyde is poisonous and can produce a stinky smell even with trivial concentration (1–2 ppm). Since it is harmful to factory operators and consumers, much attention has been drawn to formaldehyde, making it the most analyzed chemical among all poisonous materials. Various regulations and standards for controlling the release of formaldehyde from textiles are set by govern-

ments all over the world. Meanwhile, methods for eliminating free formaldehyde from treated fabrics have also been developed. Recent research has been made on multicarboxylic acid and on finishing agents with less or no formaldehyde,^{5–12} but in view of the results and price, none of them can replace the widely used amide formaldehyde finishing agent.

Part of the free formaldehyde released from treated fabrics comes from the free formaldehyde in the resin prepolymer solution, which depends on the equilibrium state of the finishing agent and the formaldehyde content in the synthesis of the finishing agent. In other words, reduction of the formaldehyde content in the synthesis can decrease the free formaldehyde content in the prepolymer solution.¹³

The experiments were conducted in several stages: First, various prepolymer mixtures (with different ratios of DMEU and MMEU) were synthesized with different ratios of ethylene urea and paraformaldehyde. After the nitrogen and total formaldehyde contents were identified, a crease-resistant finish process was applied to cotton fabrics under various conditions. Physical properties of the treated fabrics under various finishing conditions as well as their relations with the free formaldehyde content were analyzed.

EXPERIMENTAL

Materials

The cotton fabric, 40s × 40s ends (100) and picks (80), was desized, scoured, and bleached. Sodium hydroxide, sulfuric acid, a selenium mixture catalyst, boric acid, pyridine, magnesium chloride, ethylene urea, paraformaldehyde, methanol, and other chemicals were of reagent grade.

Methods

Analysis and Synthesis of DMEU Resin Prepolymer

DMEU was synthesized by the Hoover method. DMEU/MMEU with various mixing ratios can be obtained by varying the mol ratio of ethylene urea and paraformaldehyde.^{14,15} Nitrogen and total formaldehyde contents in the resin finishing agent synthesized thereafter were measured by the Kjeldahl method and the chromotropic acid method,¹⁶ respectively, while the free formaldehyde content was measured by the acid–sodium sulfite method.¹⁷

Process of Crease-Resistant Finish

The cotton fabrics were first impregnated in a solution containing the finishing agent (8% prepolymer) and magnesium chloride (10% of the weight of prepolymer) for 10 min at room temperature followed by being squeezed to a wet pick up of 80%, pinned on a frame without tension, dried at 80°C for 5 min, and cured at different temperatures (110–150°C) or for different times (30–180 s). After curing, the samples were thoroughly washed in a solution containing 2 g/L soap and dried at ambient condition.

Analysis

The tensile strength of the warp yarns was measured using an Instron tester according to ASTM standard D 1682-64. The dry and wet crease-recovery angles (DCRA and WCRA) were determined according to ASTM standard D 1295-67. The nitrogen content and total and free formaldehyde contents were measured.

RESULTS AND DISCUSSION

Analysis and Identification of Synthesized Finishing Agent

Figure 1 shows the IR spectra of various DMEU/MMEU resin prepolymer mixtures synthesized with different mol ratios of ethylene urea and paraformaldehyde by the Hoover method. Figure 1(a) shows the finishing agent (MMEU) synthesized with an equal mol ratio. Figure 1(c) shows the finishing agent synthesized with a 1 : 2 (ethylene urea : paraformaldehyde) mol ratio. The difference between Figure 1(a) and (c) is the absorption at 3364 cm⁻¹, which is not observed in the latter. This indicates the presence of the NH radical. Figure 1(b) shows the finishing agent with a 1 : 1.5 (ethylene urea : paraformaldehyde) mol ratio, which shows less absorption of NH, indicating less MMEU content. Further identification of the synthesized finishing agent was performed by analysis of the nitrogen and total and free formaldehyde contents, which are listed in Table I.

Table I shows that the nitrogen content increases with increasing paraformaldehyde while total formaldehyde content decreases. In addition, the ratio between nitrogen and total formaldehyde increases, as predicted in the calculations.

Influence of Process Conditions on the Physical Properties of the Treated Fabrics

Table II shows that the DCRA and WCRA of the treated fabrics increase with the mol ratio of

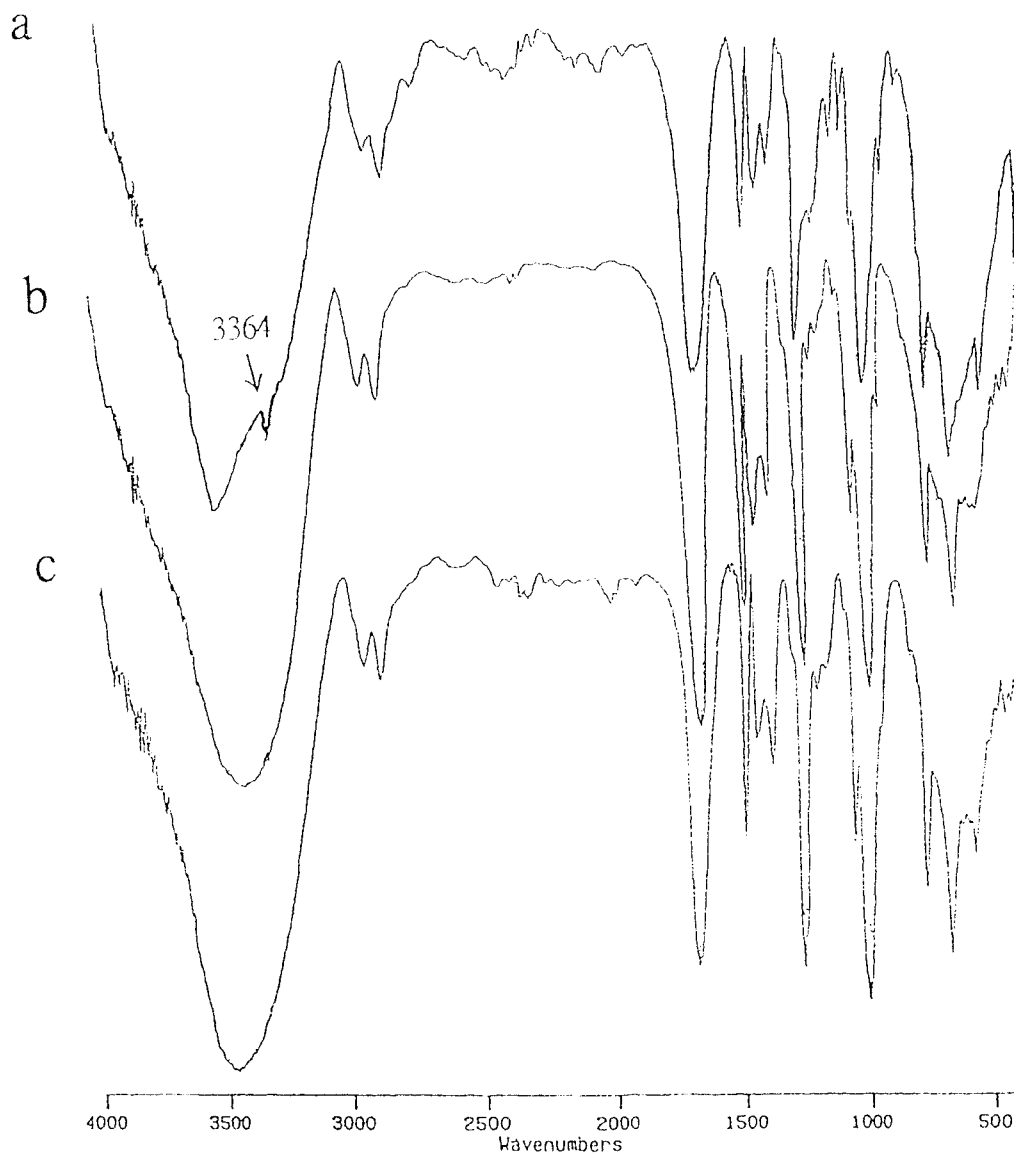


Figure 1 IR spectrum of resin finishing agent synthesized with different mol ratios of the source mixture: (a) finishing agent synthesized with 1 : 1 (EU : PF); (b) finishing agent synthesized with 1 : 1.5 (EU : PF); (c) finishing agent synthesized with 1 : 2 (EU : PF).

paraformaldehyde in the source, as well as with the curing time. This is because a high paraformaldehyde dose in the synthesis leads to a high percentage of DMEU in the finishing agent and, hence, promotes the reaction between fabrics and the finishing agent, because of the two $>N-CH_2OH$ groups in DMEU. On the other hand, tensile strength retention in the treated fabrics shows different trends. Since more crosslinks are formed when the reaction between the fabrics and the finishing agent is more active, the treated fabrics become hardened and straightened, resulting in more concentrated tensile strength. Moreover, a long curing time en-

hances the hydrolysis of fabrics in acid catalysts. Table II also shows that the DCRA and WCRA of the treated fabrics increase with the mol ratio of paraformaldehyde in the source at various curing temperatures. Similarly, tensile strength retention of the treated fabrics is reduced with increasing curing temperature and the mol ratio of paraformaldehyde in the source.

Influence of Finishing Conditions on Nitrogen and Various Formaldehyde Contents in the Treated Fabrics

Table II summarizes the nitrogen and free formaldehyde contents in the treated fabrics under

Table I Nitrogen Content and Total Formaldehyde Content of Various Resin Agents Which Were Synthesized with Different Mol Ratios of Ethylene Urea and Paraformaldehyde

Content ($\mu\text{mol}/\text{mg}$)	EU : PF ^a					
	1 : 1.0	1 : 1.3	1 : 1.5	1 : 1.7	1 : 1.9	1 : 2.0
<i>N</i>	16.96	15.60	14.83	14.15	13.87	13.68
Total CH ₂ O	8.25	9.09	9.92	11.28	12.38	13.45
Free CH ₂ O	0.02	0.05	0.08	0.13	0.16	0.21
CH ₂ O/ <i>N</i> ^b	0.49/1	0.58/1	0.67/1	0.80/1	0.89/1	0.98/1

^a Mol ratio of ethylene urea and paraformaldehyde.^b Ratio of total CH₂O and *N* content.

several conditions. It shows that the nitrogen and free formaldehyde contents in the treated fabrics increase with the mol ratio of paraformaldehyde. This is because the DMEU content in the synthesized finishing agent increases with paraformaldehyde. Since DMEU has two >NCH₂OH groups, it reacts more actively than does MMEU and results in a higher nitrogen content in the treated fabrics. Similarly, high paraformaldehyde in the synthesis also results in high formaldehyde content in the prepolymer solution. Therefore, reducing the amount of formaldehyde involved in the reaction can decrease the free formaldehyde con-

tent in the prepolymer solution. In addition, because the decomposition of NCH₂OH in the finishing agent leads to the formation of free formaldehyde, the higher the DMEU percentage in the finishing agent, the more paraformaldehyde in the source and the easier for free formaldehyde to be released in the finishing process. At high curing temperatures, the reaction between the fabrics and the finishing agent is more active, so the nitrogen content increases. Similarly, NCH₂OH in the finishing agent decomposes much easier at high temperatures, so the free formaldehyde content also increases. The total formaldehyde con-

Table II Physical Properties, Nitrogen Content, and CH₂O Content of the Treated Cotton Fabrics^a

EU : PF ^b	Curing Temperature (°C)	DCRA (W + F) ^o	WCRA (W + F) ^o	TSR (%)	<i>N</i> ($\mu\text{mol}/\text{g}$)	Total CH ₂ O ($\mu\text{mol}/\text{g}$)	Free CH ₂ O ($\mu\text{mol}/\text{g}$)
1 : 1.0	110	231	224	88.2	522	354	6
	130	244	235	82.7	554	380	12
	140	248	239	74.5	587	408	16
	150	253	242	70.7	622	437	22
1 : 1.3	110	254	244	83.6	628	428	25
	130	269	251	80.2	652	446	32
	140	280	257	71.6	696	485	42
	150	284	260	62.8	714	506	51
1 : 1.5	110	257	247	83.4	681	476	43
	130	271	253	69.2	702	498	52
	140	285	260	64.2	736	516	57
	150	293	265	57.7	753	524	63
1 : 1.7	110	259	250	81.6	694	490	50
	130	276	257	67.8	717	504	58
	140	289	262	62.8	742	518	68
	150	300	270	54.5	769	531	78
1 : 2.0	110	263	254	80.7	715	537	75
	130	281	261	65.2	742	564	82
	140	294	266	61.4	771	583	102
	150	308	274	51.7	806	594	110

^aResin concentration: 8%; MgCl₂: 0.8%; drying: 80°C × 5 min; curing time: 3 min.^b Mol ratio of ethylene urea and paraformaldehyde.

tent showing the same trend as that of the nitrogen as seen in Table II is due to the same reason as described above.

Influence of Finishing Conditions on the Relations Between Free Formaldehyde Content and Physical Properties in the Treated Fabrics

Figures 2 and 3 show the relations between the DCRA, WCRA, and free formaldehyde content at different curing temperatures. Both DCRA and WCRA increase with the free formaldehyde content when it exceeds $75 \mu\text{mol/g}$ in the treated fabrics. Since the DCRA and WCRA in some treated fabrics can reach 300° and 270° , respectively, the free formaldehyde content also increases dramatically. Therefore, an optimized relation between the free formaldehyde content and the crease-resistant angle can be obtained by mixing ethylene urea and paraformaldehyde in a 1 : 1.5–1 : 1.7 mol ratio and curing at 150°C for 3 min. Figure 4 shows the relations between the free formaldehyde content in the treated fabrics and the tensile strength retention. The free formaldehyde content for curing at 110°C is less except for a source mixing ratio 1 : 2.0. The tensile strength retention is also the highest under this condition. It reveals that the reaction between the

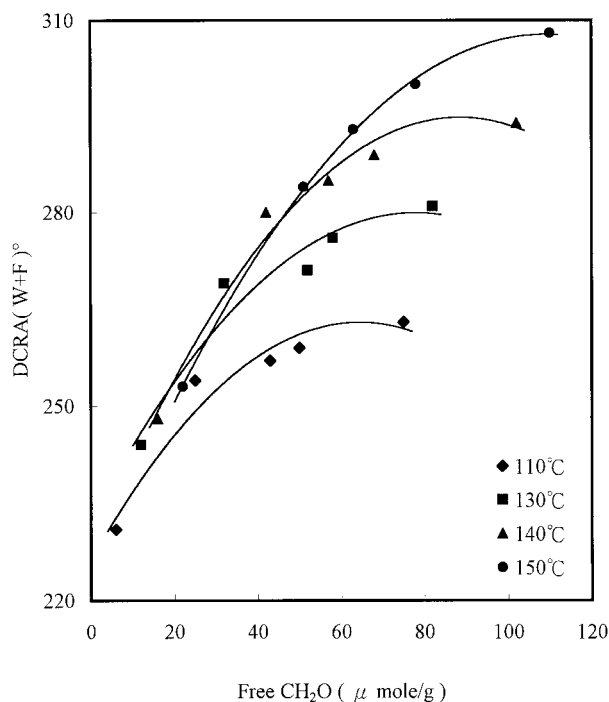


Figure 2 Relation between free CH_2O and DCRA of treated fabrics at different curing temperatures.

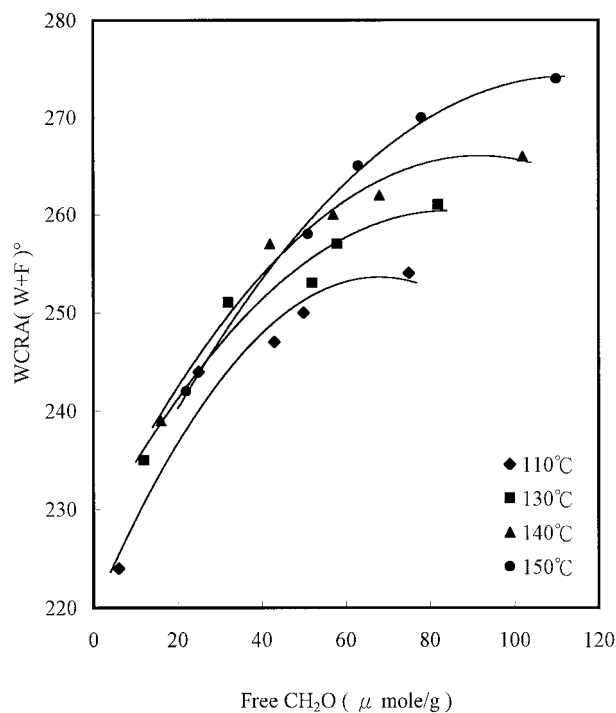


Figure 3 Relation between free CH_2O and WCRA of treated fabrics at different curing temperatures.

fabrics and the finishing agent at 110°C is less active. Even for a source mixing ratio as high as 1 : 2.0, the free formaldehyde content still reaches $83 \mu\text{mol/g}$ for curing at 110°C , while the DCRA and WCRA can only reach 263° and 254° , respectively. This result suggests that curing at lower temperature might release more free formaldehyde, even though fabrics are less reactive and the DCRA/WCRA is limited. This is because a high in-reacted formaldehyde content and more $>\text{NCH}_2\text{OH}$ groups in DMEU will release more free formaldehyde. As shown in Figure 4, tensile strength retention in the treated fabrics declines dramatically at higher curing temperature. This is because, when the fabrics and agent react more thoroughly at higher temperature, more crosslinks are formed, resulting in a highly concentrated tensile strength. Figure 4 also shows that tensile strength retention in the treated fabrics decreases slowly with increasing free formaldehyde content when it exceeds $75 \mu\text{mol/g}$ in the treated fabrics. Therefore, optimized relations between tensile strength retention and free formaldehyde content can be obtained by mixing the source materials in a 1 : 1.5–1 : 1.7 mol ratio and curing at 150°C for 3 min.

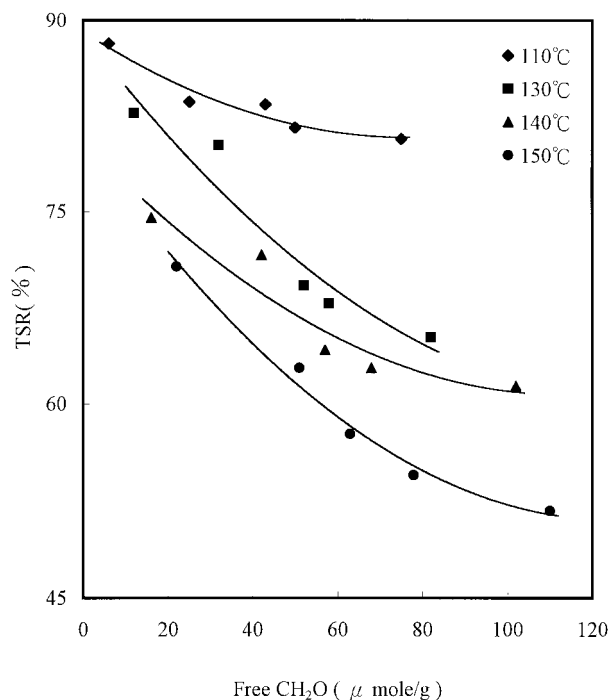


Figure 4 Relationship between free CH₂O and TSR of treated fabrics at different curing temperatures.

CONCLUSIONS

The synthesis of a DMEU/MMEU prepolymer mixture with various mixing ratios was studied by varying the mol ratio of ethylene urea and paraformaldehyde. The prepolymer mixture was applied to cotton fabrics under various conditions for a crease-resistant finish. The following results were obtained:

1. DCRA, WCRA, and the content of nitrogen, total formaldehyde, and free formaldehyde increase with increasing curing time, curing temperature, and the mol ratio of paraformaldehyde, while tensile strength retention decreases.
2. Curing conditions have less influence on the relations among the DCRA, WCRA, and the tensile strength retention with a high paraformaldehyde mol ratio.

3. Optimized relations between physical properties as well as relations between physical properties and free formaldehyde content in the treated fabrics were obtained by the following process: synthesizing a resin finishing agent in a combination of ethylene urea and paraformaldehyde with a mol ratio of 1 : 1.5–1 : 1.7, applying the finishing agent to the cotton fabrics for crease-resistant treatment, drying at 80°C for 5 min, and curing at 150°C for 3 min.

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