

# Kinetic Studies of Crease-Resistant Finishing Process for Cotton Fabrics with DMEU/MMEU Prepolymer Mixture

CHUNG-YANG SHIH, KUO-SHIEN HUANG

Department of Applied Fiber Style, Kun Shan University of Technology, Yung Kang, Tainan, Taiwan 71016, Republic of China

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**ABSTRACT:** The kinetics of the crease-resistant finishing process for cotton fabrics with DMEU/MMEU prepolymer mixture are studied. The DMEU/MMEU prepolymer resin is made from ethylene urea (EU) and paraformaldehyde (PF) with different mole ratios. The results show that the nitrogen content in the treated fabrics and the reaction rate constant increases with curing temperature and PF mole ratio. The treated fabrics with more PF in the source material have smaller  $E_a$ ,  $\Delta H^*$ , and  $\Delta S^*$ . The  $\Delta G^*$  was independent of the mole ratio in the source material, but it increases with curing temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 509–513, 2002

**Key words:** kinetics; crosslinking; curing; crease-resistant finishing

## INTRODUCTION

Conventionally, crease-resistant finish was obtained by pad-dry-cure method with *N*-methylol compounds, urea derivatives such as ethylene urea and bihydroxyl ethylene urea, or with various melamine derivatives.<sup>1</sup> During these processes, a large amount of free formaldehyde is released. Until recently crease-resistant finish for cotton fabrics with non-formaldehyde agents have been reported.<sup>2–7</sup> Our previous results showed that crease-resistant finishing process with DMEU/MMEU prepolymer mixture for cotton fabrics can help to reach equilibrium of released free formaldehyde and crease resistance.<sup>8</sup>

Kinetic studies of crease-resistant finishing process for cotton fabrics have been reported.<sup>9–17</sup> However, studies of crease-resistant finishing process with DMEU/MMEU resin mixture remain to be undertaken. Therefore, in this work, reaction kinetic parameters in the crease-resis-

tant finishing process with various resin mixtures are calculated and analyzed.

## EXPERIMENTAL

### Materials

The cotton fabric, 40s by 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, paraformaldehyde, and methanol used were of reagent grade.

### Synthesis of DMEU/MMEU Prepolymers

$x$  moles of ethylene urea were added to 250 mL of methanol and the mix was stirred vigorously and heated to 40°C to assure a complete dissolution. Meanwhile,  $y$  moles of paraformaldehyde, plus a suitable amount of alkali, was dissolved in another 250 mL of methanol likewise, resulting in a transparent solution. Then, at 50°C, the paraformaldehyde solution was gradually added to the ethylene urea solution. After the addition was complete, the mix was allowed to react at 50°C for

Correspondence to: C.-Y. Shih (scy-f@mail.ksut.edu.tw).

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**Table I** Nitrogen Content of Various Treated Cotton Fabrics with Different Prepolymer Resins<sup>a</sup>

Curing Temp. (°C)	Curing Time (min)	EU:PF		
		1:1	1:1.7	1:2
80	2	0.135	0.204	0.242
	3	0.186	0.286	0.310
	4	0.242	0.381	0.406
	5	0.271	0.434	0.452
	6	0.312	0.476	0.512
100	8	0.340	0.561	0.604
	2	0.172	0.232	0.296
	3	0.254	0.351	0.381
	4	0.311	0.447	0.470
	5	0.360	0.521	0.550
120	6	0.406	0.592	0.632
	8	0.432	0.680	0.720
	2	0.214	0.274	0.332
	3	0.306	0.402	0.436
	4	0.384	0.496	0.530
140	5	0.442	0.580	0.632
	6	0.507	0.628	0.706
	8	0.554	0.724	0.810
	2	0.254	0.314	0.372
	3	0.362	0.472	0.501
	4	0.453	0.534	0.612
	5	0.512	0.662	0.712
	6	0.572	0.726	0.798
	8	0.642	0.852	0.902

<sup>a</sup> Resins are made from EU and PF with different mole ratios.

1 additional h. The solution was filtered and the filtrate was refrigerated to cool down and form crystals. The crystals were collected and washed with cold methanol and filtered. Finally, the product was dried in vacuum. The ratios of  $x$  versus  $y$  used were 1:1, 1:1.7, and 1:2.

### Methods

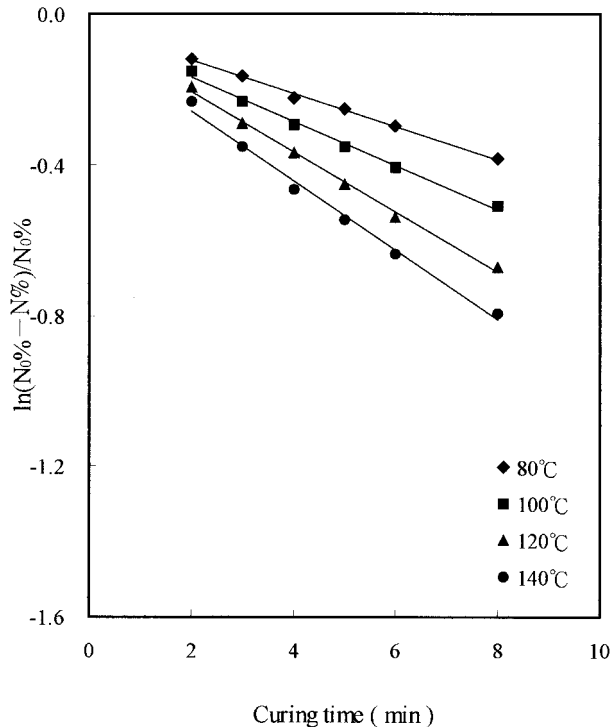
The cotton fabrics were first impregnated in a solution containing finish agent (8% prepolymer) and magnesium chloride (10% of the weight of prepolymer) for 10 min at room temperature, followed by squeezing to a wet pick up of 80%. Without predrying, the padded fabrics were heated for different intervals of time at a temperature ranging from 80 to 140°C, and then the fabric was washed with hot tap water for 15 min, and dried in an oven. The dried fabrics were weighed and tested. The nitrogen content of the fabrics was

determined by the Kjeldahl method. As for the kinetic studies, previously reported procedures were employed.<sup>18,19</sup>

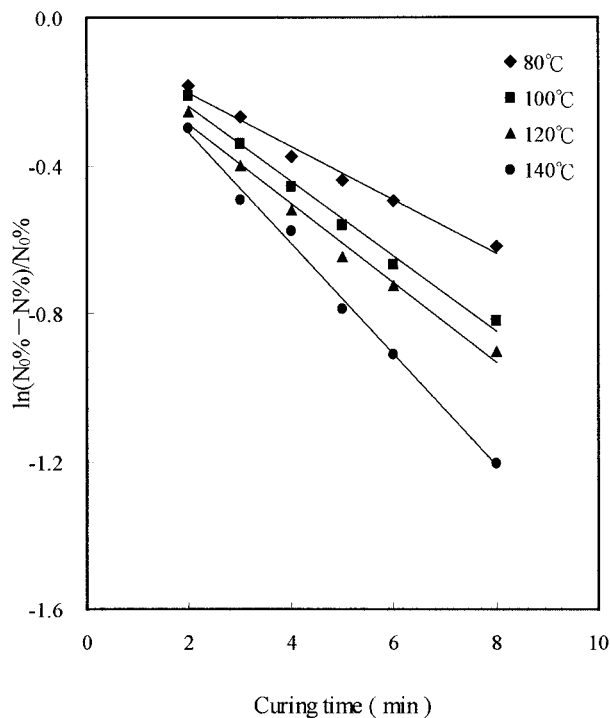
## RESULTS AND DISCUSSION

### Specific Reaction Rate Constants

The nitrogen content of the treated fabrics with different prepolymer resins under various curing temperatures and curing times are shown in Table I. When the finishing agent ( $\text{CH}_2\text{O}:\text{N} = 0.49:1$ ) with 1:1 EU/PF mole ratio was applied in the process, the nitrogen content in the treated fabrics increases with curing temperature and curing time (Table I). This is because the reaction between the finishing agent and the fabrics is more active at a higher temperature or with longer curing time. Finishing agents ( $\text{CH}_2\text{O}:\text{N} = 0.80:1$  and  $\text{CH}_2\text{O}:\text{N} = 0.98:1$ ) with different source mole ratio were applied during the crease-resistant finishing process. In comparison with Table I, the nitrogen content of the treated fabrics increases with increasing paraformaldehyde dos-



**Figure 1** The graph of  $\ln(N_0\% - N\%)/N_0\%$  versus reaction time (min) for fabric treated with prepolymer at four temperatures. The mole ratio for synthesis is 1:1.0 of EU:PF.



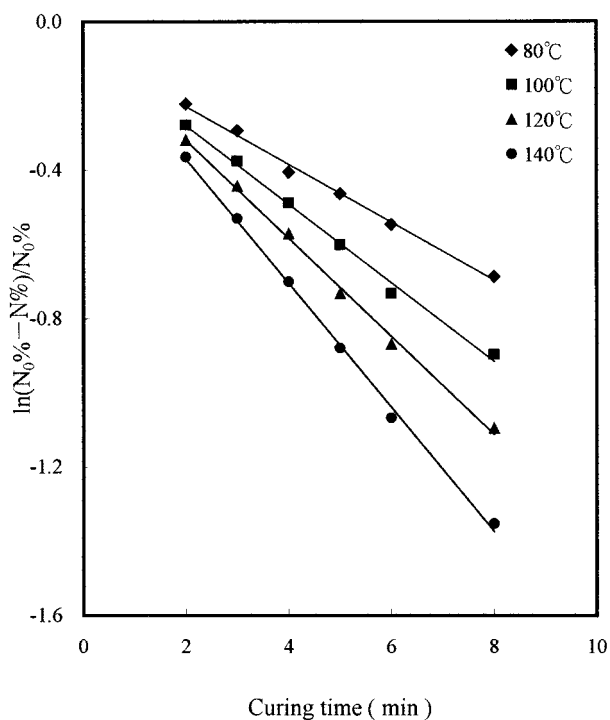
**Figure 2** The graph of  $\ln(N_0\% - N\%)/N_0\%$  versus reaction time (min) for fabric treated with prepolymer at four temperatures. The mole ratio for synthesis is 1:1.7 of EU:PF.

age in the finishing agent. Because the finishing agent with high paraformaldehyde dosage contains more DMEU, it reacts more easily with cellulose, from the presence of two reacting radicals. However, there is not much difference between the 1:1.0 and the 1:1.7 mole ratios of EU and PF.

Plots of  $\ln(1 - N\%/N_0\%)$  against curing time are shown in Figures 1, 2, and 3 for various treated fabrics, respectively. The quantity  $N_0\%$  is the nitrogen content determined from the treated fabrics by the pad-dry-cure process (i.e., 80% wet pickup, predried at 80°C for 5 min, and dried at 160°C for 3 min; the samples are thought to be fully cured at this point), and  $N\%$  is the percentage of bound nitrogen after a measured time. All data showed a linear dependence on the curing time, which suggests that the reaction was of pseudo-first-order. The specific reaction rate constant ( $k$ ) was obtained by the least-square curve fitting on the basis of a first-order reaction and is tabulated in Table II. The rate constant increases with curing temperature and PF mole ratio in the source material. The reasons are as described above.

### Activation Parameters

Figure 4 shows the Arrhenius plot of reaction rate constants with respect to the curing temperature. The activation parameters derived by Ziifle and Moore method for various fabrics are shown in Table II. According to our previous article,<sup>20</sup> among the three resin processing agents synthesized in various EU/PF mole ratios, their resulting  $\text{CH}_2\text{O}/\text{N}$  content proportion becomes larger along with an increasing molality of PF, that is, less N content. When the molality of PF gets bigger, the resulting resin mixture would contain more DMEU as the latter possesses two  $>\text{N}-\text{CH}_2\text{OH}$  groups; thus the relative N content becomes less, but with a higher total amount of  $\text{CH}_2\text{O}$ . However, Table II shows that the processed cloth showed a higher nitrogen content along with an increasing PF, which illustrates that the resin synthesized from a higher PF molality would easily form the complete ether linkage (i.e.,  $\text{cell}-\text{O}-\text{CH}_2-\text{N}<$ ). This was also reported in an earlier article.<sup>21</sup> The activation energy  $E_a$  decreases with increasing paraformaldehyde dosage in the source, because more DMEU in the finishing agent leads to more active



**Figure 3** The graph of  $\ln(N_0\% - N\%)/N_0\%$  versus reaction time (min) for fabric treated with prepolymer at four temperatures. The mole ratio for synthesis is 1:2.0 of EU:PF.

**Table II** Rate Constants and Activation Parameters of Various Treated Cotton Fabrics

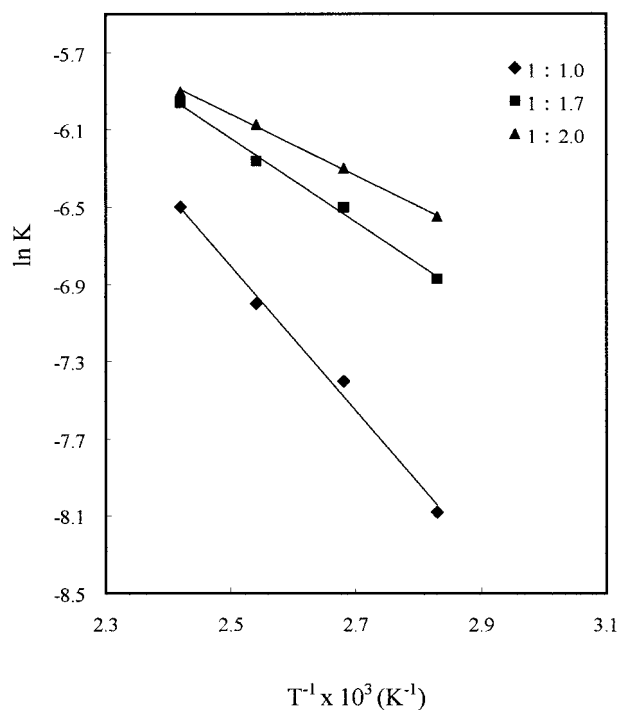
EU:PF <sup>a</sup>	Curing Temp. (°C)	Nitrogen Content <sup>b</sup> (%)	Rate Constant $k \times 10^{-3}$ (sec <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal/mole)	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (cal/°Kmole)	$E_a$ (kcal/mole)
1:1.0	80	0.340	0.323	26.405	6.713	-55.785	7.415
	100	0.432	0.635	27.453	6.674	-55.709	
	120	0.554	0.938	28.659	6.635	-56.405	
	140	0.642	1.502	29.782	6.594	-56.145	
1:1.7	80	0.561	1.037	25.608	3.641	-62.229	4.342
	100	0.680	1.546	26.797	3.601	-62.189	
	120	0.724	1.931	28.097	3.561	-62.432	
	140	0.852	2.533	29.354	3.522	-62.548	
1:2.0	80	0.604	1.435	25.377	2.921	-63.616	3.622
	100	0.720	1.807	26.681	2.881	-63.808	
	120	0.810	2.345	27.947	2.840	-63.881	
	140	0.902	2.736	29.290	2.801	-64.139	

<sup>a</sup> Mole ratio of ethylene urea: paraformaldehyde.

<sup>b</sup> The curing time was 8 min.

crosslink reaction. Therefore,  $\Delta S^*$  for the treated fabrics is negative. However, free energy  $\Delta G^*$  is positive and increases with curing temperature but shows no dependence on the PF mole ratio, that is,  $\Delta G^*$  is determined only by the curing temperature. Whereas, in the case of  $\Delta H^*$ , all the

values are positive, which means that the reaction is endothermic and there are complexes formed during the reaction. In addition,  $\Delta H^*$  decreases with increasing PF mole ratio in the source, which means that the high PF mole ratio favors crosslink reactions.



**Figure 4** Plots of  $\ln k$  based on nitrogen versus reciprocal of absolute temperature.

## CONCLUSIONS

Ethylene urea (EU) and paraformaldehyde (PF) with different mole ratios were used to synthesize DMEU/MMEU prepolymers with various combinations. The prepolymer mixtures were applied in the crease-resistant finishing process. The results show that the nitrogen content of the treated fabrics and the reaction rate constant increases with curing temperature and PF mole ratio. The treated fabrics with more PF in the source material have smaller  $E_a$ ,  $\Delta H^*$ , and  $\Delta S^*$ , wherein all the  $\Delta S^*$  values were negative. However, the  $\Delta G^*$  was independent of the mole ratio in the source material, but it increases with curing temperature.

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