

Influence of Pregrafting Cotton Fabrics on Kinetics of DMEU Finishing

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SYNOPSIS

Cotton fabrics were pregrafted with a mixture of *N*-methylolacrylamide and methacrylic acid at mixing molar ratio of 4/6. The influence of pregrafting on the kinetics of finishing with 1,3-dimethylolethylene urea was studied. The results shows that pregrafting can increase the rate constants. Values of E_a , ΔH^* , ΔS^* , and ΔG^* suggest that the pregrafting of cotton fabric not only affects the reaction action state, but also is beneficial for the reaction between cellulose and the finishing agent. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A number of articles have reported the modification of cotton fabrics by grafting with various monomers.¹⁻⁴ Some scholars have reported on the influence of pregrafting cotton fabrics with vinyl monomers on the physical properties of the resin-finished cotton fabrics.⁵⁻¹¹ Others¹²⁻¹⁵ reported that the grafting of cotton fabric with the mixture of two monomers under a certain molar ratio, which has a synergism effect and has a maximum graft yield. In addition, there are also many studies of the kinetics and activation parameters of the reaction between cellulose and the crosslinking agent under various conditions.¹⁶⁻²² However, studies of cotton pregrafted with mixed monomers are still very rare.

In this work, the influence of pregrafting on the activation parameters of resin finishing for cotton fabrics was investigated. The pregrafting of cotton fabrics was carried out using a mixture of *N*-methylolacrylamide (MAM) and methacrylic acid (MAA) at a mixing molar ratio of 4/6. The latter ratio proved to induce a higher crease recovery angle and mois-

ture regain in our earlier report.²³ The resin finishing was performed using 1,3-dimethylolethylene urea (DMEU) as per a reported method.²⁴

EXPERIMENTAL

The cotton fabric, 40s × 40s ends (100) and picks (80), was desized, scoured, and bleached before use. The sample of cotton fabric was first impregnated in freshly prepared aqueous ferrous ammonium sulfate for 15 min at 25°C. The sample was then squeezed, washed thoroughly with distilled water, and dried. An accurate weight of the Fe-containing sample was immersed in an aqueous solution containing MAM and MAA (mixing molar ratio 4/6) and H₂O₂ under various concentrations of the mixed monomer (1 or 4%). The reaction was then allowed to proceed while stirring at 75°C for 90 min. The grafted cotton fabrics were first impregnated in a solution containing 8% DMEU and 0.8% zinc nitrate for 10 min at room temperature followed by squeezing to a wet pickup of 90%. Without predrying, the padded fabrics were heated for different intervals of time at a temperature ranging from 80 to 140°C, then washed with hot tap water for 15 min, and dried in an oven. The dried fabrics were weighted and tested. The nitrogen content of the fabrics was de-

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terminated by the Kjeldahl method. The graft yield was determined by the gravimetric method.

RESULTS AND DISCUSSION

Specific Reaction Rate Constants

Figure 1 shows the variation in the nitrogen content of ungrafted cotton fabrics with reaction time at different temperatures when the fabrics were finished with DMEU under the catalytic influence of zinc nitrate. Shown in Figures 2 and 3 are the variations for the cotton fabrics pregrafted with 1 and 4% mixed monomer, respectively. Here, we can see the slightly concave shape of the relationship between nitrogen content and the initial curing time in all cases. This is because there was much water in the fabric and water could interfere with the reaction between the finishing agent and cellulose. Nevertheless, the nitrogen content will be much different if a high cure temperature or a long cure time is available. These three figures show that the nitrogen content not only was higher for pregrafted cotton fabrics than for those ungrafted, but also increased with the graft yield.

Plots of $\ln(1 - N\%/N_0\%)$ against curing time are shown in Figure 4–6 for ungrafted and grafted cottons, respectively. The quantity $N_0\%$ is the nitrogen content determined from the treated fabric by the pad-dry-cure process (i.e., 90% wet pickup, predry at 80°C for 5 min, and dry at 160°C for 3 min; the samples are thought to be fully cured at this point²³), and $N\%$ is the percentage of bound nitrogen after a measured time. All data showed a linear dependence on the curing time, which suggests

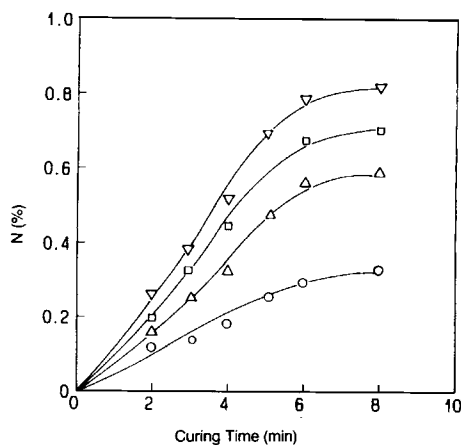


Figure 1 Changes in nitrogen content of ungrafted cotton fabric treated with 8% DMEU and 0.8% zinc nitrate as the catalyst vs. reaction time in minutes at four temperatures: (○) 80°C; (△) 100°C; (□) 120°C; (▽) 140°C.

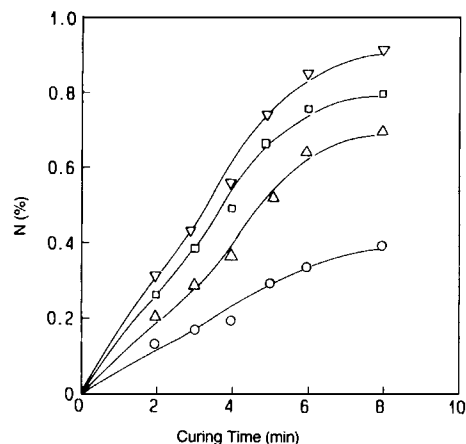


Figure 2 Changes in nitrogen content of grafted cotton fabric (2.5%) treated with 8% DMEU and 0.8% zinc nitrate as the catalyst vs. reaction time in minutes at four temperatures. The symbols are the same as in Figure 1.

that the reaction was of pseudo-first-order. The specific reaction rate constants (K) were obtained by least-square curve fitting on the basis of a first-order reaction and are tabulated in Table I. The data in Table I show that the rate constants for pregrafted cottons increased with the reaction temperature as well as the graft yield. For pregrafted fabrics, there are extra functional groups from the grafted polymer. These functional groups could react with the finishing agent; thus, the rate constants increased with the graft yield.

Activation Parameters

Figure 7 shows that the temperature dependence of the rate constant K was following the Arrhenius

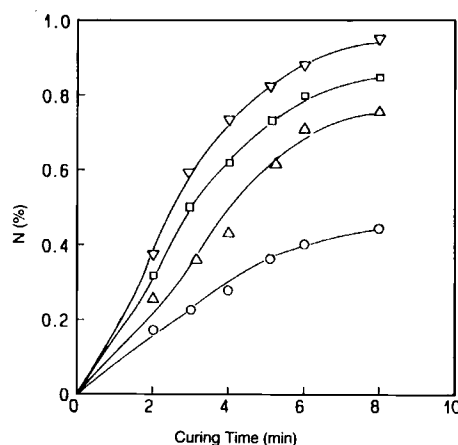


Figure 3 Changes in nitrogen content of grafted cotton fabric (10.3%) treated with 8% DMEU and 0.8% zinc nitrate as the catalyst vs. reaction time in minutes at four temperatures. The symbols are the same as in Figure 1.

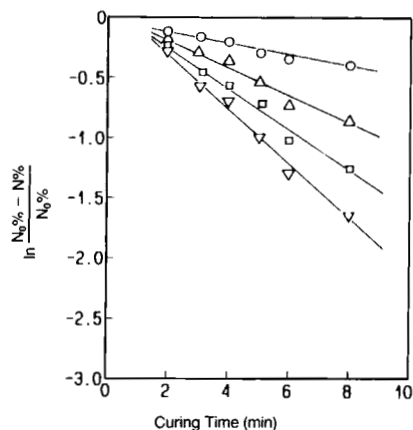


Figure 4 The graph of $\ln(N_0\% - N\%)/N_0\%$ vs. reaction time in minutes for ungrafted cotton fabric treated with 8% DMEU and 0.8% zinc nitrate as the catalyst at four temperatures. The symbols are the same as in Figure 1.

equation. The activation parameters for the various grafted cotton cellulose-DMEU reactions are listed in Table I, using the method of Ziifle et al.²⁴ and Moore.²⁵ It reveals not only that the activation energies for ungrafted fabrics were higher than those for grafted fabrics, but that they also decreased with increase of the graft yield. This phenomenon was attributed to the grafted polymer, which is beneficial to the reaction of the finishing agent and cellulose. On the other hand, the free energies of activation (ΔG^*) were all positive and increased with the curing time, while depending little on the graft yield. This suggests that the swelling effect of grafted cotton does affect the reaction state but does not affect the energy needed for the crosslinking reaction. This result is similar to Chen's report.²⁰ All the enthalpies

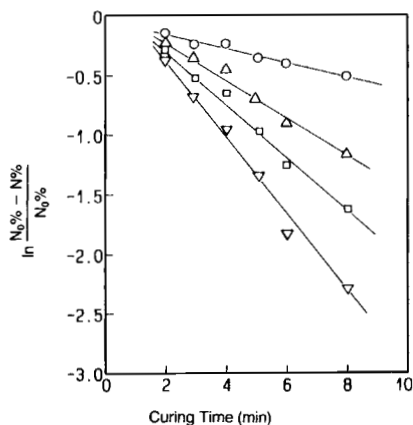


Figure 5 The graph of $\ln(N_0\% - N\%)/N_0\%$ vs. reaction time in minutes for ungrafted cotton fabric (2.5%) treated with 8% DMEU and 0.8% zinc nitrate as the catalyst at four temperatures. The symbols are the same as in Figure 1.

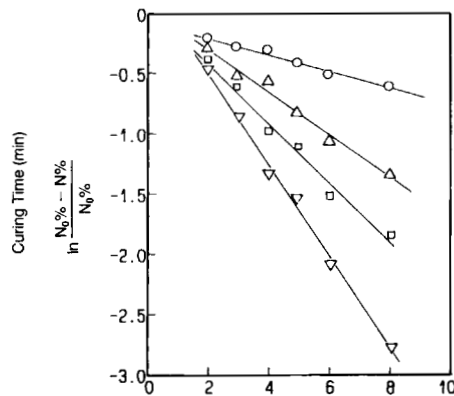


Figure 6 The graph of $\ln(N_0\% - N\%)/N_0\%$ vs. reaction time in minutes for ungrafted cotton fabric (10.3%) treated with 8% DMEU and 0.8% zinc nitrate as the catalyst at four temperatures. The symbols are the same as in Figure 1.

of activation (ΔH^*) are positive. This indicates that the formation of the transition-state complex was endothermic. The values of ΔH^* for ungrafted fabrics were higher than those for grafted fabrics. This suggests that the crosslinking reaction in the ungrafted fabrics was more difficult, since the ungrafted fabrics were less reactive than were the grafted fabrics. Entropies of activation (ΔS^*) were all negative and were more negative for higher graft yield. Thus, pregrafted fabrics were more prone to form crosslinking with the finishing agent.

CONCLUSION

The cotton fabric was pregrafted with different concentrations of MAA and MAM at a mixing ratio of 4/6. The pregrafted and ungrafted fabrics were fin-

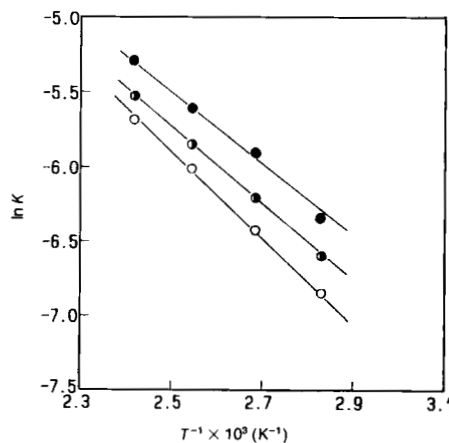


Figure 7 Plots of $\ln K$ based on nitrogen vs. reciprocal of absolute temperature: (○) 0%; (◐) 2.5%; (●) 10.3%.

Table I Rate Constants and Activation Parameters of Grafted and Ungrafted Cotton Fabrics

Graft Yield (%)	Curing Temp (°C)	Rate Constant $K \times 10^{-3} \text{ (s}^{-1}\text{)}$	ΔG^* (kcal/mol)	ΔH^* (kcal/mol)	ΔS^* (Cal/K mol)	E_a (kcal/mol)
0.0	80	1.025	25.614	4.940	-58.567	5.641
	100	1.701	26.769	4.900	-58.630	
	120	2.575	27.878	4.859	-58.571	
	140	3.297	29.209	4.821	-59.053	
2.5	80	1.428	25.378	4.568	-58.952	5.269
	100	2.158	26.485	4.529	-58.863	
	120	3.167	27.692	4.488	-59.043	
	140	4.253	28.914	4.447	-59.240	
10.3	80	1.907	25.154	4.072	-59.722	4.773
	100	2.792	26.360	4.033	-59.861	
	120	4.015	27.531	3.992	-59.896	
	140	5.125	28.772	3.951	-60.097	

ished with DMEU. From the kinetics and activation parameters of the finishing, it shows that both the nitrogen content and the rate constants for grafted cotton fabrics were higher than those for ungrafted cotton. Higher graft yield leads to higher N% and K, lower E_a and ΔH^* , and little change in ΔG^* . The independence of ΔG^* on the graft yield suggests that the swelling does not affect the energy needed for the crosslinking reaction. Entropies of activation (ΔS^*) were all negative, and the order was as follows: ungrafted > 2.5% graft yield > 10.3% graft yield. This suggests that the grafting of cotton fabric was beneficial to the reaction between cellulose and the finishing agent.

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