The Effects of Pregrafting Cotton Fabrics with MAA/MAM on the Dyeing Kinetics of Direct Dyes in a Finite Bath

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Received 14 May 1996; accepted 9 November 1996

ABSTRACT: The influence of pregrafting of cotton fabrics with mixed monomer on the dyeing kinetics of direct dyes was investigated. The results of this research show that the equilibrium absorption (a_e) and activation energy (ΔE^*) in the dyeing of grafted fabrics are smaller than those of ungrafted fabrics. The experimental results show that the value of the equilibrium absorption is smallest when the molar ratio of MAA/MAM (methacrylic acid/methylacryl amide) is 4/6. However, the rate constant (k') is larger for grafted fabrics than for ungrafted fabrics. No significant difference was observed between the structural diffusion resistance constant (n) of grafted and ungrafted fabrics. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1139–1142, 1997

Key words: dyeing; cotton; MAA/MAM; grafting; kinetics

INTRODUCTION

It is commonly known that the molecular structure of fibers will be relaxed and swelled after grafting,[1–7] and as a result, water molecules and chemicals will penetrate into the fibers more easily. This increased penetration will in turn enhance the processing characteristics of the fabrics. Our previous reports show that when cotton fabrics are grafted with methacrylic acid/methylacryl amide (MAA/MAM), the hydroscopic properties, the reaction to resin agents, and the dyeing properties of the cotton fabrics are all improved.[8,9] Results indicate that these enhanced characteristics due to grafting with MAA/MAM are maximized if the molar ratio of MAA/MAM is 4/6.

In order to ascertain how mixed-monomer grafting would influence the dyeing kinetics of direct dyes when cotton fabrics are treated with dyes in a finite bath, we use the following kinetic model[10–12] of the dyed content of a fabric to obtain various dyeing factors:

$$a = a_e[1 - \exp(-KC_0t)]^n = a_e[1 - \exp(-k't)]^n \quad (1)$$

where a is the dyed content of the fabric at the dyeing time t, a_e is the equilibrium absorption, K is the specific rate constant, k' is the reacting rate constant, C_0 is the concentration of dyes in the finite bath, and n is the structural diffusion resistance constant. Applying the value of each of the rate constants to the Arrhenius equation [eq. (2)],[10] the activation energy of dyeing (ΔE^*) can be obtained.

$$k' = k_0e^{-\Delta E^*/RT} \quad (2)$$

where T is the absolute dyeing temperature, and R is the gas constant.

EXPERIMENTAL

Materials

The cotton fabric, 40s × 40s ends (100) and picks (80), was desized, scoured, and bleached. MAM

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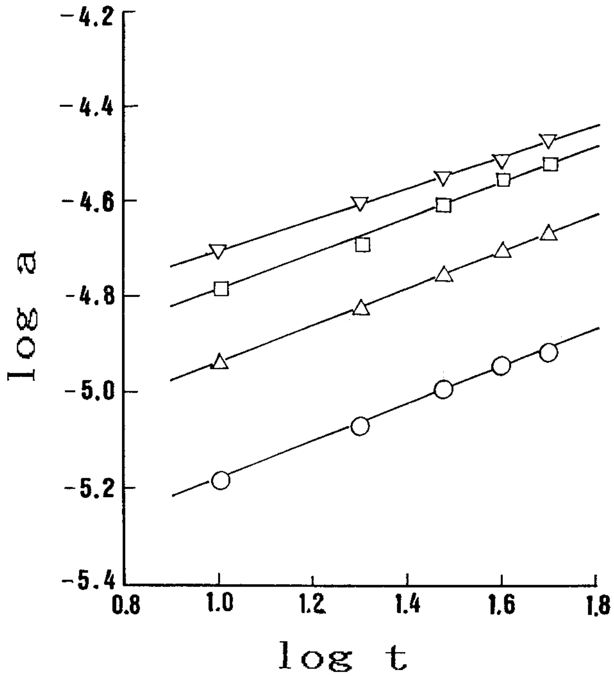

Figure 1 The plots of log a versus log t for grafted and ungrafted fabric. Mixture monomer concentration, 4%; dyeing temperature, 50°C. (○) ungrafted, grafted (MAA/MAM): (△) 10/0, (▽) 4/6, (□) 0/10.

and MAA were purified according to standard procedures.[13,14] Ferrous ammonium sulfate, hydrogen peroxide, sodium sulfate, and sodium carbonate were all extra-pure reagent grade (Hayashi Pure Chemical Industries Ltd., Japan). The dye used was Everdirect Supra Blue BRL (C. I. Blue 201; Everlight Chem. Ind. Corp, Taiwan).

Methods

Grafting Procedure

The grafting procedure was described in our previous work.[8]

Dyeing Procedure

Both the grafted and the ungrafted cotton fabrics were cut into pieces of 0.5 × 0.5 cm and dyed in a beaker with a dyeing solution containing 0.1 g/L of dye and 10 g/L of NaCl at a liquor ratio of 1 : 60. The dyeing temperature ranged from 50 to 80°C and was kept constant in a water bath.[7] The dyeing solution and cotton fabric were shaken slowly using a shaker. At a specific time interval, 0.2 mL of the supernatant dyeing solution was pipetted into 2.8 mL of distilled water in test tubes and the absorbance was measured with an ultraviolet spectrophotometer.

RESULTS AND DISCUSSION

Figures 1–4 show the relationship between the logarithm of the dye content absorbed (log a) and the logarithm of the dyeing time (log t) for various treated fabrics which were pregrafted and dyed at various temperatures. These figures show that the relationship between the logarithms of these two parameters is linear. Applying eq. (1) to the data shown in Figures 1–4, the value of the dyeing rate constant (k') and the structural diffusion resistance constant (n) can be obtained. From these figures, we can see that the value of the equilibrium absorption of each of the treated fabrics decreases with the increase in the dyeing temperature. In particular, the equilibrium absorbtion (a_e) of the grafted fabrics is lower than that of the ungrafted fabrics, with the value of a_e varying according to the concentration of the grafting monomer and the molar ratio. This is probably due to the relaxed and swelled molecular structure of the fiber after grafting. Obviously, this effect varied depending on the type and quan-

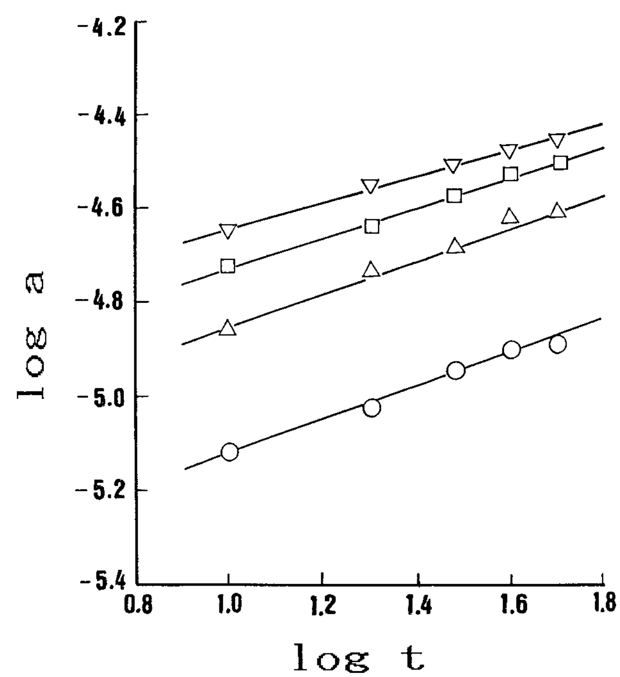

Figure 2 The plots of log a versus log t for grafted and ungrafted fabric. Mixture monomer concentration, 4%; dyeing temperature, 60°C. (○) ungrafted, grafted (MAA/MAM): (△) 10/0, (▽) 4/6, (□) 0/10.

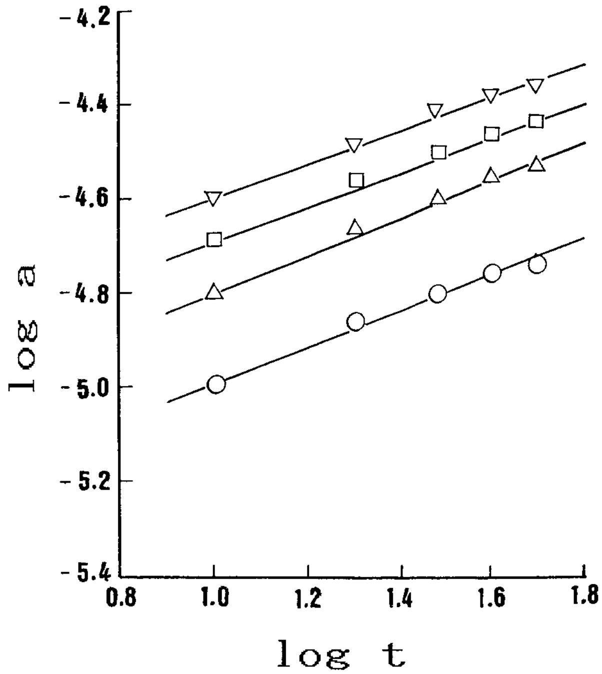

Figure 3 The plots of log a versus log t for grafted and ungrafted fabric. Mixture monomer concentration, 4%; dyeing temperature, 70°C. (○) ungrafted, grafted (MAA/MAM): (△) 10/0, (▽) 4/6, (□) 0/10.

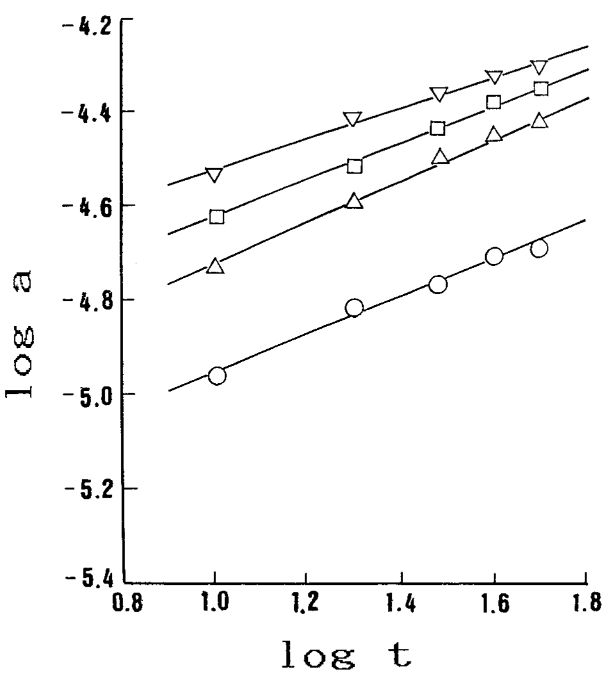

Figure 4 The plots of log a versus log t for grafted and ungrafted fabric. Mixture monomer concentration, 4%; dyeing temperature, 80°C. (○) ungrafted, grafted (MAA/MAM): (△) 10/0, (▽) 4/6, (□) 0/10.

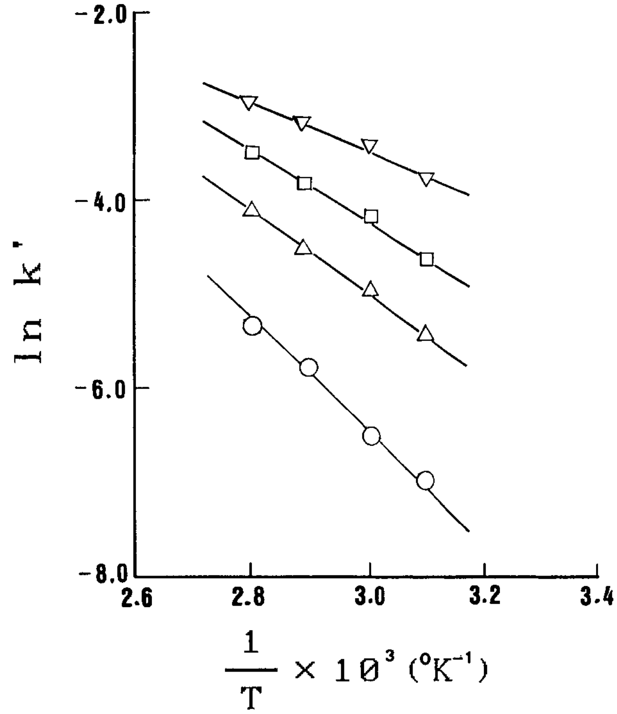

Figure 5 The plots of ln k' versus $1/T$ for various cotton fabrics. Mixture monomer concentration, 4%. (○) ungrafted, grafted (MAA/MAM): (△) 10/0, (▽) 4/6, (□) 0/10.

tity of the grafting polymer. For instance, when the ratio of MAA/MAM was 10/0, the carboxyl group of MAA and the hydroxyl group of cellulose may react into an ester group. The ester group formed will inhibit dyes from entering the grafting polymer. The absorption and diffusion of the dyes may also be hindered due to the steric effect. The values of the dyeing rate constant (k'), however, indicated that the k' of the ungrafted dyed fabrics was much smaller than that of the grafted ones. Since the structure of the fiber was relaxed and swelled after grafting, the movement of the molecular chain becomes easier. As a result, the T_g of the fiber is lowered and the absorption, penetration, and diffusion of dyes were thus improved. The k' became larger with the increase in the concentration of monomer and the dyeing temperature. The maximum value of k' was obtained when the ratio of MAA/MAM is 4/6. There was no significant change in the structural diffusion resistance constant (n), as indicated by the experimental data.

Figure 5 shows the Arrehenius plot of k' values for different types of treated fabrics. The slope of each line is shown in the figure, and each activation energy of dyeing was calculated according to

Table I Absorption Equilibrium, Rate Constant, Structural Diffusion Resistance Constant, and Activation Energy of Various Cotton Fabrics

Fabric	Monomer Conc. (%)	Molar[a] Ratio	Dyeing Temp. (°C)	$a_e \times 10^{-5}M$	$k' \times 10^{-3}$ (min^{-1})[b]	n	ΔE^* (kcal/mol)
Grafted fabric	1	4/6	50	8.406	2.564	0.394	9.786
			60	8.284	5.853	0.396	
			70	8.187	10.052	0.401	
			80	8.008	15.208	0.395	
		10/0	50	8.230	4.086	0.399	8.985
			60	8.172	6.673	0.403	
			70	7.964	9.709	0.409	
			80	7.831	16.788	0.397	
	4	4/6	50	8.403	19.255	0.412	4.621
			60	7.940	26.089	0.417	
			70	7.806	35.774	0.420	
			80	7.724	58.861	0.406	
		0/10	50	8.174	10.911	0.407	6.814
			60	8.086	14.589	0.410	
			70	7.846	22.126	0.414	
			80	7.765	30.875	0.402	
Ungrafted fabric			50	8.514	0.958	0.387	10.533
			60	8.472	1.435	0.389	
			70	8.265	3.181	0.390	
			80	8.117	4.563	0.387	

[a] Molar ratio of MAA/MAM.
[b] These data were obtained from a dyeing time interval of 15 min.

eq. (2). Table I shows that the ΔE^* of pregrafted dyed fabrics was smaller than that of ungrafted ones. Thus, MAA/MAM grafting is beneficial to the enhancement of the dyeing property of treated fabrics. The mechanism of MAA/MAM grafting is similar to that of resin agents.

CONCLUSIONS

These experiments were conducted by pregrafting cotton fabrics with MAA/MAM and applying dyes to the fabrics. The conclusions of this research are as follows. First, the value of the equilibrium absorption (a_e) and the dyeing activation energy (ΔE^*) of ungrafted treated fabrics are larger than those of grafted fabrics, and the dyeing rate constant (k') is larger for grafted fabrics than for ungrafted fabrics. Second, the changes in the structural diffusion resistance constant (n) are insignificant. Finally, except for the structural diffusion resistance constant, a_e, k', and ΔE^* are all related to the dyeing temperature, the concentration of mixed monomer, and the molar ratio of mixed monomer.

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