

Polymeric Multifunctional Carboxylic Acids as Crosslinking Agents for Cotton Cellulose: Poly(itaconic acid) and *In Situ* Polymerization of Itaconic Acid

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ABSTRACT: Multifunctional carboxylic acids have been used as nonformaldehyde durable press finishing agents for cotton. In previous research we found that maleic acid (MA) and itaconic acid (IA) polymerize *in situ* on cotton fabric at elevated temperatures when both potassium persulfate ($K_2S_2O_8$) and sodium hypophosphite (NaH_2PO_2) are present, thus imparting wrinkle resistance to the treated cotton fabric. We also found that MA and IA polymerize in aqueous solutions in the presence of $K_2S_2O_8$ and NaH_2PO_2 . In this research, we compared the effectiveness of poly(itaconic acid) (PIA) applied to cotton fabric as a polymer and IA applied as a monomer and allowed to polymerize *in situ* for crosslinking cotton cellulose. We found that IA is more effective in esterifying cotton cellulose and imparting a high level of wrinkle resistance to the fabric as it polymerizes *in situ* than PIA applied as a polymer. We also found that tensile strength loss of the cotton fabric crosslinked by IA polymerizing *in situ* as a function of fabric wrinkle recovery angle is practically the same as that crosslinked by PIA applied as a polymer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 319–326, 2001

Key words: cellulose; crosslinking; cotton; durable press finish; esterification; FTIR; Raman spectroscopy; *in situ* polymerization; itaconic acid

INTRODUCTION

Since the identification of formaldehyde as a probable human carcinogen in the 1980s, extensive efforts have been made to find formaldehyde-free crosslinking agents for cotton to replace the traditional *N*-methylol durable-press finishing agents.¹ In recent years multifunctional carboxylic acids have become the most promising non-formaldehyde crosslinking agents for cotton.^{2–5} In 1992 Choi reported that treating cotton fabric with a mixture of maleic acid (MA) and itaconic

acid (IA), in the presence of potassium persulfate ($K_2S_2O_8$) as an initiator, significantly increases the wrinkle resistance of the treated cotton fabric.⁶ Previously, we studied the *in situ* polymerization of MA and IA and found that MA and IA can polymerize on the cotton fabric at elevated temperatures when both $K_2S_2O_8$ and sodium hypophosphite (NaH_2PO_2) are present and that the concentration of $K_2S_2O_8$ in a finish system has a profound impact on the *in situ* polymerization and the performance of the treated cotton fabric.^{7,8} The concentration of $K_2S_2O_8$ required for polymerization of MA and IA is much higher than that reported previously by Choi.⁸ We also found that the molecular weight of the copolymer of MA and IA formed *in situ* on the cotton fabric is in the approximate range of 2,000–3,000.⁹

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In our previous research we used Fourier transform infrared (FTIR) spectroscopy to study the esterification of cellulose by poly(carboxylic acids), and found that a poly(carboxylic acid) esterifies cellulose through the formation of a cyclic anhydride intermediate.^{10–13} We also found that the effectiveness of a poly(carboxylic acid) for crosslinking cotton cellulose is affected by its molecular weight.¹³

MA and IA are extremely difficult to homopolymerize under conditions normally used for vinyl monomers. In our previous research, however, we found that MA and IA polymerize in aqueous solutions in the presence of both $K_2S_2O_8$ and NaH_2PO_2 .¹⁴ In this research we evaluated the effectiveness of PIA synthesized in an aqueous solution and IA polymerizing *in situ* for crosslinking cellulose and for imparting wrinkle resistance to the cotton fabric. We also investigated the relationship between tensile strength loss and the wrinkle resistance of the cotton fabric thus treated.

EXPERIMENTAL

Materials

The fabric was a desized and bleached plain-weave 100% cotton fabric weighing 100 g/m² (Testfabrics style 400). MA, IA, $K_2S_2O_8$, and NaH_2PO_2 were reagent grade chemicals supplied by Aldrich.

Polymerization of IA

Dissolved in 325 mL of water at 65°C were 125 g of IA and 50 g of NaH_2PO_2 . Then 16 g of $K_2S_2O_8$ was gradually added to the solution while stirring over a period of 30 min. The polymerization was allowed to continue for another 60 min. The PIA thus synthesized was used directly to treat the cotton fabric without further separation.

Cotton Fabric Treatment

A cotton fabric sample was first impregnated in an aqueous solution containing either PIA or IA, $K_2S_2O_8$, and NaH_2PO_2 . Both solutions maintained approximately the same carboxylic mole concentration. The wet pickup was in the range of 95%–100%. The impregnated fabric was dried at 85°C for 3 min and then cured at a specified temperature for 3 min in a Mathis curing oven.

All the concentrations were presented as percent weight of bath (% WOB).

Evaluation of Fabric Performance

The wrinkle recovery angle (WRA) and tensile strength at filling direction of treated cotton fabric were measured according to AATCC Test Method 66-1990 and ASTM Method D5053-90, respectively. All the fabric samples were tested after one washing cycle without the use of a detergent.

FTIR Spectroscopy Measurements

All the infrared spectra of the treated cotton fabric were diffuse reflectance spectra collected with a Nicolet Magna 760 FTIR spectrometer and a Specac diffuse reflectance accessory, and were presented in the absorbance mode ($-\log R/R_0$). Resolution for all the infrared spectra was 4 cm⁻¹. Potassium bromide powder was used as a reference material to produce a background spectrum. No smoothing functions and baseline correction were used. To measure the intensity of the ester carbonyl band, the treated and cured cotton fabric was first washed in deionized water to remove the unreacted acid and catalyst, then treated with a 0.1M NaOH solution at room temperature for 4 min to convert free carboxyl on the fabric to a carboxylate anion. It was then dried and finally ground in a Wiley mill to form a powder prior to FTIR spectroscopy analysis. The ester carbonyl band intensity in the infrared spectra of the treated cotton fabric was normalized against the 1318 cm⁻¹ band associated with a C—H bending mode of cellulose. To examine the anhydride formation, a treated fabric sample was analyzed by FTIR immediately after exposure to a high temperature.

FT-Raman Spectroscopic Measurements

A Nicolet 950 FT-Raman spectrometer with a liquid sample accessory and a InGaAs detector was used to collect the Raman spectra of the solutions. For the Raman spectra, the resolution was 8 cm⁻¹, and there were 200 scans for each spectrum.

pH Titration

- (1) *Titration of PIA*: 0.6 g of the reaction product of 125 g of IA, 50 g of NaH_2PO_2 , and 16 g of $K_2S_2O_8$ in 325 mL of water, as

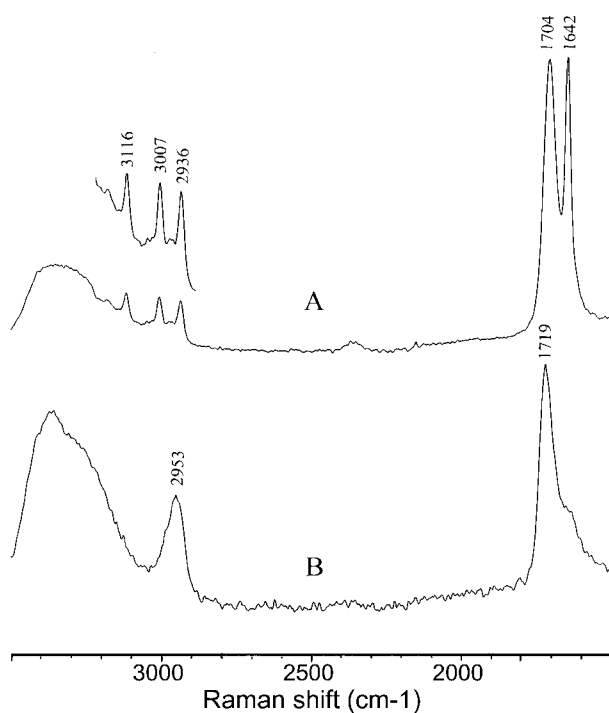


Figure 1 FT-Raman spectra of (A) the aqueous solution of IA and NaH_2PO_2 , and (B) after $\text{K}_2\text{S}_2\text{O}_8$ was added and polymerization was completed.

discussed above, was dissolved in 50 mL of CO_2 -free distilled water. The solution was titrated with a standardized sodium hydroxide solution (0.1002M). The pH values at various titration intervals were measured using a Beckman pH meter (model 310) to generate a pH titration curve of PIA.

- (2) *Titration of IA*: 0.125 g of IA, 0.05 g of NaH_2PO_2 , and 0.016 g of $\text{K}_2\text{S}_2\text{O}_8$ were dissolved in 50 mL of CO_2 -free distilled water. The titration process was the same as that for PIA.

RESULTS AND DISCUSSION

Both IA and NaH_2PO_2 were dissolved in water at 65°C . Presented in Figure 1(a) is the Raman spectrum of the IA- NaH_2PO_2 solution. The intense band at 1642 cm^{-1} is the $\text{C}=\text{C}$ stretching mode of IA, while the band at 1704 cm^{-1} is due to the stretching mode of the carboxylic carbonyl of IA.^{15,16} Two weak bands at 3116 cm^{-1} and 3007 cm^{-1} are asymmetric and symmetric stretching modes, respectively, of $=\text{CH}_2$, and the band at

2936 cm^{-1} is from the stretching mode of the saturated CH.^{15,16}

To the IA- NaH_2PO_2 solution was gradually added $\text{K}_2\text{S}_2\text{O}_8$, and the polymerization was allowed to continue for another 60 min. The Raman spectrum of the reaction product (PIA) is presented in Figure 1(b), in which the bands at 1642 and $3116/3007\text{ cm}^{-1}$ due to $\text{C}=\text{C}$ and $=\text{CH}_2$ disappeared while a relative strong band at 2953 cm^{-1} emerged because of saturated hydrocarbon. The data presented here indicate that unsaturated IA was converted to saturated PIA as IA polymerized. It can also be observed that the carboxylic carbonyl band was shifted from 1704 cm^{-1} in Figure 1(A) to 1719 cm^{-1} in Figure 1(b). In an IA molecule conjugation between $\text{C}=\text{C}$ and the carboxylic $\text{C}=\text{O}$ shifted the carbonyl stretching mode to a lower frequency at 1704 cm^{-1} [Fig. 1(a)]. When IA polymerized, the carboxylic carbonyl was no longer conjugated with $\text{C}=\text{C}$, thus shifting the carboxylic carbonyl to a higher frequency at 1719 cm^{-1} [Fig. 1(b)]. Therefore, the Raman spectroscopy data provide definitive evidence that IA polymerizes in the presence of $\text{K}_2\text{S}_2\text{O}_8$ and NaH_2PO_2 .

To further confirm the formation of PIA, we titrated IA before and after polymerization. The two systems had approximately the same carboxylic acid molar concentration and contained the same weight percentage of NaH_2PO_2 . The titration curves of IA and PIA are shown in Figure 2. The titration curve of IA shows a sharp equivalent point at pH 7–10, while PIA gradually increased its pH in the same region (Fig. 2). When IA polymerized to form PIA, partial neutralization of PIA reduced the dissociation constants of the free carboxylic groups in the molecule. The greater the number of carboxylic groups neutralized, the less acidic the PIA became. This is why the PIA titration curve does not show a sharp equivalent point in Figure 2. Thus, the titration data presented in Figure 2 corroborate the formation of PIA as demonstrated by the FT-Raman spectroscopy data in Figure 1.

The infrared spectrum of the cotton fabric treated with 6% IA is shown in Figure 3(a), in which the band at 1716 cm^{-1} is from the stretching mode of the carboxylic acid carbonyl. Two bands, at 1842 cm^{-1} and 1769 cm^{-1} , emerged in the spectrum when the treated fabric was cured at 160°C for 3 min [Fig. 3(b)]. These two bands are due to the symmetric and asymmetric stretching modes of itaconic anhydride formed at the ele-

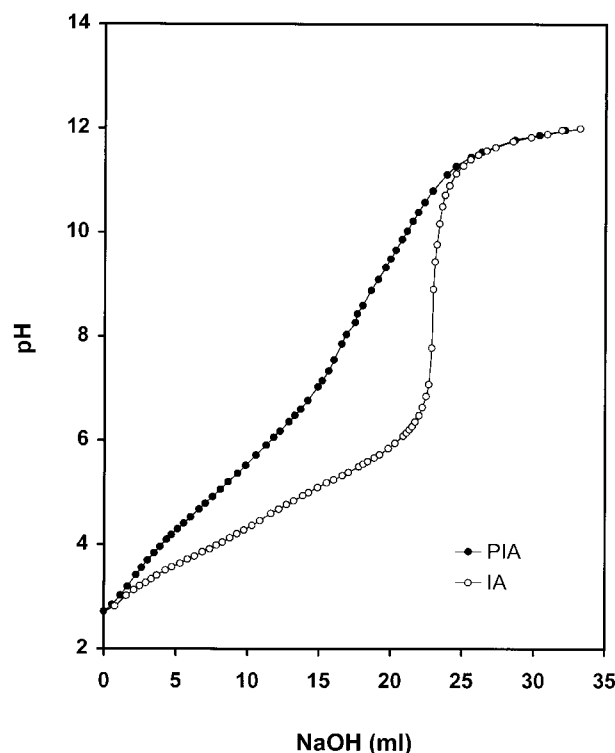


Figure 2 Titration curves of the aqueous solution of IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$ before and after polymerization (IA and PIA, respectively).

vated temperature.¹⁷ These two bands appear to be sharp in the difference spectrum [Fig. 3(c)].

Presented in Figure 4(a,b) are the infrared spectra of the cotton fabric treated with PIA (the reaction product of IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$, as discussed above) before and after curing at 160°C for 3 min. Two explicit bands at 1852 cm^{-1} and 1778 cm^{-1} , a result of symmetric and asymmetric stretching of the cyclic anhydride of PIA, are seen in the difference spectrum [Fig. 4(c)]. These two anhydride carbonyl bands of PIA, shown in Figure 4(c), appear to be broader and at higher frequencies than those of anhydride of IA [Fig. 3(c)]. The conjugation of the carbonyl and the alkene double band in an IA molecule reduces the frequencies of the two anhydride carbonyl stretching modes.¹⁷

The cotton fabric was treated with 6% IA, 4.9% NaH_2PO_2 , and 2% $\text{K}_2\text{S}_2\text{O}_8$, then cured at 160°C for 3 min. The spectra of the treated fabric before and after curing are shown in Figure 5(a,b), respectively. Two bands from the symmetric and asymmetric stretching of a cyclic anhydride appear at 1850 cm^{-1} and 1776 cm^{-1} , respectively, in the difference spectrum [Fig. 5(c)]. Apparently,

the frequencies and shapes of these two bands, shown in Figure 5(c), are very similar to those of PIA, shown in Figure 4(c), thus indicating that IA polymerized on the cotton fabric under the curing condition.

Since esterification of cotton by a poly(carboxylic acid) is pH-dependent,^{18,19} we evaluated the effect of pH on the WRA and tensile strength of the cotton fabric treated by PIA as either a polymer or formed *in situ* on cotton. The cotton fabric was treated with a solution containing 6% PIA and 4.9% NaH_2PO_2 and with a solution containing 6% IA, 4.9% NaH_2PO_2 and 2% $\text{K}_2\text{S}_2\text{O}_8$. The pH of the solutions was adjusted to a range of 2.0–3.6 using NaOH or HCl. The treated fabric was cured at 180°C for 3 min. The WRA and tensile strength of treated cotton fabric are shown in Table I. It can be observed that the fabric WRA remained statistically unchanged in the 2.0–3.2 pH range but decreased notably at pH 3.6 (Table I). The fabric tensile strength increased when the solution pH was increased from 2.0 to 3.6. This is because a higher solution pH reduces acid-catalyzed cellulose depolymerization on cotton.²⁰ Therefore, we chose 3.2 as the optimal pH for the

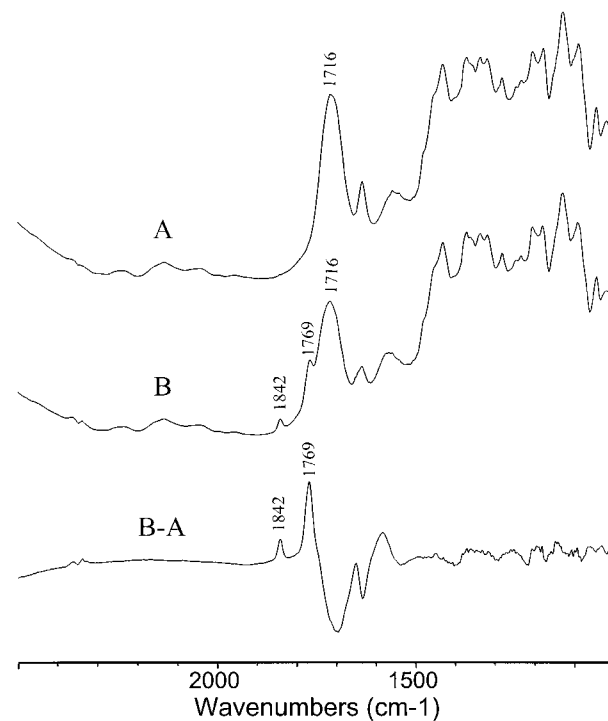


Figure 3 Infrared spectra of (A) cotton fabric treated with 6% IA; (B) cotton fabric thus treated and cured at 160°C for 3 min; and (C) the difference spectrum, $B - A$.

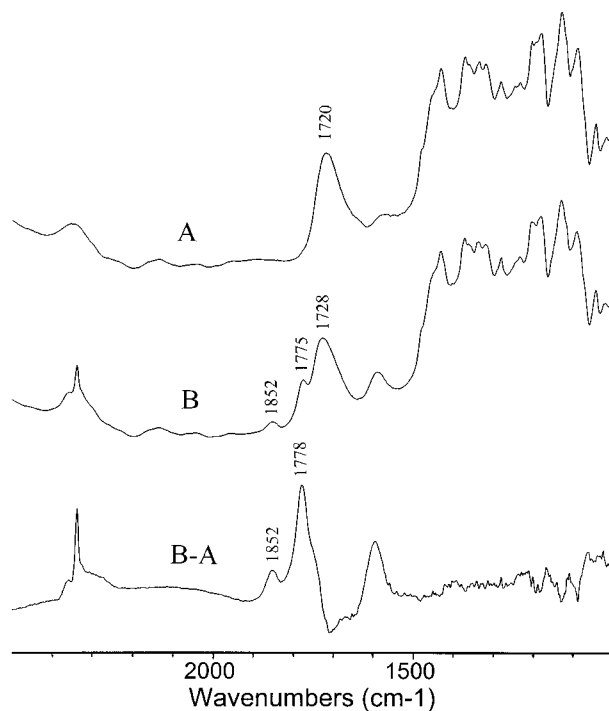


Figure 4 Infrared spectra of (A) cotton fabric treated with 6% PIA and 4.9% NaH_2PO_2 ; (B) cotton fabric thus treated and cured at 160°C for 3 min; and (C) the difference spectrum, $B - A$.

solutions used to treat the cotton fabric in order to minimize the acid-catalyzed cellulose degradation.

We investigated and compared the effectiveness as crosslinking agents for cotton of PIA applied as a polymer with that formed *in situ* on cotton. The cotton fabric was treated with, respectively, a solution containing 6% PIA and 4.9% NaH_2PO_2 and a solution containing 6% IA, 4.9% NaH_2PO_2 and 2% $\text{K}_2\text{S}_2\text{O}_8$. The treated fabric samples were cured at temperatures ranging from 140°C to 200°C for 3 min. The cotton fabric samples thus treated were rinsed in 0.1M NaOH solution to convert free carboxylic acid bound to the fabric to a carboxylate anion so that the ester carbonyl band intensity could be measured quantitatively.²¹

The ester carbonyl band intensity of the treated cotton fabric samples is presented as a function of the curing temperature in Figure 6. It can be seen that the ester carbonyl band intensity increased as the curing temperature was increased and that the ester carbonyl band intensity of the cotton fabric treated with IA polymerizing *in situ* was significantly higher than that

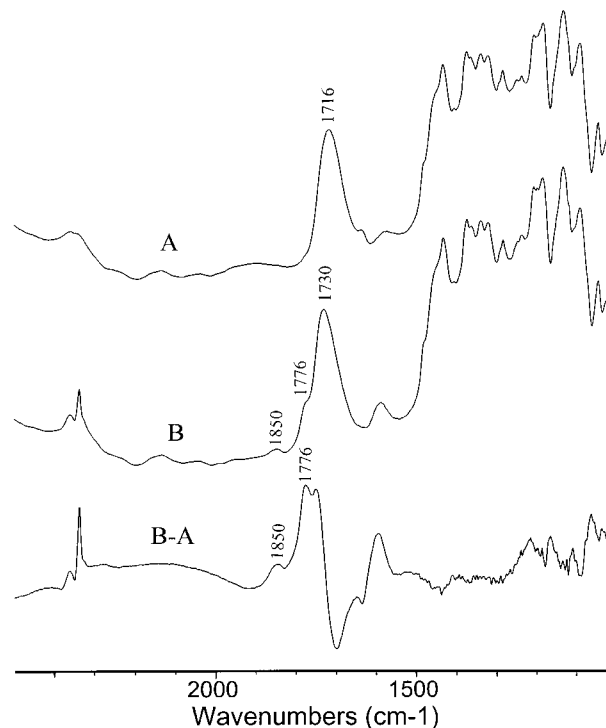


Figure 5 Infrared spectra of (A) cotton fabric treated with 6% IA, 4.9% NaH_2PO_2 , and 2% $\text{K}_2\text{S}_2\text{O}_8$; (B) cotton fabric thus treated and cured at 160°C for 3 min; and (C) the difference spectrum, $B - A$.

treated with PIA applied as a polymer. Shown in Figure 7 is the WRA of the cotton fabric treated with PIA and IA and cured at different temperatures. The cotton fabric treated with IA showed 20° or higher WRA than that treated with PIA at the same curing temperature, as indicated in Figure 7. Since the solutions of PIA and those of IA had the same carboxylic acid molar concentration, we concluded that the PIA formed *in situ* is more

Table I The WRA and Tensile Strength of the Cotton Fabric Treated with PIA and IA at Different pH

pH	WRA ($w + f$, degree)		Tensile Strength (Filling, kg)	
	PIA	IA	PIA	IA
2.0	258	279	9.9	8.2
2.4	257	272	11.8	8.9
2.8	260	272	11.6	9.3
3.2	263	274	12.8	9.8
3.6	250	265	12.7	10.7

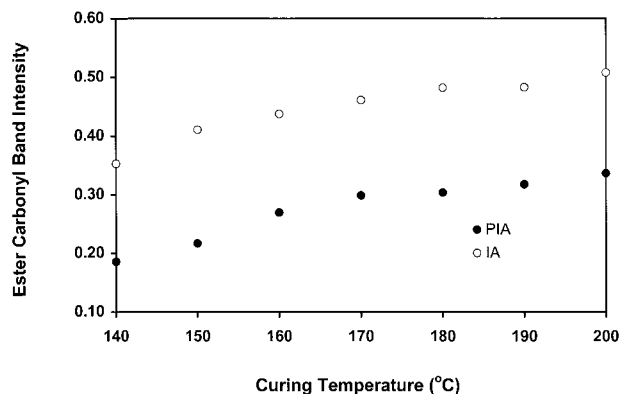


Figure 6 Ester carbonyl band intensity of cotton fabric treated with PIA and of that treated with IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$ versus the curing temperature.

effective in esterifying and crosslinking cotton than the PIA applied as polymer in the entire temperature range.

The carbonyl band intensity ratio (carboxylate-ester) for the cotton fabric treated with PIA and that treated with IA is shown in Figure 8. The amount of free carboxyl groups for the PIA-treated fabric is notably larger than that of the IA-treated fabric, as demonstrated in Figure 8. The size of the PIA molecule is much larger than that of IA, thus reducing its ability to penetrate into the bulk of cotton fibers. The mobility of the anhydride intermediate of PIA to excess cellulosic hydroxyl groups is reduced as the number of the ester linkages between PIA and cellulose increases and the bound PIA molecule becomes more restricted during a curing process. A larger portion of the PIA anhydride intermediate, com-

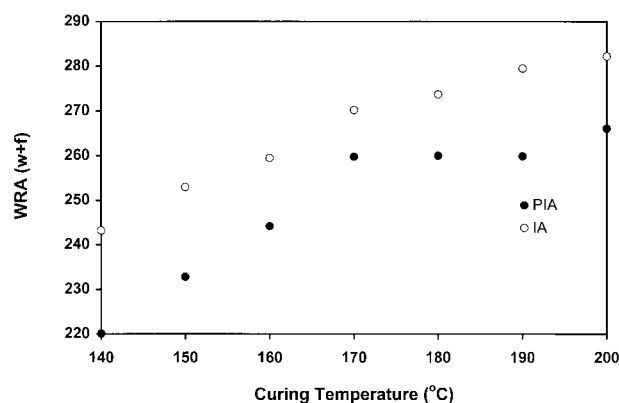


Figure 7 WRA of cotton fabric treated with PIA and of that treated with IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$ versus the curing temperature.

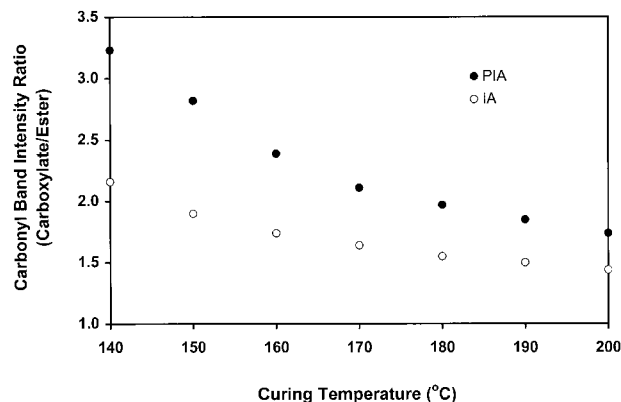


Figure 8 Carbonyl band intensity ratio (carboxylate/ester) of cotton fabric treated with PIA and of that treated with IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$ versus the curing temperature.

pared to that of the IA polymerizing *in situ*, is unable therefore to access the cellulosic hydroxyl to esterify and thus remains free. Another possible explanation is that IA is more homogeneously distributed across the cross section of cotton fibers because it is able to penetrate well into the bulk of the cotton fibers, while PIA as a polymer is more concentrated on the fiber surfaces. Therefore, cellulosic hydroxyl is more accessible for IA than for PIA.

Figure 9 shows the WRA of the treated cotton fabric as a function of ester carbonyl band intensity. Despite IA forming a larger amount of ester on the cotton fabric than did PIA, the WRA of PIA-treated fabric was higher than that of IA-treated fabric at the same ester carbonyl band intensity (Fig. 9). One possible explanation is that

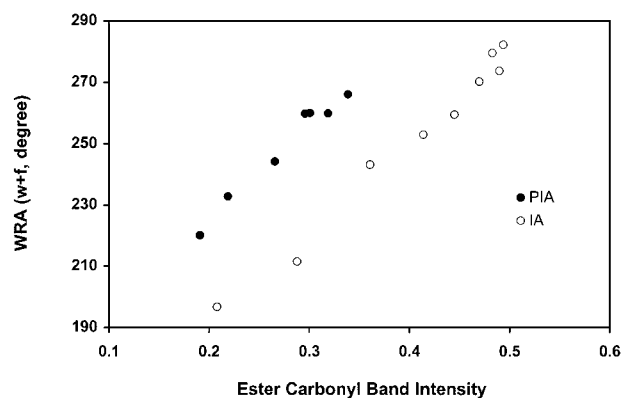
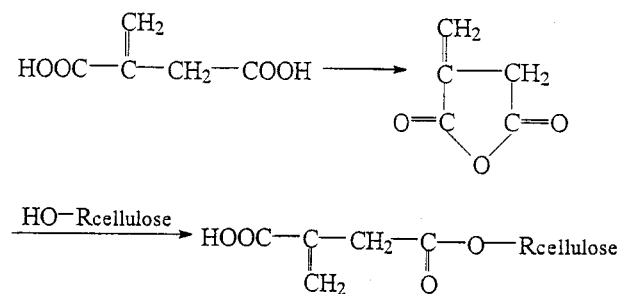


Figure 9 WRA of cotton fabric treated with PIA and of that treated with IA, NaH_2PO_2 , and $\text{K}_2\text{S}_2\text{O}_8$ versus ester carbonyl-band intensity.

a portion of IA applied to the cotton fabric esterified cotton without participating polymerization. Because *in situ* polymerization and esterification of IA take place simultaneously, a portion of IA may esterify before it polymerizes on cotton. An IA monomer has two carboxylic acid groups, only one of which is able to esterify cellulose because formation of a five-membered cyclic anhydride intermediate is necessary for a poly(carboxylic acid) to esterify cellulose^{10–13} (Scheme 1). Therefore, the portion of IA esterifying cellulose without polymerizing did not contribute to the crosslinking of cellulose and to the increase of the fabric's wrinkle resistance. In our previous research we found that approximately 20% of IA remained monomeric when the cotton fabric was treated with 6% MA, 6.7% ITA, 4% NaH₂PO₂, and 2% K₂S₂O₈, and cured at 180°C for 2 min.⁷

Previously, we found that reduction in the mechanical strength of crosslinked cotton fabric is caused by the depolymerization and crosslinking of cellulose molecules as a result of a crosslinking process.²⁰ Researchers in the past believed that a more even distribution of a crosslinking agent between the surface and the interior of cotton fiber improved the mechanical strength of the crosslinked cotton fabric.^{23–24} *In situ* polymerization was originally used to achieve a more homogeneous distribution of a crosslinking agent.^{24–25}

In this research we measured the tensile strength loss of the cotton fabric treated with PIA and of that treated with IA polymerizing *in situ* as a function of fabric WRA (Fig. 10). It can be seen that fabric tensile strength loss increased as the curing temperature and consequently the WRA were increased, and that the correlation between tensile strength loss and the WRA appeared to be linear (Fig. 10). Even though the IA-treated cotton fabric has a higher WRA than the PIA-treated one, as shown in Figure 7, the slope of the linear correlation is very close (Fig. 10). Because IA is



Scheme 1

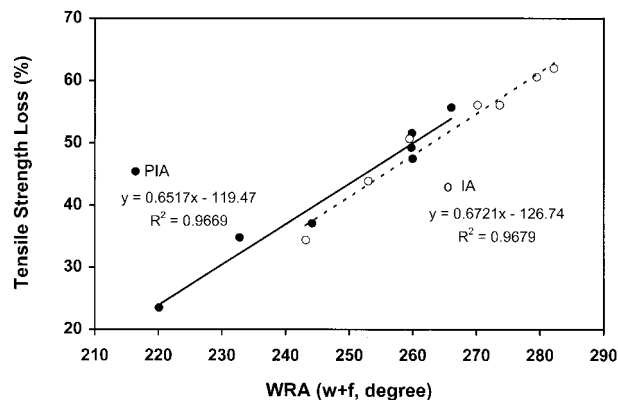


Figure 10 Tensile strength of cotton fabric treated with PIA and of that treated with IA, NaH₂PO₂, and K₂S₂O₈ versus WRA.

much smaller in molecular size than PIA, the distribution of IA in a cotton fiber is more homogeneous than PIA. The data presented here do not support the hypothesis that *in situ* polymerization of a crosslinking agent improved fabric mechanical strength because of more even distribution of the crosslinking agent, as reported previously.

CONCLUSIONS

IA is more effective in esterifying cotton cellulose and imparting wrinkle resistance as it polymerizes *in situ* on cotton than PIA applied as a polymer. The tensile strength loss of the cotton fabric crosslinked by IA polymerizing *in situ* as a function of fabric WRA is very similar to that crosslinked by PIA applied as a polymer.

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