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Formaldehyde Free Cross-linking Agents Based on Maleic Anhydride Copolymers

Kee Jong Yoon*, Jong Hyung Woo, and Young Sam Seo

Department of Textile Engineering, College of Engineering, Dankook University
San 8, Hannam-dong, Yongsan-gu, Seoul 140-714, Korea
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Abstract: Low molecular weight copolymers of maleic anhydride and vinyl acetate were prepared to develop formaldehyde free cross-linking agents. Since lower molecular weight is favorable for efficient penetration of the finishing agent into the cotton fibers in the padding process, the concentration of the initiator, chain transfer agent and the monomer ratios were varied to obtain copolymers of low molecular weights. The prepared polymers were characterized by GPC, ^{1}H-NMR, FTIR, DSC and TGA. Copolymers of molecular weights of 2 000 to 10 000 were obtained and it was found that the most efficient method of controlling the molecular weight was by varying the monomer ratios. Poly(maleic anhydride-co-vinyl acetate) did not dissolve in water, but the maleic anhydride residue hydrolyzed within a few minutes to form poly(maleic acid-co-vinyl acetate) and dissolved in water. However, the maleic acid units undergo dehydration to form anhydride groups on heating above 160 °C to some extent even in the absence of catalysts. The possibility of using the copolymers as durable press finishing agent for cotton fabric was investigated. Lower molecular weight poly(maleic anhydride-co-vinyl acetate) copolymers were more efficient in introducing crease resistance, which appears to be due to the more efficient penetration of the cross-linking agent into cotton fabrics. The wrinkle recovery angles of cotton fabrics treated with poly(maleic anhydride-co-vinyl acetate) copolymers were slightly lower than those treated with DMDHEU and were higher when higher curing temperatures or higher concentrations of copolymer were used, and when catalyst, NaH_2PO_2, was added. The strength retention of the poly(maleic anhydride-co-vinyl acetate) treated cotton fabrics was excellent.

Keywords: Cellulose, Cotton, Maleic anhydride, Poly(maleic anhydride-co-vinyl acetate), Durable press

Introduction

Formaldehyde based cross-linking agents are generally used in durable press finishing, but formaldehyde is a suspected carcinogen that is linked to nasal and lung cancer and may be released during the finishing process or even during end-use. Therefore, formaldehyde-free polycarboxylic acids (PCA) have been used to cross-link cellulose via ester linkages. Various PCAs, such as maleic acid, succinic acid, tricarballylic acid, citric acid, 1,2,3,4-cyclopentane tetracarboxylic acid (CPTA), 1,2,3,4-butanetetracarboxylic acid (BTCA), tetrahydrofurane tetracarboxylic acid etc. have been reported in the literature [1-8]. Copolymers of maleic acid, acrylic acid and vinyl alcohol whose molecular weight is approximately 1,000 developed as polymeric ester forming cross-linking agents by FMC Corporation in Europe has also been studied [2]. As cross-linking agents must penetrate into the cotton fibers within a few minutes during the padding process, it was thought that lower molecular weights would be favorable for efficient penetration.

The cross-linking of cellulose by a polycarboxylic acid is known to proceed in two steps: the formation of a cyclic anhydride intermediate by dehydration of two adjacent carboxylic acid groups, and the reaction between cellulose and the anhydride intermediate to form an ester. Yang *et al.* [2] reported that PCAs having carboxyl groups bonded to adjacent carbons on backbone, capable of forming five-membered cyclic anhydrides, esterify cotton cellulose more effectively than those polycarboxylic acids that have their carboxyl groups bonded to alternant carbons and are unable to form five-membered cyclic anhydride intermediates. Of the PCAs, BTCA was reported to be the most efficient cross-linking agent but it is not used commercially due to various reasons, such as its commercial availability and cost. This may have brought about the development of the polymeric ester forming cross-linking agents in Europe. However, it does not appear to have resulted in commercial use. A possible drawback of the polymeric cross-linking agent may have been its low diffusion rate.

Therefore, development of low molecular weight polymeric ester forming cross-linking agent was attempted in this study. Maleic acid and maleic anhydride were considered since they either can form or have 5-membered cyclic anhydride groups, known to be efficient in cross-linking cellulose. Since maleic anhydride does not form a homopolymer and forms alternating copolymers when copolymerized with vinyl acetate, it was thought that molecular weight could be controlled by using excess maleic anhydride in the copolymerization with vinyl acetate. The control of molecular weight in the copolymerization of poly(maleic anhydride-co-vinyl acetate), P(MAn -co-VAc), was attempted by changing the concentration of the initiator, incorporation of a chain transfer agent and varying the monomer feed ratios.

The anhydride group is more reactive than the carboxylic

*Corresponding author: keejyoon@dankook.ac.kr

acid groups and would be ideal for cross-linking cellulose, but it is very susceptible to hydrolysis and poly(maleic acid-co-vinyl acetate) can be formed on addition to water in the preparation of the padding bath. However, the anhydride group can be re-formed by heating. The reversibility of hydrolysis and anhydride re-formation by heating was studied using FTIR, DSC and TGA.

To study the feasibility of using P(MAn-co-VAc) as a durable press finishing agent, cotton fabric was padded with a solution containing low molecular weight P(MAn-co-VAc), a catalyst, and a wetting agent, pre-dried, cured and washed then treated with a softening agent. The effect of the molecular weight on the effectiveness of the copolymers as a durable press finishing agent was evaluated by measuring the wrinkle recovery angles of the treated fabrics.

Experimental

Materials

Scoured and bleached cotton print cloth (30s × 30s, 73 × 73/inch, plain weave) was used. Maleic anhydride (MAn, Aldrich) and 2,2'-azobisisobutyronitrile (AIBN, Aldrich) were recrystallized from chloroform and methanol, respectively. Vinyl acetate (VAc, Aldrich) was distilled under reduced pressure. Toluene and diethyl ether were used as received. Wetting agent, Triton X-100 (Aldrich) and softening agent, Snowsilicone RDS (Dae Young Chem. Co., Ltd., Korea), were used as received.

Synthesis of Copolymer and Analysis

Copolymerization of MAn and VAc was carried out by adding MAn and VAc monomers and AIBN initiator to toluene, purging the reaction mixture with nitrogen and stirring at 70 °C for 4 hours. The total monomer concentration in toluene was 10 % (wt). Dodecyl mercaptan was also added in the experiments where the effect of chain transfer agent on the molecular weight of the copolymer was studied. The copolymerization product was dissolved in warm toluene, precipitated in diethyl ether, filtered and dried in vacuum.

The molecular weight of P(MAn-co-VAc) was measured using a Waters 2414 gel permeation chromatograph equipped with Styragel HR2, HR4 and HR5 columns (Waters). The measurement was carried out using tetrahydrofuran as an eluent at 30 °C and the relative molecular weights compared with PS standards were determined. ^{1}H-NMR spectra of the copolymer in DMSO-d_6 were obtained on a Gemini 200 NMR spectrometer (Varian Co.), using tetramethylsilane as an internal reference. Infrared spectra were obtained using a Perkin Elmer Spectrum GX FTIR spectrometer by scanning 12 times at a resolution of 2 cm^{-1}. The samples for FTIR measurement were prepared by dissolving the copolymer in acetone and casting on a CaF_2 window and drying. Thermal analyses of the copolymers were carried out on a TA 2100 DSC and TA Instruments Q50 TGA at heating rates of 10 °C/min. The hydrolysis of the anhydride groups during dissolution in water and its regeneration on heating were studied using IR, DSC and TGA.

Durable Press Finishing with P(MAn-co-VAc)

The cotton fabric was padded with a solution containing 0, 4, 8, 10 or 12 % P(MAn-co-VAc), 4.8 % sodium hypophosphite catalysis and 0.2 % Triton X-100 to a wet pick-up of 100 %, pre-dried at 85 °C for 3 min., then cured at 150, 160, 170 or 180 °C for 3 min. The treated fabric was rinsed in running water at 50 °C for 30 minutes, treated with a 5 % nonionic softening agent solution and dried in a vacuum oven at 60 °C for 30 minutes. Samples were conditioned in a standard atmosphere before evaluation. The wrinkle recovery angle of the treated cotton fabric was evaluated according to KS K 0550. The tensile testing of the treated cotton fabric was carried out using a Universal Testing Machine LR10K (Lloyd, England) at 20 mm/min with 1.5 cm × 4 cm samples. The averages of five measurements are reported.

Results and Discussion

Copolymerization

The changes in the molecular weight and polydispersity of copolymer with initiator concentrations, chain transfer agent concentrations and monomer feed ratios shown in Table 1 suggest that varying the monomer feed ratio is the most effective in controlling the molecular weight. Molecular weights

Table 1. Copolymerization conditions and the GPC molecular weight data of poly(maleic anhydride-co-vinyl acetate)

Monomer feed mole ratio	Initiator concentration	Chain transfer agent concentration	GPC molecular weight		
MAn/(MAn+VAc)	AIBN (M)	Dodecylmercaptan (M)	M_n	M_w	M_w/M_n
0.5	0.001		9 800	16 200	1.66
0.5	0.005		8 100	14 600	1.79
0.5	0.010		6 300	11 900	1.88
0.5	0.020		4 200	8 300	1.99
0.5	0.040		5 700	11 400	1.98
0.5	0.005	0.001	6 400	11 100	1.74
0.5	0.005	0.005	6 300	11 700	1.86
0.5	0.005	0.010	5 800	10 400	1.80
0.5	0.005	0.020	4 900	8 700	1.76
0.5	0.005	0.040	3 700	6 400	1.75
0.1	0.005		9 300	16 100	1.73
0.3	0.005		9 800	16 800	1.72
0.5	0.005		6 500	12 700	1.94
0.7	0.005		4 500	8 500	1.88
0.9	0.005		2 200	3 700	1.66

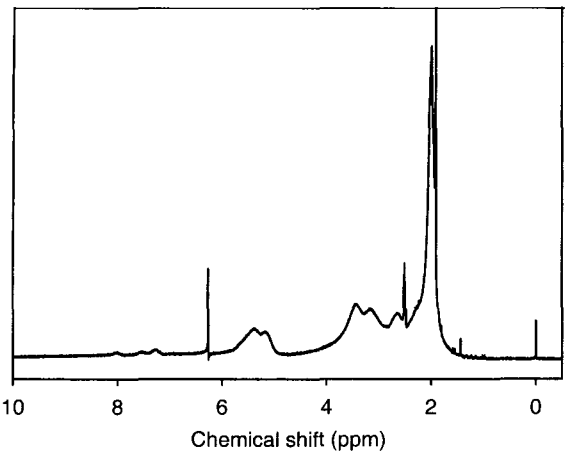

Figure 1. ^{1}H-NMR spectrum of P(MAn-co-VAc) (M_n 2 200 prepared at MAn/(MAn + VAc) = 0.9).

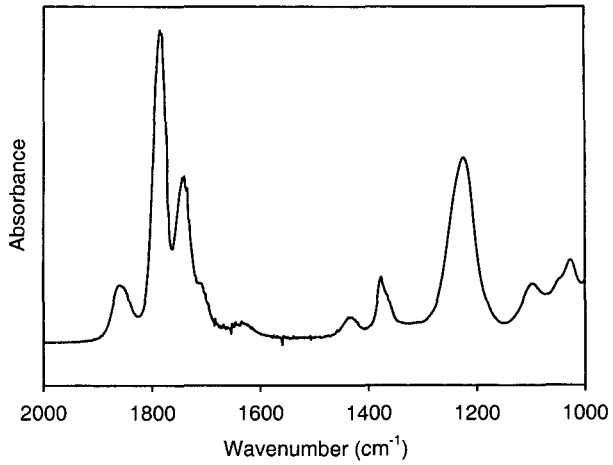

Figure 2. FTIR spectrum of P(MAn-co-VAc) (M_n 2 200 prepared at MAn/(MAn + VAc) = 0.9).

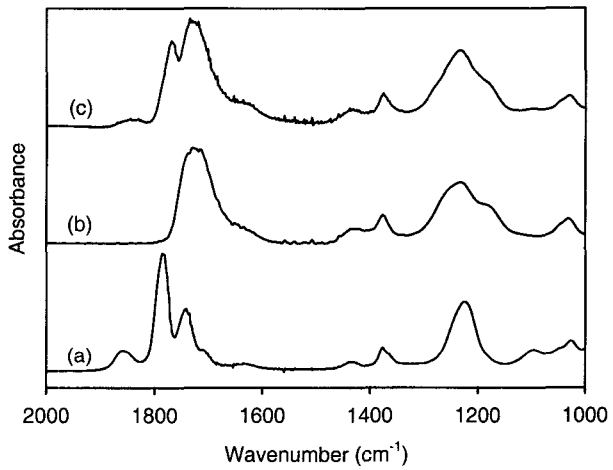

Figure 3. FTIR spectra of (a) P(MAn-co-VAc), (b) P(MAn-co-VAc) hydrolyzed in water for 30 min. at 60 °C and (c) hydrolyzed P(MAn-co-VAc) heated for 3 min. at 180 °C. (P(MAn-co-VAc): M_n 2 200 prepared at MAn/(MAn + VAc) = 0.9).

in the range 2 000 to 10 000 were obtained. The lowest molecular weight was obtained when the maleic anhydride feed ratio was 0.9, in the range studied. This can be explained by the very low reactivity ratio of maleic anhydride (M_1) in its copolymerization with vinyl acetate (M_1), r_1~0, $r_2 = 0.019$ [9]. Since these two monomers are known to exhibit alternating behavior, it appears that when vinyl acetate is consumed the propagating chain end becomes maleic anhydride and further addition of monomers is not possible. In the case when vinyl acetate is in excess, higher molecular weights were obtained in comparison with when the feed ratio was 0.5. It appears that although the reactivity ratio r_2 is very low, addition of vinyl acetate monomers onto the vinyl acetate radical may have been possible resulting in higher molecular weights at higher VAc feed ratios. Chain transfer reaction to the acetyl group may also have been possible. Relatively narrow molecular weight distributions were obtained.

The ^{1}H-NMR spectrum of P(MAn-co-VAc) copolymer prepared at a MAn feed ratio of 0.9 is shown in Figure 1. Peaks of the methine hydrogen in the vinyl acetate repeating unit (r.u.) occur around 5.4 ppm, peaks of the methine hydrogen of the maleic anhydride r.u. at 3.2 and 3.5 ppm and peaks of the methylene and methyl hydrogens of vinyl acetate r.u. around 2. The peak area of the 5.4 ppm peak to the peaks at 3.2 and 3.5 ppm were roughly 1:2 suggesting that the ratio of MAn to VAc in the copolymers were approximately 1:1 and that P(MAn-co-VAc) may be an alternating copolymer. The NMR spectra of P(MAn-co-VAc) samples prepared at MAn feed ratios of 0.5 and 0.7 were similar to Figure 1. However, the NMR spectra of P(MAn-co-VAc) samples prepared at MAn feed ratios of 0.1 and 0.3 suggested that greater amounts of VAc were incorporated into the copolymer.

The FT-IR spectrum of P(MAn-co-VAc) prepared at MAn feed ratio of 0.9 in Figure 2 exhibits characteristic peaks at 1859 cm^{-1} and 1785 cm^{-1} (C=O asymmetric and symmetric stretching band of anhydride groups), 1741 cm^{-1} (C=O symmetric stretching band of VAc), 1225 cm^{-1} (C-O-C stretching band of MAn) and 1096 cm^{-1} ($COCH_3$ stretching band of VAc). The GPC, ^{1}H-NMR and FTIR data suggest that low molecular weight P(MAn-co-VAc) containing similar amounts of maleic anhydride and vinyl acetate units can be prepared most effectively by variation of the monomer feed ratios.

Hydrolysis and Anhydride Re-formation

When the copolymer is added to water to prepare the padding bath, the copolymer does not dissolve initially but slowly dissolves as the anhydride units hydrolyze to form acid groups. The FTIR spectrum of the hydrolyzed P(MAn-

co-VAc) (prepared at a monomer feed ratio, MAn/(MAn + VAc) of 0.9) in Figure 3 exhibits no anhydride peaks and the characteristic C=O stretching band of an acid appears at 1730 cm^{-1}. However, the anhydride peak is again formed on heat treatment of the hydrolyzed P(MAn-co-VAc) at 180 °C for 3 min., even in the absence of catalyst. The re-formation of the anhydride group could be observed using DSC and TGA. The DSC data in Figure 4 showing the heating thermograms of P(MAn-co-VAc) and hydrolyzed P(MAn-co-VAc) exhibits a complex endothermic peak in the range 100-230 °C. The hydrolyzed P(MAn-co-VAc) exhibits a broad peak in the range 100-190 °C, which is absent in P(MAn-co-VAc). This broad peak appears to be due to the dehydration of adjacent

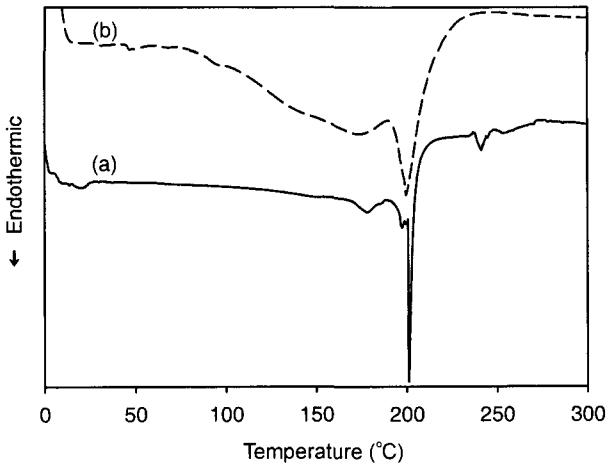

Figure 4. DSC heating thermograms of (a) P(MAn-co-VAc) and (b) hydrolyzed P(MAn-co-VAc). (P(MAn-co-VAc): M_n 2 200 prepared at MAn/(MAn + VAc) = 0.9).

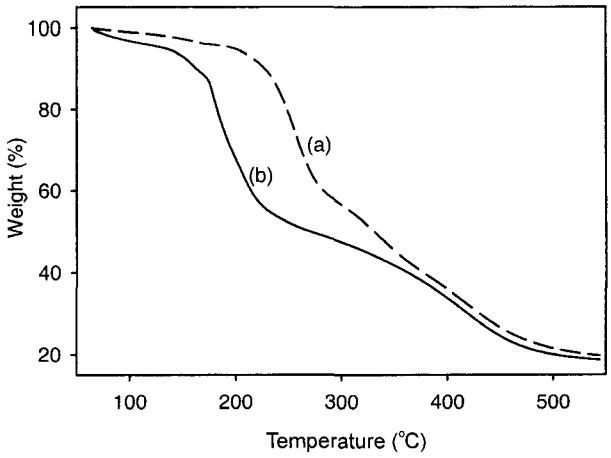

Figure 5. TGA curves of (a) P(MAn-co-VAc) and (b) hydrolyzed P(MAn-co-VAc). (P(MAn-co-VAc): M_n 2 200 prepared at MAn/(MAn + VAc) = 0.9).

carboxylic acid groups. P(MAn-co-VAc) exhibits a sharp peak near 200 °C and the hydrolyzed P(MAn-co-VAc) exhibits a slightly broader peak in the range 190-230 °C, which appears to be due mainly to the decarboxylation of the anhydride. The data of the hydrolyzed P(MAn-co-VAc) is similar to the results for poly(acrylic acid) in the literature, although the temperatures are somewhat lower than in the case of poly (acrylic acid) which forms 6-membered rings on dehydration [10,11]. The TGA data of P(MAn-co-VAc) of M_n 2 200 prepared at a feed mole ratio MAn/(MAn + VAc) of 0.9 in Figure 5 shows the weight loss due to these reactions. Significant weight loss in the case of the hydrolyzed P(MAn-co-VAc) occurs in the range 150-220 °C, while in the case of P(MAn-co-VAc) it occurs in the range 200-270 °C. The earlier weight loss in P(MAn-co-VAc) appears to be due to the re-formation of the anhydride via dehydration. However, weight loss in excess of 50 % occurs, suggesting that degradation reactions are occurring along with the dehydration and decarboxylation reactions. The FTIR, DSC and TGA data suggest that re-formation of anhydride via dehydration is possible. Thus, it appeared that the hydrolyzed copolymer could act as a cross-linking agent via the re-formation of anhydride groups in the presence of catalysts, similar to the PCAs.

Durable Press Finishing with P(MAn-co-VAc)

Based on the copolymerization experiments, P(MAn-co-VAc) of varying molecular weights for the finishing of cotton were prepared by varying the monomer feed ratio. The GPC molecular weights with respect to polystyrene standards are shown in Table 2. Although the number average molecular weight for the MAn/(MAn + VAc) = 0.9 sample is 3 100, the molecular weight corresponding to the GPC peak onset is 9 200 (Figure 6), which may still be too large for penetration into the pores of the cotton fiber.

When cotton fabric was padded with aqueous solutions of P(MAn-co-VAc), sodium hypophosphite catalyst, and wetting agent, pre-dried, cured, washed and treated with a softening agent, increases in the wrinkle recovery angles (WRA, W+F) of the fabric occurred. The effect of the curing temperature on

Table 2. Copolymerization conditions and the GPC molecular weight data of P(MAn-co-VAc) prepared for the durable press finishing of cotton fabrics

Monomer feed mole ratio	Initiator concentration	GPC molecular weight		
MAn/(MAn + VAc)	AIBN (M)	M_n	M_w	M_w/M_n
0.1	0.005	9 100	14 000	1.54
0.3	0.005	8 300	12 600	1.52
0.5	0.005	5 300	9 000	1.69
0.7	0.005	4 100	7 500	1.82
0.9	0.005	3 100	5 200	1.70

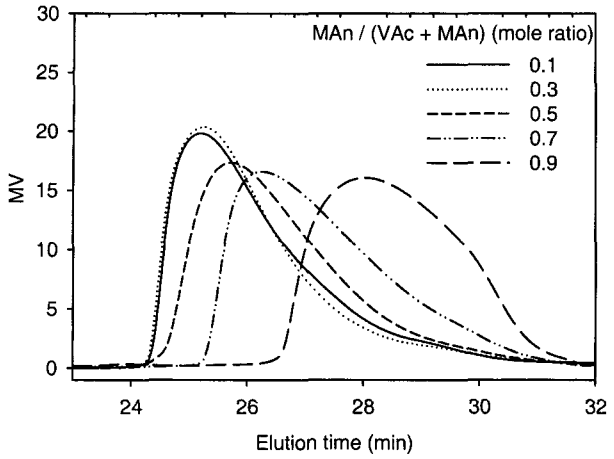

Figure 6. GPC elution curves of P(MAn-co-VAc) prepared for durable press finishing of cotton fabrics.

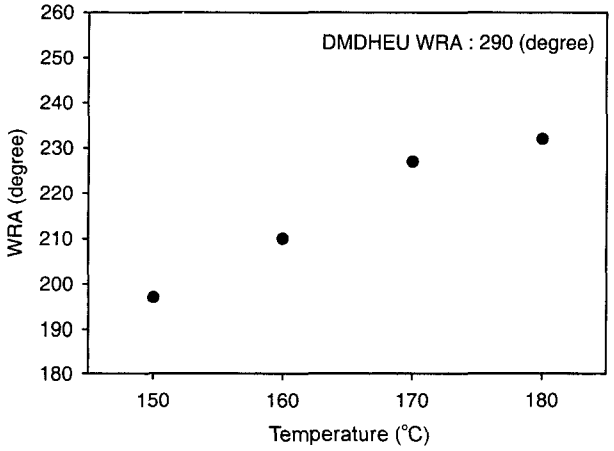

Figure 7. The effect of curing temperature on the wrinkle recovery angle (WRA, W+F) of cotton fabric padded with 10 %(wt.) P(MAn-co-VAc) of M_n 5 300 and cured for 3 min. at different temperatures.

the WRA of cotton treated with 10 % P(MAn-co-VAc) of M_n 5 300 shown in Figure 7 exhibits a gradual increase in the WRA values. This appears to be due to the more efficient re-formation of the anhydride groups, which are capable of cross-linking cellulose at higher temperatures as can be seen in Figure 8. Significant formation of the anhydride groups can be seen at 180 °C even in the absence of catalyst. Thus with the addition of sodium hypophosphite catalyst it appears that anhydride re-formation occurs at lower temperatures to result in the formation of cross-links and increase in the WRA above 150 °C observed in Figure 7. The WRA of the cotton fabric treated with different concentrations of P(MAn -co-VAc) of M_n 5 300 shown in Figure 9 exhibits slight increases at concentrations above 4 %. Curing temperature had a more significant effect compared with concentration of

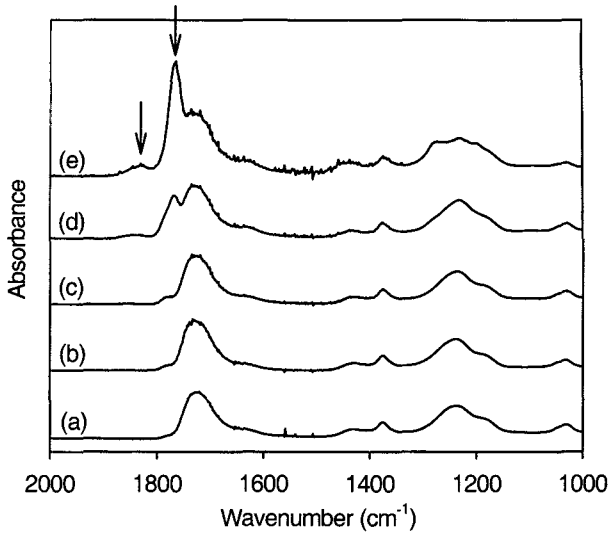

Figure 8. The effect of heat treatment temperature on the re-formation of the anhydride groups in hydrolyzed P(MAn-co-VAc) in the absence of catalyst, (a) 120 °C, (b) 140 °C, (c) 160 °C, (d) 180 °C, and (e) 200 °C.

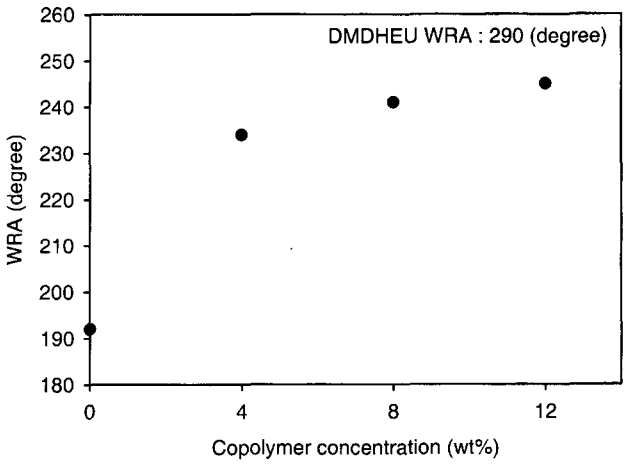

Figure 9. The effect of concentration of P(MAn-co-VAc), M_n 5 300, in the padding bath on the wrinkle recovery angle (WRA, W+F) of cotton fabric padded, cured at 170 °C for 3 min., and then treated with softening agent.

the copolymer in the padding bath, but yellowing of the fabric occurred at curing temperatures above 180 °C. The effect of molecular weight of P(MAn-co-VAc) on the WRA of treated cotton fabrics padded with 10 % (wt.) copolymer, 4 % sodium hypophosphite catalyst and 0.2 % Triton X-100 then cured at 170 °C for 3 min. is shown in Figure 10. WRA values comparable to DMDHEU treated fabrics (6 % DMDHEU, 1.5% $MgCl_2$, other auxiliaries same as in the case of P(MAn -co-VAc) treatment) were obtained with the two lower molecular weight P(MAn-co-VAc)s. The lower molecular weight appears to have been a positive factor in the penetra-

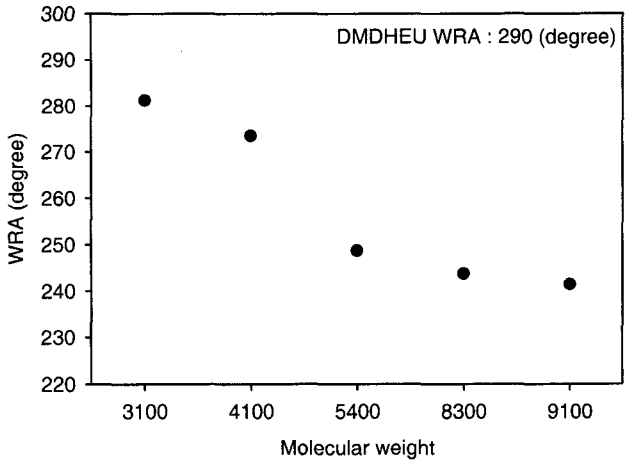

Figure 10. The effect of molecular weight of P(MAn-co-VAc) on the wrinkle recovery angle (WRA, W+F) of cotton fabric padded with 10 %(wt.) P(MAn-co-VAc) and cured at 170 °C for 3 min., then treated with softening agent.

Table 3. Tensile strength of 10 %(wt.) P(MAn-co-VAc) padded cotton fabrics cured at 170 °C for 3 min. compared with cotton, and DMDHEU treated cotton fabrics. (DMDHEU treatment: 6 %(wt.) with 1.5 %(wt.) $MgCl_2$ catalyst, cured at 170 °C for 3 min.; same softening agent treatment in DMDHEU and P(MAn-co-VAc) treated fabrics)

Sample		Load at break (N)	
		Warp direction	Weft direction
Cotton fabric		290	280
DMDHEU treated cotton fabric		240	210
Poly(MAn-co-VAc) treated cotton fabric	M_n of poly (MAn-co-VAc) 9 100	300	240
	8 300	290	240
	5 300	290	230
	4 100	290	260
	3 100	280	290

tion of the cross-linking agent into cellulose. When higher molecular weight copolymers were used, the finished fabric had a stiff starchy feel indicating that most copolymers were deposited on the surface of the fabric. The strengths of the cotton fabrics treated with P(MAn-co-VAc) were comparable to the original scoured and bleached cotton fabric, while the DMDHEU treated fabric exhibited great decrease in the strength (Table 3).

Conclusion

Low molecular weight poly(maleic anhydride-co-vinyl acetate) copolymers, P(MAn-co-VAc), were prepared to develop polymeric cross-linking agents. The control of molecular weight was efficient when the comonomer feed ratios were varied compared with when the concentrations of the initiator or the chain transfer agent were varied. P(MAn-co-VAc) of number average molecular weights below 5 000 could be obtained by adding greater amounts of maleic anhydride compared with vinyl acetate. The growth of the copolymer chain appears to have ceased on depletion of vinyl acetate. The anhydride groups hydrolyze on addition of the copolymer to water, but can be re-formed in the curing stage. The copolymer of Mn 3 100 was most efficient in enhancing the wrinkle recovery angle of the treated cotton fabric, and results comparable with DMDHEU have been obtained. The strength retention of P(MAn-co-VAc) treated cotton fabrics was superior to DMDHEU treated fabrics.

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