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Durable press finishing of cotton fabrics with polyamino carboxylic acids

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ABSTRACT

In this study, a polyamino carboxylic acid was synthesized by reaction of a commercial polyvinylamine and bromoacetic acid. The reaction product was used for crosslinking of cotton fabric by a pad-dry-cure process. Crosslinking of the finished cotton occurred via the formation of ester bonds between the carboxylic groups of the polyamino carboxylic acid and the hydroxyl groups of cellulose. Ester bonds were confirmed by appearance of the corresponding absorbance at 1730 cm^{-1} in the FTIR spectrum of the finished cotton. The created durable press effect on the finished cotton with polyamino carboxylic acid was evaluated by measuring the wrinkle recovery angle (WRA). Impact of this finishing agent on the physical properties of the cotton was studied by evaluating the tensile strength and whiteness index, and softness of the finished cotton. The easy care effect was durable against laundering. Softness, whiteness, and tensile strength of the finished cotton have not changed significantly.

1. Introduction

Cotton fibers are the most important natural fibers in apparel industry. Since cotton can readily absorb moisture, the apparels which are made by cotton fabrics are the most comfortable garments. Despite the numerous advantages, there are also some disadvantages, such as easy wrinkling of fabric in practical applications (Kadolph & Langford, 2001; Schindler, 2004). One of the first attempts to overcome this problem was crosslinking of cellulose with formaldehyde-based compounds, mainly dimethyloldihydroxyethylenurea (DMDHEU) (Berbner, 1990; Geubtner, 1990; Levin, 1983; Sharpe & Mallinson, 2003). Environmental concerns and potential danger of formaldehyde caused to introduce formaldehyde-free reagents for easy-care finishing of cotton fabric (McKerron, 1987; Yoon, Woo, & Seo, 2003). Given this, polycarboxylic acids such as 1,2,3,4-butanetetracarboxyic acid (BTCA) and citric have been used as the formaldehyde-free finishing agents of cotton (Kittinaovarat, Kantuptim, & Singhaboonponb, 2006; Sauperl & Ribitsch, 2009; Yang & Wang, 1996). The mechanism of durable press finishing of cotton with polycarboxylic acids is based on esterification of cellulose chains through the formation of an intermediate cyclic anhydride of the polycarboxylic acid and its further reaction with the hydroxyl groups of cellulose (Gillingham, Lewis, & Voncina, 1999; Gu & Yang, 1998; Schindler, 2004; Yang, 1993b). Yang et al. have studied easy care finishingof cotton fabrics using different polycarboxylic acids. They analyzed the effects of process conditions such as catalyst, pH and temperature on the crosslinking of cellulose by esterification (Yang & Andrews, 1991; Yang & Wang, 1997; Yang, 1991a, 1991b; Yang, 1993a, 1993b). Nevertheless, easy care finishing with polycarboxylic acids causes some problems, e.g. yellowing of fabric, deterioration of tensile strength, and also relative expensive cost of the reagents (Bhattacharyya, Doshi, & Sahasrabudhe, 2003; Sircharussin, Ryo-Aree, Intasen, & Poungraksakirt, 2004; Lam, Kan, & Yuen, 2011). Due to these drawbacks, there is still a great interest to develop new products for easy care finishing of cotton fabrics, which are formaldehyde-free, inexpensive, showing less yellowing effect, and less impact on mechanical properties of the finished cotton fabric.

In this regard, polyamines may be interesting compounds. Polyvinylamine is already produced on an industrial scale for various industrial applications. Polyvinylamine (PVAm) is a linear cationic polymer. The chemical structure is shown in Scheme 1 (Schröer, 1994). The primary amino groups attached at the molecular chain can be functionalized easily.

Protonated polyvinylamine has a high charge density and adsorb on negative charged surfaces. The industrial applications of polyamines can be enlarged through chemical modification of these compounds, e.g. carboxylation of polyamines leads to the formation of amphoteric polymers with excellent complexing-properties. The reaction of a linear polyvinylamine and a halocarboxylic acid (e.g. bromoacetic acid) under alkaline conditions results in a carboxylated polyvinylamine (the polyamino carboxylic acid). The carboxylated polyvinylamine may react with the hydroxyl groups of the cellulose molecule (Scheme 2).

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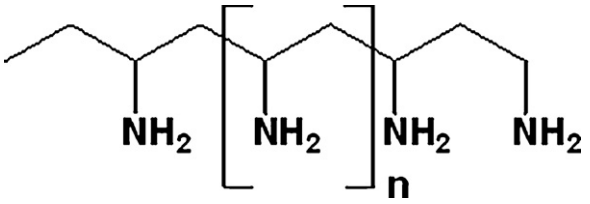
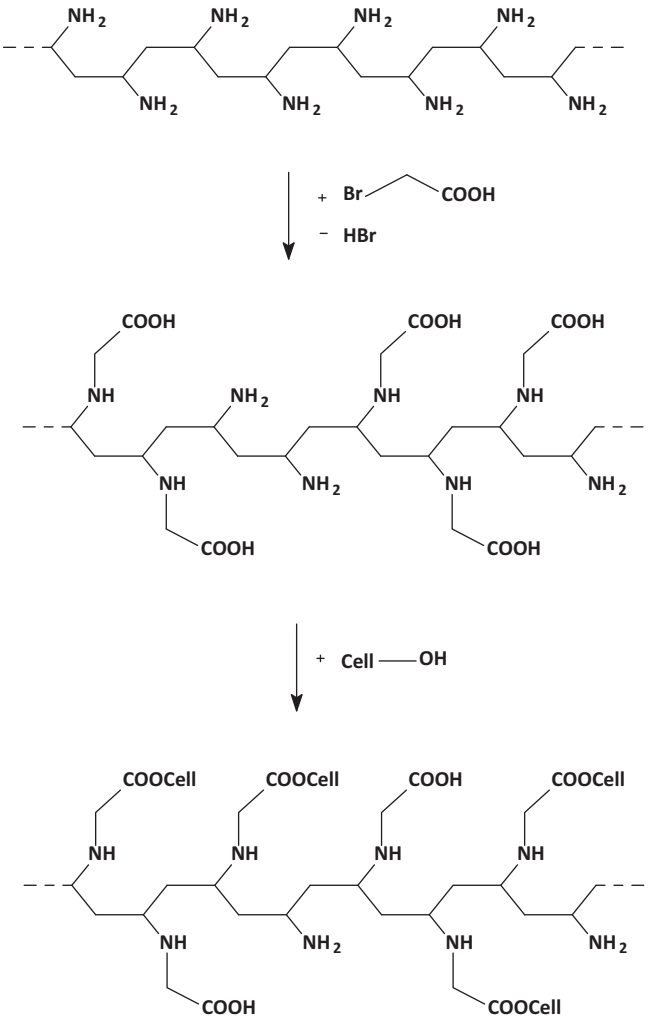


Scheme 1. Chemical structures of polyvinylamine.



Scheme 2. Carboxylation of polyvinylamine (PVAm) with bromoacetic acid and crosslinking of cellulose with the carboxylated PVAm.

The purpose of this study was the synthesis of polyamino carboxylic acid and its application on cotton fabric as a novel durable press finishing agent. The polyamino carboxylic acid has been synthesized via carboxylation of a polyvinylamine (PVAm) with bromoacetic acid. The resulted substance was purified and chemically characterized using elemental analysis, FTIR and ^{1}H NMR. The finishing effects have been investigated by measuring the wrinkle recovery angle, tensile strength and whiteness index.

2. Materials and methods

2.1. Materials

A standard scoured, bleached and desized plain woven cotton fabric (density 110.66 g/m^2) was supplied by Testex. Polyvinylamine (Lupamin 1595®, M_w 10000 g/mol, concentration 10–15%, BASF), bromoacetic acid (99%, Merck), hydrochloric acid (32%, Merck), ethanol (Merck), sodium hydroxide (99%, Merck), acetic acid (99%, Merck), phosphoric acid (85%, Merck), boric acid (Flucka), methylene blue (Merck), potassium bromide (Merck), sodium hypophosphite (Alfa Aesar), and a cation exchanger (Lewatit SC 102, Bayer AG) were used as commercial products without any further purification.

2.2. Methods

2.2.1. Carboxylation of PVAm

Polyvinylamine (PVAm) was carboxylated by adding bromoacetic acid to an alkali aqueous solution of PVAm (1–8% (w/v), pH 11, different mole ratio PVAm:bromoacetic acid; 1.00:0.25, 1.00:0.50, 1.00:0.75 and 1.00:1.00). The reaction was completed after 24 h at room temperature and the pH value of the solution was adjusted to 6–7 using hydrochloric acid. Water was removed under vacuum and the obtained solid was washed with ethanol. A cation exchanger (20 g in 200 ml distilled water) was used to extract sodium chloride and sodium bromide from the solid. The solution was evaporated under vacuum and the resulted solid washed with ethanol and dried at 60 °C for 24 h.

2.2.2. Chemical characterization of carboxylated PVAm

The degree of substitution (DS) was calculated from elemental analysis using the ratio of carbon to nitrogen (C/N) of the carboxylated PVAm. FTIR and ^{1}H NMR spectroscopy were used for further characterization of the carboxylated PVAm. FTIR spectroscopy was carried out by an IRPrestige-21 (Shimadzu) with resolution of 4 cm^{-1} and 40 scans for each spectrum. Potassium bromide was used as reference material. The elemental analysis of the synthetized carboxylated PVAm was done by EA 3000 (Hekatech). ^{1}H NMR spectra were recorded using a Bruker DMX300 with deuterated ethanol as solvent.

2.2.3. Finishing of cotton fabric with carboxylated PVAm

Finishing of cotton samples was done by a pad-dry-cure process. Each cotton sample weighted 8 g and the liquor-to-goods-ratio was 12.5:1. The cotton fabrics were stirred for 2 h at room temperature in the solutions containing carboxylated PVAm (1%, w/v) and sodium hypophosphite (60 g/l) as catalyst. Afterward, they were padded in a laboratory padding frame with 100% wet pick-up, dried at 85 °C for 10 min and cured at 170 °C for 6 min in a Matthis stenter. Finally the finished cotton fabrics were rinsed for 5 min with tap water and then 5 min with distilled water to remove unreacted chemicals from the surface of the cotton fabrics. The rinsed samples were dried at room temperature and conditioned (24 h, 20 °C, 65% humidity).

2.2.4. Gravimetric test

The conditioned cotton samples were weighted before and after finishing and the relative weight increase was calculated using the following equation:

$$\text{relative weight increase [\%]} = \left(\frac{m_2 - m_1}{m_1}\right) \times 100$$

where m_1 is the weight of original sample and m_2 is the weight of finished cotton sample. Every experiment was performed in triplicate. The precision of the obtained value of relative weight increase was ±1.2%.

2.2.5. Determination of carboxyl groups

The carboxyl group content of the finished cotton fabrics using carboxylated PVAm with different degree of substitution was

Table 1
Experimental degree of substitution of carboxylated PVAm, calculated from C/N ratio of elemental analysis (DS_{EA}) and peak area ($PA_{^1H\,NMR}$) of ^1H NMR ($DS_{^1H\,NMR}$).

Mole ratio PVAm:bromoacetic acid (±0.01)	C/N	DS_{EA} (%)	$PA_{^1H\,NMR}$	$DS_{^1H\,NMR}$ (%)
1.00:0.00	1.7	0	0	0
1.00:0.25	2.1	22.5	0.87	21.7
1.00:0.50	2.5	48.7	1.69	42.2
1.00:0.75	2.9	69.6	2.47	61.7
1.00:1.00	3.3	94.6	3.89	97.5

measured using methylene blue test (Klemm, Phillip, Heinze, & Wagenknecht, 1998).

2.2.6. FTIR spectroscopy of finished cotton fabric

An IRPrestige-21 (Shimadzu) was used for study of FTIR spectroscopy of the finished cotton with resolution of 4 cm^{-1} and 40 scans for each spectrum. The samples were treated with 0.1 M NaOH solution at room temperature to convert the free carboxyl to carboxylate, dried and finally prepared by pressed-disc technique before FTIR spectroscopy (Lewis & Voncina, 1997a, 1997b; Udomkichdecha, Kittinaovarat, Thanasoonthornroek, Potiyaraj, & Likitbanakorn, 2003; Yang, 1991b).

2.3. Measurement of wrinkle recovery angle, tensile strength, whiteness-index and wash fastness

Wrinkle recovery angle (WRA) of the cotton samples was measured according to DIN 53891 with a Monsanto wrinkle recovery tester (Karl Frank GmbH, Weinheim-Birkenau). The tensile strength was determined according to DIN 53530 (Zwick Universal Test Device 1445). The whiteness index was evaluated according to CIE-Lab method using a spectrophotometer (3880, Datacolor). WRA, tensile strength, and whiteness index were measured at least using 5 cotton samples and the mean value was recorded. Fastness of durable press effect against laundering was evaluated according to EN ISO 105-CO6: 1997 (liquor volume 150 ml, liquor-to-goods-ratio 1:30, ECE detergent 4 g/l, 30 min, 40 °C).

3. Results and discussion

The degree of substitution (DS) of carboxylated PVAm has been calculated from the C/N ratio. Due to the introduction of carboxylic groups in PVAm the C/N ratio changes. In Table 1 the results of elemental analysis are summarized. The C/N values have been obtained from the results of the elemental analysis and DS_{EA} are the calculated DS from these C/N values.

The chemical structure of the synthetized polyamino carboxylic acid was confirmed by ^1H NMR spectroscopy. ^1H NMR spectra of PVAm showed two singlets at 2.2 and 4.1 ppm with peak area of 12.02 and 6.24, respectively (Fig. 1a). These peaks have been attributed to the protons in CH_2— and CH—(—CH_2—CH—NH_2)$_n$, respectively. The carboxylated PVAm showed a new triplet at 1.2 ppm, according to the protons of methylene group (—CH_2) adjacent to the carboxyl group (Fig. 1b) Therefore, a DS value can also be calculated from peak areas of ^1H NMR spectra. The results are presented in Table 1.

Infrared spectroscopy (FTIR) was as well used to obtain information about the chemical structure of carboxylated PVAm. In Fig. 2 the FTIR spectra of PVAm and carboxylated PVAm are given. The spectrum of PVAm showed a signal at 1670 cm^{-1} and a broad signal at 3369 cm^{-1}, attributed to the primary amine group (—NH_2) and NH_2— stretching, respectively. The signal at 1175 cm^{-1} has been attributed to the stretching of C—N bond. As it can be seen from the spectrum of the carboxylated PVAm (DS 22.5%), a new intense peak was seen at 1735 cm^{-1}, belonging to the carboxyl group (—COOH).

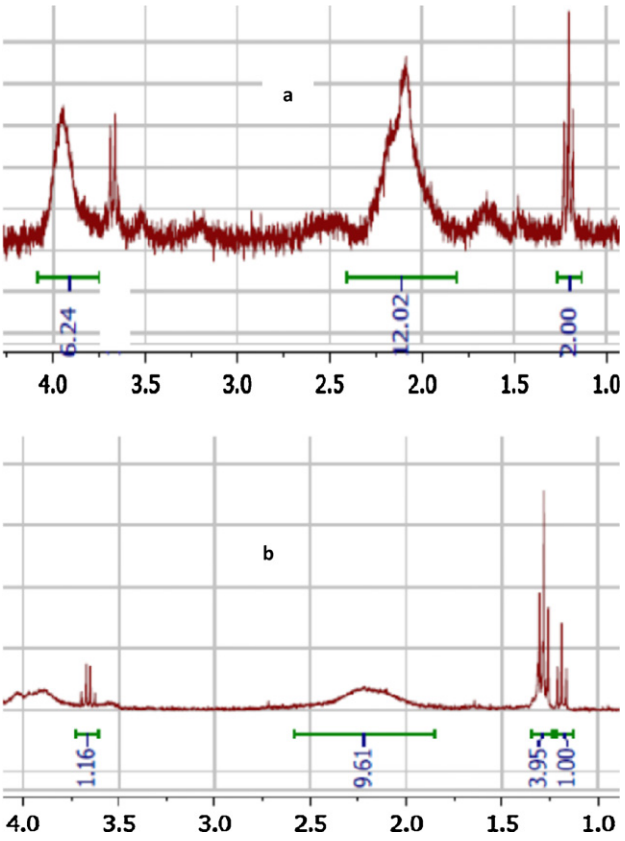


Fig. 1. ^1H NMR spectra of PVAm (a) and carboxylated PVAm (b) with a DS value of 94.6%.

The appearance of this signal confirmed the carboxylation of PVAm, too. With increasing degree of substitution the intensity of carboxyl bond at 1735 cm^{-1} also increased.

In Fig. 3 the relationship between the amounts of fixed carboxylated PVAm on cotton as a function of concentration of the carboxylated PVAm in solution (DS 94.6%) is shown. With increasing concentration of carboxylated PVAm the weight of the finished cotton increased, indicating the successful fixation of the carboxylated PVAm. The solution with an initial concentration of carboxylated PVAm of 8% in dipping process has resulted to a weight increase of 3.4%.

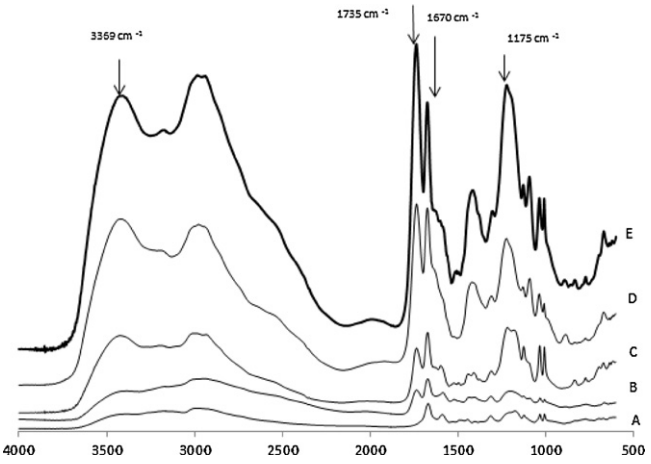


Fig. 2. FTIR-spectra of PVAm (A) and carboxylated PVAm of different degree of substitution (DS); (B) DS 22.5%; (C) DS 48.7%; (D) DS 69.6% and (E) DS 94.6%.

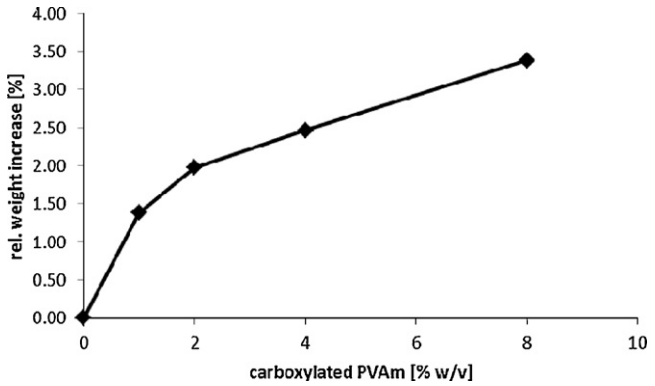


Fig. 3. Relative weight increase of cotton finished with carb. PVAm vs. concentration of carboxylated PVAm (DS 94.6%) in solution.

In Fig. 4 the weight of the finished cotton samples as a function of the degree of substitution of the carboxylated PVAm used is given. Fig. 4 shows that with increasing the degree of substitution (DS) relative weight of finished fabric increased and approving the permanent fixation of the polyamino carboxylic acid on the cotton fabric.

Fixation of the synthetized polyamino carboxylic acid on the cotton fabric has occurred through the formation of ester bond. The FTIR spectrum of cotton finished with polyamino carboxylic acid (DS 94.6%) showed a signal at 1730 cm^{-1}. This signal has been attributed to the ester bond and confirmed the esterification of the finished cotton (Gillingham et al., 1999; Yang, 1991a). The FTIR spectrum of the finished cotton is presented in Fig. 5. It has been suggested by some authors that esterification of cotton can occur through formation of 5-member or 6-member cyclic anhydride intermediates, which easily reacts with the hydroxyl groups of the cellulose chain (Gillingham et al., 1999; Welch, 1994; Yang, 1993c; Yang & Wang, 1996, 1997). However, esterification via formation of *n*-member cyclic anhydrides has been reported, too (Martel, Morcellet, Ruffin, & Weltrowski, 2002; Martel, Weltrowski, Ruffin, & Morcellet, 2000). This may be a possible mechanism for the reaction of the carboxylated PVAm with cotton.

Regarding to the crosslinking mechanism it can be supposed that the additional free carboxylic groups in the carboxylated PVAm which are accessible in cellulose reflects the effectiveness of cotton crosslinking. Thus, the quantitative measurement of free carboxylic groups in cotton is useful to evaluate the effectiveness of crosslinking (Sauperl & Ribitsch, 2009). The amount of free carboxylic groups present on the finished cotton as a function of the degree of substitution of carboxylated PVAm is shown in Fig. 6. As expected, with increasing the number of carboxylic groups bound to the PVAm,

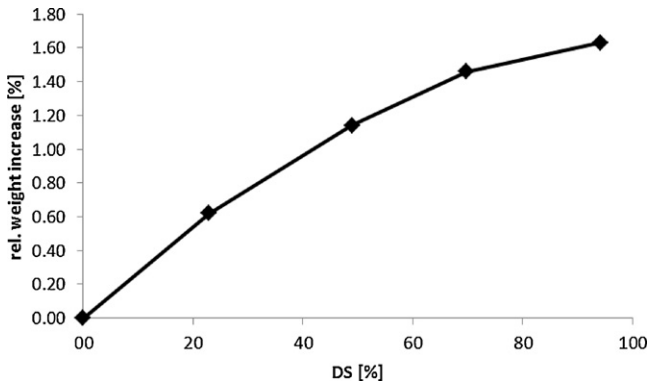


Fig. 4. Relative weight increase of the finished cotton vs. degree of substitution (DS) of the carboxylated PVAm (1%, w/v) in solution.

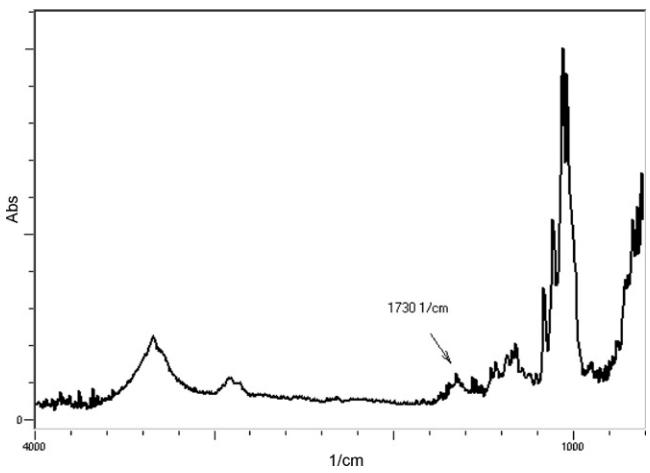


Fig. 5. FTIR-spectrum of cotton finished with carboxylated PVAm (DS 94.6%, 1% (w/v)).

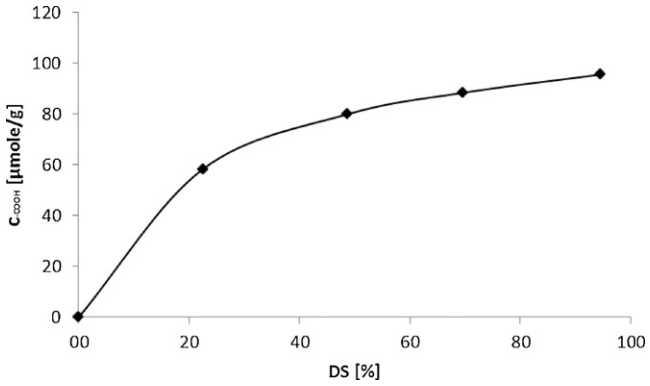


Fig. 6. Carboxyl group content of the finished cotton fabric (c_{-COOH}) vs. degree of substitution (DS) of the carboxylated PVAm (1%, w/v) in solution.

the amount of unreacted carboxylic groups on the cotton fabric increased.

To evaluate the performance of durable-press induced by carboxylated PVAm, wrinkle recovery angle (WRA) and the durability of the obtained easy-care properties to laundry washing of cotton fabrics finished with carboxylated PVAm of different degrees of carboxylation were measured. The results are presented in Table 2.

These results show that the use of carboxylated PVAm produced a durable press effect in the finished fabric. The improvement of this effect depends on the number of ester bonds formed between the hydroxyl groups of cellulose and the carboxyl groups in the polycarboxylic acids (Trask-Morrell, Kottes Andrews, & Graves, 1990; Welch, 1988, 1990). The wrinkle recovery angle from 101° in original cotton improves to 161° in the cotton finished with carboxylated PVAm (DS 94.6%).

Table 2
Wrinkle recovery angle (WRA°) of the original cotton (0) and the cotton finished with carboxylated PVAm (1%, w/v) of different degrees of substitution (DS), and its durability against laundry washing (no. washing cycles: 1–5).

DS (%)	WRA°	$WRA°_1$	$WRA°_5$	Loss in WRA°-after 5 washing cycles (%)
0	101	–	–	–
22.5	114	104	102	11.7
48.9	123	116	111	10.8
69.8	137	129	125	9.6
94.2	161	152	148	8.7

Table 3
Tensile strength and whiteness index of the original cotton (0) and the cotton finished with carboxylated PVAm (1%, w/v) of different degrees of substitution (DS).

DS (%)	Tensile strength		Whiteness index	
	Measured tensile strength (*N*)	Loss of tensile strength (%)	Measured whiteness index	Loss of whiteness (%)
0	527	–	78	–
22.5	511	3.13	43	81.4
48.9	501	5.19	54	44.4
69.8	455	15.82	58	34.5
94.2	416	26.69	64	21.2

Also in Table 2 the durability of this easy-care effect after 5 washing cycles is given. The durable-press effect was only reduced by 9% in the case of cotton finished with carboxylated PVAm with a DS value of 94.2%. With increasing number of ester bonds, the number of unhydrolyzed ester bonds and consequently the wash resistance of the durable press effect increased.

Tensile strength and whiteness index of the finished cotton fabrics have been measured to evaluate the impact of finishing with carboxylated PVAm on the physical properties of the cotton. The results are presented in Table 3. As expected, the creation of durable-press effect by crosslinking of cellulose with carboxylated PVAm reduced the tensile strength. The crosslinking of cellulose inhibited distribution of tear stress over many molecules which can slightly shift the external forces (Schindler, 2004). Also, the acidity of the finishing solution caused a reduction of the tensile strength (Schindler, 2004). Generally durable press finishing of cotton fabric with polycarboxylic acids or formaldehyde-based chemicals leads to yellowing of finished cotton. The use of carboxylated PVAm as finishing agent also caused yellowing of cotton. However, with increasing value of the DS, whiteness index increased. In addition to the measurable physical properties, the softness of the finished cotton did not change significantly.

Another important factor for a durable press finishing is kind and amount of catalyst. Sodium hypophosphite has been proven to be the best catalyst for crosslinking of cotton with polycarboxylic acids (Gu & Yang, 2000; Lammermann, 1992; Rowland, Welch, Brannan, & Galagher, 1967; Welch & Peter, 1997; Welch, 1990). In this study also sodium hypophosphite has been used as catalyst. The influence of concentration of sodium hypophosphite on durable-press properties of finished cotton is presented in Fig. 7. Using 60 g/l of sodium hypophosphite, the wrinkle recovery angle (WRA) reached an optimum and decreased at higher concentrations.

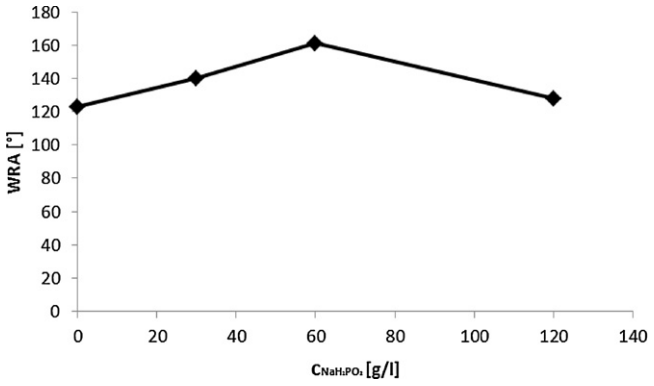


Fig. 7. The effect of concentration of sodium hypophosphite ($c_{NaH_2PO_2}$) on the wrinkle recovery angle (WRA) of cotton finished with carboxylated PVAm (DS 94.6%, 1% (w/v)).

4. Conclusion

Polyamines such as polyvinylamine can be easily converted to polyamino carboxylic acids. They can be used as effective crosslinking agents for durable press finishing of cotton fabrics. Polyamino carboxylic acid is permanently fixed on the cotton fabric via formation of ester bonds creating a durable press effect. With increasing number of carboxyl groups bound to the polyamine used, the wrinkle recovery angle of the finished cotton increases and the created effect has more durability against laundering. Tensile strength, whiteness and softness of the finished cotton do not change intensely. Unsubstituted amino groups in carboxylated polyamine are suitable for further chemical reactions on the cotton. Thus, additional finishing effects are possible. The results will be published in the near future.

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