

Alkaline Treatment of Cotton in Different Reagent Mixtures with Reduced Water Content. II. Influence of Finishing Procedure

Constanta Ibanescu,^{1,2} Christian Schimper,¹ Thomas Bechtold¹

¹Christian-Doppler Laboratory for "Textile and Fibre Chemistry of Cellulosics", Institute of Textile Chemistry and Textile Physics of Leopold-Franzens University Innsbruck, 6850 Dornbirn, Austria

²Department of Macromolecules, Faculty of Industrial Chemistry, "Gh. Asachi" Technical University, 700050 Iasi, Romania

Received 16 November 2005; accepted 10 November 2006

DOI 10.1002/app.24077

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Changes in cotton fabrics brought about by different swelling agents and different types of finishing procedures have been studied in this work, using a single-step swelling of cotton in the reagent. Cotton fabrics were treated with different alkalis and mixtures of alkalis and other additives and finished with a modified type of 1,3-dimethylol-4,5-dihydroxyethylene urea, using wet-on-wet and wet-on-dry technique. Properties generally used to characterize mercerized cotton were selected that are technologically important, such as water retention, shrinkage,

stiffness, and crease recovery angle. Water retention method has been used to compare the degree of swelling for different samples. Differences in properties among these samples were observed and some practically important conclusions were arrived at. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1194–1201, 2006

Key words: fibers; crosslinking; curing of polymer; resin; swelling

INTRODUCTION

Since Mercer and Lowe proposed the alkaline treatment to improve cotton fabric properties, a lot of work was carried out to find the right recipes and conditions for general and special purposes.¹

Swelling pretreatments for cotton fabrics are used to improve dimensional stability, dyeability, luster, softness, and textile performances both before and after crosslinking to impart smooth drying properties. Such pretreatments include caustic mercerization and liquid ammonia treatment.

The present work is a follow-up of a study on the mercerization of cellulose fabrics, using different alkali solutions and mixtures of alkali and different additives.

All types of cellulosic materials have the same crystalline structure called cellulose I. This structure is destroyed to some level by some solvating or swelling treatments. During this transformation, the original, parallel-chain crystal structure of cellulose I changes to that of cellulose II, which is based on antiparallel chains.²

Alkali treatment of fabrics usually yields different results as fiber or yarn mercerization characterized by higher swelling at surface and low penetration into interior of fabric. Therefore, a lot of attention has to be paid to the uniformity of alkali treatment that is affecting especially mechanical properties of fabrics.

Durable press finishing, used to overcome wrinkling problems in cotton fabrics, involves crosslinking agents that covalently crosslink with hydroxyl groups of adjacent cellulose polymer chains within cotton fibers.

Substantial scientific work on the development of crosslinker-systems for cotton textiles was done by Rowland and coworkers.³ These studies also covered changes in pore structure and alkali sorption behavior of the crosslinked cotton.^{4,5} As an outcome of the research activities, also information about the different reactivity of the hydroxyl groups in cellulose chains was obtained.⁶ Because of the importance of cellulose crosslinking operations for cellulose textile finishing, up to present time extensive research about the application of crosslinkers for pad-dry-cure operations has been undertaken.^{7–11}

1,3-Dimethylol-4,5-dihydroxyethylene urea (DMD-HEU) is the most widely used crosslinking agent because it provides good durable press properties at a lower cost and an acceptable level of detrimental effects on fabric strength and whiteness when compared with other *N*-methylol agents.¹²

Correspondence to: C. Ibanescu (textilchemie@uibk.ac.at).

Contract grant sponsors: CD-Research society and Vorarlberger Landesregierung.

TABLE I
Formulations Used for Alkaline Treatment

Sample no.	NaOH, (mol/L)	KOH, (mol/L)	Sodium silicate, (mol/L)	NaCl, (mol/L)	Glycerin, (mol/L)	Na-gluconate, (mol/L)	Water, (mol/L)	Label for samples
1	3.13						54.94	A
2	3.75						54.38	
3	5.00						53.83	
4	6.25						53.27	
5	7.50						51.61	
6		3.13					52.44	A
7		3.75					52.16	
8		5.00					50.22	
9		6.25					49.11	
10		7.50					46.61	
11	3.13			1.71			52.16	B
12		3.13		1.71			49.94	
13	3.13				2.17		46.34	C
14		3.13			2.17		44.12	
15	3.13		0.31				51.33	D
16		3.13	0.31				47.84	
17	3.13					0.46	51.33	E
18		3.13				0.46	49.11	
19	7.50			3.42			46.89	F
20		7.50		3.42			47.45	
Blank				Raw material				
A1				Ammonia treated - reference sample				R

A homogenous distribution of the resin in the fabric results in a more favorable balance of proprieties: shrinkage in process is reduced and crease recovery angle (CRA) is increased when compared with non-resin-finished samples.

In a previous work,¹³ the swelling of cotton fabrics in sodium hydroxide and potassium hydroxide solutions of different concentrations as well as in mixtures of these alkali solutions and some specific additives was investigated. It was proved that swelling power of the alkali hydroxides depends on the cationic size and concentration of solution. It was noted that the structure–property relationship had some specificity to the swelling agent as well, in other words, it was influenced by the type of additive added in alkali hydroxides. Alkali-treated samples were compared with ammonia-treated textiles and the results indicated a possible alternative to ammonia treatment without affecting final quality and end-use properties of fabrics.

In this part of the study, the influence of different types of finishing procedures was analyzed. The samples treated with alkali solutions and alkali mixtures were crosslinked with DMDHEU, using wet-on-wet and wet-on-dry technique. Ammonia-treated samples (reference samples) were resin finished in the same way, and some properties generally used to characterize mercerized cotton that are technologically important, such as water retention, shrinkage in process, stiffness, CRA for the two categories of textiles, were compared.

EXPERIMENTAL

Materials

The fabric used in this study was a 100% cotton plain woven fabric, with 54 ends and 30 picks per cm, and a weight of 112 g/m² (F. M. Haemmerle Textilwerke GmbH, Dornbirn, Austria). It was a blue, yarn dyed, desized, and unbleached material. Chemicals used were as follows: sodium hydroxide (NaOH) solution 50%, (K. Deuring and Co.), and potassium hydroxide (KOH) pellets, (Riedel-de Haen), sodium silicate, (K. Deuring and Co), sodium chloride (NaCl) of technical grade (SALIN, Salinen, Austria), glycerin (Merck), and sodium gluconate (Merck). The crosslinking reagent was a modified type of 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU), Clariant. Magnesium chloride (MgCl₂) of technical grade was used as catalyst in crosslinking reaction.

Methods

Fabric samples, of dimensions 30 × 100 cm², were padded using solutions described in Table I. The samples were padded through liquor in a one-dip-one-nip operation in an HVF-type horizontal padder, from Mathis AG, at a roller speed of 1.0 m/min and nip pressure of 1.0 bar. All samples were weighed after padding to determine wet pickup, the values of which ranged from 50–66%.

After padding, all the samples were rolled on glass rods, closed in plastic sheets, and stored for 4 h at

room temperature. After this period, the samples were opened, washed with soft water, neutralized in a 1 mL/L acetic acid solution, and dried at 40°C. The one-meter samples were then cut in three pieces. The first type piece was only dried at 40°C. For the other pieces two types of crosslinking agent application were used:

- wet-on-wet impregnation, involving a 5-dip-5-nip operation;
- wet-on-dry impregnation, involving sample drying for 1 min at 130°C before resin impregnation.

For impregnation, a finishing solution based on DMDHEU (40 g/L), with $MgCl_2$ as catalyst was used. After padding, both the second type samples and the third type ones were dried for 1 min at 130°C and condensed for 45 s at 170°C.

Ammonia-treated samples, kindly supplied by F.M. Haemmerle, resin finished in our laboratory, were analyzed for comparison (reference samples). The influence of the finishing method on final properties of textiles was studied.

Prior to testing, all samples were conditioned for over 24 h in a standard atmosphere at $(20 \pm 2)^\circ C$ and $(65 \pm 4)\%$ relative humidity, and all the evaluation were performed in the same atmospheric conditions.

Analyses performed in this study were as follows:

1. The water retention value (WRV) of cellulosic fabrics was determined as difference between weight of the sample dried at 105°C for 2 h and the weight of the same sample after 10 min centrifugation at $4000 \times g$ (Heraeus Labofuge M) multiplied with 100.¹⁴
2. Determination of crease resistance of textile fabrics by measuring the angle of recovery, method of horizontal fold, and erected free limb on the dry sample (DIN 53,890)—five 5×2 specimens (each along warp and fill) per sample.
3. Shrinkage in process—measuring reduction in length on warp and fill direction and calculation reduction of a definite area. Results were expressed as percentage of the same area in blank samples (raw material).
4. Stiffness—the length needed for the material to produce a 45° angle on warp and fill direction. Results were also expressed as percentage of the corresponding value of the blank sample.

RESULTS AND DISCUSSION

Water retention

Water retention as an important end-use property of cellulose is remarkably changed on crosslinking. The amount and the direction of the change depend

largely on crosslinking agent and crosslink density.¹⁵ Resin crosslinking of samples decreases to some extent the affinity for water, both for ammonia-treated and alkali-treated samples, but this was an expected result.

No essential differences have been noted for the two alkalis used when wet-on-wet procedure was used. For low alkali concentrations, WRVs are almost similar as for ammonia-treated sample, but above 3.75 mol/L accessibility to water of alkali treated samples becomes higher [Fig. 1(a)]. In the case of wet-on-dry application of crosslinker, the influence of the cation in alkali solutions used as swelling agents was noticeable. KOH penetrates into the ordered regions of cellulose at somewhat lower molar concentrations than NaOH, and KOH uptake is higher than that of NaOH up to a lye concentration of about 5 mol/L, while above that concentration, NaOH uptake tends to exceed that of KOH. This behavior is illustrated in Figure 1(c). For samples treated with NaOH solutions, a decrease of affinity for water is noticed up to 5 mol/L. Above this value a sharp increase of WRVs appeared. The image is completely changed when KOH solutions are used as swelling agents. Up to 5 mol/L, a higher affinity for water could be noticed, which remains almost constant above this value. In all cases alkali-treated sample exhibited higher accessibility to water when compared with reference sample (Fig. 1(c)).

The differences induced by the application method of the crosslinking agent could originate in the fact that the accessibility achieved by swelling is decreased by drying because of the aggregation of fibrils and to the possible formation of additional hydrogen bonds, the wet-on-dry procedure involving a supplementary drying step.

Resin finishing decreases WRV for all samples treated with alkali mixtures when compared with nonfinished samples, and a comparison of dry-crosslinked and wet-crosslinked cottons generally shows that the dry treatment reduces water absorption and wet treatment increases it, even if some exceptions could be noticed [Fig. 1(b, d)]. It could be supposed that dry-state treatment introduces covalent crosslinks between cellulose chains, which might be expected to reduce swelling. Wet-crosslinking process probably results in a more open cellulose structure, because crosslinking was performed in swollen state, thus the fibers reswell more and water can penetrate more easily.

Crease recovery angle

Chemical finishing usually improves crease recovery and wrinkle resistance of cotton fabrics, this effect is clear for all samples and this tendency does not depend on the impregnation procedure.

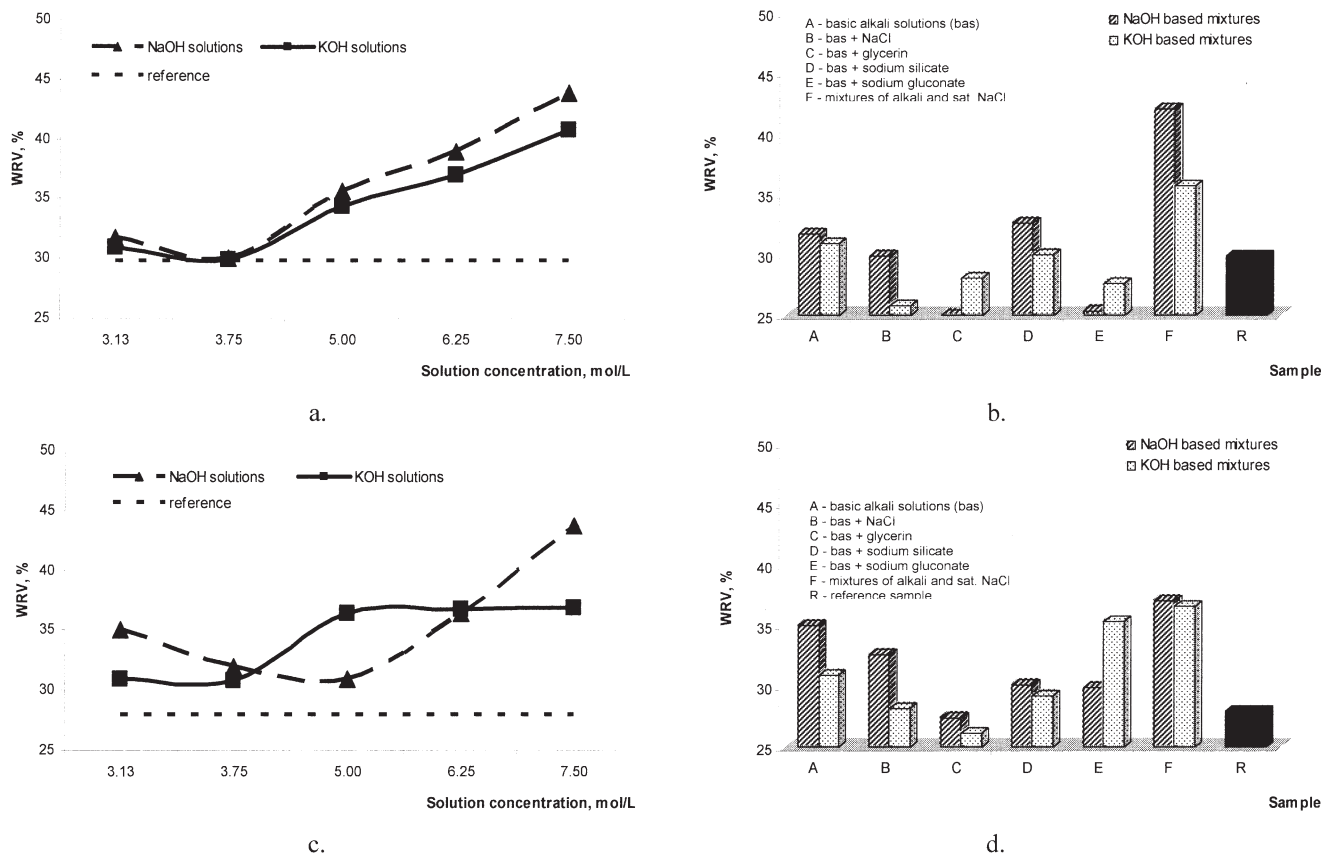


Figure 1 Variation of WRV: (a) with alkali solutions and concentration solutions—wet-on-wet technique; (b) with the type of additive—wet-on-wet technique; (c) with alkali solutions and concentration solutions—wet-on-dry technique; (d) with the type of additive—wet-on-dry technique.

The influence of finishing on crease recovery is dependent on the degree of fiber swelling during crosslinking. During drying, crosslinking in the swollen state appears to affect the initial stages of recovery, whereas crosslinking in the collapsed state influences recovery during deswelling of the fiber.¹⁶ Because two techniques of resin application were used (one involving drying of the sample before impregnation) some influence of these methods on CRA was expected.

The crosslinking of alkali-treated fabrics resulted in a significant improvement of CRA, up to 50° (w+f). Ammonia-treated (reference) samples resulted in improvements even greater than those recorded for alkali-treated materials.

For all samples, the differences between warp and fill direction were generally small. The figures taken into account are the sums of the warp and fill data obtained. For all samples, these values were measured for 5 and 30 min, respectively, and it was noticed that CRA at 30 min exhibits an increase of about 15 units when compared with CRA at 5 min. Thereby, this discussion refers only to CRA after 5 min but all conclusions are valid for CRA for 30 min, too.

An examination of the curves in Figure 2(a, c) suggests that all the crosslinked alkali-treated samples

have higher recovery values than the nonresin finished materials, which indicates the effectiveness of the treatment. However, the influences induced by the alkali treatment are kept after resin finishing, almost all samples exhibiting higher recovery than reference sample.

In the case of samples treated with alkali mixtures with reduced water content, the resin finishing increased CRA and kept resistance to creasing superior to reference sample. No essential differences could be noticed between the two methods of impregnation [Fig. 2(b, d)].

The mechanism whereby resistance to creasing is imparted to cellulose fabrics could be connected with the increase in elasticity of these materials because of the different treatments applied. The increase in elasticity would increase the resistance of the materials to deformation and this effect could be explained as due to filling of the amorphous regions with a three-dimensional resin network or to chemical crosslinking of cellulose. The composite effect over the whole material is dependent on the proportions of crystalline and amorphous regions and on water content, and this could be an explanation for the effect different mixtures had on this property.

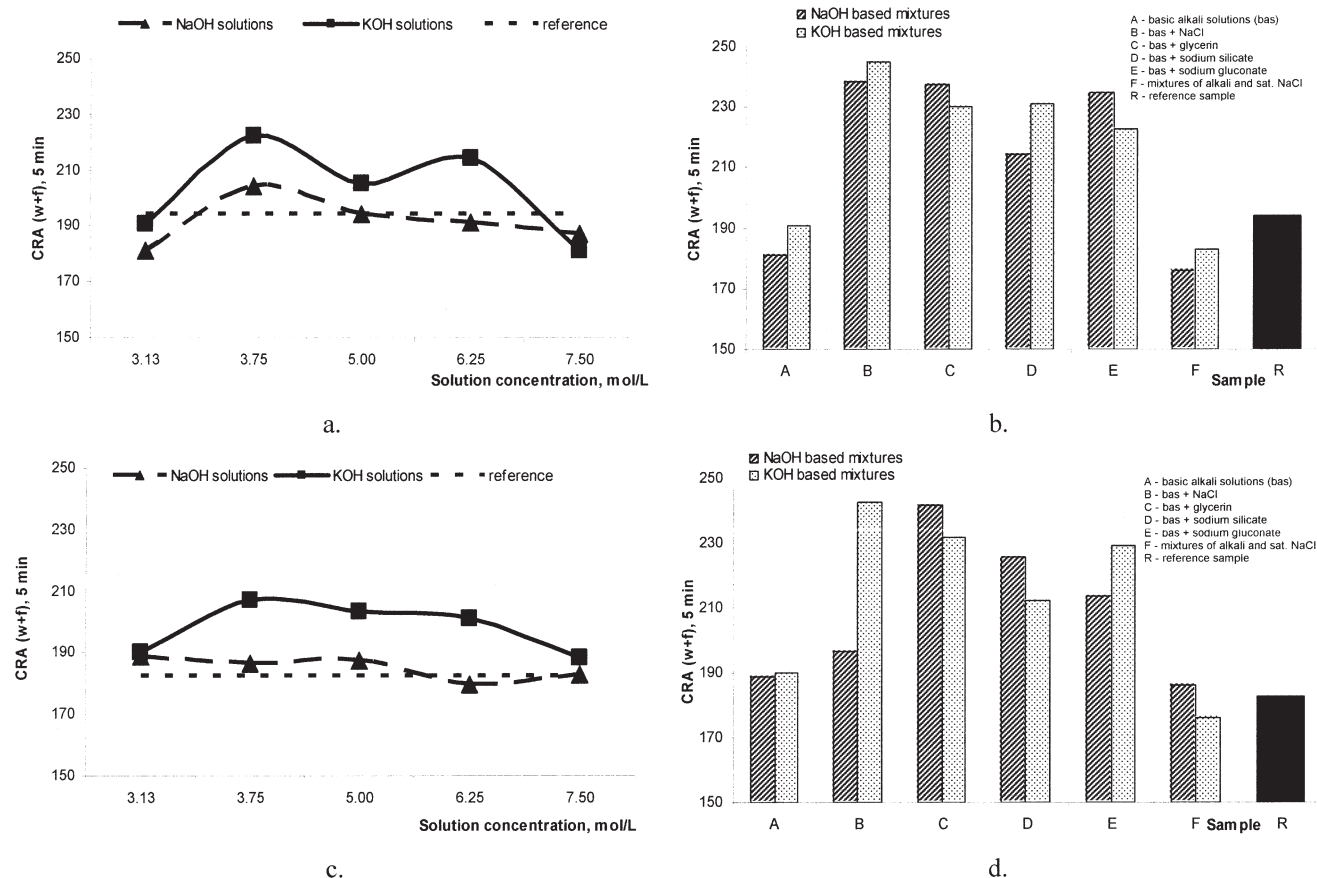


Figure 2 Crease recovery angle: (a) influence of the concentration of alkali solutions—wet-on-wet technique; (b) influence of additive type—wet-on-wet technique; (c) influence of the concentration of alkali solutions—wet-on-dry technique; (d) influence of additive type—wet-on-dry technique.

It is important to emphasize that chemical finishing improved crease resistance of all materials taken into consideration, and after finishing, the effects induced by the mixtures with reduced water content were kept, an improvement of this property when compared with reference sample being achieved. The higher CRA values could be also attributed to the even distributions of crosslinking agent in/on the treated fabrics.

Stiffness

Stiffness was determined by comparison with blank samples and it was expressed, firstly as percentage of blank sample stiffness. For a better relevance of graphs stiffness for each sample was calculated as (sample stiffness—100). So negative values represent a reduced stiffness compared with blank sample and positive values an increased stiffness.

Crosslinking, especially with formaldehyde or formaldehyde urea compounds affects decisively the mechanical properties of cellulose materials constituting the basis of commercial application of cellulose crosslinking in textile industry. Usually, the stiffness

and wrinkle resistance of fabrics are significantly enhanced by crosslinking.¹⁵

No softener was added in the finishing recipes and in this way additional influences were avoided. As expected resin crosslinking decreased samples stiffness, and both techniques used for crosslinker application kept the effects obtained by the use of alkali treatments. For ammonia-treated (reference) sample, both wet-on-wet and wet-on-dry application of resin determined a reduction of stiffness when compared with nonresin-finished sample, the best results being obtained by the use of wet-on-wet method.

Graphs in Figure 3(a, c) allow a comparison of the action of aqueous NaOH, and aqueous KOH onto cellulose on one hand, and of the finishing procedure on the other. The application of crosslinking agent improved stiffness for samples treated both with NaOH and KOH solutions when compared with nonresin-finished samples, but the shape of curves proved the differences existing between the mechanism of action of the two alkalis involved, and, of course, the influence of alkali solution concentrations. Interaction between cellulose and aqueous alkali solutions can be considered to be based on conformational and spatial

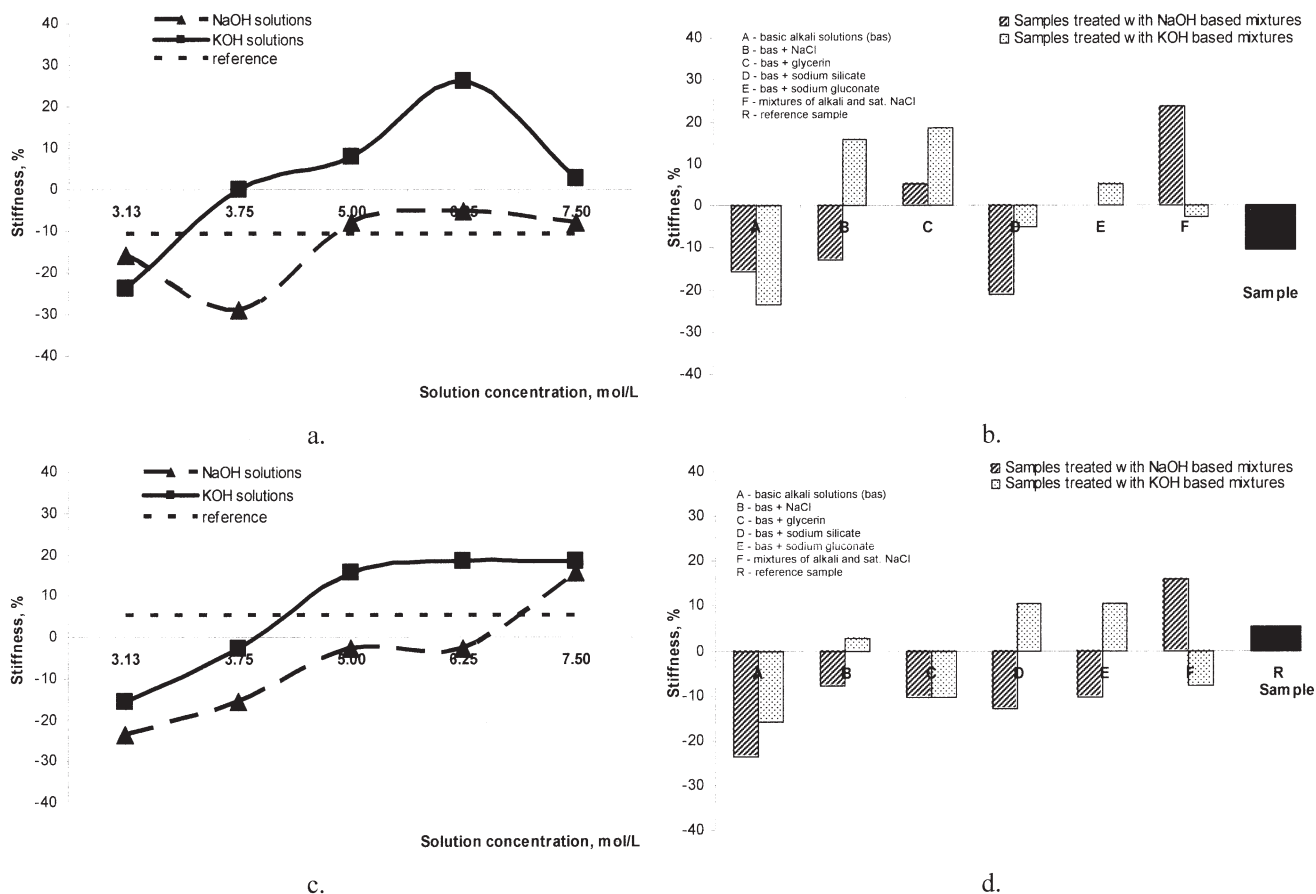


Figure 3 Stiffness: (a) influence of the concentration of alkaline solutions—wet-on-wet technique; (b) influence of additive type—wet-on-wet technique; (c) influence of the concentration of alkaline solutions—wet-on-dry technique; (d) influence of additive type—wet-on-dry technique.

changes of the polymer chains by destruction of the original inter and intramolecular hydrogen bonds in connection with concentration-dependent specific interaction between cellulosic hydroxy groups and hydrated alkali ion dipoles. For lower concentrations of alkali solutions (up to 5 mol/L), this process is governed by an incomplete accessibility of the cellulose structure to alkali penetration, while above this concentration is connected with changes in hydration of the alkali and further insertion of hydroxy groups into hydration shell of the ion dipoles.¹⁵ Differences between the powers of penetration of the two alkalis used and between the dimensions of the hydration shells of NaOH and KOH produced, probably, the differences in the shape of the curves corresponding to NaOH- and KOH-treated samples in Figure 3(a, c).

Samples treated with NaOH exhibited lower stiffness than samples treated with KOH solutions for all concentrations taken into account, and wet-on-wet application of crosslinking agent seemed to be a more favorable technique from the point of view of stiffness.

Analyzing samples treated with mixtures of alkali (NaOH or KOH) and different additives [Fig. 3(b, d)], a significant reduction of stiffness could be evidenced

when compared with nonresin-finished samples and, the most suited method of application proved to be wet-on-dry method. By this procedure almost all mixtures using NaOH as alkali produced samples with lower stiffness both compared with reference sample and blank sample.

Shrinkage in process

Fabric shrinkage was characterized by dimensional change on warp and fill direction and by dimensional change of a specific area. Therefore, if specific area shrinkage (as percent of the same area in blank sample) was calculated, the data plotted in the graphs represented (100—this percentage). Thus, a clear image of how much the shrinkage of a sample differs of blank was obtained.

The way in which shrinkage of nonresin-finished samples was influenced by the type and concentration of alkali solutions and by the different additives added in them was discussed in the first part of this work.¹³

In Figure 4, the extent to which shrinkage was influenced by the finishing method was depicted. Wet-

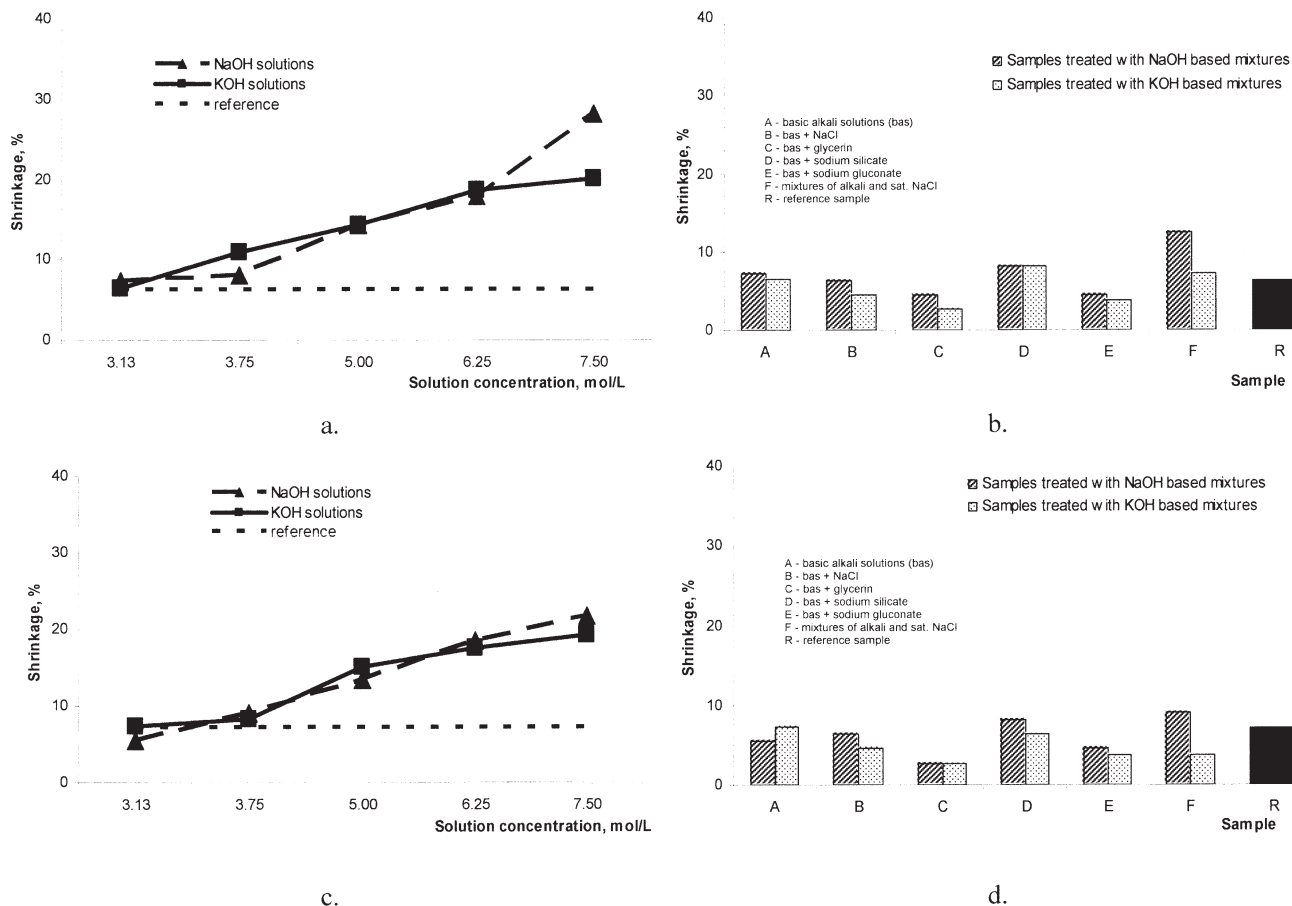


Figure 4 Shrinkage in process: (a) influence of the concentration of alkaline solutions—wet-on-wet technique; (b) influence of additive type—wet-on-wet technique; (c) influence of the concentration of alkaline solutions—wet-on-dry technique; (d) influence of additive type—wet-on-dry technique.

on-wet procedure determined a small decrease in shrinkage for ammonia-treated (reference) sample when compared with wet-on-dry method. As it was demonstrated in a previous work, an increase in alkali solution concentration determined an increase in shrinkage and this tendency is obvious for resin-finished samples, too.

Crosslinking resin treatment improves the shrinkage, especially for wet-on-dry application. A minimum shrinkage was obtained, as expected for less concentrated solutions.

If we compare the influence of additives on fabric shrinkage [Fig. 4(b, d)], the effectiveness and positive influence of resin finishing treatment is clear, the best results being obtained by wet-on-dry application. If in the absence of crosslinking almost all samples treated with mixtures exhibit a higher shrinkage than the reference ammonia-treated sample, the image is completely changed after finishing. Both techniques determine an important reduction in shrinkage when compared with the values corresponding to nonresin-finished state. The lowest values for shrinkage were obtained for the samples treated with a NaOH (or KOH) mixture with glycerin.

In the case of ammonia-treated sample, the influence of finishing procedure on shrinkage is less important than for alkali-treated samples.

CONCLUSIONS

According to all properties investigated, the effects obtained by alkali treatments with mixtures with reduced water content are kept or even enhanced after resin finishing of samples.

The influence of two procedures (wet-on-wet and wet-on-dry) for application of the crosslinking agent on some end-use properties of textiles was analyzed.

As in the case of nonresin-finished samples, the results presented indicate a possible alternative to ammonia treatment without affecting final quality of fabrics. Both types of application techniques proved to be suited for this purpose.

The most promising results were obtained when mixtures of NaOH and NaCl or glycerin were used, which also are expected to have favorable effects on further processing of textiles. Furthermore, the effect of finishing procedures proved to be favorable for the end-use properties of textiles.

In addition, the use of these mixtures for alkali treatment gave supplementary degrees of freedom for the development of new materials with special properties.

The authors thank FM Hämmerle for supplying material, Versuchsanstalt für Textilindustrie and HTL-Dornbirn for permission to use equipment, and Dr. Eduard Burtscher for interesting discussion and remarks.

References

1. Tóth, T.; Borsa, J.; Reicher, J.; Sally, P.; Sajó, I.; Tanczos, I. *Text Res J* 2003, 73, 273.
2. Okano, T.; Sarko, A. *J Appl Polym Sci* 1984, 29, 4175.
3. Rowland, S. P.; Stark, S. M.; Cirino, V. O.; Maon, J. S. *Text Res J* 1971, 41, 57.
4. Bertoniere, N. R.; Martin, L. F.; Blouin, F. A.; Rowland, S. P. *Text Res J* 1972, 42, 734.
5. Honold, E.; Rowland, S. P.; Grant, J. N. *Text Res J* 1969, 39, 1023.
6. Roberts, E. J.; Wade, C. P.; Rowland, S. P. *Carbohydr Res* 1971, 17, 393.
7. Welch, C. M. *Rev Progr Color* 1992, 22, 32.
8. Sharpe, G.; Mallinson, P. In *Textile Finishing*; Heywood, D., Ed.; Society of Dyers and Colourists: Bradford, 2003; p 337.
9. Reinert, F. *Textilveredlung* 1989, 24, 223.
10. Manian, A. P.; Abu Rous, M.; Schuster, C. K.; Bechtold, T. *J Appl Polym Sci*, to appear.
11. Schindler, W. D.; Hauser, P. J. *Chemical Finishing of Textiles*; CRC: Boca Raton, 2004. ISBN 0-8493-2825-X.
12. Udomkitchdecha, W.; Kittnaovarat, S.; Thanasoonhotnrock, V.; Potiyaraj, P.; Likitbanakorn, P. *Text Res J* 2003, 73, 401.
13. Ibanescu, C.; Schimper, C.; Bechtold, T. *J Appl Polym Sci* 2006, 99, 2848.
14. Okubayashi, S.; Schmidt, A.; Griesser, U.; Bechtold, T. *Lenzinger Berichte* 2003, 82, 79.
15. Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry, Vol. 2: Functionalization of Cellulose*, Wiley-VCH: Weinheim, 1998.
16. Ranganathan, S. R.; Elder, H. M.; McLaren, I. F. *J Text Inst* 1971, 62, 393.