CROATICA CHEMICA ACTA
CCACAA **76** (4) 293–298 (2003)

ISSN-0011-1643
CCA-2885
Original Scientific Paper

Application of Spectrophotometric Methods in Assessing the Influence of Alkaline Treatment on the Degree of Crosslinking of Cotton Cellulose with BTCA

Olivera Šauperl,* Karin Stana-Kleinschek, Bojana Vončina, Majda Sfiligoj-Smole, and Alenka Majcen-Le Marechal

University of Maribor, Faculty of Mechanical Engineering, Institute of Textile Chemistry, Ecology and Colorimetry, Smetanova 17, SI-2000 Maribor, Slovenia

RECEIVED MARCH 18, 2003; REVISED MAY 26, 2003; ACCEPTED MAY 28, 2003

Key words
BTCA
crosslinking
mercerization
cotton cellulose

Polycarboxylic acids appear to be the most promising nonformaldehyde crosslinking agents to replace the traditional, mostly formaldehyde-based, compounds. The most effective among these acids is 1,2,3,4-butanetetracarboxylic acid (BTCA). In this study, a comparison was made of the crosslinking effect on mercerized and on unmercerized as well as with different BTCA mass fractions crosslinked cotton fibres using FT-IR spectroscopy, the methylene blue method and water retention determination. The main purpose of the research was to evaluate how the structural changes of mercerized cotton (transformation of cellulose I into cellulose II) influence the crosslinking of cellulose fibres.

INTRODUCTION

Under the term crosslinking of cellulose we understand the procedure of optimizing the usable value of treated material.[1] The crosslinking agents react with hydroxyl groups of cellulose fibers in such a way that a crosslinked structure emerges. Certain exploitable and preservative properties of these materials are obtained by this treatment.[1,2] Since the noxious formaldehyde is released by most crosslinking agents, they are substituted with the so-called non-formaldehyde reagents. Among these, dymenthyl glyoxal urea (DMGU) and various polycarboxylic acids are important. Among the latter, 1,2,3,4-butanetetracarboxylic acid (BTCA)[3,4,5] has rendered the best results. The effectiveness of the crosslinking procedure of hydroxyl groups of cellulose fibres with BTCA depends on the amount of the crosslinking agent and catalyst, temperature, crosslinking reaction time and the pH of the finishing bath.[6,7] Crosslinking results from the esterification of the hydroxyl groups of cellulose fibers, which takes place in two phases. According to Yang, first a cyclic anhydride is formed, which in the next phase forms an ester with the hydroxyl group of cellulose fibers (Figure 1).[8] According to the second mechanism,[9] a mixed linear anhydride is formed in the presence of the catalyst ($NaH_2PO_2 \cdot H_2O$) (Figure 2). The degree of crosslinking increases with the increase of ester bonds. The mechanism of cellulose crosslinking with BTCA is partly understood but the influence of the accessibility of hydroxyl groups on the crosslinking with BTCA has not been completely explained so far.

It is known that mercerization influences the reactivity and accessibility of hydroxyl groups of cellulose

---

* Author to whom correspondence should be addressed. (E-mail: olivera.sauperl@uni-mb.si)

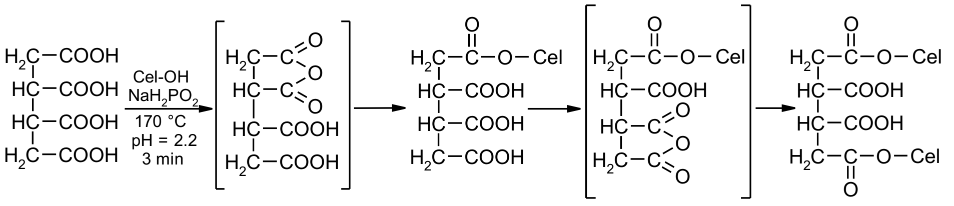


Figure 1. Mechanism of the crosslinking of hydroxyl groups of cellulose with BTCA as a result of the formation of a cyclic anhydride.[8]

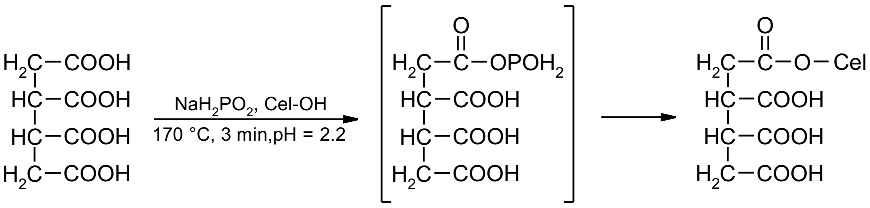


Figure 2. Mechanism of the crosslinking of hydroxyl groups of cellulose with BTCA as a result of the formation of a linear mixed anhydride.[9]

fibers. Mercerization changes the cellulose at both molecular and macromolecular levels.[10] Because of the changes in the fine structure of the fibers (cellulose I changes to cellulose II), the sorption properties of mercerized fibers are altered.[11,12] The decrease in crystallinity and the increase in amorphous regions lead to an increased accessibility of the reactive hydroxyl groups of cellulose fibers. The sorption properties of cotton cellulose are mainly defined by hydroxyl groups that take part in the esterification of cotton cellulose with BTCA. The aim of our investigations was to find out whether it is possible to use FT-IR spectroscopy and the »methylene blue« method for a quick and simple assessment of the influence of mercerization on the degree of crosslinking. Namely, we wanted to define the correlation between the accessibility and the reactivity of hydroxyl groups of cellulose fibers and the degree of crosslinking. Increased reactivity of the mercerized cotton cellulose fibers was proven by the Knecht method.[13] The sorption properties (water retention capacity) of crosslinked samples were determined in accordance with the standard DIN 53 814. The effectiveness of crosslinking was studied with FT-IR spectroscopy where the degree of crosslinking was determined on the basis of the intensity of the bands at fixed wavelength numbers in relation to the referential band. Crosslinking with BTCA produced three types of carbonyl groups in the cellulose: ester, carboxyl and carboxylate. The amount of carboxyl groups was determined using the methylene blue method.[16,17,18]

EXPERIMENTAL

Fabric Specifications

The investigations were carried out on unmercerized and mercerized 100 % cotton fabrics. The surface mass (167 g m^{-2}), warp density (47 threads cm^{-1}), filling density (24 threads cm^{-1}) and the weave (3- way basic twill) were the same in both types of fabric. Pre-treatment was carried out in the firm MTT Tekstil d.o.o. Maribor according to its technological procedure and proceeded in the following sequence: singeing, alkaline treatment mercerization (for mercerized fabric) and chemical bleaching.

Crosslinking of Fabric

Samples were crosslinked following the procedure of dry crosslinking. This included impregnation, drying and crosslinking. The contents of the finishing bath and the crosslinking conditions are shown in Table I.

After crosslinking, the samples were rinsed at room temperature until conductivity of distilled water (0.4 / µs cm^{-1}) was reached.

Assessment of the Degree of Mercerization according to the Knecht Method

According to the Knecht method, the absorption of the substantive dye on the fiber was followed. Unmercerized and mercerized samples were treated in a solution of the substantive dye Tobazol Scharlach 4BS (Cinkarna Celje). The contents of the bath and the dyeing conditions are shown in Figure 3.

The remission values of dyed samples were measured using a spectrophotometer, type Datacolor Spectraflash SF600. Numerical assessment of the dye difference between unmercerized and mercerized samples was carried out in accordance with the system CIELAB ($\Delta E_{ab}^* = 6.04$).

TABLE I. Contents of the finishing bath and the conditions of crosslinking with BTCA

w (BTCA)[(a)] / %	1, 3, 5, 7
w catalyst ($NaH_2PO_2 \cdot H_2O$)[(a)] / %	1, 3, 5, 7
pH	2.2
w liquor pick up / %	100
drying temperature T_{drying} / °C	100
drying time t_{drying} / min.	10
crosslinking temperature $T_{crossl.}$ / °C	170
crosslinking time $t_{crossl.}$ / min.	3

[(a)] Manufacturer Fluka.

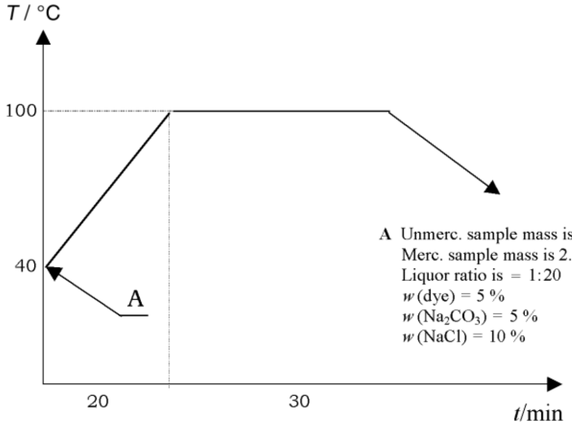


Figure 3. Dyeing conditions according to the Knecht method.

Determination of Water Retention Capacities according to DIN 53 814

The method is based on calculating the water retention capacity in the fibers (WRC), which is obtained from the difference in masses between the centrifuged and absolutely dry samples following the equation (Eq. 1):

$$\mathrm{WRC} = \frac{m_\mathrm{c} - m_\mathrm{a}}{m_\mathrm{a}} \cdot 100 \qquad (1)$$

where

WRC / %	the water retention capacity of fibers
m_c / g	mass of centrifuged fibers
m_a / g	mass of absolutely dry fibers

FT-IR Spectroscopy

In order to obtain a spectrum, the samples were shaped into KBr tablets. The measurements were taken on the Perkin Elmer 1600 apparatus under the following conditions: resolution 4, scan 16. The degree of crosslinking was determined from the proportion of intensity of the bands of ester (1725 $\mathrm{cm^{-1}}$) / carboxylate (1576 $\mathrm{cm^{-1}}$).[8] This was performed by treating the already crosslinked sample with 0.1 M NaOH (2 min) and changing the carboxyl groups –COOH into carboxylate $-\mathrm{COO^-}$ groups, which could then be assessed semi-quantitatively and more accurately by FT-IR spectroscopy.

Spectrophotometric Method of Methylene Blue[16,17,18]

The dye methylene blue binds to acid carboxylic groups of fibers according to the principle of ion exchange. Since the treatment is carried out in an alkaline medium (pH = 8.5),[17] the carboxyl groups of bound BTCA are found in carboxylate form (Eq. 2):

$$\mathrm{B^+\,A^-} + \mathrm{Cel{-}COO^-} \rightleftharpoons \mathrm{Cel{-}COO^-\,B^+} + \mathrm{A^-} \qquad (2)$$

where $\mathrm{B^+\,A^-}$ dye is in the form of salt.

The share of carboxyl groups in the mass of the absolutely dry cellulose sample can be calculated from the part of the unbound methylene blue dye as follows (Eq. 3):[16]

$$\{\rho\}\ (\mathrm{-COOH,\ absolutely\ dry\ cellulose\ sample}) = (7{,}5 - \{A\}) \cdot 0.00313 \,/\, \{m_\mathrm{a}\} \qquad (3)$$

where

ρ / 10^{-3} mol $\mathrm{g^{-1}}$	
A / mg	part of unbound methylene blue
m_a / g	mass of absolutely dry cellulose sample.

The amount of the dye in the dye bath was determined using the Perkin Elmer Lambda 2 UV/VIS spectrophotometer and the amount of dye concentration was calculated on the basis of the calibration curve. For each individual sample, three parallel measurements were taken and analyzed under the same experimental measuring conditions. The results were statistically evaluated by standard deviation.[18]

RESULTS AND DISCUSSION

Increased reactivity of mercerized cotton cellulose was confirmed by the Knecht method. From the remission value of unmercerized and mercerized samples and the calculated dye difference ΔE_ab^*, amounting to 6.04, a considerably larger absorption of mercerized cotton cellulose was observed (Figure 4).

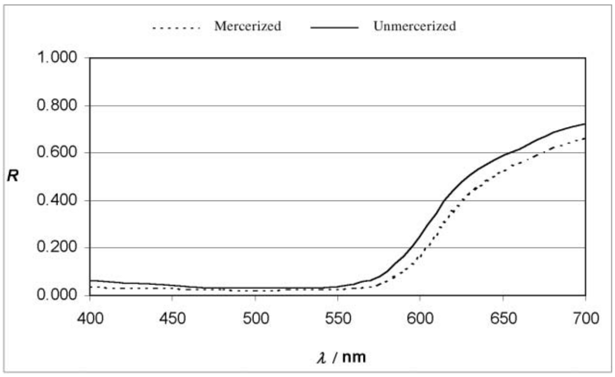


Figure 4. Remission curves of unmercerized and mercerized cotton cellulose stained by substantive dye Tobazol Scharlach 4BS.

The water retention capacity for unmercerized and mercerized cotton cellulose according to DIN 53 814 is shown in Figure 5. Table II presents the review of the degree of water retention capacity of unmercerized and mercerized cotton cellulose crosslinked with 1 %, 3 %, 5 % and 7 % mass fractions of BTCA in the finishing bath.

The percentage of water retention capacity has shown a typical difference between uncrosslinked unmercerized and uncrosslinked mercerized cotton cellulose. The uncrosslinked mercerized samples had a 7 % higher capacity of water retention than the uncrosslinked unmercerized

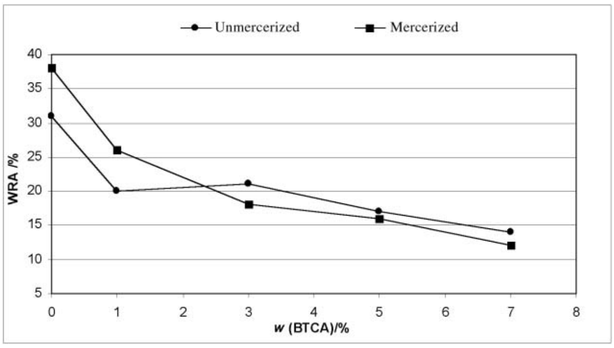


Figure 5. Graphic presentation of the degree of water retention of unmercerized and mercerized cotton cellulose samples treated with 1 %, 3 %, 5 % and 7 % mass fractions of BTCA in the finishing bath.

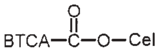
TABLE II. Table presentation of the degree of water retention of unmercerized and mercerized cotton cellulose samples treated with 1 %, 3 %, 5 % and 7 % mass fractions of BTCA in the finishing bath

	w (water retention capacity) / %			
w (BTCA) / %	unmerc. cotton	STDEV unmerc. cotton	merc. cotton	STDEV merc. cotton
0	31	0.28	38	0.37
1	20	0.29	26	0.31
3	21	0.25	18	0.30
5	17	0.36	16	0.40
7	14	0.15	12	0.10

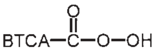
samples. The results of the determination of water retention capacity of unmercerized and mercerized cotton cellulose treated in the finishing bath with 1 %, 3 %, 5 % and 7 % mass fractions of BTCA have shown that the percentage of water retention capacity decreases with an increase in the mass fraction of BTCA. The degree of esterification along with the crosslinking of cotton cellulose with BTCA, increases proportionally to the increase in the mass fraction of BTCA. At a lower mass fraction of BTCA, more reactive mercerized samples retain a higher percentage of water capacity compared to unmercerized samples. This is to be expected due to the large number of accessible hydroxyl groups of cotton cellulose.

Treatment with 3 % mass fraction of BTCA in the finishing bath when treating an unmercerized sample gave an unexpected increase in water retention capacity, which cannot be adequately explained; however, it is obvious from both curves that with a larger degree of crosslinking capacities, water retention decreases. It seems that with mercerization structural changes in cotton cellulose improve the effect of crosslinking, particularly when the finishing bath contains a relatively high level of BTCA. This was also confirmed by the results obtained by FT-IR spectroscopy.

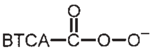
When cotton fabric is treated with BTCA and sodium dihydrogen phosphate(I) monohydrate as catalyst, an ester bond is formed between the cotton cellulose and BTCA under certain conditions. After the crosslinking reaction is completed, there are three types of carbonyl groups in cotton cellulose: ester (**a**), carboxyl (**b**) and carboxylate (**c**).[8]


$\mathrm{BTCA{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}Cel}$

a


$\mathrm{BTCA{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}OH}$

b


$\mathrm{BTCA{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}O^{-}}$

c

The band at the wavelength 1725 cm^{-1} represents the ester carbonyl group (which confirms the covalent bond between the cellulose and BTCA) as well as the uncrosslinked carboxyl carbonyl group of BTCA. Hence the intensity of the band at this wavelength does not represent the real degree of esterification. By the treatment of crosslinked samples in 0.1 M NaOH, carboxyl groups of BTCA transform into carboxylate, which absorbs at 1576 cm^{-1}. Comparison of the FT-IR spectrum before and after treatment with NaOH shows that the latter leads to a decreased intensity of the band at 1725 cm^{-1} and the increase at the wavelength 1576 cm^{-1}. The band at 1725 cm^{-1} shows the presence of ester groups only after the treatment with NaOH.

In this investigation, unmercerized and mercerized samples were treated in a finishing bath that contained BTCA (1 %, 3 %, 5 % and 7 %) and a catalyst of equal concentration. The spectra were normalized relative to a constant band of cellulose at a wavelength of 1313 cm^{-1}.[8] The degree of crosslinking was calculated from the proportion of the intensity of the bands of two wavelength numbers (ester 1725 cm^{-1}/carboxylate 1576 cm^{-1}), where a larger proportion indicates a better crosslinking effect.

Table III presents the data on the intensities of the bands at wavelengths of 1725 cm^{-1} and 1576 cm^{-1} as well

TABLE III. Band intensity at wavelengths 1725 cm^{-1} and 1576 cm^{-1} and the proportion of these intensities for unmercerized and mercerized cotton samples crosslinked in the finishing bath with 1 %, 3 %, 5 % and 7 % mass fractions of BTCA

	Unmercerized cotton cellulose				Mercerized cotton cellulose			
w (BTCA) / %	1	3	5	7	1	3	5	7
w (catalyst) / %	1	3	5	7	1	3	5	7
A_{1725} / cm^{-1}	0.19	0.26	0.27	0.27	0.23	0.26	0.27	0.31
A_{1576} / cm^{-1}	0.19	0.23	0.20	0.20	0.25	0.23	0.20	0.27
A_{1725} / A_{1576}	1	1.13	1.35	1.35	0.92	1.13	1.35	1.55

as the proportion of the intensity of the bands of these two wavelength numbers for the unmercerized and mercerized cotton samples crosslinked in the finishing bath with mass fractions of 1 %, 3 %, 5 % and 7 % BTCA.

It can be calculated from the results that in the case of mercerized as well as unmercerized cotton cellulose the proportion of intensity of the bands ester (1725 cm^{-1}) / carboxylate (1576 cm^{-1}) increased with the increased mass fraction of BTCA. This means that increasing the mass fraction of the crosslinked agent (BTCA) in the span from 1 % – 7 % leads to an improved effect of crosslinking. It was noted that, at lower mass fractions of BTCA (1 %, 3 % and 5 %), the properties were almost completely the same, irrespective of whether unmercerized or mercerized cotton cellulose was used in crosslinking. In the case of unmercerized cotton samples, the proportion of intensity of the bands ester (1725 cm^{-1}) / carboxylate (1576 cm^{-1}) reached a maximum in samples treated with 5 % BTCA in the finishing bath, while the properties in samples treated in the finishing bath containing 7 % mass fraction of BTCA remained at the same level. The rate of the bands ester (1725 cm^{-1})/carboxylate (1576 cm^{-1}) for mercerized (1.55) and unmercerized cotton cellulose (1.35) treated in the finishing bath containing 7 % BTCA is noticeably higher in the case of mercerized cotton cellulose. It is obvious that mercerization, which is known to influence the fine structure (transformation of cellulose I to cellulose II), changes the adsorption properties of cotton cellulose, additionally improves the reactivity of the hydroxyl groups, and therefore influences the degree of cotton cellulose esterification with BTCA.

A result of mercerization is the higher accessibility of the reactive cellulose hydroxyl groups on which the reaction of esterification takes place. As a consequence, the best crosslinking results were obtained on mercerized samples treated in a finishing bath with the highest mass fraction of BTCA (7 %).

Table IV gives the data on the contents of carboxyl groups (10^{-3} mol kg^{-1}), calculated on the basis of the sorption of the methyl blue dye.

On the basis of the results of the methyl blue method it was noted that in all cases the content of the carboxyl groups increased with the increased mass fraction of BTCA (Figure 6).

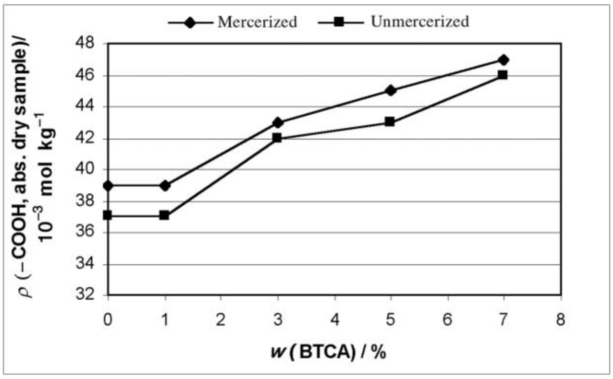


Figure 6. The content of carboxyl groups depends on the mass fraction of BTCA in the finishing bath for unmercerized and mercerized cotton cellulose. Mass fractions of BTCA in the finishing bath were 1 %, 3 %, 5 % and 7 %.

It can be seen from Figure 6 that the treatment with 1 % mass fraction of BTCA does not affect the contents of –COOH.

The amount of carboxyl groups in the case of mercerized cotton cellulose compared to unmercerized cotton was by $2 \cdot 10^{-3}$ mol kg^{-1} bigger. The biggest increase in carboxyl groups was recorded when the mass fraction of BTCA was increased from 1 % to 3 %. This amounted to $4 \cdot 10^{-3}$ mol kg^{-1} in mercerized samples and to $5 \cdot 10^{-3}$ mol kg^{-1} in unmercerized samples. This mass fraction increased the content of carboxyl groups in both cases (unmercerized and mercerized cotton cellulose) by $2 \cdot 10^{-3}$ mol kg^{-1} on average. Again it was noted that at all mass fractions the more reactive mercerized samples contained a larger share of carboxyl groups than unmercerized samples. Structural changes caused by mercerization (crystallinity of fibers can drop to 20 %) increase fiber absorption.[19] In this way, BTCA has an easier access to mercerized fibers. The results of the methyl blue method have confirmed that the change in the fine structure of cotton cellulose induced by mercerization increases the effect of crosslinking. Scattering of the results was assessed by standard deviation and good reproducibility was found. Standard deviation was adequately small in all cases.

TABLE IV. ρ (–COOH, absolutely dry sample)/(10^{-3} mol kg^{-1}) for unmercerized and mercerized samples treated in the finishing bath containing different mass fractions of BTCA (1 %, 3 %, 5 % and 7 %)

	ρ (–COOH, absol. dry sample) / (10^{-3} mol kg^{-1}) unmerc. cotton cellulose		ρ (–COOH, absol. dry sample) / (10^{-3} mol kg^{-1}) merc. cotton cellulose	
w (BTCA) / %	average	STDEV	average	STDEV
0	37	0.5	39	0.25
1	37	1.52	39	1.52
3	42	0.57	43	0.57
5	43	1.0	45	1.0
7	46	1.15	47	1.15

CONCLUSIONS

The results point to the following conclusions. Using the Knecht method it was found that the absorption properties were considerably better in mercerized fabric than in umercerized fabric. The color difference (ΔE_{ab}*) amounted to 6.04.

The water retention capacity properties of the fibers decreased with an increasing mass fraction of BTCA. It is concluded that the alkaline treatment of cotton cellulose (mercerization), especially when higher mass fractions of BTCA are applied in the finishing bath, improves the effect of crosslinking.

The results of FT-IR spectroscopy have shown that in the case of unmercerized and mercerized cotton cellulose treated in the finishing bath with different mass fractions of BTCA (1 %, 3 %, 5 % and 7 %), the proportion of intensity of the bands ester (1725 cm^{-1}) / carboxylate (1576 cm^{-1}) increases with an increased mass fraction of BTCA. The largest increase was recorded in the case of the unmercerized sample treated in the finishing bath with 7 % mass fraction of BTCA. Due to the changes in fine structure, mercerization additionally improved the degree of esterification of cotton cellulose with BTCA.

In changing the mass fraction from 0 % to 1 % BTCA, a part of the carboxyl groups did not change. The biggest increase in the carboxyl groups was recorded in the mass fraction increase from 1 % to 3 %. At all mass fractions, mercerized, more reactive samples, contained a higher proportion of carboxyl groups than unmercerized samples. The results of the methyl blue method also confirmed that mercerization favorably influences the crosslinking effect.

The results show a good reproducibility. The standard deviation is negligently small in all cases. On the basis of the results it can be concluded that both spectrophotometric methods are suitable for a quick and simple determination of the degree of crosslinking of cellulose hydroxyl groups with BTCA. It was found by both methods that mercerized, more reactive cotton cellulose, noticeably improved the effect of crosslinking.

REFERENCES

1. A. M. Grancarić, I. Soljačić, and D. Katović, *Osnove oplemenjivanja tekstila* [Textile Finishing], Vol. 2, Zagreb, 1994, pp. 12–20.
2. V. Lindtner, *Tehnologija apreture* [Technology of Textile Finishing], Vol 2, *Kemični apretirni postopki* [Chemical Processes of Textile Finishing], Ljubljana, 1971, pp. 129–138.
3. C. Q. Yang and L. Xu, *Text. Res. J.* **68** (1998) 457–464.
4. M. Welch, *Rev. Prog. Coloration* (1992) 32–41.
5. B. Vončina, *Fibres Text. East. Eur.* (1996) 69–71.
6. C. M. Welch, *Am. Dyest. Rep.* (1994) 19–26.
7. M. C. Hyung, *Text. Res. J.* **63** (1993) 650–657.
8. C. Q. Yang and W. Qilie, *Text. Res. J.* **66** (1996) 595–603.
9. E. L. Gillingham, D. M. Lewis, and B. Vončina, *Text. Res. J.* **69** (1999) 949–955.
10. E. Dinand, *Cellulose* **9** (2002) 7–18.
11. S. Tzong-Haw, L. Shyn-Min, H. W. Jiunn, and C. Cheng-Chi, *Text. Res. J.* **63** (1993) 357–361.
12. N. R. Bertoniere and King, *Text. Res. J.* **59** (1989) 114–121.
13. Knecht, *JSDC* **24** (1908) 67.
14. C. Q. Yang and W. Qilie, *Text. Res. J.* **67** (1997) 334–342.
15. C. Q. Yang, *Text. Res. J.* **61** (1991) 298–305.
16. D. Klemm, B. Phillip, U. Heinze, and W. Wagenknecht, *Comprehensive Cellulose Chemistry,* Vol. I*, Fundamentals and Analytical Methods,* Wiley-VCH Verlag GmbH, Weinheim, 1998.
17. B. L. Browning, *Methods of Wood Chemistry*, Vol. II, New York, 1967.
18. L. Fras, master thesis, University of Maribor, FS, Maribor, 2000.
19. D. Džokić, *Hemijska dorada tekstilnog materiala* [Chemical Finishing of Textile Materials], University of Beograd, Faculty of Technology and Metallurgy, Beograd, 1986, pp. 122–124.

SAŽETAK

Primjena spektrofotometrijskih metoda u procjeni utjecaja lužnatoga postupka na stupanj umrežavanja pamučne celuloze s 1,2,3,4-butantetrakarboksilnom kiselinom

Olivera Šauperl, Karin Stana-Kleinschek, Bojana Vončina, Majda Sfiligoj-Smole i Alenka Majcen-Le Marechal

Većina do sada rabljenih spojeva za umrežavanje celuloze sadrži formaldehid. U novije se vrijeme takvi spojevi sve više zamjenjuju sa spojevima koji ne sadrže formaldehid. Od svih takvih spojeva najdjelotvornije su polikarboksilne kiseline, a među njima se najviše rabi 1,2,3,4-butantetrakarboksilna kiselina. Autori su proučavali utjecaj mercerizacije na umrežavanje celuloze, koja zbog promjene fine strukture povećava adsorpcijska svojstva celuloznih materijala. Cilj istraživanja bio je utvrditi spektrofotometrijskim metodama je li mercerizacija pomoću 1,2,3,4-butantetrakarboksilne kiseline utječe na umrežavanje celuloze.