Umrežavanje celuloze limunskom kiselinom uz prisutnost FAU zeolita
Citric acid crosslinking of cellulose in the presence of zeolite FAU

Sandra FLINČEC GRGAC[1], Andrea KATOVIĆ[2], Drago KATOVIĆ[1] & Sandra BISCHOF-VUKUŠIĆ[1]
sflince@ttf.hr, katovic@unical.it, dkatovic@ttf.hr, sbischof@ttf.hr
[1] Faculty of Textile Technology, Department of Textile Chemistry and Ecology
[2]University of Calabria, Faculty of Engineering, Department of Chemical Engineering and Materials

INTRODUCTION

Polycarboxylic acids, especially 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA) in combination with phosphorus-containing catalysts, such as sodium hypophosphite (SHP), have proven to be the most effective substitutes for the formaldehyde-releasing crosslinking agents(Fig.1.) such as the N-methylol compound (DMDHEU) dimethylol-dihydroxy ethylene urea[1,2].
In our previous research CA has been used with sodium hypophosphite (SHP) catalyst, while this paper studies the possibility to replace it with an environmentally and economically acceptable zeolite catalysts (FAU and MFI, Fig 2.).
Zeolites, a family of aluminosilicates containing pores and cavities in the range of 4-18 Å, are well-known sorbents, catalysts and molecular sieves. Structure of zeolites consists of three-dimensional network $(AlO4)^{-5}$ and $(SiO4)^{-4}$ polyhedra (Fig. 3.), connected oxygen atoms. The structures are generally very open and contain channels and cavities containing cations, water molecules and other molecules. Cations and water molecules have a high degree of mobility. With respect to this property zeolites are characterized by high ion exchange capacities. Alumina / silica compounds are used in various chemical and physical processes such as heterogeneous catalytic reactions (zeolites catalyze esterification reactions too), gas separations, ion exchange and adsorption processes.[4]

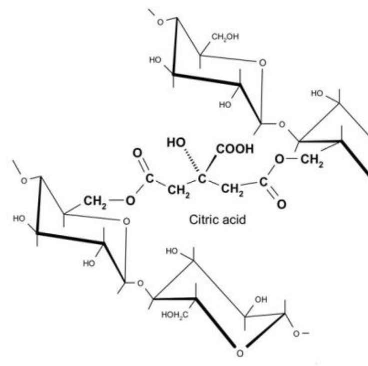
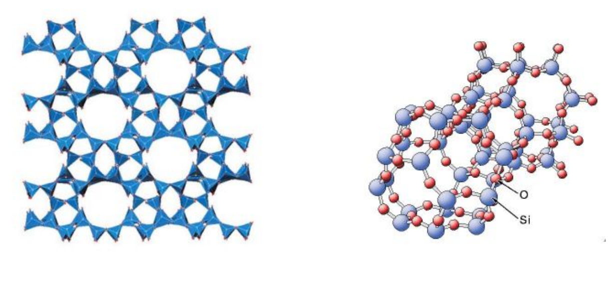


Figure1. Cross-linking via ester linkage of CA[3]



A) B)

Figure 2. Zeolite structure: a) MFI, b) Faujasite

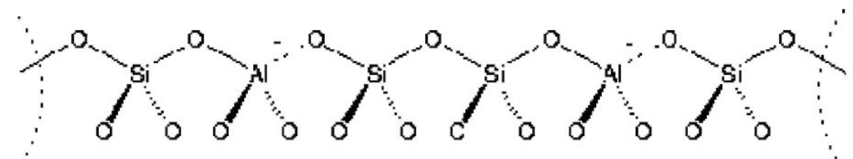


Figure3.Structure of zeolites consists of three-dimensional network $(AlO_4)^{-5}$ and $(SiO_4)^{-4}$ polyhedra [4]

EXPERIMENTAL

Samples of desized, scoured, bleached and mercerized cotton fabrics (100%; 170 g/m^2) were padded to 100% wet pickup with three different baths:
a) suspensions containing FAU zeolite powder (1.3 wt %) in aqueous solution of citric acid (CA) crosslinking agent (10 wt %)
b) suspensions containing MFI zeolite powder (1.3 wt %) in aqueous solution of citric acid (CA) crosslinking agent (10 wt %)
c) containing SHP (6.5 wt %) in aqueous solution of citric acid (CA) crosslinking agent (10 wt %)

Scanning electron microscopy is used to characterize the surface morphology and crystal size of the zeolite particles bonded to cellulose fibers. For the scanning electron microscope (SEM) study, the sample were mounted on stubs and coated with gold in a sputter coater.

FE Scanning Electron Microscope, Mira II LMU, Tescan

FT-IR Spectrum 100, Perkin Elmer

Spectraflash SF 300, Datacolor, Switzerland.

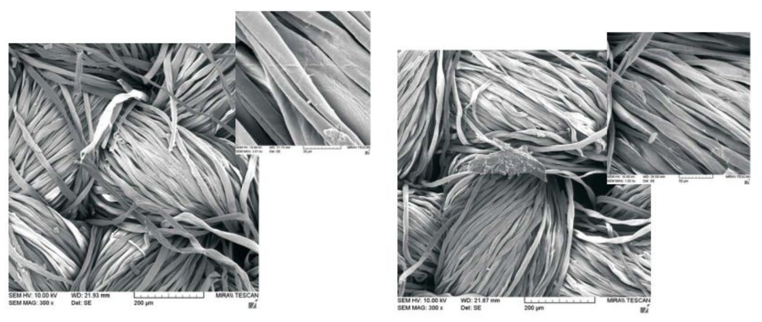
TGA, Perkin Elmer

The treated samples were analyzed by ATR-IR spectroscopy using a FTIR spectrometer (PerkinElmer, software Spectrum 100). 4 scans at a resolution of 4 cm-1 were recorded for each sample between 4000 cm-1 and 450 cm-1. To measure the intensity of the ester carbonyl band, samples were treated with a 0.1M NaOH solution at room temperature for 2 min to convert the free carboxylic acid on the fabric to a carboxylate anion so that the ester carbonyl band could be separated from that of the overlapping carboxylic acid carbonyl. The ester carbonyl band intensity in the IR spectra of the treated cotton fabric was normalized against the 1314 cm-1 band associated with the COH bending mode of cellulose.

Thermal analyses of cotton materials were performed in a flowing synthetic air atmosphere (30 % oxygen; flow rate of 90 ml/min) using a Perkin Elmer analyzer controlled by a PC system. TG measurements of the samples were obtained from ambient temperature to. 800 °C at a heating rate of 10°C/min. Prior to the thermal analysis runs the treated cotton fabrics were cut into small pieces having an average weight of ~1 mg, while the analyzed samples were approx. 5 mg

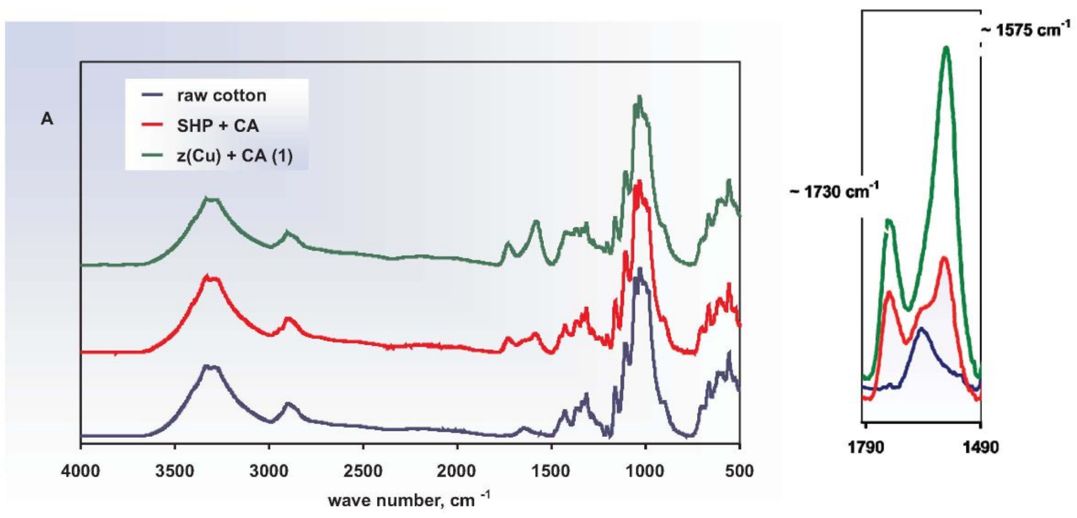
The fabric CIE whiteness (WCIE) and Yellowness (YI) index was measured according to AATCC Method 110 ('Whiteness of Textiles') using a Spectrophotometer Spectraflash SF 300,Datacolor, Switzerland.

RESULTS AND DISCUSSION



A B

SEM images of the cotton sample treated with:
a) CA and b) commercial catalyst SHP and CA

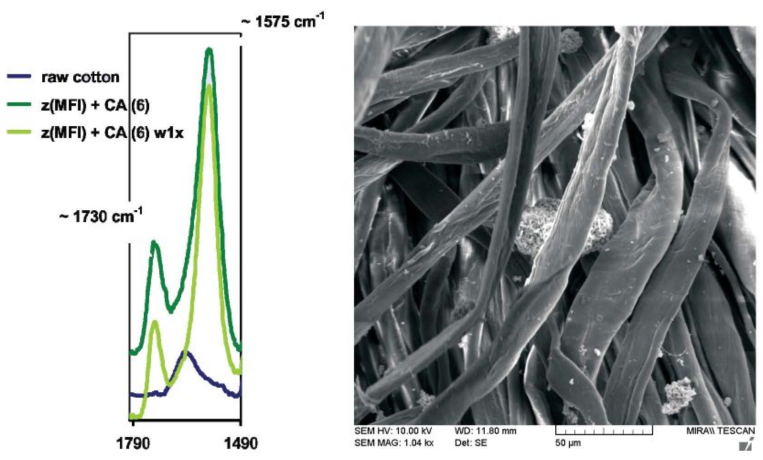


FTIR ATR spectra of the raw cotton, cotton treated with SHP and CA, and cotton treated with zeolite Cu-FAU [sample code z(Cu) + CA (1)]; within the frame the region characteristic for the esterification peaks

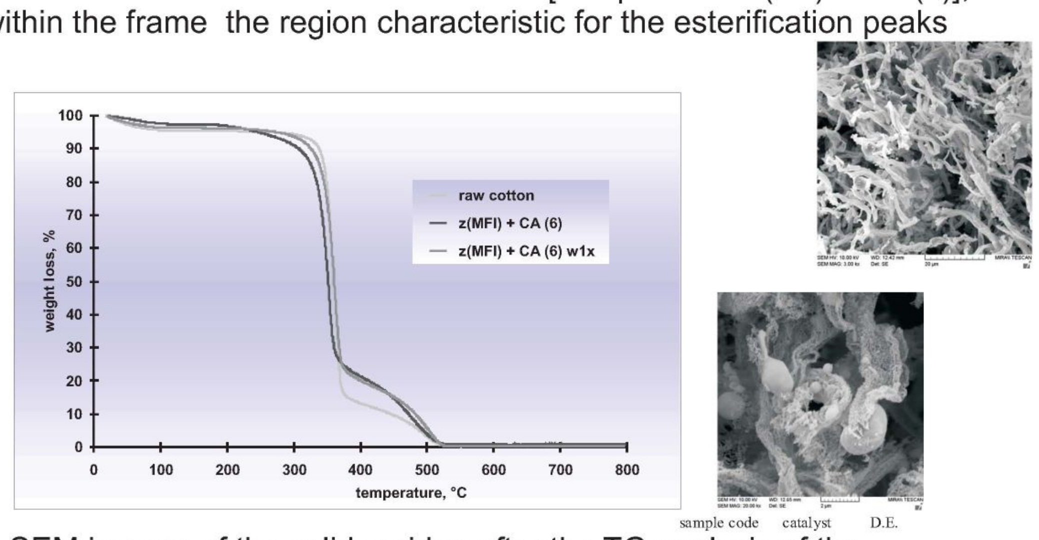
Table 1. Degree of esterification (D.E.) for the treated cotton samples calculated from the ratio of the intensities of the IR bands at wave numbers 1730 cm^{-1} and 1575 cm^{-1} corresponding to ester and carboxylate groups, respectively.

Sample code	Catalyst	D.E.	D.E. after w1x
SHP-CA	SHP	0.436	0.391
z(Cu)+CA (1)	Cu-FAU*	0.481	0.315
z(Cu)+CA (3)	Cu-FAU*	0.476	0.244
z(MFI)+CA (6)	MFI	0.423	0.292

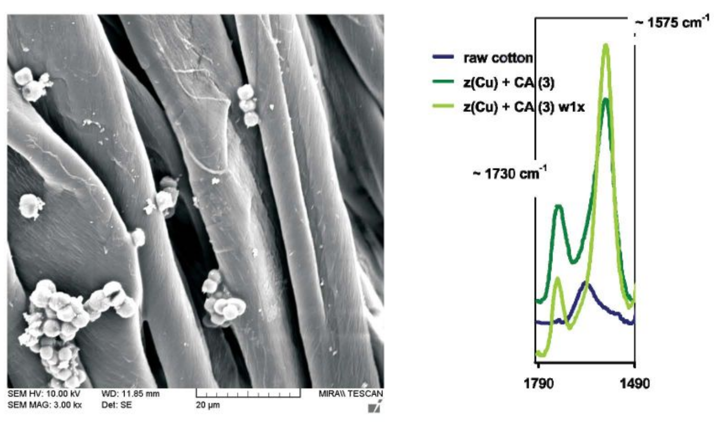
[1] initialization: microwave owen
*introduction of copper obtained by direct hydrothermal synthesis



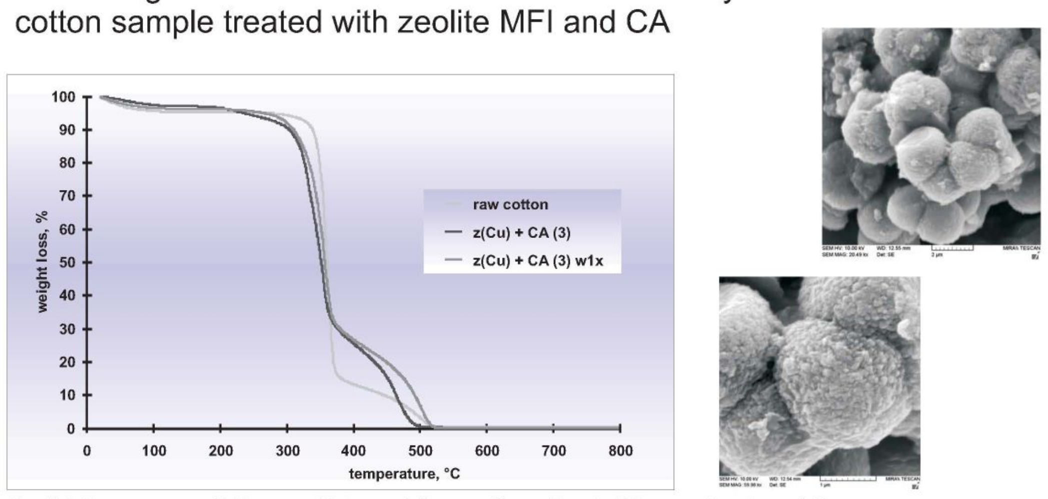
SEM images of the cotton sample treated with zeolite MFI and CA and the FTIR ATR spectra showing the region characteristic for the esterification peaks



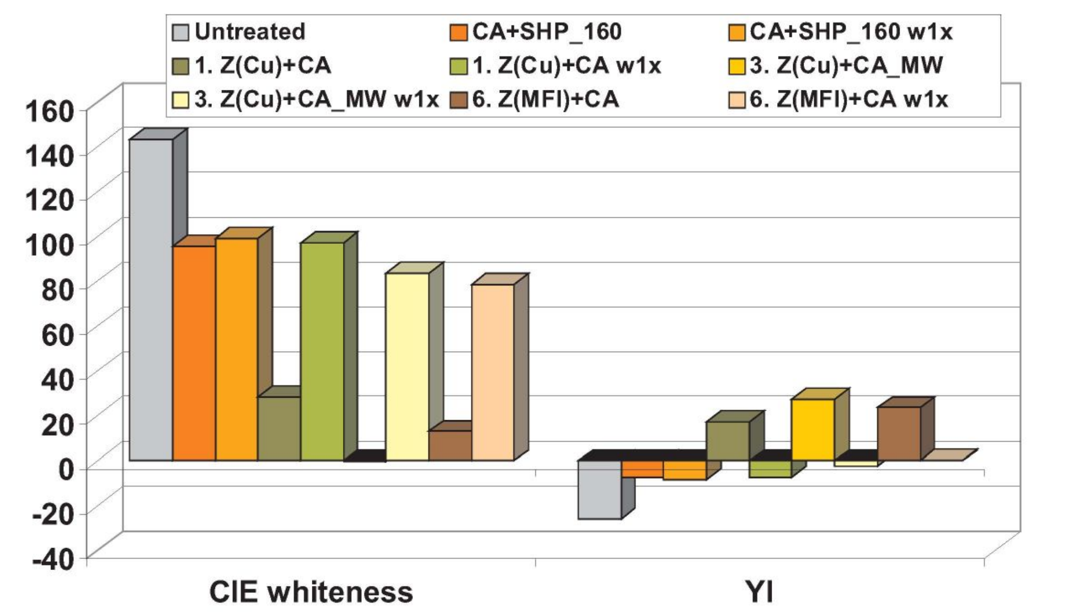
SEM images of the solid residue after the TG analysis of the cotton sample treated with zeolite MFI and CA



SEM images of the cotton sample treated with zeolite Cu-FAU and CA (MW initialization) and the FTIR ATR spectra showing the region characteristic for the esterification peaks



SEM images of the solid residue after the TG analysis of the cotton sample treated with zeolite Cu-FAU and CA



The problem of yellowness (YI), which might occur during the treatment with CA at elevated curing temperatures, has been known from our earlier research [5]. It has been proven thet the presence of hydroxyls group may cause a noticeable yellowing of the material during the heat cure [6]. Decrease of W_{CIE}(Whiteness Index International Commission on Illumination (french. Commission internationale de l'éclairage)) is, as expected, the most noticeable with the application of CA, but the W_{CIE} velues increase again after the first washing cycles, which is of great aesthetic importance. Cotton fabrics treated with CA in the presence of zeolite as a catalyst has a higher degree of yellowness thet after washing decreases while the CIE whiteness increases.

CONCLUSIONS

- **Zeolites (commercial MFI and FAU as well as Cu-FAU synthesised in our laboratory) chosen for this study confirm their catalytic role in the esterification of cellulose with citric acid.**
- **All zeolites remained on the cotton fibers and they were easily observed with SEM.**
- **The stability of the zeolites were confirmed by SEM images of the residues remained after TG analyses of the cotton samples treated with zeolite and CA.**
- **The degree of esterification in the case of zeolite treated cotton fabrics corresponds to the one obtained using the commercial SHP catalysts, so it is worthwhile to optimize the preparation procedure because zeolites are ecologicallz and economically more suitable.**

LITERATURE

[1] Yang, C., Wu, W., Fire and Materials 27 (2003) 223
[2] Katović, D., Bishof-Vukušić, S., Flinčec Grgac, S., Lozo, B., Banić, D., Fibers & Textiles in Eastern Europe 17 (2009) 90
[3] Schramm, C., Rinderer, B. Influence of additives on the formation of saturated PCA produced during durable-press curing with citric acid.Journal of Society of Dyers and Colourists. 1999; 115:306-311
[4] Franz Keller, Lutz Körner: Zeolite, ChE 735 - Kinetics and Catalysis; Professor Thatcher Root; University of Wisconsin - Madison
[5] Schramm, C., Bischof Vukusic, S., Katovic, DNon-formaldehyde durable press finishing of dyed fabrics: evaluation of cotton-bound polycarboxylic acids. Coloration Technology. 2002; 118:244-249
[6] Lu, Y., and Yang, C. Q., Fabric Yellowing Caused by Citric Acid as a Crosslinking Agent for Cotton, Textile Res.J., 1999; 69, 685-690.