In this paper, the ethyl chitosan grafting on cotton is studied by varying two parameters of polycondensation stage: temperature (140-180°C) and catalyst (1.1 mmol zinc acetate, zinc chloride or magnesium chloride). The ethyl chitosan was prepared by direct alkylation method, the chitosan concentration varying from 0.1 to 2.1 mmols; the molar ratios chitosan: alkylation agent: NaOH were (0.1-2.1): 1.1: 1.1. The FT-IR spectroscopic analysis certified the differences produced by these factors on the treated samples, confirming ethyl chitosan grafting on cotton. The grafting effects were estimated by the evaluation of values of wrinkle-recovering angles (dry WRA and wet WRA), breaking forces (on warp and weft) and mass losses after laundering and after abrasive friction. The statistical analysis of four grafting effects (dry WRA, wet WRA, breaking forces on warp and weft) led to low values for standard deviations and standard errors of the mean, showing that the obtained results have a high degree of confidence.

Keywords: ethyl chitosan, FT-IR spectroscopy, grafting, catalyst, polycondensation temperature, statistical analysis

The synthesis of alkyl chitosan is based on one of the three alkylation methods: the reductive method, Michael addition and direct alkylation [1-3]. The direct alkylation of chitosan was the subject of many research studies [4-12]. The alkyl chitosan is usually prepared by the reaction of chitosan with an alkylation agent (of alkyl iodide or alkyl chloride type) in the presence of NaOH alkaline medium [4]. An inconvenient of direct alkylation is the obtaining of O-alkylated products as well as N-alkylated ones [5]. Usually, in order to obtain a high degree of alkylation, the stages where the chitosan is kept in contact with the alkylation agent, in NaOH medium, are repeatedly applied [6, 7]. However, the efficiency of alkyl chitosan synthesis by direct alkylation method depends on several factors: the molar ratio chitosan: alkylation agent: alkali agent [5], the reaction time [8], the nature and the concentration of the alkali forming the alkaline medium [9, 10], the temperature [11, 12].

The alkyl chitosan can be applied on cotton fabric by coating method or by grafting [13]. Usually, the grafting is done by pad-dry-cure technology [13-16], like the most finishing/functionailization processes [13, 17-21]. As this technology has three distinct stages (padding, drying and finishing/functionalization processes [13, 17-21]. The working parameters for padding and drying stages were the same, but for the polycondensation stage the parameters (temperature and catalyst) were varied as follows: 140, 170 and 180°C for polycondensation temperature and 3 catalysts of metallic salt type (zinc acetate, ZnCl₂, MgCl₂). The effects of ethyl chitosan grafting on cotton were estimated by the values of wrinkle-recovering angles (dry WRA and wet WRA), breaking force (on warp and weft) and mass losses after 1-5 cycles of repeated launderings and after 500-1500 cycles of abrasive friction.

A statistical analysis of four grafting effects (i.e. dry WRA and wet WRA and breaking force on warp and weft) has been also made by computing the standard deviations and standard errors of the mean, in order to study the degree of confidence of the obtained results.

**Experimental part**

**Materials and methods**

The synthesis of ethyl chitosan (in the three forms mono-, di- and triethyl chitosan) has been made according to the indications from literature [1], proceeding at direct alkylation of chitosan (0.1-2.1 mmol CS) with 1.1 mmol alklylation agent (AA) and 1.1 mmol NaOH. The alkylation agent used was ethyl chloride, obtained by Kellen reaction, where ethanol, HCl and a catalyst (of metallic salt type: zinc acetate, ZnCl₂, MgCl₂), reacted in equimolar ratio.

The ethyl chitosans obtained have been grafted on cotton by pad-dry-cure technology. The padding stage consisted in cotton impregnation with ethyl chitosan freshly synthesized with molar ratios CS:AA:NaOH=(0.1-2.1):1.1:1.1 (in mmol), followed by squeezing (degree of squeeze - 80%); the drying was done at 100°C, for 3 min; the polycondensation consisted in the completion of grafting reaction due to the high temperature and to the presence of the catalyst.

In this research the synthesis of ethyl chitosan, of mono-, di- and triethyl chitosan type (abbreviated as MECS, DECS and TECS, respectively) was performed in the same way as in one of our previous paper, where the alkylation agent, ethyl chloride, was obtained in-situ. Then the product has been applied on 100% cotton samples by pad-dry-cure
The polycondensation stage was realized in multiple ways, varying the polycondensation temperature (from 140, 170 to 180°C), as well as the catalyst used. Three catalysts have been tested (the same three catalysts used in Kellen reaction for ethyl chitosan synthesis), namely: zinc acetate, zinc chloride and magnesium chloride.

The chemicals used for this paper were provided by the following companies: highly viscous Chitosan - Fluka AG; reagents (35%hydrochloric acid, 95%ethanol, 100%glacial acetic acid), sodium hydroxide (p.a.) - Merck Company; catalysts (zinc acetate, zinc chloride and magnesium chloride) - Sigma Aldrich and non-ionic surfactant (Romopal O) - Romtensid SA Timisoara, Romania.

The 100% cotton plain weave fabric of 100 g/m² weight was provided by IASITEX SA/România. The cotton fabric has been prepared by scouring with 2%NaOH, 1%Na₂CO₃, 1%Romopal O, liquor ratio = 1:50, at 100°C temperature, during two hours, followed by hot and cold rinsing and drying at room temperature.

FT-IR analyses

FT-IR analyses of all samples were performed on Multiple Internal Reflectance Accessory (SPECAC, USA) with ATR KRS-5 crystal of thalium bromide-iodine, having 25 reflections, and investigation angle of 45°. This accessory device was attached to the Spectrophotometer FTIR IR Affinity-1 Schimadzu (Japan); the spectra registration was realized with 250 scans in the 4000-600 cm⁻¹ rang. After the registration, the absorption spectra have been electronically superposed using the Spekwin 32 academic software.

Wrinkle-recovering angles, WRA

The wrinkle-recovering angles WRA were measured using an Metrimpex FF-01 according to German standardized method DIN 53890. WRA values were determined on samples cut on the two directions: warp and weft; the total WRA was calculated by summing the wrinkle-recovering angle on warp with the one on the weft. Ten measurements were performed out on every dry or wet samples.

Tensile strength

The tensile strength measurements have been carried out according to ASTM E83-ASTM E4 EN 100002-2-BS-3846-ISO 9531-IUP/6-IUP/8-IUP/9-IUF/470. The HSK-T dynamometer for yarns and fabrics, with QMAT TEXTILE FIRE soft, was used for testing and the input parameters were: speed: 100 [mm/min]; d (distance) = 200 [mm] and force F = 150 N; A = 100 [mm²].

The tests were repeated 30 times on each type of treated sample.

Statistical analysis

The data statistical analysis consisted in the calculation of standard deviation (SD) and standard error of the mean (SEM) for WRA and breaking force. The calculation was done using MATLAB software [22, 23] and the calculation relations are presented in equations 1 and 2.

\[
SD = \left[ \frac{\sum(X_i - \bar{X})^2}{n} \right]^{1/2}
\]

\[
SEM = SD / n^{1/2}
\]

where \(X\) is dry WRA; 2) \(X\) is wet WRA; 3) \(X\) is the breaking force on weft; 4) \(X\) is the breaking force on warp;

\[
SEM = \text{standard error of the mean; } n = \text{number of observations/experiments.}
\]

SEM is the standard error of the mean; \(n = \) number of observations/experiments.

In fact, SD shows the dispersion of the grafting effects (WRA, tensile strength) from the mean value. Values of standard deviation close to zero indicate the data tendency to get very close to the mean value, while high values indicate the data dispersion on a large scale.

Standard error of the mean (SEM) shows the precision of mean value calculation.

Mass losses

Mass losses of grafted samples have been gravimetrically evaluated in two ways: -after repeated launderings, according to SR EN ISO 105-C06/A2:1999, standard equivalent with AATCC Test Method 124-1996 Smoothness Appearance of Fabrics after Repeated Home Laundering; Samples (40 mm × 10 mm) grafted with ethyl chitosan were weighted before laundering and after 1 to 5 repeated laundering cycles. The recipe used for laundering was: Ariel gel equivalent to ECE detergent type, 4 g/L detergent (Standard Detergent 1993); solution volume: 150 mL, time = 30 min, temperature = 40°C. A hot and cold rinsing followed and then drying by hanging in open air. The tests were repeated 10 times.

Mass losses of grafted samples have been evaluated with the eq. 3 and 4:

\[
W_i = \frac{W_s - W_a}{W_s} \times 100 \% \tag{3}
\]

\[
\Delta W_i = W_a - W_s \tag{4}
\]

where \(W\) and \(\Delta W\) represent the mass losses expressed as percentage and in grams, respectively, after \(i\) laundering cycles (\(i = 1, 3\) and 5); \(W_s = \) weight before laundering; \(W_a = \) weight after laundering;

-after abrasive friction: the weight difference, namely, the mass before friction minus the mass after a number of friction cycles, was determined according to ASTM D4966/D4970, SN 198525/198529, EN ISO 12947-1:1998 on Martindale Abrasion and Piling Tester, model: 4 Stations; \(L \times W \times H = 570 \times 532 \times 362; 62\) Kg. Each test was repeated 10 times.

Results and discussions

The grafting of mono-ethyl chitosan (MECS) on cotton is confirmed by the following aspects (compared to the spectra of untreated cotton sample):

- increase of absorption bands in 3331-3275 cm⁻¹ domain with the increase of polycondensation temperature. In this domain the NH, and O-H asymmetric and symmetric stretching bands [24, 25] are recorded and these peaks increase confirm the presence of chitosan from MECS grafted on cotton; the higher the polycondensation temperature, the bigger the grafting degree (figs. 1, 2);

- increase of absorption bands in 2918-2851 cm⁻¹ domains (figs.1, 2), assigned to C-C bond [24, 25]; the highest peaks were recorded at 180°C, meaning that the temperature
favors the grafting; surprisingly, the temperature of 140°C leads to the lowest peaks.
- increase of the 1202 cm\(^{-1}\) peak assigned to ether bond, \(\text{C-O-C} [24, 25]\), proving the grafting, through ether bridges, between MECS and cotton (fig. 1 and fig. 3).
- increase of 1107 cm\(^{-1}\) peak afferent to OH secondary groups, increase due to the contribution of OH groups attached to the carbon atom no. 3 from the structure of MECS grafted on cotton (fig. 1 and fig. 4);
- slight decrease of 1053 cm\(^{-1}\) peak (assigned to primary OH groups (C-O stretching)) proving the implication of primary OH groups of cellulose and of MECS in the polycondensation stage, with ether bond forming (fig. 1 and fig. 4);

**Grafting effects**

**Dry WRA**

The influence of polycondensation stage parameters (temperature and catalyst nature) on dry WRA is shown in figure 5. The molar ratios presented in figure 5 correspond to: CS: AA: NaOH = 0.1:1.1:1.1 represent the triethyl chitosan (TECS), CS: AA: NaOH = 0.39:1.1:1.1 represent the diethyl chitosan (DECS) and the other 3 ratios (CS:AA:NaOH = (1.1-2.1):1.1:1.1 refer to monoethyl chitosan (MECS) [1].

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**Fig. 1.** FTIR spectra for monoethyl chitosan, MECS (CS:AA:NaOH = 2.1:1.1:1.1) grafted on cotton at different polycondensation temperatures

**Fig. 2.** Details of FT-IR spectra in 3600-2700 cm\(^{-1}\) domain

**Fig. 3.** Details of FT-IR spectra in 1260-1175 cm\(^{-1}\) domain

**Fig. 4.** Details of FT-IR spectra in 1180-1000 cm\(^{-1}\) domain
The information offered in figure 5 shows the increase of dry WRA with the increase of chitosan concentration and polycondensation temperature, regardless the catalyst nature (when the reference is the untreated sample). However, the biggest dry WRA was obtained when zinc acetate was used as catalyst in the polycondensation operation.

**Wet WRA**

All samples treated with ethyl chitosans have wet WRA bigger than WRA for the reference (untreated cotton sample), but smaller than dry WRA (fig. 6). When the tested samples are wet it can be noticed that wet WRA increase with the increase of CS concentration, regardless the catalyst nature. The biggest wet WRA have been obtained for polycondensation temperature of 170°C and when the catalysts used were zinc acetate, followed by ZnCl₂. The increase of polycondensation temperature to 180°C led to important decreases of wet WRA in the case of zinc acetate used as catalyst and to slight decreases when ZnCl₂ was used. MgCl₂ is less efficient compared with the other two catalysts, as it led to wet WRA smaller, regardless the polycondensation temperature; using this catalyst increases of wet WRA are obtained as the polycondensation temperature increases.

**Mechanical properties: Breaking force**

In figures 7 and 8, the sample grafted only with 2.1 mmol chitosan without chitosan alkylation has been taken as reference (abbreviated with R). Compared with R, all the samples grafted with ethyl chitosans showed lower mechanical properties. In comparison with the breaking force of untreated cotton sample (148 N on weft and 234 N on warp direction) the majority of samples treated with ethyl chitosans showed bigger breaking forces; this can be explained by the presence of ethyl chitosan on yarn surface, thus contributing to its strengthening.

The two parameters of polycondensation (temperature and catalyst nature) led to increases of breaking force with the increase of polycondensation temperature and of chitosan concentration (in molar ratios CS:AA:NaOH used for ethyl chitosan synthesis) only when zinc acetate was used as catalyst; this means that the nature of catalyst used plays an essential role: zinc acetate had the best effect, the other catalysts presenting destructive effects. It is known that, during the polycondensation stage, the metallic salt/catalyst decomposes and gives rise to an acid (acetic acid from zinc acetate and HCl from ZnCl₂ and MgCl₂, respectively); the higher is the acid strength, the more powerful are the destructive effects on cotton integrity.

**Statistical analysis**

The statistical analysis of grafting effects (namely the values dry WRA, wet WRA, breaking forces on weft and warp) was carried out for the cases in which the polycondensation temperature was 170°C, in the presence of zinc acetate as catalyst; the results are presented in table 1.

According to table 1 all SD values are small, close to zero, indicating that all WRA values and the maximal breaking forces are very close to the associated mean values.

The very small values of standard errors of the mean (SEM) denote a great computing precision of the mean value, in both conditions.
Durability of grafting effects

The durability of grafting effects was evaluated by determining the mass losses after 1-5 repeated launderings and after 500-1500 cycles of abrasive friction. Tables 2 and 3 present the mean values of mass losses at individual laundering for 10 grafted samples and at abrasive friction of these samples, after 500, 1000 and 1500 cycles of abrasive friction, respectively.

The mass losses indirectly indicate the bond strength between the grafting agent (ethyl chitosan) and polymer (cellulose). But this strength depends on the parameters used in pad-dry-cure technology: the concentration of grafting agent (ethyl chitosan) and the concentrations of all chemicals in the impregnation bath, the impregnation time, the pressure at squeezing, time of squeezing, temperature and time of drying, temperature, and catalyst nature in polycondensation.

Table 2 shows the mean values for mass losses at laundering of samples grafted with 0.1-2.1 mmol ethyl chitosan when, in the polycondensation stage, 1.1 mmol of zinc acetate was used as catalyst, at 170°C temperature.

It can be noticed that as the ethyl chitosan amount increased the losses also increased for one laundering cycle, three laundering cycles, as well as for five laundering cycles.

The grafting treatments have been well done, as the mass losses after 5 repeated launderings did not exceed 6.8%.

Table 3 presents the mean values of mass losses at abrasive friction of grafted samples, when, in the polycondensation stage, 1.1 mmol of catalyst were used, at temperatures of 140, 170, and 180°C.

The losses after 500, 1000 and 1500 cycles of abrasive friction, respectively, are small regardless the temperature used in polycondensation stage and the catalyst type, proving that MECS (obtained with the molar ratio CS:AA:NaOH = 1:1:1) is hard to remove from cellulose chains, even when forces were employed. The explanation of this behavior is based on the strength of the bond between MECS and cellulose, which, being of ether type, is hard to break.
2851 cm⁻¹ (assigned to C-H stretching) and at 1202 cm⁻¹ the grafting achievement by the increase of peaks at 2918-a chemical bond with cellulose. FT-IR analysis showed by coating on the surface of cotton yarn/fabric, but formed demonstrated that each ethyl chitosan was not deposited and after 500-1500 cycles of abrasive friction, respectively, mass losses found after repeated launderings (1-5 cycles) have been obtained at the temperature of 170°C. The small dry WRA, wet WRA and breaking force (on weft and warp) showed the temperatures tested in this paper the best values for as well as the generation of good grafting effects; among parameters play an important role in reaction completion Conclusions

In pad-dry-cure technology, the polycondensation stage parameters play an important role in reaction completion as well as in the generation of good grafting effects; among the temperatures tested in this paper the best values for dry WRA, wet WRA and breaking force (on weft and warp) have been obtained at the temperature of 170°C. The small mass losses found after repeated launderings (1-5 cycles) and after 500-1500 cycles of abrasive friction, respectively, demonstrated that each ethyl chitosan was not deposited by coating on the surface of cotton yarn/fabric, but formed a chemical bond with cellulose. FT-IR analysis showed the grafting achievement by the increase of peaks at 2918-2851 cm⁻¹ (assigned to C-H stretching) and at 1202 cm⁻¹ (assigned to C-O-C stretching vibration).

The catalysts ZnCl₂, and MgCl₂ are less suited for ethyl chitosan grafting on cotton because, at the high temperature of polycondensation stage, they give rise to HCl (by salt decomposition), affecting the samples integrity, thus leading to the decrease of maximal breaking force. Zinc acetate is a milder catalyst, unaffaeting the cellulose support, and it produce the best grafting effects, assessed by big values of dry WRA, wet WRA, breaking forces on weft and warp and small mass losses at repeated launderings and friction.

The statistical analysis of four grafting effects (dry WRA, wet WRA, breaking forces on weft and warp) showed small values of standard deviations and standard errors of the mean, indicating that the obtained results have a high degree of confidence.

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Manuscript received: 6.11.2015