Effect of Surfactant - Assisted Enzymatic Treatment on the Structure and Specific Properties of Wool Fibre

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The objective of this study is to perform an enzymatic treatment on wool fibers in the presence of a mild detergent containing surfactants obtained from renewable raw materials, in order to obtain a reduction in the felting of wool fibers. This treatment is designed to replace the classic wool fiber process using chlorine compounds, aggressive to people and the environment. FTIR spectroscopy has demonstrated the effect of enzymes by breaking down bonds from the functional groups characteristic of the keratin protein of wool. Determination of relaxation shrinkage and felting shrinkage allowed the selection of the samples that led to a minimal felting phenomenon.

Key words: enzymes, surfactants, wool fibers, anti-felting treatment

Wool is a valuable product for the textile industry. Due to its properties, such as resistance to wear, non-crease properties and good thermal insulation is used for warm clothing, overalls, knitwear and blankets. Before getting to the market, wool needs to be subjected to many treatments, some of which raising environmental protection issues through the presence of highly polluting chemical processing. The classic anti-felting wool fiber process uses chlorine-based oxidative chemical compounds, which are aggressive to people and environment. Felting is a typical property of all animal keratin fibers, caused by scales on the surface of the wool fiber as a result of a directional friction effect. The felting of the wool is a major disadvantage, resulting in irreversible shrinkage, changes in the dimensions, structure and surface of the material. Some modern alternatives, unconventional and ecological treatments have been proposed, for the dyeing of wool [1, 2], wool anti-felting, with low-plasma anti-spraying [3], laser treatment [4], use of biopolymers [5], enzymatic treatments [6-8]. Steady efforts are also being made in the field of waste recovery from the textile industry [9].

The purpose of the present paper is to replace the anti-felting operation with active chlorine-based oxidative derivatives, aggressive to the environment, by carrying out an ecological, enzymatic treatment of the wool fiber in the presence of surfactants made of renewable raw materials with anti-felting effect, but without deeply affecting the wool fiber. The evaluation of the effect of this enzymatic treatment in the presence of surfactants will be achieved by the FTIR technique, by highlighting the changes occurring after treatment.

Experimental part

Materials and methods

100% wool pile - wool band, washed, combed and *standard wool fabric,* Dorobantul- Ploiesti;

Enzymes -three types of proteases: Alcalase 2.5 L (E1); Liquanase 2.5 L (E3); Savinase16 L (E4), one type of amylase: Stainzyme 12 L (E2) and one type of lipase: Lipex 100 L (E5), Novozymes;

Detergent composition specifically designed to be compatible with the enzymes considered, consisting of 20% non-ionic surfactants obtained from renewable raw materials (alkylpolyglucosides and ethoxylated fatty alcohols), chelates, preservative agents, adjusted to *p*H 7.5.

Distilled water was used during the experiments.

The experiments were made on a laboratory washing apparatus under mechanic and thermic control Scourotester (*Textilipari Kutato Intezet* Budapest).

Surfactant-assisted enzymatic treatment of wool fibers was performed using 2 g of 100% wool pile, at a detergent concentration - 3 g/L, with different mixtures of enzymes and various amounts of enzymes, according to table 1.

Table 1
EXPERIMENTAL CONDITIONS

Sample code	Enzyme mixtures	Percentage enzyme versus detergent, (%)
10	E1+E5	30/5
11	E3+E5	30/5
12	E4+E5	30/5
13	E1+E2+E5	30/5/5
14	E3+E2+E5	30/5/5
15	E4+E2+E5	30/5/5

Washing step: fabric: washing water ratio 1:20; *p*H 7; temperature 40°C; time 45 min;

Rinsing step: temperature 30°C; 5 min;

Drying step: temperature 40°C; time 30 min.

FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were registered with a Spectrum GX spectrometer, Perkin Elmer instrument in ATR module.

Determination of relaxation shrinkage (IWS test method no. 9, 1980) and of the *felting shrinkage* (IWS test method no. 185, 1980) were performed on CUBEX apparatus, on pieces of 100% wool fabric. Shrinkage is a dimensional change in the lenght and width of a fabric sample. For the determination of relaxation shrinkage the wool fabric samples were soaked for 15 min in solution at 40°C, stirred for 5 min than rinsed and dryed. In the end, shrinkage of wool pieces is measured for both warp and weft dimensions.

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Relaxation shrinkage is calculated according to the formula (1):

$$\%Relaxation\ shrinkage = \frac{O.M.-R.M}{O.M.} x100 \quad (1)$$

where: O.M. is original measurement;
R.M. is relaxed measurement.

After the relaxation operation the samples are washed in CUBEX apparatus for 1 h at 40°C, than the wool samples are rinsed and dryed. Shrinkage of the wool pieces is measured for both warp and weft dimensions.

Felting shrinkage is calculated according to formula (2):

$$\%Felting\ shrinkage = \frac{R.M.-W.M}{R.M.} x100 \quad (2)$$

where: R.M. is relaxed measurement;
W.M. is washed measurement.

Results and discussion

Enzymatic treatment of wool fibers in the presence of surfactants, in order to achieve a smoothing of the wool scales, by which the phenomenon of anti-felting of the wool is realized, was carried out following the experimental laboratory program described in material and methods.

Wool samples subjected to treatment were analyzed by infrared spectrometry with Fourier transform. As expected, the FTIR spectra of wool samples represent a complex biological structure, composed of diverse types of proteins, made up of different amino acids, among which an important role is cystine. These samples of wool treated with the enzymes are compared with standard wool. In order to compare the intensity of the absorption bands as transmittance in % for the three samples and the standard, their spectra were normalized and corrected for the baseline.

Wavelengths corresponding to the characteristic wool fiber functional groups have been identified, which are shown in table 2.

Table 2
WAVENUMBERS CORRESPONDING TO FUNCTIONAL GROUPS OF WOOL FIBERS

Wavenumber, cm^{-1}	Functional group
3286 cm^{-1} – 3282	N-H
3076 cm^{-1} – 3075	C=C
2961 cm^{-1} – 2957 2878 cm^{-1} – 2875	CH_3-
2923 cm^{-1} – 2920 2852 cm^{-1} – 2851	CH_2-
1641 cm^{-1} – 1634	Amida I (C=O)
1538 cm^{-1} – 1535	Amida II (NH)
1452 cm^{-1} – 1451 1400 cm^{-1} – 1398	-CH-
1118 cm^{-1} – 1117	$CySO_2$-S-Cy
1077 cm^{-1} – 1076	CySO-S-Cy
931 cm^{-1} – 930	C-O-C

The samples 10, 11 and 12 were subjected to FTIR spectroscopy along with an untreated wool standard. FTIR spectra are presented in figures 1, 2, and 3.

The absorption bands characteristic for the following functional groups are presented (fig. 1-3):

N-H in the region 3287 cm^{-1} - 3281 cm^{-1}, for which the intensities of the absorption bands for this functional group decrease in order 11, then for all others are equal;

C = C in the region 3076 cm^{-1} - 3075 cm^{-1}, for which the intensities of the absorption bands decrease in order 11, then for all others are equal;

CH_3- in the regions 2961 cm^{-1} - 2957 cm^{-1} and 2878 cm^{-1} - 2875 cm^{-1}, for which the absorption band intensities decrease in the same order and the standard has the highest intensity;

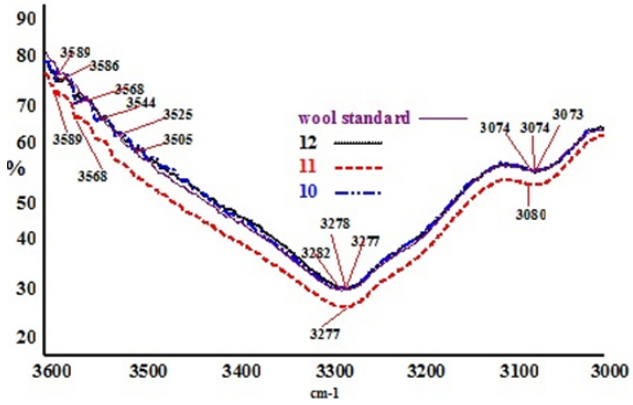

Fig. 1. FTIR spectra for samples 10, 11 and 12 and standard wool for the domain 3600-3000 cm^{-1}

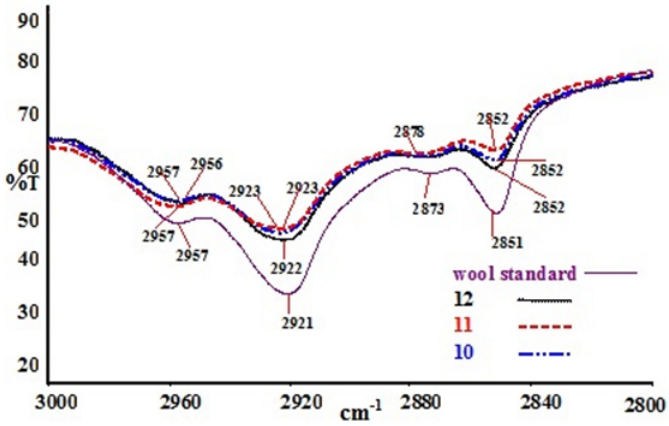

Fig. 2. FTIR spectra for samples 10, 11 and 12 and standard wool for the domain 3000-2800 cm^{-1}

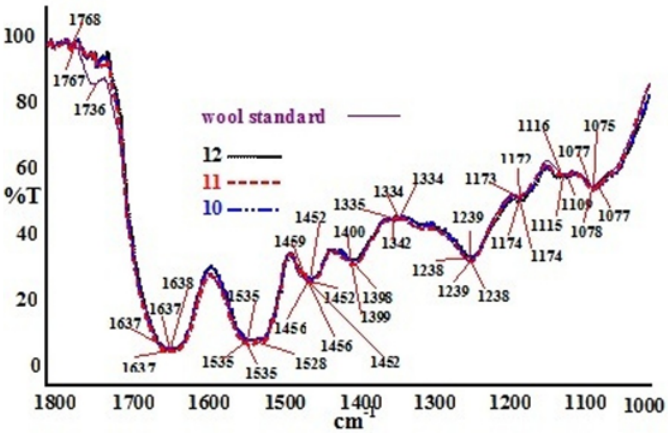

Fig. 3. FTIR spectra for samples 10, 11 and 12 and standard wool for the domain 1800-1000 cm^{-1}

CH_2 in the regions 2924 cm^{-1} - 2920 cm^{-1} and 2852 cm^{-1} - 2851 cm^{-1}, where the absorption band intensities for both spectral domains decreases in the order: standard, 12, 10, 11;

C = O in the $CONH_2$ group, Amide I, in the region 1641 cm^{-1} - 1638 cm^{-1}, where the intensity of the absorption band for samples 10, 11, 12 and standard are substantially the same;

NH of the $CONH_2$ group, Amide II, in the region 1535 cm^{-1} - 1529 cm^{-1}, has the same behavior as Amide I, and for the NH function in the $CONH_2$ group Amide III, in the region of 1239 cm^{-1} - 1238 cm^{-1}, the intensities decrease in order, 11 equal to the standard, then the rest are equal;

-CH- at 1452 cm^{-1} and at 1400 cm^{-1} - 1398 cm^{-1}, has identical behaviour, namely the intensities for all three samples studied and for the standard are substantially the same.

CySO-S-Cy, Cystine-S-mono-oxide S, in the region 1074 cm^{-1} - 1073 cm^{-1}, the intensity of the specific band decreases in the order: standard and the remaining practically equal;

C-O-C in the region 931 cm^{-1} - 930 cm^{-1}, shows a broad band and its intensity decreases in the order of 12, 10, 11, and then the standard.

The samples 13, 14 and 15 were subjected to FTIR spectroscopy along with an untreated wool standard. FTIR spectra are presented in figures 4, 5 and 6.

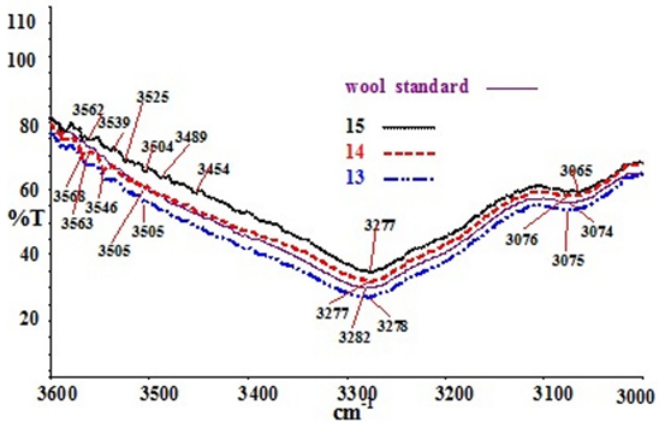

Fig. 4. FTIR spectra for samples 13, 14, 15 and standard wool for the domain 3600-3000 cm^{-1}

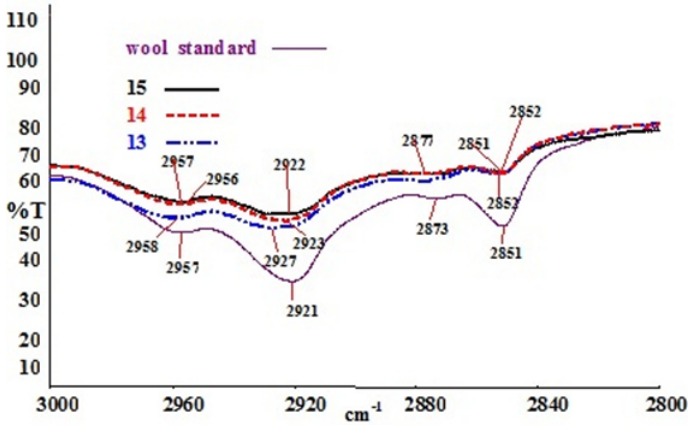

Fig. 5. FTIR spectra for samples 13, 14, 15 and standard wool for the domain 3000-2800 cm^{-1}

The absorption bands characteristic for the following functional groups are presented (fig. 4-6):

N-H in the region 3287 cm^{-1} - 3281 cm^{-1}, for which the intensities of the absorption bands for this functional group decrease in order 13, then standard, 14 and 15;

C = C in the region 3076 cm^{-1} - 3075 cm^{-1}, for which the intensities of the absorption bands decrease in order 13, then standard, than 14 and 15;

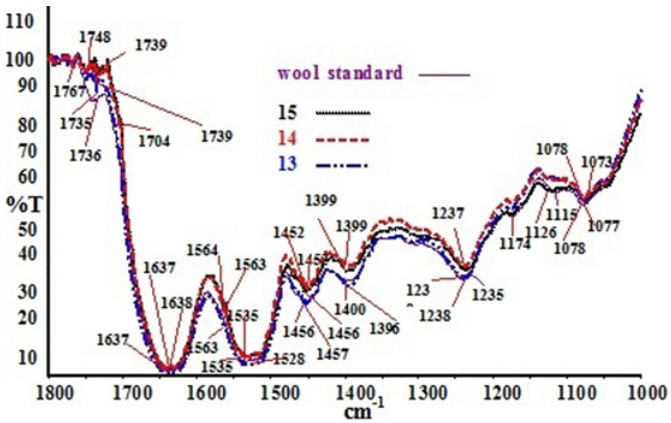

Fig. 6. FTIR spectra for samples 13, 14, 15 and standard wool for the domain 1800-1000 cm^{-1}

CH_3- in the regions 2961 cm^{-1} - 2957 cm^{-1} and 2878 cm^{-1} - 2875 cm^{-1}, for which the absorption band intensities decrease in order standard, 13, then 14 equal to 15;

CH_2 in the regions 2924 cm^{-1} - 2920 cm^{-1} and 2852 cm^{-1} - 2851 cm^{-1}, where the absorption band intensities, for both spectral domains, decrease in the same way as the one mentioned above;

C = O in the $CONH_2$ group, Amide I, in the region 1641 cm^{-1} - 1638 cm^{-1}, where the intensity of the absorption band for sample 13 is stronger, the rest being substantially equal;

NH of the $CONH_2$ group, Amide II, in the region 1535 cm^{-1} - 1529 cm^{-1}, has the same behaviour as Amide I, and for the NH function in the $CONH_2$ group Amide III, in the region of 1239 cm^{-1} - 1238 cm^{-1}, the intensities decrease in order, standard, then 13, 15, 14;

-CH- at 1452 cm^{-1}, where the intensity of standard is equal to sample 13, then 14 is equal to 15, and for the region 1400 cm^{-1} to 1398 cm^{-1}, the intensities decrease in order 13, then standard, then 14 equal to 15;

CySO-S-Cy, Cystine-S-mono-oxide S, in the region 1074 cm^{-1} - 1073 cm^{-1}, the intensity of the specific band decreases in the order: standard and the remaining practically equal;

C-O-C in the region 931 cm^{-1} - 930 cm^{-1}, shows a broad band and its intensity decreases in the order of 15, 14, standard then 11.

The dimensional changes, in both warp and weft directions (percentage relaxation and felting shrinkage) of wool fabrics 10-15 subjected to testing were compared to untreated wool fabric, as it is shown in table 3.

The analysis of table 3 shows that the best samples are 10 and 13, which exhibit the smallest felting phenomenon compared to the untreated wool. Sample 10 is formulated two enzymes: E1 (protease) and E5 (lipase). Sample 13 is formulated with three enzymes: E1 (protease), E5 (lipase) and E2 (amylase), E5 and E2 being in concentrations much

Table 3

PROPERTIES OF UNTREATED AND ENZYMATIC TREATED WOOL FABRICS

Sample	Original measurement, cm		Relaxed measurement, cm		Felting measurement, cm		Relaxation shrinkage, %		Felting shrinkage, %	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
Untreated wool	30.3	25.15	24.75	30.05	23.75	29.45	+18.3	-19.5	+4	+2
10	39.0	29.95	39.2	30.2	37.85	29.6	-0.5	-1.0	+2	+2.5
11	38.85	29.8	38.7	30.2	37.55	29.3	+0.8	-1.4	+3.1	+3.1
12	28.5	29.95	28.85	30.15	27.8	29.5	-2.1	-0.7	+3.4	+3.4
13	38.55	29.75	38.8	30.1	37.55	29.6	-0.8	-1.7	+3	+1.3
14	29.0	29.95	29.0	30.3	27.95	29.8	+1	0	+3.6	+1.6
15	38.8	29.85	38.65	30.05	37.35	29.65	+0.8	+1.5	+3.3	+1.3

lower than E1 protease, but it seems that, as we have anticipated, the enzymes are extremely specific, each of them has contributed to our technical aim, namely to smooth the edges from the overlapping *scales* of the wool fiber through a single treatment.

Conclusions

The treatment of wool fibers in the presence of surfactants was conducted with proteolytic, amylolytic and lipolytic enzymes. Samples are formulated with two or three enzymes, which are intended to smooth the scales of wool fiber, thus limiting the unwanted felting phenomenon. FTIR measurements of samples treated with enzymes in the presence of detergent indicate changes in the intensities of various functional groups of wool compared to the standard wool fabric spectrum. Two samples are found to be efficient in reduction the felting phenomenon, one formulated with protease and lipase and the other formulated with protease, amylase and lipase.

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