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INVESTIGATION OF SLENDERING ON COARSE WOOL FIBER AND ITS CHARACTERISTICS

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Abstract:In this research the influence of slendering on coarse wool fiber which then improved by m-TGase treatment was studied. The coarse wool fiber was first treated by reducing agent then it was stretched at different conditions over various periods of times and temperatures and finally steam set. The wool fibers were then tested for some mechanical and physical properties. To overcome tenacity loss of the fibers as a result of slendering treatment, after–treatment with microbial trans-glutaminases was examined. The results show that the fineness of the fiber was improved about 17 % but the tenacity decreased about 15%. XRD analysis show that the degree of crystallinity related to stretching ratio and this increasing of stretching alters the degree of crystallinity. SEM shows that the cuticle of the treated samples causes excessive damage and the reducing agent can affect on wool surface. Furthermore, alkaline solubility was increased by reduction treatment, but m-TGase can compensate a little. The fiber yellowness was significantly decreased after slendering.

Key words: XRD, crystallinity, m-TGase Enzyme, yellowness, alkaline solubility, coarse wool, slendering

1-Introduction

Iranian coarse wool fibers are used in some textile materials, such as fabrics, carpets and nonwovens. The commercial properties of wool fibers are improved by some processing. One of the most important processes to improve the wool properties is chemically treated by reductive agents then stretched and set [1]. This treatment leads to modify some characteristics such as fineness that leads to slenderness. Initially, the technology of slendering was introduced on the merino wool fibre as an Optim™ brand by CSIRO, Australia in 1992 [2-3]. In this research the slendering treatment was accomplished on the coarse wool fibre. In spite of obtaining good advantages of this process, some disadvantages may be cause on the coarse wool fibre, such as the loss of tenacity. This can be made up by applying cross-link enzyme as microbial Transglutaminase. Trans-glutaminase is a family of amino acid transferase. Protein–glutamine, amine γ-lutamyl-transferase (EC2.3.2.13), commonly known as transglutaminase (TGase), is an enzyme that catalyses the acyl transfer reaction in which a γ -carboxyamide group of a peptide-bound glutamine (Gln) residue is an acyl donor. The acyl receptor is primary amine group which is usually the ε-amino group of a lysine (Lys) residue [4-6]. Using microbial Trans-glutaminase on wool after slendering helps to raise the wool fiber yarn strength [7-9]. Also in the earlier study on the stretched wool fiber was reported that the degree of crystallinity of the wool fibers decreased whereas the degree of orientation increased during the stretching and the tensile behavior of the stretched wool also supported the $\alpha \rightarrow \beta$ microstructure transformation [10]. Course wool fiber can be modified and create novel fibre by slendering through the mixture of chemical, mechanical and biochemical process. In recent report on the slendering of the course wool fibers was concluded that the microstructure of the modified coarse wool fibre has been transformed from α-helical to β-pleated sheet conformation by using infrared spectroscopy and Raman spectroscopy [9]. This study reports some other changes in the coarse wool fiber due to the slendering with reducing agent for different time periods and concentrations and various stretching with respect to the strength, diameter, morphology as

seen by SEM, solubility in alkaline, yellowness and crystallinity which was studied by X-ray diffraction.

2-Experimental part

2.1-Materials and Methods

Raw material used - Iranian coarse wool fibre- was scoured by fineness of 37.5 μm. Reducing agent used was sodium dithionite of Merck (Germany). The fibre was first scoured with 1% non-ionic detergent Rockapon12203 from Rockapon Co. (China) at 75°C for 45 min and then washed with tap water and dried at room temperature. Stretched wool fibre was produced on the basis of the processing described by Yao et al [11] (Fig1). The scoured wool was processed in the form of sliver on manual stretching equipment, developed at Textile Department, School of Engineering Science and Research Branch of Islamic Azad University in Tehran. Different conditions of slendering was arranged and by performing primary experiments, some values as following details on the Table 1 were selected as representation of slendering. The wool sliver was treated by different conditions which are given in Table 1 for 5 times and the average results were reported. After chemical treatment, the sliver was stretched and post oxidized by air to annihilate the reducing agent residue, and then dried at room temperature and steam set at 140°C for 4 min. It should be mentioned that remaining of reducing agents such as sodium dithionite in the wool will result in the accelerated release of setting caused by the same disulphide interchange reaction reducing setting release to a minimum, thus the reducing agents must be removed, and many thiol groups oxidized to disulphides as possible. This is particularly desirable to restore the mechanical strength of the network [12].

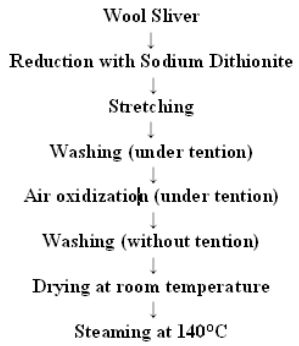

Figure 1*-Schematic diagram of stretching process of wool sliver*

2.2-Enzyme treatment

Wool fibre may loose its tenacity due to chemical and mechanical treatments. Cross-linking enzymes could restore the strength loss to some extent. Cross-linking enzyme used was microbial trans-glutaminase (amine γ-glutamytransferase EC-2.3.2.13), supplied by Ajinomoto Co., Singapore, and referred to m-TGase. It was composed of 1% (w/w) enzyme containing 99% (w/w) maltodextrin with reported activity of 86–135 units/g, where one enzyme unit is defined as the amount causing formation of 1 μmole of hydroxamic acid in 1 minute at 37°C [13]. The sample from experimental design for both optimization of fineness and tenacity was selected (sample 3 of Table 1) and treated with 20% m-TGase, pH=9-10, L:G: 40:1 at 37°C for 30 min, in order to improve wool tenacity [14].

Table 1*- The optimum values for slendering treatment*
S-Stretch Ratio, C- Sodium dithionite Concentration, Ti-Time, Te-Temperature, TG-m-Tgase

Sample	C (%)	S (%)	Ti (min)	Te. (°C)	TG (%)
1	2.5	53	7	70	0
2	1.25	57	14	55	0
3	2.5	44	10.5	75	0
4	2.5	44	10.5	75	20
5(raw) wool	0	0	0	0	0

2.3-Tenacity

Tensile properties of the fibre bundle were tested on an Elima yarn and fabric strength tester with constant rate of extension (CRE) and ASTM D1294 test method. The clamp speed and gauge length were 250 mm/min and 1 inch respectively [15].

2.4-Diameter

Fibre diameter was measured with wool Micronair instrument of Shirley Developments Ltd,(SDL) using IWTO standard methods under ASTM D 1282 [15].

2.5-Morphological study

The morphology of the fibres were observed using Scanning electron microscopy (SEM) (LEO ELECTRON MICROSCOPY (440I), England), after gold coating.

2.6-X-ray diffraction

To determine the crystallinity of the treated samples under different conditions, the sample was placed within the chamber of analytical X-ray diffract meter, X'Pert MPD Model, produced by Philips Company in Netherland. The pulp is Cu ka radiation, the generator intensity was 40 kV, and the generator current was 40 mA. The sample was then scanned from 2θ= 0-70˚, in step of 0.02˚/s. The resultant graphs were printed out on the origin graph plotting package.

2.7-Alkali Solubility

The experiment was carried on the ASTM D1283 method. One gram of wool sample after dried in an oven at 110°C for 15 min weighed and then was put into a baker containing 100 ml of sodium hydroxide of 0.1 N at 65°C for 1 h. Then the contents were filtered and rinsed with distilled water for 5min and dried in an oven at 110 °C for 1 h. After being desiccated, the alkali solubility of the samples was calculated as a percentage of the original weight according to the above equation.
Weight loss (%) was calculated from the following equation:

$$\text{Alkaline solubility} = \frac{W1-W2}{W1} \times 100 \quad (1)$$

Where W1 is the weight of the sample before treatment and W2 is the weight of the sample after treatment.

2.8-Yellowness index

The prepared test specimen is measured to give the tristimulus values X, Y and Z for the CIE* Illuminant D65 and 10º observer. Yellow index (YI) of the samples was calculated according to ASTM method E313 by following equation. Cx=1.3013, Cz=1.1498

$$YI\,E313 = \frac{100\left(C_x X - C_Z Z\right)}{Y} \quad (2)$$

3-Results and discussion

3.1-Fineness

Diameter of stretched wool with various stretch ratios and reducing treatment conditions are shown in Table 2. It varied between a minimum of 30 and a maximum of 31.3 in comparison to 37.5 for the raw wool. Therefore, fibre diameter was reduced between 15.4% and 18.9% in all tested samples. Thus the results show that the fineness of the coarse wool can be comparable with the OPTIM Fine wool [11].

3.2-Tenacity

Tenacity of the fibres is shown in Table 2. It varied for different test conditions between 1.8 and 3.2 g/Tex in comparison to 3.84 g/Tex for the raw wool. Fibre tenacity reduced differently between 16.6% and 53.12% for various samples. It can be seen that the tenacity of sample 1 to 3 decreased and after treating sample 3 with m-TGase, it was increased from 2.1(g/tex) to 3.2(g/tex). The result was predictable according to Ge and et al [1] and others [16, 17, and 18].

3.3-Tenacity of m-Tgases treated fibres

Tenacity of m-TGases treated fibers with different percentage of enzyme concentration on the sample 3 is shown in Table 3. It can be seen that the 20% m-TGases treated fibre shows the highest tenacity. Thus the concentration of 20% has been selected for further studies.

Table 2*-Average value of diameter and tenacity for different samples*

Sample	Average value			
	Diameter (μ)	CV%	Tenacity (gf/tex)	CV%
1	30	1.5	1.8	21.5
2	31.3	1.3	2.2	12.3
3	30.7	1.46	2.1	17.5
4	30.7	1.46	3.2	15.6
5(raw wool)	37.5	1.16	3.84	20.02

3.4-Surface morphology

The surface morphology of wool samples was characterized by scanning electron microscopy. Wool surface morphology is characterized by the scales, which play an important role in protecting the wool from damage and have high influence on some important properties of wool, such as luster and shrinkage [19]. The SEM in Fig. 2 shows that scales on the untreated wool fiber (raw wool-Fig2-E) are clear and arranged compactly around the fiber. But the scales in Figures (2-A, B and C) are damaged and it can be seen that the scales are separated and some of the fiber scales are striped. Also some scales are patulous. Fig 2-D for sample 4 which is after- treated with m-TGase shows that some scales are separated from the surface. Therefore it can be concluded that the slendering may damage and change the edge of some scales. Also

slendering may alter some characteristic of the fibers because of striping of some scales as indicated in the Fig.2 (A-E).

Table 3*-Mean tenacity of sample 3 treated with different percentage of enzyme concentration*

Enzyme concentration (%)	Tenacity (gf/tex)	CV (%)
5	2.2	16.5
10	2.4	12.7
15	2.9	20.3
20	3.2	15.6

3.5-XRD

The measurement of the degree of crystallinity provides useful data while characterizing fibers using X-ray diffractometry. The X-Ray Diffractograms of the samples are shown in Fig3. The degree of crystallinity of each sample was calculated by the obtained results of the graphs. Crystallinity is determined by the ratio of the whole diffraction of crystalline phase and the whole scattering of amorphous phase of a sample. Fig 3 shows the total crystallinity of stretched wool samples, which equals the sum of the α and β-Crystallinity. These losses are considered not to be significant, but may show that a small amount α-helical molecular chains transformed into amorphous material [20]. The results show that the degree of crystallinity was increased by stretching but with stretching ratio above 50%, the degree of crystallinity start to decrease gradually. Overall the maximum degree of crystallinity is related to sample 3 with 44% stretching. The results were reported in Table 4. The stretching mechanism is mainly dependent on the secondary structure transformation from α-helical structure to β-pleated-sheet structure. When the fiber is stretched longer than 50%, the mechanism of the wool fibers may dominantly rely on the slippage between the protein chains and also reduction process along with stretching. This may affect the degree of crystallinity, because of cleavage and slippage between disulphide bonds which depend on concentration of reducing agent. However the degree of crystallinity of these samples was affected by the concentration of reducing agent and stretch ratio. There is no linear correlation between stretch ratio and the degree of crystallinity. In comparison between these results and the results of the previous researches, the total crystallinity remained almost constant for wool samples stretched between 20-35% [20].

3.6-Alkaline solubility

As Table 5 shows, an increase in concentration of the reducing agent raises the percent of weight loss in dissolving of the wool fibers in alkaline, representing a higher solubility of wool in alkaline solution. This means that reducing agent may hydrolyze the polypeptide chains of proteins in wool fibers and reduces the stability of wool against the alkali, which can be a disadvantage of reducing treatment [14].

The results are in accord with their tenacity results. As both the tenacity and alkali solubility are affected by increasing the reducing agent concentration. This means that some of the linkages between chains of the polypeptide and some disulphide bonds have been broken [15, 16 &20]**.** The other point is the effectiveness of cross-linking enzyme on the wool fibre. It can be seen that alkaline solubility of sample 3 decreases after enzyme treatment i.e. alkaline solubility of sample 4. It can be concluded that some broken bonds are revived and the structure of wool fiber becomes stronger [14, 16, 17&21].

Table 4*-Degree of crystallinity of different samples calculated by XRD results*

Sample	Total area	Area[cts*2Th.]	Degree of crystallinity
Raw wool	57	9.84	17.2
1	28	7.83	27.96
2	58	12.76	22.00
3	35	11.46	32.74

Table 5 *-Alkaline solubility of different treated samples*

Sample	W2(g)	W1 (g)	Alkaline solubility(%)
1	0.83	1	17
2	0.86	1	14
3	0.84	1	16
4	0.88	1	12
5	0.92	1	8

3.7-Yellowness index

There is an improvement in the yellowness of treated wool fiber relative to the untreated one as shown in Table 6. Also Fig 4 shows the reflectance spectra of different samples. Increasing the concentration of reducing agent has decreased the yellowness index of the samples. This is comparable with other results, since the reducing treatment help to bleach the wool fiber [22-23]. However, the yellowness index of sample 4 increased again. It can be concluded that the yellowness index of those treated wool with m-TGase increased. This can be due to the action of other materials including the commercial powder enzyme.

4-Conclusion

Slendering on coarse wool fiber causes many changes in wool fiber properties. The analysis represents some advantages and disadvantages that are important for further usages. The wool fiber fineness diameter obtained is within acceptable range. The tenacity loss that can be compensated by cross-linking enzyme as m-Tgase is considerable but it may be limited. XRD results show the degree of crystallinity related to stretching ratio, increasing of stretching can be altered by the degree of crystallinity. It should be noted that the degree of crystallinity decline slowly by stretching above 50%.
SEM pictures show that the cuticle of the treated samples causes excessive damage and the reducing agent can affect on wool surface particularly on the shape of the scales. Furthermore, alkaline solubility increased by reduction treatment, but m-Tgase can compensate slightly. Yellowness was decreased after slendering but increased for the m-TGase treated samples and became close to raw wool.

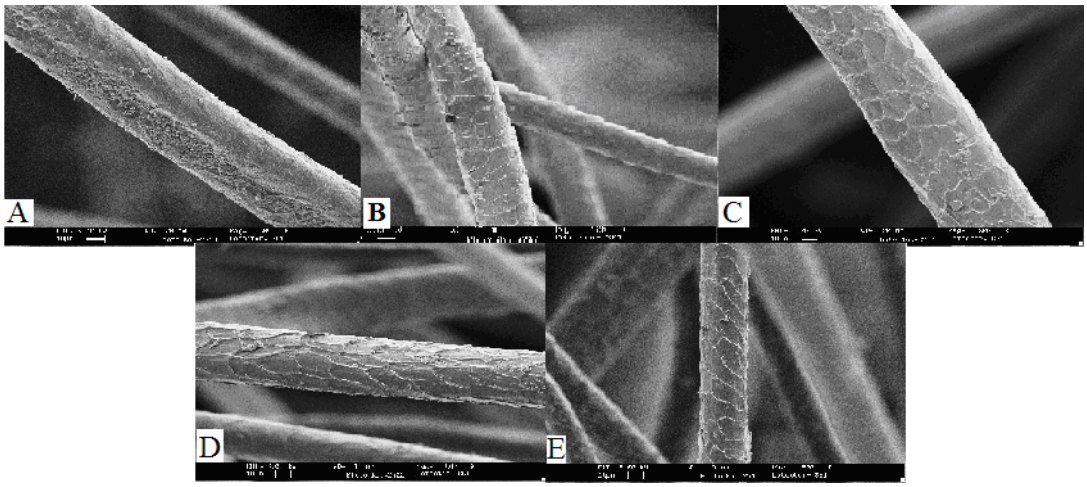

Figure 2- *Scanning Electron Microscope of samples, A-sample1, B-sample2, C-sample3, D-sample4, E-sample5(x500)*

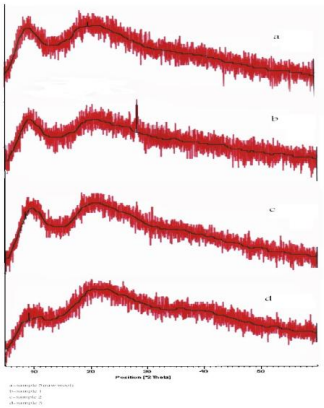

Figure 3- *X-Ray Diffractograms of the samples a-Raw wool, b-sample 1, c-sample 2, d-sample 3.*

Table 6- *Tristimulus values X, Y and Z were obtained from Reflectance graph and Yellow Index E313 for different samples*

Sample	X	Y	Z	YI(%)
1	6547.6	9436.2	8914.7	43.15
2	6437.1	9134.4	8645.8	42.14
3	5931.6	8640.6	8154.3	43.8
4	5044.4	7448.5	7092.9	46.04
5	5292.4	7872.8	7508.4	46.8

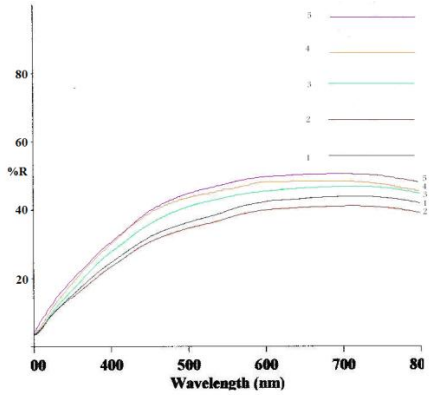

Figure 4- *Reflectance spectra of yellowness for different samples*

5-References

[1]-Tonin C, Aluigi A, Bianchetto Songia M, D'Arrigo C, Mormino M, Vineis C,: Thermoanalytical Characterisation of Modified keratin Fibers, *Journal of Thermal Analysis and Calorimetry*;Vol. 77(2004).p. 987–996.
[2]-http://www.csiro.au/science/pps7m.html. Accessed April 2009.
[3]-http://www.csiro.au/files/files/p6py.pdf. Accessed April 2009.
[4]- Lorand L, Konishi K, and Jacobsen A, Transpeptidation mechanism in blood clotting, *Nature* 1962; 194: 1148–1149.
[5]-Folk JE, Transglutaminases, *A Review of Biochemistry* 1980; 49: 517–531.
[6]-Ichinose A, Bottenus RE and Davie EW, Structure of transglutaminases , *Journal of Biological Chemistry* 1990; 265: 13411–13414.
[7]-Cortez J, Bonner P and Griffin M, Application of Trans – glutaminase in the modification of wool textile, *Enzyme and Microbial Technology* 2004; 34(1): 64-72.
[8]-Cortez J, Bonner P and Griffin M, Transglutaminase treatment on wool leads to resistance to detergent damage , *Journal of Biotechnology* 2005; 116(4): 379-386.
[9]-Motaghi Z, Eskandarnejad S, Montazer M, Ardjmand M, Bameni Moghadam M, Mechanical slenderizing of coarse wool fibre and determination of its characteristics with FTIR and Raman spectroscopy, *Journal of the Textile Institute* 2011; in press.
[10]-liu H and Yu W, Study of the Structure transformation of Wool Fibers with Raman Spectroscopy, *Journal of Applied Polymer Science* 2007; 103: 1-7.
[11]-Yao J, Liu Y, Yang S, Liu J, Characterization of Secondary Structure Transformation of Stretched and Slenderized Wool Fibres with FTIR Spectra, *Journal of Engineered Fibres and Fabrics* 2008; 3(2): 22-31.
[12]-Mckinnon J, Chemistry of the wool Industry scouring and Yarn production, *Wool Research organisatin of Newzland;* Animal product, F, Wool: 1-30.
[13]-Motoki M and Seguro K, Transglutaminase, U.S. Patent 1992; 5,156,956..
[14]-Montazer M, Ramin A, Influences of Proteases and Trans-glutaminases on Wool, *FIBRES & TEXTILES in Eastern Europe* 2010;18(2)(79): 98-102.
[15]-ASTM D 1282 and D1294, *Test Method for wool fibres Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia* 1996; *PA*, 07.01.
[16]-Truong VD, Clare DA, Catignani GL, Swaisgood HE, Cross-linking and Rheological Changes of Why Proteins Treated with Microbial Transglutaminase, *Journal of Agricalture Food Chemistry* 2004; 52: 1170-1176.
[17]-Fengyan G, Zaisheng C, Zhang H, Zhang R, Transglutaminase Treatment for Improving Wool Fabric Properties ,*Fibers and Polymers* 2009; 10(6): 787-790.
[18]-Cardamone JM, Enzyme-mediated crosslinking of wool. Part Π, Transglutaminase, *Textile research Journal* 2007; 77(4): 214-221.
[19]-Weilin X, Guizhen K, Jihong W, Xungai W, Modification of wool fiber using steam explosion, *European Polymer Journal* 2006; 42: 2168–2173.
[20]-Cao J, Billows CA, Crystallinity determination of native and stretched wool by X-ray diffraction, *Polymer International* 1999; 48: 1027-1033.
[21]-Yilmazer D and Kanik M, Bleaching of Wool with Sodium Borohydride, *Journal of Engineered Fibers and Fabrics* 2009; 4(3): 45-50.
[22]-Derbyshire AN and Lemin DR, The light Fastness of Yellow Wools, *Journal of the Society of Dyers and Colourists* 1964; 80(5): 243-248.
[23]-Gaeen J, Cegarra J and Cayuela D, Wool bleaching with reducing agents in the presence of sodium laurylsulphate. *Journal of the Society of Dyers and Colourists* 1994; 110(8): 277–279.