Effect of the Chemical Unhairing Process on Pulled Wool Characteristics

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Abstract

Textile research is being driven to find sustainable materials as an alternative to raw fibers. In fact, reusing fibrous waste, as a byproduct, is one of the most important environmental challenges that confront the world. This research focused on studying pulled wool fibers as a natural fiber to reduce environmental loading. There are large amounts of residual pulled wool fibers that can be recycled and valorised. Therefore, raw and pulled wool fibers were characterized and compared. Scanning Electron Micrographs (SEM) results show that on the pulled wool fiber, the surface became rougher and the scales appear affected and less dense. Based on the X-ray diffraction (XRD) results, the crystallinity of the pulled fiber decreased lightly. Attenuated Total Reflectance-Fourier Transform Infra Red (ATR-FTIR) spectroscopy analyzes presented some changes in chemical composition. A High-Performance Liquid Chromatography (HPLC) test showed an increase in the amount of cystic acids. The pulled wool fiber indicates that it might have damaged some crosslinks of macromolecular chains in the fiber. Thus, physical, chemical and mechanical properties are affected during the chemical unhairing process. This research purpose was to increase the potential for better value of pulled wool as it presents the natural fiber most used in several applications.

Keywords

ATR-FTIR, red face Barbary sheep, chemical unhairing process, pulled wool, SEM, X-ray.

1. Introduction

Wool is a valuable natural protein fiber. Raw wool fiber is known to have excellent intrinsic properties, and therefore it is widely used as a high-quality textile material [1]. A very important amount of post-consumer and post-industrial textile fiber wastes are being generated [2]. In this context, a high volume of wool fiber waste (pulled wool) is generated from tanneries [3] during the unhairing process, which consists of removing wool from the skin after it has been removed from the hide [4].

The unhairing process could be done by many methods, such as clipping, scalding, chemical, sweating, and enzymatic processes. Unhairing using chemical treatment is considered as the process most used in tanneries [5]. In fact, using lime and sodium sulfide in chemical treatment creates an extremely alkaline solution, resulting in the removal of the wool fiber from the hide.

To be recycled as a textile fiber, pulled wool fibers should have special characteristics that are similar to those of raw fibers. These characteristics play an important role in the functional and aesthetic properties of the final product [6].

Until now, the available literature on pulled wool is still insufficient to reflect clearly its importance as recycled fiber. Most studies are often limited to studying raw wool.

The present research was therefore aimed to conduct a comparative study between raw and pulled wool fiber characteristics. The physical and chemical properties of fibers were measured and compared. According to the results obtained, we were able to estimate suitable applications of recycled wool fibers and to determine their value and end-use.

2. Experimental

2.1. Materials

The hide of a slaughtered sheep was taken from Sahel of Tunisia's battle. Considering the significant influence of sex and breed on wool fiber properties [7], the pelts selected were of a male of the red face Barbary variety (BTR). The hide was divided into two identical parts (Figure 1a). One part was sheared and identified as raw wool (R), while the second part was pulled (P) from the hide using the chemical tanning process. Each part was divided into different zones; rump, back, side, and neck, denoted #1, #2, #3 and #4, respectively, as shown in Figure 1b.

The chemical tanning process is as follows: Sodium sulfide Na_2S was added to water until the concentration of the solution reached 18°Be. After its dissolving, lime was added to the solution in order to obtain a 35°Be concentration. Tanning involved pasting the flesh side of the skin with the obtained solution [8].

According to Standard ASTM D 584 – 96 (Reapproved 2005) to determine the percentage of clean wool weight, samples were weighed immediately, immersed in a scouring bowl solution containing 0.3% of sodium carbonate (Na_2CO_3) and 0.1% soap and EDTA stirred for 15 minutes at a temperature of 52±3°C. This procedure was repeated once more [8]. After that, the washed samples were oven-dried at 105°C and weighed.

2.2. SEM analysis

Scanning Electron Microscopy (SEM) analysis was carried out with a JEOL JSM5400 microscope at 15 kV acceleration voltage after gold coating.
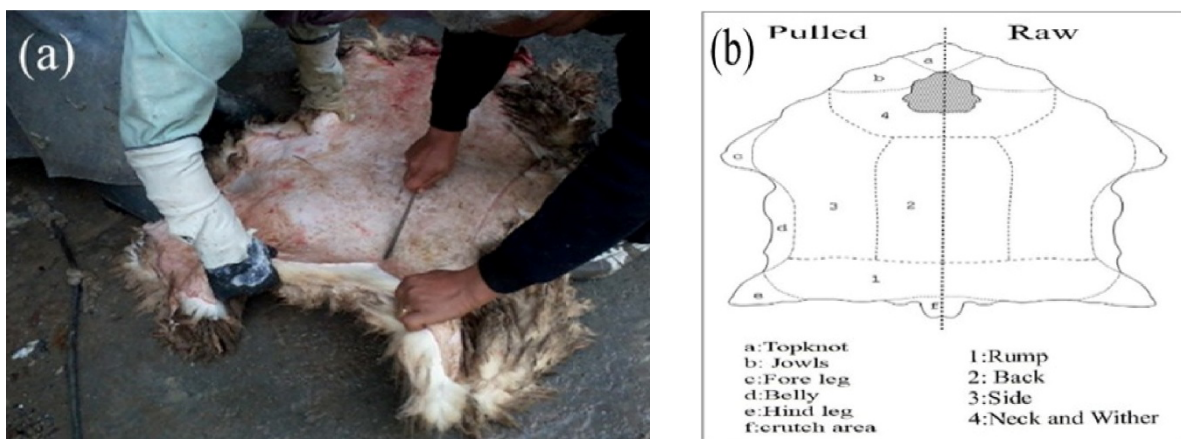
Fig. 1. Skin division along (a) longitudinal direction & (b) different sheep body parts

2.3. Determination of mean diameter and fiber length

Measurement of the apparent diameter of pulled and raw wool was taken by a projection microscope (×400 times) according to ASTM D 2130-90 (Reapproved 2001). The test was carried out on 300 randomly chosen fibers [9].

Wool fiber length measurements were performed using the direct method according to ASTM D519-04 (Reapproved 2013). Fibers from the sample were normalized and arranged one by one, over a graduated scale, to take the measurements.

2.4. Test of moisture regain

In accordance with Standard NF G 08-001, the moisture regain (MR) of the samples were tested under standard conditions (25°C, 65% RH). It was calculated using Equation 1.

$$MR(\%)=100*\frac{M_h-M_s}{M_s} \qquad (1)$$

Where M_s and M_h represent the dry weight and conditioned weight of the samples, respectively.

2.5. ATR-FTIR analysis

An ATR-FTIR instrument (Spectrum Two™ FTIR, Perkin Elmer) was used to analyse the spectra of the samples.

100 scans were made per sample with a resolution of 2 cm^{-1}. The infrared spectra were recorded in the range of 4000-400 cm^{-1}.

2.6. X-ray diffraction analysis (XRD)

To determine the crystallinity of the samples, the wool fiber was placed within the chamber of an analytical X-ray diffractometer and measured at 2θ of 5° to 80° and at a scan speed of 8 deg/min. The resultant graphs were printed out using an OriginPro 8 graph-plotting package. The degree of crystallinity (Xc) was estimated using Equation 2.

$$Xc=\frac{(A_{tot}-A_{amor})}{A_{tot}}\times100 \qquad (2)$$

Where A_{tot} is the total area under the curve of the diffracted intensity at 2θ = 5° to 45°, and A_{amor} is the corresponding area under the baseline [10]. The baseline is default to the bottom axis, but it can be customised by adding an additional line from the grids tab of the axis dialog. Using the integrations of the total area under the curve and that under the baseline, we can determine the crystallinity percentage.

2.7. Tensile properties

For the tensile testing a LLOYD Instrument machine was used at a constant gradient rate of 17mm/min

with a 20 mm length in accordance with Standard ISO 5079:1995(E). For each sample, the mechanical properties of 50 fibers were tested, and the mean value and deviation were calculated.

2.8. Amino acid analysis

Chemical analysis of the wool fibers was performed by HPLC. Wool samples were hydrolysed with 6 M HCl for 24 h at 110°C in a nitrogen atmosphere. Free amino acid residues were obtained with 6-aminoquinolyl-N-hydroxysuccimildyl carbamate (AQC by Waters) and eluted on a reversed-phase column. The quantitative amino acid composition was determined by calibration with amino acid standard H (Pierce), cysteic acid, lanthionine (TCI Europe) as an external standard and α-aminobutyric acid as an internal standard [11].

3. Results and discussion

In order to compare the physical and mechanical properties between raw and pulled wool, our samples were cleaned. Yield is a major determinant of the value of raw wool [12]. With the exception of vegetable matter, scouring removes most of the grease, wax (fat), suint, and dirt from wool fibers [13]. The percentage of clean wool weight was calculated, the results of which are shown in Table 1.

This proportion varies with the sampling points. In general, it decreases in dirty

Sheep body part (as in Figure 1b)	#1	#2	#3	#4	Mean CWY (%)
CWY of raw wool (%)	81.61±1.32	89.06±0.88	90.72±2.01	76.21±2.68	**84.40±6.75**
CWY of pulled wool (%)	57.08±2.28	62.72±4.01	51.19±4.49	55.35±3.56	**56.59±4.78**

Table 1. Clean weight yield (CWY) for raw and pulled wool fibers

places (rump, belly, and areas on which the animal lies down). The results presented in Table 1 indicate that the clean weight yield varies from 76.21± 2.68 to 90.72 ± 2.01% for raw wool. The side (#3) presents the cleanest region as it often retains impurities [14]. In addition, the clean weight yield is affected by the fiber's diameter. According to Taherpour et al., the yield of coarse wool is higher than that of medium and fine wool [15].

The average clean weight yield of raw wool, 84.40± 6.75%, is higher than that of pulled wool, which is 56.59± 4.78%. The CWY of pulled wool varies from 51.19± 4.49% to 62.72± 4.01%. This decrease is explained by the chemical product used in the tanning process and its post-treatment [16]. Despite this low value, the clean weight percentage of pulled samples can be described as acceptable referring to the American Sheep Industry Association, which considers that washing performance is between 40% and 70%, and for the Tunisian sheep breed - from 50–70% [17].

3.1. SEM Analysis

The surface structure of fiber is an important factor affecting its properties. Wool is a natural fiber, which intrinsically has a rough surface. SEM images of raw and pulled wool fibers are shown in Figure 2, revealing slight changes in the cuticle layer. For raw wool, presented in Figure 2a, it can be clearly observed that scales are sharp and that the cuticle layer has a smooth surface. However, for the pulled wool, presented in Figure 2b, the scales appear affected and less dense as compared to raw wool. Thus, the chemical treatment makes the scale edges blunt, and also some roughness is induced on the cuticle surface. Moreover,

this treatment has an etching effect on the surface of wool fiber.

For wool fiber, it is evident that the destruction is essentially caused by the attack on protein fiber by the alkaline treatment [5]. In fact, tanning involves many steps (soaking, chemical unhairing, liming, fleshing, lime removal, bating, fat removal, etc.). Thus, the morphology of pulled wool is systematically affected and its surface roughness increased. Indeed, using lime and sodium sulfide in the chemical method, especially at high concentration, creates an extremely alkaline environment, resulting in the pulping of hair and its subsequent removal [18].

Morphological details of the scales are the number of scales per 100 μm, the scale height and scale index [19]. The number of scales per 100 μm is 8.6 and 8.4 and the scale height 18.96 μm and 18.27 μm, respectively, for raw and pulled wool. These results are in agreement with those of Mahal et al. [20]. In their investigation, they proved that the average number of scales per 100 μm for medium wool is approximately eight.

The scale index, which is the ratio of scale height to fiber diameter [20], is equal to 0.743 for raw wool and 0.703 for pulled wool. Figure 2c, which presents raw wool, and Figure 2d, which presents the fiber after alkali treatment, show that scales height decreased, and as a result the scale index decreased. Therefore, it can be concluded that the chemical treatment may damage and change the edge of some scales. According to Rippon, friction is related to the scale index [21]. Its decrease for pulled wool fibers accounts for the low directional frictional coefficient reported for this wool.

3.2. Mean diameter

The average fiber diameter of wool is the single most important parameter that characterises its fineness [22]. In addition, it is to the manufacturers' advantage to know how much grade variation exists between raw and pulled wool in any given lot before determining its fair market value. For this reason, it is very crucial to assess the variation in fiber diameter between raw and pulled wool. The values obtained herein are presented in Table 2.

From Table 2, the average diameter value of raw wool is equal to 26.34± 1.19 μm. Therefore, according to the American Blood grade system, wool fibers of the red face Barbary breed belong to the middle grade "3/8 Blood" [23]. With reference to Charlet et al. [14]., the finest fibers are at the neck (#4) and on the upper part of the shoulder, on each side of the withers. The coarsest fibers are mostly on the rump (#1). Average fineness is found on the side (#3) and the back (#2). The percentage diameter difference between raw and pulled wool is in the order of 4.08, 1.10, 3.12, and 2.36%, respectively. for rump, back, side and neck. The average diameter of pulled wool is decreased to 25.62 ± 0.86 μm. The difference between the diameters of raw and pulled samples reveals significant changes ($p < 0.05$).

In fact, the chemical treatment alters scales and fragments were dislodged without modifying the inner diameter of the wool fiber, as a result, it keeps its initial fineness. This outcome is in agreement with that of Phan et al., who proved that using a chemical treatment, raw wool loses about 0.8μm to 1μm in diameter due to scales peeling [24].

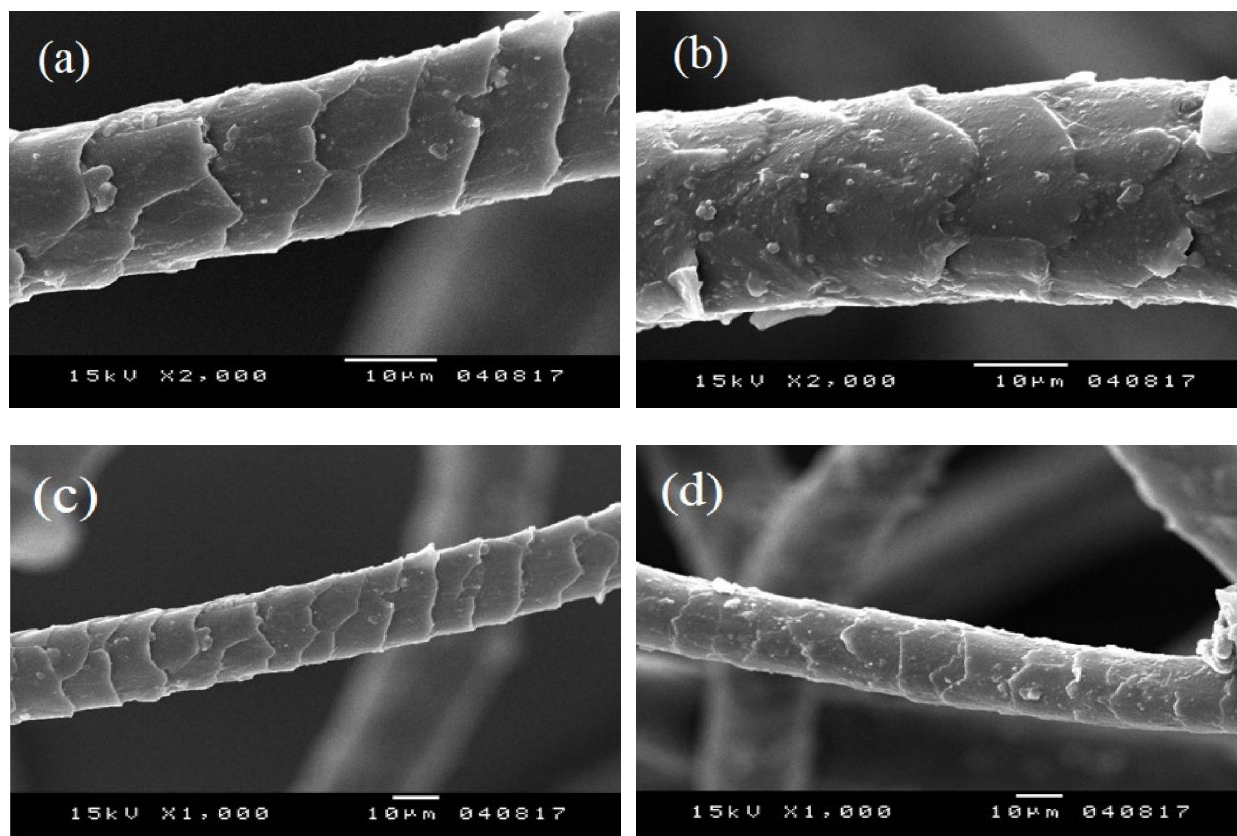According to the ASTM D 3991-94 (Reapproved 2000), those samples with

Fig. 2. Scanning electron micrographs of (a) raw, (b) pulled wool fibers (□2000), (c) raw, and (d) pulled wool fibers (□1000).

Sheep body part (as in Figure 1b)	#1	#2	#3	#4	Mean Diameter (MD)
Raw wool diameter (µm)	27.72±4.21	25.28±3.50	26.94±4.21	25.40±4.19	**26.34±1.19**
CV (%)	15.19	13.84	15.63	16.5	**15.29**
Pulled wool diameter (µm)	26.59±3.96	25.00±3.71	26.10±5.67	24.80±4.23	**25.62±0.86**
CV (%)	14.89	14.84	21.72	17.06	**17.13**

Table 2. Fiber diameter (FD) of raw and pulled wool fibers

associated diameters, standard deviation, and a coefficient of variation can be used in light upholstery coatings and in some carpets and tapestries.

3.3. Fiber length

Wool fiber length is a cornerstone factor that determines its end-use. The direct method was used to determine the fiber length of both raw and pulled wool. The results obtained are shown in Table 3.

The side (#3), back (#2) and rump (#1) fibers are always very long close to the average. However, the shortest fibers are on the neck (#4). This finding is confirmed by Charlet et al. [14].

The percentage length difference between raw and pulled wool is in the order of 14.81, 11.72, 4.94, and 15.96%, respectively, for rump, back, side and neck. It is noticeable that the higher difference value is concentrated in the zone exposed to sunlight (#1, #2 and #4). In fact, when wool or other keratin is exposed to sunlight for extended periods, it is prone to loss of lipid and eventually to loss of strength [25]. As a result, after chemical treatment, pulled fiber

unhairing from the same zones presented a higher difference percentage.

For manufacturers it is of major importance to know the range of length in order to determine its auction price [26]. The distribution of lengths is an indication of different finesses, for example the longer wool fibers are, the higher the diameter is [14].

For our samples, the mean length is 89.77± 7.79 mm with a 25.62± 0.86 µm mean diameter. According to the Canadian Sheep Federation, for a wool fineness of 26 µm to 30.1µm, the

Sheep body part (as in Figure 1b)	#1	#2	#3	#4	Mean Fiber Length (MFL)
Raw wool length (mm)	101.78±18.94	100.72±21.61	106.02±16.89	98.36±20.24	**101.72±3.20**
CV (%)	18.61	21.46	15.93	20.58	**19.14**
Pulled wool length (mm)	86.70±12.44	88..92±16.17	100.78±15.32	82.66±13.73	**89.77±7.79**
CV (%)	14.35	18.18	15.20	16.61	**16.09**

Table 3. Mean fiber length (MFL) of raw and pulled wool fibers

Sheep body part (as in Figure 1b)	#1	#2	#3	#4	Mean moisture regain (MR)
Moisture regain of raw wool (%)	15.52±0,59	14.56±0,65	15.25±0,82	14.18±0,62	**14.88±0.62**
Moisture regain of pulled wool (%)	14.42±0,66	14.41±0,78	14.70±0,73	13.18±0,57	**14.18±0.68**

Table 4. Moisture regain (MR) of raw and pulled wool fibers

suggested length is between 75 and 90 mm. Thus, the diameter-length ratio of the pulled samples tested can be considered as acceptable.

3.4. Fiber moisture regain

Moisture regain is the ability of a dry fiber to absorb moisture under set conditions of humidity. Owing to the presence of the amorphous region and the amide and carboxyl groups, wool fiber has high moisture regain [6], reaching 15.5% at 25°C [27], which is the case of our test samples.

Wool fiber is strongly hygroscopic. It has a pronounced hydrophobic character on its surface, absorbing water as vapor while the liquid water is pushed out of the fiber, thanks to the cuticles [28]. As can be seen in the table above, the moisture regain of pulled wool, 14.18± 0.68 %, is lower than that of raw wool, 14.88± 0.62 %. This phenomenon can be explained by the damage of the scales, which was the cause of hydrophobicity on the surface of raw wool.

Moreover, Frederic Élie proved that wool fiber is covered with greases and even waxes (suintine), which represents up to 50% of the weight of the fleece. The greases are mainly composed of suint (dissolvable by cold water) and lanolin (insoluble in water). Lanolin is very hygroscopic. It can absorb a third of its weight in water [29]. Furthermore, lanolin is sensitive to alkali products, as a result of which its content decreases with the chemical process of unhairing. Thus, the moisture regain of pulled samples decreased.

3.5. XRD Analysis

Measurement of the degree of crystallinity provides useful data while characterising fibers using X-ray diffractometry. The degree of crystallinity is determined by the ratio of the whole diffraction of the crystalline phase and the amorphous phase of each sample. In this part, we investigated through XRD analysis the change in the total crystallinity between raw and pulled wool.

The X-ray diffraction results of the raw and pulled samples are shown in Figure 3. They show the typical diffraction pattern, with a prominent 2θ peak at 20° and a minor peak at 10°. The crystalline scattering corresponds to that above the baseline, and amorphous scattering to that below the baseline.

The degree of crystallinity of each part of the pelt for raw and pulled wool was calculated with the results of the graphs obtained. The percentages of crystallinity X_c of raw wool fiber are 40.5, 40.4, 41.4, and 39.7, respectively, for zones #1, #2, #3 and #4, and 33.3, 35.33, 34.0, and 31.5

for pulled wool. The values of average crystallinity X_c obtained are 40.5% and 33.5%, respectively, for raw and pulled wool. The average loss is in the order of 7% between raw and pulled wool. The results show that the degree of crystallinity was decreased by alkali treatment.

The α-keratin structure presents a crystalline spacing of 0.51 nm at the prominent peak 20°and 0.98 nm at the minor peak 10°. In addition, the ß-keratin structure presents a crystalline spacing of 0.465 nm at the prominent peak and 0.98 nm at the minor peak. The total crystallinity of wool samples equals the sum of α and β-crystallinity [30]. The peak around 10° is characteristic of the hydrated crystalline structure of wool. Under standard conditions (temperature 25°C and humidity 65%), most of the hydrogen bonds in the fiber were not changed. However, the intensity of the diffraction peak at 20° of the pulled wool became lower and blunter. This difference in crystallinity may be explained by the transformation of a small amount of α-helical molecular chains into amorphous material [31]. The disulfide bonds in the fibers of pulled wool were broken, thus some crystals and amorphous regions were thoroughly destroyed, and as a result the crystallinity of the wool decreased.

Moreover, the crystallinity of wool fiber is related to its physical, chemical as
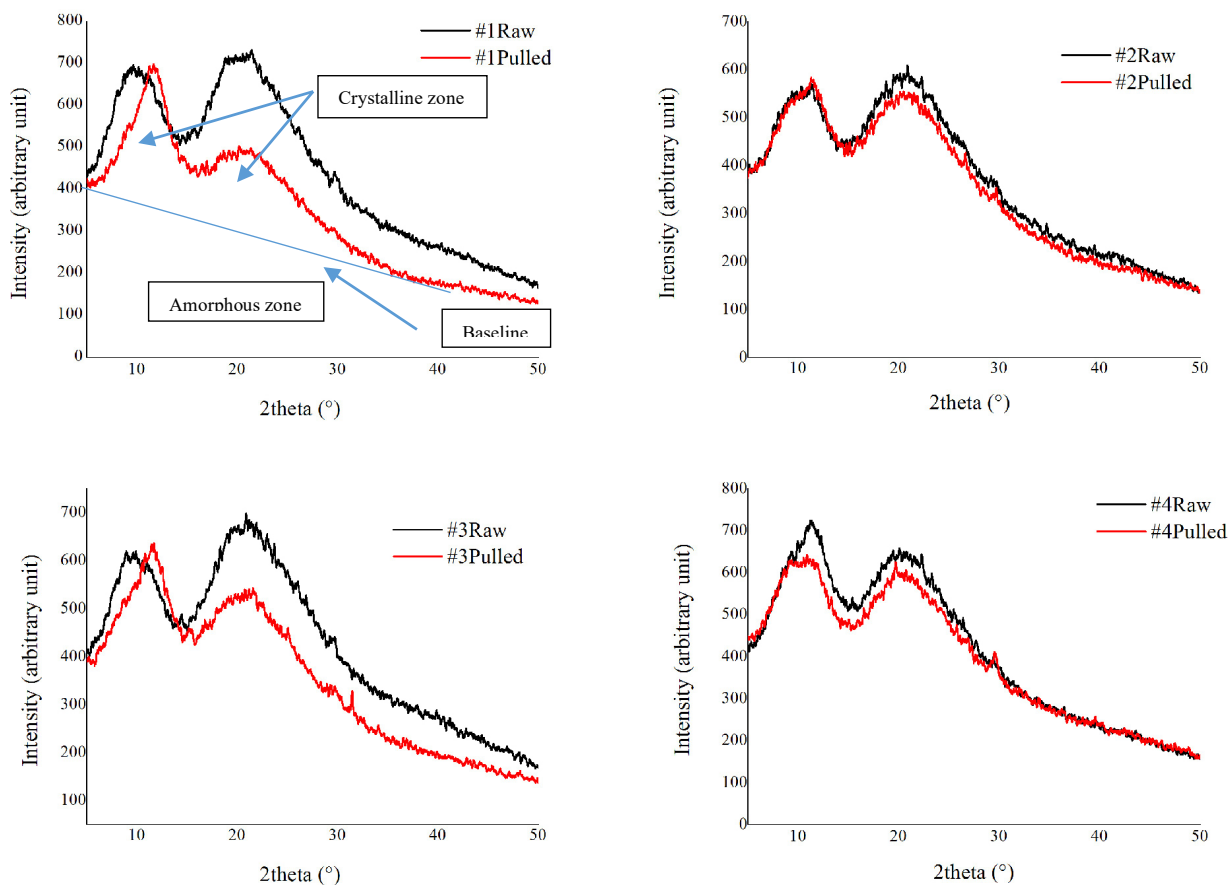
Fig. 3. X-ray diffraction spectra of different parts for raw and pulled wool fibers
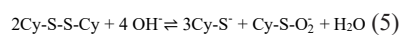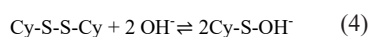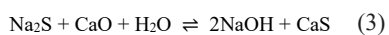
well as mechanical properties. Alkali treatment led to reducing the crystallinity on wool fiber [32], which probably can be explained by the fact that the polypeptide chain was broken during alkali treatment. A part of the crystal region was decomposed, hence the crystallinity slightly decreased. Otherwise, these changes are attributed to the breaking of disulfide bonds in the pulled wool fiber [33].

3.6. Amino acid analysis

The amino acid compositions of raw and pulled wool fibers are shown in Table 5. Indeed, we can observe that the content of ½ cystine (the sum of cystine and cysteine) decreased from 9.06 ± 0.06 to 6.24 ± 0.08 (mole %), while that of cysteic acid increased from 0.26 ± 0.01 to 0.35 ± 0.02 (mole %).

The wool hydrolysis process through alkali treatment involves the breakage of

the peptide bonds and disulfide bonds of proteins, which results in the formation of amino acids. The alkaline hydrolysis of wool with sodium hydroxide, obtained during chemical treatment (Equation 3), resulted in the breakage of disulfide, peptide, and side-chain amide bonds (Equations 4 and 5).

$$Na_2S + CaO + H_2O \rightleftharpoons 2NaOH + CaS \quad (3)$$

$$Cy\text{-}S\text{-}S\text{-}Cy + 2\,OH^- \rightleftharpoons 2Cy\text{-}S\text{-}OH^- \quad (4)$$

$$2Cy\text{-}S\text{-}S\text{-}Cy + 4\,OH^- \rightleftharpoons 3Cy\text{-}S^- + Cy\text{-}SO_2^- + H_2O \quad (5)$$

The reaction of NaOH with the disulfide bonds results, therefore, from the various chemical structures of cysteine, depending on the bonds of the sulfur molecules with the different chemical species found in the NaOH solution. We find cysteine, Cy-SH; Bunte Salt, Cy-S-SO$_3$Na; cysteic acid, Cy-SO$_3$H; cystine dioxide, Cy-SO$_2$-S-Cy, and cystine monoxide, Cy-SO-S-Cy.

A similar result was given by Norton and Nicholls, who reported that cystine is modified and that some main chain breakdown also occurs when wool is exposed to alkali [34].

Furthermore, the amounts of amino acids that contribute to the α-helix formation in intermediate filaments (e.g lysine LYS, aspartic acid ASP, histidine HIS and glutamic acid GLU) are greater in raw wool than in pulled wool [35}, which explain the decrease in crystallinity.

3.7. ATR-FTIR analysis

Infrared absorption spectra of raw and pulled wool are shown in Figure 4a. The characteristic absorption bands are assigned mainly to the peptide bond (CONH). The vibrations in the peptide bonds originate bands known as amide A, amide B, and amide I, II & III., For raw and pulled fiber, bands at 3278 cm^{-1} and 3272 cm^{-1} of amide A, and at

	Amino acid	Raw wool (mole%)	Pulled wool (mole%)
Cysteic acid	CYA	0.26±0.01	0.35±0.02
Aspartic acid	ASP	9.85±0.02	9.77±0.21
Serine	SER	11.42±0.01	11.5±0.04
Glutamic acid	GLU	16.58±0.04	15.55±0.08
Glycine	GLY	6.46±0.01	6.83±0.32
Histidine	HIS	0.52±0.03	0.36±0.01
Arginine	ARG	5.87±0.05	5.52±0.10
Threonine	THR	7.09±0.06	5.59±0.03
Alanine	ALA	5.73±0.01	5,88±0.01
Proline	PRO	3.28±0.00	7,76±0.16
Lanthionine	LANT	0.98±0.01	0,72±0.04
½ Cystine [a]	1/2CYS	9.06±0.06	6,24±0.08
Tyrosine	TYR	2.14±0.03	2,57±0.04
Valine	VAL	5.25±0.10	5,16±0.10
Methionine	MET	0.27±0.02	0,54±0.03
Lysine	LYS	3.87±0.01	3,55±0.12
Isoleucine	ILE	2.86±0.01	2,76±0.05
Leucine	LEU	6.88±0.04	7,34±0.14
Phenylalanine	PHE	1.68±0.06	2,05±0.04

[a] ½ Cystine is the sum of cystine and cysteine, expressed as cysteine (mole %).

Table 5. Amino acids compositions of raw and pulled wool fibers

3068 cm^{-1} and 3058 cm^{-1} of amide B are observed, respectively. Amides A and B are both connected with the stretching vibrations of the N-H bond. Amide I appears approximately at 1636 cm^{-1} for both pulled and raw wool. This band is connected with the C=O stretching vibration. Amide II, which occurs in 1514 cm^{-1}, is related to N-H bending and C-N stretching vibration. The amide III band falls at 1234 cm^{-1} for raw wool and 1232 cm^{-1} for pulled wool, resulting from the combination of C-N and C-C stretching as well as N-H in-plane bending with C-O bending vibrations [36].

The peaks that occur in the range between 1156 cm^{-1} and 1022 cm^{-1} (Figure 4b) are related to the asymmetric and symmetric S-O stretching vibrations of the Bunte salt residues [37].

The raw wool sample presented two peaks at around 1027 and 1042 cm^{-1}, which are assigned to cysteine–S–sulfonate (–S–SO$_3$-) and cysteic acid (–SO$_3$H), shifting to 1025 and 1039 cm^{-1}, respectively, for pulled wool fibers. Furthermore, there
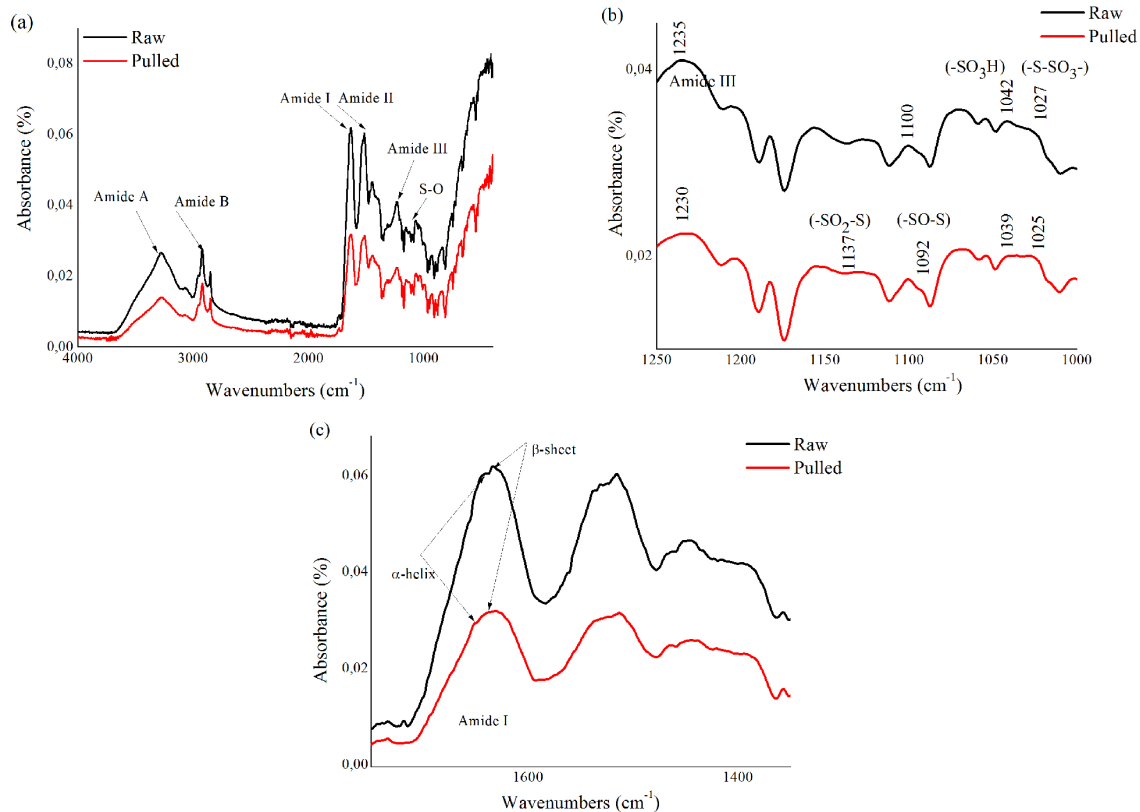

Fig. 4. ATR-FTIR spectra of raw and pulled wool fibers; (a) 400–4000 cm^{-1} region ,(b) 1000–1250 cm^{-1} region, (c) 1350–1750 cm^{-1} region

	BS (cN)	T (cN/tex)	E (%)
#1R	17.80±3.39	22.53	31.53±3.10
#1P	16.23±3.68	22.32	27.43±2.85
#2R	14.41±2.59	21.93	30.73±3.44
#2P	13.55±2,98	21.08	27.09±2.80
#3R	16.69±3.62	22.36	31.47±2.80
#3P	15.04±3.88	21.47	27.04±3.22
#4R	14.08±3.49	21.22	30.42±3.33
#4P	13.24±3.28	20.93	27.16±2.82
Raw	**15.75±1.80**	**22.01±0.58**	**31.24±0.55**
Pulled	**14.52±1.39**	**21.45±0.62**	**27.93±0.17**

Table 6. Mechanical properties of pulled (P) and raw) wool fibers (R.

appeared more cystine oxides which are assigned to cystine monoxide (–SO–S–) around 1092 cm⁻¹ and to cystine dioxide (–SO₂–S–) around 1137 cm⁻¹. This last point proves that cysteine was oxidised by alkali treatment in chemical unhairing [38,39].

According to literature, [40] the range between 1600-1700 cm⁻¹ indicates the presence of a second structure of a protein. For raw wool, the absorption at 1642 cm⁻¹ is related to the crystalline α-helix structure. For the ß-sheet, it appears at 1633 cm⁻¹. While for pulled wool, α-helix and ß-sheet occur at 1650 cm⁻¹ and 1633 cm⁻¹, respectively.

The amount of the light absorbed indicates the concentration of molecules that absorb the light [41]. As shown in Figure 4c, it is clear that the intensity of α-helix's peak decreased significantly. However, the range of the ß-sheet becomes larger.

3.8. Tensile properties

Tensile properties, breaking strength (BS), fiber tenacity (T), fiber elongation (E), and Young's modulus are the important parameters that enable the prediction of further processing behaviour. The mechanical properties of raw and pulled wool are shown in Table 6.

The breaking value of the side part (#3) often seems to approach the average. Moreover, the mean BS of pulled wool is 7.8 % lower than that of raw wool.

In this study, the average tenacity is evaluated as 22.01± 0.58 cN/tex and 21.45± 0.62 cN/tex, respectively, for raw and pulled wool. Despite the fact that the tenacity values for Barbary red face breed wool are lower than the average tenacity of Australian wool, which is around 35 cN/tex, our tested wool samples are considered to be adequate in the textile industry. In fact, wool fibers should have at least 6 cN/tex of tenacity to withstand physical and mechanical tensions and breaking [17].

In addition, the results obtained show that the elasticity of the fiber decreases from 31.24± 0.55 % for raw wool to 27.93± 0.17 % for pulled wool. According to literature [42], cystine contains sulfur, which gives the fiber high elasticity and high resistance to breakage. The decrease in the amount of cystine in pulled wool is the essential cause of the loss of elasticity (10.6 %).

4. Conclusion

This research study examined the reconsideration of pulled wool as a sustainable, biodegradable, and renewable resource, with its particular fibrous structure and high content of keratin protein. Tanning treatment using the chemical unhairing process induced significant changes in the fibers' properties (pulled wool). The fibers' qualities, such as fineness, length, crystallinity, tensile properties, and elongation were decreased from 26.34 µm to 25.62 µm, from 101.72 mm to 89.77 mm, from 40.5% to 33.5%, from 22.01 cN/tex to 21.45 cN/tex, and from 33.24% to 27.93%, respectively. Such changes could be attributed to the breakage of disulfide bridges and the removal of some substances in the pulled fibers.

Based on these results, pulled wool fiber quality was found to be influenced significantly by the hard operating conditions of the chemical unhairing process. However, these fibers' characteristics are still suitable for various textile applications. Consequently, this research opens up effective and economically feasible pathways to increase the potential for the better value of pulled wool by applying new ecological unhairing processes.

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