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Analysis of structural transformation in wool fiber resulting from oxygen plasma treatment using vibrational spectroscopy

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HIGHLIGHTS

- The α-helix structure was the highest component content of wool fiber.
- The α-helical transformed to β-pleated configuration during plasma treatment.
- The disulphide bonds content in the treated wool fiber reduced.
- The oxygen plasma treated samples presented higher cysteic acid.

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ABSTRACT

The aim of this study was to investigate the influence of oxygen plasma procedure at different time treatments on wool fiber using the micro-Raman spectroscopy as a non-destructive vibrational spectroscopic technique and Fourier transform infrared spectroscopy. The amide I and III regions, C—C skeletal vibration region, and S—S and C—S bonds vibration regions were analyzed with the Raman microscope. The Fourier transform infrared spectroscope analysis was employed to find out the effect of oxygen plasma treatment on the cysteic acid residues content of the wool fiber sample. The results indicated that the α-helix structure was the highest component content of wool fiber. Moreover, the protein secondary structure of wool fibers was transformed from α-helical arrangement to the β-pleated sheet configuration during the oxygen plasma treatment. Also, the disulphide bonds content in the treated wool fiber reduced because they were fractured and oxidized during oxygen plasma treatment. The oxygen plasma treated samples presented higher cysteic acid compared to the untreated wool samples due to produce more cleavage of disulfide linkages.

Introduction

Wool fiber contains more than 170 different proteins which are composed of 20 different α-amino acids having a complex morphological and chemical structure [1]. Physical and chemical modification of wool fiber is the particular interest for both industrial and research purposes. The targets of wool modifications include the improvement of antibacterial [2], dyeability [3–5], anti-felting [6,7], pilling propensity [8], wettability [9] etc.

The cuticle, cortex and medulla are the three main components of wool fiber. The cuticle is the layer of overlapping scales surrounding the cortex. The scales are relatively hard with sharp edges which are responsible for the directional frictional effect and shrinkage of woolen goods during felting. The scales also act as barriers for water, dye and finishing agents applied on wool fibers and adversely affect the sorption behavior [4,10]. There is a certain methods have been used to solve the felting and sorption problems of wool fiber, which is including physical means such as mechanical, thermal and ultrasonic treatments, and chemical approaches such as reduction, oxidation, enzyme and ozone treatments [11].

Low temperature plasma (LTP) treatment is a non-aqueous and environmentally friendly surface modification technique [12]. The LTP is comprised of ultraviolet radiation with a wavelength of 100 nm, electrons with energies of 1–10 eV, photons, radicals, ions and gases in an atomic state. Plasma treatment of textile fibers results in two kinds of effects, including surface and deep changes. The surface effects occur in the outer part of the fiber up to 10 nm, depending on the kind of employed gas and deep effects which

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includes the production of radicals, hydrogenation and changes in the polymer's network density occurring from 1–5 μm, irrespective of the kind of employed gas [13].

Plasma treatment can be used effectively to modify the surface of various textile substrates [14]. Compared to raw wool, plasma treated wool has a different physical and chemical properties that alter the performance of several textile processes such as finishing, dyeing and spinning to produce products with higher quality [11].

Several studies have been done on plasma treatment of wool fiber with different gases and application of various finishing agents on wool fiber to enhance selected properties of the resulting goods. Various analyzing techniques have been employed to investigate the wool fiber changes after plasma treatment, which are including FTIR [12,13,15], FT-Raman [14], XPS [15,16], WAXS [13], SEM [3,5,12] and AFM [17]. The FTIR and FT-Raman spectroscopy are the standard methods of assessing changes in protein secondary structure, including wool fiber keratin [18].

The infrared technique has been used extensively for the detection of oxidized species in the wool fiber after different treatments. The characteristic absorption band found in the infrared absorption spectra of wool fiber keratin is mainly assigned to the peptide bond (—CONH—) as the fundamental structural unit of the polypeptide chain. In strong alkaline solutions (pH = 13–14) disulphide bonds which stabilize the keratin structure and peptide bonds are destroyed due to intensive and poorly selective hydrolysis of keratin [19]. Yao et al. used the FTIR spectroscopy to characterize stretched wool fibers in terms of secondary structure transformation. They found two peaks of C—N—H and C═O bonds occurred at lower wave number positions in stretched wool fibers compared to the un-stretched samples, suggesting the transformation of secondary structure from alpha form to beta conformation [20].

The Raman technique, which is complementary in nature to that of the infrared (IR), provides a direct method to study the disulfide bonding as well as the amino acid residues with aromatic side chains within the proteins [21]. The micro Raman technique is a non-destructive analysis that can be applied even to the single fiber. It can be applied for the investigation of the plasma interaction with the surface of fiber [22].

The disulphide bond is the most reactive part of the keratin. Many chemical reactions which give stability and anti-felting to wool products are based on the reduction and modification of the cystine bonds. The advantage of Raman spectroscopy is that it provides useful information about —SS— groups through reduction and oxidation, which is impossible to measure using infrared spectroscopy, since these bands can be assigned to S—S and C—S vibrations of cystine. In addition, it can provide structural information due to amide I and amide III vibrations, and the skeletal C—C stretch [23]. Micro Raman spectroscopy was used to study the transformation of α-helical arrangement of wool fiber to the β configuration (β-sheet) due to stretching process [24]. Therefore, the Raman spectroscopy facilitates to study the changes resulting from of reactions on the conformation of the amino acidic residues of the polypeptide chains [25].

Wojciechowska et al. exposed the wool fiber keratin to the hydrolytic degradation process in alkaline environment and studied the changes in the structure of wool fiber keratin by means of Fourier-transform Infrared and Raman Spectroscopy. The main band of the untreated sample was observed at 507 cm^{-1} besides two other peaks at 521 and 530 cm^{-1} with an appreciably lower intensity. The progress in alkaline hydrolysis led to the disappearance of the main S—S bond at 507 cm^{-1}. Introduction of orthosilicic acid into the alkaline environment distinctly masked this destruction process. Experimental data achieved from the analysis of amide I bands in Raman spectrum indicated conformation changes in the secondary structure of keratin leading to the formation of α-helical regions, which occurred simultaneously with the reduction of disordered regions in the presence of orthosilicic acid [19].

In another paper, Wojciechowska et al. confirmed the conformational changes of disulphide bonds in the keratin chain of wool fiber treated with orthosilicic acid by Raman spectrum studies. The process of deuterium exchange in wool fiber, which was carried out in their experiment, decreased the conformational changes of the wool fiber keratin chain treated with orthosilicic acid. The analysis of distributed amide bands in infrared spectrum indicated a shift in the direction of lower frequencies as a result of deuterium exchange, which was due to conformational changes of the keratin chain indicating a decrease in its order [26].

The aim of this study was to investigate the influence of oxygen plasma procedure at different time treatments on the wool fiber using Raman microscope and Fourier transform infrared spectroscopy. Moreover, the internal structural changes in the wool fibers due to oxygen plasma procedure at different time treatments were analyzed using a Raman microscope.

Methods

Plasma treatment

The wool yarn was scoured with a 1% nonionic detergent (Triton X100 from Merck Company, Germany), nonionic surfactant that has a hydrophilic polyethylene oxide chain $(C_{16}H_{25}O)_{30}OH$, at 50 °C for 30 min. Then, the scoured wool yarn samples were treated with a radio frequency, low pressure plasma equipment (model: Junior plasma, Europlasma, Belgium) with oxygen gas. The oxygen flow rate was 30 sccm (Standard Cubic Centimeters per Minute) and the pressure chamber adjusted to 150 mTor. Plasma was generated at 100 W for different predefined times, which was 2.5, and 5 min. After that, air was introduced into the chamber and the plasma treated sample was removed.

Characterization

The micro-Raman microscope (Senterra, BRUKER, Germany) equipped with excitation lines at 785 nm (diode laser) with a power of 50 mW was utilized and spectra measurements of wool fiber samples were collected with continuous scans from 200 to 3500 cm^{-1}. The resolution for Raman spectra was 3 cm^{-1} and was deconvoluted with PeakFit v4.12 softwear. Micro-Raman spectroscopy enables to study the vibrations of wool molecules through the interaction of light with the vibrations. The Raman spectrum is highly sensitive to structural differences of wool molecules [27]. In order to make possible a comparison of the Raman spectra from different samples, the spectra were normalized on the strong peak at 1448 cm^{-1}, which is mainly attributed to the CH_2 and CH_3 bending vibrations of amino acid side chains. The conformation changes of main peptide chains have no influence on this band. The profile of this band is also consistent for different wool fibers. Therefore, the peak at 1448 cm^{-1} was chosen as a reference band [28–30].

The FTIR instrument (Shimadzu IRAffinity-1, Japan) was used to analyze the spectra of wool samples. Resolution for the infrared spectra was 4 cm^{-1}. A film of wool powder and KBr pellet was used for FTIR testing. Absorbance of the infrared in the prepared film was collected from 400 to 2000 cm^{-1} by this instrument.

Results and discussion

The Raman spectra of the oxygen plasma treated wool fiber at different times (2.5 and 5 min) are compared to that of untreated wool fiber are presented in Fig. 1. In the spectral region from 1100 to 1800 cm^{-1}, there is a valuable information concerning