Effects of Enzymatic Treatments on Surface Morphology and Chemical Structure of Linen Fabrics

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ABSTRACT: In previous studies; effects of enzymatic treatments on linen fabrics have been mostly investigated in terms of wettability, sorption properties, whiteness-yellowness index, and *K/S* values after dyeing. However, surface chemistry and topography of enzyme-treated linen fabrics have not been reported enough. The aim of this work was to examine the effect of pectinase treatments on surface structure and chemical properties of greige linen fabrics by using instrumental techniques. After enzymatic treatment, adequate removal of noncellulosic impurities from the fiber surface has been proved by AFM images and O_1/C_1 ratio of the treated surface. Water drop test measurement and absorbance spectrographs of FTIR analysis have supported the results. It was observed that achievement in bioscouring is familiar to conventional alkaline scouring.
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Key words: flax; enzyme; FTIR; XPS; SEM

INTRODUCTION

Flax (*Linum usitatissimium*) has been used in several areas due to its unique properties since ancient times. The flax seeds of the plant have been used for linseed oil and animal fodder whereas flax fibers separated from the stalk have been utilized mostly in textile industry. Among all natural fibers, flax fibers have competitive specifications such as handling and thermal properties for garment technology also strength properties for composite technology.[1,2]

Besides these specifications, energy consumption for fiber production is lower than synthetics due to traditional farming system from harvesting to retting of flax. Along with the improvements in biotechnology, rapid retting of flax stalks with enzymes is possible. Since the significance of recycling have been realized, remaining flax shives during yarn processes have become a source for raw material that are utilized in production of technical textiles and composites. All these advantages provide the production of flax fibers to be called as green process. Thus linen has become a research area in terms of ecology and sustainability. In recent years, research have been focused on to keep linen production as a green process by applying bioscouring instead of conventional alkaline scouring.[3,4]

Prior to dyeing and finishing, alkaline scouring of linen is necessary to remove noncellulosic impurities such as pectin which are responsible for the hydrophobic characteristic. However, alkaline treatments at high pH and temperature cause weight losses, changes in strength properties and increment in environmental pollution and energy consumption. Instead of alkaline scouring, the alternative ecological process to remove pectic substances without altering the bulk properties of fiber is to apply pectinolytic enzymes at mild conditions.[5,6]

In previous studies, effects of enzymatic treatments on linen fabrics have been mostly investigated in terms of wettability, sorption properties, whiteness-yellowness index, and *K/S* values after dyeing. It was reported that improved yarn evenness, sorption performance, and wettability have been achieved by applying enzymatic treatments to greige linen yarn or fabrics. After common bleaching and dyeing, enzyme treated samples had approximately same results on WI and *K/S* values but with better physical properties due to lower weight loss compared with alkaline-treated samples.[7–14] On the other hand, it is clear that the changes in chemical properties and surface structure have not been reported enough, when the literature have been checked out carefully.[15–17]

The aim of this work is to examine the effect of pectinase treatments on surface structure and chemical properties of greige linen fabrics by using instrumental techniques such as Atomic Force Microscopy

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(AFM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), and X-Ray Photoelectron Spectroscopy (XPS).

EXPERIMENTAL

Materials

Greige 100% linen fabric (plain weave, 116 g/m^2, 22 × 22 yarns per cm) was supplied from a local supplier. Alkaline pectinase enzyme was kindly supplied by Dystar under the commercial name of Serazyme C-PE (Bio Prep 3000L based) with an activity of 400 APSU/g. All the other chemicals were laboratory grades reagents.

Methods

Greige linen fabrics were treated with pectinase enzyme solution of 2% owf, at material to liquor ratio of 1:50. Enzymatic treatments were carried out at 55°C and pH 8 for 30 min at Linitest (ATLAS) equipment (42 rpm). For conventional alkaline scouring, greige fabric was treated at 80°C for 30 min with NaOH (40 g/L) at a liquor ratio of 1:30. Common bleaching process was applied at 80°C for 1 h with a bath containing H_2O_2 (5 g/L), NaOH (1 g/L), and Na_2SiO_3 (1 mL/L). The treated fabrics were rinsed with cold water then washed with hot water for 5 min and dried at room temperature. Prior to experiments and analysis, the samples were conditioned for 24 h at 20°C and 65% relative humidity.

Wettability

When the vertically hanged linen fabrics are sunk into polar liquid, within the first 20–40 s there have been quick decrease in diameter of capillary pores due to fast swelling of fiber cell walls. The changes in diameter of capillary pores affect capillary forces. Though wicking measurement is based on the capillary forces, misreading in wicking height results is possible. To determine the wettability performance of treated linen, water drop test was preferred to prevent probable difficulties of wicking measurements that were explained elsewhere.[18] Dissipation of the water drop (50 μL) on the fabric is observed and the elapsed time for disappearance of drops into the fabric is measured. Five readings from different parts of the treated fabrics were taken and the mean values were reported with standard deviations.

Scanning electron microscopy

Surface morphology of greige linen fibers and treated linen fibers have been observed by Phillips XL-30S FEG Scanning Electron Microscope. Each sample was sputter-coated with gold for 150 s prior to the observation. Observations were utilized at 3500× magnification.

Atomic force microscopy

Detailed analysis of surface structure was utilized by Vecoo MultiMode V Atomic Force Microscope. Tapping mode was preferred as scanning method to observe the 3D topography images of sample surfaces. Scanning speed at scanning range of 5 μm and 1 μm was 1.0 Hz whereas at scanning range of 500 nm it was adjusted to 2.0 Hz to prevent disfiguration of topographical image.

Fourier transform infrared spectroscopy (FTIR-ATR)

Chemical changes of treated samples were investigated using a Perkin–Elmer Spectrum 100 FTIR-ATR Spectrometer with a diamond/zinc selenide crystal. To ensure reproducible contact between the crystal faces and the fabric, a pressure of 80 kPa was applied to the crystal holder. Five scans were taken on average with a resolution of 4 cm^{-1}.

X-ray photoelectron spectroscopy

Quantitative analysis of sample surfaces to determine percent composition of C and O atoms was utilized by SPECS X-Ray Photoelectron Spectroscope with a Mg Kα X-ray source operated at 10 kV and 200 W. Survey scans were taken with a pass energy of 48 eV.

RESULTS AND DISCUSSIONS

Wettability

Hydrophilic characteristic of linen fabric depends on pectin, lignin, and waxy materials content. Washing process in weak alkaline conditions removes the waxy materials; however removal of lignin is not as easy since it is connected to cellulose by pectin. Thus partial removal of pectin is the key to improve the hydrophilic characteristic.

Conventional alkaline treatment and enzymatic treatment with pectinase was applied to untreated linen fabric. Wettability performances of samples were tested by drop test. There have not been observed any dissipation of water drops on the untreated sample even after 300 s. Average disappearance time of water drops on alkaline and enzyme treated samples were respectively, 10.46 ± 1.34 s and 50.38 ± 8.79 s. When the standard deviations of the results are taken in account, it is clear that homogeneity of alkaline scouring is better than the bioscouring. However after common bleaching

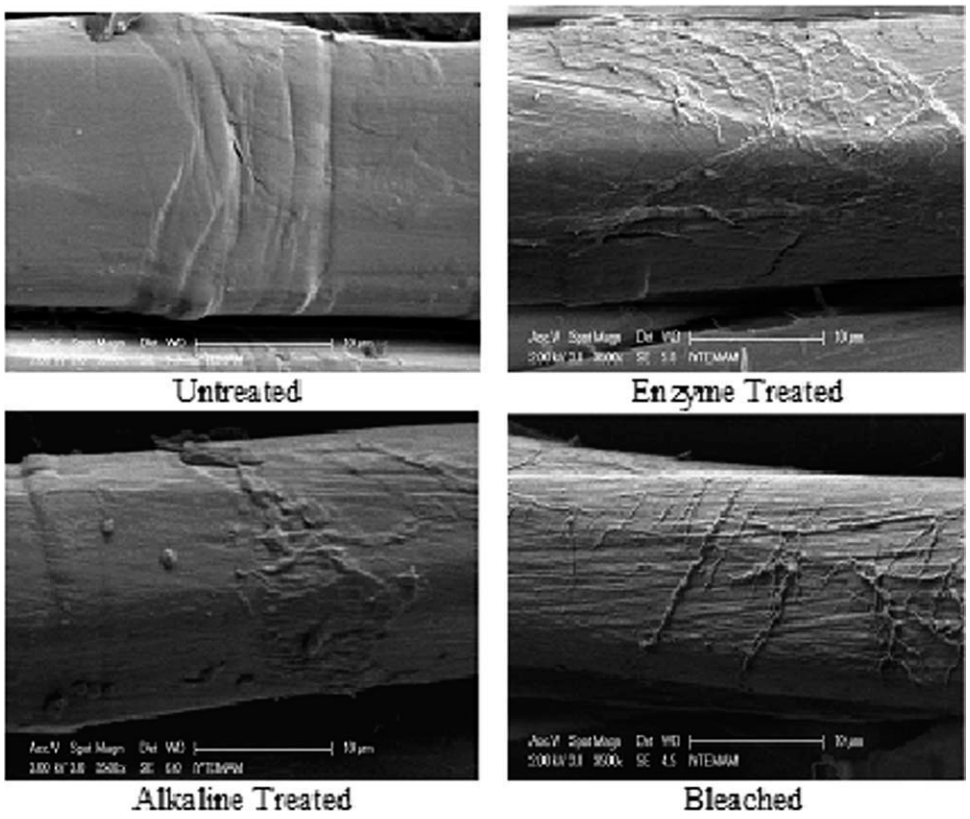

Figure 1 SEM images of untreated and treated linen fabrics.

of both alkaline and enzyme-treated samples, drop test results of both alkaline and enzyme treated samples were lower than 10 s.

Surface morphology

It is already known; enzymes can not go deep inside the fibers due to having bigger sizes than the pores of fibers. Thus, enzymes react with their specific substrate on the sample surface. To investigate the modifications occurred on the surface of fibers after the treatments, SEM and AFM images of untreated and treated linen fabrics were examined. SEM was utilized to check if there has been any visible difference between untreated and treated surfaces. SEM images of the samples are given in Figure 1.

Multicellular flax fibers are connected to each other by pectin and the outer surface of fibers consist of pectin, lignin, and waxy materials. As seen in the SEM image of untreated fibers, the outer surface of noncellulosic materials around the fiber bundles forms a smooth surface. The aim of bioscouring with pectinase is to remove pectin and lignin that are connected to surface of fibers by pectin. In Figure 1, the wavy surface structure of enzyme treated sample has proved the influence of pectinase on removal of noncellulosic outer surface around the fibers. Compared to alkaline treated sample, both the wavy surface structure and the drop test result of enzyme-treated sample have indicated a partial removal of noncellulosic material. When the SEM images of untreated and alkaline treated samples are considered, alkaline one had rougher surface than untreated one due to an effective cleaning. Hardly identified individual fibers from the SEM image of alkaline-treated sample are distinctive in the SEM image of alkaline-treated bleached sample.

SEM images dedicated that scouring efficiency of enzymatic treatments are slightly lower than the alkaline ones. AFM is utilized to achieve detailed information about the treated surfaces. Several scanning have been applied on an area of 5 μm × 5 μm. 3D images of the samples are given in Figure 2(a).

Besides SEM images, AFM images dedicate a distinct view of the efficiency difference between alkaline scouring and bioscouring. Individual fibrils, hardly identified in the SEM image, can be seen clearly in the topographical image of alkaline treated sample. Alkaline treatment has almost removed the outer layer from the surface of fiber thus the individual fibrils could be identified. On the other hand, not only the wavy structure seen in SEM images but also the rough surface structure seen in AFM images of enzyme-treated fibers have stated that outer layer of noncellulosic impurities are remained partially. To examine the rough structure on the surface of

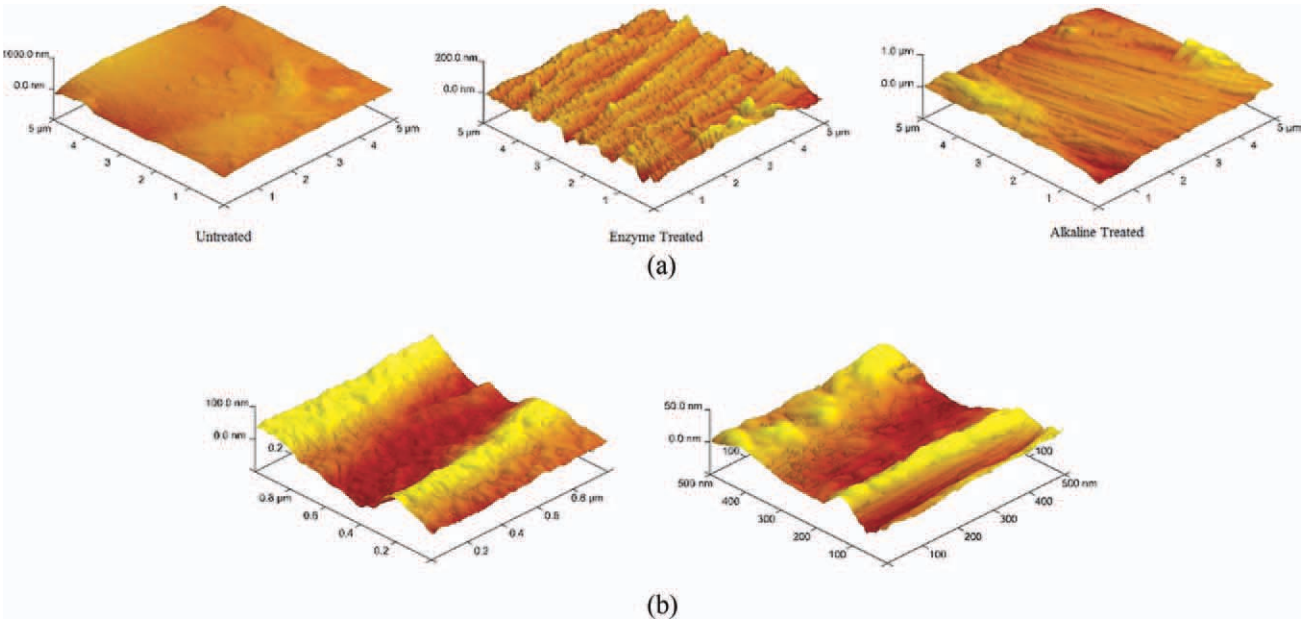

Figure 2 (a) AFM images (5 μm) of untreated and treated linen fabrics. (b) AFM images (1 μm, 500 nm) of enzyme treated linen fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

enzyme treated fibers, more scanning have been applied on an area of 1 μm × 1 μm and 500 nm × 500 nm. 3D images of the enzyme-treated fibers are given in Figure 2(b).

In spite of the remained noncellulosic impurities that are indicated by rough surface structure, individual fibrils could be observed in Figure 2(b). Thus significant achievement in removal of hydrophobic outer layer from the fiber surface by bioscouring should not be ignored.

Surface chemistry

Removal of noncellulosic impurities by pretreatments decreases the intensity of noncarbohydrate components in fiber content. FTIR Spectroscopy is utilized to observe the changes in quantity of noncarbohydrate components by comparing the intensity of characteristic peaks at certain bands of pectin, lignin, and waxes. The absorbance spectrographs of untreated, alkaline, and enzyme-treated samples are given in Figure 3.

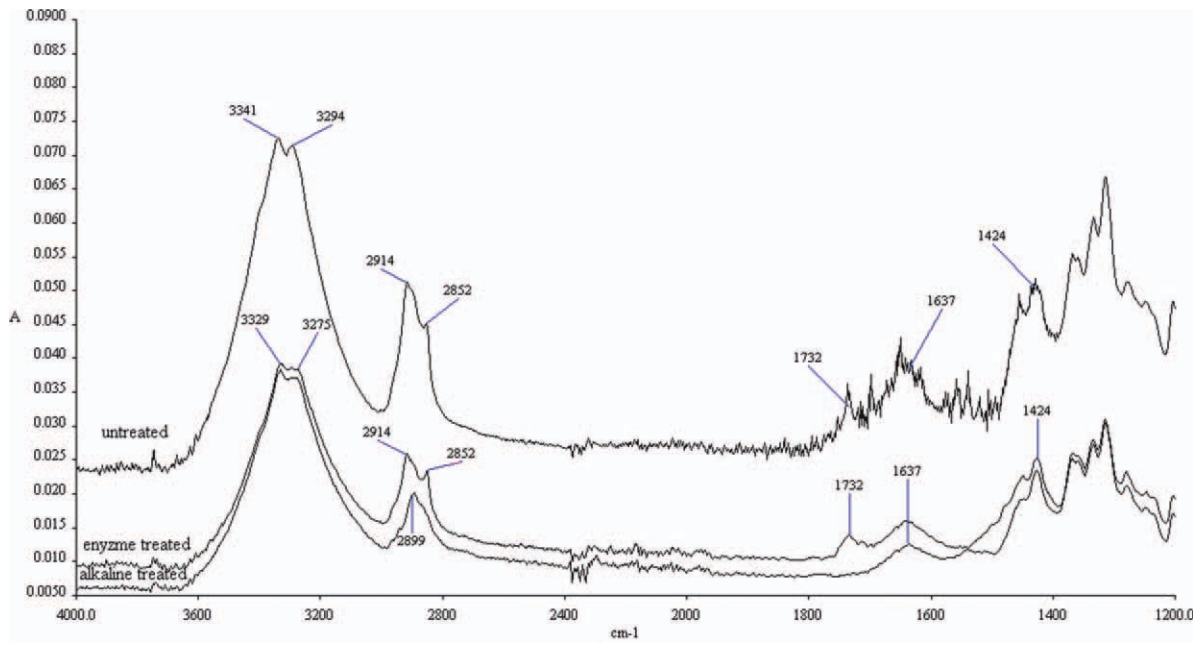

Figure 3 IR spectra of untreated and treated linen fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Elemental Composition of the Surface of Untreated and Treated Linen Fabrics

Linen fabric	O_1 %	C_1 %	O_1/C_1
Untreated	15.5	84.5	0.1834
Enzyme treated	28.1	70.7	0.3974
Alkaline treated	31.9	67.9	0.4698

Waxes and fatty acids are identified by characteristic peaks of —CH_2— groups in long alkyl chains at around 2918 cm^{-1} and 2849 cm^{-1}. Peaks at around 1740 cm^{-1} and 1600 cm^{-1} determine carboxylic esters and ionized carboxylate of pectin.[19,20] Untreated fabric has two peaks at 2914 cm^{-1} and 2852 cm^{-1} representing the presence of waxes. After enzymatic and alkaline treatments, the peak at 2914 cm^{-1} has moved to 2899 cm^{-1} and become less sharp while the one at 2852 cm^{-1} has almost disappeared. The intensity of peak at 1732 cm^{-1} has decreased after enzymatic treatments whereas it has almost become invisible after alkaline treatments. In addition, less remarkable changes in the intensity of peaks at 1637 cm^{-1} is observed. Since the peaks at 1732 cm^{-1} and 1637 cm^{-1} represent —C=O— and —COO^-— stretching, the decrease in intensity of peaks state significant removal of pectin.

Upon the removal of noncellulosic components, cellulose content of linen increases. Because of increased cellulose content after alkaline and enzyme treatments, O_1/C_1 ratios of treated linen samples are expected to get closer through the O_1/C_1 ratio of pure cellulose (0.83). To determine the O_1/C_1 ratio after treatments, XPS measurements were carried out. O_1%, C_1% contents and O_1/C_1 ratios of samples are given in Table I.

Because of the obtained achievement in pectin removal by enzymatic and alkaline treatments, significant increment in O_1/C_1 ratio of untreated linen was measured as 116.7% and 156.2%, respectively.

CONCLUSIONS

The main goal of this study was to investigate the surface morphology and chemistry of linen fabrics after enzymatic and conventional alkaline treatments by instrumental techniques. The treated samples were characterized by water drop test, SEM and AFM images, FTIR spectra, and XPS results.

The water drops have kept their drop shape on untreated samples even after 300 s whereas the disappearance time of water drops on pectinase and alkaline treated samples were respectively, 50.38 and 10.46 s. Though the disappearance time of water drops on pectinase treated samples were much higher than alkaline treated ones, the results decreased up to less than 10 s by application of bleaching process after enzymatic treatments. The removal effeciency of treatments on noncellulosic impurities were examined by SEM and AFM images to observe the changes in surface morphology. In AFM images, individual fibrils of alkaline treated samples were observed clearly whereas visibility of individual fibrils of enzyme treated samples were prevented by the partially remained outer layer. XPS results represented a remarkable increase in the O_1/C_1 ratio of fiber surface after pectinase and alkaline treatments such as 116.7% and 156.2%, respectively. In addition, the decline in the presence of waxes, fatty acids, and pectin was observed in the FTIR spectra of enzyme-treated sample.

After pectinase treatments of linen fabrics, both rough surface structure and the increment in the O_1/C_1 ratio proves significant removal of outer layer that consist of noncellulosic impurities.

Thus it can be concluded that; for removing noncellulosics from linen fabrics at the pretreatment process, pectinase treatments could be preferred instead of conventional alkaline treatments to reduce environmental pollution.

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