EVALUATING THE INFLUENCE OF CHEMICAL MODIFICATION ON FLAX YARN

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Abstract

Natural fibres are used in polymer composites as reinforcement for its comparable characteristics with traditional fibre reinforcements. To attain good mechanical performance for natural fibre reinforced composites, good adhesion between fibre and matrix is essential. Most of the polymers are hydrophobic in nature and are more or less incompatible with hydrophilic natural fibre. Hence to reduce the hydropilicity of fibres, different surface modification methods have been adopted. In this investigation attempt to chemically modify natural fibre in the form of flax yarn is done through alkalization, silylation and acetylation. FT-IR was used to characterize the changes induced by the yarn modifications. Since these treated yarns are intended to be used as reinforcement in thermoplastic matrix, the knowledge on the thermal properties of treated yarns is necessary. For analyzing thermal stability of yarns TGA was adopted. Moisture absorption test and SEM images of modified yarn surface provide with the information on effect of chemical treatment.

1. Introduction

An archeological study by Kvavadze et al. [1] lead to an inimitable finding of wild flax from an excavation site in Republic of Georgia which indicates the usage of these fibres date back thirty thousands of years during upper paleolithic period. It could be assumed that to resist from adverse climates, human might have begun to use fibres that were naturally available as clothing’s which in future turn out to be one of his basic needs. Later with advancement in science and technology, synthetic fibers are also now being produced alongside with natural fibres as textile structures. Among these, natural fibres occupy the lion share in the production of textiles in different form. Textile structures could be classified as one dimensional and two dimensional with respect to the macroscopic perception of structure and dimension [2]. An example for one dimensional structures are linearly ordered one dimensional group of fibres called yarns, which are interlaced or interloped to form two dimensional planar structures called fabrics. In general the natural plant fibre yarn has approximately 100 fibres in its cross section and linear density in range of 5 – 50 tex [2]. Different plant fibres including cotton, jute, hemp, flax and more of those kinds are used for production of yarns. Among these, flax is a class of fibre with its mechanical properties comparable to glass fibres [3]. This make flax a perfect choice to replace conventional fibres used as reinforcement in polymer composites. Numerous studies have been reported on various aspects of composites reinforced with flax in form of fibres, yarns, fabrics and are still a relevant research area [4-6].

To achieve a good mechanical performance by composites it is necessary to attain a good stress transfer between matrix and the fibre. Eventually there should be better adhesion between both fibre and matrix. In the case of natural fibre reinforced composites, the main issue faced is with the incompatibility of hydrophobic polymer matrix and hydrophilic natural fibre. The polar nature of fibres is due to presence of hemicellulose and amorphous region of cellulose. Several methods have been adopted to modify the surface of natural fibre to make it compatible with polymer matrix. Li et al [7] and John et al. [8] have comprehensively reviewed the chemical and physical methods used for surface modification of natural fibres. The purpose of the present investigation is to study the influence of alkalization, silylation and acetylation on flax yarn through FTIR, TGA and SEM. Moisture absorption of chemical treated yarns in a given interval of time against untreated yarns where also verified.

2. Materials and methods

2.1. Materials

Flax yarn used to study the surface modification in this work is low twist yarn from Safilin, France. Organo silane, 3 aminopropyltriethoxysilane (APS) 99% pure from Acros chemicals was used for silane treatment. Sodium hydroxide and acetic anhydride was purchased from Merck. Ethanol used for silane treatment is analytical grade.

2.2. Fibre modification

2.2.1. Alklalization

Flax yarns were treated with 4% solution of NaOH for 30 min at room temperature. The fibers were washed with water until it was neutral as indicated from pH paper. The washed fibers were dried overnight in an oven at 70^{o}C.

2.2.2. Silane treatment

An alcohol-water solution (95% - 5%) was prepared and APS were added with stirring into the alcohol/water medium to yield 2% silane solution. Yarns were dipped in the solution for 5 minutes. In next step the yarns where left to dry at room temperature for 30 minutes and then it was kept in an oven at 110^{o}C until yarns where fully dried.

2.2.3. Acetylation

Acetylation was done by modifying the procedure of Rowel [9] Oven dried yarns were dipped into glass container with acetic anhydride for 1 minute. Then the yarns were filtered using a stainless steel mesh and for 3 minutes the mesh was left for draining of excess acetic anhydride. Finally the treated yarns were dried at 110^{o}C for 2 hours.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The surface of the treated flax yarns was characterized by FT-IR. IR spectra were acquired using a Bruker optics-Tensor 27, FTIR spectrometer equipped with diamond ATR accessory. The spectra were recorded over the range 4000 cm^{-1} - 400 cm $^{-1}$ averaged over 32 scans. Two specimens for each treatment were analyzed.

2.3.2. Thermogravimetric analysis (TGA)

TGA was performed using a Netszch TG 209 C. The test was carried out in nitrogen atmosphere by heating from 25^{o}C to 800^{o}C at a heating rate of 20^{o}C/min. Approximately 10 mg of sample was taken to run the test and at least two specimens were analyzed for each treatment.

2.3.3. Moisture absorption test

Moisture absorption test was done in a climatic test chamber, Vötsch VC 4060, Vötsch Industrietechnik, Germany. The test condition was set at a temperature of 25^{o}C and relative humidity of 65%RH and 95%RH for 24 hours. All the yarns were dried in an oven for 70^{o}C for 24 hours and were cooled in a desiccator for 1 hour. Moisture absorption was calculated from the difference in weight gain of fibre after test and initial weight of fibre before test.

2.4.4. Scanning electron microscopy (SEM)

Zeiss EVO 50 VP was used to examine the effects of chemical modifications upon the yarn surface.

3. Result and Discussion

3.1. Surface modification of fibre

3.1.1. FTIR

FTIR spectra of untreated and treated flax yarn are shown in Figure1. The main spectral characteristics of natural fibres were found in the untreated flax within the range of 900–1700 cm^{-1}. The symmetric glycosidic stretch C–O–C at 1103 cm^{-1} and the C– OH stretching vibration of the cellulose backbone at 1060 cm^{-1} and 1029 cm^{-1} which arise from the polysaccharide components are evident from Figure 1. The 1429 cm^{-1} band was attributed to the CH_2 bending of cellulose. The peak at 896 cm^{-1} is assigned to the out of phase ring stretching which is characteristic of the cellulose backbone. A peak at 1731 cm^{-1} in carbonyl region is related to hemicellulose in natural fibre. During the process from natural fibre to yarn, flax fibre undergoes several chemical treatments including mercerization. So a large amount of hemicellulose is removed at this stage of yarn production which is evident from the presence of corresponding low intense peak. In spectra of natural fibres, peak at 1635 cm^{-1} correspond to adsorbed/absorbed water in the fibre which is evident from spectra of untreated flax. The peak at 3342 cm^{-1} in spectra of untreated flax corresponds to hydroxyl group present in fibre. Another peak at 2896 cm^{-1} is due to –CH stretching vibrations [10].

Alkalization reveals significant differences in spectra of treated and untreated flax yarn. Intensity of peak at 3342 cm^{-1} which corresponds to OH stretching, decreases for treated flax. Untreated flax fibre exhibits a low intense peak at 1733 cm^{-1} in carbonyl region which is related to hemicellulose in natural fibres. But this peak is not visible by alkalization giving evidence of removal of hemicellulose. The intensity of peak at 1641 cm^{-1} assigned to adsorbed/absorbed water reduces compared to untreated flax. This may be due to reduction in polar nature of flax yarn induced by alkali treatment.

The spectrum of 3-aminopropyltriethoxysilane (APS) treated flax yarn shows the peak at 1558 cm^{-1} which is typical of the amine group that might be hydrogen bonded to the hydroxyl groups of both silanol and fibre[11]. Since Si-O-Si and Si-O-C peak is in the fingerprint region of 600-1200 cm^{-1}, it is difficult to completely assign the Si-O-Si and Si-O-C. The intensity of the peak at 1029 cm^{-1}, which is an overlap of Si-O-Si band and the C-O stretching of cellulose [12], is increased after silylation giving further evidence of reaction. The last spectra in Figure1 represent the acetylated flax yarns. The appearance of peak in carbonyl region near 1731 cm^{-1} is visible from the spectrum. This gives the evidence for acetyl group substitution which is further supported by the reduction in intensity of peak at 3342 cm^{-1} corresponding to –OH group in fibre. Another notable change in spectra of acetylated flax compared to untreated flax is reduction of intensity near 1635 cm^{-1} of absorbed water in fibre. From this it could be assumed that the acetylation might have reduced the hydrophilicity of natural fibre.

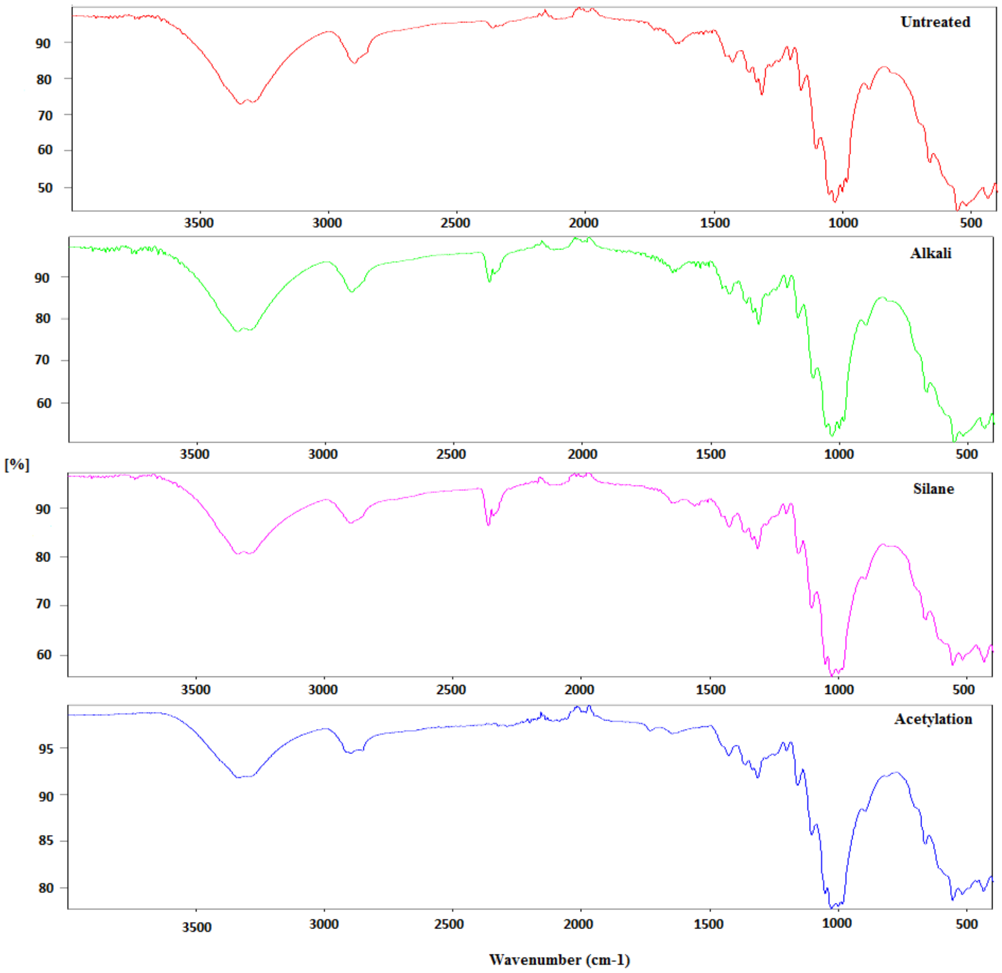


Figure 1: FTIR spectra for untreated and treated flax yarn

3.1.2. Thermal analysis (TGA)

Thermal stability of fibre was studied from the thermogram. The onset temperature for untreated and treated flax yarns is listed in Table 1.

Treatment	**Onset temperature (°C)**
Untreated	347 ±2
Alkali	350 ±1
Acetylation	347 ±3
Silane	355 ±3

Table 1: Onset temperature for untreated and treated flax yans

Onset temperature of Untreated, alkalized and acetylated yarn remains almost constant. Meanwhile the onset for silylated yarn exhibits a small increase in thermal stability when compared to untreated yarn. This might be influence of the silane coupling agent which has a higher thermal stability. From this, it could be also assumed that the organosilane is well bonded on the surface of yarn which was also evident from the FTIR spectrum. DTG curve given in Figure 2, display the degradation of the untreated as well as treated yarns. Obviously two stage degradation can be seen from it in the temperature range of 25°C – 120°C and from 200°C – 400°C. Since flax is hydrophilic in nature, it will easily absorb moisture and the first degradation step could be ascribed to loss of absorbed water [13]. This behaviour of natural fibres should be credited to presence of –OH functional group. The second degradation step between 200°C and 400°C is faster and a major weight loss occurs due to the degradation of cellulose, hemicellulose and lignin [14]. Inset picture in Figure 2 illustrates degradation temperature in range of 200°C – 325°C. Thermal degradation of hemicellulose is supposed to occur in this range [15]. Even though the yarns undergo various chemical treatment including mercerization in its pathway from fibre to yarn, small trace of hemicellulose is still remaining in the untreated yarn. However alkali treatment with 4% concentrated NaOH helps in removing the left out hemicellulose from the yarn. Alkali treatment is established in partial removal of hemicellulose and lignin [15].

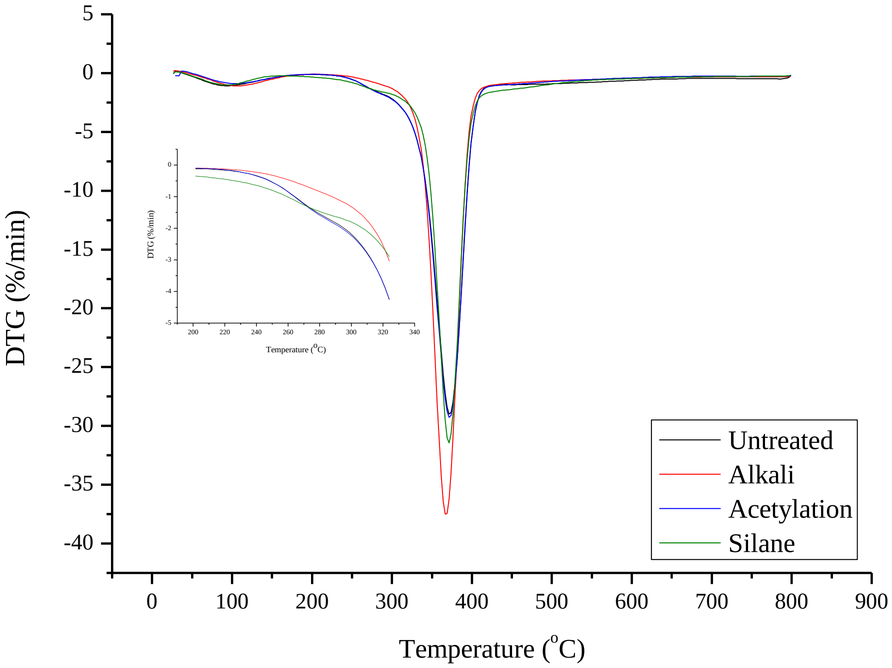


Figure 2: DTG curves of untreated and treated flax yarns

3.1.3. *Effect of chemical treatments on moisture absorption*

The influence of chemical treatment on flax yarn was studied through moisture absorption test conducted in a climatic chamber. In a given period of time the absorption of moisture by the yarns where calculated by the equation (1)

$$\mathrm{WG}(\%) = \frac{\mathrm{W(f)} - \mathrm{W(i)}}{\mathrm{W(i)}} \times 100 \tag{1}$$

Where WG (%) is the weight gain percentage at 24 hours, W (f) is weight at 24 hours, W (i) is initial weight before the test.

Weight gain percentage of the treated and untreated fibres is illustrated in Figure 3. Under the condition of 65% RH, alkali treatment proves to be less absorbing the moisture compared to other treated and untreated yarns. When the test where conducted at 95% RH, It seems that there is no notable difference in weight gain percentage. Even though a small decrease in weight gain could be found in the case of silane treated and acetylated yarns compared to untreated yarn. Related kind of work has been reported by Wong et al. [16] in which they have studied the moisture absorption of treated flax fibres in a climatic chamber and have reported a comparable results for the silane treatment at both 65% RH and 95% RH. It could be assumed that all kind of yarns reached its maximum moisture content within 24 hours under relative humidity of 95%. As this study was only intended to see the effect of chemical treatment on moisture absorption in a given period of time, it is not sufficient to give any idea on the equilibrium moisture content and it would be of interest to carry out further studies on moisture absorption in future.

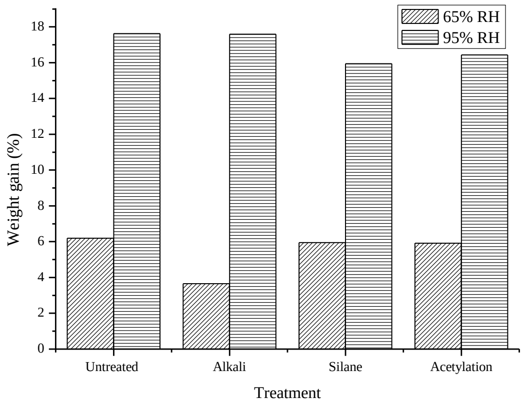
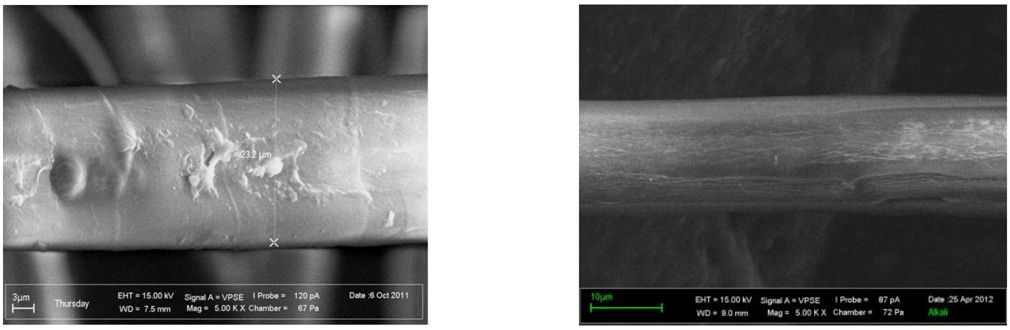


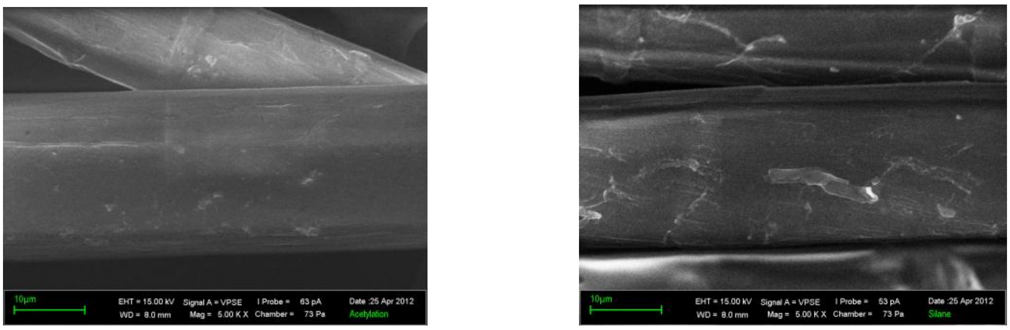
Figure 3: Moisture absorption of flax yarns in a time period of 24 hours

3.1.4. SEM examination of treated yarns

Scanning electron micrographs of untreated and treated yarns are shown in Figure 4 (a) – (d). The surface of untreated fibre covered with a kind of waxy substance which agrees with previous studies [17]. This indicates that even though the yarn during its production has undergone mercerization or some other modifications there is still left over of the waxy substances and probably hemicellulose on the surface. SEM picture of alkali treated yarn in Figure 4(b) seems to have a clean and rough surface. Acetylation gives a smooth surface which could be explained by removal of waxy materials and to substitution of surface hydroxyl group by acetyl groups [18]. SEM picture of silane treated yarn seems to have a layer which covers the surface of yarn. It should be taken into consideration that alkali treatment was done prior to silane treatment. In that point of view neither the waxy substance nor the roughness imparted by alkali treatment is visible on the surface. It shows that the surface of the yarn has been silylated.



(a) Untreated (b) Alkali



(c) Acetylation (d) Silane treatment

Figure 4: SEM photographs of flax yarns after treatment

4. Conclusion

In the present study, the influence of alkalization, acetylation and organo silane coupling agent on the flax yarn have been analyzed. FTIR analysis gives the evidence for the impact of the above discussed treatments on the yarn. Thermal stability for organo silane treated yarns exhibited an increase, while other two modifications equal the stability of untreated. Scanning electron microscopic pictures reveals that treatment induces change on the surface of flax yarn. Moisture absorption of treated yarns under a constant temperature and time for two different relative humidity was verified to see the effect of treatment. Even though it is difficult to conclude an order from the results, weight gain percent of all the three treated yarns is better than untreated. Furthermore extended study of moisture absorption might give clear information on this. The reduction in polarity of flax yarns undergone treatment is further proven by the reduction in the intensity of peak corresponding to adsorbed/absorbed water and also from DTG curve of thermal analysis. Finally we can conclude that a correlation of the investigated results gives the information that the polar nature of flax yarns have been reduced by treatments and in turn could be anticipated to have good adhesion with the thermoplastic matrix.

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