Effect of Alkali, Esterification and Silane Surface Treatments on Properties of Flax Fibres

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Authors' contributions

This work was carried out in collaboration between all authors. Author JZ designed the study, made the experiments, and wrote the first draft of the manuscript. Author HA checked the results of the study performed the infrared spectroscopy analysis and thermogravimetric analysis. Authors JB and HZ managed the draft corrections and other analysis.

Original Research Article

ABSTRACT

In the recent decades, flax fibres can be used as laminate reinforcements with polymer matrix materials to form natural composites, providing outstanding environmental benefits and other characteristics such as reduced cost and light weight. The composite properties are limited by the poor natural fibre/polymer matrix adhesion, which could be improved by chemical modifications. The fibre properties, such as thermal and mechanical properties, after the treatments have a direct effect on the composite behaviors. In order to investigate the effect of treatments on fibre properties, non-woven flax fibre mats were subjected to alkali, esterification and silane treatment. Fourier transformation infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and tensile tests were conducted on the virgin and treated flax fibres. It was found that all the treatments resulted in the removal of pectin and lignin component within the primary cell wall as evidenced by the characteristic IR peak change. The results showed that the thermal stability of non-cellulose part of flax fibres was highly improved by esterification modifications. However, the decrease (20-30%) in fibre tensile properties after the treatments was possibly offset by the improvement in fibre/matrix adhesion.

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1. INTRODUCTION

Flax fibre reinforced bio-polymers offer environmental benefits and desirable characteristics that may help to reduce the environmental footprint of superlight electric vehicles [1-3]. The hydrophilic property of flax leads to the poor interfacial adhesion with the nonpolar hydrophobic polymer matrix and difficulties in mixing. Surface modifications such as mercerization, acetylation, silane treatment etc. were investigated to increase the hydrophobicity of the flax fibres [4-7].

The flax fibre mainly comprises of polysaccharides including cellulose (64.1%), hemicellulose (16.7%), lignin (2.0%) and pectin (1%), with minor components such as bound water, waxes, and other inorganic materials [8]. The fibrils of cellulose in the crystalline form are deposited within the hemicellulose and lignin acting as an amorphous phenolic polymer matrix. The hydroxyl groups in flax fibres could be modified for hydrogen bonding or to introduce new moieties that form effective interlocks within the system. In addition, the rougher fibre surface resulting from dissolution of primary cell walls during treatment could enlarge the fibre/matrix contact area and hence improve the wettability [9].

Mercerization has an effect on the chemical composition of the flax fibres, degree of polymerization and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicellulose [10]. Alkali treatment also produces fine cellulose fibres by transferring crystalline form cellulose I into cellulose II [11]. The extent of this transformation is to some extent reflected by the IR (infrared spectroscopy) intensity ratio of the symmetric (C-O-C) and asymmetric (C-O-C) stretching modes as observed by Jahn et al. [12]. About 25% tensile and flexural strength improvement in 18% acetylated flax fibre with PP-flax fibre composites (30% fibre) was recently reported [13].

Acetylation is a well-known esterification method originally applied to wood cellulose to stabilize the cell walls against moisture, improving environmental degradation [14]. In lignocellulosic material the acetic anhydride reacts with more reactive hydroxyl groups (OH), which are in lignin and hemicellulose (amorphous material), whereas the hydroxyl groups of cellulose (crystalline material) prevent the diffusion of reagent and result in low extent of reaction [15]. Tensile and flexural strengths of flax/PP (polypropylene) composites were found to increase with increasing degree of acetylation up to 18% [16].

Xie and his coworkers [17] reviewed silane coupling agent modification to natural fibre composites and found out improvements in strength, moisture absorption and fungal resistance for unsaturated polyester (UP) and epoxy composites. The silane modification for fibres in epoxy composites was aminopropyltriethoxysiloxane (APS) and methacryloxypropyltrimethoxysilane (MPS). 3% APS solution combined with alkali treatment was found to provide better moisture resistance [18]. Silane was hydrolysed forming reactive silanols and then adsorbed and condensed on the fibre surface (sol-gel process-see in Fig. 1). The hydrogen bonds may be further converted into covalent bonds at elevated temperature.

Except the improved fibre/matrix adhesion, the properties of fibres themselves, such as thermal stability and mechanical properties could also play an important role in the final material performance and applications [9,15,19]. Thermal degradation of flax fibres is crucial to the development of natural fibre composites in order to ensure good composites with wide operating and service temperature range. The thermal degradation of the fibres depends on the chemical content and the energy to break down the chemical bonds or to degrade the chemicals [19]. Ahmed and his coworkers [20] have pointed out that the addition of $Mg(OH)_2$ can produce low combustible flax/PP composites with improved thermal stability. Saiah et al. [21] referred that an observed mass loss in 300-360°C range of wheat flour thermoplastic based flax composites increased significantly as a result of the fibre content increase. The heat treatment on non-woven flax also increased the air flow resistivity, reducing the sound absorption of hemp/PLA (polylactide) composites [22]. Bledzki et al. [13] reported that the degradation temperature of flax fibres increased from 319°C to 360°C after acetylation (34% acetylation). It was also stated that the thermal stability of flax fibres increased after alkali treatment due to the composition change of the removal of lignin and hemicellulose [23].
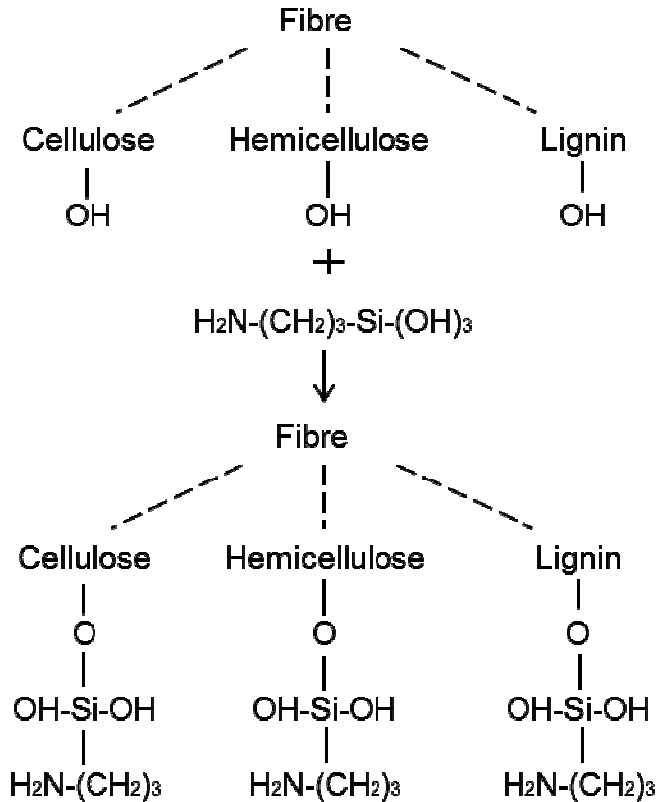
Fibre

Cellulose   Hemicellulose   Lignin

OH   OH   OH

$+$

$H_2N\text{-}(CH_2)_3\text{-}Si\text{-}(OH)_3$

Fibre

Cellulose   Hemicellulose   Lignin

O   O   O

OH-Si-OH   OH-Si-OH   OH-Si-OH

$H_2N\text{-}(CH_2)_3$ $H_2N\text{-}(CH_2)_3$ $H_2N\text{-}(CH_2)_3$

Fig. 1. Grafting of silanols on flax fibre surface [18]

In addition to the thermal stability, the surface treatment may have a great effect on mechanical properties of fibres. Li and his colleagues [24] also observed a decrease in flexural modulus (-6.1%) for MPS-g-PLA (Polylactide-grafted-r-metha-acryloxypropyltrimethoxysilane) treated sisal/PLA composites in comparison to the untreated composites.

Currently, there aren't many reports on the thermal and mechanical properties of flax fibres influenced by different treatments. In this paper, alkali, acetylation, silane treatment and enzymatic treatment were selected to modify non-woven flax mats. The SEM images to some extent reflected the removal of primary wall or other changes during treatments. The chemical changes of flax fibres from pretreatments were also indicated from Fourier transformation infrared spectroscopy (FTIR) spectrums. The effects of fibre pretreatments on thermal degradation and tension performance of flax fibres were investigated through thermal gravimetric analysis (TGA) and traction testing.

2. METHODOLOGY

2.1 Materials and Treatments

Dry non-woven flax fibre mats (600 g/m^2, carding/cross-lapping/needle punching) supplied by Eco Technilin Ltd were sent to Valtion Teknillinen Tutkimuskeskus (VTT Ltd) for surface treatments Table 1. Aminopropyltriethoxysilane (APS), butane tetracarboxylic acid (BTCA) and NaOH were obtained from Sigma-Aldrich. The alkali treatment was made by immersing the flax mats into 5 wt% NaOH solution for one hour, washing them two times thoroughly with water and drying in 50°C for 12 h. This NaOH treatment was made as pre-treatment also for BTCA and APS treated mats. The BTCA treatment was done by spraying 2.5 wt% BTCA-water solution on both mat surfaces to contain 5% of BTCA, followed by heating at 80°C for 20 min and drying at 50°C for overnight (to 24h). APS treatment was done with ethanol (98%): water-solution (80:20) containing 1% APS.

Table 1. Untreated and treated flax fibres for investigations

Fibre type	Treatment method	Detail
Untreated	None	-
NaOH treated	5% NaOH	Mercerisation
BTCA treated	NaOH+BTCA	Esterification
APS treated	NaOH+APS	Silane treatment

The mats were sprayed 'full' with solution on both sides and let stand in room temperature for 2 h. APS is attached on fibres in heat oven at 80°C for 4 h followed by washing with ethanol-water solution and water and drying in heat oven in 50°C for overnight.

2.2 Characterization and Tests

2.2.1 Fourier transformation infrared spectroscopy

ATR (attenuated total reflectance) -FTIR spectroscopy was conducted using a Shimadzu FTIR 8400S to characterize all the samples to identify the chemical change of flax fibres. The scan number was 64 per minute with the band range from 600 to 4000 cm^{-1}.

2.2.2 Thermogravimetric analysis (TGA)

The thermal analysis of untreated and treated flax fibres, and tannin resins were carried out by a TGA STA 449 instrument supplied by Netszch at Cracow University of Poland. Around 20mg of each specimen was heated from room temperature to 600°C at the heating rate of 10°C/min.

2.2.3 Tension test

Tension tests were carried out according to ASTM D 5035-11 standard. The standard cut strip size was 150×25 mm for non-woven fibre mats with a gauge length of 75 mm. The tensile tests were conducted by an Instron 5/100

machine at a loading rate of 300 mm/min with a 5KN load cell. The use of aluminate plates was necessary to give a tight clamping. At least 4 specimens were tested for each type.

3. RESULTS AND DISCUSSION

3.1 Effects of Surface Treatments on Fibre Compositions

The FTIR full spectra of untreated and treated flax fibre are plotted in the Fig. 2. The important characteristic band assignments for the untreated flax fibres are summarised in Table 2. The peak at around 1735 cm^{-1} is associated with C=O stretching for ester groups, indicating the presence of galacturonic acid from pectin in the fibres. Two peaks appearing at around 1600 cm^{-1} and 1505 cm^{-1} are attributed to the aromatic C=C in-plane stretching from lignin. The results are in agreement with the investigation of Garside and Wyeth [25].

The difference between the major chemical constituents of unmodified and 5% NaOH mercerised flax fibres could be identified clearly. The peak around 1735 cm^{-1} indicating the existence of pectin as mentioned before disappeared in the FTIR spectra of flax fibres modified with 5% NaOH. The absence of this peak was attributed to the removal of the pectin component within the primary cell wall. The peak at 1505 cm^{-1} disappeared after NaOH treatment, indicating the possible dissolution of lignin. As a result, the presence of absorbed

Table 2. Infrared band characteristics for neat flax fibres [25]

Position/cm^{-1}	Assignment	Belonged chemicals
~3335	v (OH) free	-
~2850	v (CH2) symmetrical	Organic compounds
~1735	v (C=O) ester	Pectin
~1635	Adsorbed water	All the chemicals
~1595	v (C=C) aromatic	Lignin
~1505	v (C=C) aromatic	Lignin
~1155	v (C-C) ring breathing	Largely from cellulose
~1105	v (C-O-C) glycosidic	Cellulose

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water mainly contributes to the peak of 1582 cm^{-1}, shifted from 1632 cm^{-1} in the IR spectra of neat fibres. Three main effects of the sodium hydroxide modification on cellulose fibres can be demonstrated [12,26]: (i) transform of crystalline structure from cellulose-I to polymorphous cellulose-II; (ii) removal of non-cellulosic cementing constituents (pectin, lignin and hemicellulos), creating the rougher topography; (iii) neutralisation with substances like acidic hydroxyl groups and carboxyl groups to reduce the hydrophilicity.

The most significant change in the FTIR spectra after NaOH-BTCA treatment was observed in the range of 1500^{-1} to 700cm^{-1}. The appearance of the peak around 1730 cm-1 does not arise from the C=O bonds of pectin removed during the NaOH treatment is contributed from the ester bonds introduced by BTCA reacting with OH groups. The peak (1635 cm^{-1}) representing the absorbed water in cellulosic crystalline shifted towards the low-frequency side (1563 cm^{-1}) along with a new partially-overlapped peak at 1540 cm^{-1}. The shift of the peak position was correlated with the carboxylate carbonyl via NaOH treatment.

Efficiency of silane treatment, such as aminopropyltriethoxysiloxane (APS), was reported to be higher than that for the untreated fibre because more reactive sites can be generated for silane reaction [18]. The combined NaOH treatment in NaOH-APS type removed the waxy epidermal tissues, lignins, adhesive pectins and hemicellulose. It resulted in the disappearance of peaks at 1735 cm^{-1} and 1505 cm^{-1} assigned to C=O in pectin and aromatic C=C in lignin, respectively. In addition, the well-defined absorption band at around 690 cm^{-1} was obtained due to the symmetric stretching of –Si-O-Si- structure on the APS treated fibres. The increment of the peak intensity at 1000 cm^{-1} and 982 cm^{-1} was attributed to the presence of Si-O-C bonds derived from the silane chemical treatment.

3.2 Effects of Surface Treatments on Fibre Thermal Properties

Fig. 3 shows the mass loss of flax fibres as a function of temperature. The decomposition profile of untreated flax fibres shows strong agreement of the typical TGA-air of flax fibres [27]. Cellulose is the main component of natural fibres, and thus controls the major degradation

behaviour of flax fibres. The degradation routes for cellulose upon heating were discussed in the literature [28]. The glycosyl units are decomposed at low temperature, followed by their depolymerisation at high temperatures. Then the formed substances like levoglucosan decompose into gas at higher temperatures. According to the TGA curve in Fig. 3, it was obvious that some weight loss of around 5.47% occurred up to 200°C due to the evaporation of absorbed water of flax fibres upon heating. Then the biggest weight loss of 65.94% mainly due to the cellulose degradation occurred in the approximate temperature range of 250°C to 380°C, followed by the second weight loss of 24.99%, largely attributed from non-cellulose components (from 380°C to 420°C). After that, a weight loss of 3.28% took place until 600°C and left the residual content of 0.32%. The main decomposition temperature was obtained at 305°C, which is similar to the temperatures observed in the publications [10,29,30]. However, the onset of degradation started at much lower temperature of approximate 200°C, in line with literature findings [8,27,31]. The onset of degradation of treated fibres was also observed around 200°C, whereas their decomposition temperature decreased from 305°C to about 250-260°C after the treatments. For the pure NaOH treated flax fibres, the non-cellulose decomposition was observed at a higher temperature of 500°C than those of neat and NaOH-APS flax fibres, which were found around 410°C Table 3. NaOH-BTCA exhibited the lowest weight loss between 300-500°C with 35% residue, indicating the improved thermal stability for non-cellulose content.

To further understand the degradation of untreated flax fibres, the resultant DTG curve Fig. 4 was used to present the kinetics upon heating. For untreated fibres, the first DTG peak was broad and below 100°C as a result of water removal. The second DTG peak is caused by cellulose degradation while the third DTG peak of around the 417°C is largely attributed to the degradation of non-cellulose components. It is worth noting that the cellulose degradation continued after the first peak until 500°C since cellulose suffered different degradation reactions depending on temperatures. Generally, in the temperature range from 300°C to 500°C, cellulose is firstly converted into active form to yield phenol, followed by the ring scission at approximately 340°C to form anhydrosugars such as levoglucosan and formation of polycyclic aromatic compounds
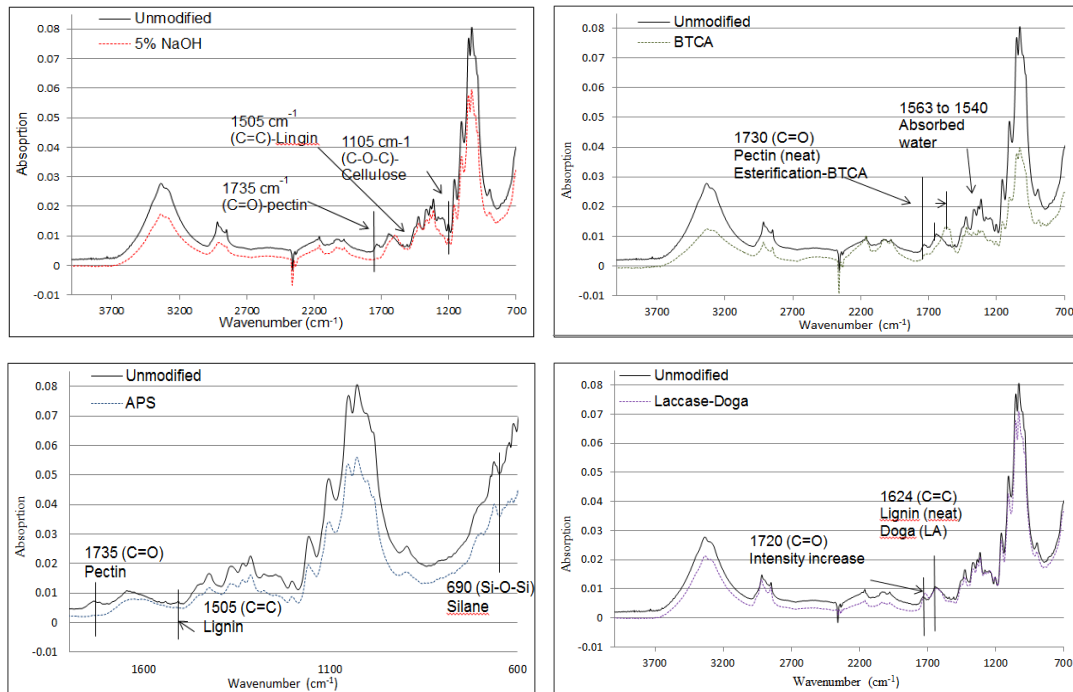
Fig. 2. FTIR spectrum of unmodified and treated flax fibres

Table 3. Summary of TGA results for treated and untreated flax fibres

Flax type	Moisture ($_{wt}$%)	Main decomposition temperature (°C)	DTG peaks (°C)		
			1st	**2nd**	**3rd**
Untreated	5.47	305.5	50.2	336.5	417.4
NaOH	5.88	250.3	59.6	293.0	528.1
NaOH-BTCA	5.83	258.5	78.2	301.5	451.3
NaOH-APS	6.49	261.8	48.3	299.9	421.4

(350°C) that mainly constitute the ash content in the 400-500°C temperature range [28]. After the third DTG peak, most of the decomposition products integrated into tar, volatile hydrocarbons and condensable gases (e.g. H_2O, CO), and left around 0.3% inorganic residue after 600°C. Hornsby et al. [29] found that TGA of flax fibres showed nearly 10% carbonaceous residual formed between 300 to 500°C because of a nitrogen atmosphere. The degradation progressed much faster in air condition than in a nitrogen or inert atmosphere because free radicals are easier to generate in air. Among all the fibres, the highest 1st peak

temperature of 80°C of NaOH-BTCA sample indicated that BTCA treatment ledto strong hydrogen bonding with water. The second peak temperature related to cellulose degradation decreased from 336°C of untreated fibres to the temperature range of 290-300°C for the modified samples. This may correlate to the increase of amorphous cellulose. In addition, the 2nd peak magnitude, which is the maximum decomposition rate, of all modified samples decreased compared to that of untreated flax fibres. This reduced decomposition rate is attributed to the removal of part of lignin and hemicellulose, which exhibits lower degradation
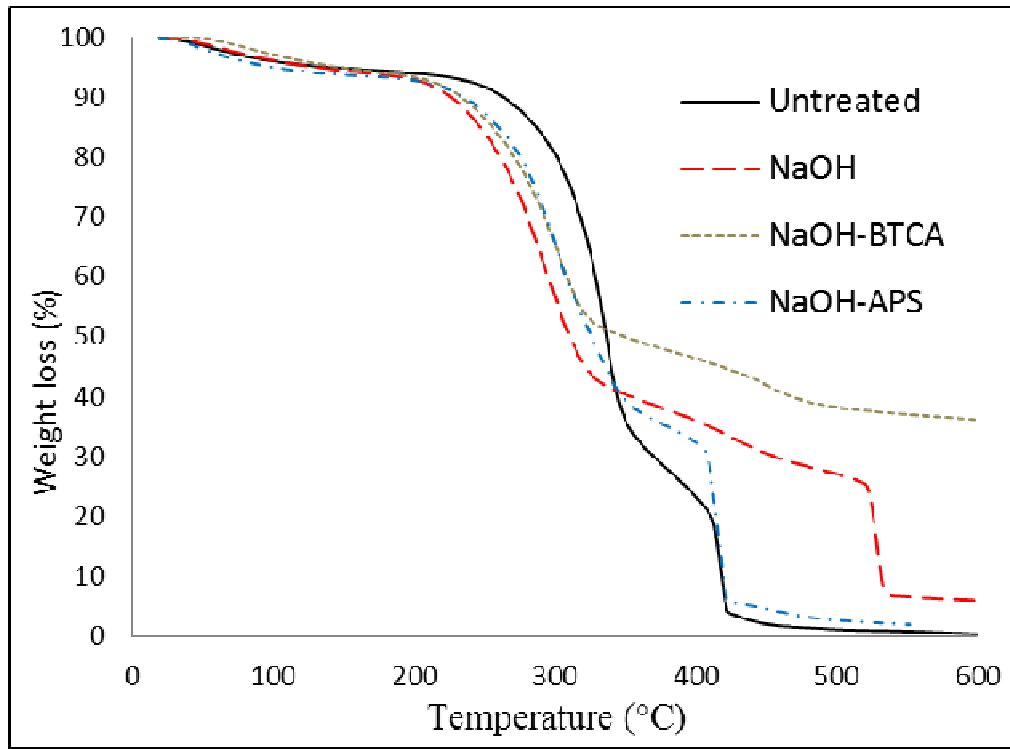
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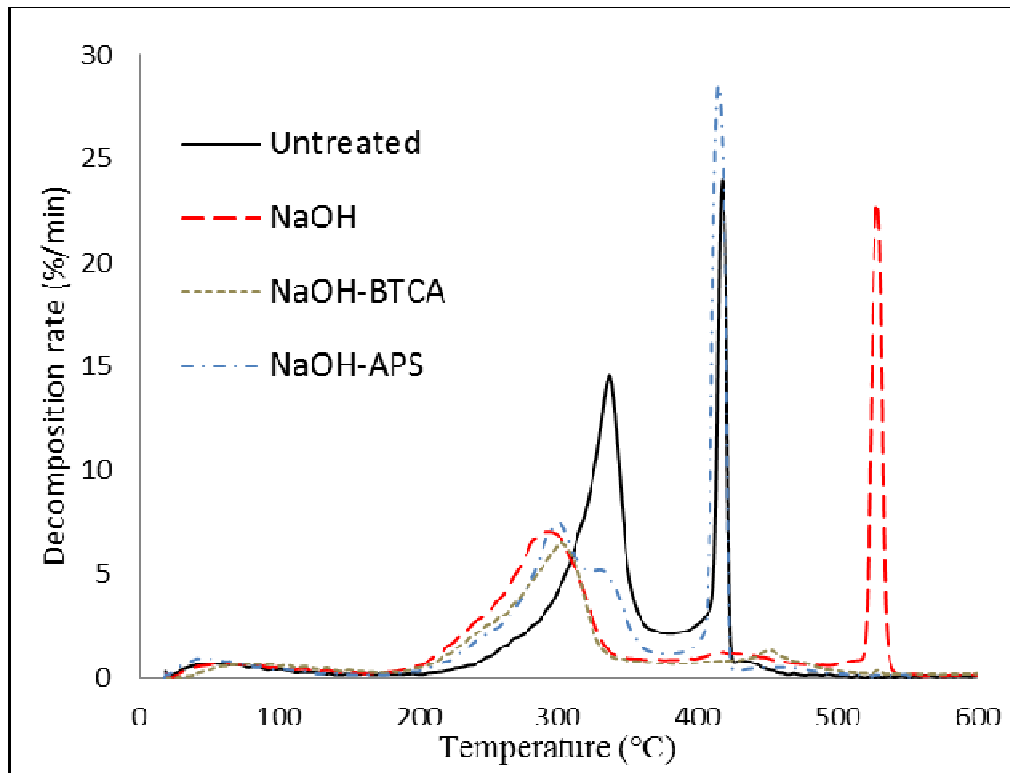**Fig. 3. TGA curves of investigated flax fibres**

Fig. 4. DTG curves of investigated flax fibres

stability. The degradation of hemicellulose happened in the 200-280°C, and the degradation at high temperature of 280-300°C was from lignin (activation energies: hemicellulose-28 kcal/mol; lignin-25kcal/mol) [32]. Many researchers [28,33,34] reported the positive influence of alkali treatment on thermal stability of natural fibres. The 3rd peak temperature of pure NaOH treated flax fibres was around 100°C higher than that of untreated sample. Apparently the thermal stability of non-cellulose part is highly improved by alkali treatment on flax fibres. BTCA flax sample showed a low 3rd peak value, indicating that esterification may result in the slowest decomposition stage of non-cellulose components.

3.3 Effects of Surface Treatments on Fibre Tensile Properties

Tension properties like breakage force and apparent elongation were obtained for the non-woven flax mats with and without treatments as shown in Table 1. Neat flax mats exhibited the breakage force and apparent elongation of 131 N and 48%. Based on the results, to various extents, the surface treatments deteriorate the tensile properties of non-woven flax mats. NaOH, APS treated fibres show average values of breakage force around 110 N, 20 N less than that of untreated flax fibres. The highest reduction about 33% in peak load was observed for BTCA treated non-woven flax mats. As discussed before, the hemicellulose (pectin) and lignin was removed from fibres after the treatments. However, it can be concluded that the excess removal of these constituents leads to the severe loss of inter-fibrillra matrix, causing less load transfer between elementary fibres compared to the near fibres. Singha et al. [18] reported that the APS treatment destroyed packing of the cellulose chains to a certain extent, causing disorder in the crystalline pattern of the main polymeric backbone. The reduced properties of non-woven flax mats after acrylic acid and other acid treatments were found by Erasmus and Anandjiwala [35] and were attributed to the possible fibre degradation resulting from the harsh treatment environment. However, hydroxyethyl-cellulose (HEC) treatment can improve the mechanical properties of stiffness of twist flax fibres by 75% [36]. Apparently, the flax fibre mechanical properties can be affected either positively or negatively by using different surface treatments.

In terms of the apparent elongation, non-woven flax mat represents the highest value of around 50%. Again BTCA treated fibres showed the lowest elongation value at 30%. The high apparent elongation of non-woven mat is the consequence of the re-alignment of flax fibres in the load direction. A plastic-deformation-like behaviour of non-woven flax mat during tension was shown in Fig. 5. Due to the rule of mixturesfor fibre/matrix composites, the decreased tensile properties of flax fibres may compensate the effect of improved fibre/matrix wettability. The resulting composite tensileperformance may not be able to achieve the best improvement degree from the treatments. Li and his colleagues [28] observed the increase in tensile strength (6.7%) and decrease in flexural modulus (-6.1%) for MPS(γ-metha-cryloxypropyltrimethoxysilane)-graft-PLA treated sisal/PLA composites in comparison to the untreated composites.
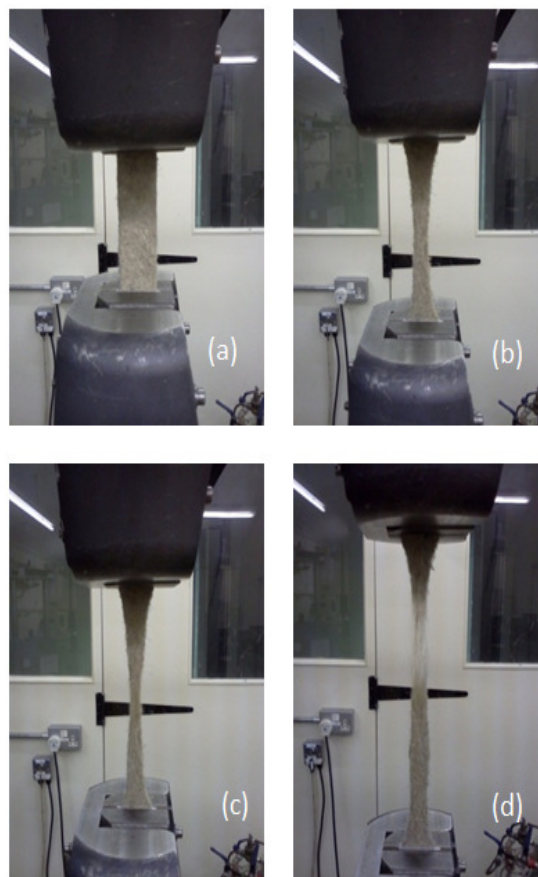

Fig. 5. Tensile deformation of the non-woven mat (from a to d)

Table 4. Effects of treatments on tension properties of non-woven flax mats

Type	Max. Force (N)	Apparent elongation at Load peak (%)	Max elongation (load<10%)
Untreated	131.2±5.3	48±4.2	67.5±2.4
NaOH	107.1±2.1	45.6±3.5	60.9±2.6
NaOH+BTCA	87.7±5.8	30.9±4.3	47.7±2.5
NaOH+APS	109.6±10.2	45.0±4.7	58.5±3.8

4. CONCLUSION

The effect of fibre treatments on the thermal and mechanical properties of flax fibres was investigated. The physical changes like the removal of pectin and lignin (form the primary cell wall) during the NaOH treatment were verified by the disappearance of their characteristic IR band at 1735 cm^{-1} and 1505 cm^{-1} respectively. FTIR results also indicated the presence of cross-linked BTCA (ester bond) and the new APS (Si-O-Si) bond. As a result of the changes in fibre physical structure, the treated fibre can potentially provide good fibre/matrix contact. The onset degradation temperature for flax fibres occurred at around 200°C, indicating the processing and service temperature below 200°C. NaOH-BTCA was found to provide the best improvement on thermal stability of the non-cellulose content in the flax fibres. Additionally, the fibre tensile properties decreased to some extent after the treatments, possibly due to the loss of inter-fibrillar matrix or the degradation from harsh reaction environment. Apart from the improved fibre/matrix adhesion, the property (thermal and mechanical) change intreated flax fibres is also very important to understand the behavior of final bio-composites through the rule of mixture. New bio-sourced matrix such as bio-epoxy and bio-phenolic resins, could be used in the future with untreated and treated flax fibres to analyze the composite performances.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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