

Aging studies on flame retardant treated lignocellulosic fibers

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ABSTRACT: The study deals with chemical and flame retardant (FR) treatment of flax fabric. Sheets of flax fabric were subjected to chemical treatments using NaOH and silane coupling agents. A phosphate-based flame retardant (DAP) was also applied to improve the flammability of the fabric. The effects of the chemical treatments and FR treatments on flax fabric were investigated using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and vertical flame resistance test. Aging studies were carried out by exposing the samples in an environmental chamber at specified conditions for two weeks. The mechanical properties of the fabric, before and after environmental aging, were investigated. Flammability of flax fabric was improved after FR treatment. Thermal studies revealed a shift of decomposition temperature to lower temperatures and an increase in char residue after FR treatment. Despite treatment of the fabric with NaOH and silane, the tensile strength of FR-treated flax fabric declined by more than 90% after aging for two weeks at 90 °C and 50% RH. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44175.

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INTRODUCTION

The use of natural fibers as reinforcement materials has been extensively studied over the past years due to the growing demand for sustainable and eco-friendly products. The most important application sectors are construction (decking, siding, and fencing) and automotive industries. According to the report¹ on Global Natural Fibre Composites Market 2014–2019: Trends, Forecast and Opportunity Analysis, natural fiber composites market is expected to be worth US\$531.2 million with an expected annual growth rate of 11.2% during 2014–2019. The prime driving force for the rising incorporation of natural fiber composites in automotive interiors is to reduce the overall weight of the vehicle in order to achieve better fuel efficiency. The automotive industries have been using natural fibers for interior components for several years.^{2–4} Natural fibers are mainly used for door and instrument panels, package trays, glove boxes, arm rests, and seat backs and recently in exterior components as well.

The difficulties with using natural fibers are their hydrophilic nature and their high flammability which can be problematic for many applications. Natural plant fibers, being hydrophilic in nature, absorb moisture from the environment.⁵ This is due to the presence of strongly polarized hydroxyl groups.⁶ The high moisture absorption of natural fibers can create debonding problems when incorporated in composites. Reducing moisture

absorption of natural fibers is an effective way to modify the mechanical properties of these materials. Researchers have employed a number of fiber surface treatments to reduce moisture sensitivity of natural fibers.^{7–9} The treatments aim to chemically modify the surface of the fiber to reduce moisture absorption. John *et al.*,¹⁰ Punyamurthy *et al.*,¹¹ and Abdelmouleh *et al.*¹² have reported on the effectiveness of NaOH and silane treatment in reducing moisture absorption of natural fibers. In their work, John *et al.* reported that sisal-oil palm reinforced composites treated with 0.5% NaOH showed higher water uptake than composites treated with 4% NaOH. The authors reasoned that an increase in NaOH concentration created more adhesion between the fiber and the matrix leading to a decrease in moisture uptake.

The other problem with natural fibers is their high flammability and burning potential, therefore addition of flame retardants would expand their uses in some specific applications.¹³ Different flame retardants have been utilized to treat natural fibers to overcome this challenge to be used in textiles or composites. The most commonly used flame retardants are based on halogens, phosphorus, boron, ammonium compounds, graphite, and alkaline earth metallic compounds.

Phosphorus containing compounds have been commonly used to render natural fibers flame retardant.^{13,14} They have been

Table I. Properties of Flax Fabric

	Warp	Weft
Yarn Tex (average)	38 (3.4)	37 (3.6)
Ends and picks (CV %)	Ends/cm: 1.9 (1.71)	Picks/cm: 21 (2.71)
Fabric density (CV %)	180 g/m ² (0.85)	

used both as a physical additive as well as part of the polymer structure. The non-toxic phosphorus-based compounds can effectively initiate the charring of fibers.^{14,15} Acid fire retardants produce char via a dehydration process. Phosphorus-acids remain liquid and exhibit strong acidic properties up to 864 °C, and therefore phosphate derivatives are considered better fire-retardants than sulfate, borax, nitrate, etc.¹⁵ Continuing work on phosphate-based flame retardants is reported in literature, for example on cotton fabric^{16,17} and on bast fiber fabrics which are finding use in composite materials. Sonnier *et al.*¹⁸ improved the flame retardancy of flax fabrics by radiation grafting of phosphorus compounds. They reported that 1.5 wt % of phosphorus compounds was enough to make flax fabric self-extinguishing. Szolnoki *et al.*¹⁹ reported that the treatment of hemp fabric with phosphorus flame retardant reduced the flammability of hemp fabric reinforced epoxy composites characterized with increased limiting oxygen index (LOI) values and by 25% reduced heat release rate.

The use of natural fiber-based composites is increasing in automotive and aerospace applications. In these sectors, most of the components are exposed to varying conditions of temperature and humidity during the service life. Hence, it is crucial to establish data on the properties of flame retardant and chemically treated fibers (nonwoven or woven) under variable aging conditions. Also it is apparent from the literature that studies on the effect of aging of FR-treated natural fibers and composites are scarce and hence needs to be addressed. In this research work, the effect of alkali, silane, and FR treatment on thermal, mechanical, and flammability properties of woven flax fabric was studied. The mechanical properties of the treated fabric before and after aging were also studied.

EXPERIMENTAL

Materials

Commercial woven flax fabric (plain weave) was obtained from Libeco, Belgium. The fabric parameters are presented in Table I (obtained from supplier). Sodium hydroxide and (3-aminopropyl) tri-ethoxy silane (A1100) were supplied by Sigma-Aldrich, South Africa. The flame retardant Flammentin TL833 was supplied by ACTI-Chem, Durban, South Africa. Flammentin TL833 is a liquid based on ammonium salts of inorganic acids. It contains diammonium phosphate (DAP) as the major flame retardant in the composition.²⁰ The chemical formula of DAP is (NH)₂HPO₄. Flammentin TL833 is a non-durable flame retardant; however, the intended use of the fabric is in composite materials where the fabric will be the reinforcement in a resin matrix.

Flax Fabric Modification

Alkali Treatment. Sheets of flax fabric with dimensions 300 mm × 300 mm were immersed in a 5% (m/vol) NaOH solution for 2 h. After treatment, the sheets of flax fabric were washed with distilled water. Finally, the sheets of fabric were washed with water containing 2% acetic acid until the pH was about 7. The sheets of flax fabric were dried at 70 °C in an oven for 24 h.

Silane Treatment. The silane coupling agents used for modifications of flax fabric was (3-aminopropyl)tri-ethoxy silane. Approximately 0.5% solution of the silane was prepared by measuring out the required volume of silane and then diluting it in the appropriate volume of an ethanol water mixture (6 : 4 ratio). The pH of the solution was adjusted to 4 with the drop-wise addition of acetic acid. The sheets of fabric with dimensions 300 mm × 300 mm were immersed in this solution and were allowed to stand for 2 h. The solution was drained out and the sheets of fabric were washed with distilled water. Finally the sheets of fabric were dried in an oven at 70 °C.

Flame Retardant Treatment. Flax fabric was first chemically modified by alkalization and silanization. The flame retardant (FR), Flammentin TL833, was diluted with water and applied using a padder (roaches BVHP) at a speed of 1 m/min and pressure of 1.2 bar to give a wet pick up of ~100% on the weight of the fabric. After padding the fabric was oven-dried on a pin frame at 120 °C for 2 min. The final add-on of the FR was 10% on the weight of the fabric. Figure 1 shows the stages involved in the treatment of flax fabric. The sample codes of different flax fabric are given in Table II.

CHARACTERIZATION

Fourier Transform Infrared Spectroscopy

Attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) of the untreated and untreated flax fabrics were carried out on a Spectrum 100 FTIR (PerkinElmer, Waltham, MA). The spectra were analyzed over the range of 500–4000 cm⁻¹.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out in a PerkinElmer Pyris thermogravimetric analyzer. The samples (5–10 mg) were heated from 30 to 700 °C at a rate of 10 °C/min under nitrogen atmosphere (flow rate at 20 mL/min). Three specimens were tested and the average data have been reported.

Vertical Flame Test

Flammability studies on flax fabric were carried out using vertical burning test according to ASTM D6413 [Standard Test

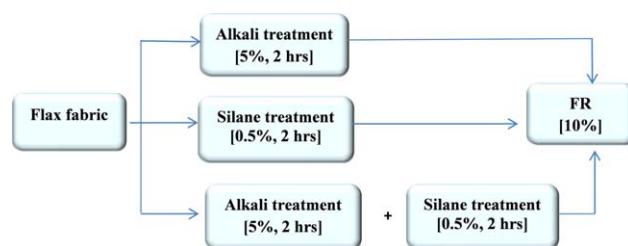


Figure 1. Stages in the chemical treatment of the fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Sample Codes

Name	Description
U	Untreated flax fabric
N	NaOH treated flax fabric
S	Silane treated flax fabric
N-S	Flax fabric pre-treated with NaOH first followed by silane treatment
U-FR	FR treated flax fabric
N-FR	Flax fabric treated with NaOH first followed by FR
S-FR	Flax fabric treated with silane first followed by FR
N-S-FR	Flax fabric treated with NaOH and silane first followed by FR

Method for Flame Resistance of Textiles (Vertical Test)]. Flax fabric samples of dimensions 150 mm × 50 mm were used. Specimens were tested in the weft direction. The specimen was positioned vertically above a controlled flame and exposed for a specified period of time (12 s) according to the method. The flame was then removed, and after flame-time and after-glow time were measured. Char length was measured under total tearing force of 100 g.

Tensile Characterization of Flax Fabric

Tensile testing was carried out on the Instron tensile tester model 3345 J9529. Samples of dimension 150 mm × 50 mm were tested according to ASTM 5035 (Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)). Fabric samples were raveled for tensile tests and were characterized both in the warp and the weft direction. Samples were tested to failure under tension at a cross head speed of 120 mm/s. Four specimens were tested for each type of fabric. Tensile strength of the samples was recorded in Newton. The error bars on tensile graphs represent standard deviation.

Environmental Conditioning of Flax Fabric

Treated and untreated flax fabric of dimensions 150 mm × 50 mm were placed in a Binder GmbH environmental chamber model APT.line™ KMF (E5.2) with program control. Samples were exposed for two weeks at a fan speed of 5% under specific conditions of temperature and humidity as shown in Table III. The aged fabric was then subjected to tensile testing to

Table III. Environmental Conditions

Temperature (°C)	Relative humidity (%)
60	50
75	50
90	50
25	60
25	75
25	90

determine the effect of temperature and humidity on mechanical properties.

RESULTS AND DISCUSSION

FTIR Analysis

The effects of NaOH, silane, and FR treatment on flax fabric were analyzed using FTIR spectroscopy. Figure 2 shows the FTIR spectra of the untreated, NaOH-, and silane-treated flax fabrics. FTIR spectrum of flax fabric demonstrate OH, CH, C=O, C—O—C, and C—O stretching vibrations.²¹ The peak at 1641 cm⁻¹ may be attributed to C=O ester band from pectin.²² The peak at 1440 cm⁻¹ corresponds to lignin.²³ The peak around 2896 cm⁻¹ has been associated to the CH stretching vibration from the CH₂ group of hemicellulose. It has been reported that the CH and CH₂ groups of oils and waxes can also occur around the same band.²² The increase of transmittance peaks at 1641 cm⁻¹, 1440 cm⁻¹, and 2896 cm⁻¹ corresponds to the decrease in the proportion of hemicelluloses, pectin, and lignin in the fiber. The peak at around 3327 cm⁻¹ may be attributed to the —OH stretching vibration in the fiber. The increase of transmittance of hydroxyl group peak for the chemical treated fibers corresponds to the decrease of the hydroxyl group in the fiber. These results confirm that there was some reaction between the used chemicals and the fiber components. However, the use of chemical treatments did not completely remove the hydrophilic group in the fiber, exposing the fabrics to wet environments may still cause the available hydroxyl groups to form hydrogen bonds with water molecules. The order of increase in transmittance peaks values of the fibers after chemical treatment was as follows:

$$\text{Silane (S)} > \text{NaOH-Silane (N-S)} > \text{NaOH (N)} > \text{Untreated (U)}$$

To observe the effects of the FR on flax fabrics, the FTIR spectrum of the untreated and FR-treated flax fabrics are shown in Figure 3. The weak band around 3250 cm⁻¹ [Figure 3(b)] can be attributed to NH₄ vibration of the DAP on the FR-treated

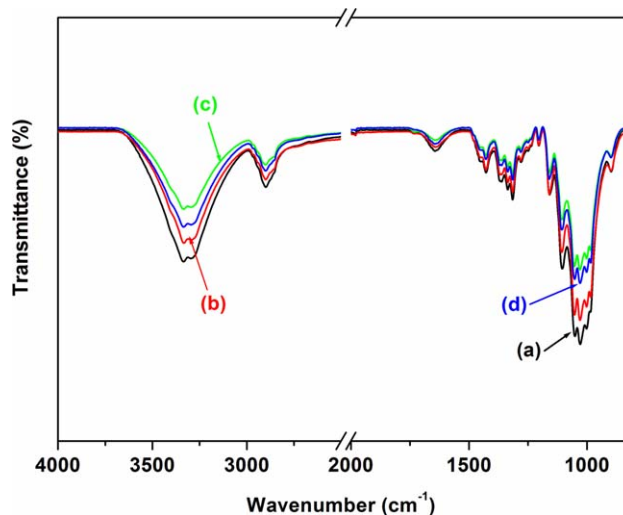


Figure 2. FTIR spectrum of (a) U, (b) N, (c) S, and (d) N-S. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

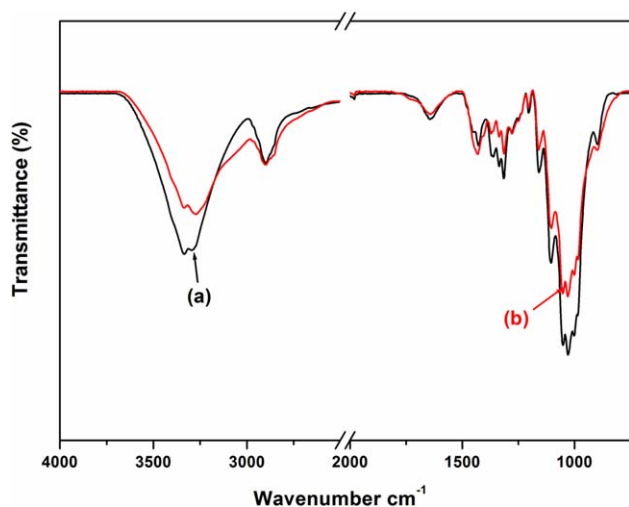


Figure 3. FTIR spectra of (a) U and (b) U-FR flax fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fabric. The presence of DAP in the fabric resulted in increases in transmittance. The most significant difference was observed around 3327 cm^{-1} , at this wavenumber the transmittance peak value which corresponds to —OH stretching vibration of the fiber increased and appeared to be shifting to lower wavenumber. This may be due to the coating of the fibres with DAP. An increase in transmittance at around 3327 cm^{-1} and $1160\text{--}1040\text{ cm}^{-1}$ (OH groups) could also be due to the phosphorylation of cellulose primary hydroxyl groups to form cellulose phosphate esters.²⁴

Thermogravimetric Analysis

Thermograms of all samples are shown in Figure 4(a,b) and the results are tabulated in Table IV. It can be seen in Figure 4(a) that the untreated and chemically treated flax fabric samples showed a single step thermal degradation process. From the DTG thermogram [Figure 4(b)], it can be seen that the untreated flax fabric (U) shows a main degradation peak temperature at around $369\text{ }^{\circ}\text{C}$. It is interesting to observe that NaOH treatment of flax fabric (N) decreased the T_{max} (maximum peak temperature from the DTG thermogram) of the sample to around $351\text{ }^{\circ}\text{C}$. The residual char left at $600\text{ }^{\circ}\text{C}$ was increased from 13.2% to 20.0%. This is in agreement with some findings in literature²⁵; however it is in disagreement with other authors who found that NaOH treatment may result an increase in thermal stability and little change in char residue.^{26,27} The reason for this may be variation in treatment conditions which cause different chemical reactions:

- Treatment with NaOH can remove binding pectins and lignin which may result in a decrease in thermal stability.
- Higher concentrations of or prolonged treatment with NaOH can change the crystalline structure of cellulose (cellulose I to cellulose II). This results in an increase in the amorphous phase and corresponding decrease in crystallinity which can reduce thermal stability.

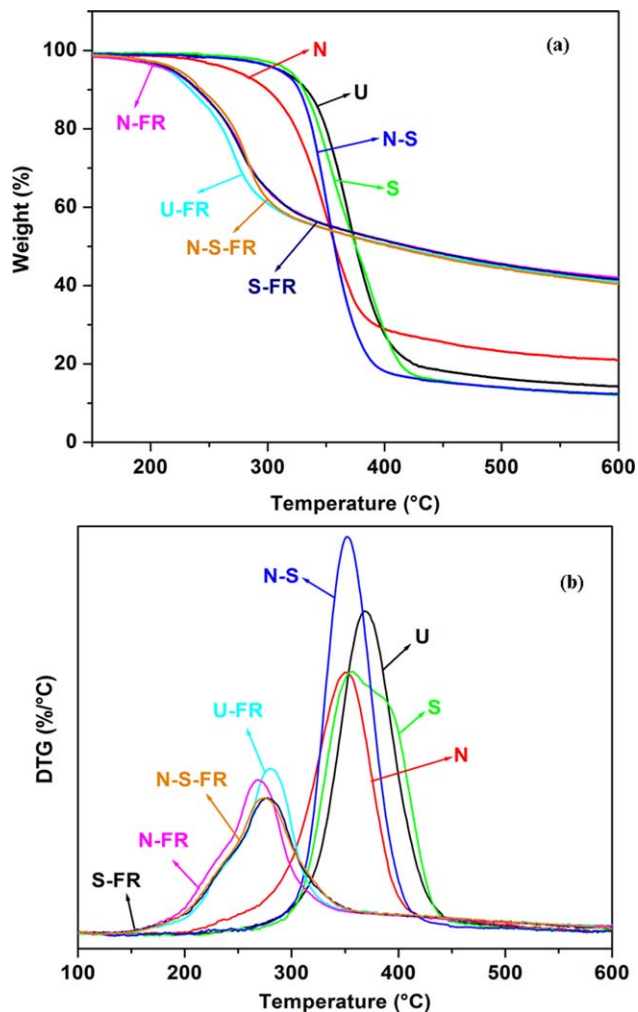


Figure 4. Thermograms [(a) TGA and (b) DTG] of untreated and chemically treated flax fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It can be observed in Figure 4(a) and Table IV that, compared to untreated (U), the decomposition temperature of silane treated (S) flax fabric decreased to $356.5\text{ }^{\circ}\text{C}$ and the char residue was slightly reduced to 10.9%. The reason could be that silane

Table IV. Thermal Data from Figure 5

Sample	$T_{\text{max}}^{\text{a}}$ ($^{\circ}\text{C}$)	Char residue at $600\text{ }^{\circ}\text{C}$ (%)
U	369.2	13.2
N	351.4	20.0
S	356.5	10.9
N-S	352.8	11.2
FR	280.1	37.9
N-FR	268.6	38.3
S-FR	278.5	39.7
N-S-FR	274.3	39.2

^a T_{max} : Maximum peak temperature from the DTG thermogram.

Table V. Burning Behaviour of Untreated and Chemical Treated Flax Fabric

Sample ID	After-flame \pm SD (s)	After-glow \pm SD (s)	Char length \pm SD (cm)
U	10.2 \pm 0.1	25.2 \pm 1.0	N.R
S	14.1 \pm 1.3	17.5 \pm 4.1	N.R
N	10.4 \pm 2.4	109.3 \pm 7.8	N.R
N-S	24.5 \pm 2.7	47.2 \pm 11.1	N.R
U-FR	0	0	9.0 \pm 0.07
N-FR	0	0	10.8 \pm 0.6
S-FR	0	0	9.2 \pm 0.2
N-S-FR	0	0	8.6 \pm 0.1

SD: Standard deviation.

N.R: Denotes no record due to complete destruction of the fabric.

coupling agents decreased the mobility of cellulose chains and that will strain and weaken the existing hydrogen bond thus decreasing the thermal stability. For alkali-silane treated flax fabric (N-S), the decomposition temperature shifted to 352.8 °C and the char residue was found to be 11.2%.

Compared to untreated and chemically treated fabric, flax fabric treated with DAP (FR) showed two changes: (1) DAP promoted the formation of solid residues and char; (2) the regions of major weight loss of DAP treated fabric shifted to lower temperatures. From Table IV, it can be seen that the decomposition temperature shifted to 280.1 °C, 268.6 °C, 278.5 °C, and 274.3 °C for U-FR, N-FR, S-FR, and N-S-FR, respectively. The decrease in decomposition temperature is due to the catalyzed dehydration of cellulose by phosphoric acid, which was formed by the decomposition of DAP at lower temperatures than that for cellulose degradation.²⁸ The char amount for the untreated and chemically treated fabric was between 11 and 20%, whereas for the DAP-treated fabric this increased to between 38 and 40%. Therefore it can be deduced that the application of DAP results in a delay in the formation of volatile pyrolysis products and the promotion of char formation when the flax fabric is subjected to heat. A decrease in decomposition temperature of FR-treated natural fibers has been reported by other authors.^{29,30} Bocz *et al.* reported a decrease in decomposition temperature and an increase in char residue of flax fibres treated with ammonium phosphate (AP).¹³ The char amount at 500 °C for

AP-treated flax fibres was found to be 41.1%, almost double than that of the untreated flax fibres.

Vertical Burning Test

Table V presents the burning behavior (flame resistance test) of untreated and chemically treated flax fabric with and without FR. The flax fabric without FR disintegrated completely during the test as a result of after-flaming and glowing combustion (after-glow); consequently there was no result for the char length. FR-treated flax fabric exhibited good flame retardant properties compared to the untreated ones. The fabric exhibited no after-flame or after-glow after removal of the test flame. The flame retardancy of FR-treated flax fabric was not greatly affected by NaOH (N) and silane treatments (S). It is well known that the phosphorus containing compounds render natural fibers flame retardant.^{31,32} DAP has been found to be the most effective among non-durable and durable FRs in imparting FR properties to cellulosic materials and in yielding a char.^{14,33} Vertical flame test for untreated and FR-treated nonwoven cotton fabric was studied by Nam *et al.*³¹ They reported that after-flame time for untreated nonwoven cotton fabric was found to be 0.8 s and the fabric was completely destroyed after vertical flame test. Flame combustion was prolonged for 4.2 s after the flame source had been removed for DAP-treated fabric and resulted in the entire specimen turning into a sturdy char. Zhang *et al.* also studied vertical flame test of untreated and FR-treated ramie fabric.³² They reported that for untreated

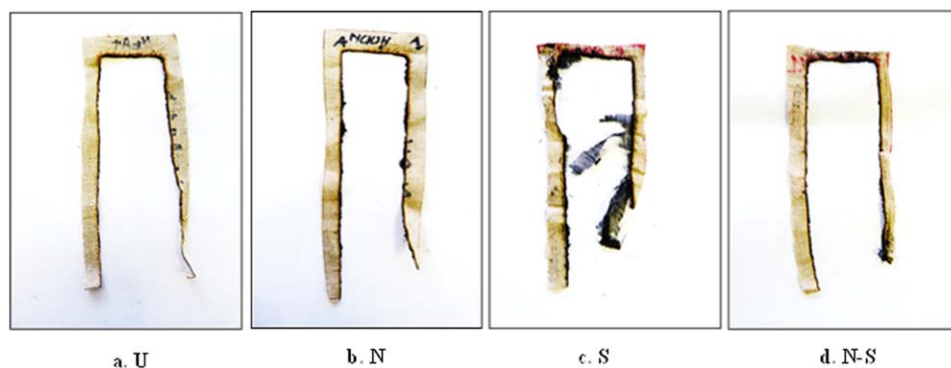


Figure 5. Images of the final residues of FR treated flax fabric after flammability test in vertical configuration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

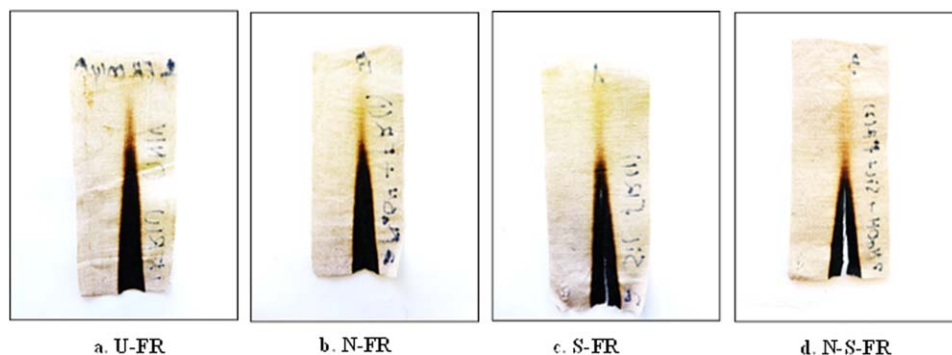


Figure 6. Images of final residues of flax fabric after flammability test in vertical configuration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ramie fabric, the flame was vigorous and spread upwards rapidly. The char was porous and formed loose fabric fragments during the vertical flame test. The fabric coated with a flame retardant consisting of polyelectrolyte polyethylenimine (PEI) and AP showed self-extinguishing ability and the char was more compact.

It has been reported that when phosphorus-based flame retardant decomposes, phosphoric acid and ammonia are formed.³⁴ The phosphoric acid formed can phosphorylate the primary hydroxyl group of cellulose to form a phosphorus ester. Ester decomposition occurs at high temperatures to form double bond and an acid molecule, which becomes available for further reaction. By successive esterification and elimination reactions, stable conjugated structures are built up. Conjugated structures of this kind are the precursors for the formation of char. The acid may also crosslink with cellulose, changing the normal pathway of pyrolysis to yield less flammable products.³⁵ NH_3 gas can reduce the concentration of O_2 that supports combustion.³⁶

Figures 5 and 6 show images of flax fabric after flame resistance test. It can be seen that in Figure 5(a–d) flax fabric without FR disintegrated completely; only silane-treated fabric showed some fabric remnants. As seen in Table V, the afterglow time for the silane-treated fabric was also lower, about 17.5 s compared to about 25.2 s for the untreated fabric. In addition, there was slower burning of the fabric after flame removal (longer after-flame time). This could be a result of the initial bonding of the silane with fiber hydroxyl groups as noted in the FTIR results. Bonding of the silane somehow reduces after-glow and retards the burning process slightly, but does not prevent burning. The presence of the silane in the fabric and then the char acts as a partial barrier to oxygen/heat thereby retarding burning and reducing the after-glow process.³⁷ The flame retardant property of the FR-treated fabric is clearly observed in Figure 6(a–d).

Tensile Testing

Figure 7 presents the tensile strength of treated and untreated flax fabric both in the weft and warp direction. The tensile strength of untreated, chemically treated, and FR-treated flax fabric was found to be higher in the weft direction [Figure 7(a)] than in the warp direction [Figure 7(b)]. The tensile properties of woven fabric depend on the fabric structure, i.e., yarn twist, yarn strength, weave, crimp, and cover.³⁸ A woven fabric

is formed by interlacement of two sets of threads namely, warp and weft threads. The warp threads are termed as ends and the weft threads as picks. The strength of the fabric can be greater either in the warp or weft direction depending on a number of factors such as the number of yarns, yarn twist, and yarn size.

Chemical treatment of natural fibers has been reported to increase the tensile strength of natural fibers.³⁹ However, in this study, chemical treatment of flax fabric with NaOH and silane coupling agents did not achieve significant improvement in tensile strength. It can be seen in Figure 7(a) that the strength of

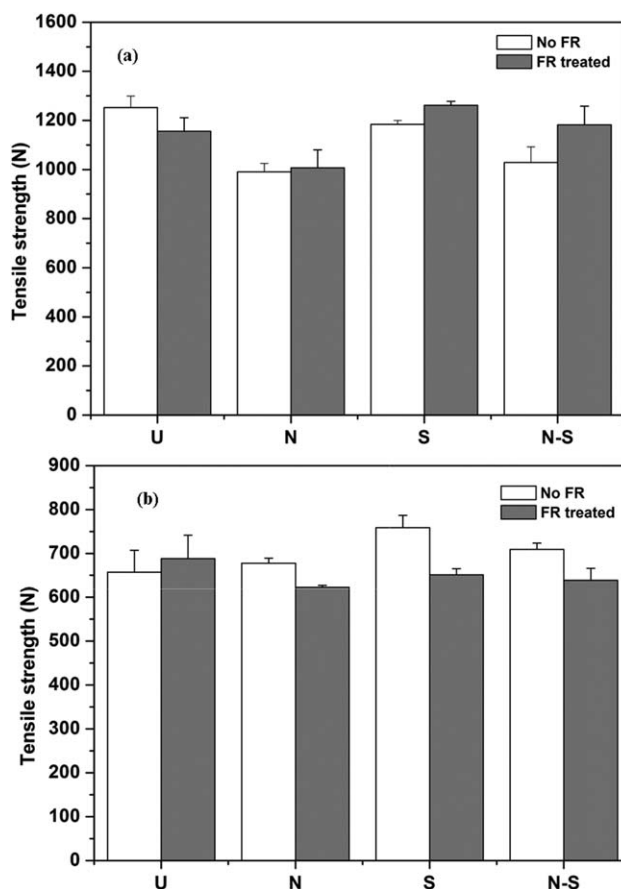


Figure 7. Tensile strength of treated and untreated flax fabric (a) weft and (b) warp.

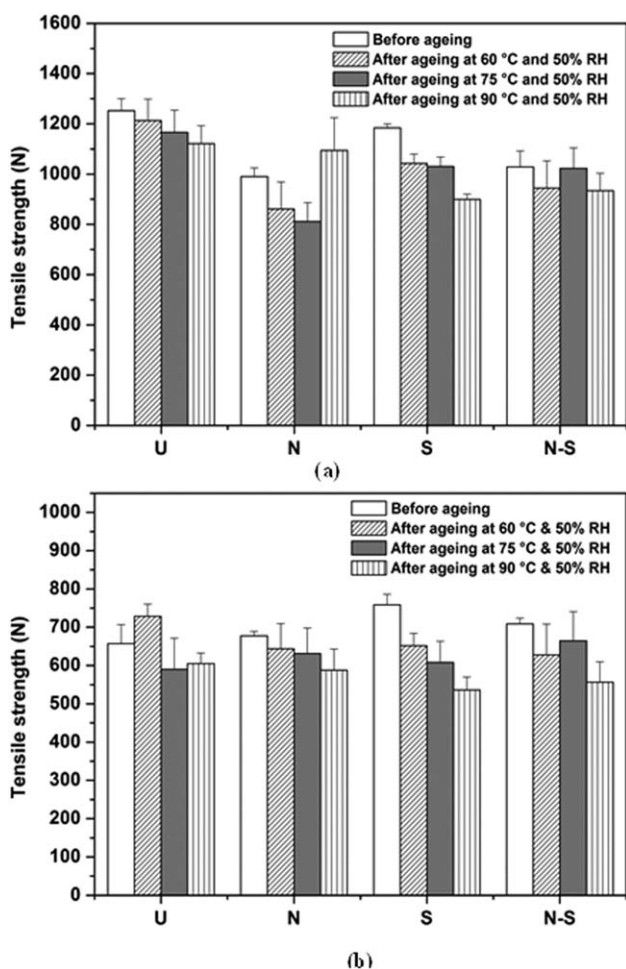


Figure 8. Tensile strength of the untreated and treated fabric after aging at different temperatures (a) weft and (b) warp direction.

NaOH-treated flax fabric was reduced after alkali treatment. Fiber pull out from the fabric was observed after alkali treatment. Fiber damage and loss of bonding hemicellulose, pectin, and lignin might be the reason for the decrease in strength. Shrinkage of the fabric was observed after NaOH treatment which might also have affected the tensile strength. It has been reported that even at low NaOH concentration, fibers can fibrillate resulting in a reduced fiber diameter.⁴⁰ In the case of woven fabric the following affects the strength:

- Major contribution to strength in woven fabrics is alignment of yarns in warp and weft direction. Chemical treatment results in partial unwinding of yarns and results in a less compact arrangement.
- The reduction in strength of NaOH-treated natural fabrics can also be attributed to the reduction of hemicellulose rendering the cellulose chains unconnected and hence unable to carry any load. Cellulose is insoluble in strong alkaline solution while hemicellulose is soluble and can be extracted with weak aqueous alkaline solution.⁴¹

For the FR-treated flax fabric, it can be observed that the presence of FR reduced the tensile strength in the weft direction for

the untreated flax fabric. For the chemically treated and FR-treated flax fabric, there are cases of increase (N) and decrease (S), but the results are not statistically significant. Yang *et al.* reported a decrease in tensile strength of cotton fabric both in the warp and the weft direction after treatment with MDFA (*N*-methylol dimethylphosphonopropionamide) flame retardant. The author explained that fabric treated with MDFA required phosphoric acid as catalyst and when the fabric were dried at high temperature (>165 °C) for 3 min this resulted in damage to the fabric.

Environmental Conditioning

Tensile Strength after Aging for Two Weeks at Different Temperatures. Figure 8 represents the tensile strength of flax fabric before and after aging at different temperatures and at constant relative humidity for two weeks. The tensile strength of flax fabric in the warp and the weft direction decreased as the aging temperature was increased. For flax fabric tested in the weft direction [Figure 8(a)], the tensile strength decreased by 10.5%, 24.1%, and 9.2%, for U, S, and N-S after aging at 90 °C and 50% RH. However, there was a slight increase of 10.5% in tensile strength of NaOH-treated flax fabric. It has been reported that NaOH reacts with fiber -OH groups according to the following reaction⁴²:

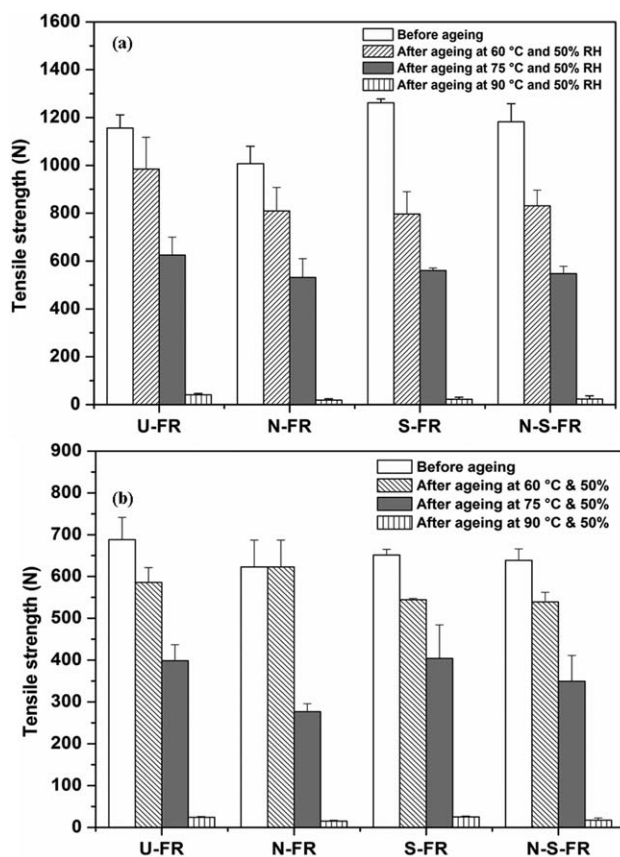


Figure 9. Tensile strength of the untreated and treated fabric with FR after aging at different temperatures (a) weft and (b) warp direction.

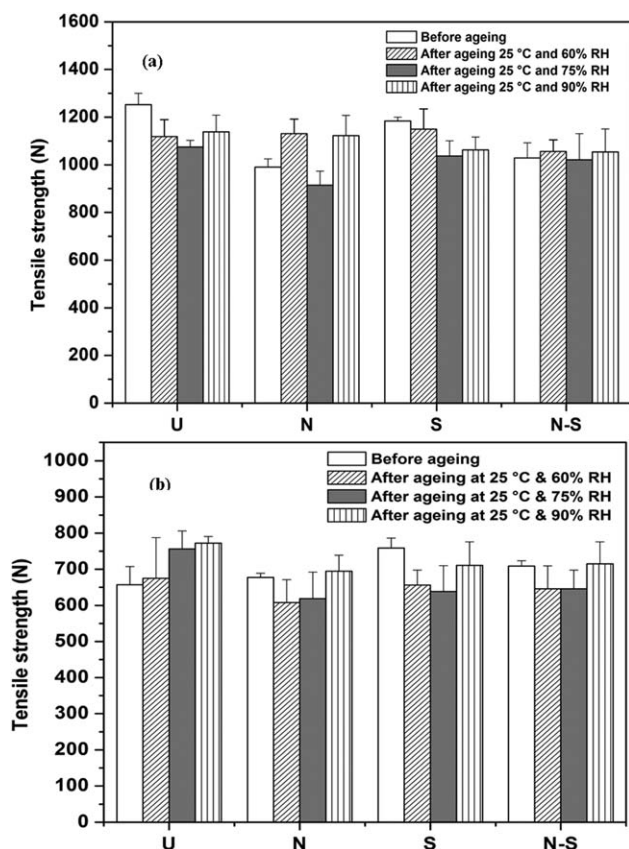


Figure 10. Tensile strength of the treated and untreated fabric after aging at different humidity levels (a) weft and (b) warp direction.

The increase in tensile strength may be due to the reduced number of fiber —OH groups available at the fabric surface for hydrogen bonding with water molecules. NaOH did not prevent water absorption but compared to the other treatment it gave better results for flax fabric in the weft direction. Tensile strength in the warp direction [Figure 8(b)], decreased by 8.0%, 13.3%, 29.3%, and 21.5% for U, N, S, N-S, respectively, for fabric aged at 90 °C and 50% RH.

Figure 9 shows the tensile strength of FR-treated flax fabric conditioned at different temperatures and constant relative humidity for two weeks. The decrease in strength was most prominent for samples aged at 90 °C and 50% RH, where the tensile strength was observed to decrease by more than 90% in both the weft and the warp directions. Despite the treatment of the fabric with NaOH and silane coupling agents, addition of FR showed a negative impact on the tensile strength when the fabric was exposed at elevated temperatures. For flax fabric tested in the weft direction [Figure 9(a)], the tensile strength decreased by 96.4%, 98.2%, 98.3%, and 98.1% for U-FR, N-FR, S-FR, and N-S-FR, respectively, after aging at 90 °C and 25% RH. The tensile strength for flax fabric tested in the warp direction [Figure 9(b)] decreased by 96.5%, 97.6%, 96.2%, and 97.3% for U-FR, N-FR, S-FR, and N-S-FR, respectively, after aging at 90 °C and 50% RH.

Studies on the strength degradation of wood after FR treatment have been reported,^{43,44} but reports on the tensile strength of

FR-treated natural fibers are scarce. In this case, when DAP is exposed to high temperatures and humidity it dissociates to form phosphoric acid and ammonia; the acid formed results in degradation of the flax fabric leading to deterioration in mechanical properties. Deng *et al.* studied the water solubility of AP and AP coated with polysiloxane (Si-AP) in distilled water at 70 °C and 25 °C.⁴⁵ They reported that all the AP particles dissolved in hot water, indicating that AP could easily be attacked by moisture or water, especially at high temperatures. The study did not focus on strength degradation but provide proof that phosphorus-based flame retardants tend to hydrolyze when exposed to high temperatures which can then facilitate fiber damage.

Tensile Strength after Aging for Two Weeks at Different Humidity Levels. Figure 10 shows the tensile strength of flax fabric after aging at different humidity conditions and constant temperature (25 °C) for two weeks. It was observed that the tensile strength decreased by 9.1% and 10.3% for untreated (U) and silane (S) treated, flax fabric, respectively, at 90.0% RH and 25 °C [Figure 10(a)]. An increase of 13.3% and 2.2% was observed for sample N and N-S. For flax fabric tested in the warp direction [Figure 10(b)], the tensile strength decreased by 6.3% for silane treated fabric, respectively. An increase of strength by 17.5%, 2.6%, and 0.8% was observed for sample U, N, N-S, respectively. Increasing humidity levels did not have a

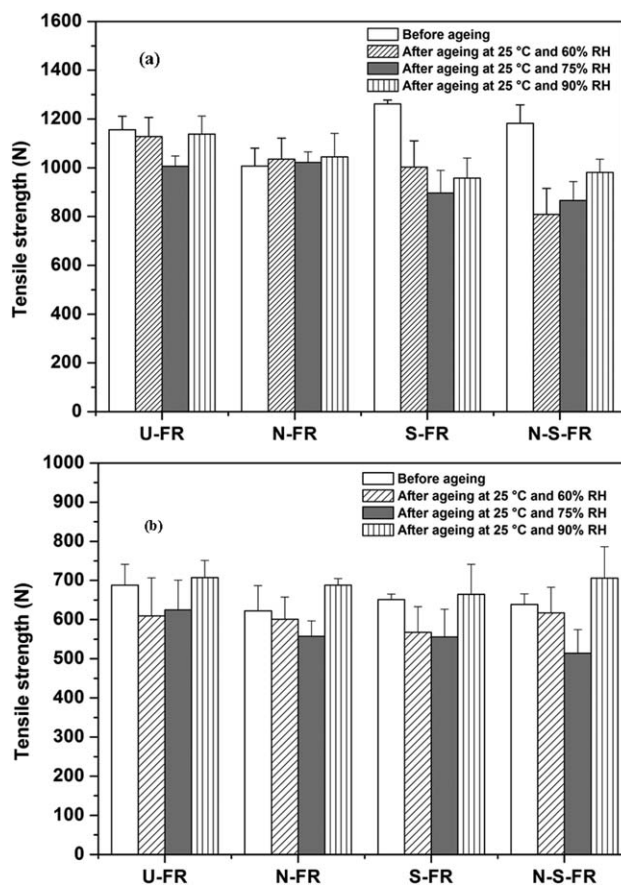


Figure 11. Tensile strength of the treated and untreated fabric with FR after aging at different humidity levels (a) weft and (b) warp direction.

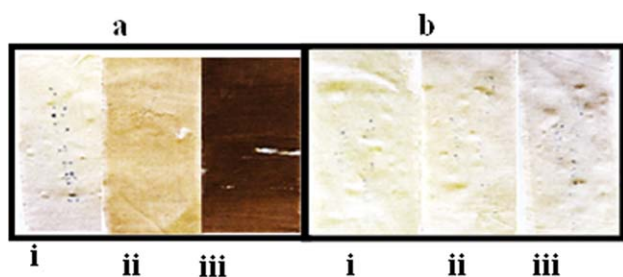


Figure 12. Images of the fabric after aging at [a](i) 60 °C (ii) 75 °C, and (iii) 90 °C at a constant humidity of 50%, [b] (i) 60% RH (ii) 75% RH, and (iii) 90% RH at a constant temperature of 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant effect on the tensile strength of flax fabric. There are reports in literature where moisture absorption has resulted in an increase of strength for natural fibers. Chen *et al.* reported that moisture absorption was found to cause a small increase in the tensile strength of bamboo fiber at high relative humidity conditions.⁴⁶ In another study by Stamboulis *et al.*, green flax fibers exhibited increased tensile strength by 20% after being humidified at 90%.⁴⁶ They suggested that the availability of free water molecules had a plasticizing effect which was advantageous to increasing the strength of cellulose fibers.

Water is able to penetrate into cellulose network of the fiber. It makes its way into capillaries and spaces between the fibrils and into less tightly bound areas of the fibrils themselves and attaches itself by chemical link to groups in the cellulose molecules.⁴⁷ In this way, water molecules tend to force the molecules of cellulose apart, lessening the forces that hold the cellulose molecules together and destroying some of the rigidity of the entire cellulose structure. Water acts, in this way as a plasticizer for the fiber. The penetration of water into the mass of tightly bound cellulose molecules permits the molecules to move freely relative to one another. The cellulose molecules in wet fiber are so well lubricated by the water molecules that the fibres become quite plastic and deformed.

Figure 11 shows the tensile strength of flame retardant treated flax fabric after aging at different humidity conditions and constant temperature (25 °C) for two weeks. FR treatment of the flax fabric did not show great decrease in strength at 90% RH and 25 °C. For fabric tested in the weft direction, a decrease of 1.6%, 24.1%, 17.0% was observed for U-FR, S-FR, N-S-FR, respectively, [Figure 11(a)]. A slight increase in tensile strength of 3.8% was observed for N-FR. For flax fabric tested in the warp direction [Figure 11(b)], an increase in strength of 2.8%, 10.5%, 2.1%, and 10.6% was observed for U-FR, N-FR, S-FR, and N-S-FR, respectively. FR treatment does not cause excessive strength degradation at high humidity levels, but the fabric did absorb moisture because fabrics were found to be wet. DAP is a hygroscopic material and as such water absorption was increased.

Flame retardant treated fabric after aging at 90 °C and 50% RH were also found to be brittle and darker in visual appearance [Figure 12(a)]. The brittleness and darkening of the fabric

indicates fiber degradation and the onset of charring as a result of the breakdown of the FR into phosphoric acid and subsequent acid dehydration of fiber cellulose. Under these extreme aging conditions the FR starts to react much as it would do when exposed to heat in a fire. When samples are aged at different humidity conditions there is no change in color but the fabric was found to be moist at 90% RH and 25 °C [Figure 12(b)]. Similar studies on the changes in visual appearance of FR-treated natural fibers have not been found in literature so far.

CONCLUSIONS

The purpose of this study was to investigate the effects of chemical treatments and flame retardant treatments on (i) tensile properties of flax fabric, (ii) thermal and flammability properties of flax fabric, and (iii) mechanical properties after environmental aging of flax fabric. Vertical flame test results showed that the application of a FR improves the flammability properties of the fabric. Compared to the untreated fabric, FR-treated fabric exhibited no after-flame and after-glow time due to the charring of the fabric after removal of the flame source. TGA showed that chemical treatment resulted in a decrease in thermal stability which is in contrast to some reports in literature on the improvement in thermal stability after silane and NaOH modification. The decomposition temperature of the fabric shifted to lower temperatures with the application of a FR and the char residue was increased. The applied FR decomposes at lower temperature forming phosphoric acid. The acid influences the decomposition of the fabric by hindering the formation of flammable gases and promoting the formation of char. Treatments of the fabric with NaOH and silane coupling agents did not provide significant improvements in tensile strength after environmental aging. Tensile strength decreased with an increase in aging temperature. The chemical treatments did not protect the fabric against moisture. The application of the FR showed further negative effects on tensile strength after exposure to elevated temperatures. At 90 °C and 50% RH, the tensile strength decreased by more than 90% and the flax fabric changed in color and became brittle. This was attributed to the dissociation of DAP to form phosphoric acid and ammonia when exposed to high temperatures and humidity. The acid formed results in degradation of the flax fabric leading to deterioration in mechanical properties. At high humidity conditions, flax fabric was found to be moist but a high decline in tensile strength was not noticed.

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