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Influence of sodium hydroxide, silane, and siloxane treatments on the moisture sensitivity and mechanical properties of flax fiber composites

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Abstract

Natural fibers are a sustainable alternative to synthetic fibers due to their high weight-specific Young's moduli and strengths. However, the mechanical properties of natural fibers are very sensitive to their moisture content. Therefore, chemical treatments are often applied to natural fibers to lower their water absorption and enhance fiber-matrix interaction. The aim is to study the effects of fiber modifications with sodium hydroxide, silane, and siloxane on the water uptake and tensile properties of flax fiber composites produced via prepreg technology. In addition, the effect of moisture on the composites' tensile properties was investigated by conditioning one part of the tensile specimens according to DIN EN 2823 (at 70°C and 85% relative humidity). The NaOH treatment was the only modification that had positive effects on the Young's modulus and tensile strength in the unconditioned and conditioned state. The increase of the tensile modulus and strength are most likely due to changes in flax fiber composition, crystallinity of the cellulose and the rougher fiber surface of NaOH modified fibers. This shows that chemical treatment of natural fibers may improve the performance level of natural fiber composites and prevent a loss in their mechanical properties in humid environments.

Highlights

- Flax fiber modifications with sodium hydroxide, silane, and siloxane.
- Flax fiber composite production via prepreg technology.
- Water uptake after conditioning at 70°C and 85% relative humidity.
- Tensile tests before and after conditioning.
- SEM images of modified flax fibers.

KEYWORDS

fiber modifications, flax fibers, mechanical properties, natural fiber composites, prepreps

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1 | INTRODUCTION

In recent years, the utilization of fiber reinforced polymer composites has gained increasing significance in various industries, including sports, automotive, wind energy, and aerospace, owing to their remarkable weight-specific modulus and strength.^{1,2} The application of prepregged fiber products, commonly referred to as prepregs, enables precise control over the fiber volume content within the composite, while simultaneously reducing the processing time.³ However, the production of synthetic fibers, such as glass and carbon necessitates substantial energy consumption, resulting in significant CO₂ emissions.⁴ In contrast, plant-based fibers like flax or hemp require comparatively less energy during their production and processing stages.⁵ Moreover, natural fibers are biodegradable, offering an environmentally friendly alternative to synthetic fibers. Consequently, the utilization of natural fibers leads to reduced CO₂ emissions and a lesser environmental impact.

Natural fibers exhibit lower density and cost compared with glass or carbon fibers.⁶ However, in terms of mechanical properties, plant fibers demonstrate inferior strength and modulus when compared with their synthetic counterparts.⁷ Consequently, they can serve as a sustainable alternative to glass and carbon fibers in applications where the highest strength and modulus are not required. Nevertheless, the hydrophilic nature of natural fibers presents a challenge,⁸ as it leads to variations in thermo-mechanical properties due to water absorption.^{9,10} To address this, fiber modifications are employed to minimize water uptake, mitigate the sensitivity of natural fibers to moisture, and enhance the adhesion between fiber and matrix.¹¹ Various approaches are utilized to achieve this, including alterations to the fiber structure, chemical composition, functional groups on the fiber surface, as well as adjustments to the degree of polymerization and crystallinity of cellulose.^{12,13}

The most widely employed methods for modifying natural fibers encompass chemical treatments utilizing alkali solutions, silanes, and siloxanes.^{14,15} These treatment agents interact with the hydroxyl groups present on the surface of the fibers or modify the fiber composition itself. Through the reduction of available hydroxyl groups, the hydrophilic nature of the fibers is diminished, leading to enhanced compatibility with hydrophobic matrices.¹⁶ Furthermore, the reaction between the treatment agent and the hydroxyl groups can result in the formation of novel functional groups. Subsequently, these newly introduced functional groups can engage in reactions with the functional groups present in thermosetting matrices, thereby significantly improving the adhesion between the fibers and the matrix.¹⁷

Chemical treatment with alkali solutions serves the dual purpose of removing impurities from the surface of natural fibers and inducing surface roughness, thereby enhancing fiber-matrix adhesion.¹⁸ The efficacy of alkali treatment is influenced by factors, such as the concentration of the alkali solution, treatment duration, and temperature conditions.¹⁹ Furthermore, alkali treatments lead to alterations in the chemical composition of natural fibers by partially removing hemicellulose, lignin, and waxes.^{12,13}

Gassan et al.¹⁹ conducted a study in which flax fibers were treated with a 20% NaOH solution for 20 min at room temperature. Composites were subsequently prepared using an epoxy matrix. The chemical treatment induced reorientation of cellulose fibrils in the fiber direction, resulting in improved tensile and flexural properties of the flax fiber composites compared with untreated fibers. Yan et al.²⁰ demonstrated that treatment with NaOH (5%) led to a 13.3% increase in tensile modulus and a 21.9% increase in tensile strength of flax fiber composites. Van de Weyenberg et al.²¹ prepared unidirectional flax fiber composites with an epoxy matrix using untreated flax fibers as well as flax fibers treated with 1–3% NaOH solutions for 20 min. The alkalization treatment resulted in increased longitudinal and transverse flexural modulus and strength, attributable to improved fiber-matrix adhesion. Specifically, the longitudinal flexural modulus increased from 18 to 22 GPa, and the longitudinal flexural strength increased from 218 to 283 MPa after treatment. Huner²² conducted experiments involving the treatment of flax fibers with sodium hydroxide, acetic anhydride, and silane. The treatments significantly enhanced the tensile and flexural properties of flax fiber composites, with the NaOH treatment of flax yarns resulting in the greatest improvement in modulus and strength compared to composites made from untreated fibers.

In contrast to alkali treatments, silane modifications introduce silanol groups as functional groups onto the surface of the fibers.²³ These silanol groups can undergo reactions with epoxy groups, leading to improved fiber-matrix adhesion.²² Furthermore, treatment with silane coupling agents causes a decrease in the hydrophilicity of cellulosic fibers.²⁴ Alix et al.¹⁷ conducted a study where flax fibers were treated with four different chemicals, and the tensile properties of both treated and untreated individual flax fibers were compared. The results revealed that silane treatment enhanced the tensile strength, while modifications using anhydrides or styrene had adverse effects on the tensile properties. Le Moigne et al.²⁵ performed silane treatment on flax fibers and observed a 25% increase in tensile strength for flax fiber composites with a PLA matrix.

In this study, modern semi-finished reinforcements from flax fibers were subjected to various treatments

including sodium hydroxide, silane, and siloxane. These treated fibers, as well as untreated fibers, were then impregnated with a bisphenol A based epoxy resin system (DGEBA/dicyandiamide) using a prepreg production line. The main objective of the research was to investigate the influence of fiber modification and moisture on the tensile properties of unidirectional flax fiber composites. To achieve this, flax fiber laminates were manufactured from the prepregs and subsequently subjected to tensile testing under different conditions. Specifically, the tests were performed on both unconditioned samples and samples conditioned at 70°C and 85% humidity for a duration of 240 h, following the guidelines outlined in DIN EN 2823.²⁶ The aim of this work is to contribute to the development of more sustainable materials suitable for applications where limitations in material behavior due to hygro-thermal exposure are critical.

2 | EXPERIMENTAL

2.1 | Materials

The epoxy resin used in this study was D.E.R. 331, sourced from Blue Cube Assets GmbH & Co., KG, Olin Epoxy (Stade, Germany), with an epoxy equivalent weight of 187 g/mol. The resin was cured using dicyandiamide, specifically DYHARD[®]100S from Alzchem Group AG (Trostberg, Germany). The active hydrogen equivalent weight (AHEW) of DYHARD[®]100S was assumed to be 12.05 g/mol. As an accelerator, DYHARD[®]UR500 from Alzchem Group AG (Trostberg, Germany) was employed.

The natural reinforcement utilized in this study was the non-crimp flax fabric FUSE 200 FLX obtained from SachsenLeinen GmbH (Markkleeberg, Germany). FUSE 200 FLX consists of unidirectional, nontwisted yarns that are held together by a thermoplastic fiber binder, which accounts for approximately 5% of the total fabric weight. Supplied in roll form as a semi-finished product, FUSE 200 FLX has a surface weight of approximately 200 g/m² and a fabric width of 20 cm.

2.2 | Fiber modification treatments

In order to influence fiber-matrix interaction at the fiber surface, three fiber treatments, that is sodium hydroxide, silane, and siloxane, have been investigated in this work.

2.2.1 | Sodium hydroxide

The initial fiber treatment involves immersing the non-crimp flax fabrics in a NaOH solution to enhance, clean,

and homogenize the fiber surface, thereby promoting increased interaction with the epoxy resin. The chosen treatment parameters include a NaOH concentration of 5% in a water-based solution for a duration of 5 h at room temperature. To facilitate the NaOH treatment of an entire roll of flax non-crimp fabrics, the Cotex installation from Andreas Junghans GmbH & Co., KG (Frankenberg, Germany) is employed. This system enables active and uniform pretreatment. It utilizes two orifices located at the base of the reactor, one at the center and the other near the reactor wall, through which the NaOH solution can be introduced and circulated back and forth. By winding the flax fabric onto a perforated metal tube, both the internal and external layers of the roll can be effectively impregnated with the NaOH solution. Subsequently, the pH value of the treated fabrics reaches approximately 13 and must be neutralized through repeated washing with deionized water.

2.2.2 | Silane

The second fiber treatment method involves the use of an epoxy-silane binder to enhance the adhesion between the fiber and the matrix. Specifically, 3-glycidoxypropyltrimethoxysilane (GPTMS, depicted in Figure 1) is employed for its ability to form chemical linkages. One part of the GPTMS molecule, the GPTMS-epoxide group, links with the epoxy resin via the curing agent, while the other part, the GPTMS-silane group, forms oxygen bridges with the hydroxyl groups of the flax cellulose.²⁷ However, the formation of the oxygen bridge requires two steps: hydrolysis of GPTMS and subsequent

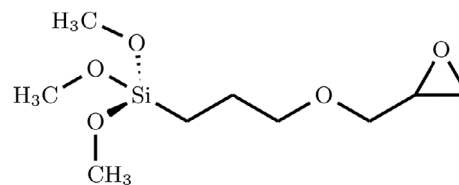


FIGURE 1 Chemical structure of 3-glycidoxypropyltrimethoxysilane (GPTMS).

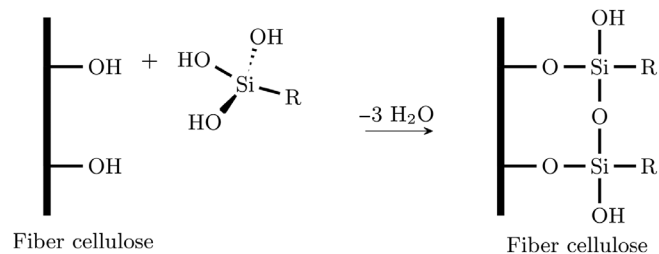


FIGURE 2 Chemical grafting and formation oxygen bridge between trimethoxysilane compound and flax cellulose.

condensation. During hydrolysis (as shown in Figure 2), the CH_3O group of GPTMS is replaced by a hydroxyl group. This step occurs in a solution composed of 80% ethanol and 20% water, with an acidic environment (pH around 4) maintained by the addition of acetic acid. The hydrolysis process takes place for 30 min. Following hydrolysis, the solution contains H^+ ions necessary for the subsequent condensation step.²⁸ To apply the treatment, the roll of non-crimp flax fabric is immersed in the GPTMS solution for 15 min, allowing for the adsorption and chemical grafting processes to occur, resulting in the formation of the oxygen bridge. The appropriate quantity of GPTMS should be approximately 2% of the total weight of the flax fibers.

2.2.3 | Siloxane

The third fiber treatment method involves the use of a water-based siloxane emulsion called Tegopren 6879-50, which is a bi-functional siloxane manufactured by Evonik. The purpose of this treatment is to impart hydrophobic properties to the fiber surface and minimize the formation of voids resulting from moisture absorption at the fiber-matrix interface.²⁹ To apply the treatment, the roll of flax fabric is immersed in a solution containing a concentrated 2.5% Tegopren emulsion for a duration of 15 min. This allows for the interaction between the siloxane molecules and the fiber surface.

2.2.4 | Drying process

Following the chemical treatment stage, the fibers undergo a drying process using an infrared drying machine with a process way measuring 6 m in length. This machine employs an infrared field arrangement on both sides of the wet treated fiber fabrics. The dried fibers are then wound onto a paper tube to create a dried semi-finished product. To ensure efficient drying without causing thermal degradation, the infrared fields are set to operate at approximately 40%–50% of their maximum capacity. This allows for effective removal of moisture from the wet fibers. The winding speed used during this process is approximately 1.2 m/min, resulting in a residence time of approximately 5 min for drying.

2.3 | Resin formulation, prepreg production, and laminate curing

A mixture comprising D.E.R. 331, DYHARD[®]100S (with a stoichiometric ratio $R = 1$), and DYHARD[®]UR500

(1 wt%) was prepared using a dual asymmetric centrifuge speed mixer manufactured by Hauschild Engineering (Hamm, Germany). The mixing process was conducted at a rotational speed of 3000 1/min for a duration of 120 s. Subsequently, the formulated mixture was placed in a vacuum oven at 45°C and 10 mbar for 1 h to ensure the removal of trapped air.

Flax fiber prepregs were produced using a hot-melt procedure on a small-scale prepreg impregnation line provided by Roth Composites Machinery GmbH (Steffenberg, Germany).^{30,31} The resin was heated to 40°C to enhance its flow and facilitate the impregnation of fibers. A slot with a height of 130 μm was used to coat the resin onto a carrier paper. Prior to prepreg production, the flax fibers were thoroughly dried at 110°C for 15 min to promote effective interaction and wetting between the fibers and the resin. Consequently, the resulting prepreg exhibited a fiber volume content of approximately 50%, with a ply thickness of around 0.3 mm.

Following impregnation, the prepreg was cut into sheets measuring 300 mm by 250 mm. For tensile testing, unidirectional laminates were prepared by stacking four layers on a steel plate. The prepreg layers were covered with a bleeder cloth to enhance surface quality. Subsequently, the stack was enclosed in a PET bag and subjected to vacuum packing at 1 mbar. Curing was carried out using a Langzauner heating press from Langzauner GmbH (Lambrechten, Austria) within a pressurized steel mold at an air pressure of 4 bar. The curing cycle involved an initial step at 100°C for 1 h, followed by a second step at 120°C for 2 h. The heating rate between the individual curing steps was 5°C/min.

2.4 | Specimens preparation and conditioning of specimens

Tensile specimens, adhering to the dimensions specified by the EN ISO 527-5 standard, with measurements of 250 \times 10 \times 1 mm, were obtained by cutting laminates using the M-1600 CO₂ laser system from eurolaser GmbH (Lüneburg, Germany). The manufactured composite specimens were divided into two groups for conditioning. One group underwent conditioning under standard air conditions at 23°C and 45% relative humidity, while the other group was stored in a Vötsch VCS₃ 7060-5 climate chamber from Weiss Technik GmbH (Balingen-Frommern, Germany) at 70°C and 85% relative humidity for a duration of 10 days, following the guidelines provided by DIN EN 2823.²⁶ The conditioning period mentioned corresponds to the required time for the specimens to attain a steady-state weight, considering moisture absorption and temperature effects. The change in weight due to moisture absorption was

determined by measuring the weight of the specimens before and after the conditioning process.

2.5 | Tensile tests

In accordance to DIN EN ISO 527-5, tensile tests are performed with a Zwick/Roell testing machine Z010 from ZwickRoell GmbH & Co., KG (Ulm, Germany), equipped with the extensometer MacroXtens. In all tests, a gage length of 50 mm was employed, and a cross-head speed of 2 mm/min was applied during the testing procedure.

2.6 | Scanning electron microscopy

The Zeiss Gemini 1530 scanning electron microscope, manufactured by Carl Zeiss AG (Oberkochen, Germany), was employed to examine the tensile specimens. A 5 kV acceleration voltage was applied, and the surfaces were coated with a platinum layer of approximately 5 nm in thickness.

3 | RESULTS AND DISCUSSION

3.1 | Water absorption

Figure 3 illustrates the water absorption behavior of tensile specimens fabricated from flax fiber laminates following conditioning at 70°C and 85% relative humidity for a duration of 240 h. Among the tested specimens, those incorporating untreated flax fibers exhibit the lowest water uptake, measuring approximately 3.02%. This aligns with the findings of Berges et al.,³² who observed a water uptake of approximately 3.3% for unidirectional flax fiber composites under the same conditions after 6 days. Subsequently,

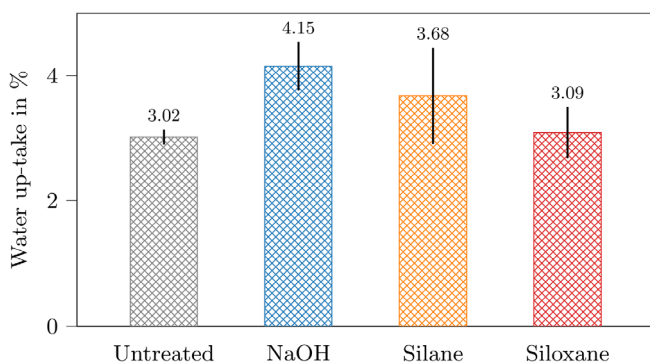


FIGURE 3 Water uptake of tensile specimens made from flax fiber laminates conditioned at 70°C and 85% relative humidity for 240 h.

specimens fabricated from flax fibers treated with siloxanes demonstrate a water uptake of approximately 3.09%. In contrast, the silane treatment leads to a higher water absorption level, measuring approximately 3.68%. Remarkably, the tensile specimens made from flax fibers treated with sodium hydroxide exhibit the highest water uptake, measuring approximately 4.15%. This finding is consistent with the research conducted by Murayama et al.,³³ where composites were prepared using bamboo fibers with various fiber modifications and PLA matrix. The water uptake of these composites was measured during immersion in water for 250 h. In accordance with our results, the alkali-treated bamboo fiber composites demonstrated the highest water uptake, reaching 23%. On the other hand, the water uptake of the silane-treated bamboo fibers was nearly identical to that of the untreated bamboo fibers, measuring 17.6%. The water absorption during conditioning is influenced by factors, such as the volume and structure of the pores within the fiber wall, as noted by Moudood et al.³⁴ The overall water uptake includes both capillary flow and water penetration into the fibers. It is likely that the treatment with sodium hydroxide resulted in surface roughening and increased pore volume, thereby contributing to the higher water uptake observed. These findings deviate from previous investigations on the water absorption behavior of modified flax fibers.³⁵ A potential explanation for these observed effects is discussed in Section 3.3.

3.2 | Tensile tests

3.2.1 | Stress–strain behavior of flax fiber composites

Figure 4 illustrates representative stress–strain curves obtained from tensile tests performed on flax fiber composites with different fiber modifications, both in the unconditioned and conditioned states. All flax fiber composites show a linear elastic behavior for small tensile strains. However, at around 0.2% tensile strain, all composites exhibit a “knee-point” in their stress–strain curves, that is showing continuously digressive stress–strain behavior, and thereby deviating from the initial linear elastic behavior. At tensile strains larger than 0.3%, the stress–strain curves continue linearly. Consequently, the Young’s moduli obtained at higher tensile strains are significantly lower than the Young’s moduli determined between 0.05% and 0.25% tensile strain. The final failure of the specimens is preceded by sudden drops in stress. For better clarity, the stress–strain curves are only displayed until the ultimate tensile strength since the data following the ultimate tensile strength mainly shows stepwise drops in tensile stress during failure.

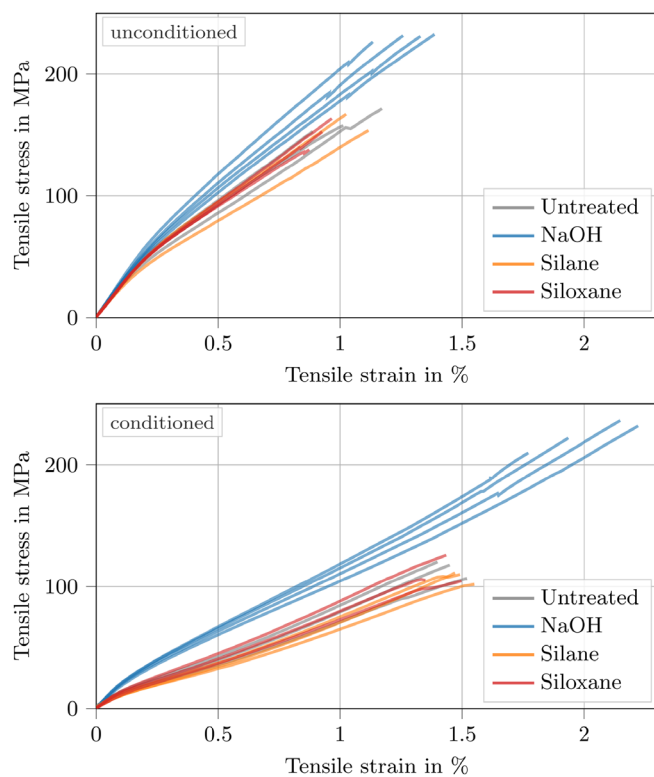


FIGURE 4 Stress–strain curves derived from tensile tests of flax fiber laminates with different fiber modification treatments in the unconditioned (top) and conditioned (bottom) state.

Explaining the stress–strain behavior of natural fiber composites includes two main aspects: (I) changes in the internal structure by reorientation of cellulose microfibrils of natural fibers as a result of the applied stress, and (II) changes in composite morphology resulting from crack initiation and crack growth in the matrix, matrix–fiber interface and fiber. While the first aspect is often regarded as a visco-plastic effect, the later one is, for regular matrices, irreversible and critical to the composite's structural integrity.³⁶ Considering only the aspect of internal changes in the flax fibers as a response to the applied stress, it was argued several times in literature that the nonlinear behavior results from the nonlinear behavior of the natural fiber itself. The stress–strain curves of flax fibers may be divided into three regimes: a linear one until 0.3%, a digressive part between 0.3% and 1.5%, followed by a progressive stress–strain behavior from 1.5% until fiber rupture.³⁷ However, other studies found three distinctly different stress–strain curves of flax fibers, of which two show the digressive regime described by Charlet et al.³⁸ Usually, all types may be found in one harvest and the proportion of types varies with the type of flax fiber used. The hypothesis that the nonlinearity of flax fiber composites results from the nonlinear behavior of flax fibers is supported by several studies.^{36,39,40} However, these studies did not contemplate the damage

evolution in the matrix itself which contradicts basic composite mechanics.⁴¹

On the other hand, considering crack initiation and crack growth in the composite, it becomes clear that the progressive damage evolution in the matrix and the matrix–fiber interface is at least in parts responsible for the nonlinear behavior of natural fiber composites. Similar deviations from linear elastic behavior were already observed in sheet molding compound, which, like the flax fiber composite, is also a long fiber reinforced polymer.^{42–44} The stress–strain curves can be divided into three regimes: in the first regime, the material behaves linearly elastic.^{45,46} At a certain stress level, the “knee-point” indicates the damage initiation and beginning of crack formation in the matrix and fiber–matrix interphase.⁴⁷ Afterwards, the stress–strain curves continue in a linear elastic fashion.

In long fiber reinforced polymers, heterogeneous stress distributions arise by nonuniform fiber orientation and heterogeneous fiber volume distributions.⁴⁸ Crack initiation occurs in regions with a higher concentration of matrix material perpendicular to the direction of tensile loading.

The surrounding fibers impede crack propagation by acting as barriers.⁴⁹ Consequently, localized damage in the matrix increases the load on the fibers, resulting in elevated shear stresses at the fiber–matrix interface. When individual fibers deviate from the loading direction, micro-cracks develop at the fiber–matrix interface, leading to eventual debonding of the fiber. Crack initiation in natural fiber composites at lower stress levels has already been documented via synchrotron x-ray tomographic microscopy and acoustic emission detection.^{50,51} In conclusion, both aspects may contribute to the overall nonlinear behavior at small tensile strains.

The stress–strain curves of all fiber modifications display kinks at stress levels proximate to the ultimate tensile strength of the respective specimens. The sudden drops in tensile stress before the failure of the specimens may be accredited to matrix crack growth, fiber–matrix debonding and individual fiber breakage, resulting in an instantaneous reduction of the load-carrying cross-section.⁵² The failure of individual fibers precedes the overall failure of the specimens, as fibers, especially natural fibers, exhibit variations in their moduli and strengths.^{53,54} Consequently, fibers with larger defects fail first, followed by fibers with smaller defects.⁵⁵

3.2.2 | Tensile properties of flax fiber composites

In the unconditioned state, the Young's moduli of the composites exhibit comparable values, ranging from

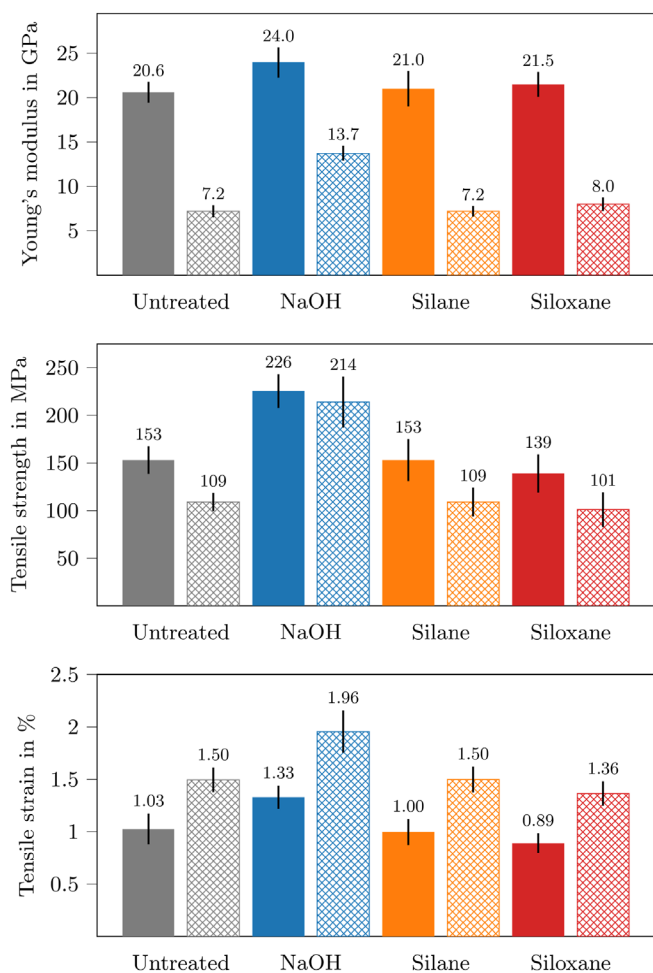


FIGURE 5 Young's modulus, tensile strength, and tensile strain of flax fiber laminates with different fiber modification treatments in the unconditioned (full bars) and conditioned (crosshatch bars) state.

approximately 20.6 GPa for untreated fibers to 24 GPa for fibers modified with NaOH, as depicted in Figure 5. The influence of silane and siloxane treatments on the tensile moduli of flax fiber composites in the unconditioned state is minimal, considering the standard deviations associated with the Young's moduli. In contrast, the flax fibers that were modified with NaOH showed a slightly higher Young's modulus, most likely resulting from changes in fiber composition as well as changes in cellulose crystallinity.^{12,13} It is important to note that the determination of Young's modulus, according to DIN EN ISO 527-5, occurs within a small strain range of approximately 0.05%–0.25%. However, this range captures only a limited portion of the stress–strain curve.

Since the stress–strain curves deviate from the linear elastic behavior at tensile strains at which the Young's modulus is evaluated, tensile moduli at small strains E_S (evaluated between 0.025% and 0.05% tensile strain) and large strains E_L (evaluated between 0.3% and 0.5% tensile

strain) were calculated (see Table 1). As the moduli at small strains remain unaffected by the deviation from the linear elastic regime, the E_S are about 3 GPa higher than the Young's moduli. According to the linear rule of mixture,⁵⁶ the Young's modulus of a composite reinforced with unidirectional endless fibers (fiber volume content $\varphi_F = 50\%$, fiber modulus $E_F = 66$ GPa,⁵⁷ matrix modulus $E_M = 3$ GPa) should be about 34.5 GPa. It is important to note that the assumptions made in this model, including ideal unidirectional fiber orientation and the presence of infinitely long fibers, are not directly applicable to long fiber reinforced natural fiber composites. Subsequently, the estimated model value (34.5 GPa) differs significantly from the E_S values (24.7–27.1 GPa).

Although the E_S values of all fiber modifications are relatively close, particularly considering their standard deviation, the tensile moduli at large tensile strain E_L of flax fibers treated with sodium hydroxide exhibit a slight increase compared with the other chemical treatments. Specifically, the moduli after the “knee-point” measure at 13.1, 16.4, 13.3, and 13.1 GPa for untreated, NaOH, silane, and siloxane treatments, respectively. This underscores the positive impact of sodium hydroxide treatment on flax fibers.

The strengths of the flax fiber composites, which underwent different modifications, exhibit significant variations. Specifically, the tensile strength of the composites with sodium hydroxide-treated fibers ($\sigma_T = 226$ MPa) is approximately 48% higher than that of the other modifications, including the nonpretreated flax fiber composites (see Figure 5). Interestingly, the tensile strengths of the untreated and silane-treated composites are approximately equal (153 MPa). However, the strength of the flax fibers treated with the siloxane is minimally lower (139 MPa).

The significant enhancement in tensile strength and the slight increase in tensile modulus observed in the NaOH-treated composite can be attributed, in part, to the activation of functional groups present on the surface of flax fibers. This activation promotes the chemical reaction between the epoxy resin and the fibers, facilitating a stronger bond among them. Furthermore, the treatment with sodium hydroxide leads to decomposition of impurities and natural pigments, as well as partial dissolution of lignin and hemicellulose, thereby increasing the cellulose content of the fibers.³⁵ Moreover, NaOH treatments contribute to an increased degree of crystallinity of the cellulose.⁵⁸ The high modulus and strength of natural fibers predominantly stem from the cellulose fibrils present within them. Additionally, the chemical treatment with NaOH induces a roughening of the fiber surface, as evidenced in the observations made in Section 3.3. This rougher surface facilitates improved interaction between the fibers and the matrix, thereby further enhancing the fiber–matrix adhesion.⁵⁹

TABLE 1 Overview of the tensile moduli before the “knee-point” E_S (evaluated between 0.025% and 0.05% tensile strain), the Young's moduli E_T (evaluated between 0.05% and 0.25% tensile strain) and the tensile moduli after the “knee-point” E_L (evaluated between 0.3% and 0.5% tensile strain) of flax fiber composites with different fiber modifications before and after conditioning at 70°C and 85% relative humidity (average \pm one standard deviation).

Unconditioned	E_S [GPa] (0.025% to 0.05%)	E_T [GPa] (0.05% to 0.25%)	E_L [GPa] (0.3% to 0.5%)
Untreated	26.0 \pm 1.6	20.6 \pm 1.2	13.1 \pm 0.9
NaOH	27.1 \pm 2.0	24.0 \pm 1.7	16.4 \pm 1.3
Silane	24.7 \pm 2.0	21.0 \pm 2.0	13.3 \pm 1.2
Siloxane	25.5 \pm 1.5	21.4 \pm 1.4	13.1 \pm 1.4
Conditioned according to DIN EN 2823:2017	E_S [GPa] (0.025% to 0.05%)	E_T [GPa] (0.05% to 0.25%)	E_L [GPa] (0.3% to 0.5%)
Untreated	11.9 \pm 0.9	7.2 \pm 0.7	6.1 \pm 0.5
NaOH	19.8 \pm 1.8	13.7 \pm 0.9	10.0 \pm 0.6
Silane	11.6 \pm 0.8	7.2 \pm 0.6	6.0 \pm 0.5
Siloxane	13.3 \pm 1.8	8.0 \pm 0.8	6.5 \pm 0.7

In contrast to the findings observed in flax fiber composites treated with sodium hydroxide, the chemical modifications using silane and siloxane do not result in any significant improvement or deterioration in the mechanical properties. The adhesion between the epoxy matrix and the modified fibers appears to be comparable to that between the matrix and the nonmodified fibers. Similar results regarding the coupling performance of silane-modified sisal fibers in epoxy matrix composites were reported by Bisanda et al.⁶⁰ In their study, the tensile modulus and tensile strength were unaffected by the surface modification of the fibers.

In line with the observations for Young's modulus and tensile strength, only the treatment involving sodium hydroxide demonstrated a beneficial impact on the tensile strain at failure of the flax fiber composites (see Figure 5). Specifically, the NaOH-treated flax fiber composites exhibited a tensile strain approximately 29%–49% higher compared with the untreated counterparts. This increase in tensile strain is accompanied by heightened tensile strength, consequently resulting in a greater amount of energy stored during deformation.

3.2.3 | Influence of conditioning on the tensile properties

During the conditioning process at a temperature of 70°C and relative humidity of 85%, the Young's moduli and tensile strengths of natural fiber composites exhibit a decrease, while the tensile strains at failure show an increase by approximately +45%–50% (see Figure 4). Specifically, for the untreated flax fiber composites, the Young's modulus decreases from 20.6 to 7.2 GPa (–65%),

and the tensile strength decreases from 153 to 109 MPa (–29%). Similar trends can be observed for the flax fibers treated with silane. Likewise, the Young's modulus and tensile strength of siloxane-modified flax fiber composites decrease to 8.0 GPa (–63%) and 101 MPa (–27%), respectively. In contrast, the treatment with sodium hydroxide limits the loss in tensile modulus and tensile strength. In this case, the Young's modulus decreases to 13.7 GPa (–43%), while the tensile strength of 214 MPa only experiences a minor decrease (–5%).

Similar to the stress–strain curves observed for the unconditioned flax fiber composites, the stress–strain curves of the tensile specimens after conditioning at a temperature of 70°C and a relative humidity of 85% exhibit deviations from the linear elastic regime at small tensile strains. However, in the conditioned state, the “knee-point” occurs at much smaller strains (0.1%) and stresses compared with the unconditioned state. This may be attributed to a reduction in the strength of the matrix. The tensile moduli after the “knee-point” for the untreated, NaOH-treated, silane-treated, and siloxane-treated composites are measured as 6.1, 10.0, 6.0, and 6.5 GPa, respectively. Once again, the composite reinforced with NaOH-treated fibers exhibits a higher modulus compared with the other modifications. However, in the conditioned state, the differences between the moduli of the composites become much more significant. Therefore, the modification of the chemical composition of flax fibers through NaOH treatment effectively prevents the loss in mechanical properties and outweighs the increased water absorption during conditioning. On the other hand, the other investigated fiber pretreatments do not have a significant impact on the mechanical properties compared with the composite reinforced with untreated fibers, even after moisture absorption.

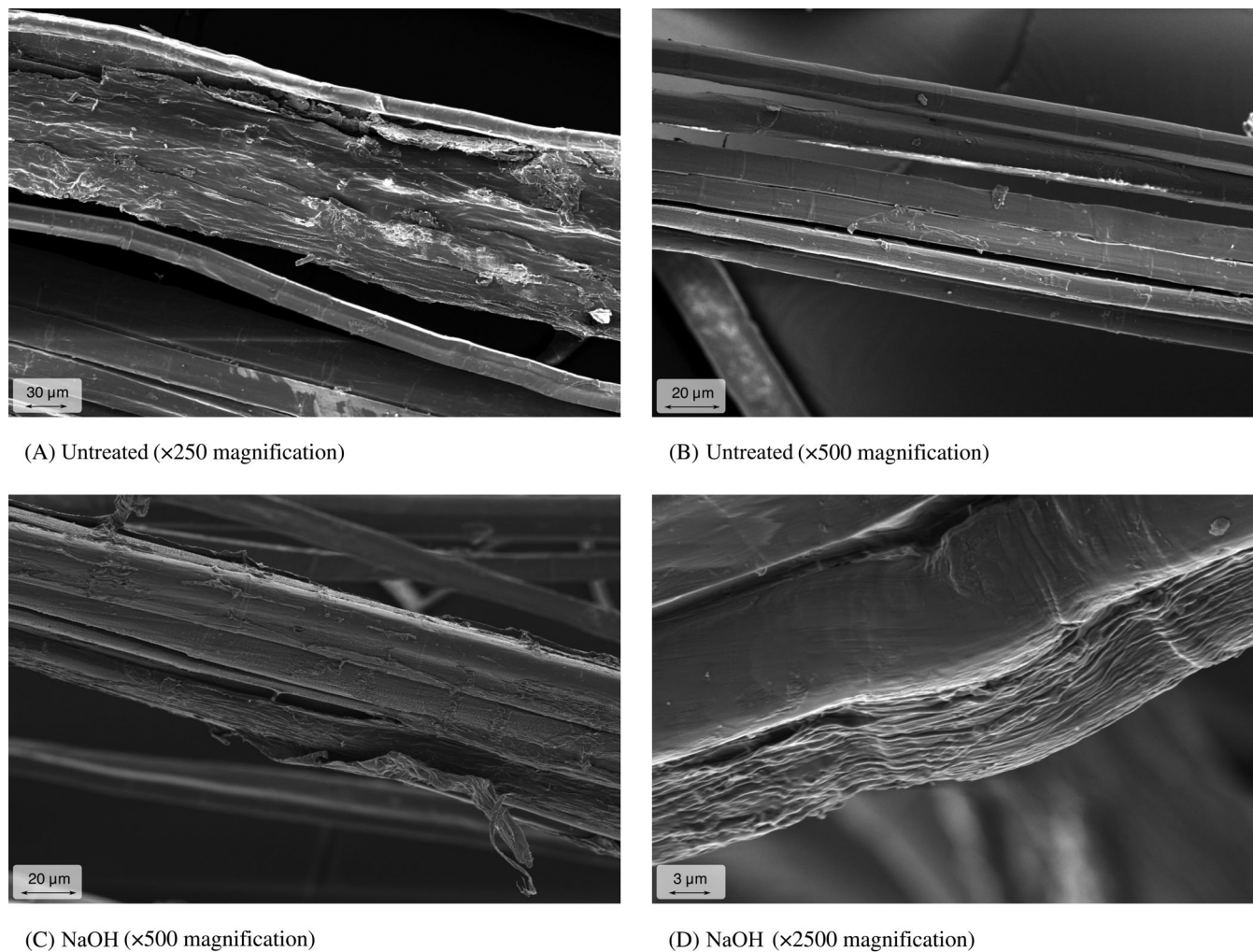


FIGURE 6 Flax fibers before the impregnation with epoxy resin at various magnifications. Some of the untreated flax fibers are completely covered with the thermoplastic binder (A). Untreated fibers that are not covered in the thermoplastic binder show impurities at their surface (B). In contrast, the flax fibers that were treated with the NaOH solution are not covered in thermoplastic binder and show a much rougher surface (C, D).

3.3 | Scanning electron microscopy

Figure 6 displays the untreated flax fibers before impregnation with epoxy resin and after NaOH treatment at various magnifications. As mentioned in the materials section (see Section 2.1), the untreated flax fibers are interconnected by a thermoplastic binder, which aids in the handling of the fabric during processing. In Figure 6A, some untreated flax fibers are fully enveloped by the thermoplastic binder, while others are not covered. While the thermoplastic binder enhances fabric rigidity during textile handling, it hinders the impregnation of flax fibers by the epoxy resin mixture. Consequently, there is no adhesion between the fibers in the encased fiber bundle and the epoxy matrix. Thus, these fiber bundles not only fail to contribute to tensile load-bearing but also act as defects in the composite.

Another contributing factor could be the presence of waxes and impurities on the surface of the flax fibers, as shown in Figure 6B. These substances further reduce the fiber-matrix adhesion, consequently leading to a decline in Young's modulus and tensile strength.

In contrast, the NaOH-treated flax fibers exhibit minimal coverage by the thermoplastic binder, as depicted in Figure 6C. Instead, the outer layer of the individual fibers appears to have undergone partial deterioration due to the strong alkali. This deterioration exposes the fibrous structure of the fibrils within the flax fibers. A closer view of a NaOH-treated flax fiber with its outer layer removed by the chemical treatment is shown in Figure 6D.

These observations provide valuable insights into the results of the water absorption and tensile tests discussed previously. First, the rougher surface of NaOH-treated flax fibers offers a larger surface area for water absorption.

Second, the NaOH treatment partially removes the thermoplastic binder and surface impurities from the fibers. Consequently, it is highly likely that the combined effects of these factors partially contribute to the observed increase in Young's modulus and tensile strength compared with composites fabricated from untreated flax fibers.

4 | CONCLUSION

The present study investigates the effects of chemical treatments on the water absorption and tensile properties of flax fiber composites. None of the chemical treatments impose any limitations on water absorption. In contrast, the rough surface of NaOH-treated flax fibers facilitates increased water uptake. Remarkably, composites fabricated from NaOH-treated flax fibers exhibit the highest tensile modulus and tensile strength among all modifications. The improvement in these mechanical properties can be attributed to a change in fiber composition, an enhanced fiber-matrix adhesion, achieved by the removal of the thermoplastic binder and the introduction of a rougher fiber surface.

Conversely, the silane or siloxane modifications fail to enhance the tensile properties of the composites compared with the untreated counterparts. This outcome remains consistent even after conditioning the composites at 70°C and 85% relative humidity. While conditioning results in a significant decrease in the Young's modulus of the composites fabricated from NaOH-treated flax fibers, it leads to an increase in their elongation before failure. Consequently, the tensile strength of the NaOH-treated fiber composites remains relatively stable.

In conclusion, the NaOH treatment of flax fibers is the preferred method due to its positive effects on the tensile properties of the resulting composites. Future studies should explore the effects of repeated conditioning on the mechanical properties of natural fiber composites and investigate the resulting degradation of the fiber-matrix adhesion.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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