ENHANCEMENT OF TENSILE PROPERTIES OF FLAX-MAT EPOXY COMPOSITES VIA CLICK CHEMISTRY WITH SURFACE FIBRILLATION AND COMPACTION OF THE FIBER PREFORMS.

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ABSTRACT

The mechanical properties of composite materials are strongly related to the fiber-matrix interface properties. This study focuses on the click chemistry modification of short flax fibers using the Cu(I)-catalyzed Huisgen cycloaddition type, to strengthen the fiber-fiber interface for composite applications. The flax fibers are functionalized in three steps: A mechanical fibrillation pre-treatment of the fibers surface, followed by a chemical cleaning treatment to eliminate pectin, lignin, hemicelluloses and waxes, allowing exposure of the hydroxyl groups in flax fibers in view of the final treatment of click chemistry. The chosen strategy allows the adaptation of propargylation and tosylation reactions to flax fibers in aqueous media. FTIR and EDX analysis of fibers treated at intermediate stages confirmed the presence of various surface functions of modified fibers with a very high degree of substitution. The properties obtained are strongly improved for reinforcements containing covalent fiber-fiber contacts. Tensile, tearing and bursting tests performed on dry mat reinforcements showed increases in the tensile index, elongation at break, tensile stiffness, burst and tear indexes of 519%, 355%, 201%, 304%, and 421% respectively. Resin transfer molding (RTM) was used to fabricate epoxy composites made of click chemistry-treated short fiber flax mats at a fiber volume content (V_f) of 40%. Tensile tests results showed the positive effect of the click chemistry treatment, with increases in the tensile modulus, strength and strain at break of 41.5%, 64.3%, and 30.8% respectively. Marked improvements in strength and Young's modulus were obtained for composites made of pre-compacted and cross-linked flax mat preforms.

Keywords

Flax fiber, surface treatment, click chemistry, mechanical properties, epoxy composites.

1. INTRODUCTION

Natural fibers derived from renewable sources such as plants have received significant attention in recent years due to their environmentally friendly characteristics. These fibers, possessing intrinsic biodegradability, have emerged as sustainable alternatives to synthetic counterparts, becoming key players in the field of composite materials. Their low energy consumption during production, combined with a reduced carbon footprint, is part of the global trend favoring sustainable materials [1-3]. However, despite their undeniable merits, natural fibers also exhibit limitations that have restricted their use, particularly in high performance applications [4]. Natural fibers demonstrate lower tensile strength and modulus of elasticity compared to synthetic fibers [5]. Moreover, their hydrophilic nature poses challenges when incorporated into hydrophobic polymer matrices, leading to incompatibility that can result in reduced interfacial adhesion or wetting difficulties during molding, thereby limiting the overall mechanical properties of the composite [6]. Additionally, natural fibers are susceptible to environmental degradation, especially under humid conditions, further complicating their utilization in certain applications [7]. The quest to unlock the full potential of natural fibers has prompted an in-depth exploration of various methodologies encompassing mechanical and chemical treatments. Mechanical treatments aim to enhance the properties of natural fibers by altering their structure. One of the main mechanical treatments is fibrillation, a process that separates individual fibrils from the bulk fibers. Fibrillation increase the overall surface area of fibers, thereby improving their ability to interlock with the matrix in composite materials or other fibers [8-11]. Compaction, another mechanical treatment, involves compressing fiber bundles to increase the fiber-fiber contacts and their interactions, resulting in increased composite mechanical properties [12]. Physical and physico-chemical modifications of cellulosic fibers, such as treatment with electron beams [13] and gamma rays [14] have also been studied. A comprehensive examination of mechanical treatments reveals their role in enhancing the properties of natural fiber composites, but the impact of these treatments may be limited in addressing certain challenges, such as the hydrophilic nature of natural fibers and their susceptibility to environmental degradation [15]. To address these issues, researchers are increasingly turning to chemical treatments [16]. The chemical modification of cellulosic fibers can be achieved through alkaline treatment, silane treatment, permanganate treatment, acetylation, benzoylation treatment, isocyanate treatment and copolymerization grafting, among others [17-24]. Suhas et al. [25] treated flax fibers with potassium permanganate ($KMnO_4$) and stearic acid. For treatment times ranging from 10 to 30 minutes, tensile strength (TS) increased from 65% to 106% and interfacial adhesion strengths (IAS) from 184% to 532% compared to the untreated reinforcement. These tests were conducted on single flax fibers. Atiqah et al. [26] treated sugar palm fibers with alkali (6% mass NaOH), silane (2% mass), and a combination of both to enhance their physical and mechanical properties for use with thermoplastic polyurethane matrices. Silane treatment notably improved the tensile strength by 161% compared to untreated fibers and significantly enhanced the interfacial adhesion strength (IFSS) by 115% [26]. Huo et al. [27] analyze various surface treatments, including acetic anhydride and acrylic acid treatments, to improve the adhesion between hydrophilic flax fibers and hydrophobic structural polymers in composite materials. They found enhanced interfacial bonding and improved mechanical properties, with the acetic anhydride treatment yielding the highest tensile strength [27]. The surface treatments were conducted to clean the surface of the fibers by eliminating non-cellulosic compounds (lignin, hemicellulose and pectin) and introducing chemical functions to alter the surface energy of fibers or facilitate additional reactions, such as the formation of covalent bonds between the fibers themselves. For this, chemical treatment aims to replace polar hydroxyl (OH) groups on the surface of cellulosic substrates with chemical functions capable of strengthening interactions between fibers [28-31]. In addition to chemical treatments on flax fibers, surface modification on other natural substrates such as cellulose nanocrystals (CNCs) have gained significant attention for improving fiber-matrix compatibility. Zhang et al. highlighted the use of surface-initiated atom transfer radical polymerization (SI-ATRP) as an efficient method to functionalize CNCs, enabling precise control over grafting density and chain length, and broadening their application in composite materials [32]. Recently, CNCs have also been explored as stabilizers in Pickering emulsions for the fabrication of antibacterial PLA composites. Zhang et al. demonstrated that anchoring polyethyleneimine (PEI) on CNCs through polydopamine-mediated surface modification significantly enhances both antibacterial properties and mechanical performance of PLA films, further illustrating the versatility of CNCs in polymer composites [33]. The reported research shows that chemical modification brings significant advantages and, therefore, further enhance the need to explore various options.

Thus, the emergence of click chemistry as a tool for modifying natural fibers has also opened new avenues for enhancing the properties of composite materials. Click chemistry is dedicated to creating strong, precise, and controllable covalent bonds, offering the potential to overcome adhesion issues that natural fibers often encounter when used in composite materials [34, 35]. One remarkable feature of click chemistry is its ability to form bonds under mild reaction conditions, minimizing the risk of fiber degradation [36]. But what truly makes click chemistry transformative in the context of natural fibers is its potential to introduce covalent bonds at the fiber-fiber or fiber-matrix interface. Unlike physical interactions, covalent bonds are highly stable and durable, ensuring the long-term mechanical integrity of composites [37]. While click chemistry is widely used in modifying synthetic polymers, its application to natural fibers has been relatively limited [38]. Therefore, there is an evident opportunity to harness the power of click chemistry to unleash the full potential of natural fibers in composite materials [39]. Wang et al. obtained enhanced epoxy-graphene oxide composites by chemically modifying graphene oxide (GO) through thiol-ene click chemistry [40]. They grafted nano-SiO_2 onto GO and incorporated it into an epoxy matrix. This treatment significantly improved the mechanical properties, with a notable increase in the tensile strength and flexural properties compared to untreated GO/epoxy and nano-SiO_2/epoxy composites [40].

In a previous work, the application of click chemistry was used successfully and led to significant improvements in the mechanical strength and tensile stiffness of kraft pulp sheets, thereby demonstrating its significant potential for natural fiber composites [41]. Building on this foundational work, the primary aim of this study is to extend the application of this chemical treatment to short flax fibers, with a specific focus on improving the mechanical performance of flax fiber mat reinforcements and their flax-epoxy composite laminates. The second objective is to integrate click chemistry with mechanical treatments, such as the surface fibrillation of short flax fibers and the pre-compaction of flax mat stacks before molding. This combined approach aims to increase the overall surface area of fibers and the number of fiber-fiber contact points to increase the efficiency of the click-chemistry treatment, thus increasing the tensile properties of the dry fiber preforms and the resulting flax-epoxy composites. This innovative methodology, blending chemical treatment with mechanical treatment techniques, seeks to overcome the traditional limitations associated with natural fiber-reinforced composites.

2. EXPERIMENTAL METHODS:

2.1. Materials

Flax fibers were supplied by Safilin Inc (Szczytno, Poland) in the form of a Tex 5000 ribbon, which was subsequently cut into short fibers of approximately 6 ± 1 mm in length. Propargyl bromide (80% in toluene), p-toluenesulfonyl chloride and sodium azide were purchased from Alfa Aesar (Haverhill, Massachusetts, USA). Sodium hydroxide and copper sulfate ($CuSO4-5H_2O$) were acquired from Acros Organics (Geel, Belgium). Dimethylformamide (DMF), sodium ascorbate and triethylamine were obtained from Sigma-Aldrich (Saint-Louis, Missouri, USA). All chemicals were used as received without further purification. For the composite plates, the resin system used consisted of

SikaBiresin CR72 resin mixed with a SikaBiresin CH72-3 hardener at a ratio of 18 g of hardener per 100 g of resin, both supplied by Sika Advanced Resins (USA).

2.2. Fiber preparation and treatment before fabrication of the flax mat reinforcement.

In this study, a series of mechanical and chemical treatments were undertaken to prepare and modify the short flax fibers. Each treatment was carefully selected for its specific potential to enhance the reinforcing effect of click chemistry on the dry mat reinforcement and ultimately, in the final composite. But to evaluate the direct influence of click chemistry on the properties, each intermediate chemical and mechanical treatments (detailed in what follows) respectively realized on the fibers and mat reinforcements have also been tested to assess the influence of these pretreatments on the mechanical properties.

Untreated fibers (referred to "Untreated"): Untreated fibers were used in the fabrication of flax mat reinforcements to serve as a benchmark for the other treatments below.

Alkaline pretreatment of fibers (NaOH): We have used a NaOH solution to clean the fibers and facilitate molecular adhesion in subsequent chemical reactions. Three different treatment durations were established to meet specific analysis and comparison needs. The first treatment consists in exposing the fibers to a NaOH solution for one day. The second batch of fibers underwent a longer treatment lasting 7 days (NaOH-7). The third batch was treated over 30 days (NaOH-30) by adjusting the pH conditions to those of the three main click chemistry reactions used in the study (propargylation: pH=7.8, tosylation: pH=12.6, and azidation: pH=10.2). This was done to ensure that the improvements in the mechanical properties of the dry reinforcement were attributed to the click chemistry reactions rather than the cleaning effect resulting from the NaOH treatment used in the process. The pretreatment procedure involves dispersing 25 g of short fibers in 2 L of deionized water for at least four hours. Next, the fibers were treated in a standard disperser for ten minutes at 1000 rpm to create a homogeneous fiber suspension. The fibers were then soaked in a 5% w/w NaOH solution for 24 hours (or for 7 or 30 days for the other two durations) at room temperature. After the soaking period, the fibers were thoroughly rinsed with deionized water followed by acidified water to neutralize any remaining NaOH. A final washing cycle allowed to prepare the pretreated fibers, which were then dispersed in an alkaline medium (2.5% m/v) for 30 minutes, marking the beginning of propargylation and tosylation reactions described later.

Fibrillation of fibers (FIB): Fibrillation of fiber surface, using a PFI (Paper and Fiber Research Institute) refining mill supplied by Noram Quality Control and Research Equipment Limited (Canada), was carried out to improve the fiber-matrix adhesion (by a mechanical effect) while maximizing the response of click chemistry process with a greater number of reactive sites obtained after fibrillation (thus increasing the chemical effect). This part of the study involved producing two types of samples: fibrillated flax fibers (FIB) and fibrillated flax fibers that had previously undergone NaOH treatment (NaOH-FIB). The fibrillation process was conducted according to the protocol suggested by Amir et al. [11]. Initially, short fibers weighing 25 g were immersed in 2 L of deionized water and allowed to soak for at least four hours. Next, the solution was mixed in a standard disperser for ten minutes at 1000 rpm. Following the findings reported by Amir et al. [11], fibrillation was performed at 500 revolutions in the PFI refiner. In the process, a refining cylinder (the rotor) is rotated at a constant speed, for the required number of revolutions, while applying a vertical loading on the fibers maintained inside the stator (the static drum) to generate the shear and compressive forces resulting in fiber surface fibrillation. The reader is referred to reference [11] for more details.

Click chemistry reactions and treatments: The last treatment involves the click chemistry principles to introduce various functional groups at the surface of fibers to create the planned fiber-fiber covalent bonds. The primary focus was on three distinct chemical reactions: propargylation, tosylation, and azidation. Each of these three reactions is necessary for the click chemistry reaction to occur. The treatment processes for each intermediate reaction (along with the final click chemistry reaction) are detailed in a previous article by the authors and will be shortly described here [41]. Figure 1.a shows the propargylation reaction, which introduces propargyl groups to both primary and secondary cellulose hydroxyls using propargyl bromide. Figure 1.b illustrates the tosylation reaction that makes the fibers more susceptible to subsequent azide substitution. Figure 1.c depicts the azidation reaction, which completes the functionalization process by substituting azide to tosyl groups, using sodium azide. Figure 1.d presents the final click chemistry reaction occurring between azidated and propargylated fibers to create covalent bonds upon contact between the two types of functionalized fibers.

Table 1 summarizes all treatment conditions performed. In the third column of the table, PB, T, TC and SA stand for the chemical reagents used, that is, propargyl bromide (PB), triethylamine (T), tosyl chloride (TC) and sodium azide (SA) respectively. Propargylation, tosylation, and azidation were performed on the four categories of flax fibers: untreated fibers (Untreated), fibrillated fibers (FIB), fibers treated with NaOH (NaOH), and fibrillated fibers treated next with NaOH (NaOH-FIB). For Pr-3 to Pr-5, Ts-3 to Ts-5 and Az-3 to Az-5 treatments, the exact same procedures as those described in [39] have been followed except that higher reagent quantities and extended treatment durations (compared to Pr-1, Pr-2, Ts-1, Ts-2, Az-1 and Az-2) have been used considering that more extractible must be remove from the short flax fibers to get high DS in comparison to Kraft pulp fibers composition used in [41]. The same approach applies for the NaOH and NaOH-FIB treatments, the protocol was implemented with higher reagent quantities and extended durations compared to the previous works on click chemistry with kraft pulp [41]. The alkaline treatment (NaOH) and alkaline combined to fibrillation (NaOH-FIB) aimed strategically to maximize the number of covalent bonds created during the final click chemistry reaction. This was obtained by fibrillating the surface of the fibers to increase the number of fiber-fiber contacts and by maximizing the reaction yields (with longer treatment durations) to achieve the desired degree of chemical substitution (DS), thus increasing the functionality of modified fibers. The variation in propargylation, tosylation and azidation treatment durations from 4 or 5 days for Untreated and FIB fibers to 7 and 10 days for NaOH and NaOH-FIB fibers was introduced considering extended periods were necessary for NaOH and NaOH-FIB fibers to capitalize on their increased reactive capacity. This gradation in treatment times was designed to find a balance between efficient chemical modifications and the risk of fiber degradation. For the final reticulation reaction, the propargylated and azidated fibers, each in a proportion of 50% of the total mass of fibers, were dispersed in 2 L of distilled water. Next, 1.48 g (5.9 mmol) of copper sulfate pentahydrate and 2.34 g (11.8 mmol) of sodium ascorbate were added to the mixture, which was mechanically stirred at room temperature for 7 days. After the reaction, the medium was filtered and washed with 2 x 1 L of hot water and 1 L of hot ethanol 95%.

Figure 2 provides a visual roadmap of the click chemistry treatments described in Table 1. The flowchart illustrates the step-by-step process from initial fiber selection to the final click chemistry reactions. It also shows the durations for the NaOH treatment to maximize the functionalization. The treatments 1 and 2 (Pr-1, Ts-1, Az-1, Pr-2, Ts-2 and Az-2) have not been considered for the final click chemistry because their DS was considered too low. All tests shown in Table 1 have been NaOH treated for one day only (so the NaOH acronym in the table). For NaOH-7 and NaOH-30, these longer treatments were conducted to ensure that the final improvements were due to click chemistry (and the creation of covalent bonds) rather than a lack of fiber cleaning (NaOH acting as a cleaning treatment) induced by too short cleaning times. The final click chemistry treatment was thus applied on the third treatments (Pr-3, Ts-3 and Az-3) after the NaOH only pretreatment, and on the fourth and fifth treatments (Pr-4, Ts-4, Az-4, Pr-5, Ts-5 and Az-5) after the combined NaOH-FIB pretreatments.

2.3 Preparation of flax fiber mats.

Figure 3 shows the dynamic former used for the preparation of flax the flax fiber mats. Two basic surface densities of flax mats (shown in Figure 3d) were prepared: 50 g/m² for dry testing of the reinforcement and 300 g/m² for composites testing. The lower surface density was used to reproduce the mat binder used in the UD-mat reinforcement developed in other works by the authors [11, 12] and to reduce the volume of chemicals and fibers required for the treatments considering only dry testing was performed on the 50 g/m² mat (mentioned in Sections 2.3 and 2.5.2). The higher 300 g/m² was prepared to mold the composite plates. The manufacturing process follows a technique that is well described in previous works by the authors [11, 12]. The dynamic forming machine (Figure 3b), provided by ALIMAND (France), consists of a mixing tank, a pump, and a high-speed perforated spinning drum used to form the mat by draining the excess of water (the drum being perforated, like a washing machine). This is a laboratory equipment well known in the paper industry. A homogeneous mixture (Figure 3a) consisting of 12 or 72 g (for the 50 or 300 g/m² mat densities) of short flax fibers in 20 L of water was prepared and dropped in the mixing tank of the dynamic former (right of Figure 3b). It is then pumped and projected over the inner wall of the spinning drum (middle of Figure 3b) to form a mat of short fibers. After forming, the mat is carefully removed and dried at 100 °C using an E-100 drum dryer (Figure 3c) manufactured by Adirondack Machine Corporation (Hudson Falls, NY, USA) to eliminate any residual moisture.

Table 2 shows all mat reinforcements produced for the dry tests of this study. To increase the number of fiber-fiber contacts and, consequently, the number of covalent bonds after the click chemistry reaction, mat compression has been introduced prior to testing for several mats as shown in column 2 of the table. For compression, a pressure of 2.2 MPa was applied for 5 minutes using a 50-ton DAKE press provided by DAKE Corp. (Grand Haven, Michigan, USA). After compaction, the reinforcement was heated at 70 °C for two hours prior the mechanical tests. The fiber treatment applied on the short flax fibers (detailed in Table 1) prior to the preparation of the mat reinforcement is found in the last column of Table 2. The dry reinforcements shown, which have all been tested following the procedures described later in Sections 2.5.1 and 2.5.2, are divided in three groups. The first group, M1 to M9, corresponds to reinforcements made of untreated fibers and fibers submitted only to NaOH or fibrillation (FIB) treatments. They have been fabricated to separate the influence of these basic treatments from the other chemical treatments (related to the click chemistry treatment) on the mechanical properties. The second group corresponds to reinforcements prepared after the propargylation treatment only (tests M10 to M13), the tosylation treatment only (tests M14 to M17), and the azidation treatment only (tests M18 to M21). Similarly, this second group of tests have been introduced to obtain the individual influence of these pre-treatments (required for the final click chemistry reaction to occur) on the mechanical properties. For these tests, the protocols shown in Table 1 have been followed. Looking at Table 1, this means that the applied fiber treatment (last column of Table 2) for this second group of tests also includes the NaOH and FIB treatments of the first group performed before the propargylation, tosylation, and azidation treatments. Finally, the third group tests M22 to M29, corresponds to reinforcements made of 50% of propargylated fibers and 50% of azidated fibers, combination allowing the click chemistry reaction to occur during the drying step of the reinforcement immediately after removing the mat from the dynamic former. To demonstrate the unique impact of the click chemistry-induced covalent bonds, the mechanical properties of the third group were directly compared with those of the initial and intermediate groups. Finally, the third group is divided in two sub-groups, one without the addition of a catalyst (tests M22 to M25) to promote the click chemistry reaction by simple contact between the propargylated and azidated fibers, and the other one using a copper(I) azide-alkyne cycloaddition (CuAAC) catalyst to activate the click chemistry reaction and possibly create more covalent bonds (tests M26 to M29).

2.4. Preparation of composite plates:

Selection of the reinforcements for plate molding: Based on the mechanical test results obtained on the dry reinforcements of Table 2, composite plates have been molded using those showing the best mechanical properties. Increasing the properties of the dry mat reinforcement is one aspect of this study, but ultimately the most important aspect is to show how increasing the modulus and strength of the dry reinforcement contributes to improving the mechanical properties of the final composite.

Composite plate molding process: Composite plates were fabricated using the resin transfer molding (RTM) process. Further details about the mold and the molding procedure are available in previous works [11, 12]. For the composite plates, mat reinforcements of 300 g/m² were used to limit the number of layers in the plates. Before molding, the reinforcements were dried at 70°C for 2 hours to minimize the moisture content. SikaBiresin CR72 resin premixed with a SikaBiresin CH72-3 hardener were used, both supplied by Sika Advanced Resins (USA), in a weight ratio of 18% following the supplier's datasheet. After mixing the hardener with the resin, the mixture was degassed under vacuum for 10 minutes to remove the entrapped air. Before molding, the mold containing the stack of reinforcements was preheated to 80°C to reduce the resin viscosity and facilitate impregnation. When ready for the injection and after degassing, the pressure pot was connected to the mold and slowly pressurized to 4 bars for the injection. After filling, the injection and vent ports were sealed, and the mold transferred to the oven for the resin cure at 80°C for 4 hours. This was followed by an additional 3 hours of post-cure at 100°C to ensure a complete cross-linking of the resin. The composite plates prepared were made of six distinct types of flax fiber reinforcements, according to the treatments described in Table 2. These include the untreated flax mat (C1) used as reference, the mat made from fibrillated fibers only (C2), the fibrillated and compacted fibers only (C3), and the chemical click treated mats (C4, C5, and C6) which include NaOH (C3), NaOH plus fibrillation (C5) and NaOH, fibrillation and compaction (C6) along with the click chemistry final reaction. To maintain a consistent fiber volume fraction (V_f) of 40 ± 2% in all plates, the mold cavity thickness was adjusted using aluminum shims positioned between the mold halves and V_f was calculated using equation (1),

$$\mathbf{V_f}(\%) = (\mathbf{n} \times \mathbf{m}_{\boldsymbol{o,R}}) \,/\, (\boldsymbol{h} \times \boldsymbol{\rho}_{\mathbf{f}}) \tag{1}$$

where n is the number of layers in the laminate, $m_{o,R}$ is the average surface density of each mat reinforcement (g/cm^2), ρ_f is the fiber density (g/cm^3) and h the laminate thickness (cm). Here, to consider the effect of fiber treatments on ρ_f (and V_f), both the fiber density of 1.44 g/cm^3 proposed by the supplier ($\rho_{f,S}$) and that measured experimentally ($\rho_{f,E}$) were considered. Flax fiber density was measured following ASTM D297 method based on Archimedes' principle. Considering the high sensitivity of flax to water (rapid water absorption), hydrophobic Canola oil (ρ = 0,917 g/cm^3) was used to measure the submerged weight of fibers [42, 43]. The results of the average density (based on ten repetitions) are presented in Table 3 and the characteristics of each composite plate, including the reinforcement type, V_f and the final plate thickness are detailed in Table 4. The low influence of the treatments on the fiber density results in fiber volume contents all around 40%, except for C3 with a value slightly higher at 42.9%. Thus, and considering the standard deviations, fiber treatments had no significant effect on V_f.

2.5. Characterization methods

The characterization of the different fiber treatments was realized using three approaches, focusing on the effectiveness of fiber treatments through chemical, mechanical, and tensile testing. The chemical analysis was performed to confirm the success of the intermediate and final click chemistry reactions. The mechanical testing of dry mats provided insight into the treatments' impact on the reinforcement properties while allowing to choose the best reinforcements to be used for the molding of composite plates. Finally, tensile tests on composite plates gauged how these modifications transfer to the composite level. Overall, these different approaches allowed assessing the effectiveness of the different fiber treatments on the final properties of the composite plates, especially the click chemistry treatment combined to different mechanical treatments (such as fiber fibrillation and reinforcement compaction).

2.5.1. Chemical characterization

Infrared spectroscopy was performed using a Thermo Scientific Nicolet iS10 FTIR spectrometer, 32 acquisitions at room temperature at a resolution of ±4 cm-1. These tests were performed to identify the functional groups introduced onto the fibers surface through various treatments, facilitating the detection of propargyl, tosyl, and azide groups. Scanning electron microscopy (SEM) was used to assess the effect of click chemistry and chemical treatments on the fiber morphology. SEM images were obtained using a Hitachi SU1510 microscope operating in secondary electron mode with a beam current of 100 mA and an accelerating voltage of 15 KV. It is equipped with an energy-dispersive X-ray spectroscope (EDX, Oxford instrument X Max 20 mm2), enabling detailed chemical characterization of the fibers. To enhance the quality of the SEM images and facilitate EDX analysis, the fibers were sputter-coated with gold following standard practice procedures. This entailed preparing a compact sample, or "pellet," from the treated fibers, which was subsequently coated with a conductive metal layer, achieving a uniform thickness of a few nanometers. This metallic layer ensured accurate imaging and analysis by preventing charging effects. The EDX analysis data complements the findings from the FTIR analysis, as they both provide evidence for the successful modification of the flax fibers using different treatment methods. The propargyl, tosyl, and azide groups present on the functionalized surface of fibers are mainly composed of carbon, sulfur, nitrogen, and oxygen. In this work, we are more interested in the external surface than the internal part of the fibers since the interfacial interaction occur when the fibers come into contact. Wich is compatible with EDX surface analysis.

2.5.2. Mechanical characterization on flax mat

Mechanical tests were conducted on the dry reinforcements (surface density of 50 g/m^2) presented in Table 2, using testing methods currently used in the paper industry. This allowed the use of known and recognized standards for testing dry reinforcements for which the thickness cannot be measured with precision. The burst strength (the maximum pressure the reinforcement can withstand without breaking) was measured using a Mullen-type burst tester following the TAPPI T 403 om-97 technique. The burst index (B.I.) is reported in kPa.m2/g. Measurements were made at two different locations on each mat. The tear index (T.I.) is performed according to the TAPPI T 414 om-98 method using the Elmendorf Tearing Tester Thwing-Albert. The tear index is expressed in mN-m2/g. Finally, tensile tests on 25 mm x 150 mm samples are carried out to measure the elongation at break (E.B), the tensile strength in the form of the rupture index (R.I) (expressed in N-m/g), and the tensile stiffness St (kN/m) was calculated from the force per unit width versus strain curves according to:

$$\boldsymbol{St} = (\boldsymbol{\Delta f} \times \boldsymbol{L}) / (\boldsymbol{w} \times \boldsymbol{\Delta L}). \tag{2}$$

Here, Δf (kN) is the difference between two force levels, L (m) is the initial specimen length, w (m) is the initial specimen width and ΔL (m) is the change in length induces by Δf. These tests were conducted on an Instron 4201 tensile machine, mounted with a 0,5 kN load cell, according to the TAPPI T 494 om-01 method.

2.5.3. Tensile testing of composites

Tensile testing was a crucial aspect of evaluating the mechanical properties of composites. They were conducted in compliance with ASTM D3039 for tension testing of polymer matrix composite materials. An Instron-U150 LM testing machine, equipped with a 50 kN load cell, was used. The axial extension was measured with a 50 mm Instron 2620 extensometer. The tests were conducted at a constant velocity of 2 mm/min, adhering to the standard specifications. Each type of composite plate (in Table 4) underwent at least six tensile tests.

3. Results and Discussion

3.1. Chemical characterization of modified flax fibers

3.1.1. Functionalization (FTIR Analysis)

Figure 4 shows FTIR analysis curves of propargylated (a), tosylated (b), azidated (c), and unmodified flax fibers (d), providing a clear contrast between chemically modified and natural fibers. The spectral analysis of propargylated, tosylated, and azidated fibers confirms the successful grafting of these functional groups onto the fiber surface. Characteristic peaks illustrate the success of the modification. The alkyne group found in propargylated fibers is visible as a unique strong and sharp peak at 2109 cm^{-1} (Figure 4. a). This alkyne peak, absent in the Pr-1, is evident for Pr-5 due to the extended exposure of fibers to propargyl bromide (Table 1). For tosylation, the S=O stretching peaks around 1160 and 1360 cm^{-1} (Figure 4. b) are also clearly visible, but their intensity increases from Ts-1 to Ts-5. The most intense S=O peak is observed for Ts-5, indicating a successful grafting when increasing reactant quantities and treatment duration. Azidation is confirmed by a weak sharp peak at 2034 cm^{-1} for the Az-5 spectrum (Figure 4. c). The peak intensity increases with sodium azide weight and longer treatment, especially for NaOH pre-treated fibers, emphasizing its importance. Az-1 lacks this peak, indicating unsuccessful azidation. The comparison of the spectra of untreated, NaOH-treated, and chemically treated fibers (Pr-5, Ts-5, Az-5) in Figure 4.d, along with the reaction conditions given in Table 1, reveals the successful chemical modifications of flax fibers, especially when larger quantities of reactants and longer treatments are involved. The NaOH-treated fibers exhibit FTIR spectra similar to those of untreated fibers, showing that NaOH primarily cleans the fiber surfaces without altering their intrinsic chemical structures (see Figure 4.d). Additionally, note that the second and fourth levels of treatments (Pr-2, Ts-2, Az-2 and Pr-4, Ts-4, Az-4) are not shown in the spectra. For the former, the spectra were similar to the initial treatments (Pr-1, Ts-1, Az-1), indicating that the reaction conditions used did not advance the functionalization any further, while for the latter, the spectra were similar to those of the fifth level (Pr-5, Ts-5, Az-5), indicating that at this stage, a saturation point in functional group grafting may have been reached.

3.1.2. SEM-EDX Analysis

The SEM images in Figure 5, all taken at 100X magnification, provide comparisons of the morphological changes resulting from the different chemical modifications. Figure 6 shows the EDX analysis of the fibers in Figure 5 while Table 5 shows the elemental composition statistics. The morphology of the fibers could impact the mechanical properties of composites, fibers with a more irregular surface may lead to higher mechanical properties, due to improved interfacial bonding with the polymer matrix. Untreated fibers show a relatively smooth surface (Figure 5. a) with a primary carbon and oxygen composition, which is typical of natural flax fibers (Figure 6. a). After NaOH treatment, some increase in surface roughness and oxygen content are observed (Figures 5. b and 6. b), indicating the removal of hemicelluloses and lignin, thereby exposing more cellulose fibrils and a possible increase of surface hydroxyl groups. Subsequent chemical treatments result in further morphological alterations. Propargylated (Pr-5) and tosylated (Ts-5) fibers develop rougher textures and surface irregularities, possibly due to the reaction conditions. (Figures 5.c and 5.d). This is corroborated by the EDX mapping, which shows a homogeneous increase in carbon for Pr-5 (Figure 6. c) and a significant rise in sulfur content for Ts-5 (Figure 6.d), reflecting the successful introduction of respective functional groups propargyl and tosylate. Azidated fibers (Az-5), show a different surface morphology with notable irregularities (Figure 5.e).

As presented earlier, Table 5 shows the elemental composition but also the degree of substitution at the surface of modified flax fibers. Significant changes occurred in the elemental composition during the modification process. Untreated fibers contained 67.1% of carbon and 32.1% of oxygen. After the NaOH treatment, a marked increase in the oxygen content to 40.0% was observed while the carbon content decreased to 58.6%. This treatment produced the breakage of some carbon bonds in the cellulose structure, leading to an increase in the availability of hydroxyl groups (and therefore oxygen atoms). Looking at propargylation, tosylation, and azidation treatments, changes in the elemental composition further validate FTIR findings of Figure 4. For instance, the absence of sulfur in untreated and propargylated fibers (Pr-1 to Pr-5) was expected as no sulfur-containing reagent is used in these treatments. The appearance of sulfur in tosylated fibers (Ts-1 to Ts-5) confirms the successful tosylation process, as also reflected by the FTIR results. The increasing sulfur percentage in Ts samples, from Ts-1 to Ts-5, suggests that a higher amount of tosyl chloride and a longer reaction time indeed led to a higher degree of tosylation, consistent with the increasing intensities of the S=O peak in the FTIR spectra. Nitrogen in the azidated fibers (Az-3 to Az-5) confirms the azidation process. However, the absence of nitrogen in Az-1 (and Az-2, not shown) supports the FTIR results, which suggest that azidation failed under the conditions used for these samples. The changes in the O/C ratio for the different treatments also demonstrate the impact of these modifications. Untreated fibers have an O/C ratio of 0.48, which increases to 0.68 in NaOH-7, the general trend of a decreasing O/C ratio observed as treatment conditions are intensified (from treatments 1 up to treatments 5), particularly with the lowest ratios seen in Ts-5 and Pr-5 samples, indicates a high degree of modification. This decrease can primarily be attributed to the addition of carbon-rich functional groups, such as tosyl and propargyl, that increase the carbon content on the fiber surface. In the elemental analysis and for reasons mentioned above, the Pr-2, Ts-2, and Az-2 treatments are not separately listed in the table as they yielded results similar to Pr-1, Ts-1, and Az-1, respectively. Similarly, the fourth treatments (Pr-4, Ts-4, and Az-4) are not shown because their results closely mirror those of the more intensive fifth treatments (Pr-5, Ts-5, and Az-5). The degree of substitution (DS), which quantifies the extent of chemical modifications, shows an increasing trend from Pr-1 to Pr-5, Ts-1 to Ts-5, and Az-1 to Az-5. The highest DS is observed in Az-5, suggesting that these conditions lead to the highest degree of modification.

3.2. Mechanical testing of flax mats

All intermediate chemical modifications applied to the fibers, including fibrillation, mat compaction, alkaline pretreatment using NaOH, propargylation, tosylation, azidation, and finally the crosslinking with or without a catalyst, have been evaluated for their individual (and cumulative) effect on the mechanical properties of the dry mat. The results of all tests, including tensile, burst and tear indexes are summarized in Table 6. Looking at the table, the uncompressed tests (M3, M6, M8, M12, M16, M20, M24 and M28) show results very similar to the compressed tests prepared under the same conditions (M4, M7, M9, M13, M17, M21, M25 and M29).

The results are reproduced as bar charts in Figures 7 to 11 for analysis purposes and better visual appreciation where, to clarify and ease the reading, the uncompressed tests have been omitted. The results can be grouped in four categories. First, test M2 (the untreated and compressed mat) serves as the base reference instead of test M1. M1 and M2 show comparable results (Table 6) while test M2 is closer to the reality of preforming in RTM where the reinforcements always undergo compression to fit the mold geometry, which remains true for flax reinforcements [11]. Second, tests M3 to M9 correspond to the preliminary cleaning (NaOH-7 and NaOH-30) and fibrillation (FIB) treatments (named preliminary treatments group below). Third, tests M10 to M21, corresponding to the propargylated, tosylated and azidated fibers (named grafting treatments group below), tested individually under the non-compressed and compressed form before the click chemistry reaction occurs. Finally, the fourth group, tests M22 to M29, corresponding to reticulated fibers after the click chemistry reaction between the propargylated and azidated fibers (named click treatment group below). Looking at the preliminary treatments group (M3 to M9), a low but continuous increase is observed for the burst, tear, and tensile indexes except for M7 and M4 for the tensile index where a drop is observed. NaOH can fragilize the fibers when long treatment durations are applied, but here M4 has been treated for 7 days while M5 shows a higher tensile index after a NaOH treatment of 30 days. Similarly, M9 shows a much higher tensile index than M7 with fibrillation applied for both coupons except M9 has also been NaOH treated for one day. So, no clear explanation can be given for the lower tensile index of M4 and M7. However, and for all other tests, the combination of NaOH pretreatment and fibrillation played a role in improving the properties of flax mat reinforcements, especially for M5 and M9 showing much higher properties than the M2 reference in all types of tests. These improvements are partly attributed to the fiber-to-fiber (mechanical) interaction between fibrillated fibers [11]. Combined to the cleaning action of NaOH, which lead to the removal of lignin and hemicellulose, this could result in better interlocking and improved mechanical properties. Further analyses are however required to confirm this hypothesis. For the grafting treatments group (M10 to M21) and compared to the M2 reference, significant increases in the properties are observed compared to the preliminary M3 to M9 treatments. For propargylation (M10 to M13), tosylation (M14 to M17) and azidation (M18 to M21) and for most tests in Figures 7 to 11, the level of enhancement correlates with the degree of substitution, which increases when going from level 3 to level 5 of treatments in Table 5. This is especially true for the propargylation Pr-5 of M13 (up 347% for the tear index), tosylation Ts-5 of M17 (up 285% for the tear index), and azidation Az-5 of M21 (up 260% for the burst index, 228% for the tensile index and 355% for the elongation at break) compared to the untreated M2 mat. The presence of azide groups may have enhanced the inter-fiber adhesion [44]. Finally, for the fourth group, after the cross-linking reactions occurred with or without a catalyst (M22 to M29), another level of improvements is observed in the properties. This is especially true for the tensile index in Figure 9 with M29 reaching 519% of improvement compared to the non-treated M2, while compared to the highest DS click chemistry precursors M21 (Az-5) and M13 (Pr-5), the increase is 89% and 101% respectively. This means that creating covalent bonds is equivalent to almost doubling the tensile index. This is less evident for the other tests, however. There is still some effect on tear, burst and tensile stiffness but with lower levels of increase for M29 compared to M21 and M13. But globally and compared to M2, while the grafting treatments group (third group) showed important improvements for the tensile, burst and tear indexes, the click treatments group (fourth group) shows that the cross-linking mechanism propelled the metrics further to 519%, 304%, and 421%, respectively. And as shown by the red arrows in Figures 7 to 11, for the third and fourth groups (grafting treatments and click treatment), the properties increase with the duration of the treatment and the concentration of reactants (see Table 1) which result in higher DS levels (Table 5). This is true except for the elongation at break of the fourth group showing decreases with the treatment duration. This contributes to the very high tensile stiffness of tests M25 and M29, i.e., a high tensile index combined with a low elongation at break, both leading to a steeper initial "stress-strain" curve. Finally, it is worth mentioning that the highest properties were obtained for the highest DS levels with fiber mats subjected to compression, i.e. for tests M13, M17, M21, M25 and M29, with the best properties obtained after the click chemistry reaction occurred.

The improvements produced by the click chemistry reaction, compared to the azidated and propargylated precursors (third group), are mainly due to the formation of covalent bonds at the fiber-fiber interface. The preliminary treatments (cleaning with NaOH and fibrillation) followed by the compaction of the mat reinforcement significantly increase the number of contact points, and consequently the creation of covalent bonds. Interestingly, the click treatment without the use of catalysts (M25) showed mechanical properties comparable to the catalyzed version (M29) in most cases. This means that the use of Cu catalyst may not be necessary for the reaction to occur, which is an interesting aspect of the treatments because not only the adding of catalyst is a step that can be avoided, but it is also better to avoid it considering its negative environmental impact. Finally, the type of test realized affect the results within a given group of treatments. For example, and within the fourth group (M22 to M29), relatively consistent results are observed for the burst, tensile and elongation at break results, while large differences were obtained for the tear index and tensile stiffness. These deviations could be linked to differences in the distribution and density of cross-linking sites across the fiber surfaces and the complex way the fibers react to strong covalent bonds and different solicitation modes (burst, shear, and tension modes). So potential influences, such as the degree of cross-linking, the homogeneity of cross-linking sites, and the intrinsic reaction of fibers (which are highly non-isotropic natural fibers) to the incorporation of covalent bonds, emerge as areas for more extensive research.

The thorough testing conducted on flax mats (presented above) is important to guide the selection of treatments for preparing composite plates because the increased strength and stiffness of the reinforcement will partly transfer to composite laminates. Additionally, stronger reinforcements result in more robust dry preforms, contributing to the preparation of geometrically consistent fiber preforms for liquid molding processes like resin transfer molding (RTM). So, it is crucial to examine how these treated reinforcements behave when used in composite materials, which is the objective of the next section.

3.3 Tensile testing of composite plates

Figure 12 shows typical stress-strain curves for the tensile tests of the composites described in Table 4, while Table 7 gives precise values of the modulus of elasticity (MOE), strength, and fracture strain for the same tests, along with the variances with respect to test C1. First, the curves of Figure 12 show distinct regions, with a first linear region covering strains from 0% to around 0.3%, followed by a second region from around 0.3% up to fracture where a globally non-linear behavior is observed with a mixture of linear and non-linear portions depending on the test. A bilinear behavior is well known for UD flax fiber composites [45] where the realignment of the microfibrils inside the fibers are invoked to explain such a behavior. But we are here in presence of composites made of short fiber mats which usually behave in a non-linear manner (as raised in [11]), which is clearly not the case in view of Figure 12. Indeed, and as shown by the red lines, tests show such a bilinear behavior while the other tests are more or less non-linear. The homogeneity of the treatments inside the reinforcements could be involved as also mentioned for the dry reinforcements in the last section. But clearly, the new fiber-fiber interactions created by the treatments promote a tensile behavior not observed in composites using untreated mats.

According to Table 7 for the composite strength, the reference value C1 of 109.6 ± 7 MPa aligns with the findings of Bernaoui et al. [11], who observed a value of 110.8 ± 2.9 MPa for short fiber flax composites at a V_f of 40%. Increases in strength of 11.7% and 3.4% are obtained when using fibrillated (C2) and fibrillated-compressed (C3) reinforcements, respectively. These represent relatively small ameliorations compared to the C5 and C6 composites made of click treated mat reinforcements without and with precompression (including fibrillation in both cases), with important 46.2% and 64.3% increases in strength. The propargylation and azidation treatments, by preparing the fibers to the creation of covalent bonds, make them more hydrophobic and compatible with the epoxy resin [46]. The high increases in properties for C5 and C6 come from a combination of strong fiber-to-fiber covalent bonds and a better wettability of the fiber preform, which has a crucial role in enhancing the fiber-matrix interface for a more efficient transmission of mechanical loads. So, two important conclusions are drawn from these results. First, the increases in strength for C5 and C6 are in a large part due to the covalent bonds created by the click chemistry treatment (not from fibrillation and compression) and second, the compression in C6 increases the number of fiber-fiber contacts (and the covalent bonds created) creating an additional increase of 18.1% in strength compared to C5. Good results were also obtained for the fracture strain and modulus of elasticity. Increases in modulus of 23% and 41.5 % and in the fracture strain of 38.4% and 30.8% were obtained for C5 and C6, respectively. A huge increase of 134.8% is observed for the fracture strain combined to a drop in modulus of elasticity of 11.8% for test C3 (this is also observed in Figure 12). This very high fracture strain for C3 is not supported by the very low elongation at break for the M7 reinforcement in Figure 10, suggesting that something happened with the fiber-matrix interface (or at least the fiber-matrix interaction) when fiber fibrillation and reinforcement compression are combined without click chemistry treatments. It is known that surface fibrillation alone reduces the permeability to liquid resin of the reinforcement [10]. This was also observed in the present work with longer impregnation times. So, combining fibrillation with compaction could amplify the problem, by strongly reducing the preform porosity and permeability. In such a case, the ameliorations in composite properties could be counterbalanced by a higher porosity in the resulting composite, leading to lower strength and modulus as shown in Figure 12 and Table 7. Preform permeability is an important aspect to consider when fibrillation is involved, especially with pre-compacted fiber preforms. Future works should be oriented towards an optimization of the parameters involved in the mechanical treatments, mainly the fibrillation and compression, with those of the chemical treatments such as the treatments duration and reactants quantities.

Figure 13 compares the fracture surfaces of test C1 (untreated) and test C6 (treated). C1 (Figure 13a) exhibits a rough and uneven fracture surface, indicative of extensive fiber pull-out and weak fiber-matrix adhesion. In contrast, the treated C6 composite (Figure 13b) shows a more uniform fracture surface, suggesting a stronger fiber-matrix adhesion. This initial visual assessment is further corroborated by the detailed SEM analysis presented in Figure 14 which presents SEM micrographs of the fracture surfaces for composites C1 to C6. Matrix cracking and fiber-matrix decohesion are evident for all composites. The C1 composite (Figure 14a) displays very low matrix cracking accompanied by fiber pull-out, signifying poor fiber-matrix adhesion consistent with the irregular fracture surface in Figure 13a. In contrast, the most pronounced treatment effects are observed in C6 (Figure 13f), which exhibits a lot of matrix cracking, almost no fiber pull-out and the matrix still bonded to some of the fibers (red arrow). This suggests a much better stress transfer between the fibers and the matrix to maximize tensile properties. Comparison of the fibrillated C2 (Figure 14b) and fibrillated-compacted C3 (Figure 14c) indicate some improvement in adhesion with much more matrix cracking in C3. This highlights the nuanced effect of fibrillation (C2) and compaction (C3), which have also a different impact on the properties as shown in Table 7. With the introduction of NaOH treatment and click chemistry (C4 and C5), an increase in matrix cracking is observed, suggesting again a strong fiber-matrix adhesion, effect maximized with C6 where the reinforcement compression was performed after the click chemistry reaction. In summary, Figures 13 and 14 illustrate the significant enhancement in fiber-matrix adhesion due to the combined mechanical and chemical treatments. These observations support the improvements in tensile strength and fracture strain in Table 7, as the series progresses from purely mechanical to advanced chemical treatments.

CONCLUSION

In summary, this study successfully demonstrates the modification of flax fibers using various chemical treatments, including propargylation, tosylation, azidation, and cross-linking. The success of this work has relied on the implementation of diverse reaction conditions, along with the NaOH treatment and fibers fibrillation implemented to increase the number of reactive sites before initiating the click chemistry reactions. These pretreatments have facilitated subsequent click chemistry processes, resulting in improvements in the degree of substitution of chemical treatments and the mechanical properties of the dry reinforcements tested under different conditions. Interestingly, it was observed that the use of a catalyst was not necessary in the creation of covalent bonds in the click chemistry rection, thus avoiding the use of polluting chemical products while simplifying the treatment process. Further investigations will be undergone on this matter.

The results illustrate that click chemistry modifications strongly enhance the mechanical properties of flax mat reinforcements. Mat reinforcements containing modified fibers exhibited significantly higher tensile strength compared to those with untreated fibers, regardless of whether they were fibrillated or compacted. While NaOH treatment and fibrillation alone resulted in a decrease in the tensile index of the dry reinforcement, they played a pivotal role in enhancing the reinforcement's properties when applied to the fibers before processing with the intermediate chemical reactions and final click chemistry reaction. The NaOH pretreatment effectively removed undesirable surface contaminants such as pectin, lignin, and hemicellulose, while fibrillation increased contact surface area, making the cellulose hydroxyl groups more accessible for further chemical modifications. These preparatory stages led to notable improvements in the mechanical properties. The most important increases have been observed after the click chemistry reaction, where the tensile index, burst index and tear index test results showed that the cross-linking mechanism increased these properties by 519%, 304%, and 421% respectively. In terms of composite performance, the treated flax mat reinforcements have contributed to increased tensile strength and modulus of elasticity in the plates. The composites made from chemically treated mats (C5 and C6) displayed substantial improvements in strength and modulus of elasticity, with increases of 46.2%, 64.3%, 23.0%, and 41.5% respectively, over the untreated reference composite (C1). SEM micrographs of the fracture surfaces provided further insights into the material characteristics. Composites made from chemically treated mats showed less fiber pull-out and matrix cracking, which is consistent with improved fiber matrix adhesion and effective stress transfer factors essential for superior mechanical performance. The most significant enhancements were observed in composites C5 and C6, where a combination of NaOH treatment, fibrillation, and click chemistry resulted in a stronger interface and less visible damage post-fracture.

Overall, crosslinked fibers, both with and without catalyst, exhibited improvements in all mechanical properties, emphasizing the impact of covalent bond formation between the fibers on the mechanical performance of the flax mat reinforcement and on composites materials obtained from the modified reinforcement. This work provides valuable insights into the potential of click chemistry for modifying flax fibers, enabling the creation of materials with improved properties. It sets the stage for further research and developments in the realm of advanced materials and green chemistry.

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AUTHOR CONTRIBUTIONS

Abdelhadi Blal: Writing-Original draft, Conceptualization, Methodology, Experimental testing, Validation, Data curation, Investigation and Formal analysis.

Gilbert Lebrun: Supervision, Conceptualization, Project administration, Methodology, Writing-Reviewing and Editing, Visualization, Analysis.

François Brouillette: Co-Supervision, Conceptualization, Project administration, Methodology, Analysis, Writing-Reviewing.

Éric Loranger: Co-Supervision, Conceptualization, Project administration, Methodology, Reviewing.

DATA AVAILABILITY

Data will be made available on request.

COMPLIANCE WITH ETHICAL STANDARDS

Conflict of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

[1] A. K. Mohanty, M. Misra, and L. T. Drzal, "Surface modifications of natural fibers and performance of the resulting biocomposites: An overview," Composite Interfaces, vol. 8, no. 5, pp. 313–343, Jan. 2001

[2] P. Wambua, J. Ivens, and I. Verpoest, "Natural fibres: can they replace glass in fibre reinforced plastics?" Composites Science and Technology, vol. 63, no. 9, pp. 1259–1264, Jul. 2003.

[3] S. O. Ismail, E. Akpan, and H. N. Dhakal, "Review on natural plant fibres and their hybrid composites for structural applications: Recent trends and future perspectives," Composites Part C: Open Access, vol. 9, p. 100322, Oct. 2022.

[4] I. Elfaleh et al., "A comprehensive review of natural fibers and their composites: An eco-friendly alternative to conventional materials," Results in Engineering, vol. 19, p. 101271, Sep. 2023.

[5] A. Karimah et al., "A review on natural fibers for development of eco-friendly bio-composite: characteristics, and utilizations," Journal of Materials Research and Technology, vol. 13, pp. 2442–2458, Jul. 2021.

[6] C. H. Lee, A. Khalina, and S. H. Lee, "Importance of Interfacial Adhesion Condition on Characterization of Plant-Fiber-Reinforced Polymer Composites: A Review," Polymers, vol. 13, no. 3, p. 438, Jan. 2021.

[7] M. Ahmed. Musthaq, H. N. Dhakal, Z. Zhang, A. Barouni, and R. Zahari, "The Effect of Various Environmental Conditions on the Impact Damage Behaviour of Natural-Fibre-Reinforced Composites (NFRCs)—A Critical Review," Polymers, vol. 15, no. 5, p. 1229, Feb. 2023.

[8] T. Senthilkumar, A. K. Bharimalla, C. Sundaramoorthy, P. G. Patil, and N. Vigneshwaran, "Fibrillation of Coconut Fibers by Mechanical Refining to Enhance Its Reinforcing Potential in Epoxy Composites," Fibers and Polymers, vol. 21, no. 9, pp. 2111–2117, Sep. 2020.

[9] L. A. Sanchez-Echeverri, E. Ganjian, J. A. Medina-Perilla, G. C. Quintana, J. H. Sanchez-Toro, and M. Tyrer, "Mechanical refining combined with chemical treatment for the processing of Bamboo

fibres to produce efficient cement composites," Construction and Building Materials, vol. 269, p. 121232, Feb. 2021.

[10] A. Khakalo, A. Vishtal, E. Retulainen, I. Filpponen, and O. J. Rojas, "Mechanically-induced dimensional extensibility of fibers towards tough fiber networks," Cellulose, vol. 24, no. 1, pp. 191–205, Nov. 2016.

[11] A. Bernaoui, G. Lebrun, and E. Ruiz, "High performance natural fiber composites from mat and UD flax reinforcements backed with a mat Binder: A study of mat fiber surface fibrillation," Composites Part A: Applied Science and Manufacturing, vol. 160, p. 107064, Sep. 2022.

[12] R. S. Mbakop, G. Lebrun, and F. Brouillette, "Effect of compaction parameters on preform permeability and mechanical properties of unidirectional flax fiber composites," Composites Part B: Engineering, vol. 176, p. 107083, Nov. 2019.

[13] U. Henniges, M. Hasani, A. Potthast, G. Westman, and T. Rosenau, "Electron Beam Irradiation of Cellulosic Materials—Opportunities and Limitations," Materials, vol. 6, no. 5, pp. 1584–1598, Apr. 2013.

[14] R. Ahmad, R. Hamid, and S. A. Osman, "Physical and Chemical Modifications of Plant Fibres for Reinforcement in Cementitious Composites," Advances in Civil Engineering, vol. 2019, pp. 1–18, Mar. 2019.

[15] D. Thapliyal et al., "Natural Fibers Composites: Origin, Importance, Consumption Pattern, and Challenges," Journal of composites science, Dec. 04, 2023

[16] M. Z. Rong, M. Q. Zhang, Y. Liu, G. C. Yang, and H. M. Zeng, "The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites," Composites Science and Technology, vol. 61, no. 10, pp. 1437–1447, Aug. 2001.

[17] G. Siqueira, J. Bras, and A. Dufresne, "New Process of Chemical Grafting of Cellulose Nanoparticles with a Long Chain Isocyanate," Langmuir, vol. 26, no. 1, pp. 402–411, Nov. 2009.

[18] Y. Jia and B. Fiedler, "Influence of Furfuryl Alcohol Fiber Pre-Treatment on the Moisture Absorption and Mechanical Properties of Flax Fiber Composites," Fibers, vol. 6, no. 3, p. 59, Aug. 2018.

[19] Y. G. Thyavihalli Girijappa, S. Mavinkere Rangappa, J. Parameswaranpillai, and S. Siengchin, "Natural Fibers as Sustainable and Renewable Resource for Development of Eco-Friendly Composites: A Comprehensive Review," Frontiers in Materials, vol. 6, Sep. 2019.

[20] Y. Xie, C. A. S. Hill, Z. Xiao, H. Militz, and C. Mai, "Silane coupling agents used for natural fiber/polymer composites: A review," Composites Part A: Applied Science and Manufacturing, vol. 41, no. 7, pp. 806–819, Jul. 2010

[21] S. Sismanoglu, U. Tayfun, and Y. Kanbur, "Effect of alkali and silane surface treatments on the mechanical and physical behaviors of date palm seed-filled thermoplastic polyurethane eco-composites," Journal of Thermoplastic Composite Materials, vol. 35, no. 4, pp. 487–502, Dec. 2019.

[22] M. Abisha, R. K. Priya, K. P. Arunachalam, S. Avudaiappan, E. I. Saavedra Flores, and P. F. Parra, "Biodegradable Green Composites: Effects of Potassium Permanganate (KMnO4) Treatment on Thermal, Mechanical, and Morphological Behavior of Butea Parviflora (BP) Fibers," Polymers, vol. 15, no. 9, p. 2197, May 2023.

[23] M. Sood, D. Dharmpal, and V. K. Gupta, "Effect of Fiber Chemical Treatment on Mechanical Properties of Sisal Fiber/Recycled HDPE Composite," Materials Today: Proceedings, vol. 2, no. 4–5, pp. 3149–3155, 2015.

[24] M. Wang et al., "Chemical grafting of nano-SiO2 onto graphene oxide via thiol-ene click chemistry and its effect on the interfacial and mechanical properties of GO/epoxy composites," Composites Science and Technology, vol. 182, p. 107751, Sep. 2019.

[25] S. Y. Nayak, S. Shenoy Heckadka, A. Seth, S. Prabhu, R. Sharma, and K. R. Shenoy, "Effect of chemical treatment on the physical and mechanical properties of flax fibers: A comparative assessment," Materials Today: Proceedings, vol. 38, pp. 2406–2410, 2021.

[26] A. Atiqah, M. Jawaid, M. R. Ishak, and S. M. Sapuan, "Effect of Alkali and Silane Treatments on Mechanical and Interfacial Bonding Strength of Sugar Palm Fibers with Thermoplastic Polyurethane," Journal of Natural Fibers, vol. 15, no. 2, pp. 251–261, Jun. 2017.

[27] S. Huo, A. Thapa, and C. A. Ulven, "Effect of surface treatments on interfacial properties of flax fiber-reinforced composites," Advanced Composite Materials, vol. 22, no. 2, pp. 109–121, Apr. 2013.

[28] S. Ru, R. Yang, S. Yang, and C. Zhao, "Effects of Physical and Mechanical Properties of Coir Fiber and Reinforced Epoxy Composites Treated with Acetic Anhydride and Alkali," Journal of Natural Fibers, vol. 20, no. 2, Nov. 2023.

[29] A. S. Madival, S. Maddasani, R. Shetty, and D. Doreswamy, "Influence of Chemical Treatments on the Physical and Mechanical Properties of Furcraea Foetida Fiber for Polymer Reinforcement Applications," Journal of Natural Fibers, vol. 20, no. 1, Nov. 2022.

[30] M. Bayart, M. R. Foruzanmehr, P. Y. Vuillaume, P. Ovlaque, M. Robert, and S. Elkoun, “Poly(lactic acid)/flax composites: effect of surface modification and thermal treatment on interfacial adhesion, crystallization, microstructure, and mechanical properties,” Composite Interfaces, vol. 29, no. 1, pp. 17–36, Mar. 2021.

[31] S. Sulardjaka, N. Iskandar, P. Manik, and D. S. Nurseto, “The effect of alkalization and esterification treatment on mechanical properties of water hyacinth fiber reinforced epoxy-resin composite,” Eastern-European Journal of Enterprise Technologies, vol. 1, no. 12 (121), pp. 26–33, Feb. 2023.

[32] Z. Zhang, G. Sèbe, Y. Hou, J. Wang, J. Huang, and G. Zhou, “Grafting polymers from cellulose nanocrystals via surface-initiated atom transfer radical polymerization,” Journal of Applied Polymer Science, vol. 138, no. 48, Aug. 2021.

[33] Z. Zhang et al., “Antibacterial polylactic acid fabricated via Pickering emulsion approach with polyethyleneimine and polydopamine modified cellulose nanocrystals as emulsion stabilizers,” International Journal of Biological Macromolecules, vol. 253, p. 127263, Oct. 2023.

[34] H. C. Kolb, M. G. Finn, and K. B. Sharpless, “ChemInform Abstract: Click Chemistry: Diverse Chemical Function from a Few Good Reactions,” Chem Inform, vol. 32, no. 35, Aug. 2001.

[35] J. E. Moses and A. D. Moorhouse, “The Growing Applications of Click Chemistry,” Chem Inform, vol. 38, no. 44, Oct. 2007.

[36] C. E. Hoyle and C. N. Bowman, “Thiol–Ene Click Chemistry,” Angewandte Chemie International Edition, vol. 49, no. 9, pp. 1540–1573, Feb. 2010.

[37] S. Anand et al., “A continuous interfacial bridging approach to fabricate ultrastrong hydroxylated carbon nanotubes intercalated MXene films with superior electromagnetic interference shielding and thermal dissipating properties,” Advanced Composites and Hybrid Materials, vol. 7, no. 1, Feb. 2024.

[38] X. Meng, Y. Dong, W. Tan, Y. Xia, and L. Liang, “Click-based Chemical Modification of Cotton Fabric and Its Oil/Water Separation Application,” Journal of Natural Fibers, vol. 19, no. 14, pp. 8738–8749, Oct. 2021.

[39] X. Zhang, S. Zhang, S. Zhao, X. Wang, B. Liu, and H. Xu, “Click Chemistry in Natural Product Modification,” Frontiers in Chemistry, vol. 9, Nov. 2021.

[40] M. Wang et al., "Chemical grafting of nano-SiO2 onto graphene oxide via thiol-ene click chemistry and its effect on the interfacial and mechanical properties of GO/epoxy composites," Composites Science and Technology, vol. 182, p. 107751, Sep. 2019.

[41] A. Blal, F. Brouillette, É. Loranger, and G. Lebrun, "Click chemistry modifications for the selective crosslinking of wood pulp fibers - Effect on the physical and mechanical properties of paper", RSC Advances, vol. 14, pp. 9656-9667, 2024.

[42] M. L. Gall, P. Davies, N. Martin, and C. Baley, "Recommended flax fibre density values for composite property predictions," Industrial Crops and Products, vol. 114, pp. 52–58, Feb. 2018.

[43] A. Amiri, Z. Triplett, A. Moreira, N. Brezinka, M. Alcock, and C. A. Ulven, "Standard density measurement method development for flax fiber," Industrial Crops and Products, vol. 96, pp. 196–202, Dec. 2016.

[44] G. Mangiante et al., "Biohybrid cellulose fibers: Toward paper materials with wet strength properties," Carbohydrate Polymers, vol. 193, pp. 353–361, Aug. 2018.

[45] L. Yan, N. Chouw, and K. Jayaraman, "Flax fibre and its composites – A review," Composites Part B: Engineering, vol. 56, pp. 296–317, Jan. 2014.

[46] N. S. A. Rahman, N. A. Ahmad, M. F. Yhaya, B. Azahari, and W. R. Ismail, "Crosslinking of fibers via azide–alkyne click chemistry: Synthesis and characterization," Journal of Applied Polymer Science, vol. 133, no. 25, Mar. 2016.

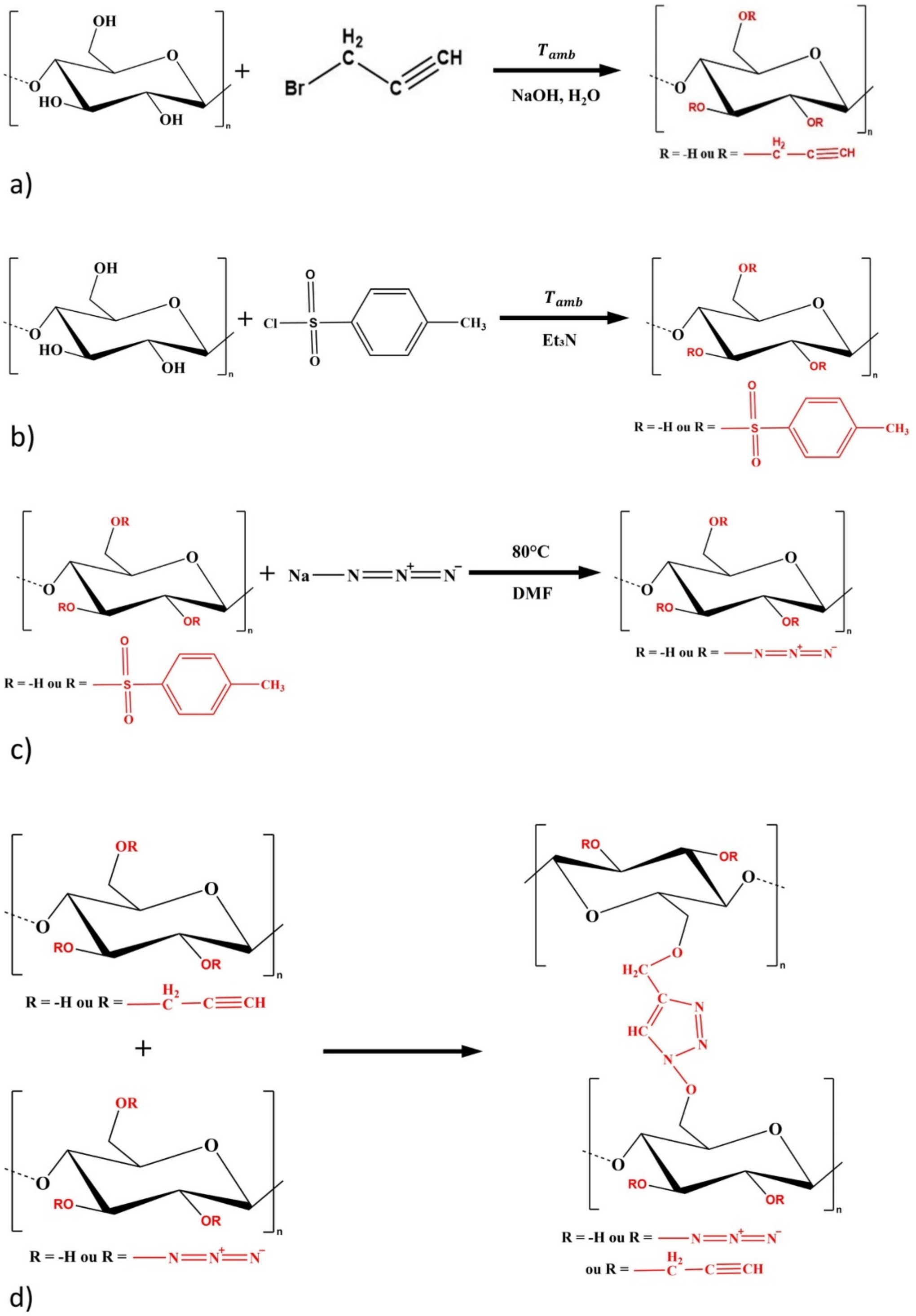

Figure 1. Schematic representation of the chemical reactions involved in the functionalization of cellulose fibers including: (a) Propargylation, (b) Tosylation, (c) Azidation and (d) click chemistry reactions.

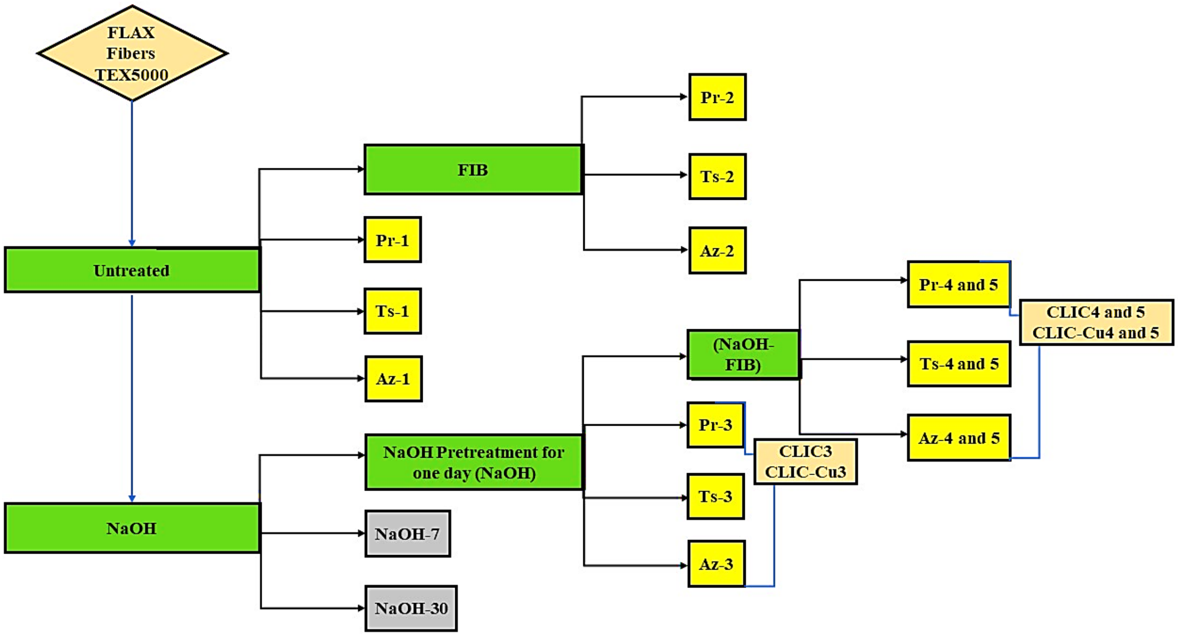

Figure 2. Experimental flowchart of flax fiber treatments.

Figure 3. Overview of the flax fiber mat preparation process. (a) A sample of the initial fiber-water slurry used for mat formation. (b) The dynamic forming machine. (c) The E-100 drum dryer employed for drying the formed mats. (d) An example of the finished flax fiber mat.

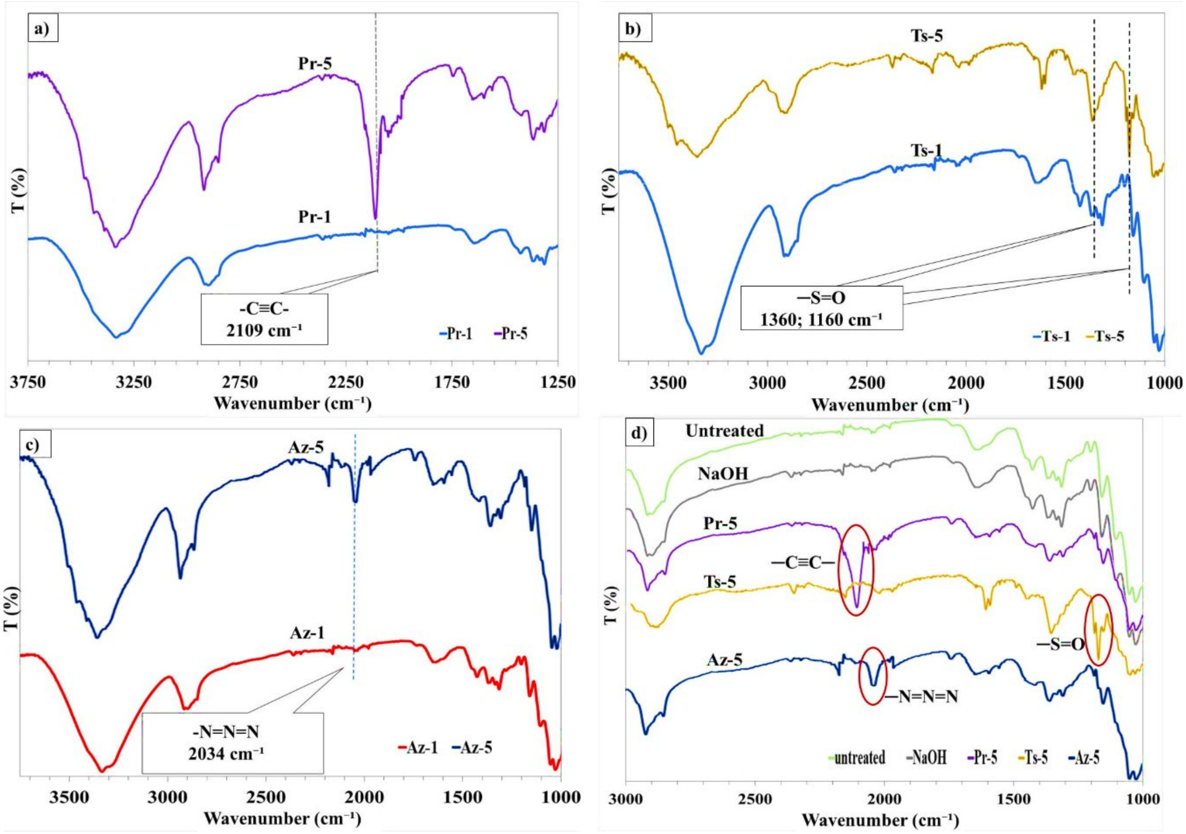

Figure 4. FTIR spectra of flax fibers: a) Propargylation, b) Tosylation, c) Azidation, and d) Global evolution along the modification process.

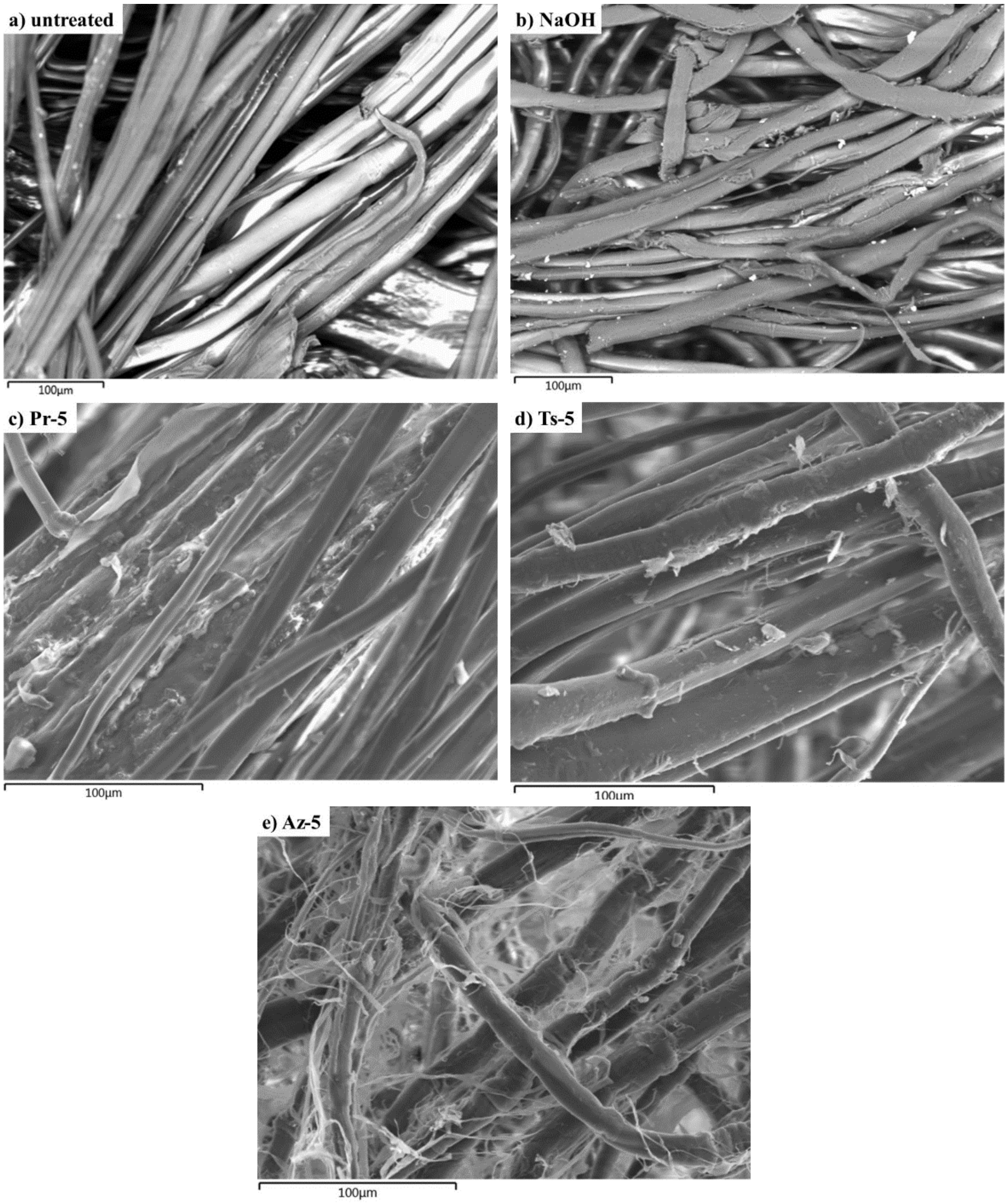

Figure 5. SEM images of untreated (a) and modified flax fibers: (b) pretreated fibers; (c) propargylated fibers; (d) tosylated fibers; and (e) azidated fibers.

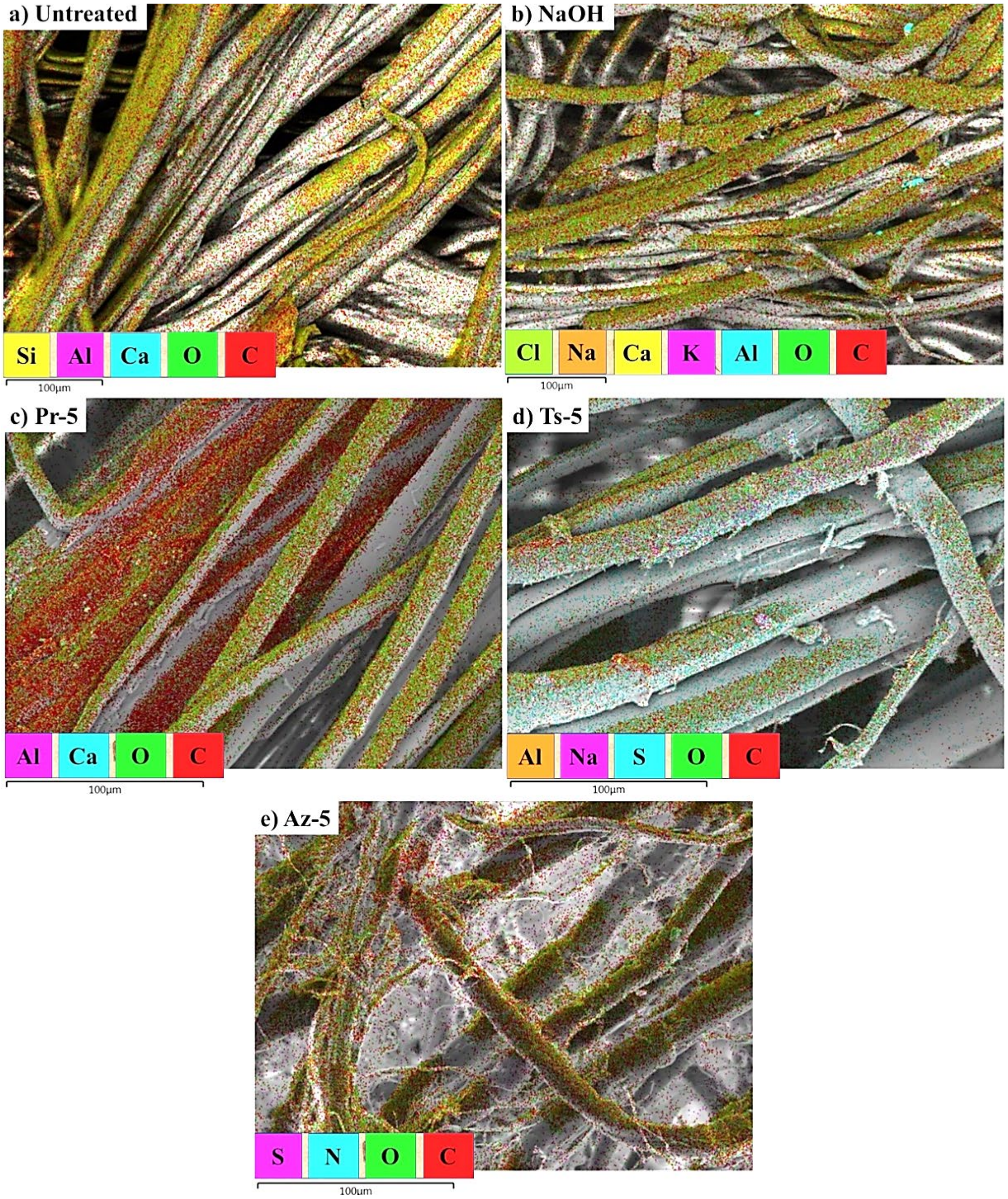

Figure 6. Energy Dispersive X-ray (EDX) mapping of untreated (a) and modified flax fibers: (b) pretreated fibers; (c) propargylated fibers; (d) tosylated fibers; and (e) azidated fibers.

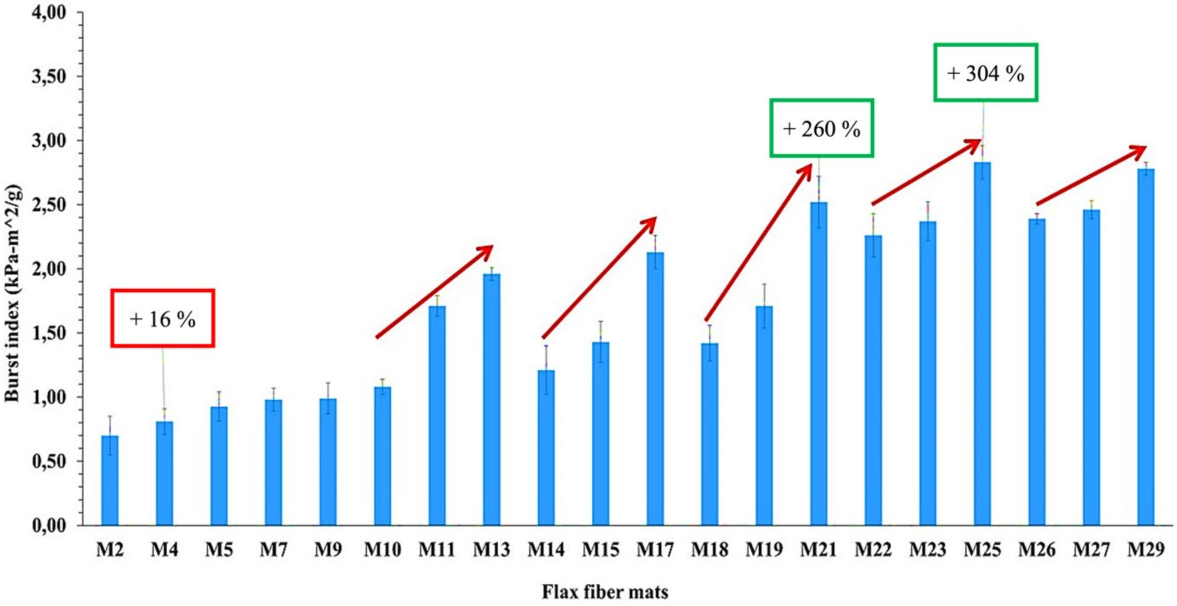

Figure 7. Burst index (kPa-m^2/g) of flax mat made from different fiber types.

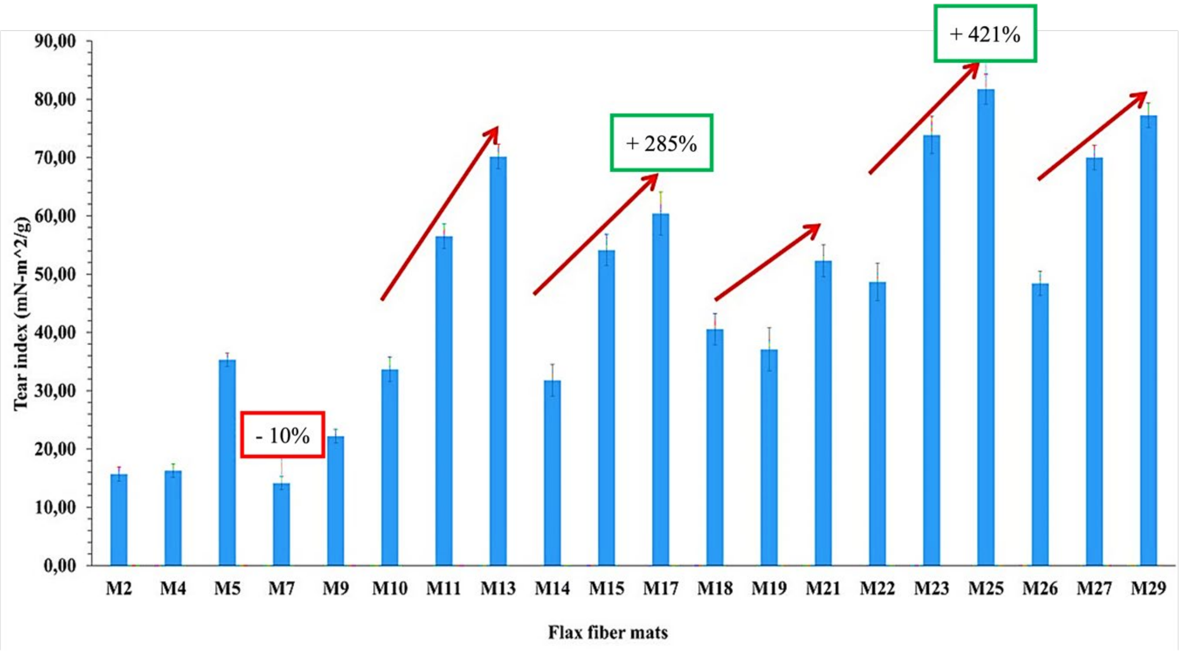

Figure 8. Tear index (mN-m^2/g) of flax mat made from different fiber types.

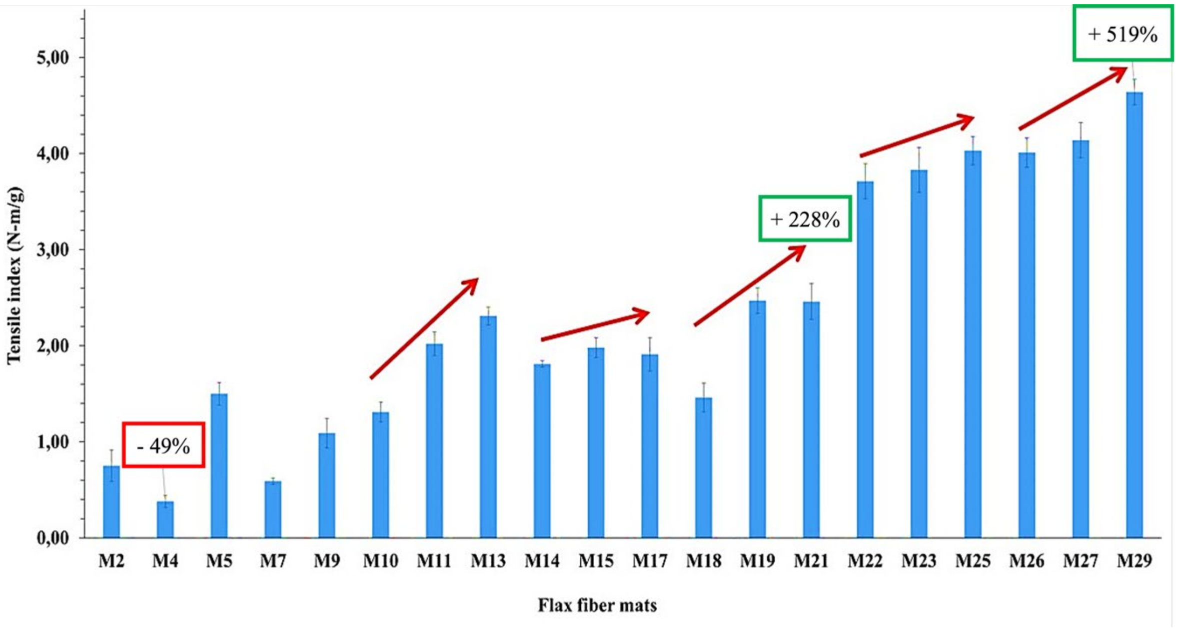

Figure 9. Tensile index (N-m/g) of flax mat made from different fiber types.

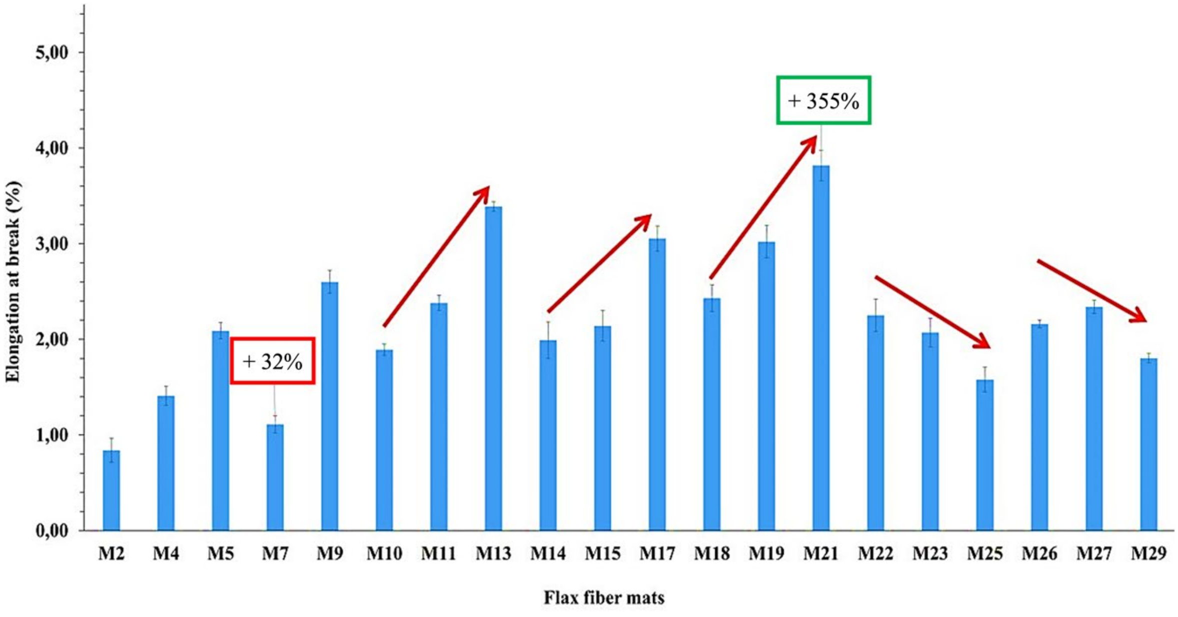

Figure 10. Elongation at break (%) of flax mat made from different fiber types.

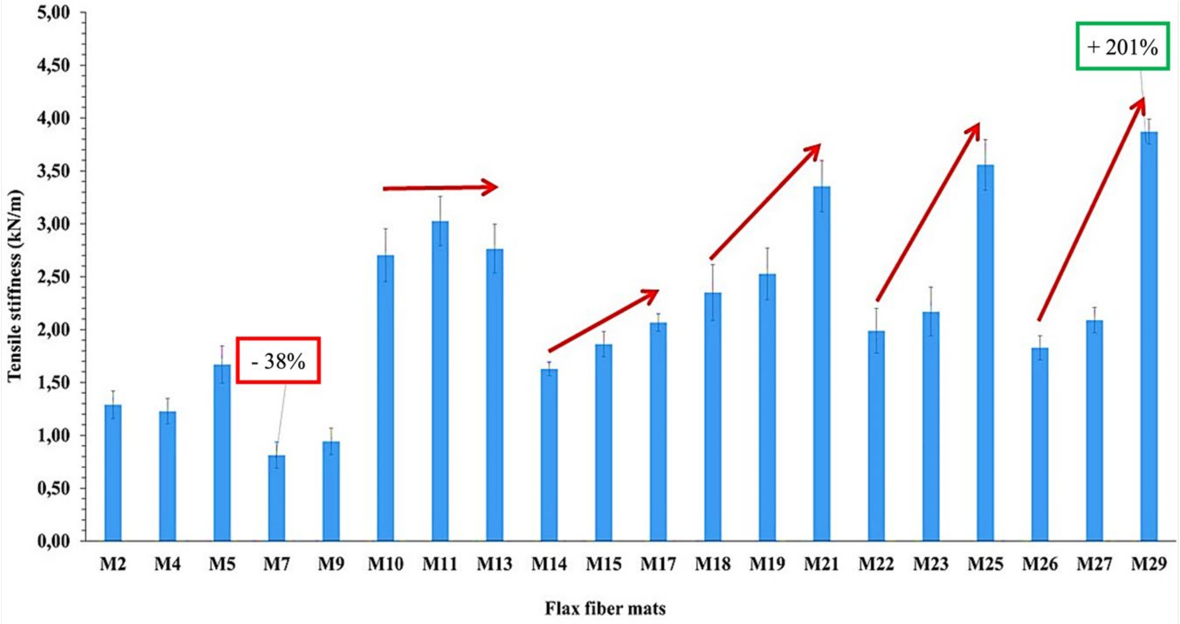

Figure 11. Tensile stiffness (kN/m) of flax mats made from different types of fiber after treatment.

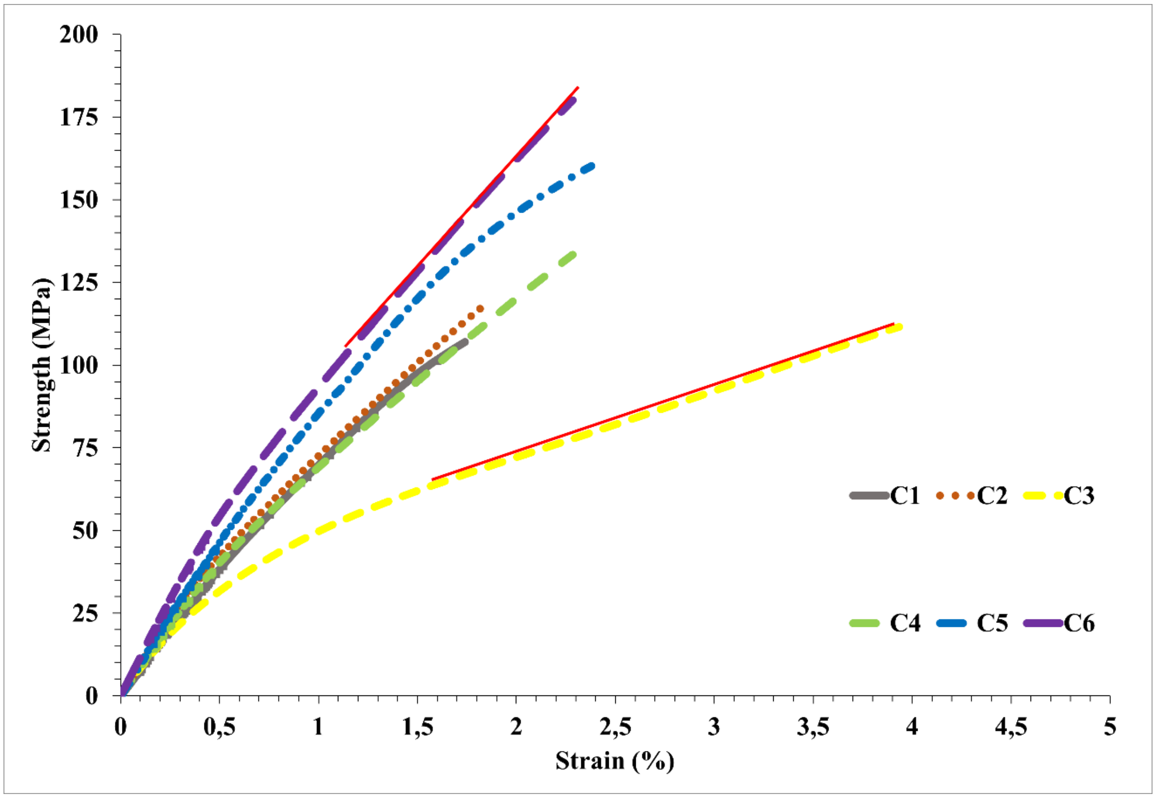

Figure 12. Typical tensile stress–strain curves for untreated and chemical treated flax fiber reinforced composites.

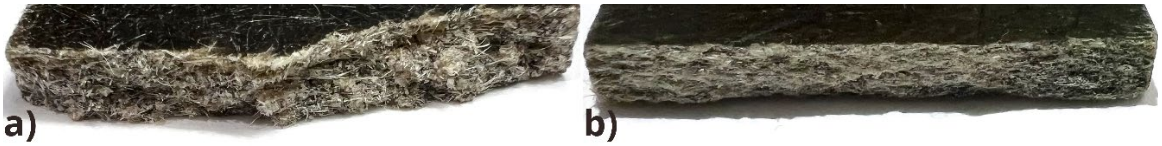

Figure 13. Fracture surfaces of composite specimens: a) C1 (untreated), b) C6 (treated).

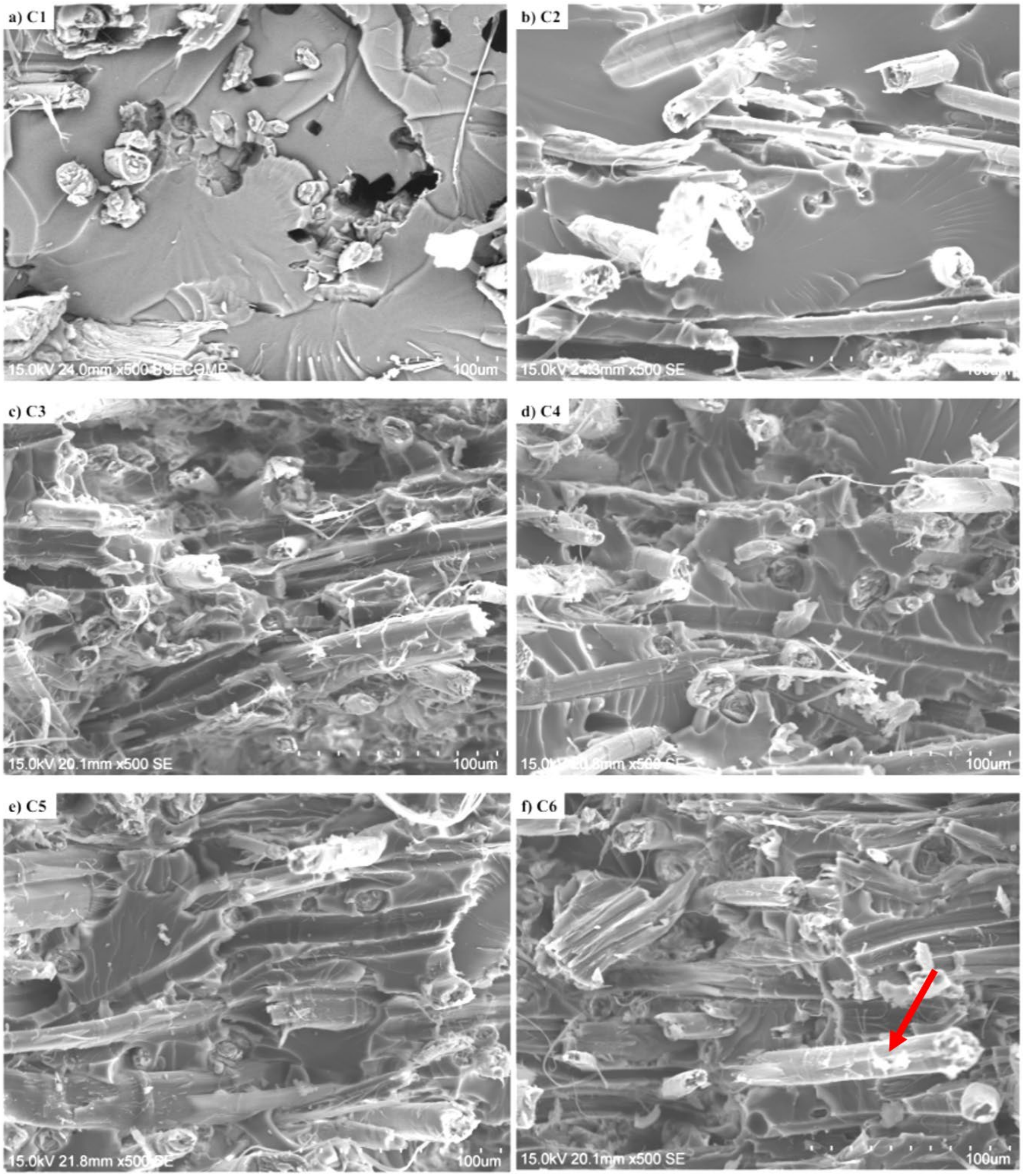

Figure 14. SEM micrographs of mechanically and chemically treated flax-epoxy composites for tests: a) C1, b) C2, c) C3, d) C4, e) C5 and f) C6.

Table 1. Chemical reaction parameters for the different types of fibers.

Chemical reaction	Fiber type (25 g)	Reactant volume/weight	Temp. (°C)	Duration (days)	Designation
Propargylation	Untreated	75 mL PB	RT	4	Pr-1
	FIB	75 mL PB		4	Pr-2
	NaOH	110.4 mL PB		7	Pr-3
	NaOH-FIB	110.4 mL PB		7	Pr-4
	NaOH-FIB	114 mL PB		10	Pr-5
Tosylation	Untreated	104 mL T + 142.2 g TC	RT	5	Ts-1
	FIB	104 mL T + 142.2 g TC		5	Ts-2
	NaOH	136.84 mL T + 181.5 g TC		7	Ts-3
	NaOH-FIB	136.84 mL T + 181.5 g TC		7	Ts-4
	NaOH-FIB	166.37 mL T + 221.06 g TC		10	Ts-5
Azidation	Untreated	32.108 g SA	75°C	7	Az-1
	FIB	32.108 g SA		7	Az-2
	NaOH	40.135 g SA		7	Az-3
	NaOH-FIB	40.135 g SA		7	Az-4
	NaOH-FIB	55 g SA		10	Az-5

Table 2. Test designation. corresponding mat type. and fiber treatment used for dry tests.

Test designation	Mat type	Fiber treatment
M1	Non-compressed mat	Untreated
M2	Compressed mat	
M3	Non-compressed mat	NaOH-7
M4	Compressed mat	
M5	Compressed mat	NaOH-30
M6	Non-compressed mat	FIB
M7	Compressed mat	
M8	Non-compressed mat	NaOH-FIB
M9	Compressed mat	
M10	Non-compressed mat	Pr3
M11		Pr4
M12		Pr5
M13	Compressed mat	
M14	Non-compressed mat	Ts3
M15		Ts4
M16		Ts5
M17	Compressed mat	
M18	Non-compressed mat	Az3
M19		Az4
M20		Az5
M21	Compressed mat	
M22	Non-compressed mat	CLIC3
M23		CLIC4
M24		CLIC5
M25	Compressed mat	
M26	Non-compressed mat	CLIC-Cu3
M27		CLIC-Cu4
M28		CLIC-Cu5
M29	Compressed mat	

Table 3. Density measurements of flax fiber (ten measurements).

Flax fibers Type	**Density (g/cm^3)**
Untreated	1.41 ± 0.03
Fibrillated	1.40 ± 0.02
Click chemistry	1.45 ± 0.04
Propargylated	1.37 ± 0.03
Azidated	1.47 ± 0.08
NaOH pretreated	1.37 ± 0.04

Table 4. Characteristics of prepared composite plates based on flax fiber reinforcement types.

Test designation	**Reinforcement type used**	**V_f calculated from $\rho_{f,S}$ (%)**	**V_f calculated from $\rho_{f,E}$ (%)**	**Plate thickness. h (mm)**
C1	untreated and non-compacted mat (M1)	39.8 ± 0.1	40.5 ± 0.1	2.95 ± 0.08
C2	fibrillated and non-compacted mat (M6)	38.8 ± 0.3	39.7 ± 0.3	2.84 ± 0.04
C3	fibrillated and compacted mat (M7)	41.8 ± 0.4	42.9 ± 0.4	2.68 ± 0.05
C4	NaOH pretreated and click chemistry treated mat (M26)	40.7 ± 0.2	40.5 ± 0.2	2.86 ± 0.03
C5	NaOH. fibrillated pretreated. click chemistry treated. and non-compacted mat (M27)	41.5 ± 0.2	41.3 ± 0.2	2.91 ± 0.06
C6	NaOH. fibrillated pretreated. click chemistry treated and compacted mat (M29)	40.2 ± 0.1	40.0 ± 0.1	2.79 ± 0.03

Table 5. Elemental composition and degree of substitution in modified flax fibers by EDX.

Flax fibers	Element percentage from EDX (%)				O/C	DS
	C	O	S	N		
Untreated	67.10	32.10	N.D.	N.D.	0.48	N.A.
NaOH-7	58.60	40.00	N.D.	N.D.	0.68	N.A.
Pr-1	60.10	39.60	N.D.	N.D.	0.66	1.06
Ts-1	61.80	37.40	0.50	N.D.	0.61	0.51
Az-1	60.40	39.20	0.20	0	0.65	0
Pr-3	62.70	36.90	N.D.	N.D.	0.59	1.66
Ts-3	62.80	35.20	1.60	N.D.	0.56	1.86
Az-3	59.20	31.00	0.40	1.60	0.52	1.62
Pr-5	67.30	32.50	N.D.	N.D.	0.48	2.90
Ts-5	75.80	20.50	2.70	N.D.	0.27	2.85
Az-5	58.50	33.40	0.70	2.90	0.57	2.97
N.D. Not detected. N.A. Not applicable						

Table 6. Mechanical properties of flax mat made from the different fiber samples.

	Burst index (kPa-m^2/g)	**Tear index (mN-m^2/g)**	**Tensile index (N-m/g)**	**Elongation at break (%)**	**Tensile stiffness (kN/m)**
M1	0.68	14.98	0.72	0.79	1.22
M2	0.70	15.69	0.75	0.84	1.29
M3	0.79	16.46	0.34	1.26	1.19
M4	0.81	16.28	0.38	1.41	1.23
M5	0.93	35.31	1.50	2.09	1.67
M6	1.03	14.84	0.52	1.04	0.78
M7	0.98	14.15	0.59	1.11	0.81
M8	0.93	21.82	1.03	2.54	0.92
M9	0.99	22.21	1.09	2.60	0.94
M10	1.08	33.67	1.31	1.89	2.70
M11	1.71	56.51	2.02	2.38	3.03
M12	1.82	68.14	2.23	3.46	2.43
M13	1.96	70.18	2.31	3.39	2.76
M14	1.21	31.77	1.81	1.99	1.63
M15	1.43	54.13	1.98	2.14	1.86
M16	2.06	59.56	1.81	2.96	1.96
M17	2.13	60.40	1.91	3.05	2.07
M18	1.42	40.56	1.46	2.43	2.35
M19	1.71	37.10	2.47	3.02	2.53
M20	2.43	51.40	2.38	3.73	3.26
M21	2.52	52.29	2.46	3.82	3.35
M22	2.26	48.68	3.71	2.25	1.99
M23	2.37	73.88	3.83	2.07	2.17
M24	2.71	80.14	3.93	1.49	3.33
M25	2.83	81.74	4.03	1.58	3.56
M26	2.39	48.40	4.01	2.16	1.83
M27	2.46	70.00	4.14	2.34	2.09
M28	2.67	76.56	4.49	1.76	3.63
M29	2.78	77.23	4.64	1.8	3.87

Table 7. Effect of click chemistry treatment's flax on the tensile properties of mat/epoxy laminated composites.

Composite	MOE (GPa)	Variance (%)	Strength (MPa)	Variance (%)	Strain (%)	Variance (%)
C1	8.0 ± 0.1	---	109.6 ± 7.0	---	1.7 ± 0.1	---
C2	8.9 ± 0.3	11.2	122.4 ± 6.3	11.7	1.6 ± 0.2	-6.4
C3	7.1 ± 0.2	-11.9	113.4 ± 1.3	3.5	4.0 ± 0.2	134.8
C4	8.2 ± 0.4	2.5	135.6 ± 2.5	23.7	2.2 ± 0.1	26.7
C5	9.8 ± 0.7	23	160.2 ± 5.5	46.2	2.4 ± 0.1	38.4
C6	11.3 ± 0.4	41.5	180.1 ± 7.6	64.3	2.3 ± 0.1	30.8