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EFFECT OF CLICK CHEMISTRY MODIFICATIONS AND NANOCELLULOSE INCORPORATION ON THE PERMEABILITY OF MAT AND UNIDIRECTIONAL-MAT FLAX REINFORCEMENTS

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ABSTRACT

In the field of composite materials, the permeability of natural fibre reinforcements is a critical parameter influencing the efficiency of liquid composite molding (LCM) processes such as resin transfer molding (RTM). This study investigates the effects of the Huisgen 1,3-Dipolar Cycloaddition click chemistry reaction and the incorporation of nanocellulose on the permeability of mat (M) and unidirectional-mat (UDM) flax reinforcements. This research encompasses a series of treatments involving fibrillation (FIB), compaction (COMP), and the incorporation of different weight fractions of nanocellulose along with click chemistry modifications (Click) on M and UDM reinforcements. Permeability was assessed using the radial flow method. The introduction of nanocellulose caused a reduction of permeability (Kx and Ky) in UDM of 95 and 96% respectively proportional to the amount added (1,5-9 % w/w) and the degree of reduction correlating with the weight fractions of incorporation. The results indicate that while the mechanical properties of flax reinforcements can be improved by these treatments, their impact on the molding process must also be considered. The results underscore the necessity of aligning mechanical property enhancements with the practical requirements of composite material molding processes.

1 INTRODUCTION

Composite materials, known for their high strength/weight and stiffness/weight ratio, are evolving rapidly with natural fibres emerging as a competitive and sustainable alternative for synthetic fibres, especially glass fibres. This change is primarily promoted by the biodegradability, low prices, and lower environmental impact of natural fibres [1]. However, the widespread use of composite materials is hindered by limitations such as their relatively lower stiffness and strength, their lower adhesion to the polymer matrix and their higher moisture absorption compared to synthetic fibres. To overcome these limitations, it is necessary to improve the properties and modify the characteristics of natural fibres (NFC) through the use of mechanical and chemical fibre surface treatments [2]. One of the strategies for resolving this problem is the use of click chemistry, specifically the Huisgen 1,3-dipolar cycloaddition, which creates strong covalent bonds between an alkyne and an azide, generally with the assistance of a copper catalyst (CuAAC). This approach is known for its efficiency in improving the interfacial bonding of natural fibres, with the potential of enhancing the mechanical properties of dry fibre reinforcements and, by extension, the composite properties [3]. Furthermore, the integration of nanocellulose into the fibre reinforcement presents an opportunity to further reinforce the composite materials. Nanocellulose, due to its high strength and stiffness, can significantly impact the mechanical properties of the fibre reinforcements when appropriately integrated.[4]Treatments applied to the surface of fibres such as the addition of nanocellulose and click chemistry modifications, introduce challenges for the molding of parts with liquid composite molding (LCM) processes, particularly the resin permeability of reinforcements which is a critical factor in resin transfer molding (RTM). Permeability plays a crucial role in determining the efficiency of composites molding, as it influences the filling time, quality, and cost of the molded parts. Previous studies by Bernaoui et al. on flax fibre composites have shown that surface fibrillation of short flax fibres can enhance the tensile properties of UDM flax-epoxy composites, but at the same time reduces the permeability of the reinforcements [5]. Similarly, Mbakop et al. have demonstrated that precompacting the same UDM flax reinforcements can increase the modulus of elasticity and tensile strength, but with a significant decrease in permeability [6].

This work analyses the impact of mat and UDM flax reinforcements modifications on their permeability to liquid resin. Specifically, it looks at the influence of surface fibrillation, precompaction, addition of nanocellulose, and click chemistry surface reaction on the permeability of reinforcements. Such analyses are important because they put into perspective the potential advances in terms of mechanical properties of composites with the important requirements related to part molding. By adding various percentages of nanocellulose while implementing the treatments required for the click chemistry reaction, this work explores avenues to enhance the mechanical properties without compromising the molding capacity.

2 EXPERIMENTAL PROTOCOLS

2.1 Materials.

Flax fibres were sourced from Safilin Inc. (Szczytno, Poland), provided as Tex 5000 ribbon, which were manually cut into short fibres (approximately 6 ± 1 mm in length) for flax mat, and as Tex 400 yarn for the unidirectional (UD) phase of the UDM reinforcement. A nanocellulose gel was prepared from oxidized kraft pulp fibres using a shear processing approach facilitated by an IKA defibrillation system. Chemicals including propargyl bromide (80% in toluene), p-toluenesulfonyl chloride, and sodium azide were purchased from Alfa Aesar (Haverhill, Massachusetts, USA). Sodium hydroxide and copper sulfate ($CuSO4·5H2O$) were obtained from Acros Organics (Geel, Belgium). Dimethylformamide (DMF), sodium ascorbate, and triethylamine were supplied by Sigma-Aldrich (Saint Louis, Missouri, USA). The reinforcements prepared were made of untreated and treated flax fibres, which include the propargylated (Pr), tosylated (Ts), azide-modified (Az), crosslinked (CLICK), NaOH-treated (NaOH for 7 days at 2.5% w/v) and fibrillated fibres (FIB).

2.2 Preparation of nanocellulose.

Nanocellulose gel was prepared, according to the procedure described by Lassoued et al. [7], produced by dispersing 30 g of dry kraft pulp in deionized water, mixing 2.2 g of TEMPO and 5 g of sodium bromide in a minimal volume of water, and adding this to a reactor with enough deionized water to total 3 L at 1% consistency. The mixture was kept at 25°C with a pH between 10 and 11. The oxidation, started with 250 ml of sodium hypochlorite and lasting two hours, was stopped by adding 75 ml of 3% hydrogen peroxide. The oxidized pulp was filtered, weighed, and then processed in a defibrillation system with heat control, resulting in a 2.5% nanocellulose gel with a carboxylate content of 1559.7 mmol/kg after two hours.

2.3 Fibre activation: alkaline pretreatment and fibrillation.

To prepare flax fibres for modifications, 25 g of short fibres were dispersed in 2 L of demineralized water and soaked for a minimum of four hours to ensure thorough saturation. Next, the fibre were treated in a standard disperser for ten minutes at 1000 rpm to create a homogeneous fibre suspension, and subsequently treated mechanically using a PFI laboratory refiner. The fibres were then soaked with stirring in a 5% w/w NaOH solution for 24 hours at room temperature to remove a fraction of other surface components such as pectin, lignin, and hemicelluloses., enhancing hydroxyl group exposure. Following this alkaline treatment, fibres were thoroughly washed with demineralized water and neutralized with acidified water (pH around 4). A final rinse with water was also done to remove any residual chemicals.

2.4 Click chemistry reactions and treatments.

Chemical modifications of flax fibres were achieved through a series of treatments adapted from previous work by Abdelhadi et al. [3]. Propargylated fibres (Pr) were prepared by adding propargyl bromide to a suspension of pretreated fibres, stirred at room temperature for 10 days, and then washed with deionized water and ethanol. Tosylated fibres (Ts) underwent a 24-hour NaOH pretreatment, followed by the addition of triethylamine and tosyl chloride, with the mixture similarly agitated and washed. Azidated fibres (Az) were produced by adding sodium azide to tosylated fibres in dimethylformamide (DMF), heated and stirred, then cooled and cleaned. Cross-linked fibres (CLICK) were created by combining 50 % w/w propargylated and 50% w/w azidated fibres in water stirred for 10 days at room temperature and subsequently washed.

2.5 Characterization of Treated Fibres

Infrared (IR) spectroscopy was conducted using a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer, with 32 acquisitions at room temperature and a resolution of ± 4 cm^{-1}, used to identify the functional groups introduced onto the surface of fibres through the various treatments. Scanning electron microscopy (SEM) assessed the morphological impacts of click chemistry and chemical treatments on fibre morphology, employing a Hitachi SU1510 microscope in secondary electron mode, 100 mA beam current, and 15 kV accelerating voltage. The SEM was equipped with energy-dispersive X-ray spectroscopy (EDX, Oxford X-Max 20 mm^2 instrument) for chemical characterization of a metalized, homogenously ground sample pellet.

2.6 Reinforcement fabrication

Using the chemically and mechanically treated fibres, two distinct types of reinforcements have been fabricated: A short-fibre mat (M) and unidirectional-mat (UDM) flax reinforcements. For both reinforcements, the fabrication process use a dynamic former from ALIMAND Inc. (France). The steps involved in the manufacturing of reinforcements are well described in previous works [5,6] and will not be described in detail here. Using this fabrication process, different reinforcements were produced to investigate the effects of each treatment on the measured permeability. This includes the raw mat reinforcement (used as reference) and a series of chemically and mechanically treated reinforcements: the fibrillated mat (M-FIB), the mat fibrillated and compacted (M-FIB-COMP), the mat with NaOH treatment (M-NaOH), the propargylated mat (M-Pr), tosylated mat (M-Ts), azidated mat (M-Az), and the mat after the click treatment (M-CLICK). Similarly for the UD-mat reinforcement, the list contains the untreated UDM reinforcement (the reference) was fabricated along with variations such as the fibrillated (UDM-FIB), compacted (UDM-COMP), the fibrillated and compacted combination (UDM-FIB-COMP), and the fibrillated with click chemistry treatment (UDM-FIB-CLICK). To evaluate the influence of nanocellulose incorporation, UDM reinforcements with different percent contents of nanocellulose were fabricated, specified as UDM-1,5, UDM-3, UDM-6, and UDM-9, the number corresponding to the weight percentages. Further modifications included the combination of fibrillation, compaction, and 3% nanocellulose (UDM-FIB-COMP-3), as well as the fibrillation, click chemistry treatment and 3% nanocellulose (UDM-FIB-CLICK-3).

2.7 Permeability Measurement

To measure the planar non-saturated permeability of the reinforcements, the radial flow method was employed, allowing for measurements in the longitudinal (in the UD fibre direction) and transverse directions (perpendicular to UD fibres). To mimic the liquid epoxy resin, a 20W-50 grade motor oil was chosen for its hydrophobic nature and low viscosity (440 mPa-s at 21°C). Each reinforcement underwent three individual tests to ensure reliability. Test samples, composed of five layers of 140 mm by 140 mm reinforcements, were perforated at their centre with a 12 mm diameter hole used as inlet cavity. For each test, the evolution of the flow front was recorded on video and subsequently transformed into a sequence of images at one-second intervals. Measurements of the Rx and Ry radii derived from the ellipses allowed the determination of permeability in the longitudinal (Kx) and transverse (Ky) directions.

3 Results

3.1 Chemical Analysis of Treated Fibres

The FTIR spectrum (Figure 1) illustrates the different functional groups in raw and chemically treated flax fibres. The broad band around 3400 cm^{-1}, attributed to O-H stretching vibrations, is observed in all samples, with modifications in the NaOH, Pr and Az treated fibres suggesting changes in hydrogen bonds The peaks near 2900 cm^{-1} correspond to C-H stretching vibrations. After propargylation (Pr), a new peak attributed to the alkyne C≡C stretching appears around 2108 cm^{-1}, confirming the addition of propargyl groups. The azidated (Az) sample shows an absorption band at 2037 cm^{-1}, characteristic of the azide N≡N stretching, verifying the presence of azide groups. Alterations in the C-O-C vibration frequencies and intensities across samples point towards chemical modifications influencing the cellulose structure. This spectral evidence confirm the successful functionalization of flax fibres.

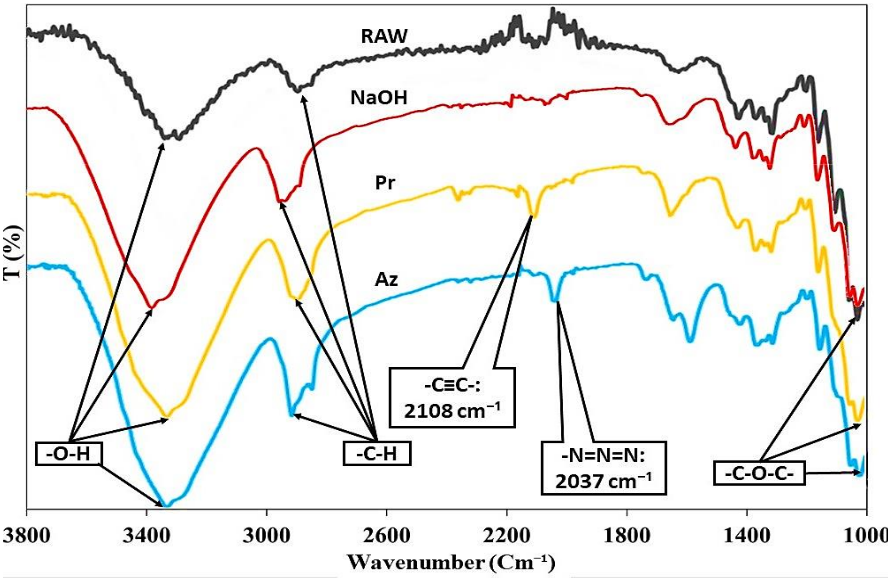

Figure 1. FTIR spectra of unmodified flax (RAW) and modified fibres (NaOH, propargylated (Pr), and azidated (Az)).

Surface and compositional changes in flax fibres due to various chemical treatments were analyzed using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX). The elemental composition of flax fibres as measured by EDX is presented in Table 1. The NaOH treatment increased oxygen content, likely from the exposure of hydroxyl groups after removing non-cellulosic substances. Propargylation followed, significantly increasing carbon content, which lowered the O/C ratio to 0.5 with degree of substitution (DS) of 2.1, suggesting effective substitution with propargyl groups. Tosylation further enhanced carbon levels to 75.3% and introduced sulfur at 2.3%, resulting in the lowest O/C ratio of 0.3 and the DS of 2.3, finally the azidation adjusted the carbon to 61.5% and oxygen to 33.4%, introduced nitrogen at 2.5%, and maintained a slight sulfur presence.

Table 1. Chemical composition and degree of substitution for chemically treated flax fibres.

Modified Flax fibres	Element percentage % (by EDX)				O/C	D.S
	C	O	S	N		
Untreated	67,1	32,1	0,0	0,0	0,5	-
NaOH	58,6	40,0	0,0	0,0	0,7	-
Pr	64,6	35,1	0,0	0,0	0,5	2,1
Ts	75,3	22,5	2,3	0,0	0,3	2,3
Az	61,5	33,4	0,6	2,5	0,5	2,2

3.2 Effect of chemical and mechanical treatments on the permeability of reinforcements

Figures 2 and table 2 show histograms and table values for the permeability of both UDM (Figure 2) and MAT (Table 2) flax fibre reinforcements. They provide a visual representation of how permeabilities in the longitudinal (Kx) and transverse (Ky) directions are affected by the various treatments. The untreated UDM samples showed the highest permeability, with Kx at 4.98×10^{-11} m² and Ky at 0.93×10^{-11} m², highlighting a significant anisotropy favoring the longitudinal direction. Compared to the UDM untreated reinforcement, the mechanical treatments like fibrillation and compaction led to notable permeability decreases of about 29% and 25 % for UDM-FIB-COMP in the longitudinal and transverse directions respectively. The incorporation of nanocellulose (UDM-1.5 to UDM-9) further alters permeability. The UDM-6 shows extremely reduced permeabilities of about 95% for Kx and 96% for Ky, suggesting that the presence of nanocellulose at this concentration fills the gaps between fibres, thus drastically reducing the preform porosity and overall fluid flow. But even at a very low level of 1.5% of nanocellulose, the reduction in Kx reaches about 71%, suggesting that the incorporation of nanocellulose to increase the mechanical properties of composites has a very negative influence on the molding capacity of the fibre-fibre preforms. In consequence, lower levels of nanocellulose addition should be considered to mitigate this effect. The combinations of mechanical and chemical treatments with nanocellulose (UDM-FIB-COMP-3 and UDM-FIB-CLICK-3) also show notable permeability reductions, although these reductions are less pronounced than those observed with higher percentages of nanocellulose alone (UDM-6). For the MAT reinforcements, the highest permeability was observed in the untreated samples. The mechanical processes slightly reduce the permeability by about 76% and 81% in the longitudinal and transverse directions respectively, whereas the chemical treatments, starting with NaOH, induced much more reductions of around 80% and 83%. This could be attributed to the elimination of certain components at the surface of fibres, leading to modifications in the pore structure. The NaOH treatment, followed by propargylation (Pr), tosylation (Ts), azidation (Az), and click chemistry (CLICK) treatments, greatly reduce the Kx and Ky permeabilities. The most significant drop is observed with the CLICK treatment, where permeability falls to 0.22×10^{-11} m² for Kx, and 0.11×10^{-11} m² for Ky, indicating a marked tightening of the porous architecture.

The findings of this study demonstrate that the incorporation of nanocellulose and the application of click chemistry significantly influence the permeability of the studied M and UDM flax fibre reinforcements. This means the use of lower percentages of nanocellulose along with optimized combinations of chemical and mechanical treatments are required to effectively manage the permeability to reach levels acceptable for LCM processes.

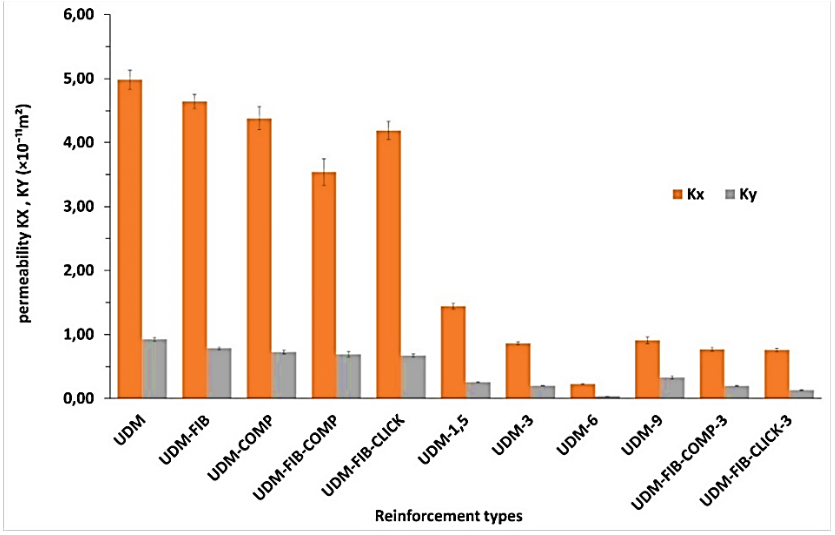

Figure 2. Effect of chemical, mechanical modifications and nanocellulose percentage on the permeability of UDM reinforcements.

Table 2: Effect of chemical, and mechanical modifications on the permeability of MAT reinforcements.

Reinforcement types	MAT	MAT-FIB	MAT-FIB-COMP	MAT-NaOH	MAT-Pr	MAT-Ts	MAT-Az	MAT-CLICK
Kx ($\times 10^{-11}$ m^2)	1,41	1,08	1,06	0,34	0,28	0,29	0,34	0,22
Ky ($\times 10^{-11}$ m^2)	1,20	1,08	0,88	0,23	0,20	0,20	0,22	0,11

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