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EFFECT OF MOISTURE CYCLING DURATION AND TEMPERATURE ON THE STRENGTHENING AND STIFFENING OF CYCLED FLAX FIBRES

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Abstract
The aim of this study was to determine the effect of moisture cycling (environmental relative humidity cycles) on the durability of flax-epoxy composites and investigate the influence of cycling duration and temperature on the stiffening and strengthening of flax fibres. Four moisture cycling protocols for flax fibres were employed in this research which includes 4D21 (4days per cycle at 21°C), 4D60 (4days per cycle at 60°C), 3H27 (3hours per cycle at 27°C) and 3H60 (3hours per cycle at 60°C). To measure the impact of high-low humidity cycling at different cycling durations and temperature, tensile testing of impregnated fibre bundle test (IFBT) samples was done. Results of the back-calculated properties revealed that the applied cycling protocols enhanced both the tensile strength and modulus of the fibres. Better improvement of tensile properties was observed in fibres cycled at longer duration. The fibres undergoing 4 days of cycling at 21ºC (4D21 fibres) showed the highest improvements in tensile strength (18%), as well as tensile moduli E1 (19%) and E2 (18%) after 10 cycles. Interestingly, all fibres showed increased stiffness (E1) in the range of 8-20% after 10 cycles and 4-8% after 20 cycles. This fibreimprovement in mechanical strength and stiffness of the fibres can possibly be attributed to a phenomenon similar to a hornification effect in wood or possibly by fibre repair due to pectin migration, which produces the strengthening and stiffening effect.

1. Introduction

Natural fibre reinforced polymer composites based on renewable sources such as flax fibres, present environmentally friendly solutions with notable specific mechanical properties. However, despite their advantages in lightweight design and cost-effectiveness, their inherent hydrophilic nature poses a significant challenge, leading to moisture absorption and subsequent performance degradation [1-7]. Previous studies have already made attempts to address this issue.

Some related studies investigated the effect of moisture cycling on plant fibre properties but mostly on wood fibres. These studies revealed that exposure to high-low humidity cycling can significantly change the mechanical and physical characteristics of the materials. For instance, research by Stamboulis et al. (2001), Scida et al. (2013) and Ferreira et al. (2017) have demonstrated that moisture cycling can induce a phenomenon known as "hornification" in natural fibres, which can result in increased stiffness and strength. Hornification, a term commonly used in the context of wood and lignocellulosic materials, refers to the irreversible changes in the structure and properties of natural fibres when subjected to drying and rewetting cycles. This process can reduce the fibre's water-uptake capacity and enhance mechanical properties, as reported by several researchers [1,3-10].

This study will aim to investigate the effect of different moisture cycling regiments on the evolution of properties of flax fibre epoxy composites (particularly fibre stiffness and strength). This includes the influence of cycling duration and temperature on the stiffening and strengthening of flax fibres after exposure to alternating relative humidities, based on a recent study [1]. Subsequently, we will aim to unravel the underlying mechanisms behind the previously observed stiffening of the lignocellulosic flax fibres after moisture cycling.

The acquired understanding will pave the way for the development of strategies to further improve the durability of flax fibre reinforced composites when subjected tohigh enviromental humidity variations. Furthermore, the findings of this study can help optimize the performance and long-term reliability of flax-based biocomposites, paving the way for their increased adoption in various applications.

2. Materials and Methods

2.1. Materials

FlaxTape™200, a unidirectional flax fibre tape with an areal density of 200g/m^2 and measuring 400mm in width, was procured from EcoTechnillin. The epoxy resin employed in the research was Epikote™ 828 combined with 1-2-diaminocyclohexane hardener in a ratio of 100 parts resin to 15.2 parts hardener. The potassium salts utilized for the long-duration moisture cycling were sourced from Sigma-Aldrich.

2.2. Moisture Cycling

FlaxTape200 was subjected to alternating high (wetting phase, 85% RH) and low (drying phase, 23% RH) relative humidities. Four moisture cycling protocols (4D21, 4D60, 3H27, 3H60) were implemented to investigate the effect of temperature and duration of cycling on the tensile strength and modulus of flax fibres. The long duration cycling (4 days per cycle, 4D) was done inside salt boxes with standard potassium salt solutions while the short duration cycling (3 hours per cycle, 3H) was done inside a Weiss Technik WKL64 humidity chamber. For the moisture cycling protocol at a lower temperature of 21ºC and 4 days per cycle (4D21), the wetting condition was controlled using potassium chloride, and potassium acetate for the drying step. At an elevated temperature of 60ºC (4D60), high relative humidity was maintained using potassium nitrate, and potassium acetate for the low relative humidity condition. Due to the limitations of the humidity chamber, the shorter duration cycling at lower temperature was set to 27ºC (3H27) instead of 21ºC to attain the same level of low relative humidity (23% RH). The high temperature - short duration protocol (3H60) was maintained at 60°C with the same alternating humidity conditions. The process was repeated for the designated number of cycles for all moisture cycling protocols: C0 (uncycled), C1 (1 cycle), C5 (5 cycles), C10 (10 cycles) and C20 (20 cycles). After each set of cycles, the samples were stored in a conditioned room set at 21ºC and 50% RH.

2.3. Impregnated Fibre Bundle Test (IFBT) Method

The fibre properties were determined through a back-calculation method after impregnating flax fibre bundles within an epoxy matrix based on the rule of mixtures. This method, along with sample preparations, was adapted from ASTM D2343 [1,12]. Flax fibres underwent a pre-drying stage at 60°C for at least 24h. The fibres were cut into 25 cm lengths, and weight measurements were noted to determine the actual fibre volume fraction (v_f) of each specimen after processing using Eq. 1. In the equation below, m_f denotes the mass of the fibre, ρ_f stands for the density of the fibres (1.45 g/cm^3), m_c is the mass of the composite, and ρ_m indicates the density of the epoxy matrix (1.16 g/cm^3). The targeted v_f for each test sample was 40%.

$$v_f(\%) = \frac{\frac{m_f}{\rho_f}}{\frac{m_f}{\rho_f}+\frac{m_c-m_f}{\rho m}}\ x\ 100 \quad (1)$$

A thin coating of release agent (Chemtrend Chemlease® PMR 90 EZ) was applied on the IFBT moulds, countermoulds, vacuum films and metals spacers before usage for easy removal and to prevent damage of the composites when demoulding the samples afterwards. The pre-conditioned fibres were placed inside the mould cavities lined with vacuum film. Homogenized epoxy resin was poured onto the fibres ensuring it thoroughly saturated the entire bundles. A counter mould was applied on each cavity and metal spacers were placed at both ends of the mould cavities to maintain a consistent composite thickness of 2mm. Curing was carried out at 70°C for 1 hour, followed by post-curing at 150°C for another hour. Then, the samples were allowed to cool down before removing from the mould to prevent any thermal effects. The cured IFBT samples were then conditioned at standard conditions of 21ºC and 50% RH for at least a week before undergoing mechanical testing [1]. All tests were conducted on six samples, and mean values were computed.

2.4. Tensile Test

ASTM 3039 standard was used as basis for performing the tensile tests on the IFBT samples (250 mm × 10 mm × 2 mm) with a gauge length of 150 mm. The impregnated fibres were tested using a universal testing machine (Instron 5567) equipped with a 30 kN load cell and operated at a cross-head speed of 2 mm/min. To prevent slippage, rectangular end tabs were put at the ends of the specimens using Araldite® epoxy adhesive. Strain measurement was facilitated using an extensometer with a 50 mm gauge length. Tensile modulus and tensile strength for each cycled fibre were back-calculated using Equations 2 and 3, employing the rules of mixtures. E_f represents the stiffness of the fibre in the longitudinal direction, E_C is the modulus of the composite, and E_m signifies the stiffness of the matrix. Additionally, σ_f is the longitudinal strength of the fibre, and σ'_m represents the stress in the matrix at the failure strain, where $\sigma'_m = E_m * \varepsilon_c$. Furthermore, σ_c and ε_c are the strength and strain at failure of the composite, respectively. For tensile modulus, both E1 (Young's modulus) and E2 (elastic modulus associated with non-linear behavior) were computed [1,12-13].

$$E_f = \frac{E_c - E_m * (1-v_f)}{v_f}\ x\ 100 \quad (2)$$

$$\sigma_f = \frac{\sigma_c - \sigma'_m * (1-v_f)}{v_f}\ x\ 100 \quad (3)$$

2.4. Scanning Electron Microscopy

Scanning electron micrographs were taken to analyze the fibre microstructure, topography and internal features of a fractured C10 IFBT composite. The sample was examined using a Philips XL-30 FEG scanning electron microscope. Before SEM analysis, the sample was first degassed and coated with gold using a plasma sputter coater to enhance its conductivity. High-resolution images were obtained using a 10kV acceleration voltage and a back-scattered electron (BSE) detector. The BSE detector aided in achieving excellent image contrast and depth analysis.

3. Results and Discussion

3.1. Tensile Properties

Tensile testing was performed after each set of moisture cycles (C0, C1, C5, C10 and C20) to assess its impact on the durability of flax fibres. Results of the impregnated fibre bundle tests, used to back-calculate the tensile properties of the flax fibres, demonstrated significant stiffening and strengthening of the moisture-cycled fibres after several cycles. Figure 1 summarizes the tensile strength of the fibres while Figure 2 shows tensile moduli from the four moisture cycling protocols.

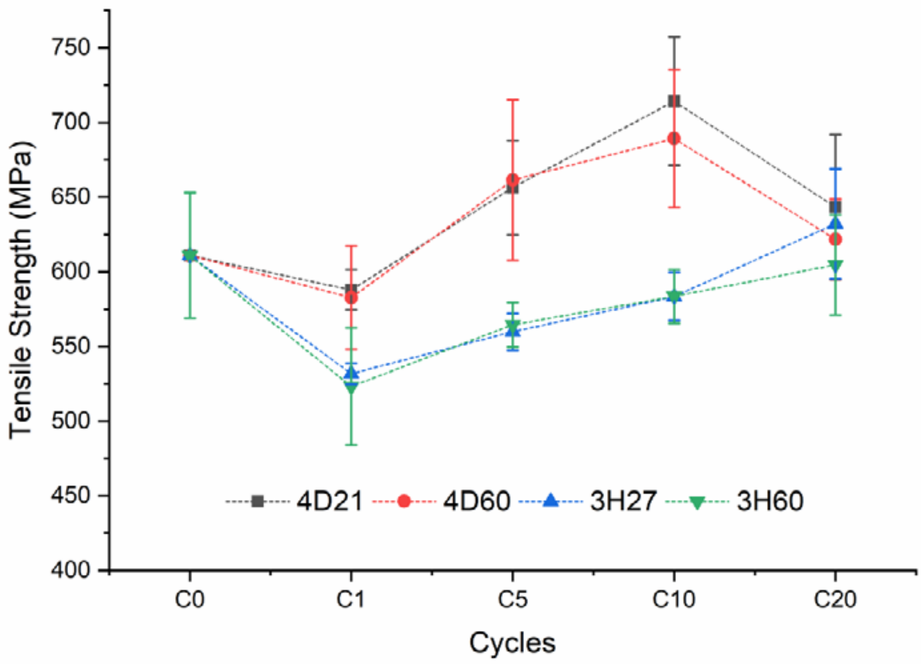

Figure 1. Tensile strength of moisture-cycled flax fibres.

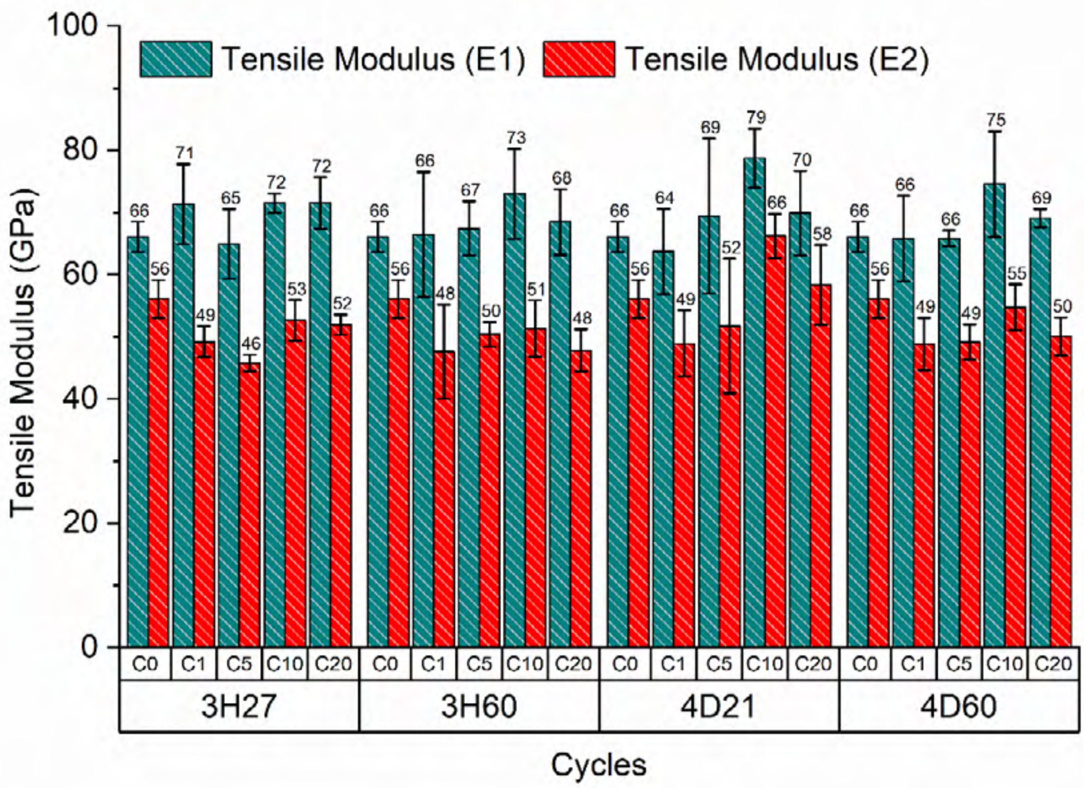

Figure 2. Tensile moduli of moisture-cycled flax fibres.

After one high-low relative humidity cycle, there is a noticeable decrease in the tensile strength which is due to the damage caused by the swelling and shrinking of fibres [2]. Interestingly, subjecting the fibres to repeated cycles of high and low humidity environments led to a phenomenon akin to "fibre repair" on both stiffness and strength. After some time, the fibre properties exhibited an upward trend. Figure 1 demonstrates the remarkable increase in fibre strength, with enhancements of 18% (C10-4D21) and 13% (C10-4D60) after ten cycles. An increase of 7% (C10-4D21) and 8% (C10-4D60) were also observed after five cycles. Moreover, even after twenty cycles, the fibers continued to show indications of repair, ranging from 2 to 5 percent. It shows that 10 cycles is the optimum number of high-low humidity cycles for 4D flax fibres. This result is similar to the research findings of Ferreira et. al (2017) on sisal fibres after wetting (water immersion, 22°C, 3h) – drying (oven-drying, 80°C, 16h) treatments which improved its bond mechanisms. For overall mechanical performance, they concluded that 5 cycles for both curaua and sisal fibres produce enhanced properties [5]. It is also apparent from Figure 1 that longer duration cycling (4D) results in greater improvements in tensile strength. It is possible that 1.5h at high %RH and 1.5h at low %RH of the 3H moisture cycling protocols is insufficient to prompt the fibre repair effect. Moreover, while an increase in temperature might have been expected to affect this phenomenon, the results contradicted this hypothesis. While temperature elevation enhance diffusion, the damage caused by the increased water uptake was balanced by the fibre repair effect. In a related study, Scida and colleagues observed a marginal increase in mechanical property reduction of flax-epoxy composites after hygrothermal ageing (40°C, 90%RH, around 40 days) [4]. In this study, 4D21 fibres showed higher improvements in tensile properties than 4D60 due to more degradation at higher temperature. During shorter duration cycling, the effects were not significant because of the brief exposure to high relative humidity conditions.

Figure 2 clearly illustrates significant improvements in tensile modulus (E1) of all moisture cycled fibres and is independent on both temperature and cycling duration. For all moisture cycling protocols, highest E1 improvements were observed after ten cycles. The fibres exhibited stiffness enhancements of 20% (C10-4D21), 13% (C10-4D60), 11% (C10-3H60) and 8% (C10-3H27) after ten cycles. Furthermore, twenty cycles of exposure to high-low relative humidities produced an improvement of 8% (C10-3H27), 6% (C10-4D21), 5% (C10-4D60) and 4% (C10-3H60). The observed increase in stiffness values and strength is similar to improvements during wood hornification which is attributed to increased hydrogen bonding in literature. This increase in hydrogen bonding results to increase in dimensional stability of the fibres [5].

The observed strengthening and stiffening effect could be due to changes in the distribution and chemistry of the primary constituents of flax, such as pectin, cellulose, lignin, and hemicellulose, accompanied by changes in the microstructure of the flax fibres. It is known from wood hornification that lignin and hemicellulose inhibits this phenomenon by preventing hydrogen bond formation affecting the cross-linking between the cellulose microfibrils [8-9]. The role of pectin in this strengthening and stiffening effect is also considered. Hornification in flax fibres may be linked to the migration of pectin, which fills gaps and defects within the fibres. This process contributes to the fibre repair effect observed after exposure to high-low humidity cycling. It was also found in a recent study that residual pectin improved the storage modulus of cellulose nanofibril dispersions from ramie fibres indicating more rigidity and better mechanical strength [14]. The reason for the improvement in stability and strength is the possible formation of pectin-hemicellulose/lignin-cellulose composite nanostructure.

3.2. Fibre Microstructure

Figure 3a shows perfectly straight and well-aligned fibres within the composite which could possibly explain the remarkable tensile strength and modulus of C10 fibres [1]. This good orientation of the fibres might have facilitated better load transfer and uniform load distribution. Additionally, it reveals properly impregnated fibres, suggesting the possibility of good adhesion between the fibers and the matrix. Future research will aim to validate this through adhesion tests. Figure 3b shows fibre shear failure due to misalignment caused by the force from matrix cracking (shown in Figure 3c) in the surrounding region.

But no obvious differences between samples subjected to the various regimes of cycling could be seen, so the exact mechanism of the fibre improvement upon cycling stays as yet elusive, and is subject to further research.

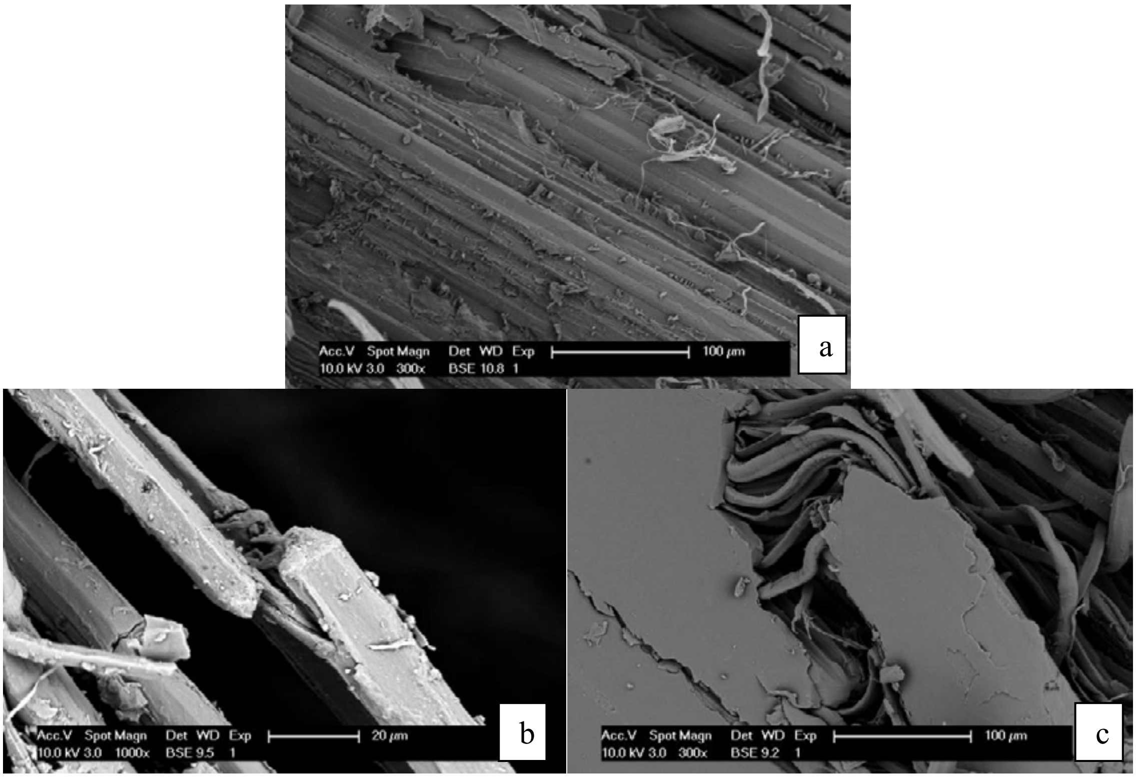

Figure 3. C10 IFBT composite (a) straight and aligned fibres, (b) fibre failure, (3) matrix crack.

Conclusion

This research employed the Impregnated Fibre Bundle Test (IFBT) method to determine fibre stiffness and strength using a fibre volume fraction of approximately 40%. Four moisture cycling protocols: 4D21(4days per cycle at 21°C), 4D60 (4days per cycle at 60°C), 3H27 (3hours per cycle at 27°C) and 3H60 (3hours per cycle at 60°C) were implemented in this study. Flax fibres were subjected to different number of cycles (C0, C1, C5, C10 and C20) of alternating high (85%) and low (23%) humidities. Analysis of the back-calculated properties from flax-epoxy composites revealed that the applied cycling protocols enhanced both the tensile strength and modulus of the fibres. The apparent fibre repair effect on tensile strength is more pronounced at longer duration cycling after 10 cycles with values of 18% (C10-4D21) and 13% (C10-4D60). Even after 20 cycles, good improvements were still observed compared to untreated fibres C0. For tensile modulus, all cycling protocols produced significant increase in stiffness. The improvement in stiffness values is in the range of 8-20% and 4-8% after 10 and 20 cycles, respectively. This strengthening and stiffening is comparable to wood hornification which is attributed to increased and permanent hydrogen bonds as mentioned in previous studies. Alternatively, the role of pectin migration contributing to a fibre repair effect will be the subject of future studies. The strengthening and stiffening effect could be due to changes in the distribution and chemistry of the primary constituents of flax, such as pectin, cellulose, lignin, and hemicellulose, accompanied by changes in the microstructure of the flax fibres.

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