NON-DRIED FLAX FIBRE REINFORCED THERMOPLASTIC COMPOSITES IN WET ENVIRONMENTS

Farzin, Javanshour[a], Alexandros, Prapavesis[b], Rama Kanta, Layek[c], Aart Willem, Van Vuure[b], Essi, Sarlin[a]

a: Department of Materials Science and Environmental Engineering, Tampere University, Tampere, Finland – farzin.javanshour@tuni.fi

b: Department of Materials Engineering, KU Leuven, Heverlee, Belgium

c: Department of Separation Science, LUT University, Lahti, Finland

Abstract: *The long-term performance of natural fibre reinforced thermoplastic (NFRP) composites is critical for developing more sustainable structures. The defects developed in NFRP due to fibre swelling and shrinkage in wet service conditions constitute a significant issue. Here, a method for restricting the in-service swelling and shrinkage of NFRP is proposed. The NFRP composites were processed with swollen fibres stored in moist conditions before thermoplastic resin infusion. The swelling of water-saturated NFRP was decreased up to 56% by non-dry fibres. The similar in-plane shear strength and transverse tensile strength of NFRP composites processed with oven-dried and preconditioned fibres (at 50% RH) showed the in-situ polymerisation of poly (methyl methacrylate) (PMMA) to be insensitive to moisture. Processing composites with preconditioned fibres (at 90% RH) decreased the water immersion ageing sensitivity for in-plane shear properties of NFRP from 30% to nearly zero.*

Keywords: Biocomposites; Adhesion; Durability; Mechanical testing; X-CT analysis

1. Introduction

Flax fibre reinforced thermoplastic (NFRP) composites offer low density, good stiffness and damping properties for structural applications [1,2]. The thermoplastic infiltration is often realised at elevated temperatures (above 100 °C). The intrinsic moisture bound to hydrophilic fibres is removed by oven-drying to avoid processing induced porosities due to fibre moisture evaporation. The water absorption of composites processed with oven-dried fibres can create residual stresses (up to 11 MPa, for 50% RH [3]) due to the high radial swelling coefficient of flax fibres ($\beta_{f,r}$: 1.9 [4]). Such residual stresses can create matrix cracking and debonding around fibre and matrix interface [4]. The hydrothermal swelling of NFRP can be restrained by using high stiffness polymer matrix systems [5] and potentially using swollen (namely non-dry) fibres [6]. The advantages of processing NFRP with non-dry fibres are not yet explored.

In this article, the hydrothermal durability of non-dry flax fibre reinforced poly (methyl methacrylate) (PMMA) thermoplastic composites was investigated. It was hypothesised that in-situ polymerisation of PMMA could be insensitive to water molecules as the MMA monomers are emulsion polymerised in an aqueous medium [7]. The microstructure of composites was studied by X-ray computed tomography. The hydrothermal durability of composites was studied by the water immersion method. The effect of ageing on the interfacial adhesion of composites was studied based on quasi-static in-plane shear and transverse tensile testing.

  doi:10.5075/epfl-298799_978-2-9701614-0-0

2. Materials and methods

Non-crimp flax yarn fabrics of unidirectional (UD) types with an areal density of 300 g/m^2 were provided by Bcomp (Fribourg, Switzerland). A liquid thermoplastic resin based on methyl methacrylate (Elium® 188, Arkema, Colombes, France) and an organic dibenzoyl peroxide powder with phthalate (BP-50-FT1, United Initiators GmbH, Pullach, Germany) with 3 wt% initiator to resin ratio were used as the polymer matrix system. The in-situ polymerisation of Elium® 188 was realised at 23 °C to reduce moisture evaporation present in non-dry flax fibres. The resin system in this article (Elium® 188) was named PMMA throughout the text.

Flax fibre reinforced PMMA composite panels with a fibre volume fraction (V_f) of 40% were manufactured based on the vacuum-assisted resin infusion (23 °C, 0.6 bar vacuum pressure) method. After infusion, composites were placed in a hydraulic press with steel-made spacers (2 mm in thickness) to assure consistent thickness values. Composites manufactured with oven-dried fibres (115 °C, 2 h), fibres preconditioned at 50% RH (23 °C, 24 h), and fibres preconditioned at 90% RH (23 °C, 24 h) were respectively labelled as Dry, RT, and RH. The moisture content of fibres was measured by an analytical balance (model GR-202, A&D Ltd, Tokyo, Japan). For these measurements, the average weight for three pieces of fabrics (10 mm × 10 mm; width × length) was measured consecutively after oven-drying and humidity conditioning. The weight gains of RT and RH fabrics after conditioning were respectively 8.1 ± 0.2 wt% and 16.8 ± 0.2 wt% compared to oven-dried (Dry) fabrics. After manufacturing, composite laminates were stored at 50% RH (23 °C) for three months to reach equilibrium before ageing and mechanical testing. Upon reaching equilibrium, the composites' microstructure and fibre volume fraction were characterised by X-ray computed (X-CT) tomography (Phoenix Nanotom, General Electric, Germany). All humidity conditioning protocols were performed in a humidity chamber (model VC 0018, Vötschtechnik, Balingen, Germany).

The hydrothermal ageing of composites was performed by immersing the panels into a sealed container filled with deionised water at 23 °C for 40 days. Prior to the water immersion ageing, the free edges of composites panels were sealed with PMMA resin. The weight gain of the panels was measured in 2 h intervals during the first day and then in 24 h intervals for the remaining period. The surface water of the panels was wiped before weight measurements. The thickness swelling of the panels right after the saturation point was measured with a micrometre. Composite panels were then stored in 50% RH (23 °C) for two months to reach equilibrium.

Quasi-static tensile testing was carried out with a universal tester (model 5967, Instron, MA, USA). The effect of water immersion ageing on the interfacial adhesion in composites was examined based on quasi-static transverse tensile testing (with $[90]_4$ composite lay-up, 500 N load cell, and 1 mm/min crosshead movement rate) and in-plane shear testing of composites (with $[+45/-45]_{SE}$ lay-up, 30 kN load cell, and 5 mm/min crosshead movement rate) according to ASTM D3039 and ASTM D3518 standards, respectively. Full-field deformation was measured with a stereo optical extensometer (StrainMaster Compact, LaVision, Göttingen, Germany).

Rectangular-shaped specimens with dimensions of 150 mm × 25 mm × 2 mm and 200 mm × 25 mm × 2 mm (length × width × thickness) were prepared respectively for transverse tensile and in-plane shear testing. Specimens were cut from the composite panels with a band sawing machine (model RBS904, Ryobi). Tapered glass epoxy tabs were used to reduce the stress concentration at the gripped section of the specimens.

3. Results and discussions

3.1 X-ray computed (X-CT) tomography of composites

The internal microstructure of flax PMMA composites processed with oven-dried (namely Dry) fibres and precondition fibres (namely RH) after three months of stabilisation at 50% (23 °C) are presented in Figure 1. Both composites are almost free of voids regardless of the initial fibre moisture content during flax PMMA resin infusion. The void-free structure of composites indicates that the in-situ polymerisation of PMMA is not sensitive to the presence of moisture. The moisture insensitivity of the resin can be relevant to the synthesis type of methyl methacrylate, which is emulsion polymerisation in an aqueous medium [7]. Minimal traces of interfacial debonding between fibre and matrix are evident within fibre yarns in Dry composite (Figure 1A). Those limited debonding lines (cracks) in Dry-type composite can be related to the swelling of oven-dried flax fibres during the stabilisation period at 50% RH. On the contrary, highly swollen RH fibres have shrunk during the drying (stabilisation) period at 50% RH (Figure 1B). The extensive interfacial debonding lines (cracks) within fibre yarns are evident for RH-type composite. The average size of crack openings (width) in RH is 9.7 ± 3.1 µm, which is 177% higher than the average crack opening size in Dry-type composite (3.5 ± 0.3 µm). The large debondings can dramatically reduce the interfacial shear strength of RH composites. The results here accentuate the significance of hygroscopic residual stresses in non-dry flax PMMA composites due to flax fibres' high radial swelling coefficient ($\beta_{f,r}$: 1.9 [4]).

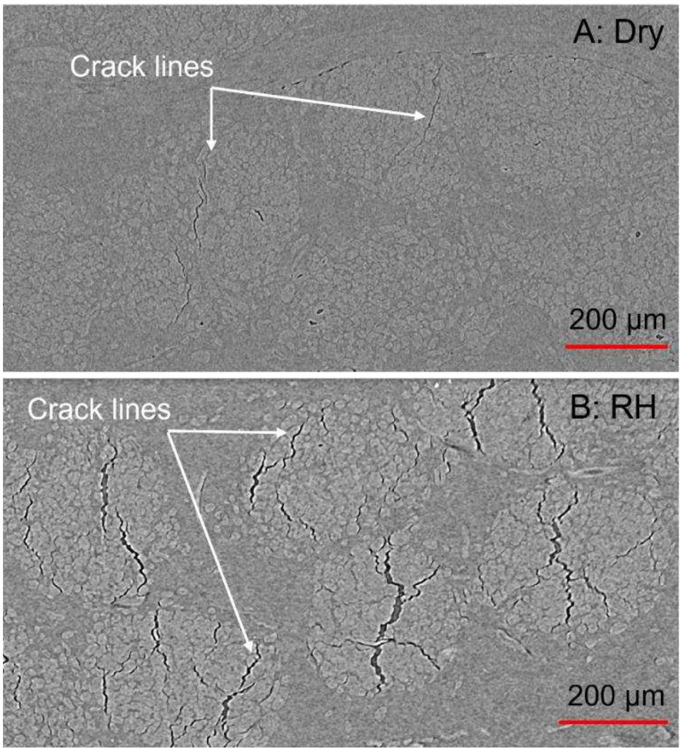

Figure 1. Non-destructively captured microstructure of composites based on X-CT after three months stabilisation period at 50% RH (23 °C).

3.2 Water sorption characteristics of composites

The water sorption-time histories of flax PMMA composites are presented in Figure 2A. After reaching equilibrium (at 50% RH, 23 °C for three months), the composites' moisture content is

  doi:10.5075/epfl-298799_978-2-9701614-0-0

shown as zero water sorption. Composites stabilise after the first 4 days of rapid water sorption and reach the saturation point with weight gain of 9.6% (Dry), 9.1% (RT), and 8.9% (RH) after 28 days. Processing composites with swollen (non-dry) RT and RH fibre reduces the thickness swelling at the saturation point of flax PMMA by 47% and 56%, respectively (Figure 2B). In conclusion, processing composites with swollen (non-dry) fibres limited the hygroscopic swelling and shrinkage of composites which can reduce the hygroscopic residual stress-induced defects.

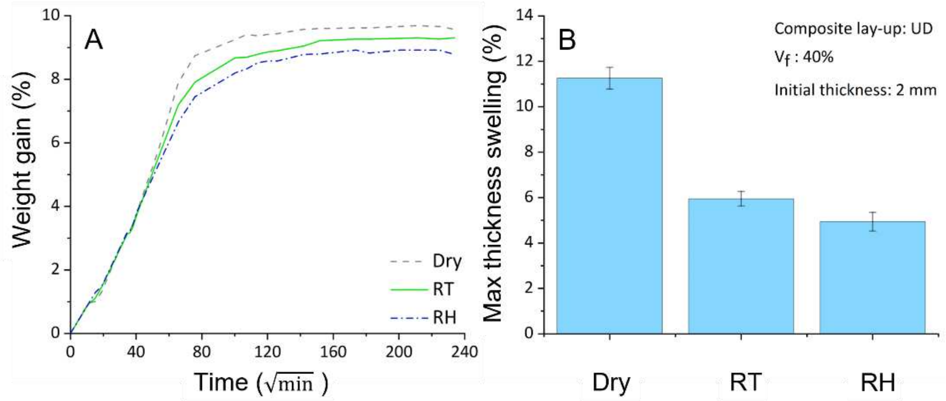

Figure 2. Water sorption-time history (A) and thickness swelling of composites (B)

3.3 Transverse tensile properties of composites

The transverse tensile strength (S_T) and elastic modulus (E_T) values of flax PMMA composites are presented in Figure 3. Before water immersion ageing, composites processed with oven-dried fibres (namely Dry) and conditioned fibres at 50% RH (namely RT) have similar transverse tensile strength (Dry: 14.5 ± 0.3 MPa, and RT: 13.7 ± 0.5 MPa) and elastic modulus (Dry: 3.1 ± 0.3 GPa, and RT: 3.1 ± 2 GPa) values. It is worth noting that the transverse tensile moduli of Dry and RT composites are in the same range as the tensile elastic modulus of the matrix (E_{PMMA}: 3.17 ± 0.2 GPa). Similar S_T and E_T values of RT and Dry composites show that in-situ polymerisation of PMMA is not sensitive to fibre moisture during resin infusion. However, the RH composites processed with non-dry fibres conditioned at 90% RH have 38% and 48% lower S_T and E_T than Dry composites. RH's inferior S_T and E_T values can be ascribed to the debonding cites between fibre and matrix (see Figure 1) due to the shrinkage of highly swollen RH fibres from 90% RH during manufacturing to 50% RH during the stabilisation period.

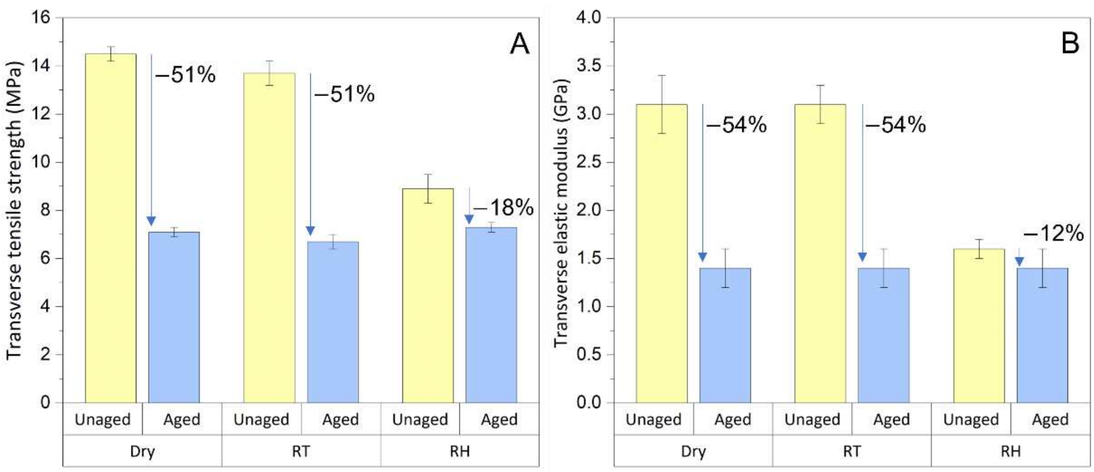

Figure 3. Transverse tensile strength (A) and elastic modulus (B) of flax PMMA composites

In Figure 3, the S_T and E_T properties of Dry and RT composites deteriorate by approximately 50% after one ageing cycle, including 40 days of water immersion, followed by a stabilisation period of 2 months at 50% RH (23 °C). For the similar ageing cycle, the deterioration in S_T (18%) and E_T (12%) properties of RH composites is notably limited compared to Dry and RT. Interestingly, the S_T and E_T properties of Dry, RT, and RH are in the same range after one water immersion ageing cycle.

In summary, the processing of flax PMMA composites with non-dry fibres conditioned at 50% RH did not alter composites' interfacial adhesion (based on S_T values). Especially, similar E_T values of Dry and RT composites indicated that in-situ polymerisation of PMMA is not sensitive to moisture. After one cycle of water immersion ageing, the S_T and E_T values of composites were in the same range regardless of the initial moisture content of fibres during the resin infusion. The mechanical performance of RH composites was relatively stable before and after the water immersion ageing.

3.4 In-plane shear properties of composites

The typical representative in-plane shear stress-strain curves of flax PMMA composites with $[+45/-45]_{SE}$ lay-up are presented in Figure 4. In this section, the offset in-plane shear strength (τ_{12}^{offset}) is defined as the stress value at 0.2% engineering shear strain. The maximum in-plane shear strength (τ_{12}^{max}) is defined as the stress value at 5% engineering shear strain according to the testing standard (ASTM D3518). The shear chord modulus of elasticity (G_{12}^{Chord}) is determined in the engineering shear strain range of 2000 $\mu\varepsilon$ to 6000 $\mu\varepsilon$.

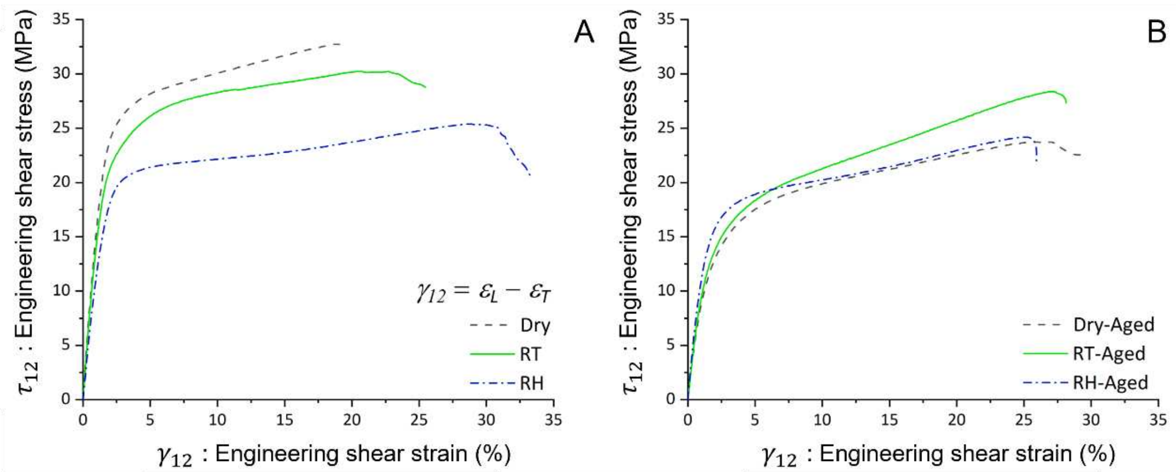

Figure 4. In-plane shear stress-strain plots of flax PMMA composites before water immersion ageing (A) and after ageing (B)

Before water immersion ageing (Figure 5), Dry and RT composites have similar τ_{12}^{max} and G_{12}^{Chord} values. The RH composites manufactured with highly swollen fibres conditioned at 90% RH have respectively 23% and 18% lower τ_{12}^{max} and G_{12}^{Chord} values than the Dry specimens processed with oven-dried fibres.

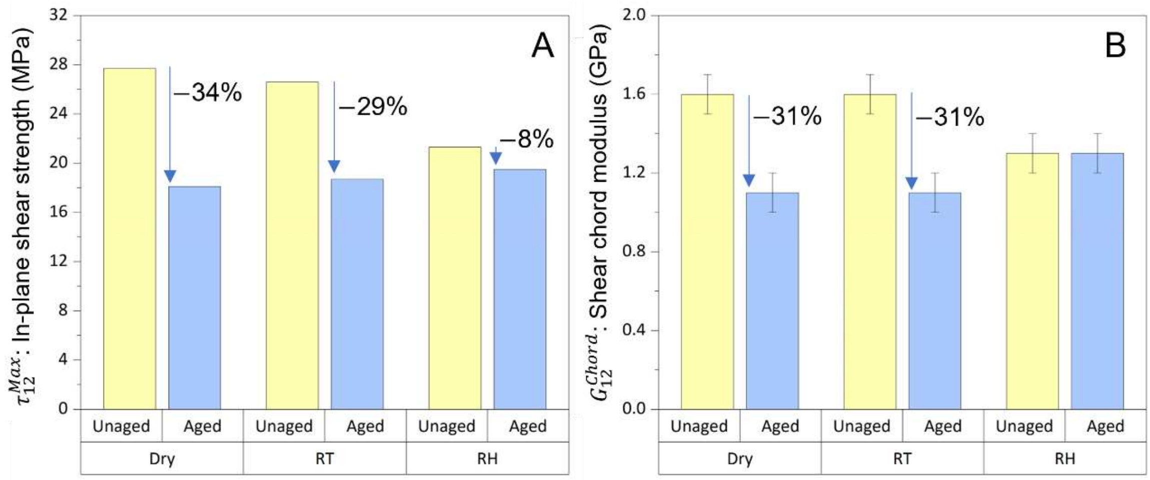

Figure 5. Effect of water immersion ageing on τ_{12}^{Max} (A) and G_{12}^{Chord} (B) values of composites

In Figure 5, one ageing cycle (water immersion and stabilisation) reduces the τ_{12}^{max} and G_{12}^{Chord} of Dry and RT by approximately 30%. Ageing has only a minor effect (8%) on the τ_{12}^{max} of RH composites. Interestingly, the G_{12}^{Chord} of RH is not sensitive to ageing and offers a higher G_{12}^{Chord} value (by 18%) compared to aged Dry and RT. Composites processed with oven-dried and non-dried fibres present similar τ_{12}^{max} values after one ageing cycle. It is worth noting that the in-plane shear strength of composites is less sensitive to the hydrothermal ageing than the transverse tensile strength (see Figures 3 and 5). The overall in-plane shear performance of flax PMMA composites is summarised in Table 1.

Table 1: In-plane shear properties of flax PMMA composites with [+45/-45]$_{SE}$ lay-up

Composite	G_{12}^{Chord} (GPa)	τ_{12}^{Offset} (MPa)	τ_{12}^{Max} (MPa)	$\gamma_{12}^{Failure}$ (%)
Dry	1.6 ± 0.1	17.6 ± 0.7	27.7 ± 0.9	19.4 ± 1.2
Dry-Aged	1.1 ± 0.1	8.6 ± 0.4	18.1 ± 0.7	29.6 ± 1.3
RT	1.6 ± 0.1	16.6 ± 0.4	26.6 ± 0.3	27.6 ± 1.3
RT-Aged	1.1 ± 0.1	13.2 ± 0.6	18.7 ± 0.4	28.6 ± 1.4
RH	1.3 ± 0.1	13.2 ± 0.8	21.3 ± 0.5	34.4 ± 1.9
RH-Aged	1.3 ± 0.1	12.3 ± 0.8	19.5 ± 0.3	26.1 ± 1.5

In summary, the results in this article presented a possibility to tailor the hygroscopic expansion and hydrothermal durability of flax PMMA composites based on the initial fibre moisture content during the in-situ polymerisation. The findings here can be beneficial for manufacturing natural fibre reinforced thermoplastics (NFRP) for various applications such as 3D/4D printing [8] and out of autoclave processing of large NFRP products. The fatigue testing of flax PMMA composites after water immersion ageing will be performed in future work to understand the effect of non-dry fibres on the interfacial adhesion over dynamic loading ranges.

4. Conclusions

This article showed that flax PMMA thermoplastic composites manufactured with oven-dried and non-dry fibres conditioned at 50% RH offer similar interfacial adhesion properties. Composites processed with preconditioned fibres at 50% RH (namely RT) and 90% RH (namely RH) had respectively 47% and 56% lower thickness swelling due to water sorption compared to NFRP with oven-dried fibres (namely Dry). Lower thickness swelling of non-dry composites can reduce the hygroscopic residual stresses and debond cites between fibre and matrix in wet service conditions. For both Dry and RT composites, the transverse tensile strength (S_T) and in-plane shear strength (τ_{12}^{Max}) respectively reduced by 50% and 30% after a water immersion ageing cycle. The RH composites were least affected by ageing in S_T (by - 18%) and τ_{12}^{Max} (by - 8%). After one ageing cycle, the S_T and τ_{12}^{Max} of all three types of composites were in the same range regardless of the initial fibre moisture content during the manufacturing. Interestingly, the shear chord modulus of elasticity (G_{12}^{Chord}) of RH composites was not affected by the ageing cycle and was 18% higher than aged Dry and RT.

Acknowledgements

This project was funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 764713-FibreNet.

5. References

1. Liu T, Butaud P, Placet V, Ouisse M. Damping behavior of plant fiber composites: A review. Compos Struct. 2021 Nov 1;275:114392. Available from: https://doi.org/10.1016/j.compstruct.2021.114392.
2. Javanshour F, Prapavesis A, Pärnänen T, Orell O, Lessa Belone MC, Layek RK, et al. Modulating impact resistance of flax epoxy composites with thermoplastic interfacial toughening. Compos Part A Appl Sci Manuf. 2021 Nov 1;150:106628. Available from: https://doi.org/10.1016/j.compositesa.2021.106628.
3. le Duigou A, Merotte J, Bourmaud A, Davies P, Belhouli K, Baley C. Hygroscopic expansion: A key point to describe natural fibre/polymer matrix interface bond strength. Compos Sci Technol. 2017 Oct 20;151:228–33. Available from: https://doi.org/10.1016/j.compscitech.2017.08.028.
4. Lu MM, Fuentes CA, Van Vuure AW. Moisture sorption and swelling of flax fibre and flax fibre composites. Compos Part B Eng. 2022 Feb 15;231:109538. Available from: https://doi.org/10.1016/j.compositesb.2021.109538.
5. Fruleux T, Castro M, Sauleau P, Matsuzaki R, Le Duigou A. Matrix stiffness: A key parameter to control hydro-elasticity and morphing of 3D printed biocomposite. Compos Part A Appl Sci Manuf. 2022 May 1;156:106882. Available from: https://doi.org/10.1016/j.compositesa.2022.106882.
6. Lu MM, Van Vuure AW. Effects of water immersion ageing on composites made of non-dry flax fibres. Mater Today Proc. 2020 Jan 1;31:S206–8. Available from: https://doi.org/10.1016/j.matpr.2019.11.061.

7. Krys P, Matyjaszewski K. Kinetics of Atom Transfer Radical Polymerization. Eur Polym J. 2017 Apr 1;89:482–523. Available from: https://doi.org/10.1016/j.eurpolymj.2017.02.034.

8. Le Duigou A, Correa D, Ueda M, Matsuzaki R, Castro M. A review of 3D and 4D printing of natural fibre biocomposites. *Mater Des*. 2020 Sep 1;194:108911. Available from: https://doi.org/10.1016/j.matdes.2020.108911.