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RESEARCH ARTICLE

One step production from the monomer of poly(L-lactide)/flax biocomposites by thermoplastic resin transfer molding: Mechanical properties and aging

Bernard Miranda Campos [ID] | **Jordan Beauvois** [ID] | **Serge Bourbigot** [ID] | **Gaëlle Fontaine** [ID] | **Grégory Stoclet** [ID] | **Fanny Bonnet** [ID]

University of Lille, CNRS, INRAE, Centrale Lille, UMR 8207, UMET—Unité Matériaux et Transformations, Lille, France

Correspondence
Fanny Bonnet, University of Lille, CNRS, INRAE, Centrale Lille, UMR 8207, UMET—Unité Matériaux et Transformations, F-59000 Lille, France.
Email: fanny.bonnet@univ-lille.fr

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Abstract

Development of biocomposites is becoming a necessity due to environmental concerns. Polylactide is a matrix of choice, regarding its bio-sourced and compostable nature along with its mechanical properties. In this study, poly(L-lactide)/flax biocomposites were produced using thermoplastic resin transfer molding (TP-RTM) in one step process from the monomer, affording sustainable and fully compostable composite materials. The polymerization of L-lactide (L-LA) monomer was promoted by tin octoate, affording poly(L-lactide) (PLLA) matrices displaying monomer conversions superior to 96% and mass-average molar masses above 140,000 g/mol. Flax fibers were used as received without any functionalization which is usually conducted to prevent the hydroxyl groups to conduct side reactions. Mechanical testing revealed bending modulus of 9.3 GPa and bending strength of 177 MPa comparable to existing literature values for PLLA/flax composites produced by other techniques. Digital microscopy analysis provided insights into impregnation quality and void characterization within the composites. In addition, the durability of these biocomposites was also evaluated via accelerated aging tests.

Highlights

- PLLA/flax biocomposites were produced by TP-RTM for the first time.
- In situ polymerization of the PLLA matrix associated with non-functionalized flax fabrics was conducted.
- Bending properties were found in line with those of PLLA/flax composites produced by compression molding.
- Aging tests under UV at 50°C of PLLA/flax biocomposites were conducted.

KEYWORDS

aging tests, biocomposite, natural fibers, polymer-matrix composites (PMCs), thermoplastic resin transfer molding (TP-RTM), thermoplastic resins

1 | INTRODUCTION

Among bio-based materials, polylactide (PLA) has emerged as a material of choice thanks to its compostable character, *in vivo* biodegradability, biocompatibility and relatively low cost, making it suitable in biomedical and short-lifetime applications.[1–4] In particular, PLA shows properties close to those of polyethylene terephthalate (PET), enabling its use in packaging industry. However, PLA displays some intrinsic characteristics, such as low Tg (around 60°C) and low elongation at break (2%–6%), which limit its use in various applications.[3] To address these problems and to allow PLA to be used for a wider range of long-lifetime applications, it is often used in blends with other polymers[5,6] or as matrix in composite materials.[7]

Regarding composites, in the last two decades PLA has been associated with synthetic and natural fibers to improve its mechanical properties.[7–9] Among natural fibers, flax is undoubtedly the most commonly used reinforcement with PLA in order to produce fully bio-based composites, as an alternative to oil-based ones.[10] The substitution of synthetic fibers with natural ones as reinforcement in composites for engineering applications has become increasingly popular in the recent years due to growing environmental concerns and the demand for the development of sustainable materials.[10,11] However, flax fibers display some disadvantages compared to synthetic ones, most notably the variability in their properties and environmental effects, that is, high relative humidity, which can degrade their tensile properties.[11] The production of PLA/flax composites is currently conducted by compression molding, injection molding or film stacking.[8–12] In these techniques, melted PLA is injected or molded by compression into a mold with pre-disposed flax fibers. More recently, PLA/flax composites were produced via 3D printing.[13,14] In most cases, authors report the formation of voids in these composites which they postulated to arise from the lack of wettability between the flax and the PLA matrix. In order to increase the hydrophobicity of cellulosic substrates, flax is currently treated prior use via different techniques.[11,15–18] In a recent work, flax was also modified by surface-initiated ring-opening polymerization of ε-caprolactone to increase the hydrophobicity of the reinforcement.[19] The main drawback linked to the processes used to produce PLLA/flax composites, is the high viscosity of the melted PLA involved which reduces the impregnation kinetics significantly, resulting in the formation of voids and unfilled areas in the final composites. Due to its high viscosity, the melted PLA cannot be used in liquid composite molding (LCM) techniques which are known to produce composites with low number of voids, generally in one-step synthesis from the monomer, and commonly employed for high-volume production of parts.

Among LCM techniques, resin transfer molding (RTM) is used for the production of thermoset matrix composites since 1980, in particular for polyurethane and epoxy resins. The use of thermoset resins in RTM is mainly due to their low viscosities, an important parameter for which resins have to present a viscosity below 1 Pa.s to be employed in this process.[20] Recently, the development of thermoplastic resins displaying low viscosity has allowed the production of composites via RTM, a process aptly named thermoplastic resin transfer molding (TP-RTM).[21] To date, the only thermoplastic resins commercially available for TP-RTM are polyamide-6 (PA-6), polymethyl methacrylate (PMMA, Elium®) and poly(butylene terephthalate) (PBT).[21,22] Other thermoplastic resins have been used in TP-RTM in academic works such as poly(ε-caprolactone) (PCL) and polyamide-12 (PA-12).[22,23]

Recent studies conducted in our lab, reported the production of poly(L-lactide) (PLLA) matrix composites reinforced by glass fibers in TP-RTM process, via *in situ* polymerization of L-lactide (L-LA) into a mold containing pre-disposed fibers.[24] More recently, our research group published novel PLLA-based copolymer/glass fabrics composites, with statistical poly(L-lactide-co-ε-caprolactone) copolymer as the matrix, the resulting composites displaying a rubbery character along with high impact resistance.[25] Despite the innovative character of these works, a step forward should be done in order to replace synthetic fibers by natural ones to produce fully compostable composites.[26]

In the present study, PLLA/flax composites were produced by TP-RTM in one step process from the monomer for the first time. This represented a major challenge due to hydroxyl groups from cellulose and hemi-cellulose in flax fibers which could react with the catalyst, either preventing the polymerization and/or undergo chain transfer reaction, lowering the overall molar masses of the resulting matrices. As mentioned above, flax fibers commonly used for biocomposites production are pre-treated to prevent some interactions with thermoplastic matrices.[11,15–18] Our experimental conditions allowed the use of non-functionalized flax fibers to produce PLLA/flax composites from the monomer. Finally, bending properties of the resulting PLLA/flax composites were evaluated, as well as their aging to investigate their durability.

2 | MATERIALS AND METHODS

2.1 | Materials

L-lactide (L-LA) monomer was purchased from Corbion (Netherlands) and used without any further purification

TABLE 1 Principal characteristics of reagents used in this study for the production of the matrix.

Reagent	Supplier	Commercial name	Shape	Assay (%)	Molar mass (g.mol^{-1})	Density (g.cm^{-3})	Water content (%)
L-lactide	Corbion (Netherlands)	PURASORB® L	White crystalline solid	99.9	144.13	1.186	0.008
Tin(II) octoate	Alfa Aesar (USA)	-	Pale yellow viscous liquid	97.2	405.12	1.251	-

TABLE 2 Principal characteristics of flax fibers used in the production of composites.

				Mechanical properties		
Pattern	Supplier	Areal weight (g.m^{-2})	Density (g.cm^{-3})	Young modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Cross-stitched unidirectional	Ecotechnilin (France)	180	1.33	35	330	0.83
Twill 2/2	Ecotechnilin (France)	300	1.29	12	113	1.7

(see Table 1). Tin (II) 2-ethylhexanoate (Sn(Oct)$_2$) was purchased from Alfa Aesar and used as received (see Table 1). Two types of woven flax fabrics supplied by Echotechnilin (France) were used: cross-stitched unidirectional (UD) and balanced 2/2 twill (TW) (see Table 2 for characteristics). The flax fabrics were dried at 80°C during 24 h prior use.

2.2 | Production of PLLA / flax composites

Two distinct composites were produced: PLLA reinforced with unidirectional flax fabric (PLLA/UD) and PLLA reinforced with 2/2 twill flax fabric (PLLA/TW). The woven flax fabrics were cut with a roll-cutter and placed into the cavity of a 3-part mold with dimensions of 120 × 120 × 5 mm. Ten layers of cross-stitched unidirectional flax fabric were placed into the mold in the same orientation. Regarding composites reinforced with balanced 2/2 twill flax fabric, only five layers of fabric were used, due to its high areal weight.

L-LA (200 g, 1,38 mol) and Sn(Oct)$_2$ (279 mg, 6,92.10^{-4} mol) catalyst, with monomer over catalyst molar ratio of [L-LA]/[Sn] = 2000, were placed into the TP-RTM injection tank under dynamic vacuum (−0.5 bar), pre-heated at 150°C during 30 min to enable the melting of L-LA (Scheme S1). The mixture was then stirred for 30 s and injected through PTFE tubes (4 × 6 mm) into the mold with pre-disposed flax fabric using N$_2$ flow. Once the mold was filled, the PTFE tubes were clamped with a steel clamp. The mold was kept under pressure (30 kN) during 2 h at 185°C to enable the polymerization reaction. After 2 h, the plates

were cooled to room temperature and the plates demolded. The TP-RTM parameters, monomer over catalyst ratio, polymerization temperature and polymerization time were set based on our previous studies.[16] For the sake of reproducibility, all experiments were conducted at least twice.

2.3 | Characterization of composites

2.3.1 | Proton nuclear magnetic resonance spectroscopy

^{1}H NMR spectroscopy was used to assess the conversion of L-LA into PLLA. The analyses were carried out on a Bruker Avance 300 MHz spectrometer. The samples (about 5–15 mg) were dissolved in 1 mL of CDCl$_3$, in a 5 mm diameter tube. The number of scans was set to 32 and the delay between each scan was set to 4 s. The calibration of the spectra was made via the residual peak of CHCl$_3$ in the deuterated solvent at 7.26 ppm. The conversion of L-LA was determined by integrating the methine (-CH) signal of monomer centered at 5.05 ppm and polymer at 5.15 ppm.

2.3.2 | Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was used to determine the number-average molar mass (M_n), the mass-average molar mass (M_w) and the dispersity (Đ) of the poly(L-lactide) (PLLA) matrices. The samples were prepared with a concentration of 1 mg.mL^{-1}, using chloroform (CHCl$_3$) as the solvent and were filtered through a 0.45 μm pore-size membrane. Measurements were

performed on an Agilent system (1260 Infinity II LC System) equipped with three columns (Shodex K-802.5, 803 et 804) placed in series and coupled with a differential refractometer (Wyatt Optilab). The PLLA samples were analyzed at 25°C in $CHCl_3$ and flow rate of 1 mL.min^{-1}. Molar masses were corrected by a factor of 0.68.[27,28]

2.3.3 | Thermal properties (TGA and DSC)

TGA measurements were performed on a TG 209 F1 Libra® to determine the thermal stability of flax fibers prior use and of the resulting PLLA matrix. Approximately 10 mg of samples were placed into an open silica pans and submitted to an isotherm at 50°C for 10 min followed by a heating ramp of 10°C.min^{-1} until 800°C under N_2, with purge flow rates set at 15 and 100 mL.min^{-1}. The thermal properties of PLLA matrix were determined on a differential scanning calorimetry (DSC) (TA Instruments). During the first scan, samples of 5–10 mg were cooled at −80°C and heated to 200°C at 10°C.min^{-1}. The enthalpy of fusion (ΔH_f) and the melting temperature (T_m) were determined from the first scan. The second scan was conducted from −80 to 200°C at 10°C.min^{-1} to determine the glass transition temperature (T_g). The degree of crystallinity (X_c) was calculated from Equation (1):

$$X_c = \frac{100\left(\Delta H_f - \Delta H_{cc}\right)}{\Delta H_f^0}$$ (1)

where ΔH_{cc} is the enthalpy of cold crystallization and $\Delta H_f^0 = 93J$ is the enthalpy of fusion of 100% crystalline PLLA.

2.3.4 | Determination of fiber mass and volume ratios

The fiber mass ratio (FMR) and the fiber volume ratio (FVR) were calculated according to the equations below:

$$M_f = \frac{mf}{mc}$$ (2)

where m_f is the mass of fibers and m_c is the mass of the composite

$$V_f = \frac{M_f}{M_f + \left(\frac{\rho_f}{\rho_m}\right)\left(1 - M_f\right)}$$ (3)

where, V_f is the volume fraction of fibers, M_f is the mass fraction of fibers, ρ_f is the density of fibers (1.33 and

1.29 g/cm^3 for UD and TW flax fibers respectively) and ρ_m is the density of the matrix (here PLLA, 1.25 g/cm^3).

2.4 | Density measurement

Densities of the composite materials were measured using an electronic density tester TWS-300E from Matsu-Haku (Taiwan). The samples tested are randomly selected parts of the composite. Each of the four samples were tested three times. The six values obtained from the UD composites were averaged to give an average density. In the same way, the six values of the TW composites allowed the calculation of an average density.

To check the consistency of these measurements with the values of V_f for the two types of composite materials, the density of these composites were calculated using the rule of mixtures.

$$\rho_c = V_f\rho_f + \left(1 - V_f\right)\rho_m$$ (4)

where ρ_c is the density of the composite material, V_f is the fiber volume fraction, ρ_f is the density of the fabric and ρ_m is the density of the matrix.

	Calculated from the rule of mixtures	Measured
Density of PLLA/UD composites (g/cm^3)	1.258	1.251
Density of PLLA/TW composites (g/cm^3)	1.255	1.203

2.4.1 | Three-point bending test

Three-point bending test was used to determine the bending strength (σ_B) and the bending modulus (E_B). A universal testing machine (Instron 5867) was used, and the specimen was placed on two support anvils and bending it through an applied force at 10 mm.min^{-1}. Five specimens with valid failures were tested. The dimensions of the specimens were adapted from ISO 14125 standard (Fiber-reinforced plastic composites – Determination of flexural properties), with length of 60 mm, width of 15 mm and thickness of 5 mm.

2.5 | Digital microscopy

Digital microscopy (Keyence VHX-7000 series) was used to investigate the quality of the impregnation of the

matrix through the reinforcements, to analyze the presence and the morphology of the voids, and to analyze the morphology of the fractures in the specimens tested in three-point bending. The morphology of the fractures was evaluated directly in the specimen after samples were prepared for the investigation of the impregnation and the voids characterization. Cross sections between $25 \times 5 \times 5$ mm^3 and $10 \times 5 \times 5$ mm^3 were cut from $120 \times 120 \times 5$ mm^3 composite plates using a bandsaw. The cross sections were cold mounted into a 30 mm diameter mold, ground with abrasive papers and flushed with water (P80, P180, P600, P1200), and polished with silicon carbide papers (800/P2400 and 1200/P400).

2.6 | Aging test

The accelerated aging of composite plates was performed in an accelerated weathering tester chamber (QUV Q-Lab). The specimens for the bending tests were used to investigate the aging and placed in holders inside the chamber. The weathering conditions chosen are from the ISO 4892-3 standard (Plastics — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps). The samples were exposed to a UVA irradiation (UVA-351 lamp) at 50°C with no moisture or condensation in 24 h cycles, with a total test duration of 720 h. These conditions simulate the UV solar radiation behind window glass. Thermal properties were evaluated by DSC after 15 and 30 days of aging. The molar mass and bending properties were evaluated after 30 days of aging.

3 | RESULTS AND DISCUSSION

3.1 | Production of PLLA/flax composites

In order to produce PLLA/flax fabrics composites by TP-RTM, it was necessary to first investigate the thermal degradation of flax fibers to ensure that flax fabrics remain stable at the polymerization temperature of the matrix of 185°C. In that frame, TGA analyses were conducted on the two types of flax fibers used in this study, that is, unidirectional flax (UD) and twill flax (TW) (Figures S1 and S2). The thermograms show a first weight loss at 100°C for both flax fabrics types, corresponding to the release of water. A second weight loss starts around 200°C for both TW and UD flax which can be attributed to hemicellulose degradation.[29,30] The maximum DTG is observed at 357°C for both flax fibers, which corresponds to cellulose degradation.[31] At 800°C, a residual mass of 18% for TW flax and 10% for UD flax are observed, corresponding to the residue left from hemicellulose and lignin.[31,32] The degradation of the components of flax fibers initiates above the selected polymerization temperature, that is, 185°C, thereby ensuring the thermal stability of the fabrics throughout the polymerization process.

The presence of flax fabrics in the TP-RTM can be a major issue as in this process the polymerization of the monomer is conducted in situ in the mold containing the reinforcement. Actually, the presence of the hydroxyl groups (–OH) of the cellulose and hemicellulose of the flax can react with the catalyst, preventing the polymerization or interacting with the growing polymer chain to undergo chain scission via transfer reactions, lowering the molar masses of the resulting PLLA matrix. Thus, studies report the functionalization of flax prior use for the production of composites.[11,15–18] In the present work, the experiments were conducted without any pre-treatment of the flax fabrics, which were just dried 24 h at 80°C prior use. The polymerization being quite efficient according to our previous studies with glass fabrics,[24] one could expect that the propagation would be faster than chain transfer side reactions. Actually, conversions of L-LA up to 96% were obtained after 2 h for all experiments (Figure S3) with both flax fabrics types, what is comparable to our previous study with inert glass fabrics (Table 3, Figure 1).[24] In addition, very high mass-average molar masses (M_w) ranging from 128,800 to 143,300 g.mol^{-1} were measured for PLLA/flax(TW) and PLLA/flax(UD) composites matrices along with narrow dispersities ranging from 1.62 to 1.74 (Figure S4). One can conclude regarding the conversions and M_w values of the PLLA matrices, that the presence of flax fibers does not hinder the ring opening polymerization of L-LA in TP-RTM experimental conditions. For the sake of reproducibility, all experiments were conducted at least twice.

The PLLA matrices of composites produced with both flax fabrics types were analyzed by TGA in the absence of reinforcement (Figures S5 and S6). Comparable thermal degradation behaviors were observed, with $T_{5\%}$ values of 235 and 236°C and $T_{95\%}$ of 317°C and 319°C for PLLA/flax(UD) and PLLA/flax(TW) respectively. In addition, the maximum DTG for both matrices was around 294°C. Regarding the DSC analysis of the PLLA matrices, still in the absence of reinforcement, they showed melting temperatures ranging from 169 to 173°C, glass transition temperatures around 53–54°C and crystallinity from 49% to 54% which is in line with literature values for high molar masses PLLA (Table 1).[33,34]

In contrast to synthetic fibers such as glass fabrics, flax fibers exhibit an irregular and non-uniform structure, contributing to irregularities and voids within the composite

TABLE 3 PLLA/flax fabrics composites produced by TP-RTM[a].

Sample	Reinforcement	L-LA conversion[b] (%)	$M_w{}^c$ (g.mol^{-1})	Đ[c]	$T_g{}^d$ (°C)	$T_m{}^d$ (°C)	ΔH^d (J.g^{-1})	X^d (%)
1-UD	Unidirectional flax fabric (UD)	94	143,300	1.62	54	169	45.5	49
2-UD		94	143,300	1.62	54	173	46.4	50
1-TW	Twill 2/2 flax fabric (TW)	96	128,800	1.74	53	173	49.0	53
2-TW		96	131,900	1.62	53	170	50.7	54

[a]Experimental conditions: all experiments were doubled for reproducibility (X-UD and Y-UD are identical). Catalyst Sn(Oct)$_2$, [L-LA]/[Sn] = 2000; polymerization temperature: 185°C; polymerization time: 2 h.

[b]Determined by ^{1}H NMR in CDCl$_3$.

[c]Determined by SEC in CHCl$_3$ with molar masses correction factor of 0.68.[22,23]

[d]Determined by DSC analysis, T_g was determined at the first scan and T_f at the second one.

FIGURE 1 (A) PLLA/unidirectional flax(UD) and (B) PLLA/twill flax(TW) composite plates (120 × 120 mm).

material. The inherent irregularities in flax fibers can cause disruptions in the resin flow during the injection process, leading to the formation of voids and unfilled areas. Digital micrographs of cross sections of PLLA/flax (UD) composites show the presence of meso-voids between the longitudinal flax fibers (Figure 2). These meso-voids are predominantly found among the flax yarns and range from 500 to 2000 μm.

In longitudinal cut, the morphology of the elementary fiber (lumen) is distinctly visible within flax bundles (Figure 3A,B). These individual fibers exhibit an irregular structure, and when put together, form bundles that also possess irregular shapes and arrangements (Figure 3C,D). Despite the irregular structure of these elementary fibers, which might potentially lead to uneven resin flow during injection, no voids were detected in this particular region.

Regarding PLLA/flax(TW) composites, meso-voids between the flax fiber bundles were also identified (Figure S7). Even if these meso-voids could not be quantified by digital microscopy, visually the number of voids was higher than in PLLA/flax(UD) composites. It suggests that the flax(TW) fabric architecture promotes more disruptions in resin flow, leading to the formation of voids.

The PLLA/flax(UD) composites display fiber mass ratio (FMR) of 26 wt% and fiber volume ratio (FVR) of 25 vol%, while PLLA/flax(TW) analogs present FMR of 31 wt% and FVR of 30 vol%. These values in FMR and FVR are related to the numbers of layers of fabrics used (10 layers for UD and 5 for FW due to their different areal weight) but also to the impregnation of the fibers by the matrix. As observed previously, the impregnation in PLLA/flax(UD) composites was more effective compared to PLLA/flax(TW) ones, primarily due to the difference in fibers architecture. Consequently, a larger amount of PLLA matrix was injected, resulting in a decrease in both the FMR and FVR. Densities of both composite materials were measured and found to be 1.251 and 1.203 g.cm^{-3} for UD and TW reinforced composites respectively. In order to check the consistency of these measurements with the values of Vf for the two types of composite materials, the theoretical densities of these composites were calculated using the rule of mixtures (see experimental section). Regarding the UD-reinforced composites, a density of 1.258 g.cm^{-3} was mesaured, what is quite close to the calculated one of 1.251 g.cm^{-3}, but slightly inferior due to the presence of voids in the composite material. As expected, the measured density of 1.255 g.cm^{-3} for TW is much lower than the calculated one of 1.203 g.cm^{-3}, which is consistent with the fact that these composites types display the highest voids amount.
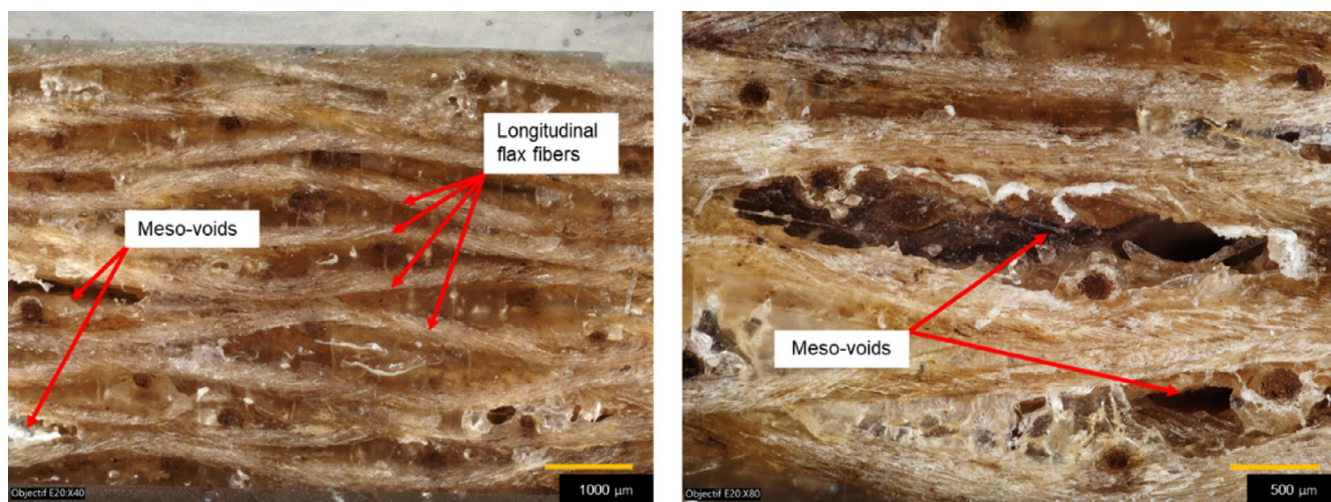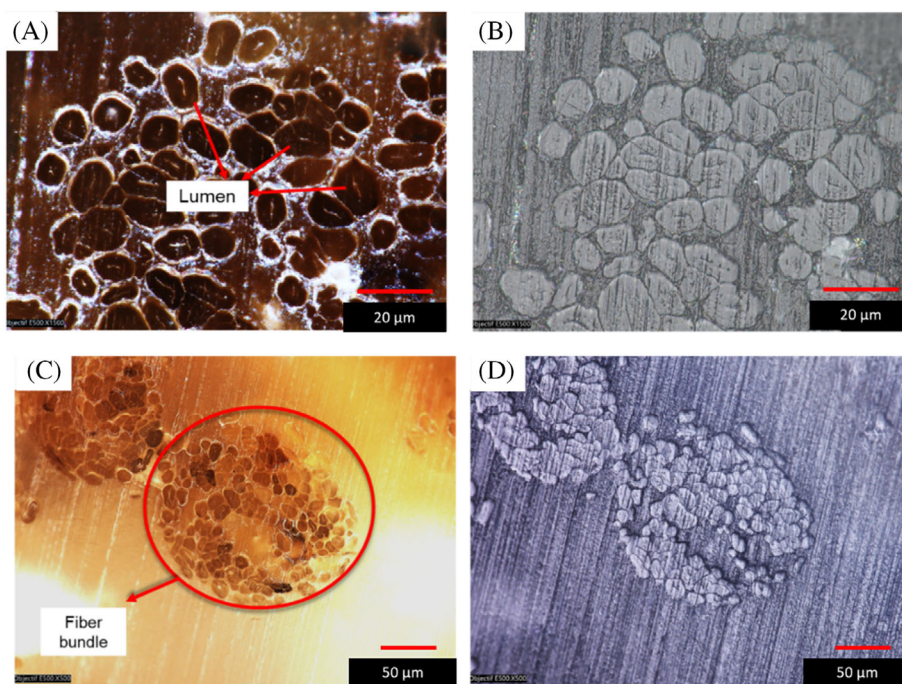
FIGURE 2 Digital micrographs of cross section of PLLA/flax(UD) composites.

FIGURE 3 Digital micrographs in a longitudinal cut of PLLA/flax(UD) plate.

3.2 | Mechanical properties of composites

The mechanical properties of PLLA/flax(UD) and PLLA/flax(TW) composites produced by TP-RTM were assessed by three-point bending tests (see experimental section). PLLA/flax(UD) samples display bending modulus (E_B) of 9.3 GPa, bending strength (σ_B) of 177 MPa and a strain at break of 2.86% (Figure 4A). Regarding the failure, all PLLA/flax(UD) composites showed a tensile fracture with interlaminar shear (Figure 5A–C). Translaminar cracks and intralaminar matrix cracks were observed next to the tensile fracture (Figure 5B).

Since no PLLA/flax composites produced in one-step TP-RTM process were reported to date, the bending test results were compared with values from the literature for PLLA/flax composites manufactured through different processes. For the sake of comparison, PLLA/flax composites with unidirectional fibers displaying FMR of 49 wt%, produced by compression molding with a flax preform and PLLA fibers, display an elastic modulus of 18 GPa and a tensile strength of 215 MPa.[35] Another study, focusing on PLLA/unidirectional flax composites with FMR of 22 wt% produced via film stacking present an elastic modulus of 13.8 GPa and a tensile strength of 160 MPa.[36] Both studies reported the presence of voids and their negative
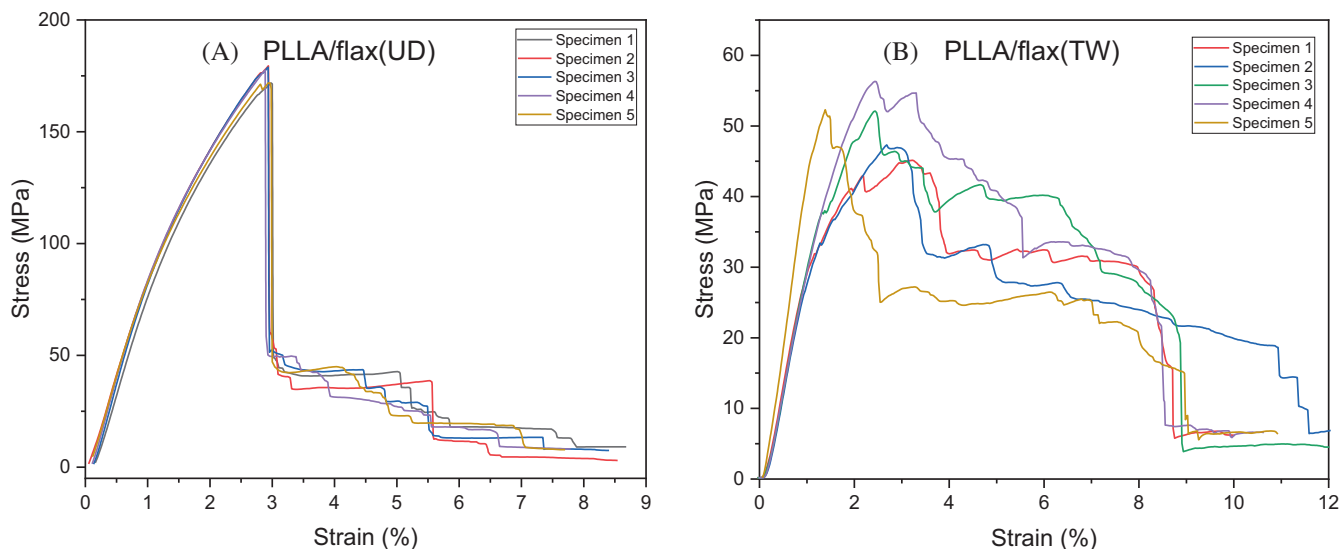
FIGURE 4 Strain-stress curves on three-point bending test of (A) PLLA/flax(UD) and (B) PLLA/flax(TW).
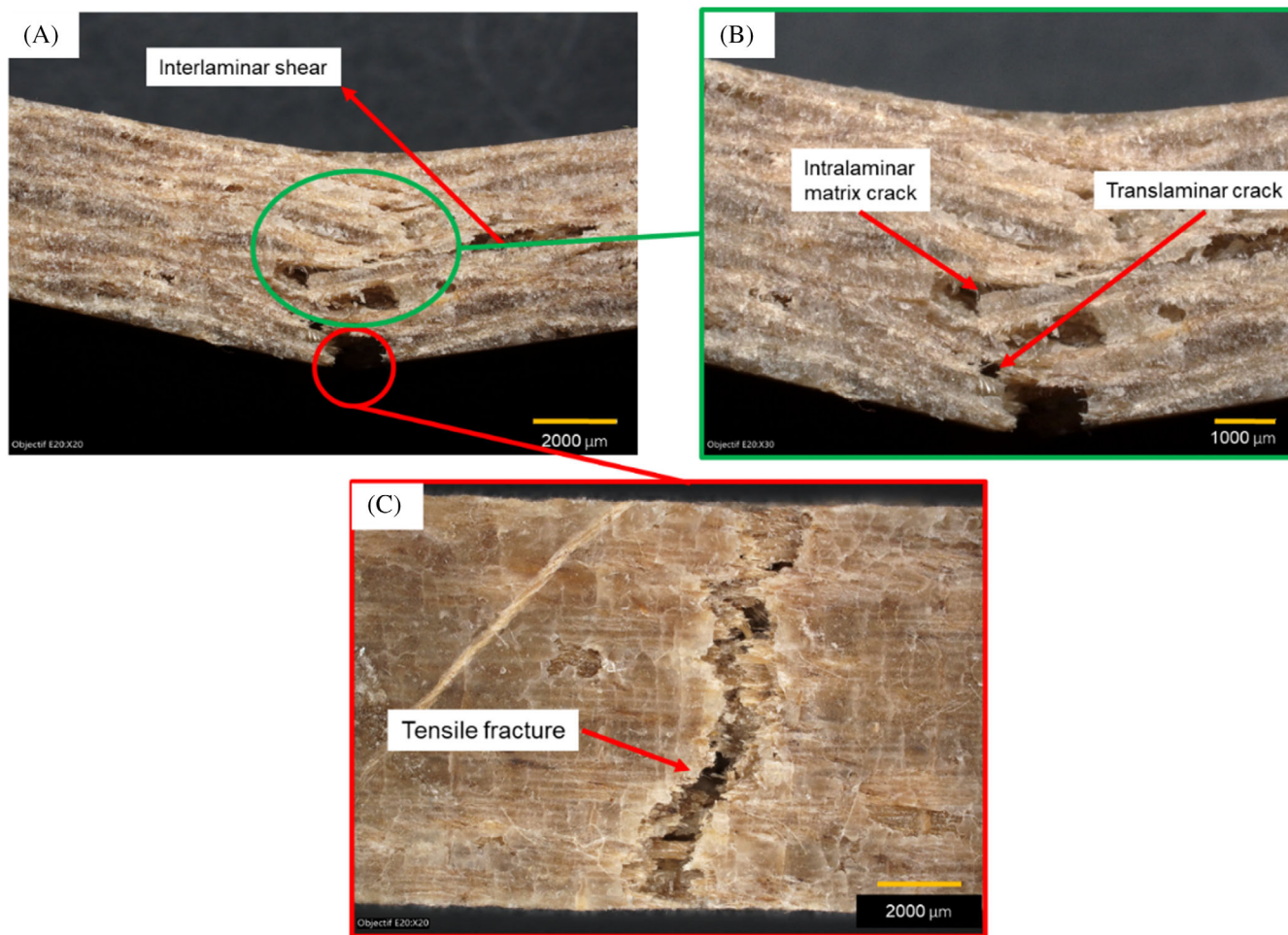

FIGURE 5 Digital micrographs of failure observed in the PLLA/flax(UD) specimen after bending test.

impact on the bending characteristics of the composites. Considering variations in manufacturing processes and fiber volume ratios, one can conclude that the bending modulus and bending strength values obtained for PLLA/flax(UD) composites produced by TP-RTM align closely with those reported in existing literature.

Regarding PLLA/flax(TW) composites, they display bending modulus (E_B) of 3.66 GPa, bending strength (σ_B) of 50 MPa and a strain at break of (εB) 2.90% (Figure 4B). Compared to PLLA/flax(UD), the bending properties of PLLA/flax(TW) composite are lower, as a decrease of almost 40% and 30% was observed in bending modulus and bending strength respectively. While the matrices in both PLLA/flax(UD) and PLLA/flax(TW) composites display identical thermal properties (same T_m and T_g) and crystallinity of 49%, which can influence their bending properties, any discrepancies in the values of E_B and σ_B are directly attributed to the differences in fibers architecture and matrix impregnation. The presence of numerous voids in PLLA/flax(TW) composites explains the lower values of E_B and σ_B measured. The major failure identified in PLLA/flax(TW) composites after three-point bending test was the delamination (Figure 6A,B). This failure could be induced by the presence of voids localized between the flax fabrics, but also by the roughness of flax fibers present in the twill 2/2 fabric. Compared to the UD flax fibers, the TW flax fibers possess a higher roughness, inducing the formation of voids as the wettability was less effective. Another problem observed in PLLA/flax(TW) composites was the impregnation at the surface of the plate. The high level of roughness of these fibers provoques a less effective impregnation by the matrix since the resin flow is not homogeneous. In that way, some unfilled areas appeared, and the external layer of the matrix, supposed to cover the reinforcement, is not uniform (Figure 6C).

3.3 | Aging test

Aging tests were conducted on the two types of PLLA/flax fabrics composites (Table 2). The samples were exposed to UVA irradiations (UVA-351 lamp) at 50°C with no moisture or condensation. After 30 days of aging, the flax-reinforced composites specimens displayed a significant color change, from brown to white (Figure 7).

The impact of UV irradiation on the degradation of PLLA was previously studied in the litterature.[37–41] It suggests two distinct photo-degradation mechanisms, depending on the wavelength of UV irradiation. The Norrish II mechanism is proposed for UV light irradiation under 300 nm (UV-B), while a radical mechanism is suggested for irradiation under UV light between 300 and 400 nm (UV-A). In our study, the accelerated aging was conducted with a UV light settled at 340 nm (UVA-A) and so the radical mechanism of photodegradation of PLLA seems to be the most probable.
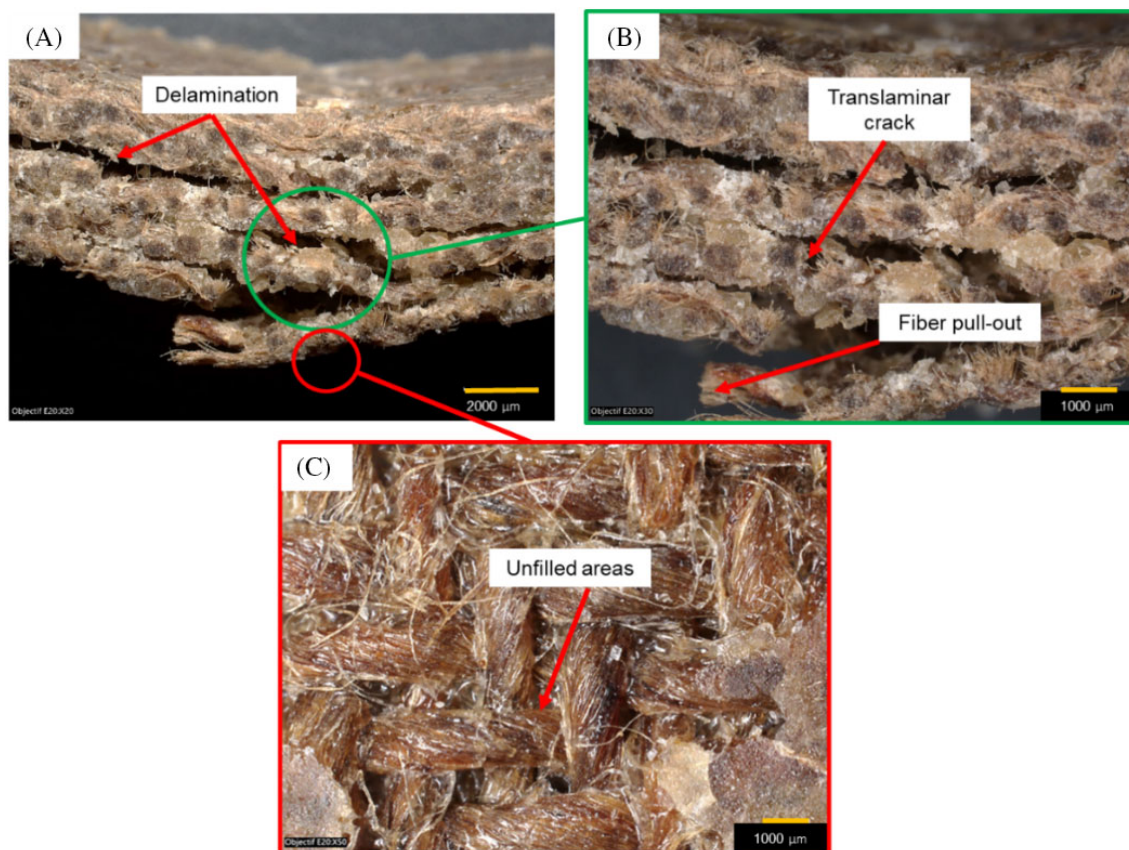

FIGURE 6 Digital micrographs of failure observed in the PLLA/flax(UD) specimen.

An efficient method for detecting chain scissions is the measurement of molar masses of the polymer matrix before and after aging. The decrease in molar masses is responsible for the damage in thermal and mechanical properties of the matrix and thus the composite material. In our samples, after 30 days of aging the M_w of the PLLA matrices dropped by 53% and 83% for PLLA/flax (UD) and PLLA/flax(TW) respectively, along with an increase of dispersities in both cases, what is consistent with the occurrence of high rates of chain scissions (Table 4).

Regarding thermal properties, T_g of PLLA/flax (UD) matrix increased from 3°C and its T_m decreased from 173 to 168°C, phenomena which were observed in the literature.[33,34] The T_g of PLLA/flax(TW) matrix did not change drastically after 30 days, however the T_m was affected with a decrease from 170 to 160°C (Table 4). The highest number of voids in the PLLA/flax(TW) composite increased the exposed area of the plate to UV irradiation which may cause more degradation to the matrix than in PLLA/flax(UD) one. Actually, the crystallinity of the PLLA matrix decreased drastically after 30 days of aging from 49.9% to 37.3% for PLLA/flax(UD) and from 57.1% down to 24.7% for PLLA/flax(TW). Previous studies suggest that the crystallinity of PLLA tends to increase when exposed to UV irradiation.[41,42] However, one have to mention that these studies report the aging of neat PLLA and no data on the aging of PLLA/flax composites exposed to UV irradiation are available.

The evolution of the mechanical properties of the composites were evaluated after 30 days of aging by three-point bending tests (Figures S10). The E_B of PLLA/ (flax)UD remained constant after aging, maintained at 9.3 GPa, while the σ_B decreased from 177 to 150 MPa. The bending strain also decreased by 21%. The aged specimen showed a tensile fracture with intralaminar matrix cracks, translaminar cracks, and some delamination at the top of the specimen (Figure 8A). These fractures were the same as those observed in the unaged samples. The changes in bending properties are not dramatic in PLLA/flax(UD) samples as a decrease of only 25% crystallinity was measured.

Regarding PLLA/flax(TW), the E_B decreased from 3.66 to 2.40 GPa and the σ_B decreased from 50 to 35 MPa while the strain only decreased by 3% (Figure S11). These decreases in bending properties can be attributed to the important loss of crystallinity, which has dropped by 57% for the aged sample compared to the unaged one. The aged specimen showed an interlaminar shear fracture with an important delamination after bending test (Figure 8B). All five layers of composite plate were delaminated, indicating that the capacity of the matrix to keep the layers cohesive was impacted by the aging.
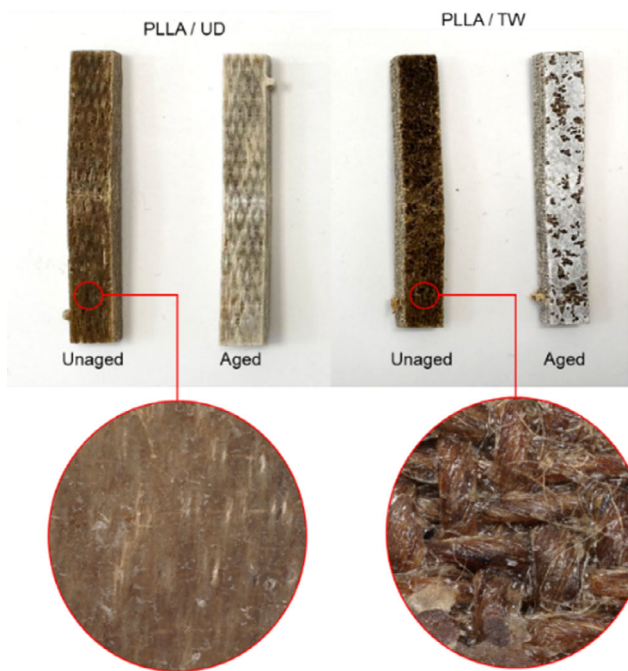

FIGURE 7 Unaged and aged FFRC specimens.

TABLE 4 Evolution of thermal properties and molar masses of PLLA matrix during aging.[a]

Sample	Composite composition	Aging time[1] (days)	T_g[b] (°C)	T_m[b] (°C)	X[b] (%)	M_w[c] (g.mol^{-1})	Đ[c]
F-1	PLLA/flax(UD)	0	54	173	49.9	143,300	1.64
		15	56	167	35.2	-	-
		30	57	168	37.3	58,600	3.12
F-2	PLLA/flax(TW)	0	53	170	57.1	131,900	1.62
		15	51	163	22.1	-	-
		30	52	160	24.7	22,200	2.91

[a]Aging conditions: under UVA irradiation (UVA-351 lamp) at 50°C with no moisture or condensation.
[b]Determined by DSC, T_g was determined from the first scan and T_f from the second scan.
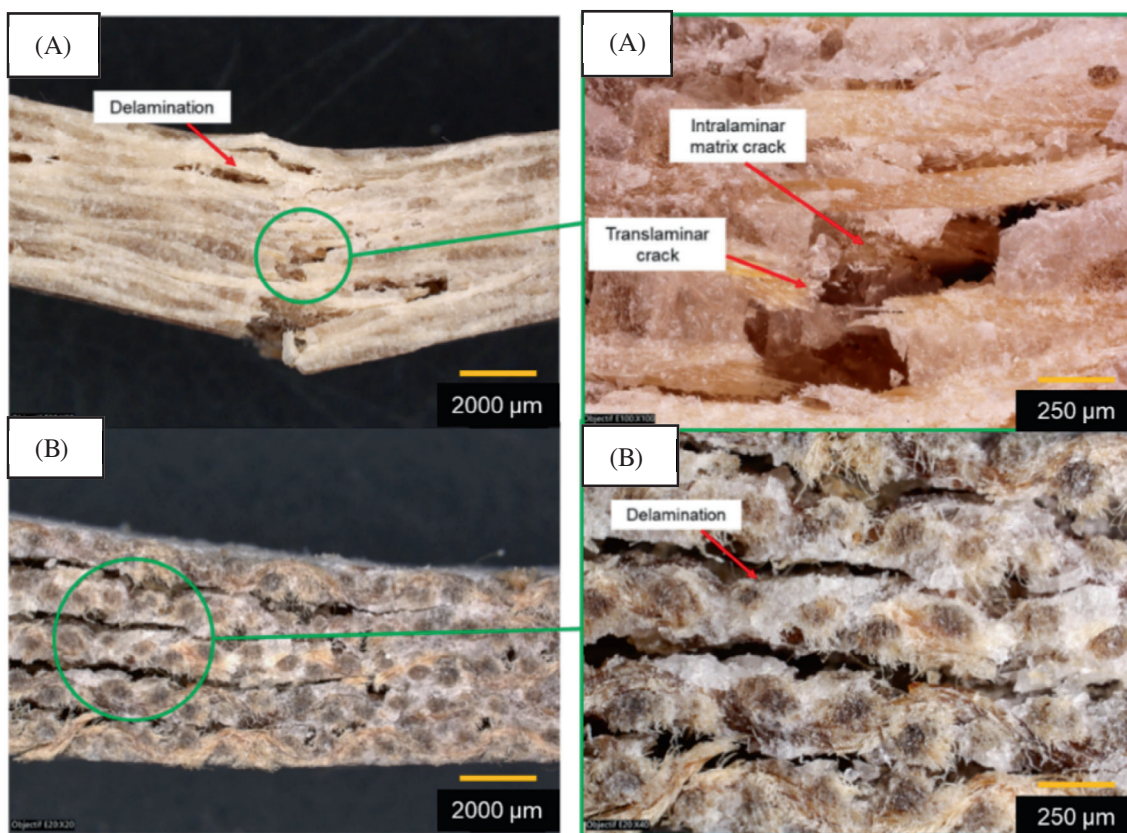[c]Determined after 30 days of aging by SEC in CHCl$_3$.

FIGURE 8 Optical micrographs of aged FFRC after bending test. (A) PLLA/flax(UD) and (B) PLLA/flax(TW).

4 | CONCLUSION

In this study, we achieved the production of PLLA/flax biocomposites by TP-RTM in one-step synthesis from the monomer via *in situ* polymerization of L-lactide. The flax fabrics, used as the reinforcement, were not functionalized as often conducted prior composite production to reduce the number of hydroxyl groups from cellulose and hemi-cellulose. Actually, in our case these functions could prevent the polymerization by reacting with the catalyst or decrease the molar masses of the resulting matrices via chain transfer reactions. One could observe that the presence of the natural fabrics did not hinder the polymerization of L-LA, as high conversions up to 96% along with very high M_w up to 143,300 g.mol^{-1} were obtained. Two types of flax fabrics were used, that is, unidirectional fabric (UD) and 2/2 twill fabric (TW) inducing some differences regarding the properties of the resulting composites. Fabrics impregnation was observed to be more effective with UD fabrics, affording PLLA/flax(UD) composites displaying higher bending properties compared to PLLA/flax(TW) analogs. Nonetheless, the former exhibits bending modulus and strength of 9.30 GPa and 177 MPa respectively, of similar magnitude as the values found in the literature for the same PLLA/flax composites produced by other manufacturing techniques. Additionally, the accelerated aging of the resulting biocomposites was studied under UV radiations at 50°C in the absence of moisture for 30 days. Aged composites experienced a slight decrease in bending properties due to the loss of crystallinity. Chain scissions occurred during aging in PLLA matrix composites, leading to a decrease in molar masses along with increase of the dispersities.

This study provides valuable insights into the production, characterization and aging behavior of PLLA/flax biocomposites, contributing to potential applications of these fully compostable biomaterials. The production of PLLA/flax fabrics in one-step synthesis from L-LA monomer by TP-RTM without non-functionalized flax fabrics, is a major step forward for the valorization of polylactide and biocomposites in general.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Bernard Miranda Campos https://orcid.org/0000-0003-1086-2037

Jordan Beauvois https://orcid.org/0009-0006-4366-7229

Serge Bourbigot https://orcid.org/0000-0003-1536-2015

Gaëlle Fontaine https://orcid.org/0000-0002-7113-1687

Grégory Stoclet https://orcid.org/0000-0003-1510-0234

Fanny Bonnet https://orcid.org/0000-0002-3776-6638

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