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Material Properties

Monitoring temperature effects on flax cell-wall mechanical properties within a composite material using AFM

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ABSTRACT

PeakForce Quantitative Nano-Mechanical property mapping (PF-QNM) was applied to explore the nano-mechanical properties of the cell wall of two kinds of flax fibre preparation: isolated and within a poly-(butylene succinate) (PBS) or maleic anhydride grafted poly-(propylene) (PP-MAPP) matrix in unidirectional flax (UD) composites. Isolated flax fibres were subjected to a thermal cycle of 8 min from ambient temperature to 250 °C. At the same time, flax fibres in a matrix were subjected to an identical cycle from 140 °C to 250 °C, depending on the nature of the matrix. At the macroscopic scale, tensile tests on both types of sample preparation showed the same trends in temperature effects on the mechanical properties. At the cell wall scale, although no gradient in the cell-wall indentation modulus was revealed by PF-QNM for isolated fibres, a very slight global loss was observed above 210 °C, in accordance with the literature. This decrease was more pronounced for flax fibres within a matrix due the confinement effect of the polymer matrix which isolates fibres from the external environment during thermal treatment. The evolution of the mechanical behaviour of the cell walls leads to embrittlement of the UD composite, underlining the importance of time-temperature couple monitoring during the processing of plant fibre composites.

1. Introduction

Over the last decade, the development of biobased composite materials has become of major industrial importance. Plant fibres can be used in many industrial products as a substitute for synthetic materials, such as glass fibre, for composite reinforcement [1,2]. In Europe, flax fibres have attracted much attention due to their specific mechanical properties [3], their environmental benefits [4] and moderate cost.

Due to the low degradation temperature of plant cell walls [2,5], matrix selection is a crucial parameter in maintaining good fibre properties. Excessively high temperatures (> 170 °C), or aggressive processes [2] lead to a modification [6] or alteration of the plant cell wall structure and mechanical properties [7–9]. Multiscale analysis should be applied to quantify the changes in behaviour and damage mechanism due to high temperatures. At the nanoscale, nanoindentation is widely used for the characterization of plant cell wall mechanical properties [10]. For example, Li et al. [11], studied the micro-mechanical properties of bamboo using thermal treatments to establish a relation between indentation modulus and hardness with increasing temperature. Zickler et al. [12] studied the behaviour of pyrolysed spruce wood as a function of very high temperature up to 2400 °C, and described different variations depending on the temperature range. Stanszl-Tschegg et al. [13] compared three samples (one reference, 160 °C and 220 °C) of beech wood by nanoindentation, showing a slight increase of the indentation modulus with temperature as well as a significant increase of the hardness. This increase of hardness is generally explained by a cross linking reaction of lignin and xylan at high temperatures [14].

Most previous studies focus on the effect of thermal treatment on isolated fibres, but it remains to establish whether this effect applies to fibres inside a composite during its processing. Moreover, it is difficult to establish a correlation between the properties of fibres and those of the composite because this depends mainly on the matrix and fibres properties but also on the individualization of the latter (*i.e.,* the fact that each fibre is well surrounded by the matrix and is not in contact with other fibres) and the composite material microstructure (including the interface between fibres and matrix). In fact, UD properties are improved if there is a high level of separation of fibres, which is the case for samples with homogeneous isolated fibres and material microstructures [15].

With the development of atomic force microscopy (AFM), new tools have become available to access mechanical properties at the

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submicron scale inside composite laminates. Nowadays, different techniques based on AFM exist to measure mechanical properties (*i.e.*, indentation modulus that results from the contact stiffness between the AFM tip and the sample surface). PeakForce Quantitative Nano-Mechanical equipment (PF-QNM) provides force-displacement curves at relatively high frequencies (*i.e.*, a few kHz) of each point during topographic imaging [16]. Different parameters such as the indentation modulus or adhesion force can be obtained at the same time at nanoscale resolution. This AFM mode has already been used for plant fibres such as bamboo or flax [17] [18].

The aim of the present study is to investigate the effect of thermal cycle treatment on the mechanical properties of flax cell walls, both on (single) isolated fibres and within a composite laminate. First, PF-QNM was used to measure the evolution of indentation modulus in thermally treated fibres. The PF-QNM approach was chosen due to its better spatial resolution compared to nanoindentation, which allows access to local mechanical gradients. Finally, the same approach was applied to flax fibres within a thermoplastic composite to compare the trends observed in flax fibres with the macroscopic tensile performances of composite materials.

2. Materials and methods

2.1. Isolated fibre thermal treatments

Technical flax fibres were obtained from flax plants, Marylin variety (2003), cultivated at Le Neubourg (Normandy, France) with a seeding density of 1800 plants/m^2, which corresponds to the conventional density for flax culture [19]. The stems were pulled and submitted to dew-retting for about six weeks until the harvest. Then, they were scutched and hackled by the company Coopérative de Teillage de Lin du Plateau du Neubourg (CTLN, Le Neubourg, Normandy, France).

A Volca (v50e, Prolabo) muffle furnace was used and thermal cycles were run in an air atmosphere at 140 °C, 190 °C, 210 °C and 250 °C for 8 min, which corresponds to a conventional thermoplastic composite process time. This time is really shorter than others found in literature but corresponds for us to a precise time of processing during which fibres undergo heating.

2.2. Film polymer production and composite laminate preparation

Biocomposite materials were manufactured with two different polymer matrixes, PP-MAPP and PBS. They were chosen according to their melting temperature, 114.5 °C [20] and 163.5 °C [21], respectively, as well as to their good thermal stability. Thus, no degradation of PP (which is the main component of PP-MAPP) is observed up to 250 °C, but occurs in the range from 300 °C to 500 °C [22]. For PBS, results of the literature indicate no significant degradation before 200 °C [23]. The poly-(butylene succinate) (PBS), poly-(propylene) and maleic anhydride grafted polypropylene (PP-MAPP) used in this study were PBS Bionolle 1020 MD (Showa Denko, Tokyo, Japan), OREVAC CA 100 (Arkema) and PP 10642 (Total Petrochemical) grafted with maleic anhydride, respectively.

Cast film extrusion was performed with a Brabender (Germany) single-screw extruder at 40 rpm for PBS and PP-MAPP, using the following temperature profile: 130/135/140 in the barrel and 140 °C and in the nozzle or 190/190/190 and 190 °C for PBS and PP-MAPP, respectively. Unidirectional flax (UD) was made from Lineo® FlaxTape (200 g m^{-2}). The supplier claims that no treatment (chemical or physical) was performed on these fibres. PBS was used to make composite plates of Flaxtape/polymer at 140 °C, while PP-MAPP was used for the other temperatures (190 °C, 210 °C and 250 °C).

Unidirectional flax composites were manufactured by film stacking [24–26] using a Labtech© 50T (USA) moulding press with a 25 × 25 cm^2 heating plate. A total of eight unidirectional flax tape layers were stacked on top of each other to obtain samples without interleaved PP-MAPP or PBS films. This assembly was placed between two aluminium cover plates, which were then inserted into the moulding press. The press was preheated for 1.5 min, and the composite assembly was maintained for 1.5 min at this temperature at 20 bars: then, a pressure of 35 bar was applied after 3 successive 1-min steps at intervals of 5 bars and a final step held for 2 min at 35 bars. Thus, the duration of the total hot cycle was 8 min. After the dwell time, the assembly was cooled to 30 °C in 3 min. The fibre volume fraction varied from 55% to 60%. Then, 250 mm × 15 mm x 2 mm samples were cut by milling for tensile characterization.

2.3. Tensile properties of polymer matrix and composites

Static tensile tests were carried out using a universal MTS type tensile testing machine equipped with a 10 kN capacity load cell. All the tests were performed at laboratory conditions of 23 °C and 48% relative humidity. The crosshead speed was 1 mm/min for composites and 50 mm/min for pure polymers. An extensometer was used with a nominal gauge length of 25 mm for the composite tensile tests. Tests were carried out at least five times for each specimen and results were averaged. All tests on composites were carried out in the direction of the fibre axis. The Young's modulus of polymers and composites was calculated from the initial segment of the stress/strain curve (*i.e.*, corresponding to a longitudinal strain between 0.025 and 0.1%).

2.4. Sample preparation for PF-QNM analysis

Both isolated fibres and UD composites had to be prepared before AFM mechanical testing as their measured cross-section surface should be as flat as possible at the nanometre scale to ensure reliable results.

Thermally treated fibres were dehydrated with a concentration series of ethanol/deionised water (50%, 75%, 90% and 100%) and then embedded in a mixture containing increasing ratios of Agar epoxy (AGAR low viscosity resin kit, AGAR Scientific Ltd., Stansted, UK)/ethanol (25%, 50%, 75% and 100%). The flax fibres were embedded to maintain their cell wall structure during the sample surface preparation by microtome. Final embedding resin polymerisation was carried out in an oven (60 °C, overnight).

UD samples were embedded in an epoxy resin (Struers Epofix) to maintain the global composite and fibre structure during preparation of the sample surface by microtome. Final coating resin polymerisation took place at ambient temperature (overnight).

Embedded samples were then machined to reduce their cross section to 1 × 2 mm, and an ultramicrotome (Leica Ultracut R) with diamond knives (Diatom Histo and Ultra AFM) was used to cut a series of very thin sections (about 50 nm thick in the last step) at reduced cutting speed (≈1 mm/s) to minimize compression and sample deformation during the cutting process. This preparation method results in much reduced surface roughness, which makes it possible to obtain relevant AFM PF-QNM measurements.

2.5. AFM PeakForce QNM

AFM mechanical characterization was performed on both isolated fibres and composite samples, after embedding described above, with a Multimode AFM Instrument (Bruker Corporation, Santa Barbara, USA) using PF-QNM imaging mode, which is an extension of the peak force Tapping™ mode where the vertical motion of the cantilever oscillates far below its resonant frequency (2 kHz). Each tapping event is an action of the probe indenting into the surface of the sample (typically 1–3 nm). Measurements were carried out using a RTESPA-525 (Bruker) probe with a cantilever spring constant of around 200 N/m. The probe was calibrated with the so-called Sader method [27] using a Scanning Electron Microscope (Jeol JSM 6460LV) to determine cantilever length and width, and AFM in Tapping™ mode to record its frequency response (resonance frequency and quality factor). The tip radius,