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In-situ evaluation of flax fibre degradation during water ageing

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ABSTRACT

The lifetime of a plant fibre biocomposite in an aggressive environment is highly influenced by the evolution of the properties of its components (fibre, matrix and interface) during ageing. This article aims to estimate the evolution of flax fibre stiffness during two months immersion of a flax/PLLA biocomposite in water, using in-situ measurements involving nanoindentation. The evolution of the nanoindentation modulus is found to be correlated with water uptake. In addition, the degradation mechanism is assessed using biochemical analyses such as total sugar and uronic acid and also by SEM observations.

Fibre stiffness reduction can be primarily explained by fibre cracking induced by differential swelling between internal cell-wall layers (S1-S2-S3) and between components within each cell-wall layer. A supplementary mechanism is the dissolution of fibre polysaccharides such as pectins that could ensure load transfer between cellulose microfibrils within the S2 Layer.

1. Introduction

The study of plant fibre biocomposites is hampered by a poor knowledge of their durability in an aggressive environment. Unlike glass fibres, plant fibres such as flax or hemp have a high affinity with water which leads to composite materials with a higher water uptake (Hill et al., 2009, Azwa et al., 2013). Water sorption generally provokes the swelling of fibres, especially when free volume is available (Clair, 2001). Several authors claim that differential swelling between plant fibres and matrix generates swelling stress, thus causing degradation, cracking, and delamination of the fibre/matrix interface and, finally, a loss of the mechanical properties which vary linearly with water uptake (Dhakal et al., 2007; Le Duigou et al., 2009; Dhakal et al., 2012; Azwa et al., 2013; Le Duigou et al., 2014). Some authors (Stamboulis et al., 2000) claim that enzymatic degradation occurs after long-term immersion, even if no specific studies have been carried out.

The sensitivity of plant fibres to water can be explained by their biochemical composition and structure. Flax fibres are composed of layers in a similar way to composite plies (Hearle, 1963). The layer sequence in the case of flax fibres consists of a primary outer wall (0.1–0.5 μm) (Burgert, 2006), followed by a secondary wall representing 80% of the fibre section which is made up of 3 layers S1 (0.5–2 μm), S2 (5–10 μm) and S3 (0.5–1 μm). In the centre of the fibre, a cavity known as a lumen may be present if the fibre is not completely filled during its growth.

The S2 layer, which consists of highly crystallized microfibrils embedded in an amorphous polysaccharide matrix (pectins and hemicelluloses), controls the mechanical properties of the whole fibre. According to (Hearle, 1963), water does not penetrate the crystallized cellulose area but rather remains within the amorphous zone. Pectins and hemicelluloses are known to play an important role in water uptake (Davies and Bruce 1998) (Zykwinska et al., 2008) as they exhibit an amorphous structure with a high amount of available hydroxyl groups (Baley et al., 2004). Water can be either located on the fibre surface or within the bulk of the fibre in the secondary cell-wall.

To improve our understanding of the aging mechanism of plant-fibre reinforced composites, we require an individual analysis of each of their components. Most published studies deal with the influence of relative humidity on mechanical properties rather than the aging mechanism. For example, (Davies and Bruce 1998) report a decrease in Young's modulus of flax fibre as a function of relative humidity (0.39 GPa per % RH in the range 30–70% RH). This trend towards higher ductility, due to plasticisation, is supported by the work of (Alix et al., 2009) on flax fibres and on PET/Hemp composites with RH in the range 35–85% (Madsen et al., 2007). However, the recent studies of (Placet et al., 2012) have highlighted an opposite trend, with an increase of hemp fibre stiffness with increasing RH due to microfibril realignment.

Very little information is available on the effect of immersion time and thus on the ageing mechanism of plant fibres in a water environment. (Stamboulis et al., 2001) claim that after 3 days expo-

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sure to 93% RH, flax fibres show the development micro-organisms on their surface which could be influenced by the retting process. (Bourmaud et al., 2010, le Duigou et al., 2012) have shown that immersion of flax fibre bundles or single fibres in deionised water for 72 h leads to only slight changes in tensile properties. However, their structural cohesion could be altered, as indicated by the observation of a cell-wall peeling process during microbond tests (le Duigou et al., 2012).

Mechanical properties of plant cell-walls can be directly measured within the composite by in-situ techniques such as nanoindentation. A previous study (Bourmaud and Baley 2010) has revealed a 35% reduction in the relative stiffness of flax fibre within a flax/PLLA biocomposite after a film-stacking manufacturing stage, as compared with native flax fibres. While the measurement of nanoindentation is a powerful tool for monitoring the evolution of local properties, discrepancies can be observed between the modulus obtained from nanoindentation and tensile tests, thus restricting the use of nanoindentation to comparative analysis (Bourmaud and Baley 2009).

The present study aims to evaluate the effect of two months water ageing on the flax fibre properties of a PLLA matrix polymer. Firstly, we measured the water uptake of a PLLA matrix reinforced by unidirectional flax fibres. Then, we carried out *in situ* measurements of fibre stiffness within the biocomposite by nanoindentation on driedsamples. Supplementary chemical analyses were performed on products released into the water.

2. Materials and methods

2.1. Materials and manufacturing

Fibres of flax, *Linum usitatissimum*, harvested in France, were dew-retted before being scutched and hackled. Then, fibre slivers were assembled with a cotton yarn to form a unidirectional reinforcement with an overall weight of 150 g/m^2. These products were supplied by Biorenfort®. PLLA 7001D from Naturworks® and are used in pellet form. Then, 40 μm-thick films were extruded and calendared.

Biocomposites were manufactured using the vacuum film stacking method as described previously (Le Duigou et al., 2011). The fibre weight fraction is set at 50%, while samples are machine–milled with the following dimensions: L = 30 mm, W = 12 mm, T = 2.1 mm. Edge-protection with Sikaflex® mastic is carried out on half of the samples to prevent water absorption through the edges, hence reducing the kinetics of water absorption. The remainder of the biocomposites have no protection. Thus, for a similar immersion time, two mechanical and degradation states are obtained.

2.2. Gravimetric analysis

Five samples of each batch were immersed in a 100 ml container filled with deionised water, with a magnetic stirrer being used for homogenization. The temperature was set at 23 °C. Water was not renewed during sample immersion to allow the subsequent analysis of sugar in the released products.

Samples were periodically removed to be weighed and characterized. Weight gain (Δw) is determined as the difference between initial weight (W0) and weight (Wt) after immersion time in minutes using Eq. (1):

$$\Delta W = \frac{\text{Wt-W0}}{\text{W0}} x100 \quad (1)$$

2.3. Nanoindentation measurement

Indentation tests were performed using a continuous stiffness measurement (CSM) technique with a commercial nanoindentation system (Nanoindenter XP®, MTS Nano Instruments) in a laboratory kept at a temperature of 23 °C and a relative humidity of 48%. The hardness and elastic moduli were measured with CSM, the values being obtained from curves according to the method of Oliver and Pharr (Oliver and Pharr, 1992). This method is described in a previous study by our team (Bourmaud and Baley 2009).

We used a three-sided pyramid (Berkovich) diamond indenter, with a measured tip angle of 65.31°, an equivalent cone angle of 70.32° and a tip radius of 16 nm. Prior to the experiments, the area function used to calculate the contact area Ac from contact depth hc was carefully calibrated with a fused silica sample.

Strain rate during loading was maintained at 0.05 s^{-1} for all the samples. We operated with a 70 Hz oscillation of 3 nm amplitude, using identical load rate conditions. The nanoindentation tests were carried out in the following sequence: firstly, after the indenter touched the surface, it was driven into the material at a constant strain rate, 0.05 s^{-1}, to a depth of 300 nm; secondly, the load was held at maximum value for 60 s; and, finally, the indenter was withdrawn from the surface at the same rate as during loading until 10% of the maximum load was reached.

For the nanoindentation tests, we used composite samples as described above (L = 30 mm, W = 12 mm, T = 2.1 mm). The samples were taken out of the water, air-dried until constant weight and then tested. They were not returned into water for further sorption and nanoindentation tests. Nanoindentation experiments were performed on flax fibre cell walls within dried biocomposites.

To select the indents to calculate the average nanoindentation modulus, we used optical images of our samples after indentation. Thus, we selected only indents in the S2 layer and not those located near the lumen or in the interphase areas (Fig. 1). After this first selection, we only kept samples showing stable nanomechanical properties so as to avoid heterogeneities in cell-wall depth. Around 40 fibres were used for each batch, and a Poisson's ratio of 0.35 (Baiardo et al., 2004) was applied in all modulus calculations. The values are averaged for an indentation depth of 200–300 nm.

2.4. Chemical analysis: sugar and polygalacturonic acid

Based on previous studies (Bourmaud et al., 2010, Lecompte et al., 2015), colorimetric analyses were performed to identify and evaluate the concentration of released matter. Sugar analysis data from (Dubois et al., 1956) were firstly used to estimate the overall amount of sugar released during ageing. The proposed correction is applied to avoid underestimation of total sugar released with increasing concentration of uronic acid. The method due to (Blumenkrantz and Asboe Hansen 1973) is used for uronic acid quantification.

2.5. SEM observation

After the nanoindentation tests, samples were sputter-coated with a thin layer of gold in an Edwards Sputter Coater, and analysed with a Jeol JSM 6460LV scanning electron microscope.

3. Results and Interpretation

3.1. Gravimetric analysis

Fig. 2 shows the water uptake of neat PLLA (Fig 2.A) as well as protected and unprotected biocomposites (Fig. 2.B). Neat PLLA samples exhibit low water absorption in deionised water at 23 °C,