

IMPROVING THE INTERFACE IN NATURAL FIBRES REINFORCED PLA BIOCOMPOSITES BY OPTIMIZED ORGANOSILANE TREATMENTS

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Abstract

In this study, we investigated the effect of an organosilane treatment on the surface properties of flax fibres and the resulting mechanical properties of flax fibres reinforced poly(lactic acid) biocomposites. Optimizing the organosilane treatment conditions increases the hydrophobicity of the fibres, and improves significantly the stiffness, the ultimate stress and the impact strength of the biocomposites, while reducing largely the scattering of their properties. Dynamic mechanical analysis reveals a decrease in damping of treated biocomposites because of the formation of a thicker layer of immobilized macromolecular chains resulting from strong interactions at the interface. Crack propagation is observed on notched samples by in situ tensile tests in a scanning electron microscope. The treated biocomposites show a cohesive failure at much higher loads which highlights the enhanced load transfer from the PLA matrix to the flax fibres.

1 Introduction

In the last decade, a growing interest has been shown for fully biobased and biodegradable composites based on natural fibres and thermoplastic biopolymer as poly(lactic acid) (PLA). Some products of natural fibres reinforced PLA are already on the market for various applications: automotive, mobile phone or plant pots [1]. This new class of composites is more environmental friendly due to its lower gross fossil energy requirement and its potential industrial compostability and recyclability. They also present good mechanical properties similar to conventional petroleum based polymer composites reinforced with glass fibres. Besides the intrinsic properties of natural fibres and PLA, the interfacial adhesion in between is a key parameter. Numerous studies deal with the improvement of interfacial adhesion in natural fibres reinforced composites to optimize their mechanical performances. Chemical as well as physical treatments have been developed to improve the reactivity and hence the interactions between the natural fibres and the matrix [2, 3]. Among all these treatments, organosilanes used for many years at the industrial scale for glass fibres, are promising and versatile coupling agents that can improve the interface in various natural fibres reinforced composites. However, the organofunctionality of silanes must be adapted to achieve a chemical bonding with the polymer matrix used [4]. Literature shows that the conditions of organosilane treatments applied to natural fibres are not well controlled [3] and vary widely leading to a limited enhancement of the interface and hence of the biocomposites properties. The most comprehensive studies on silane treatments have been conducted by Abdelmouleh et al. [5, 6]. The authors investigated the kinetic of silanes adsorption and grafting on pure cellulose substrates and lignin substrates [7] and developed enhanced treatments to reinforce a low density polyethylene and a natural rubber matrix [8]. Improved mechanical performances

were obtained when silanes were covalently bonded with the matrix, whereas entanglements with an organosilane bearing aliphatic chains were not efficient. Flax fibres are nowadays the most advanced natural technical fibres. They present high mechanical performances [2, 9, 10]. They can be used as short fibres in thermoplastics for injection moulding applications and can also be transformed in complex technical fabrics to be impregnated and formed with thermosets and thermoplastics. In this study, we investigate the influence of the conditions of silane treatment on the mechanical performances of short flax fibres/PLA biocomposites for injection moulding applications. A detailed study of the surface properties of flax fibres is conducted as a function of different treatment parameters. Then, the mechanical properties of the resulting biocomposites produced at the pilot scale, i.e. several kilos, are evaluated. Finally, the origins of the reinforcement and the role of the interface are characterized and discussed.

2 Materials and testing methods

2.1. Materials

NatureWorks® PLA polymer 7000D, supplied by Resinex (France) was used in this study. Technical flax fibres, FIBRA-S6A, in the form of bundles of 6 ± 0.5 mm in length and 260 ± 150 in diameter were supplied by Fibres Recherche Développement (FRD®, France).

2.2. Fibre treatment

2.2.1. Alkaline pretreatment

For the alkaline pretreatment prior to the organosilane treatment, fibres were soaked in a NaOH aqueous solution 5% w/w for 1 hour at room temperature then washed until the pH was neutral and dried in a ventilated hood at room temperature during 24 hours.

2.2.2. Organosilane treatment

The flax fibres were treated in various conditions with an organosilane coupling agent GPS, (3-Glycidyoxypropyl)trimethoxysilane (Dow Corning® product Z-6040) chosen for its potential reactivity with PLA by an esterification reaction [11]. The influence of the concentration and temperature of the organosilane solution, the soaking time and the heating temperature were tested. The procedure of treatment was the following: the organosilane were hydrolyzed under continuous stirring during 1 hour in a 2 L ethanol / distilled water (60/40 w/w) bath adjusted to pH 5 with acetic acid, 150 grams of flax fibre bundles were then soaked in the bath at defined soaking times and temperatures. Fibres were then washed until the pH was neutral, dried in a ventilated hood at room temperature during 24 hours and cure in an air oven during 2 hours. Fibres were stored in a climatized chamber (2% relative humidity). The different fibre treatment parameters tested in this work are resumed in Table 1.

Fibre samples	Tested treatment parameters				
	Alkaline pretreatment	Silane concentration (fibre weight basis) (%)	Soaking time (hours)	Bath temp. (°C)	Curing temp. (°C)
Flax NT	No treatment				105
Flax T1	no	1	1	20	105
Flax T2	no	5	1	20	105
Flax T3	no	10	1	20	105
Flax T4	no	5	0.08 (5 min)	20	105
Flax T5	no	5	24	20	105
Flax T6	no	5	1	20	60
Flax T7	no	5	1	70	105
Flax T8	yes	5	1	20	105

Table 1. Designation of untreated and treated fibre bundles with their corresponding conditions of treatments. Figures in bold indicate the conditions that were compared for each parameters, other conditions being fixed.

2.3. Surface properties of untreated and treated fibre bundles

The wettability of the untreated and treated fibre bundles were determined using a LPR 902 Wettability Meter (KSV Instruments LTD), based on the principle of capillary rise. 1 gram of fibres were placed in a tube and packed at a constant compacity. The bed of fibres was placed in contact with ethanol that rises by capillarity. The squared absorbed volume is plotted as function of time. The slope A of the curve is expressed by the formula:

$$A = \eta / (\gamma_L * C * \cos \theta) \quad (1)$$

Where η is the ethanol viscosity (1.2 mPa.s), C is a constant that depends on the porosity and the packing of the particles and independent of the solvent used, γ_L is the free surface energy of ethanol (22.39 mJ/m²), θ is the contact angle. The evolution of $C \cos \theta$ quantifies the affinity between the fibres and ethanol. At least five experiments were done for each fibre samples.

2.4. Biocomposites preparation

Blends of PLA loaded at 20 %wt (18.15 % v/v) of Flax NT, Flax T7 and Flax T8 were compounded in a co-rotating twin-screw extruder BC21 (Clextral, France) using a barrel to die temperature profile from 60 to 175°C with a screw speed of 300 rpm. Prior to compounding, PLA matrix was dried at 80°C overnight to avoid hydrolysis upon extrusion. Melted blends were cooled in a water bath at the exit of the die, then pelletized to 3 mm diameter and dried overnight at 50°C under vacuum (100 mbar). About 2 kg of granules were collected for each blend. Pelletized blends were molded by injection into test specimens (ISO 527-1A) for the measurement of mechanical properties. Temperatures in the barrel and nozzle ranged from 180 to 210°C, the screw speed was 80 rpm.

2.5. Mechanical properties

Tensile properties of the biocomposites were measured according to ISO 527 standard with a Zwick 10TH2S testing machine equipped with an extensometer Zwick clip-on for the determination of the Young modulus. The displacement speed was 1 mm/min and 50 mm/min for the determination of the Young modulus and the ultimate tensile strength, respectively. 10 samples per blend were tested for each testing procedure. Charpy impact test was performed on unnotched samples with a Zwick test machine, equipped with a pendulum of 2 J, according to ISO 179-1 standard. Charpy impact strength was measured on 15 samples per blend.

2.6. Dynamic Mechanical Thermal Analysis (DMTA)

The visco-elastic properties of the biocomposites were investigated using a VA 815 Metravib RDS in the dual cantilever bending mode. The samples were cut from injected specimens with dimensions of 40*10*4 mm³. The experiments were conducted in the linear viscoelastic domain at a strain value of $\pm 5 \mu\text{m}$, i.e. 0.012 %. Measurements were performed at 5 Hz, and the temperature was varied from 25 to 100°C at a rate of 3°C/min.

2.7. Scanning Electron Microscopy (SEM)

Failure mechanisms were observed with a Philips XL30 ESEM FEG equipped with an in-situ tensile apparatus by direct observations of the crack propagation at a displacement speed of 0.1 mm/min on notched specimens with dimension of 40*10*4 mm³ and a notch of 4 mm depth and 45° opening.

3 Results and discussion

3.1 Surface properties of unmodified and modified fibre bundles

Technical natural fibres as flax fibres are made of tens of elementary fibres (cells) of 5 to 35 μm in diameter packed into bundles, fibre cells themselves being composed of several concentric layers made of cellulose macromolecules arranged in microfibrils and embedded in a matrix of hemicelluloses, lignin, pectins and proteins [2]. Numerous free and reactive hydroxyl groups from cellulose and lignin arise at the surface of fibre bundles which make them highly hydrophilic. These hydroxyl groups are potentially substitutable with reactive molecules as organosilanes. As assumed by several authors [2, 3, 4, 5, 6], hydrolyzed organosilanes, i.e. silanols $-\text{Si}-\text{OH}$, can be adsorbed on fibre surface while self-condensing in polysiloxane, and could be grafted on it to a measurable extent after an appropriate heat treatment. Abdelmouleh et al. [5, 6] assumed that the heating must be carried out at 120°C under nitrogen conditions to guarantee an irreversible chemical bonding of the silane onto the cellulose surface. To compare the effect of the different treatment parameters, the wettability of the different treated fibre bundles was investigated. The GPS grafted at the surface of the treated fibre bundles should decrease their hydrophilic character and thus their wettability with ethanol, epoxy function being less polar than hydroxyl groups. This decrease of wettability should be function of the degree of self-condensation of GPS molecules and their condensation with hydroxyl groups, the lowest wettability corresponding to the highest number of GPS grafted.

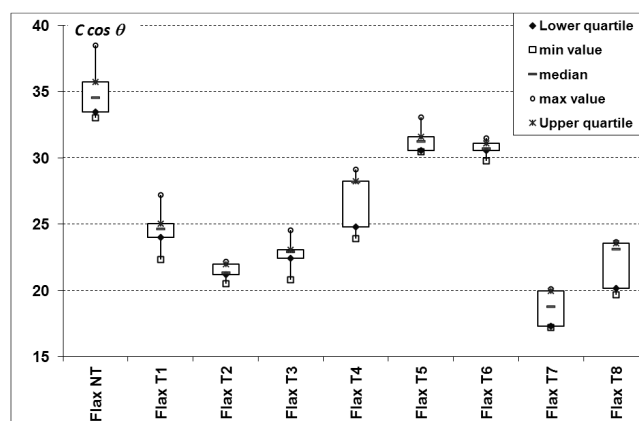


Figure 1. Wettability towards ethanol of untreated and treated fibre bundles

As shown on Figure 1, the wettability of treated fibre bundles towards ethanol is indeed significantly lower than the untreated ones, $C \cos \theta$ values are decreased up to 45%. The GPS concentration in the solution (Flax T1, Flax T2 and Flax T3) does not appear to be a very influential parameter. The lowest wettability was reached at 5%wt of GPS (Flax T2) and 1%wt of GPS was not enough to react with all the hydroxyls groups present on the fibre surface explaining the higher wettability of Flax T1. The soaking time appears to control significantly the efficiency of the treatment. The lowest wettability was found for 1 hour of soaking (Flax T2). The heating temperature is a key parameter. We found that the sample cured at the highest temperature (105°C for Flax T2 as compared to 60°C for Flax T6) presents a lower wettability. Also, heating the bath at 70°C (Flax T7) led to the lowest wettability and thus to an efficient self-condensation and grafting of silanols on fibre surface. We did not find a positive influence of the alkaline pretreatment, the wettability of the sample being higher (Flax T8 compared to Flax T2). This increase in wettability could come from the increase of hydrophilicity due to the removal of hemicelluloses, waxes, and lignin from the surface [12] and/or the increased porosity of the alkaline treated fibres that enhance the capillary rise. The grafting of GPS molecules could also be less efficient due to the lower

reactivity of cellulose surface towards silanols as assumed by Castellano et al. [7]. Based on these results, we choose Flax NT, Flax T7 and Flax T8 fibre samples to produce biocomposites and to evaluate the influence of the alkaline pretreatment and the GPS treatment on their mechanical properties and their behaviour at the fibre/matrix interface.

3.2 Mechanical properties of the biocomposites

Tensile and impact properties have been evaluated for neat PLA and biocomposites, all prepared by extrusion and injection moulding. All the materials produced can be considered as fragile and exhibit elongations at break that do not exceed 5.6% in average for neat PLA and 2.6%, 3.5% and 3.8% in average for PLA / 20%wt Flax NT, Flax T7 and Flax T8, respectively. The young modulus increases significantly by 56% when incorporating 20%wt of non-treated fibres. The increase of modulus related to the two treatments is 64% and 67% for PLA / 20%wt Flax T7 and Flax T8, respectively. There is thus an additional increase of the modulus due to the alkaline and GPS treatments but as it is usually the case, the young modulus in axially oriented composites is not very sensitive to interface modifications. The fibres are in fact mainly oriented along the specimen axis during the processing by injection moulding and the interfacial zone is therefore slightly exposed during tensile test. The ultimate stress and impact strength of biocomposites are in contrast much more sensitive to interface modifications (Table 2).

Biocomposites	In comparison with neat PLA		In comparison with PLA / 20% Flax NT	
	Ultimate tensile stress	Impact strength	Ultimate tensile stress	Impact strength
PLA / 20% Flax NT	-13 %	-15 %	-	-
PLA / 20% Flax T7	+4.5 %	-12 %	+20 %	+4 %
PLA / 20% Flax T8	+9 %	-4.5 %	+25 %	+12 %

Table 2. Mechanical properties variations of biocomposites.

As shown on Figure 2, the incorporation of 20%wt non-treated fibres leads to a drastic decrease of the ultimate tensile stress and the impact strength as compared to the neat PLA. Moreover, the scattering of the results is largely increased. It is explained by a poorer interface between the fibres and the matrix that favours the formation and the propagation of cracks and leads to an early breakage of the specimens. Contrarily, treated fibres Flax T7 and Flax T8 stabilize or even improve the matrix properties and reduce drastically the scattering of the results which indicates that the treatments lead to a homogenization of the biocomposites microstructure, i.e. a better continuity at the interface between the matrix and the fibres.

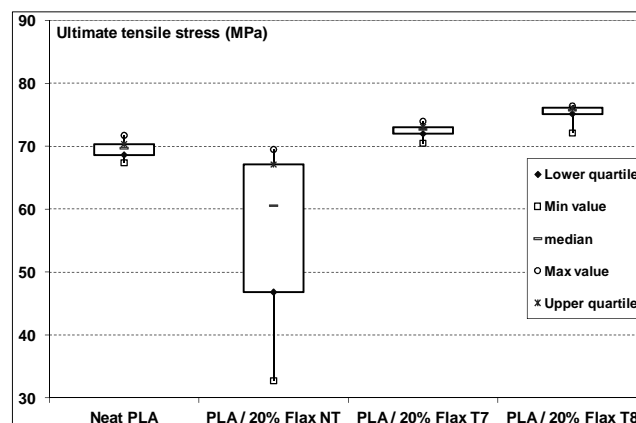


Figure 2. Ultimate tensile stress of neat PLA and the biocomposites

The overall mechanical properties of biocomposites are thus greatly enhanced by the alkaline pretreatment and GPS treatment. It has to be pointed out that the PLA / 20% Flax T8 composite always exhibit higher mechanical performances than PLA / 20% Flax T7, although surface modification analysis revealed that Flax T8 fibres could be less grafted than Flax T7. It is now interesting to better characterize the fibre/matrix interface for the different biocomposites produced.

3.3. Characterization of the interphase

3.3.1. Viscoelastic behaviour of the biocomposites

The decoupling of the elastic (storage modulus E') and the viscous (loss modulus E'') response of the material by DMTA allow to quantify the damping ($\tan \delta = E'' / E'$) which is a sensitive indicator of molecular motions and relaxations. In a composite, the molecular motions of the interfacial region contribute to the damping in addition to those of the matrix and the fibres. The analysis of the damping at the interface enables to quantify the interface bonding [13]. The maximum damping for a polymer is reached at the α transition which is related to the glass transition of its amorphous region. DSC and X-ray experiments revealed that the PLA matrix was always amorphous in the injected specimens (not shown here). As a consequence, the damping magnitude was particularly high (up to 2.8 for the neat matrix) for all the samples. As shown on Figure 3, incorporating 20 wt% of non-treated flax fibres in the PLA matrix leads to a strong decrease of the damping from 2.75 to 1.51 (45.2% of decrease) related to the elastic response of the fibres and the increase contact surface between the fibres and the matrix. In the case of an ideal composite for which the interfaces simply play their role of transferring load and do not contribute to damping, Nielsen [14] suggested that the damping of the composites $\tan \delta_c^0$ can be estimated from the mixing rule:

$$\tan \delta_c^0 = (1 - V_f) \tan \delta_m \quad (2)$$

Where V_f is the volume fraction of fibres and $\tan \delta_m$ the damping of the matrix. Considering this equation, the damping of the biocomposites would be 2.25 which is much higher than the damping measured: 1.51 and 1.44 for PLA / 20% Flax NT and PLA / 20% Flax T8, respectively. This indicates that, for all biocomposites, interactions occur at the interfaces and tend to reduce the damping due to the formation of an interphase with reduced molecular mobility. The effect of such an interphase on the damping was described by Ziegel and Romanov [15] with the following equation:

$$\tan \delta_c^0 = (1 - B V_f) \tan \delta_m \quad (3)$$

Where B is a parameter that correct the volume fraction of fibres because of the formation of an interphase. As explained by Dong and Gauvin [13], the stronger the interfacial interactions, the thicker the immobilized layer and the higher the value of parameter B . The parameters B were 2.50 and 2.62 for PLA / 20% Flax NT and PLA / 20% Flax T8, respectively. It is thus shown that, even with non-treated fibres, the parameter B is high. This indicates that interactions naturally occur between flax fibres and PLA, possibly through van der Waals and hydrogen bonding as postulated by Raj et al. [16]. As shown on Figure 3, the damping is lowered of 0.07 for PLA / 20% Flax T8, the parameter B being in turn higher. This is representative of enhanced interactions due to the alkaline pretreatment and the GPS treatment. Both mechanical and chemical coupling are responsible for these increased interactions. As a comparison, a decrease of damping of about 0.025 was observed by Abdelmouleh et al. [8] with LDPE composites reinforced with 25 wt% cellulose fibres treated with MRPS silanes. Huda et al. [17] observed a decrease of damping also accompanied by a

shift of the glass transition with laminated composites made of PLA and 40 wt% kenaf fibres treated with APS silanes. Based on the values of parameter B, it is possible to calculate an equivalent thickness of interphase. The calculation gives equivalent interphase thickness of 5.80 μm and 6.20 μm for PLA / 20% Flax NT and PLA / 20% Flax T8, respectively. It has to be emphasized that in reality, the interphase is not homogeneous around all fibres. Only the circumference of the fibre bundles undergoes the alkaline pretreatment and the GPS treatment and they are then dispersed in elementary fibres during extrusion [10].

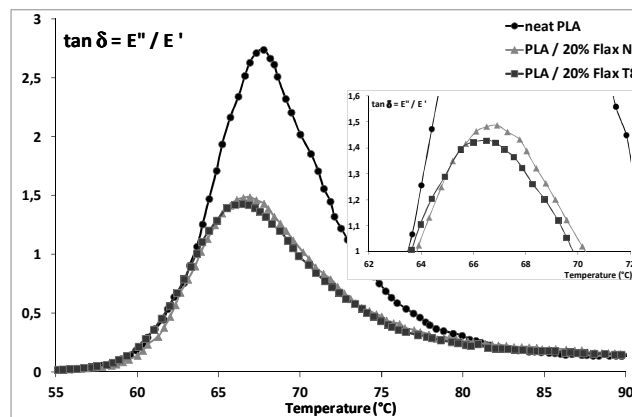


Figure 3. Damping at the α transition of neat PLA and biocomposites from 55°C to 90°C.

3.4.2. Failure mechanisms at the interphase

The failure mechanisms have been observed by direct visualization of the crack propagation on notched samples. This experiment can be assimilated to a pull-out test at a larger scale, i.e. not only one fibre but all the fibres are extracted from the matrix during the crack propagation. As shown on Figure 4, PLA / 20% Flax NT and PLA / 20% Flax T8 composites present very different behaviour during failure. In the case of non-treated fibres, the crack occurs by a clear break of the matrix and a decohesion of the fibres at the interface which is characteristic of an adhesive interfacial failure. In contrast, Flax T8 fibres leads to a cohesive interfacial failure with a tearing of the matrix and a breaking of the fibres that remain bonded to the matrix. This is confirmed by the force-elongation curves recorded during the experiments. The PLA / 20% Flax NT composite breaks at 830 N in average with maximum elongation of roughly 2 mm, while PLA / 20% Flax T8 composite break at 1250 N in average, i.e. 50% higher, with maximum elongation of 6 mm. The increased area under the force-elongation curves is representative of a higher tenacity for PLA / 20% Flax T8.

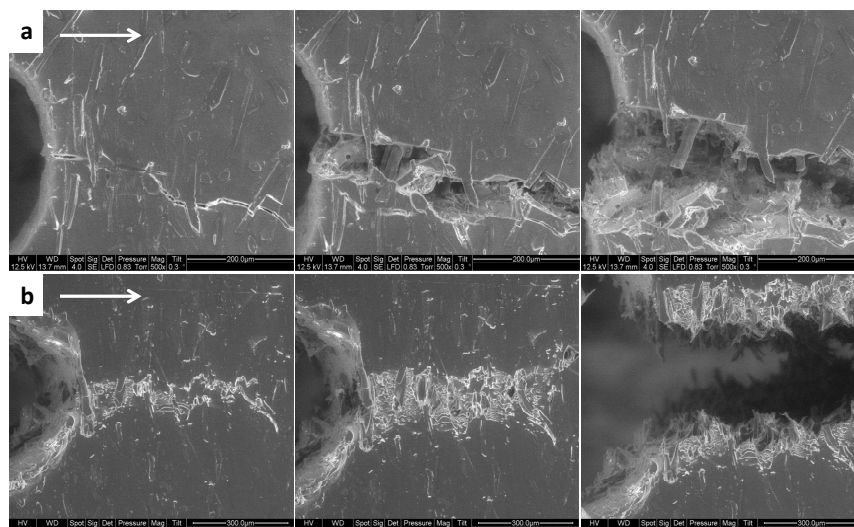


Figure 4. SEM observations during crack propagation for (a) PLA / 20% Flax NT and (b) PLA / 20% Flax T8

4. Conclusions

Optimizing the organosilane treatment conditions increases the hydrophobicity of the fibres, and improves significantly the stiffness, the ultimate stress and the impact strength of the flax/PLA biocomposites, while reducing largely the scattering of their properties. Dynamic mechanical analysis reveals a decrease in damping of treated biocomposites because of the formation of a thicker layer of immobilized macromolecular chains resulting from strong interactions at the interface. The treated biocomposites show a cohesive failure at much higher loads which highlights the enhanced load transfer from the PLA matrix to the flax fibres thanks to the organosilane treatment. Further work will concentrate on the optimization of the treatment by the use of continuous processes and on the study of the durability of these biocomposites.

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