IMPROVEMENT OF THE INTERPHASE STRENGTH AND THE MOISTURE SENSITIVITY OF FLAX FIBRE REINFORCED BIO-EPOXIES: EFFECT OF VARIOUS FIBRE TREATMENTS

D. Perremans[a*], Y. Guo[a], J. Baets[a], A. W. Van Vuure[a], I. Verpoest[a]

[a]*Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44 bus 2450, 3001 Heverlee, Belgium*
**dieter.perremans@mtm.kuleuven.be*

Keywords: Interphase, moisture, flax, bio-epoxy

Abstract

In this paper, the joined effects of an alkalization and a silane treatment are explored to improve the durability of flax fibre reinforced bio-epoxies. Additionally, the effect of a water treatment on the interphase strength is investigated. Transverse 3 point bending tests have been performed to estimate the efficacy of each of the treatments. Both alkali treatment and silane treatment lead to a threefold increase in interphase strength, given the right processing parameters. Only alkali treatment is able to increase the longitudinal tensile strength though, as the water and silane treatment both decrease the plasticity of the composites. Finally, it is shown that the division of the longitudinal tensile stress-strain response in three linear regions separated by two in-between transition zones is valid for UD flax fiber bio-epoxy composites, irrespective of the humidity conditions or fibre pre-treatment.

1. Introduction

Nowadays, more and more attention is diverted to the use of sustainable materials. In that sense, natural fibre reinforced bio-composites, being composed of fully naturally derived building blocks, offer an enormous potential. The potential is further reflected in the mechanical properties and the embodied energy of the composites, exemplified in table 1.

Material	Embodied energy per unit mass (MJ/Kg)	Embodied energy (MJ)
Bricks	8	1968
Aluminium	218	1177
Glass/polyester	100	540
Hemp/polyester	69	249

Table 1: Embodied energy of a 1x1m² facade panel with equivalent mechanical performance. The use of natural fibre reinforced synthetic matrix composites reduces the embodied energy by a factor of 8. The substitution of the synthetic matrix by a bio-derived polymer is presumed to further decrease the embodied energy.[1]

Due to their low density of around 1.4g/cm³, the specific mechanical properties of natural fibres are rather high. Flax fibres are for instance reported to outmatch synthetic glass fibres in terms of specific stiffness.[2] However, the excellent mechanical properties of natural fibres are only transferred to the composite level in case the interfacial shear strength is sufficiently

high. A study by Van De Weyenberg et al. proves that for untreated flax fibre reinforced synthetic epoxy composites the interfacial shear strength is limited to 12MPa.[3]

Moreover, most natural fibres consist of similar molecular building structures (pectines, hemicellulose, cellulose and lignines), albeit in various quantities and compositions. These molecular entities, apart from lignines, are rich in hydroxyl groups and thereby prone to heavy water absorption. The diffusion of water molecules weakens the inter-fibre bonds and therefore leads to natural fibres with an increased strain-to-failure and an unfavorable decrease in stiffness. Assarar et al. show that the longitudinal tensile stiffness of flax fibre reinforced synthetic epoxy composites is reduced by 40% after room temperature immersion in water until saturation. Similarly, the ultimate strain-to-failure is increased by 60%. Equivalent glass fibre composites only yield a reduction in longitudinal tensile stiffness of around 8%.[4]

So, despite their enormous potential, the industrial implementation of natural fibre reinforced bio-composites is currently to a major extent limited by their high sensitivity towards moisture absorption and their low interfacial shear strength. These two effects result in the degradation of the mechanical properties over time. Usually, the moisture resistance and the interfacial shear strength are increased through the application of fibre treatments.[5-6] In this paper, the joined effect of an alkalization and a silane treatment are explored to improve the durability of flax fibre reinforced bio-epoxies. Additionally, to separate the effect of the solution components, the effect of a water treatment on the interphase strength is investigated. For all treatments, the effect of concentration and immersion time will be handled. In a last section, it is explored whether the increase in interfacial shear strength as well procures an increase in the longitudinal tensile strength of the unidirectional composites.

2. Materials and Methods

This research uses UD hackled flax fibres with an areal weight of 250g/m². The flax starting material is kindly delivered by Terre de Lin. In order to treat the fibres, the UD fibres are taped on both ends and immersed in water (water treatment), a NaOH water solution (alkali treatment) or a (3-Aminopropyl)triethoxysilane water solution (silane treatment) respectively. The treatment time and solution concentration are the investigated parameters. In case of the alkali treatment, the fibres are subsequently heavily rinsed with water to ensure neutrality. After treatment, the fibres are dried for at least 24h at 60°C.

The composite samples are produced through vacuum infusion, in which a top plate controls the thickness and surface quality of the samples. The matrix consists of an EPIKOTE 828 LVEL epoxy resin and a NOVOCARD XRF-1400 bio-based novolac hardener in a mass ratio of 320/80. After mixing for 15minutes, the matrix is degassed for 20minutes at 60°C. The infusion takes place at 75°C. The curing cycle comprises of 2h curing @135°C and 1h post-curing @150°C. The obtained degree of cure is measured with DSC and yields 99.7%.

Transverse three-point bending tests are performed in accordance with the ASTM D790 standard. The dimensions of the samples are 100mm x 10 mm x 1.5 mm. The tests are applied on an Instron 5567 with a 1kN load cell, a sample cross-head velocity of 1.3mm/min and a span length of 64mm. Longitudinal tensile tests are executed according to the ASTM D3039 standard on an Instron 4505 with a load cell of 100kN. The cross-head velocity is set at 1mm/min and an extensometer with a gauge length of 50mm is applied. The dimensions of the samples are 250 mm x 20 mm x 1.5 mm.

A Philips SEM XL30FEG equipped with a Schottky based field emission gun is used to investigate the fracture area of the longitudinal tensile samples. The applied voltage is around 10kV and the scanning mode is to set to detect secondary electrons. Prior to scanning, the composite samples are covered with a thin gold layer by using a S159A Sputter Coater to prevent charging effects. After coating, the samples are placed in a degassing chamber with a pressure of 350 mbar for at least 12 hours to remove moisture.

3. Results and discussion

3.1. Transverse three-point bending tests at 55% relative humidity

Figure 1 represents the results of the transverse three-point bending tests that are performed on the alkali treated fibre composites. The untreated composites are included as a reference. For untreated flax reinforced bio-epoxy composites, the transverse flexural strength is around 11.9 MPa with a corresponding average transverse flexural stiffness of 1.1 GPa. The transverse flexural strength is similar to the one measured in the study of Van De Weyenberg et al.[3]

Figure 1 further indicates that moderate concentrations and short treatment times of alkali treatment lead to the most beneficial improvements in transverse three-point bending results. A 4wt% 5 min alkali treatment is sufficient to improve the transverse three-point bending strength by a factor 2.5 and the transverse three-point bending stiffness by a factor 3.

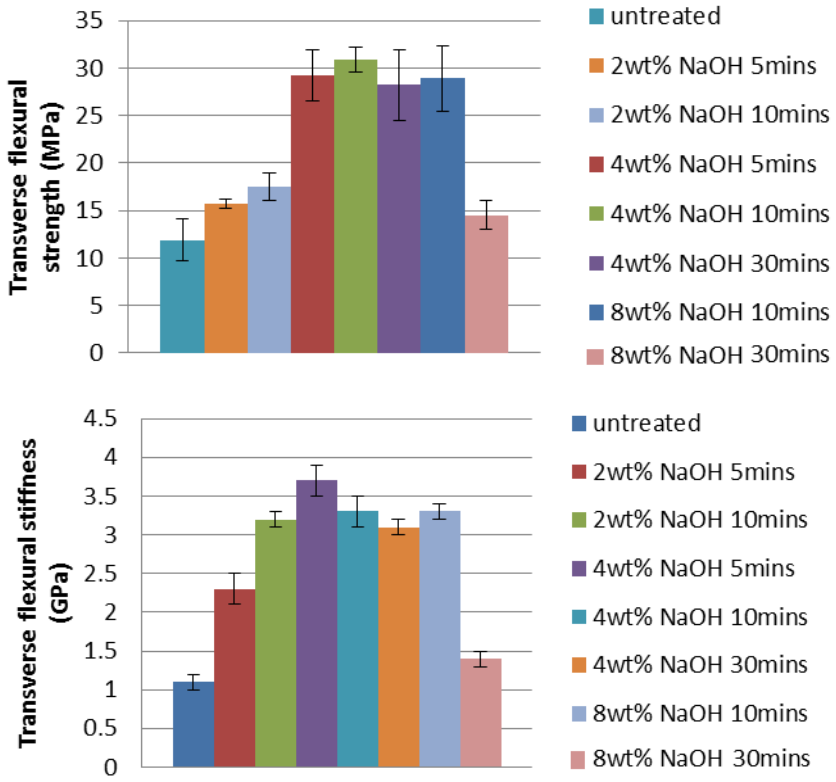

Figure 1: Overview of the transverse flexural strength (top) and stiffness (bottom) of the alkali treated composite samples. Moderate concentrations and short treatment times of alkali treatment lead to the most beneficial improvements in transverse flexural properties. (Vf=35%)

The improvements in composites' transverse three-point bending strength after alkali treatment are dedicated to a higher interphase strength between the flax fibres and the bio-epoxy matrix. This increase in interphase strength is linked to the removal of various organic substances with low mechanical properties, inherent to the flax fibre structure. According to several authors, a small amount of water containing solution is already sufficient to remove pectin components.[7-8] The removal of fibre hemicellulose is forwarded by an increasing alkali concentration, giving rise to a maximal removal content of 3.5 %.[9] This leads to an increased amount of hydroxyl groups at the surface of the flax fibres that increase the interaction with the bio-epoxy matrix. The increased interaction can be chemically or physically. The latter is explained by a larger extent of hydrogen bonding. However, given the magnitude of the increase in transverse flexural strength, it is more likely that a chemical reaction takes place. In this light, the moderate improvements at lower concentrations can be linked to an incomplete wax layer removal.

Table 2 indicates the results of the transverse three-point bending tests of the combined alkali and silane treated samples. It shows that application of silane treatment after alkali treatment does not lead to further improvements in the transverse flexural properties. The reason behind this lies in the fact that the silane molecules that constitute the surface layer of the fibres after treatment are already quite well bonded to the untreated flax fibres, as will be explicated in next paragraphs.

Treatment	Transverse flexural strength (MPa)	Transverse flexural stiffness (GPa)
4wt% NaOH 5mins	29.2±2.7	3.7±0.2
+2vol% silane 10mins	22.3±1.7	2.1±0.1
+2vol% silane 30mins	28.3±0.9	2.2±0.2
+10vol% silane 30mins	28.1±1.1	2.2±0.1

Table 2: Overview of the transverse flexural strength and stiffness of the alkali + silane treated composite samples. Application of silane treatment does not lead to further improvements in the transverse flexural properties. (Vf=35%)

Figure 2 visualizes the results of the transverse three-point bending tests that are performed on the silane treated fibre composites. The untreated composites are as well included as a reference. From this figure, it is clear that silane treatment is able to improve the transverse flexural strength of the flax bio-epoxy composites to the same extent as alkali treatment. The transverse flexural stiffness is only improved by 66% compared to the alkali treated specimens. A 10wt% 10min silane treatment is sufficient to improve the transverse three-point bending strength by a factor of 2.5 and the transverse three-point bending stiffness by a factor of 2.5.

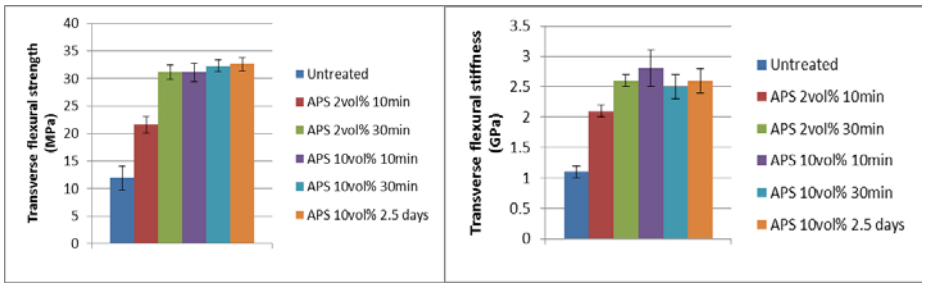

Figure 2: Overview of the transverse flexural strength (left) and stiffness (right) of the silane treated composite samples. Moderate concentrations and short treatment times of silane treatment already constitute a maximal improvement in transverse flexural properties. (Vf=35%)

The authors assume that the fortifying mechanism implies the formation of an amorphous coating structure at the surface of the flax fibres. Presumably, on the one hand the hydrolyzed silane molecules physically adhere to or chemically react with the exposed hydroxyl groups at the surface of the flax fibres, while on the other hand they chemically react with the bio-epoxy matrix. During treatment, diffusion kinetics determine the thickness of the coating layer, implying that longer treatment times or increased concentration magnify the silane deposition rate. With long treatment time and/or high concentration, this coating presumably consists of multiple layers of silane molecules that form an open network, held together by weak Van Der Waals forces and hydrogen bridges. Under application of a transverse tensile load to the coated fibres, the weakly held silane molecules will easily adjust their position to accommodate the imposed deflection, procuring a low stiffness. At higher strains, the mobility of the silane molecules is more restricted. In this case, the interphase strength will be governed by the extent of hydrogen bonds within the coating.

To undoubtedly link the improvements in transverse three-point bending strength to the presence of silane molecules in the solution, the effect of water treatment is verified. Table 3 summarizes the results of the transverse three-point bending tests that are performed on the water treated fibre composites. The untreated composites are as well included as a reference. Comparison of table 3 and figure 2 reveals that the major improvement in transverse flexural properties is assigned to the presence of silane molecules in the solution. Water treatment allows for a 50% increase in transverse flexural stiffness and strength compared to the untreated composites. This improvement is linked to the removal of pectin components in the flax fibre structure, which follows the above stated strategies to account for an increase in interphase strength and by weakest link extrapolation an increase in transverse three-point bending strength.

Treatment	**Transverse flexural strength (MPa)**	**Transverse flexural stiffness (GPa)**
Untreated	11.9±2.2	1.1±0.1
Water 30mins	18.2±0.6	1.4±0.2
Water for 2 days and a half	18.9±1.1	1.7±0.2

Table 3: Overview of the transverse flexural strength and stiffness of the water treated composite samples. Water treatment leads to moderate improvements in the transverse flexural properties. (Vf=35%)

3.*2. Longitudinal tensile tests at 50% relative humidity*

The previous sections indicate that the treatments succeed in improving the interphase quality of the flax fibre reinforced bio-epoxy composites. The improvement in interphase strength should lead to a better load transfer between adjacing fibres and should therefore also constitute an improvement in the final tensile properties of the treated composites. In order to investigate this hypothesis, a series of longitudinal tensile tests is performed on both treated and untreated composites. The result of this tensile test series is visible in table 4.

Table 4 validates that the different treatments lead to a significant improvement in the longitudinal tensile stiffness of the composites. These improvements are supported by better interfacial adhesion between the flax fibres and the bio-epoxy matrix. All treatments seem to improve the longitudinal tensile stiffness by around 15%. Regarding the longitudinal tensile strength of the composites, only alkali treatment yields a significant improvement of around 15%. Both water and silane treatments decrease the plasticity of the fibre composites, which opposes the improvement in flax bio-epoxy interphase strength.

treatment	Longitudinal tensile stiffness (GPa)	Longitudinal tensile strength (MPa)	Longitudinal strain-to-failure (%)
Untreated	25.1±0.9	224±7	1.2±0.1
Water (30min)	29.2±1.0	225±20	0.9±0.1
Silane (10vol% 10min)	28.8±1.0	230±18	0.9±0.1
Alkali (4wt% 5min)	28.5±0.9	256±16	1.1±0.1

Table 4: The longitudinal tensile properties of both treated and untreated flax fibre reinforced bio-epoxy composites. The longitudinal tensile properties are back-calculated to a fibre volume fraction of 40 % using the rule of mixtures. The table shows that all treatments succeed in increasing the longitudinal tensile stiffness due to improved interfacial adhesion between the technical flax fibres and the matrix.

The improvement in fibre/matrix interfacial shear strength is also observed under SEM microscopy. Figure 3 shows SEM images of the cross-section of an untreated (A) and various treated (B-D) flax fibre composites after tensile test failure. Figure 4 further reveals that the fibre/matrix interphase is broken in untreated composites after tensile testing. This debonding is presumed to happen at low strains, giving rise to a global decrease in longitudinal tensile stress-strain response. The debonding between flax fibres and matrix is absent in the SEM microscopy analysis of the cross-section of treated flax fibre composites after tensile test failure.

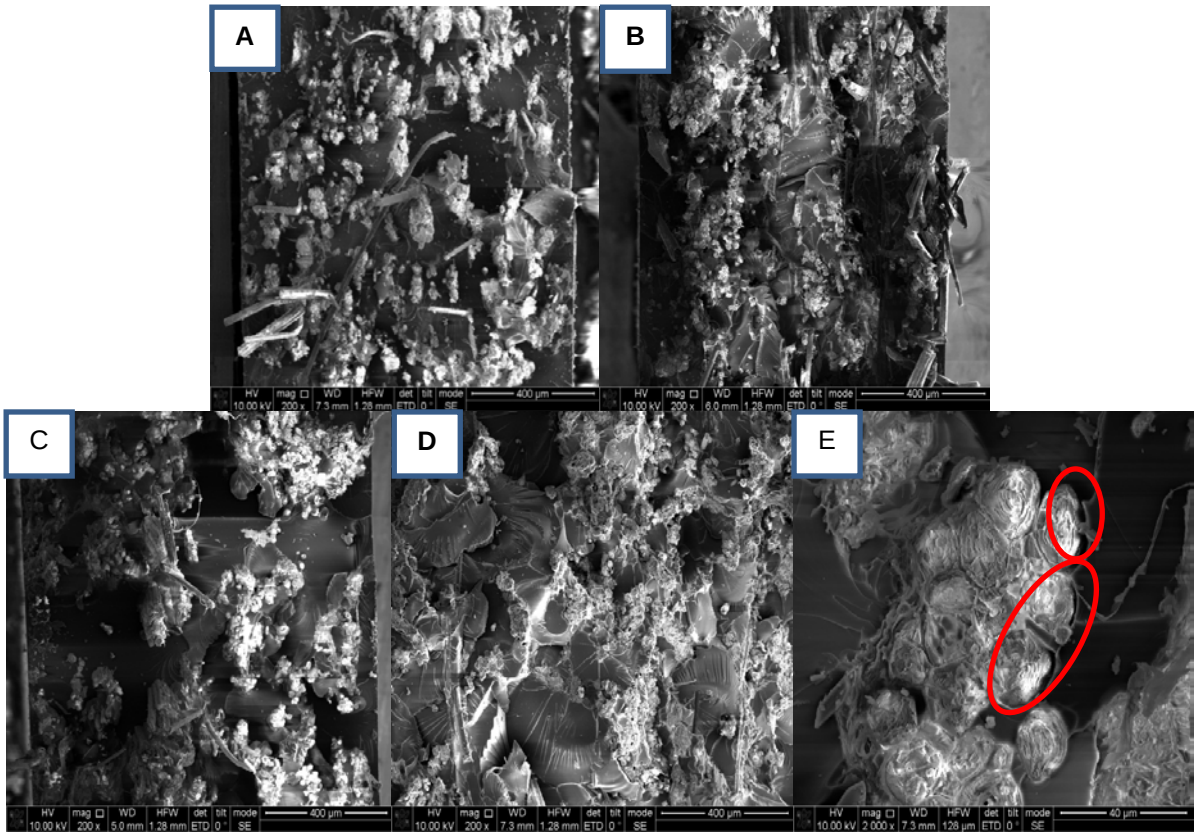

Figure 3: SEM images of the cross-section of untreated (A), alkali treated (B), water treated (C) and silane treated (D) composites after tensile test failure. All images indicate a brittle failure with fibre pull-out. (E) SEM image at larger magnification of the cross-section of an untreated fibre composite after tensile test failure. The image indicates that the technical fibres primarily debonded from the matrix, implying an extremely weak technical fibre/matrix interphase.

3.3. *Longitudinal tensile tests at 90% relative humidity*

Figure 4 shows a typical longitudinal tensile stress-strain curve for untreated UD flax fibre reinforced bio-epoxies tested at 55 and 90 % relative humidity. Figure 5 portrays the local longitudinal tensile stiffness as a function of strain for the same samples. It becomes clear that the division of the longitudinal tensile stress-strain response in three linear regions separated by two in-between transition zones continues to hold for the samples tested at increased humidity. In fact, similar shapes of the tensile stress-strain curves remain visible after fibre treatment, so that the upcoming discussion can also be transferred to treated composites.

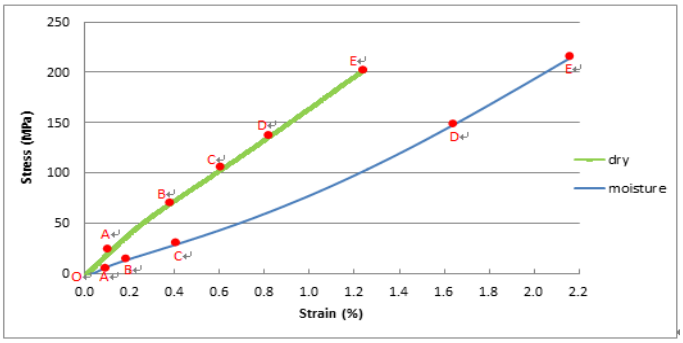

Figure 4: Comparative plot of the longitudinal tensile stress-strain curve of untreated flax fibre reinforced bio-epoxies tested at a relative humidity of 50% (dry) and 90% (moisture).

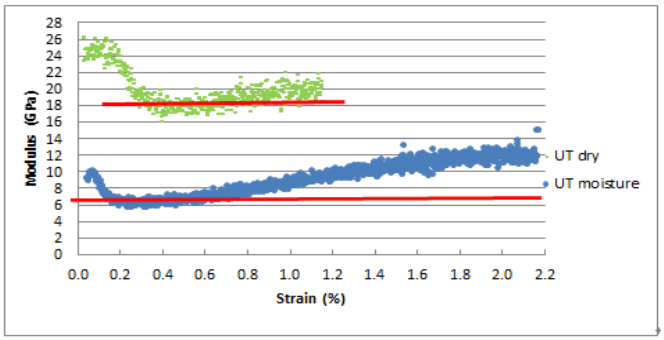

Figure 5: Local longitudinal tensile stiffness as a function of longitudinal tensile strain for the untreated UD flax fibre reinforced composites tested at a relative humidity of 50% (dry) and an increased humidity of 90%. In both cases, the division of the longitudinal tensile stress-strain response in three linear regions separated by two in-between transition zones is visible.

From figures 4 and 5, it becomes clear that the longitudinal tensile stress-strain curve of UD flax fibre composites is composed of three linear regions, separated by two in-between transition parts. The first linear region, represented in figure 4 by line segment OA, is accounted to the general elastic behaviour of the composite. The second linear region with decreased local longitudinal tensile stiffness, represented in figure 4 by line segment BC, is linked to the slippage of elementary fibres within the technical flax fibres and the gradual plastic deformation of the amorphous components in the elementary fibre interphase. Finally, the third linear region with increased local longitudinal tensile stiffness, represented in figure 4 by line segment DE, is assigned to the system in which the micro-fibrils and corresponding crystalline cellulose chains are immobile. The first in-between transition zone (AB) in this light represents the onset of visco-elastic deformation of the amorphous components in the elementary fibre interphase. The second in-between transition zone (CD) represents the gradual alignment of the micro-fibrils with the loading direction. In this way, the entire tensile stress-strain shape can be explained.

4. Conclusion

In this paper, the effect of silane, alkali and water treatment on the mechanical properties of flax fibre reinforced bio-epoxies is investigated. Transverse three-point bending tests are applied to investigate the optimal treatment parameters for each treatment. A 4wt% 5 min alkali treatment increases the transverse flexural composite strength from 11.9±2.2 to 29.2±2.7 MPa. The optimal silane treatment (10wt% 10min) is able to statistically yield the same transverse flexural strength. Furthermore, the water treated composites show a minor improvement in the transverse flexural strength (18.2±0.6 MPa). In all cases, the improvement in transverse bending properties is linked to changes in the internal flax fibre composition, increasing the reactivity with the bio-epoxy matrix. In order to investigate the improvement of the fibre treatments on the longitudinal tensile properties of UD flax fibre reinforced bio-composites, a series of tensile tests is carried out. It is shown that all treatments increase the longitudinal tensile stiffness by around 15%. This improvement is supported by an increase in fibre/matrix interphase strength, as confirmed by SEM microscopy. However, only alkali treatment is able to increase the longitudinal tensile strength. The water and silane treatment decrease the plasticity of the composites, which opposes the improvement in fibre/matrix interphase strength. Finally, it is shown that the division of the longitudinal tensile stress-strain response in three linear regions separated by two in-between transition zones is valid for UD flax fiber bio-epoxy composites, irrespective of the testing conditions or fibre pre-treatment.

Acknowledgements

The authors wish to thank the EU-FP7-financed BioBuild project for its contribution.

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