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A multi-scale study of the interface between natural fibres and a biopolymer

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Abstract:

A significant recent development in the composite field is the appearance of biocomposites (biopolymers reinforced by plant fibres) which combine mechanical performance and low environmental impacts. However, to replace conventional composites a significant effort is needed to understand their mechanical behaviour under complex loading (both in-plane and out-of-plane). The interfacial behaviour (fibre/matrix) of these materials also requires particular attention in order to optimize mechanical properties. With this aim modified Arcan, transverse tension and microdroplet debonding tests have been performed on flax reinforced PLLA biocomposites, as very few data of this type are available.

The out-of-plane tensile and tensile-shear properties of these biocomposites are lower than those measured in shear. Manufacturing parameters, and particularly consolidation pressure, are critical for these materials. Out-of plane apparent shear strengths are similar to those from debonding tests. A common feature of the tests performed at the three scales is the appearance of fibre peeling.

Keywords : A natural fibre composites ; B interfacial properties ; B out-of-plane properties ; B microbond test

1. Introduction

High performance composites are used in many applications such as automotive, aeronautical and nautical structures. In addition to functional properties such as mechanical behaviour, information on environmental behaviour is increasingly being requested by designers, particularly when an eco-design is considered. A significant recent development in this area has been the appearance of biocomposites (biopolymers reinforced by plant fibres) which combine good mechanical performance and low environmental impacts. The latter can be significantly reduced when fibres such as flax reinforce a biosourced thermoplastic polymer such as PLA (poly(lactic acid) [1], [2], [3], [4], [5] and [6]. The inclusion of plant fibres is of particular benefit to reduce weight in transport applications [7].

However, in order to replace conventional composites (glass/Polypropylene or glass/polyester) a significant effort is needed in order to understand the mechanical behaviour of these biocomposites under complex loading, both in- and out-of-plane. The interfacial behaviour (fibre/matrix) of these materials also requires particular attention in order to optimise mechanical properties, as the extensive experience with glass fibres does not exist yet for these relatively new materials. Most of the published work on biocomposites is based on results from tests at a single scale, often macroscopic (tensile or flexure tests), which makes analysis of the interfacial phenomena very difficult, especially when the fibres are randomly dispersed. Alternatives, staying at the macroscopic scale, are to use special mechanical tests such as mode I delamination which are sensitive to the interface [3, 8], recording acoustic emission on tensile specimens to determine damage threshold values [9] or to work on particular lay-ups such as ± 45° in order to favour interfacial damage mechanisms [3, 10-12]. Another solution is to work at the ply scale (mesoscopic) in order to simplify the phenomena. For example, off-axis tensile tests (at 15, 30, 45, 60 and 90°) have been performed on unidirectional flax/Polyester [10, 13], hemp/PET [14] and flax/Epoxy [11] composites.

Direct information on fibre/matrix interface behaviour can be obtained at the microscopic scale using micro-mechanics tests (pull-out, microbond, fragmentation…). Various studies on fragmentation and microdroplet debonding have been performed to characterize the interface between a flax fibre and matrix resins such as epoxy [15, 16], polyester [17], polypropylene [18] and more recently polylactide (PLA) [19].

Combining these different approaches within the study of one system should help to improve the understanding of the mechanisms governing the interface behavior, and comparing different characterization methods should enable the strengths and weaknesses to be clarified [20]. However, to date few studies have worked with this multi-scale approach. Herrera franco *et al.* [21] examined the influence of silane treatments on Hennequen fibres (with a HDPE matrix) using macroscopic tests (Iosipescu shear and flexure), mesoscopic (tensile and transverse flexure on unidirectional specimens) and microscopic tests (fragmentation and pull-out). The results at each scale showed the same trends for the treatments, even though absolute values cannot be compared directly. In a similar way, Nam *et al.* [22] performed pull-out and longitudinal tension tests on composites with a PolyButylene Succinate matrix reinforced by coir fibres in order to evaluate the influence of an alkaline treatment.

Following on from those studies, the present paper proposes a multi-scale characterization of the properties of a biocomposite which is recyclable and compostable, based on a PLLA matrix reinforced by randomly dispersed flax fibres. The properties at the macroscopic scale will be evaluated using an original experimental set-up (the modified Arcan test) which allows loading in the through-thickness direction [23]. Transverse tensile tests combined with in-situ scanning electron microscope observation will be used at the mesoscopic level and microdroplet debonding tests complete the study at the microscopic scale.

2- Materials and Methods

2.1 Material

2.1.1 Fibres

All the samples were manufactured with flax fibres grown in France. Plants were subjected to dew retting before mechanical scutching and hackling.

For samples characterized with the Arcan fixture (macroscopic scale), flax fibres were organized into a randomly oriented in-plane mat structure. Flax mats were manufactured using a semi-industrial paper-making route [24]. Fibre length was 10 ± 1 mm, which results in a high aspect ratio (L/d ≈470) due to separation of fibre bundles during the process. However some fibre bundles remain in the mat. The weight per unit area of the flax mats was around 230 g/m².

Unidirectional biocomposites (microscale scale) were manufactured with unidirectional flax ribbon with transverse knitted cotton yarn supplied by Biorenfort® (France). The areal weight of the UD flax was around 150 g/m².

2.1.2 Matrix

The bio-polymer matrix used for all the samples was Poly-L-(lactic) acid (PLLA) of molecular weight (M_n) 63000 g/mol produced by Natureworks®.

2.2 Composite manufacturing

PLLA/flax mat composites were manufactured by the film stacking route. The stack of 6 PLLA extruded films and 5 flax mats was placed in a hot press (T=190°C) according to a protocol published previously [25]. Fibre fraction was 30% by weight corresponding to 26.5% by volume. Arcan samples were milled from the panel with the following geometry: 88x24x2 mm^3. Transverse tensile samples were also manufactured by film stacking with the same protocol with various fibre weight content (20, 30 and 40%). The specimen geometry is that of the NF T 57-101 standard with a 25 mm width. Microbond specimens were prepared by placing a PLLA microdroplet on a single flax fibre. To obtain single fibres, flax bundle separation was performed under an optical microscope using tweezers for extraction. A fibre specimen was then bonded to a thin paper frame which has a central longitudinal slot of fixed gauge length (10mm). Each specimen was then re-examined under a microscope to check the fibre diameter and microdroplet geometry. The variability of fibre cross-section must be considered when working at the micro-mechanics scale on natural fibres. We assume that the drop length is small enough (<150 µm) to be able to neglect fibre diameter variation along the bonded length of the droplet.

Heating time and cooling rate were kept constant ($t_{190°C}$ = 8 min and Cooling = 10°C/min) for all manufacturing processes in order to limit different stress states and microstructure variations. It should be noted that no physical or chemical pre-treatments were used for any of the samples.

2-3 Mechanical characterization

2-3-1 Modified Arcan test

The modified Arcan fixture (Figure 1) was designed to analyze adhesives and bonded assemblies over a range of tensile/shear and compression/shear loads [26, 27]. The fixture is carefully positioned between the jaws of a test machine using articulated connections (Figure 1). The use of machined beaks reduces edge effects and stress concentrations [23]. Tests were performed under displacement control at 0.5mm/min.

Figure 1

In order to analyze the movements of the assembly an image analysis system was used, based on image correlation (ARAMIS, GOM). This enables the behaviour of the adhesive and the composite to be identified. The biocomposite specimens were lightly abraded, then bonded to aluminium substrates using the procedure described previously [23]. Tests were performed with loads in three directions: 0, 90 and 45° as shown in figure 2. Five samples were tested for each loading condition.

Figure 2

2-3-2 Transverse tensile test

Tensile tests were performed on the composites to investigate possible correlation with 0° Arcan tests. They were carried out according to French standard NF T 57–101 on parallel sided specimens of width 25 mm. Elongation was measured using an extensometer. Loading rate was 1 mm/min.

2.3.3 Microdebonding tests

In order to observe the damage mechanisms, samples were also tested on a small tensile test machine (DEBEN microtest) inside a scanning electron microscope (SEM), a Jeol JSM 6460LV.

The force and displacement were recorded during each test allowing an apparent interfacial shear strength (IFSS) to be determined. At least 50 microdroplets were tested in order to be able to apply a statistical approach. The load–displacement behaviour was linear for all tests up to debonding. An apparent interfacial shear strength τ_{app} (IFSS) was determined using simple micro-mechanics equations [28] which assumes a uniform interface stress distribution. The contribution of residual stresses and friction are not taken into account [29] even though friction strength after debonding is analysed separately. The interfacial shear strength will be compared to to pure shear 90° Arcan tests.

3- Results and Discussion

3-1 Arcan characterization

The flax mat/PLLA bio-composite was characterized using the Arcan fixture and loading in 3 directions: tension (0°), shear (90°) and tension/shear (45°). Figures 3A, B and C show the mechanical behaviour of each set of samples.

Figure 3

For the through-thickness tensile tests the results from the different specimens show considerable scatter (Figure 3A). Three of the samples show an irreversible damage threshold (knee), the others are nearly linear up to failure. The slopes of force versus displacement are different but the break loads are all quite similar, around 6.5 kN (Table 1). This gives an apparent failure strength of 9.4 ± 0.4 MPa (Table 1).

Table 1

Fracture surface observations indicate an intralaminar failure in the composite within the flax mat rather than at the epoxy adhesive joint (Figure 4A). Therefore the tests characterize the out-of-plane properties of the Flax/PLLA biocomposite, not the adhesive or interface. The fracture surfaces observed are similar to those revealed in a previous study on the same materials, after interlaminar crack propagation failure [3].

Figure 4

Fracture surface observations in a scanning electron microscope show there are some fibre bundles apparent as this is a prototype mat material. In addition, many fibres fail in a cohesive manner, within the outer fibre layers (Table 2). Control of the fibre/matrix interface is not the only challenge in these materials as the resistance of shared lamellae within fibre bundles and of the fibre layers to out-of-plane loads may be the weakest link. The observations also indicate quite ductile matrix behaviour, again confirming previous results [3]. At this scale, the fibre/matrix interface appears to be of good quality.

The response to shear loading (90°) shows little scatter (Figure 3B). A bi-linear behaviour is noted, the quasi-linear section extending from 0 to around 8000 N, the damage threshold at which cracks appear and the stiffness decreases. From this point onwards the extension continues to increase, as other energy dissipating mechanisms exist (debonding, friction at the fibre/matrix interface, plastic deformation of the matrix…). The break strength in shear is around 19 MPa, twice the value obtained in tension (Table 1). Final failure occurs once again within the flax mat layer (Figure 4B). Different failure modes can be observed in the mat fibres due to the quasi-isotropic fibre orientation, but the majority of the fibres show a clean break (Table 2). There is some peeling but it is mostly very superficial. The matrix shows a different aspect to that of the 0° fracture surfaces, with very little ductility apparent. However, there is some evidence of debonding, with the impressions of fibres left in the matrix after the fibres have been removed (Table 2). It should be noted that the displacements in shear are around 10 times larger than those measured in tension.

The plots from the tension-shear tests at 45° (Figure 3C) also show little scatter. Here the biocomposites show a quasi-linear behaviour with brittle failure, the failure strains are in the same range as those measured during tensile loading at 0°. The failure strengths are also similar to the tensile strengths, around 9 MPa (Table 1). Fracture surface observations (Figure 4C) indicate failure in the flax mat once again, with an intermediate failure between those observed at 0° and 90°. Considerable peeling is noted, the matrix is similar to that observed in tension and the residual PLLA on the fibres suggests a reasonable fibre/matrix interface quality (Table 2).

Table 2

The results from the different loading combinations can be summarized in a plot showing a failure envelope such as the one presented in Figure 5.

Figure 5

There are few data available for similar material in the published literature to compare with these results. However some recent studies with the same modified Arcan, fixture as the one used here, have characterized various structural adhesives [30, 31]. Apparent tensile failure stresses for these materials vary from 30 to 40 MPa and shear strengths from 30 to 50 MPa. Finally, Sohier *et al.* [32] presented some values for 45° glass/carbon/epoxy composites manufactured in an autoclave. The failure stresses in tension and shear were around 45MPa, around 5 times the values for the biocomposites tested here.

3-2 Mesoscopic scale: Transverse tension on unidirectional composite

Figure 6 shows the behaviour of PLLA composites reinforced by unidirectional flax reinforcement under transverse tensile loading for different fibre contents. For a 20% weight fraction (v_f = 17.2 %), the biocomposite shows brittle behaviour. As the fibre content is increased the tensile behaviour tends to become non-linear. A similar trend has been noted previously for composites with flax fibres in a polyester matrix (v_f =21.5%) [33]. One has to keep in mind that the unidirectional reinforcement includes both single fibres and bundles of fibres, which may induce strain field heterogeneity [34, 35].

Figure 6

Figures 7A and 7B show how the transverse modulus (E_T) and transverse failure stress (σ_T) change with fibre content. The transverse modulus increases when fibres are added to the matrix (20%) from 3600 MPa to 4100 MPa. The transverse modulus of the flax fibres has been estimated to be slightly higher than that of the matrix ($5<E_{fT}< 9$ GPa) [13, 33]. However, increasing the fibre content from 20 to 40% results in a very small further increase in E_T. Again these results are similar to those measured on flax/polyester, and are significantly lower than those for glass/polyester [33].

The transverse failure stress drops sharply as fibres are added, from around 60MPa for the unreinforced matrix to around 30 MPa for the composite with 20% by weight of fibres. This value is significantly higher than those reported for flax/polyester, glass/polyester [33]. The presence of fibres affects the strain field in the surrounding matrix, particularly when the fibre distribution is heterogeneous and fibre diameters vary [35]. The presence of both fibre bundles and single fibres results in a highly non-uniform strain field. Increasing fibre content from 20 to 40% results in only a slightly lower value of σ_T.

Figure 7

Additional information on transverse damage in these biocomposites can be obtained by performing transverse tensile tests inside an SEM. Figures 8 A, B and C show different damage mechanisms during such tests.

Figure 8

Flax/PLLA biocomposites show different types of damage:

- In the matrix, in particular in the zones between fibres (Figures 8A and B), where the highest strain concentrations occur.
- Debonding at the fibre/matrix interface (Figures 8A et 4B)

- Damage within the fibre bundle interfaces, in particular debonding between neighbouring lamella and between lamella and the matrix (Figure 8A). In these zones stress concentrations will occur. In addition to these areas, inside the bundle impregnation may not be complete especially with thermoplastics resins.
- Within the fibres themselves, by crack propagation (Figure 8C) or peeling of outer layers. Similar mechanisms have been noted in some carbon fibre (pitch based)/epoxy composites [36].

Therefore separation of fibre bundles in single fibres is of great importance to control damage mechanisms and to improve mechanical performance, as highlighted by Coroller et *al* .[34].

3-3 Microdroplet debonding

Microdroplet debonding tests were performed on the same materials in order to examine the apparent shear strength (IFSS) of the flax/PLLA interface directly. Typical flax/PLLA interface behavior is shown on figure 9A. The debonding force in this case is the maximum load required to break the fibre/matrix interface. The friction force is a residual force which remains after debonding due to residual stresses. These two forces are plotted as a function of the bonded area (Figure 9B) in order to determine the apparent interfacial shear strength τ_{app} and the friction stress τ_f. The relationship between these two forces and the bonding area is quite linear.

Figure 9

The values of apparent shear strength and friction strength are 18.2 ± 1.2 MPa and 8.2 ± 1.9 MPa [37]. The friction strength is quite high, almost half the shear strength. The origins of this adherence between flax fibres and PLLA are now reasonably well known [19, 37-40]. The main contributors are van der waals forces, acid/base interactions, and capillary effects, in particular through the presence of hydroxyl groupes and water at the fibre surface and carbonyl groups in the PLLA. Clearly residual stresses also contribute to the strength of this interface, as well as friction energy dissipation between fibre and matrix.

Examination of failed debonded samples in the SEM (Figure 10 A and B) provides indications of failure mechanisms. In most cases failure is interfacial, (Figure 10A), however, in a small number of cases surface peeling of the fibre is noted (Figure 10B) which can influence the friction behaviour [19].

Figure 10

4- Discussion

Examination of results from multi-scale testing such as those presented here can bring additional information on interfacial behaviour of flax/PLLA biocomposites. Table 3 summarizes the failure strengths from the modified Arcan, transverse tensile and debonding tests.

Table 3

It is interesting to note that the values from the Arcan shear test (macroscopic) and micro-droplet debonding (microscopic) are similar. Both these tests load the fibre/matrix interface in shear. In addition, displacements recorded at the start of debonding during the microbond tests (around 0.05 mm) are in the same range as the displacement corresponding to the loss of linearity in the Arcan shear test. Therefore, the large friction contribution measured after droplet debonding may also be one of the mechanisms contributing to the energy dissipation after the yield point in the Arcan shear tests which show a ductile failure mechanism (Figure 3B).

It should nevertheless be noted that the debonding test does not involve a pure shear stress state [41].

The transverse tension properties are significantly higher than those measured in the out of plane tension Arcan test at 0°. Although the response to both tests will involve loading of the fibre/matrix interface, the properties of the constituents and the reinforcement distribution also play a role [42]. The Arcan test at 0° will also involve the interlaminar region, the quality of which depends on the consolidation during manufacture which differs from transverse tensile tests. The Arcan tensile specimen is also constrained over a much larger area, limiting Poisson effects

The tension-shear loading tests (45° with Arcan) are more complex and difficult to relate to the other loadings, but are probably closer to most real loading situations.

Analysis of results from tests at different scales is particularly complex for bio-composites, where the fibre distribution is very heterogeneous. This confirms observations published previously [3]. Fibre bundles introduce particular defects and can agglomerate during manufacture to result in clusters of fibre bundles. The multi-layer composite nature of the flax fibres themselves also makes the transfer between scales difficult to quantify. Nevertheless, at least qualitatively, certain phenomena such as fibre peeling are noted at each scale and would benefit from more study in order to establish to what extent the microscopic structure of flax fibres limits the macroscopic composite properties, in particular as an energy dissipation mechanism. This is also a key issue in the development of fibre surface treatments. Further work is in progress to pursue this.

5- Conclusion

The integration of vegetable fibres in a polymer matrix is enabling composites with interesting properties to be developed with a low environmental impact. In order to extend this development it is essential to possess a thorough understanding of the mechanical behaviour of these materials, not only in-plane but also in the through-thickness direction. With this aim modified Arcan, transverse tension and microdroplet debonding tests have been performed, as very few data of this type are available.

The out-of-plane tensile and tensile-shear properties of these biocomposites are lower than those measured in shear. Manufacturing parameters, and particularly consolidation pressure, are critical to obtain good impregnation without fibre degradation. Out-of plane apparent shear strengths are similar to those from debonding tests. A common feature of the tests performed at the three scales is the appearance of fibre peeling. This is an unusual failure mechanism, rarely observed in traditional composites, and indicates that a better understanding of the role of flax fibre micro-structure is essential if biocomposite properties are to be optimized.

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Figure caption

Figure 1 Modified Arcan test set-up

Figure 2 Representation of the assembly and loading directions

Figure 3 Mechanical behaviour of flax mat/PLLA biocomposites under out-of-plane loads, - A tension (0°), B shear (90°) and C tension/shear (45°)

Figure 4 Observation of biocomposite fracture surfaces, indicating failure within the flax mat. A : Loading at 0°. B : 90°. C : 45

Figure 5 Failure envelope, out of plane loads, for flax mat/PLLA

Figure 6 Transverse stress-strain curve for PLLA/UD Flax biocomposites as a function of fibre weight content

Figure 7 Evolution of transverse Young's modulus (A) and transverse failure stress (B) of flax/PLA biocomposite versus fibre content

Figure 8 SEM images of damage mechanisms during transverse tensile tests in SEM. A: fibre bundles, B: region between single fibres, C: focus on a single fibre. Red arrows indicate loading direction

Figure 9 A Typical debonding behavior. B - Debonded Force and Friction force versus embedded surface

Figure 10 SEM Micrograph of debonded PLLA microdroplet on single flax fibre. A Interfacial failure. B Heterogeneous cohesive failure

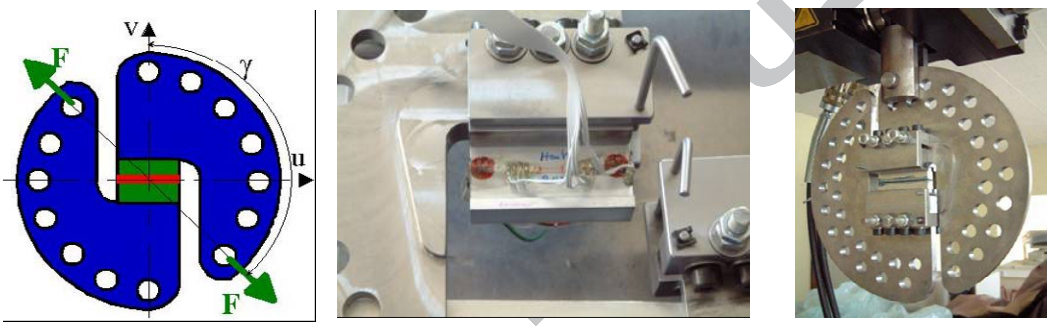


Figure 1 Modified Arcan test set-up

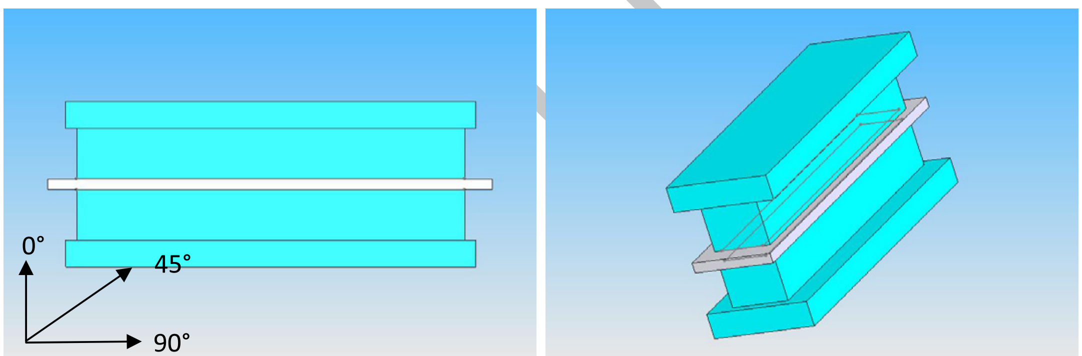


Figure 2 Representation of the assembly and loading directions

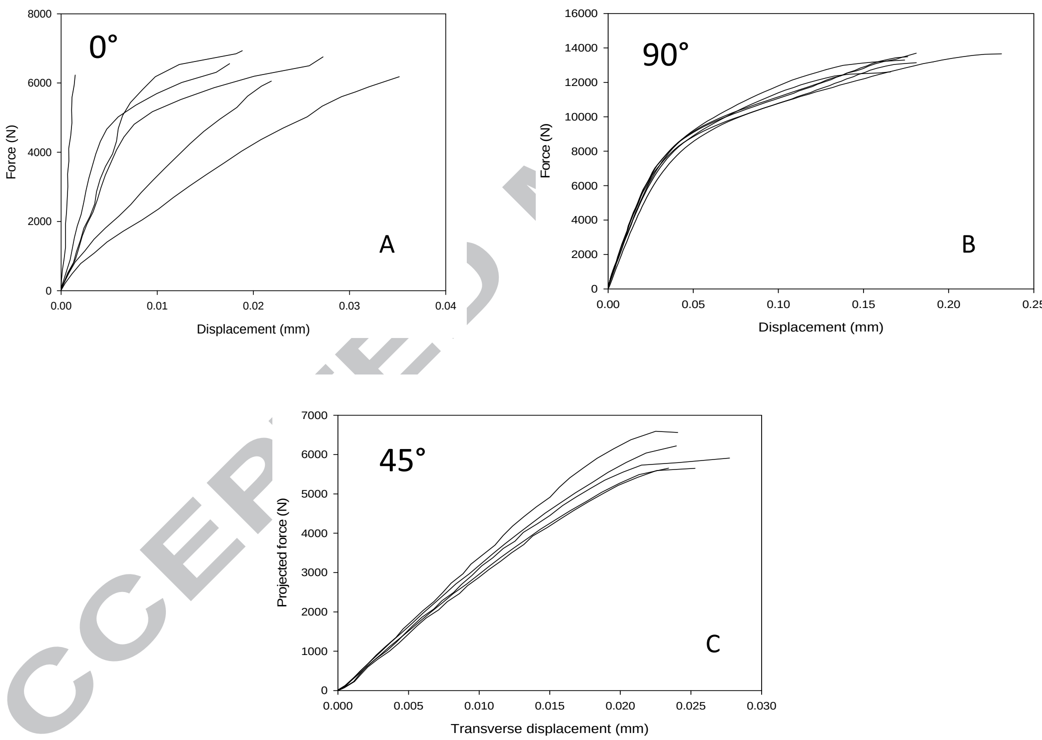


Figure 3 Mechanical behaviour of flax mat/PLLA biocomposites under out-of-plane loads, - A tension (0°), B shear (90°) and C tension/shear (45°)

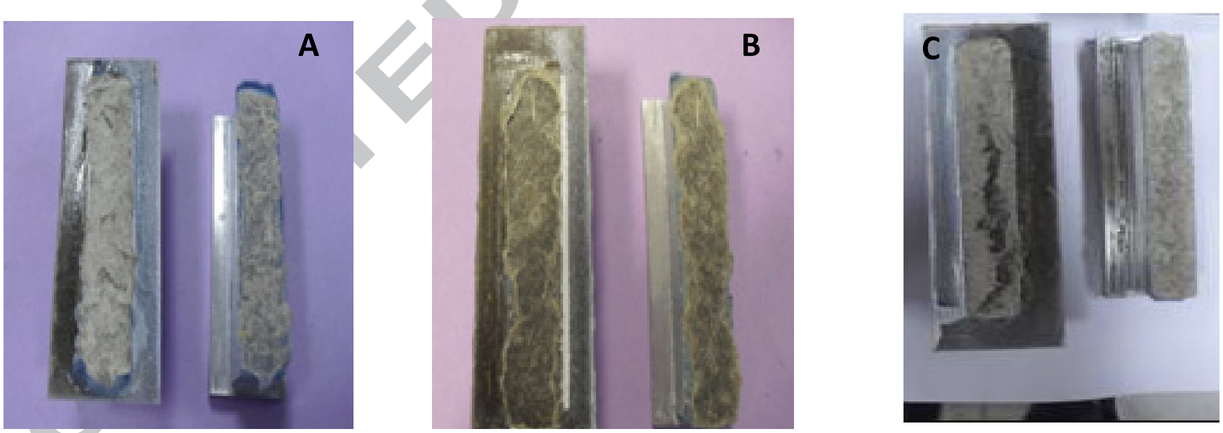


Figure 4 Observation of biocomposite fracture surfaces, indicating failure within the flax mat. A : Loading at 0°. B : 90°. C : 45°

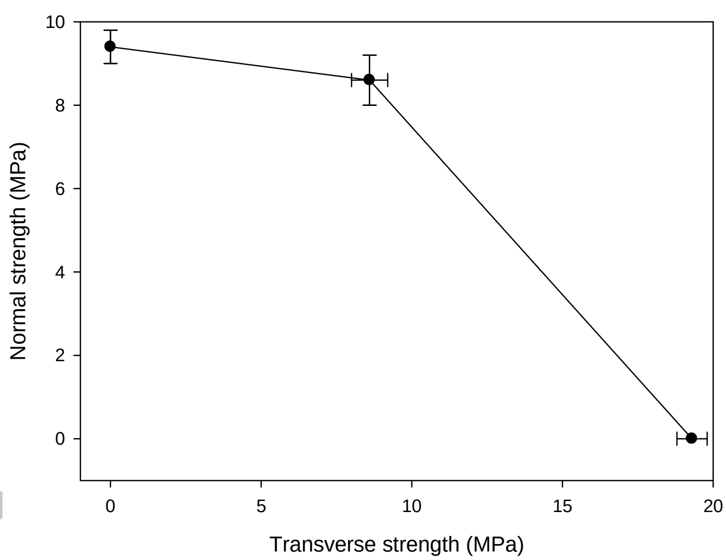


Figure 5 Failure envelope, out of plane loads, for flax mat/PLLA

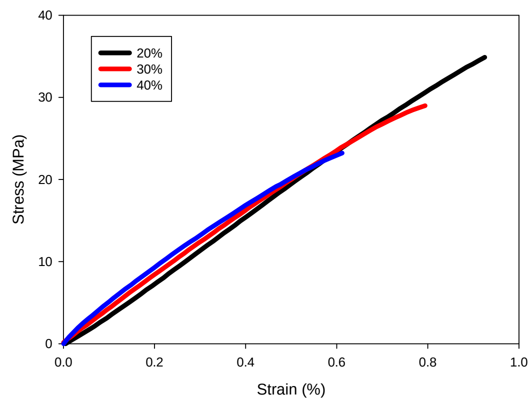


Figure 6 Transverse stress-strain curve for PLLA/UD Flax biocomposites as a function of fibre weight content

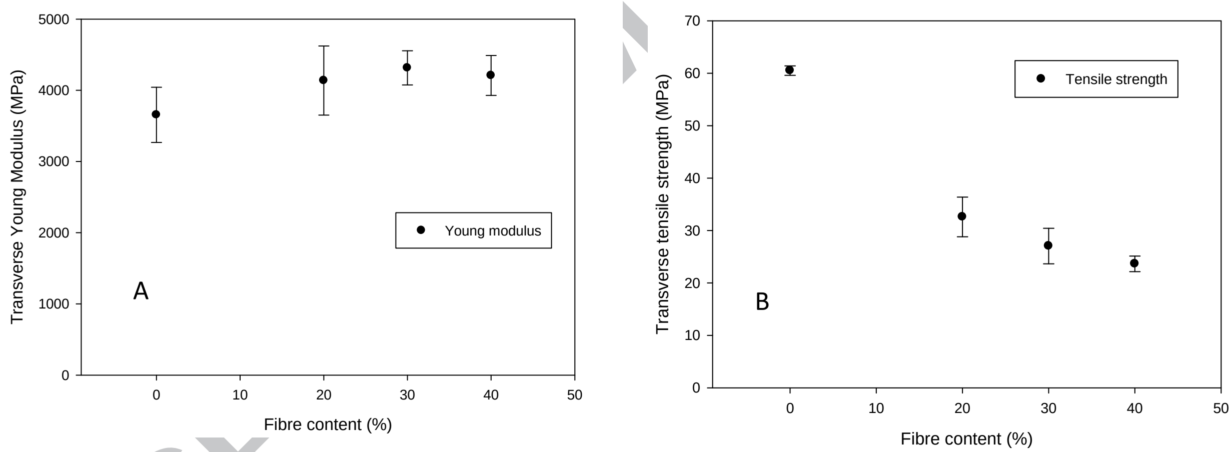


Figure 7 Evolution of transverse Young's modulus (A) and transverse failure stress (B) of flax/PLA biocomposite versus fibre content

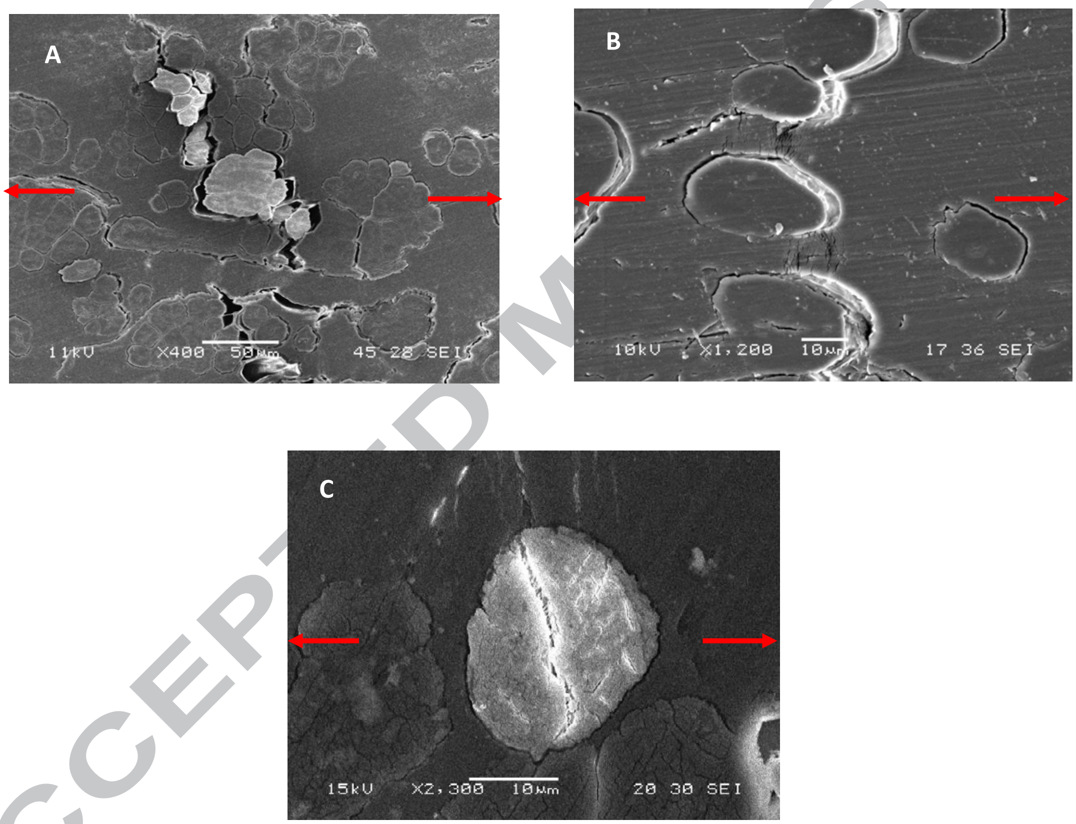


Figure 8 SEM images of damage mechanisms during transverse tensile tests in SEM. A: fibre bundles, B: region between single fibres. C: focus on a single fibre. Red arrows indicate loading direction

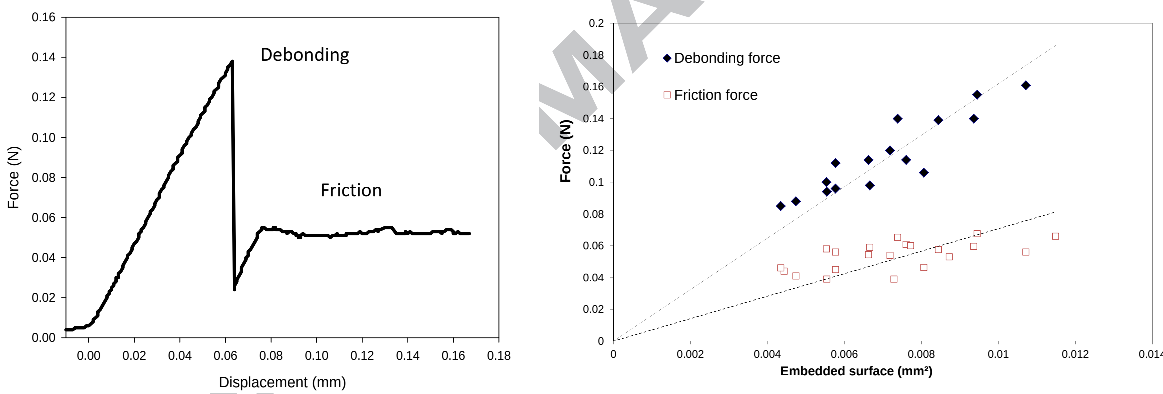


Figure 9 A- Typical debonding behavior. B- Debonded Force and Friction force versus embedded surface

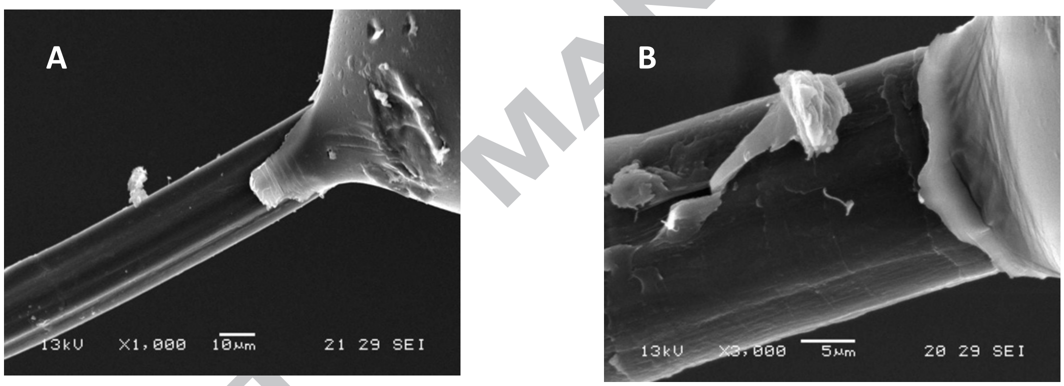


Figure 10 SEM Micrograph of debonded PLLA microdroplet on single flax fibre. A Interfacial failure. B Heterogeneous cohesive failure

Table caption

Table 1 Out-of-plane mechanical properties measured using the modified Arcan fixture.

Table 2 Damage mechanisms in PLLA/flax mat biocomposite after different loadings in Arcan tests

Table 3 Mechanical properties from tests at different scales (m_f = 30% except for microdroplet) : Modified Arcan, transverse tension, microdroplet debonding

	Tension (0°)	Shear (90°)	Tension/Shear (45°)
Break load (N)	6529 ± 266	13316 ± 370	5912 ± 408
Apparent failure strength (MPa)	9.4 ± 0.4	19.3 ± 0.5	8.6 ± 0.6

Table 1 Out-of-plane mechanical properties measured using the modified Arcan fixture.

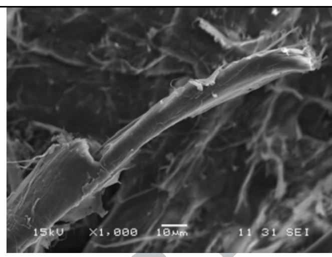
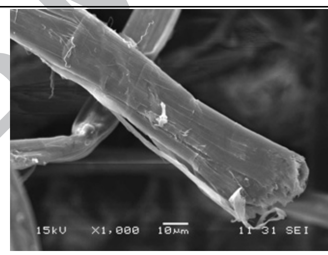
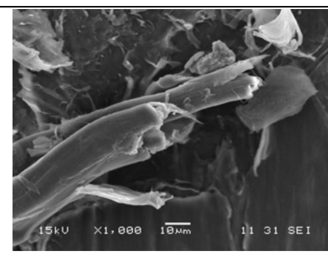
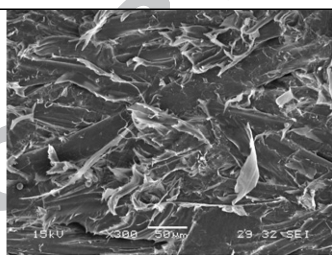
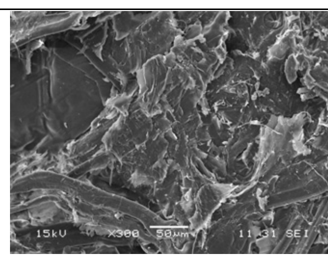
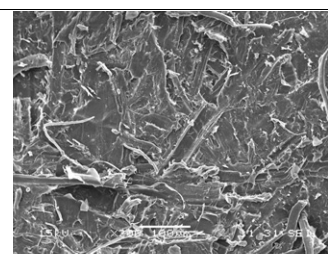
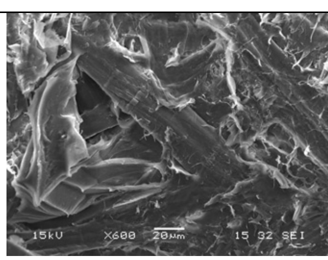
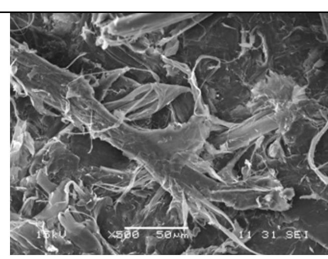
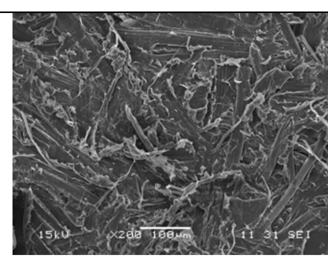
	Tension at 0°	Shear at 90°	Tension/Shear at 45°
Fibre			
matrix			
fibre/ matrix Interface			

Table 2 Damage mechanisms in PLLA/flax mat biocomposite after different loadings in Arcan tests

	Macroscopic			Mesoscopic	Microscopic
	Tension 0°	Tension –shear 45°	Shear 90°	Transverse tension	Debonding
Failure stress (MPa)	9.4 ± 0.4	8.6 ± 0.6	19.3 ± 0.5	27 ± 3.3	18.2 ± 1.2

Table 3 Mechanical properties from tests at different scales (m_f = 30% except for microdroplet) : Modified Arcan, transverse tension, microdroplet debonding