Thermo-mechanical performance of poly (lactic acid) /flax fibre-reinforced biocomposites

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Abstract

In this study, the thermo-mechanical performance of flax fibre reinforced poly lactic acid (PLA) biocomposites was investigated for the potential use in load bearing application such as body-in-white and body structures in the automotive sector. Focus was given into the relationships between the thermal and mechanical properties, and the material response under different loading and environmental conditions. The strength (72 MPa) and stiffness (13GPa) of flax/PLA composites investigated indicate a very promising material to replace traditional choices in load bearing application. The PLA's crystallinity was measured to approximately 27%. Annealing above 100 °C for an hour decreased that value to 30%, but analysis of tensile results of annealed specimens reveals a significant reduction of both the tensile strength and modulus. This reduction is associated with micro-cracking that occurred on the surface of PLA during the heating as well as deterioration of the flax properties due to drying. The study results show that strength and modulus increased with increasing strain rates, while elongation at break reduces respectively. A modulus of 22 GPa was recorded in 4.2 m/sec crosshead velocity. Further, flax/PLA showed significantly higher modulus than flax/epoxy for the composites studied. Improvement of the interfacial bonding and the temperature characteristics, combined the thermoplastic nature of PLA, demonstrates that flax/PLA composites is ideal for use in structural automotive applications.

Keywords*:* Polymer-matrix composites; Mechanical properties; Mechanical properties; Mechanical testing; Thermal analysis;

1 Introduction

Natural fibre composites are fast emerging as viable alternative to traditional materials and synthetic composites. Their low cost, lightweight, good mechanical performance and their environmentally friendly nature makes them an ideal choice for the automotive [1]. The automotive industry has already embraced these composites for several years for the production of non-structural components and their use is predicted to constantly increase in coming years. On-going efforts are aimed at developing 100% structural composites utilising bio-sourced polymers as a matrix for natural fibres reinforcement as an alternative to synthetic fibres.

Flax fibres are considered to be one of the strongest and commercially available plant fibres. Its strength varies between 350 and 1500 MPa whilst its modulus can be as high as 80 GPa [2-8]. These properties combined with its very low density and excellent damping properties make flax fibres a very good alternative to glass fibres in structural applications. To date, research has shown that flax fibre reinforcements considerably improve the stiffness and strength of the matrix, whether thermoset or thermoplastic [9-11], with the performance being affected by the fibre length, volume fraction within the composite and the interfacial adhesion between the fibres and the matrix [11; 12].

One of the most promising and suitable bio-sourced polymers is poly(L-lacctide) (PLA). It is an aliphatic thermoplastic polyester derived from lactic acid found in renewable resources, such as corn, wheat, barley, cassava, and sugar cane [13]. Lactic acid is then polymerised to PLA, either by gradual polycondensation or by ring-opening polymerisation. Due to the chiral nature of lactic acid, several distinct forms of PLA exist: poly-L-lactide (PLLA) is the product resulting from the polymerisation of L,L-lactide (also known as L-lactide), while poly-D-lactide is produced from D-lactide. Polylactic acids are hydrophobic in nature and are among the few polymers in which the stereochemical structure can easily be modified by polymerising a controlled mixture of the L- or D-isomers to yield high molecular weight amorphous or crystalline polymers that can be used for food contact applications.

Recent research has shown that PLA is a highly suitable polymer matrix for natural fibres –reinforced composites. For instance, Tokoro et al [14] mixed three types of bamboo fibres into a PLA matrix to improve its impact strength and heat resistance. Their studies resulted in good quality composite materials with the presence of the bamboo fibres increasing greatly the impact performance and thermal properties. Ochi [15] investigated kenaf/PLA composites with different fibre proportions. He reported that the Young's modulus, tensile and bending strength linearly increased up to a 50 wt.% fibre content in the composite. The study observed that unidirectional biodegradable composites fabricated using an emulsion-type PLA resin and kenaf fibres at a fibre content of 70 wt.% had high tensile and flexural strengths of 223 MPa and 254 MPa respectively. Shibata et al. [16] study prepared composites with PLA/lyocell fabric by compression moulding. The tensile modulus and strength of

lyocell/PLA composites improved with increasing fibre content. Impact strength was considerably higher than that of pure PLA. Pan et al. [17] also produced PLA/kenaf composites by injection moulding with kenaf fibre contents ranging between 0% and 30%. At 30% a tensile strength improvement of 30% was observed.

The extended use of bio-composites for the manufacturing of vehicle components would benefit largely the industry, but to date their low mechanical properties associated mainly to the thermal stability and the interactions between the fibres and the matrix, restrict their use. Although studies report the properties and potential improvements of biocomposites, the overall mechanical behaviour from a structural point of view is not completely understood and mechanical performance is below the target. The properties of the biocomposites and their mechanical performance under different environments and their effect of different loading conditions are still not understood well enough for adoption in mass products in the transport industry.

In this work, therefore, we focused on developing further understanding on thermo-mechanical behaviour of PLA/flax biocomposites manufactured using compression moulding. The primary aims were to determine the phenomena dominating their mechanical behaviour and their potential use in structural automotive applications. The mechanical properties were evaluated through tensile testing in varying environmental and loading conditions simulating typical operational conditions. Thermal studies including dynamic mechanical thermal analysis and calorimetry were conducted. Microscopy was employed to in order to investigate fracture surfaces and fibre/matrix interactions.

2 Materials and methods

2.1 Materials

A commingled/pre-impregnated PLA/flax fabric (mixed flax and PLA fibres) was used to manufacture the specimens. The poly($_L$-lactide) acid (PLA) was based on lactides acquired from corn starch fermentation (supplied by Natureworks@) and had 1.25 g/cm^3 density. The reinforcement used was a 2x2 twill flax weave with an approximate unconsolidated thickness of 0.8mm (once consolidated the thickness is around 0.3mm). All samples were prepared using a hot press moulding process with 12 layers of the fabric for the 3 mm samples and 16 layers for the 4 mm samples. The parts were moulded at 180°C, 15 bar pressure and held there at maximum temperature for 5 mins before cooling stage. The manufacture plates had 1.4 g/cm^3 density and they were then machined to produce test specimens. The manufacturing was tuned to result in samples with 40 vol.% flax. The volume fraction has a critical effect on the properties of natural fibre bio-composites. A value between 30-40% has been used in numerous studies and was proven to give natural fibre composites of high quality and thermo-mechanical properties [2, 3, 14, 21, 24]. It was observed that the properties will

generally improve with an increased volume fraction, up to a certain value, after which further increase result in weaker components.

For PLA/fibre reinforced composites to be successful for structural applications, they will have to perform as well appreciated epoxy-based fibre reinforced composites presently used in the automotive industry. Hence good reference material for performance evaluation in this study.

Epoxy resins are widely used as structural adhesives in the aerospace and automotive, the aerospace and a wide range of products where high strength bonds are required. Epoxy resins are also very commonly selected from the automotive industry [1] for the manufacturing of natural fibre bio-composites, and are among the most studied resins to be combined with natural fibres [24] in the literature. Further, there is today a wide range of available bio-sourced epoxy resins (extracted from natural sources such as epoxidised vegetables oils (EVOs) like pine oil waste and soya oil, or waste streams of other industrial processes, such as wood pulp and bio-fuels production) in the European market and an increasing number of companies with extended knowledge on the production of natural composites using these resins. All epoxy/flax composite samples were manufactured by MaHyTec (France). In a typical process, a $0/90^0$ balanced woven fabric (FlaxPly BL300) provided by LINEO was combined with a bio-sourced epoxy resin based on epoxidised pine oil waste (Epobiox LV with hardener Ca23) supplied by Amroy with a 50 vol.% fibre fraction. The plate samples (1.274 g/cm^3) were manufactured through compression resin transfer moulding (RTM) process. A pressuring force of 10kN was used, with a sequential cycle of 2 hours in 800 ^{0}C and 3 hours with a temperature of 1250 ^{0}C. Finally the test samples were then cut out using a milling machine to meet the ASTM 3039 standard.

2.2 Characterisation

2.2.1 Microscopy

For the study of fracture surfaces obtained as a result of mechanical testing of samples and the morphology of the composite, a Scanning Field Emission scanning electron microscope (FE-SEM) was used; model XL30 from FEI, with an acceleration voltage of 15 kV. Before examination all samples were sputtered coated with gold/palladium for 2 minutes to avoid charging.

2.2.2 Dynamic Mechanical Analysis

To assess the temperature of decomposition and the rate of degradation of the materials DMA testing was performed. The DMA instrument used was a Q800 from TA Instruments equipped with a dual-cantilever bending fixture. The frequency was constant at 1Hz and the temperature was set at 25°C

and then linearly increased by 1°C per minute until 150°C. The samples were cut into rectangles of 35 mm × 13 mm × 3 mm to accommodate the DMA. At least three samples per material were tested.

2.2.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a TA instruments Q200 with aluminium sample pans, to evaluate the degree of crystallinity of the PLA in the composite. The glass transition temperature (T_g), cold crystallization and melting temperatures (T_m) were also determined. PLA was pulverized using a blade to scratch from composite panels' surface. The powdered samples, between 5-10 mg in weight, were packed into a stainless steel high volume DSC pan and sealed. Five samples were tested and heated between 25°C and 200°C with a rate of 1°C/min in a nitrogen atmosphere. Two of the samples were also tested in cooling with the same rate for better understanding of the materials transitions.

2.3 Mechanical testing

All mechanical tests were carried at room temperature (ca.23°C) and constant humidity environment. The specimens were firstly conditioned in the same environment for at least 24 hours before testing. Their dimensions were measured with a calliper in at least three locations.

The tensile tests were performed according to the ASTM 3039 standard on an Instron 5500R electro-mechanical machine. Five samples were tested per material at a 2mm/min cross-head velocity. The length and width of the samples were 250mm and 25mm respectively with a 3 mm thickness. Aluminium tabs were added to avoid stress concentrations and damage of the samples by the fixing jaws (see Figure 1).

Figure 1

For the temperature studies a thermal chamber was attached on the Instron machine that allows temperature control from -40 to 150°C with a step of 1°C. The specimens were put into the chamber and tested after the temperature measured on the samples with a thermocouple was stabilized.

A high precision laser extensometer was used throughout the tensile testing. This equipment uses a high speed laser scanner to measure the spacing between two parallel reflective tape strips positioned on the sample during the test [18]. A visible laser light is aimed at the specimen, and reflected back from the tape strips set at the gage length desired. The extensometer displays the actual measured length between the strips or, if desired, the difference between the actual and initial distances.

Advantages of the method include the non-contacting nature of the method which allows measurements without affecting the sample and through chambers, the high resolution, and the fact that maximum strain or strain rates do not affect the results measurement.

3 Results and discussion

3.1 Thermal properties

The percentage of crystallinity is directly related to many of the key properties exhibited by a semi-crystalline polymer including brittleness, toughness, stiffness or modulus, optical clarity, etc. [22]. In order to calculate the percentage of crystallinity of the PLA and relate it later to the mechanical properties measured, DSC studies were carried out in a temperature range of 25-220 °C and a variable heating rate. The glass transition temperature (T_g), melt temperature (Tm), cold crystallization temperature (T_{cc}), as well as the heat of melting (H_m) and crystallization (H_c) are determined for all the samples. The degree of crystallinity is then calculated using the relationship

$$X_c\,(\%\,crystallinity) = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m\%}}.100 \qquad (1)$$

Where ΔH_m and ΔH_c are obtained via integration of the corresponding endothermic and exothermic peak of the melting and crystallization process respectively, and $\Delta H_{m\%}$ is the melting enthalpy of a totally crystallized PLA sample. $\Delta H_{m\%}$ is reported in the literature equal to 93 J/g [22; 23]. This calculation works under the assumption that after the exothermic transition only a small and unknown part of the amorphous material gets crystallized.

Figure 2 shows the DSC thermograms of the PLA as acquired from the composites as a function of the heating rate.

Figure 2

The exothermic peak of cold crystallization is apparent in all three cases signifying the presence of an amorphous part into the polymer. The glass transition is also visible at about 60 °C in each case. However, its duration and temperature range are affected by the heating rate. The exothermic transformation of the cold crystallization is visible at 90-100 °C - after which the heat flow remains constant. It has been observed that the cold crystallization peak increased and shifted towards higher temperatures as the heating rate increased. Interestingly, another exothermic peak appears prior to the melting temperature at around 150°C. This second exothermic reaction is apparent in previous studies

with PLA in the literature but has never been discussed. The increased mobility of the chains close to the melting point, allows the crystallization of an amorphous component not able to transform during the cold crystallization [17; 22; 23]. As the PLA samples were obtained through the composites, this could be associated with the presence of fibre particles, and the fact that the mobility near the fibres is reduced. In higher heating rates this exothermic peak is eliminated. The melting process starts at around 155°C and is completed before 170°C, after which the heat flow remains again constant. The heating rate seems to have again an effect on the starting temperature of the melting process and the associated enthalpy. However the peak temperature of melting remains constant. The re-crystallization of the material to a solid state after melting was observed between 90 and 100 °C for the faster to the slower cooling rates respectively, a typical observation for polymeric materials attributed to the dynamics of a nucleation-area. All temperatures and transitions observed with the DSC, fit nicely with the results acquired above from the dynamic mechanical analysis (DMA).

The degree of crystallinity was calculated between 26-28% from three different samples using equation (1), meaning that the manufacturing parameters do not promote high crystallization of the PLA, although studies have shown that natural fibres help the crystallization process as their surface topography and roughness assists the crystallization acting a nucleating agent [17]. In general, crystalline PLA has better mechanical properties in comparison with amorphous PLA, but the crystallization of PLA requires an annealing process after the moulding which could delay the manufacturing time creating an extra cost.

The fact that enthalpy of melting is close to a third of that of 100% crystallized PLA ($\Delta H_{m\%}$=96 J/g, $\Delta H_m \approx$30 J/g) reveals that only a small portion of the amorphous material changes state after during the exothermic transition. To understand this fact and investigate further the thermal properties of PLA and the process of the thermodynamic transitions a test with repetitive cycles between heat and cooling was conducted. The samples were heated from 25°C past the exothermic transition (120°C) and then cooled down to the initial temperature to start another heating process. The temperature change rate was kept constant to 10 °C/min. The results are depicted in Figures 3 and 4.

Figure 3

Figure 4

In the first heating process the T_g, and cold crystallization temperatures are clearly visible at the same temperature and with same characteristics as described above. However the material after these first transitions shows a very stable and repetitive behaviour. During cooling the heat flow remains constant (with an insignificant decrease in heating capacity in cooler temperatures most probably associated to thermal expansion/contraction of the material) while during the reheat a glass transition is repetitively appearing. Independent of the number of cycles no other exothermic transition is visible, or change in the thermal reaction of the PLA. This observation is opposite to the expected behaviour that every cycle would gradually increase the amount of crystallinity and decrease the ΔH_c to eventually reach zero [22].

3.2 Dynamic mechanical analysis

In general, the dynamic mechanical properties of a composite material depend on the fibre content, presence of the additives like fillers, compatabiliser, fibre orientation and the mode of testing. Natural fibre reinforced composites, are presently used to a great extent for the interior lining of cars and commercial vehicles. For these applications, the strength and stiffness properties have to satisfy the requirements of low temperatures at about −20 °C and higher temperatures of up to 100 °C. For establishing such a wide range of temperature-dependent material data, dynamical mechanical analysis is essential.

Dynamic mechanical thermal analysis is a sensitive technique that is used in studying the effect of temperature on the mechanical properties of materials including polymers and composites. The technique separates the dynamic modulus of materials into two distinct parts: an elastic (storage) part and a viscous (loss) component. The elastic storage modulus is the component of the dynamic modulus where the strain is in phase with the applied stress and the loss modulus is the component of the dynamic modulus |E| where the strain is 90° out of phase with the applied stress. The ratio gives the tangent of the phase angle δ and tanδ is known as the damping and is a measure of energy dissipation. Such parameters provide quantitative and qualitative information about material behaviour.

The glass transition temperature of room temperature for composites studied does not seem to vary significantly (Figures 5).

Figure 5

This value can be improved by changing the curing conditions of the resin (i.e., high temperature curing or post curing), by altering the chemical structure of the resin, or by improving the adhesion

between the fibre and the matrix. Figures 5 and 6 show the results from the DMA and the variation of storage modulus and tan(δ) for the flax/PLA and flax/epoxy composites with respect to the temperature.

Figure 6

Storage modulus is the expression of the ratio of the in-phase stress to the applied strain, representing the energy stored in the material in every cycle of deformation [17]. The glass transition temperatures are between 63-65 °C and 74-76 °C for the flax/PLA and flax/epoxy respectively, showing a disadvantage of the PLA composite in terms of thermal properties. Further, the properties for both materials start deteriorating after about 60-65 °C with the epoxy showing a more gradual loss compared to the PLA which loses more than 80% of its storage modulus before 70 °C. However the glass transition of pure PLA as found in the literature is within 50 and 60 °C with a tan(δ) of more than 2 [17; 20], which signifies that the flax fibres had a positive effect on the properties of the PLA. A possible explanation for this is associated with the fact that the presence of fibres restricts the chain mobility of the neat PLA [17]. Incorporation of the fibres gave rise to a considerable increase of the storage modulus (stiffness) and to a decrease of the tan delta values.

Close and above 80 °C the storage modulus of the PLA composites starts increasing again, an effect associated with the cold crystallization of the amorphous part of the thermoplastic PLA (as will be better described later with the DSC results). No such transition occurs to the epoxy. The properties after the crystallization seem to be very promising. Tokoro et al. [14] experimented with bamboo/PLA composites and the effect of annealing on the properties of the composite. They proved that specimens with 100% crystallinity (annealing at 110 °C for 5h) had significantly improved thermal properties and heat resistance than non-annealed ones [14]. However, the effect of this process on the mechanical properties of the composite has not been discussed.

3.3 Tensile strength and stiffness

The mechanical properties of flax/PLA composites were compared to flax/epoxy. The measured mechanical properties for the both the PLA and epoxy composites are summarized in Table 1.

Table 1

The flax/epoxy has tensile strength of 90 MPa and a modulus 7.6 GPa, compared with 72.2 MPa and 13 GPa respectively of the flax/PLA as shown on Figure 7.

Figure 7

The elongation at break was measured 1.85% and 1.5% for the flax/epoxy and flax/PLA material respectively. The epoxy shows an advantage in terms of strength but its modulus is more than 40% lower than that of flax/PLA. The modulus and strength of the pure PLA are 3.3-3.6 GPa and 50-55 MPa respectively, while those for epoxy are 3 GPa and 63-66 MPa strength. According to these results, the addition of flax will increase the modulus of elasticity of both materials, but will not significantly improve the tensile strength. This could be the result of the poor interfacial adhesion between the fibres and the matrix as observed in the SEM photographs, which results in failure of the composite when the stress reaches the matrix limits. The transfer of load to the fibres is insufficient. On the relevant literature on natural fibres it is widely reported that addition of natural fibres to a polymer matrix has no effect on the ultimate stress of the resulting composite, explained by the quality of fibres and adhesion with matrix [16; 19; 20; 24]. The fracture strain has been reduced with the addition of the flax fibres (both pure PLA and epoxy have an elongation at break of about 2%), possibly due to stress concentration in the fibre/matrix interface that promotes crack propagation.

Oksman et al. [20; 24] have studied PLA with 40 wt.% flax composites, and reported a tensile modulus of 8.3 GPa modulus and a strength of 53 MPa. They also found that by increasing the percentage of flax the mechanical properties were getting lower possibly due to manufacturing issues. These values are very low compared to the ones we measured, showing an improvement on the preparation methods as well as the composite components individually. Another possible explanation could also be the very low processing temperature used in this work (50°C). Packett et al. [19] experimented with jute/PLA composites of 40% by weight fibre content. They concluded increasing the process temperature has a positive effect on the strength and stiffness of the resulting composite due to the reduced viscosity of the PLA which led to better flow properties and hence better wetting of the fibres. Ochi et al. [15] reported very high properties with strength of more than 200 MPa and a modulus higher than 20 GPa on kenaf/PLA composites. The use of an emulsion type PLA and high kenaf fibre content allowed them to get properties comparable to glass fibre reinforced plastics.

Figure 8 shows the stress strain curves obtained from the tensile testing of the flax/PLA and flax/epoxy composites.

Figure 8

A non-linear behaviour can be observed for both the elastic and plastic region, with no clear yield point or transaction area, typical in polymeric materials. The curves show a monotonic increasing behaviour up to a sudden failure point with brittle characteristics. The epoxy specimens have a less steep onset of the stresses due to the lower stiffness and keep rising steadily up to the ultimate strength, in comparison with the PLA specimens were the high stiffness is obvious followed by a faster constant reduction of the curve's derivative.

To investigate the transition point between elastic and plastic regions of the flax/PLA, and understand the nonlinearities of the stress strain curve of the material, cyclic tests were conducted on tensile samples. The curve was divided into at least 5-6 points (areas) according to the strain. The specimens loaded up to specific strain and then unloaded to a zero stress condition, to be reloaded up to the next strain target. Five specimens were tested. Figure 9(a) shows the results of the cyclic test on the flax/PLA samples. The elasticity limit was found between 0.3 and 0.4% of the strain.

Figure 9

The material before that point had a non-linear behaviour but unloading would bring the specimens back to the initial dimensions. The non-linearity continues in the plastic region. Observation of the modulus progress throughout the test leads to the conclusion that there is some damage accumulation during the loading possibly due to debonding between the matrix and fibres. Figure 9(b) shows the degradation of the tensile modulus as a function of the applied strain. Although the reduction of modulus is apparent, this damage is limited (%) and could possibly be neglected (e.g. in material modelling). Varna et al. [25] in the effort to create a material model for natural fibre biocomposites, used short flax fibres in a PLA matrix to investigate the nonlinearities of the stress-strain curves often related to these composites. They concluded that the non-linearity is a combination of micro-damage, viscoelasticity and viscoplasticity, with the damage however not having an important role before the higher stress of the curve, and therefore could be disregarded. Although the composites used in the study had a different behaviour compared to those in the present study because of the short fibres and the very small fibre content (10 wt.%), the findings show a similarity and could be extrapolated. Conclusions drawn on Hemp/PP composite studies by Gehring et al. [26], showed that the dissipating phenomena reducing the material stiffness throughout the testing were mainly due to damaging of the PP matrix.

Figure 10 shows the SEM photographs of the fracture surface of the Flax/PLA composite after mechanical testing.

Figure 10

Extensive fibre pull-outs together with corresponding holes were observed in all specimens, suggesting a poor interfacial adhesion between the PLA and the flax fibres, besides the hydrophilic nature of the PLA. The clean surface of the pulled fibres strengthens this conclusion. The visible voids between fibres and the matrix puts forward the question whether those gaps are the result of debonding during the testing or existed already from the manufacturing. Either indicates poor adhesion resulting in insufficient transfer of the loads between the composite components, and hence reduced mechanical performance. Observation of the fracture reveals the brittle characteristics of the PLA with the surface being clean and perpendicular to the loading. The fibre edges suggest that the fibres also failed in a rather brittle manner and without plastic deformation or necking.

Further, the SEM micrographs show that the flax fibres in the material are often very tightly collected into bundles with very little or no resin between them. This fact proves poor separation of the fibres prior to the weaving that could harm the overall properties. Finally, the fibre cross-section is random with often the lumen and kink bands along the fibre length visible. The dimensional instability of natural fibres and their random shape and form explained through the different extraction processes as well as environment, age and treatment of the plants, is among the main disadvantages of natural fibre composites affecting their quality and performance [19]. Better separation and dispersion through the composite could also be beneficial [20]. Previous studies on natural fibre/PLA composites had similar conclusions with respect to the fibres and the resin adhesion. Bax et al. [21] worked with flax and cordenka fibres mixed with PLA, and observed poor adhesion and extensive fibre pull-outs. In MAPP (maleic anhydride-grafted polypropylene) as a matrix for flax fibres showed improved performance and reduced pull-outs after testing. SEM photographs from bamboo/PLA composites studied by Tokoro et al. show the same weakness in the composite, with the two components being insufficiently attached [14]. However, treatment of the fibres to remove the surface lignin from the bamboo fibres had a considerable effect on the performance of the specimens.

3.4 The effect of degree of crystallinity changes

The cold crystallization temperature of PLA matrix used was found to be between 90-110 °C (dependent on the heating rate) with a relatively low degree of crystallinity (X_c) between 26-28%

with an average value of 27.2%. The effect of annealing to increase the degree of crystallinity and study the effect on the resulting mechanical parameters was therefore investigated. Tokoro et al. [14] results with bamboo/PLA composites proved that specimens with 100% crystallinity (annealing at 110 °C for 5h) had significantly improved thermal properties than non-annealed ones. However, the effect of this process on the mechanical properties of the composite has not been discussed.

Three tensile samples' sets were heated at 110 °C for 1 h in a temperature control chamber and tested following the same standards as above. The degree of crystallinity was calculated using equation (1), and was found to be in average 30.3% for the annealed specimens compared to 27.2% of the untreated. Table 2 contains the obtained values compared to the properties of the original flax/PLA material.

Table 2

Figure 11 shows the characteristic stress-strain curve from these tests compared to that of the original composite studied.

Figure 11

Despite the increase of X_c from the annealing process, a significant decrease of the tensile strength and modulus was observed. Observation of the surface with naked eye and the optical microscope shows already a discoloration of the samples and different surface texture indicating a significant transformation of the material. SEM observations (Figure 12) show that the deterioration of the properties is related to cracks formed on the matrix surface due to shrinkage of the PLA during heating.

Figure 12

During testing, the cracks grow progressively and eventually intersect to create separated PLA micro-plates that either flow attached to the fibres or are detached from the specimen. SEM micrographs

(Figure 12) depict this phenomenon as observed close to the failure point of the tested samples. In the same micrographs the poor adhesion is again apparent as clean fibre surfaces can be observed.

An additional possible explanation, could be the water evaporation from the samples at the annealing temperature (110 °C), causing the reduction of the mechanical performance of the flax fabric. After testing a weight reduction was observed on the annealed samples, and further investigation showed that the weight reduction from exposing the specimens in 110 °C for 1 h, is as high as 1.4%. Figure 13 depicts the data gather in different time intervals from heating flax/PLA specimen in constant temperature of 50 °C and 110 °C.

Figure 13

Moisture content influences significantly the properties of flax fibres. Baley et al. [27] have shown that drying of flax fibres has negative influence on the mechanical properties of both the fibres alone and combined with epoxy resin in composite samples. They also conclude that a number of different phenomena are responsible for this loss of performance, ranging from the fibre microstructure to the fibre constituents, to stress concentration in the fibres/matrix interface due to geometrical changes of the fibres [27]. Van de Velde et al. [28] observed that exposure to different temperatures results in weight decrease and affect the mechanical properties of the fibres, with strain being more influenced than stress.

3.5 Influence of temperature dependency

The properties of thermoplastics are temperature dependent. The increase of temperature reduces the Young's modulus and tensile strength but increases the failure strain leading to a material more ductile and less stiff [29]. With increasing temperature, thermal transitions occur which can impart dramatic step-changes in material behaviour. As observed and discussed in the results above, PLA is semi-crystalline and exhibits a complex combination of thermal transitions occurring in the crystalline as well as in the amorphous phase, in relatively short range of temperatures. Furthermore, the mechanical properties of a composite and hence the effect of temperature alterations, depend on both the polymer matrix characteristic and the reinforcing fibres. Additional energy dissipation mechanisms can be activated thanks to the addition of fibres [30], and very little is known on how temperature will affect the properties of the flax reinforcement.

Although a number of studies have been conducted at room temperature, little is known on the effect of temperature on flax/PLA reinforced composites properties such as tensile strength and modulus. In

order to evaluate this effect, studies were undertaken and the resulting stress–strain curves were plotted over a temperature range of 25 to 110°C.

Figure 14 reveals a strong dependence of the material properties on temperature, as of the deformational behaviour changes from brittle to more ductile-like characteristics.

Figure 14

The material deforms up to higher strains with both the modulus and strength reduced significantly. Already around 50°C, prior to the T_g point, the stiffness is reduce by half. This result combined with the results from the thermal studies of the PLA signifies the deterioration of the PLA during the constant heating. On the DMA graphs this high deterioration is not visible, as the storage modulus reduces at 50 °C but not more than 10%. This could be related to the fact that the heating rate during the DMA test was set to 1 °C/min whilst for the tensile testing the samples were first left to reach the desirable temperature for several minutes. The above observation denotes a thermal inertia and is evidence of a strong viscous behaviour of flax/PLA. The prolonged exposure to temperature deteriorates further the mechanical properties resulting in a very weak material. Table 3 summarizes all the values acquired from the testing of the material under different temperatures.

Table 3

The effect of temperature on the properties of flax/PLA composites is more explicitly shown in Figures 15 and 16 where it can be seen that the tensile stiffness and strength decrease with an increasing temperature following a non-linear relationship, while the elongation has an opposite but similar increase with increasing temperature.

Figure 15

Figure 16

It should be noted that the present work has not investigated the effect of increase of fibres volume in the matrix, though this is expected to decrease the thermal stability of the composites. This will require variation of vol.% fibre/matrix ratio coupled with thermogravimetry and therefore a scope for follow up research work.

Interestingly, at a temperature of 65 °C (glass transition point, T_g) an increase of the modulus together with a decrease of the elongation at break were measured compared to the same values for 50 °C. The material becomes stiffer with a modulus of 7 GPa and elongation of around 2%. An explanation for this unexpected behaviour can be the higher mobility of the chains together with the increased ductility of the PLA matrix past the T_g that results in less debonding between the resin and the fibres, thus better transfer of loads between the composite constituents. Further, the temperature effect on the mechanical properties of composites derives partly from the internal stresses introduced by the differential thermal coefficients of composite components. Such internal stresses change magnitude with temperature, and can control the matrix cracking. The strength however, related mainly to the decreased load limits of the matrix, is reduced to more than 50% of that in room temperature, with a characteristic higher reduction gradient than between 25-50 °C and 65-110 °C.

The mechanical performance of flax/PLA in around 110 °C is relatively low, with the modulus decreasing another 30% from the 65 °C case, but with the strength remaining being only 15.5 MPa in comparison with 72 MPa at ambient temperature. It is also worth noticing that the stress-strain law also changes from a 2^{nd} order non-linear curve, to an approximately bilinear response. After the elastic linear region at around 2.3-2.5% strain, the material yields at a constant stress, with a visible hardening after 1-1.5% strain. The elongation at break at this temperature is on average 3.2%, more than double of that in room temperature.

Although the mechanical curves depict a shift from a brittle to a ductile material, the characteristic modes of failure do not show the same. The failure remains brittle up to 65 °C, with the matrix snapping in a 90° angle to the loading direction, no formation of neck or any material yield. At 100 °C, due to the high deterioration of the matrix (PLA), the material debonds and reacts as if no resin is present. This result can be explained through the SEM observation and conclusions drawn above from testing of the annealed samples. The loading appears to be only carried through the fibres, which after a load limit, and as they consist of fibre bundles, start slipping apart and unwrapping (Figure 17).

Figure 17

Further, the temperature and heating time had also an effect on the fibres through reduction of the moisture content [31-33].

3.5.1 Strain rate effect

Some polymers exhibit significant rate dependency while others do not. At lower strain rates a polymer usually exhibits a more ductile behaviour while at increased deformation rates the response of the material becomes brittle-like, with a significant increase of the ultimate strength and yield points. This increase in stress can be directly related to the secondary relaxation processes ($T<T_g$), or/and the decreased molecular mobility of the polymer chains at high rates of deformation [34]. The stress dependency on strain rate is often expressed as a power-law relationship that can be represented as:

$$\sigma = B.\dot{\varepsilon}^m \qquad (2)$$

where B is a constant and m is the strain-rate sensitivity coefficient, which is always greater than or equal to zero. For materials with negligible strain-rate sensitivity, m is near zero, making σ constant as a function of strain rate($\dot{\varepsilon}$). Materials with greater strain-rate sensitivity have greater values of m.

This feature of the mechanical behaviour is particularly relevant for applications with polymeric components required to resist impacts. In the automotive, impact resistance of exterior panels and components exposed to road debris is critical. Up to date very little is reported on the effects of strain rate on the mechanical characteristics of natural biocomposites. Omar et al. [35] investigated the dynamic mechanical properties of jute and kenaf fibres combined with a polyester resin. They reported that the modulus and strength of both materials were highly dependent on the strain rate, and showed a significant amount of rate sensitivity dependant on the deformational speed. Gehring et al. also observed an increase of the maximum stress supported by hemp/PP composites at an increased strain rate, and concluded that the mechanical responses of the material show a high sensitivity to the strain rate up to failure [26].

Monotonic tensile tests at different cross-head velocities were conducted to investigate the effect of strain rate on the mechanical performance of flax/PLA. Three speeds were used, 2mm/min (quasi-static), 0.5 m/sec and 4.2 m/sec, limited by the capabilities of the equipment used. For each velocity at least three samples were tested. The results for the modulus, strength and elongation at break are summarized in Table 4.

Table 4

Figure 18, depicts the stress-strain curves obtained in different testing speeds. The material mechanical properties are strongly affected by the strain rate.

Figure 18

Already in 0.5 m/sec cross-head velocity, the ultimate strength of the material is increased by 20% compared to the quasi-static velocity, with an increase of the modulus from 13 to 14 GPa. Further increasing the strain rate, results in 22 GPa tensile modulus (70% increase), with a strength as high as 95.7 MPa, representing a 32% increase. As observed the above results illustrate a change of both the strength and modulus of the flax/PLA as a function of the rate of deformation. The material at higher strain rates becomes stiffer and stronger, whilst its elongation at failure decreases. In all cases the failure mode has brittle characteristics, with failure occurring without necking or signs of plasticity. Studies with higher strain rates with the use of a Hopkinson bar are needed for the investigation of the strain rate sensitivity, and would be reported in follow up studies.

4 Conclusions

Aim of this work was the study of the thermo-mechanical performance of flax/PLA biocomposites, going beyond the typical investigation of the properties to an understanding of the mechanical behaviour of such composites from a structural point of view, for the potential use in load bearing application in the automotive sector. Focus was given into link between the thermal and mechanical properties, and the material response under different loading conditions and environments.

The strength and stiffness of flax/PLA samples – 72 MPa and 13GPa respectively – indicate a very promising material to replace traditional choices in load bearing application. However, SEM micrographs show that the interfacial adhesion of the constituents is still poor and modifications need to be applied on the fibre's surface in order to improve it. The poor adhesion is confirmed through tensile testing and the comparison of the mechanical properties of pure PLA with those obtained from the flax/PLA specimens. The need for better fibre separation prior to the manufacturing process is also underlined. The PLA matrix shows brittle characteristics, with an average failure strain of 1.5%. The stress-strain law is non-linear with the non-linearity introduced due to viscous behaviour of the material combined with a certain level of damage accumulation throughout the testing.

DMA results show deterioration of the composite properties with a tan delta peak at around 74-76 °C. An increase of the storage modulus is however visible after 80 °C, explained due to the cold

crystallization transition of the amorphous part of the PLA. The flax fibres have a positive effect on the thermal response delaying the loss of stiffness to higher temperatures compared to that of pure PLA. The crystallinity of PLA was measured to be approximately 27%. Annealing above 100 °C for an hour brings that value to 30%, but analysis of tensile results of annealed specimens reveals a significant reduction of both the tensile strength and modulus. This reduction is associated with micro-cracking that occurred on the surface of PLA during the heating as well as deterioration of the flax properties due to drying.

Temperature affects enormously the properties of flax/PLA. At 50 °C the stiffness is reduced by half, and the ultimate strength is reduced significantly. 110 °C bring the modulus further down to about 5GPa with a remaining strength of 15.5 MPa. With increasing temperature the elongation at break increases. The failure characteristics remain brittle for the temperatures up to 65 °C, while at 110 °C high degradation of PLA is observed and the load seems to be carried through the fibres which progressively slip apart.

Strain rate has an effect on the material and its viscous behaviour. Strength and modulus increase with increasing strain rates, while elongation at break reduces respectively. A modulus of 22 GPa was recorded in 4.2 m/sec crosshead velocity. Studies with a Hopkinson bar would be required for the calculation of the material's strain rate sensitivity.

The mechanical properties of flax/PLA were compared with a more commonly used a studied flax/epoxy material. Although flax/epoxy has some advantages in terms of strength and thermal stability, flax/PLA has significantly higher modulus. Improvement of the interfacial bonding and the temperature characteristics, combined the thermoplastic nature of PLA, will make flax/PLA composites ideal for use in structural automotive applications.

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Caption of Tables and Figures

Tables

Figures

Table 5: Tensile properties for flax/PLA composites; Comparison with flax/epoxy

	Modulus [GPa]	Strength [MPa]	Elongation [%]
PLA	3.5[35]	70[35]	-
Flax/Epoxy	7.6 (0.4)	90 (4.8)	1.85 (0.2)
Flax/PLA	13 (0.9)	72.2 (2.0)	1.5 (0.08)

Table 6: Tensile properties of annealed and non-annealed flax/PLA samples

	Modulus [GPa]	Strength [MPa]	Elongation [%]
Flax/PLA (27% crystalline)	13	72.2	1.5
Flax/PLA (30% crystalline)	10	40.2	2.2

Table 7: Tensile properties of flax/PLA for all four temperatures tested

	Modulus [GPa]	Strength [MPa]	Elongation [%]
Flax/PLA - 25 °C	13 (0.9)	72.2 (2.0)	1.5 (0.08)
Flax/PLA - 50 °C	6.2 (1.0)	53.2 (3.2)	2.4 (0.14)
Flax/PLA - 65 °C	7 (1.5)	35.7 (2.8)	2.04 (0.19)
Flax/PLA - 110 °C	5 (0.3)	15.5 (1.6)	3.2 (0.4)

Table 8: Tensile properties of flax/PLA as a function of the crosshead displacement

Crosshead velocity	Modulus [GPa]	Strength [MPa]	Elongation [%]
2 mm/min	13 (0.9)	72.2 (2.0)	1.5 (0.08)
0.5 m/sec	14 (0.7)	87.1 (3.8)	1.5 (0.09)
4.2 m/sec	22 (2.2)	95.7 (6.2)	1.3 (0.15)

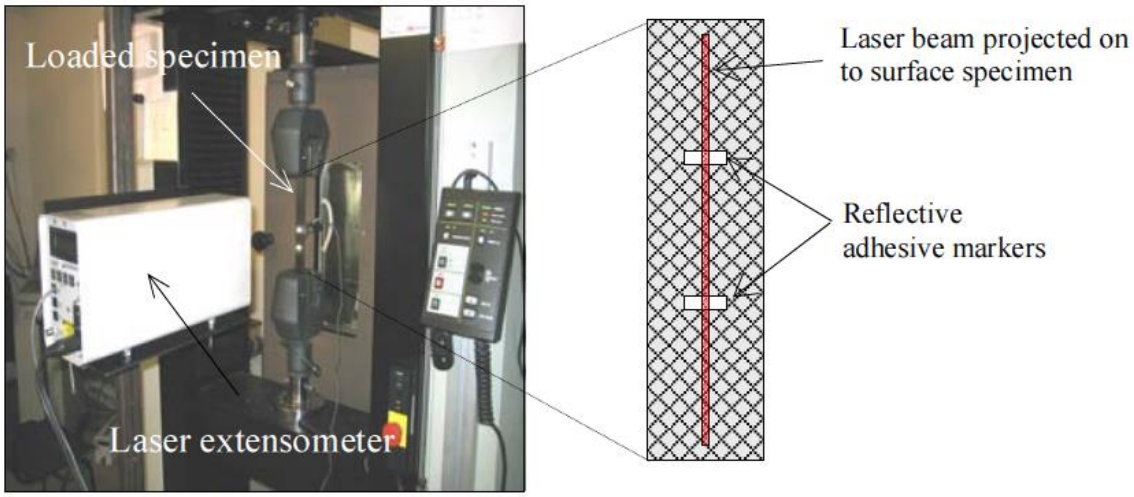


Figure 10: Experimental set up for laser extensometer measurements method

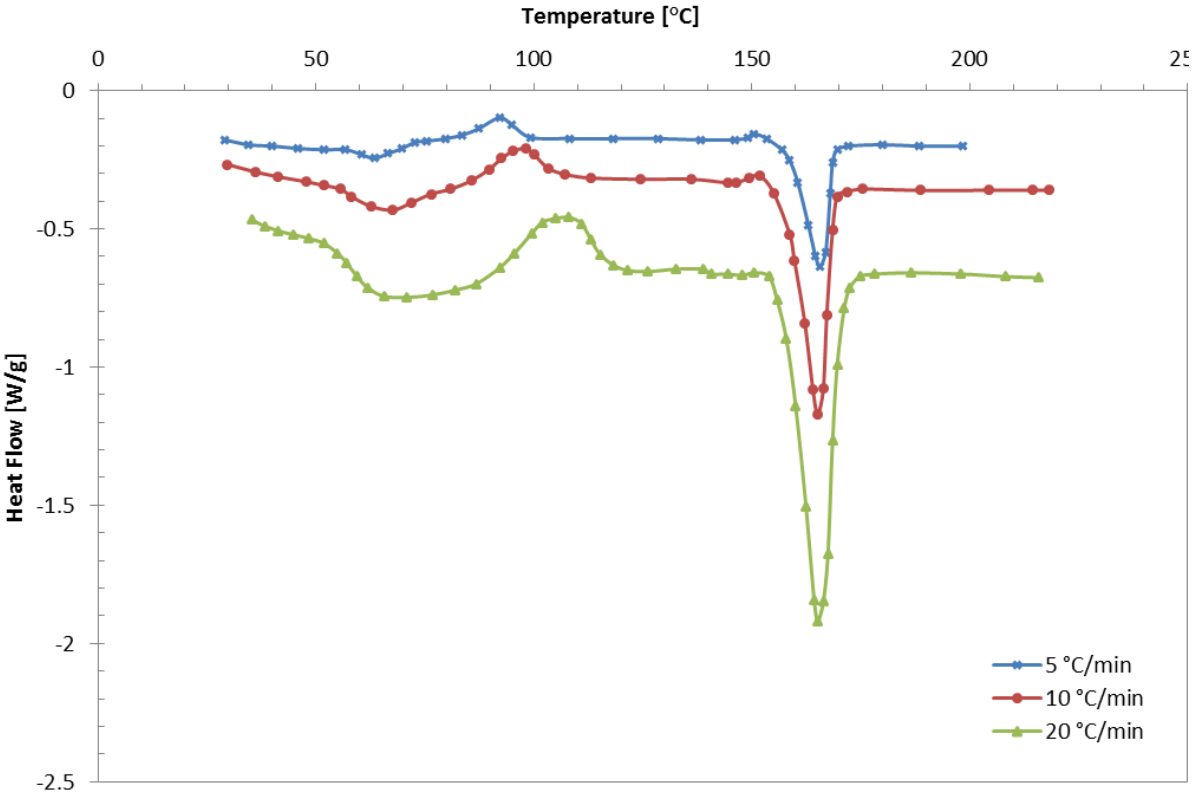


Figure 2: Effect of heating rate on DSC curves of flax/PLA

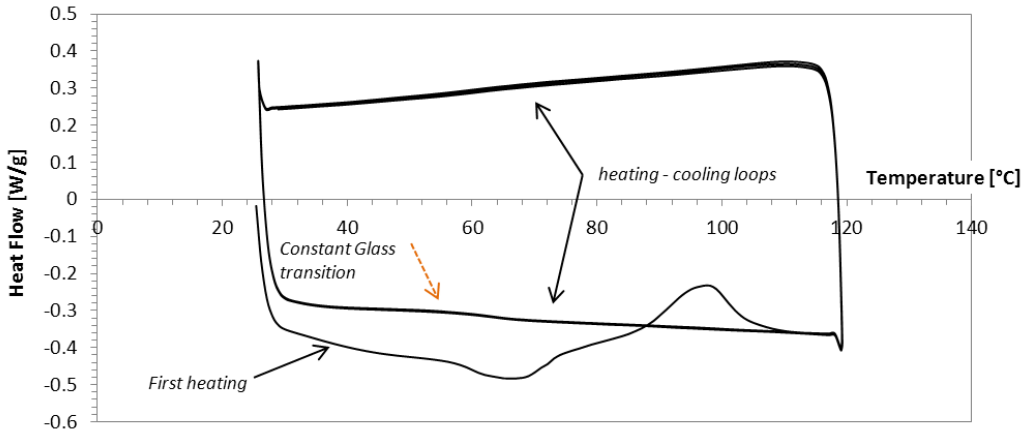


Figure 4: DSC thermograms with repetitive heating-cooling cycles

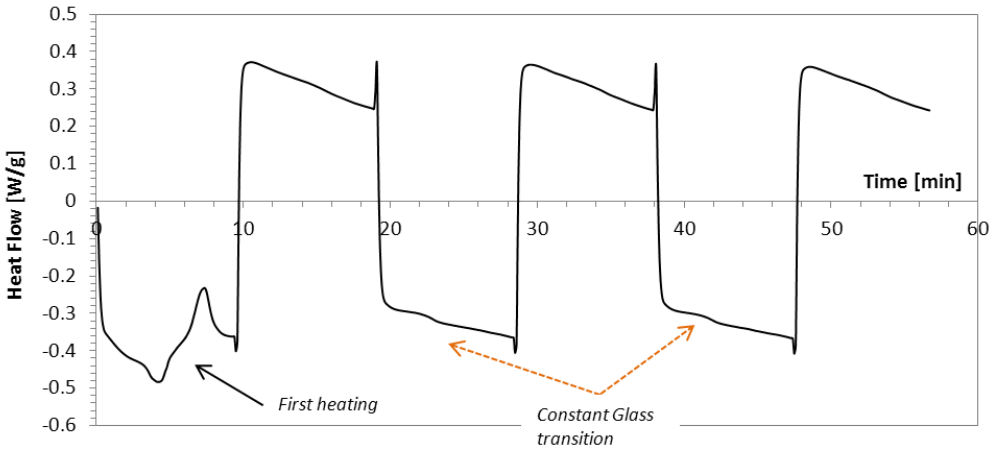


Figure 4: Heat flow as a function of time for repetitive heating-cooling cycles of flax/PLA

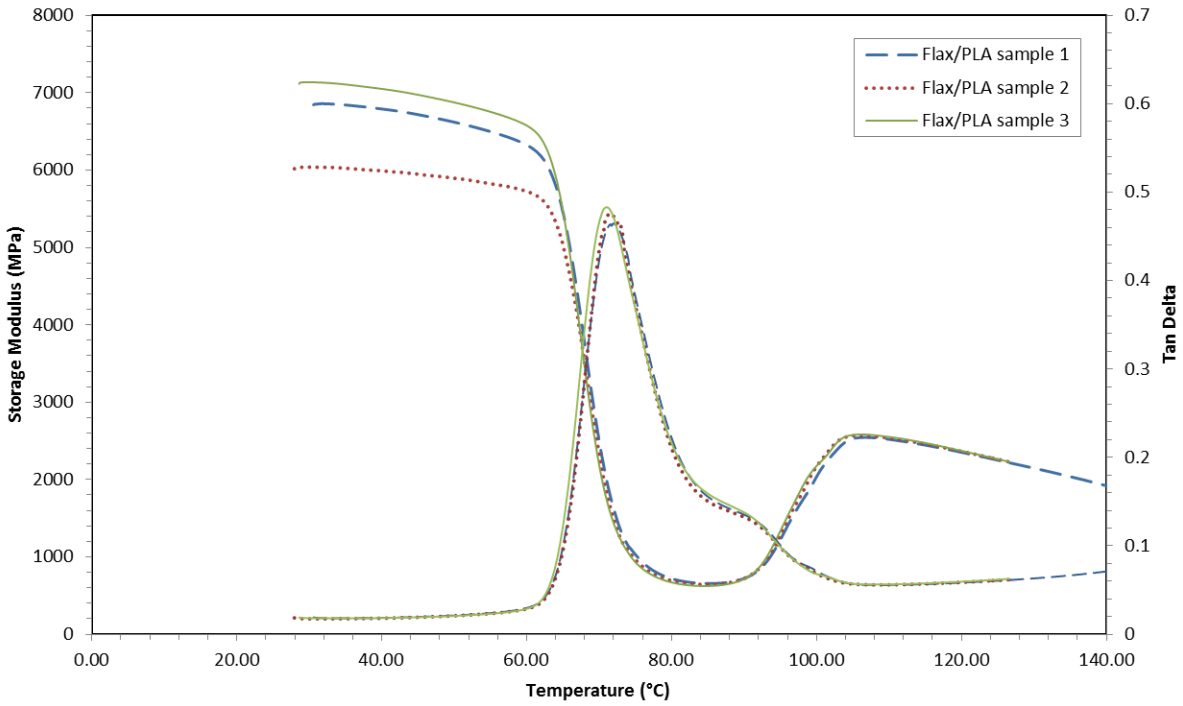


Figure 5: DMA runs for flax/PLA; Storage modulus and tan delta

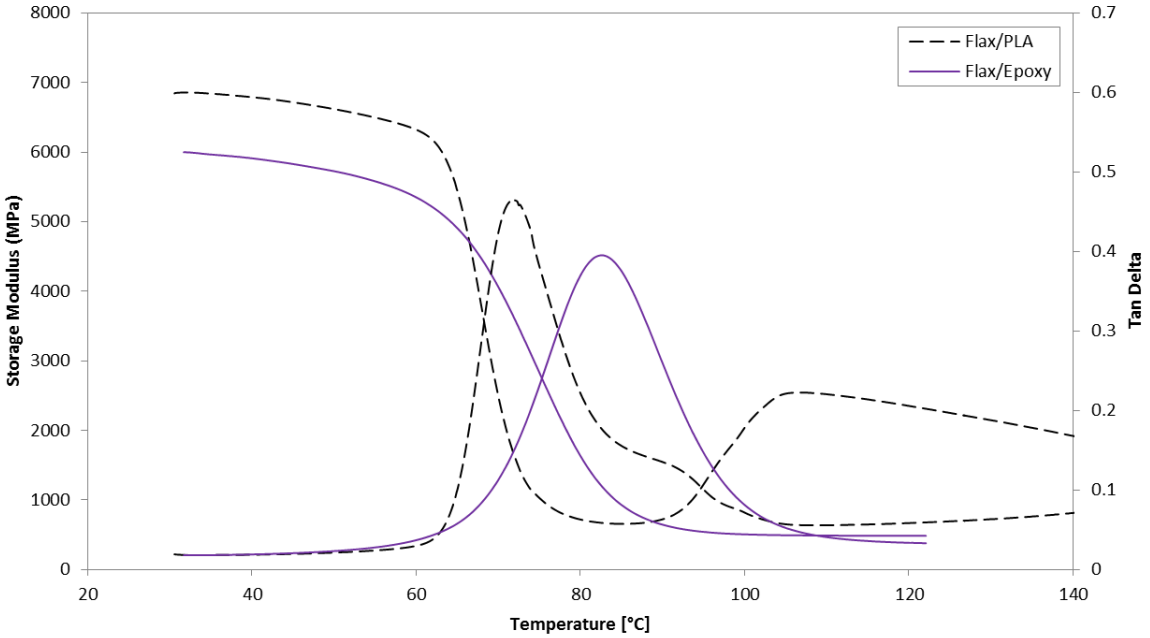
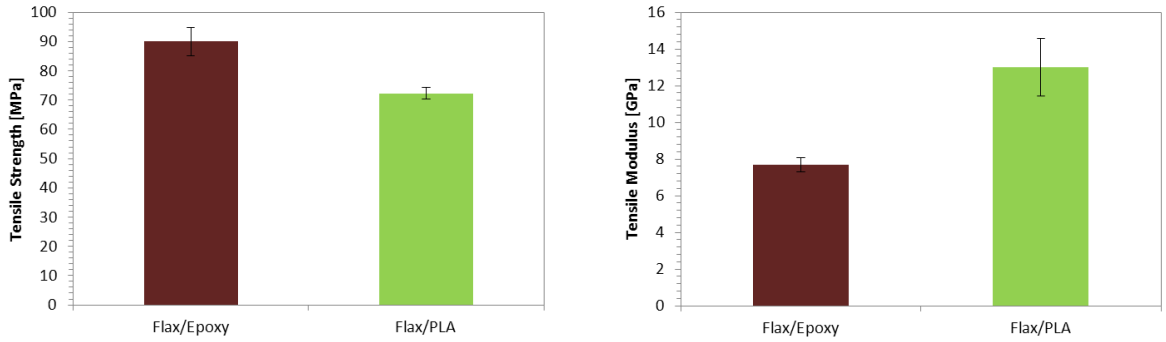


Figure 6: Comparison of **s**torage modulus and tan delta from DMA runs of flax/PLA and flax/epoxy composites



(a) (b)

Figure 7: Tensile strength (a), and Young's modulus (b) for flax/PLA and flax/epoxy composites

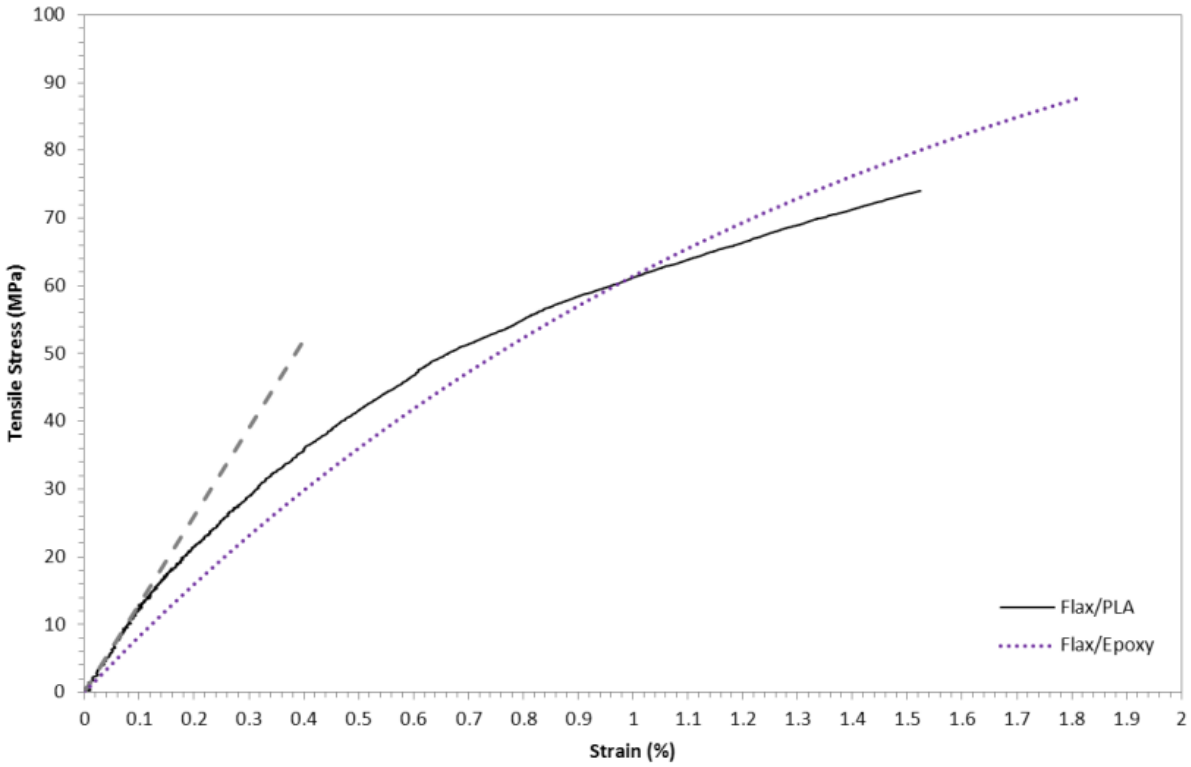
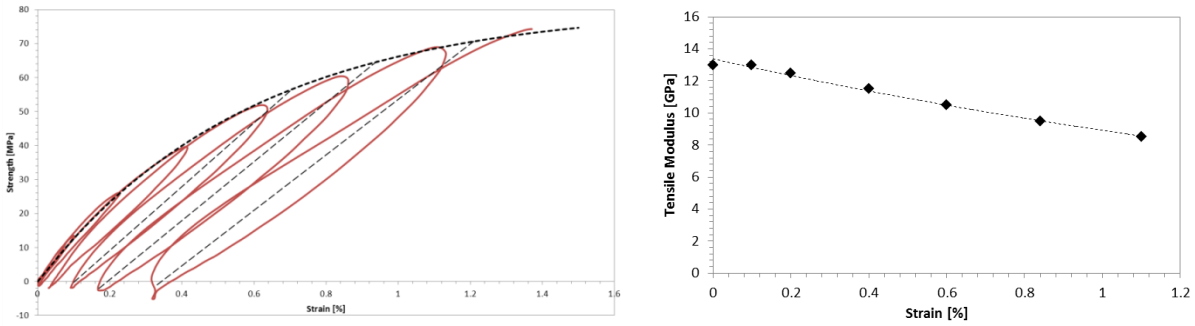


Figure 8: Stress-strain curve from tensile testing of flax/PLA and flax/epoxy



(a) (b)

Figure 9: (a) Cyclic test for flax/PLA and (b) tensile modulus reduction as a function of strain due to damage accumulation during testing

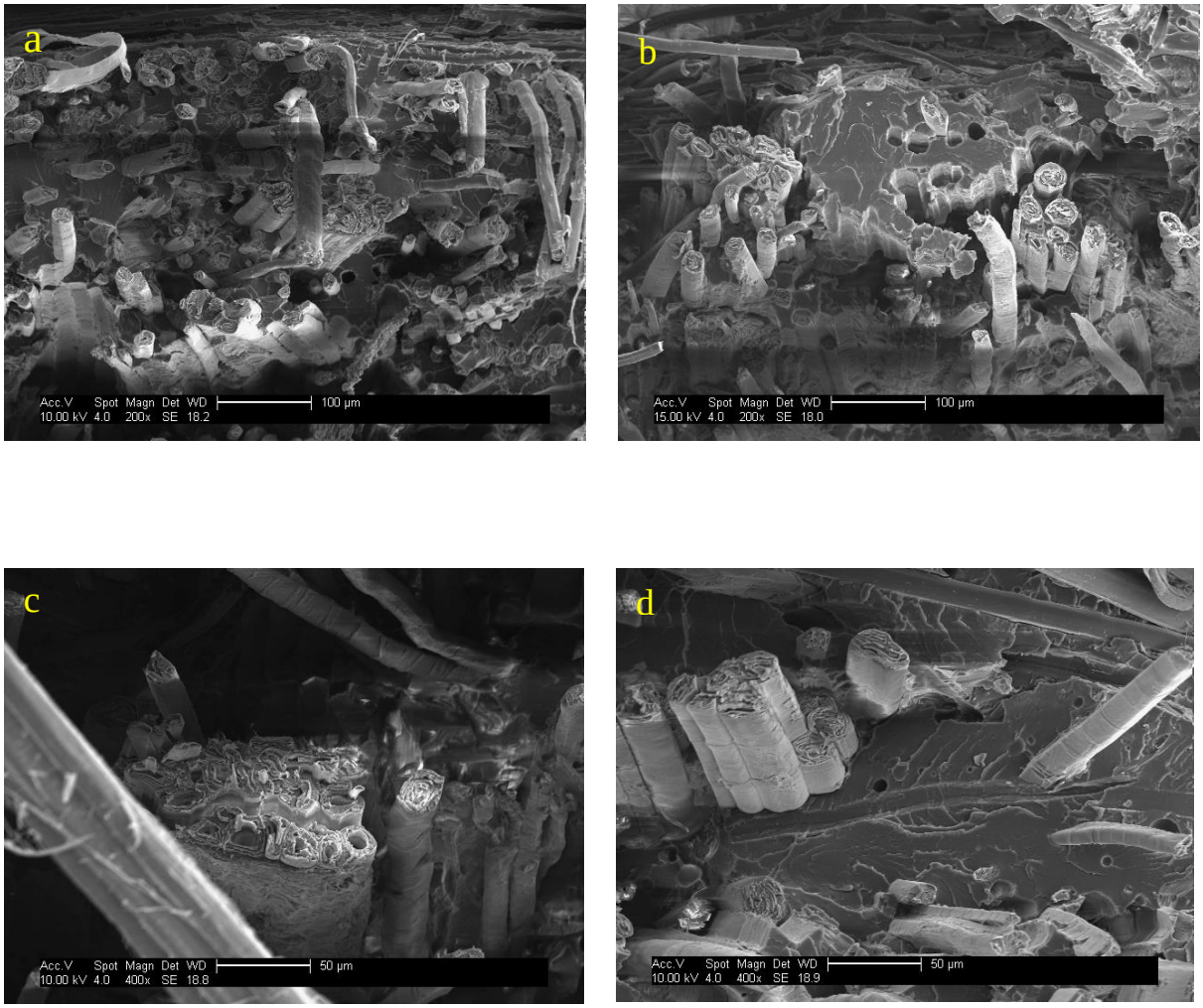


Figure 10: Overview of the fracture surfaces of flax/PLA tensile specimens

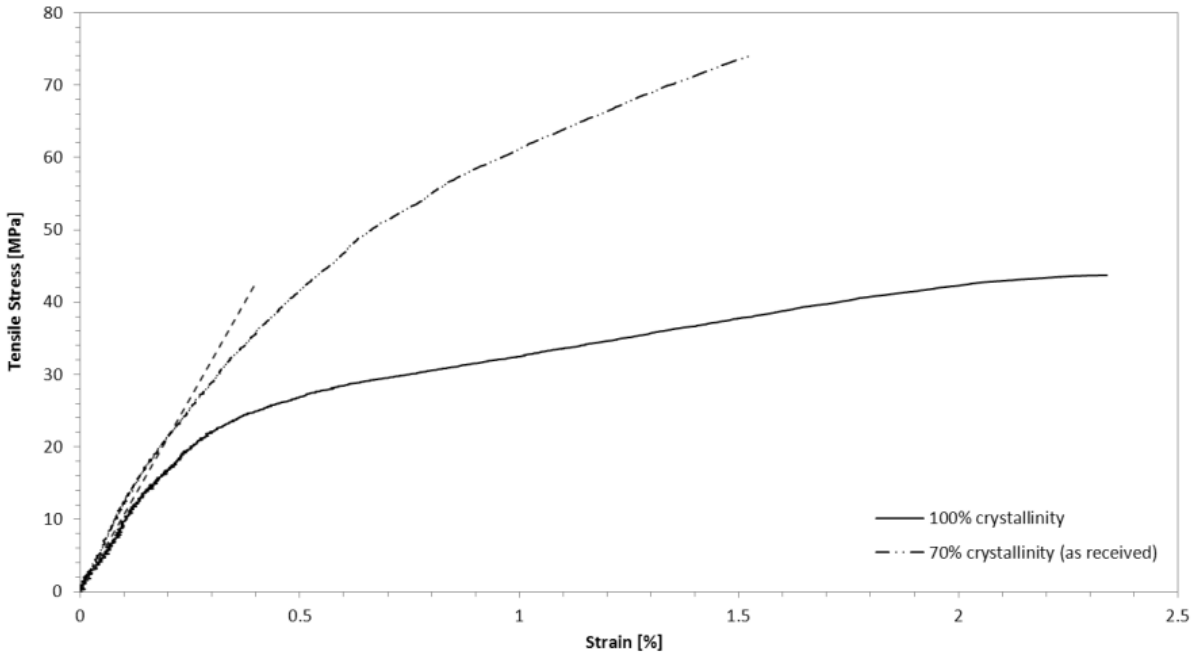
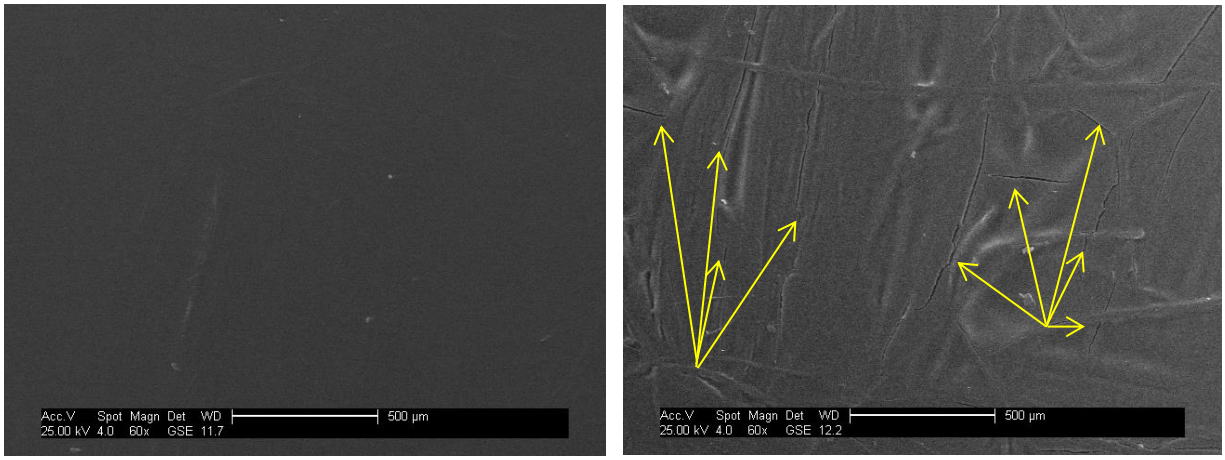
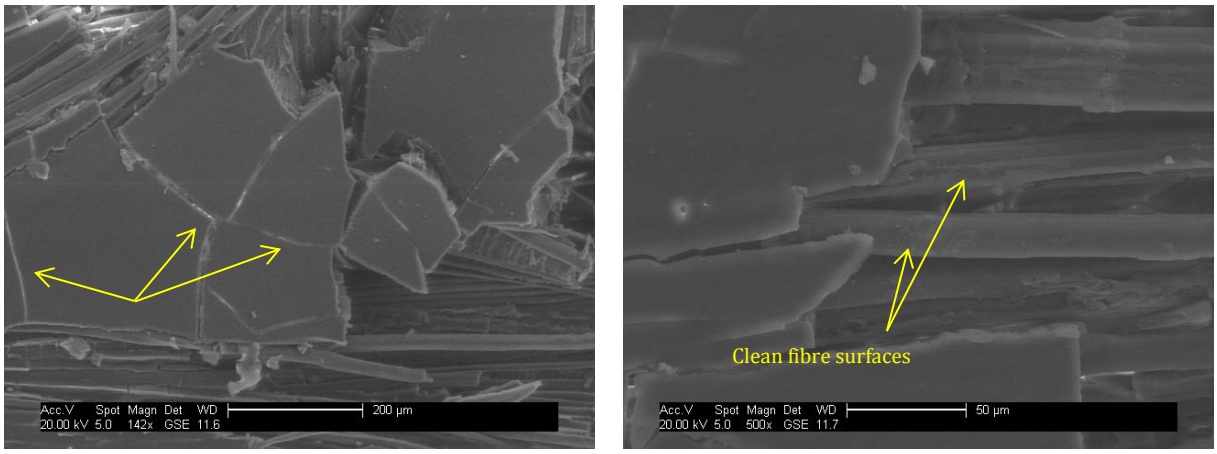


Figure 11: Stress strain curve of annealed flax/PLA samples compared to original samples (as a function of X_c)



(a) (b)



(c) (d)

Figure 12 Detailed SEM photographs from (a) original flax/PLA samples compared to the surface of (b) annealed samples. The formation of cracks and the deterioration of the PLA's surface is visible. During testing, the crack growth results in breakage of the PLA (c). Poor interfacial adhesion was observed as the fibre surfaces were clean (d)

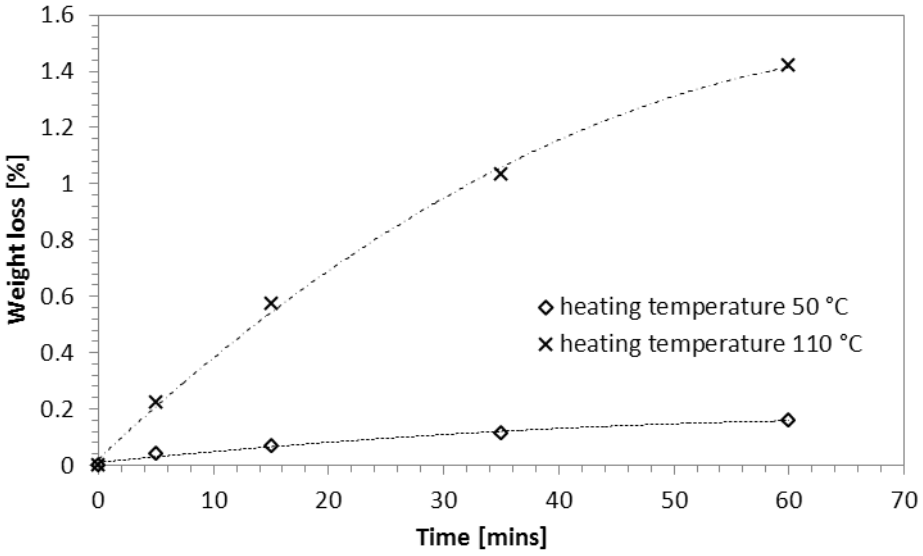


Figure 12: Weight loss of flax/PLA due to drying for 1h at 50 °C and 110 °C

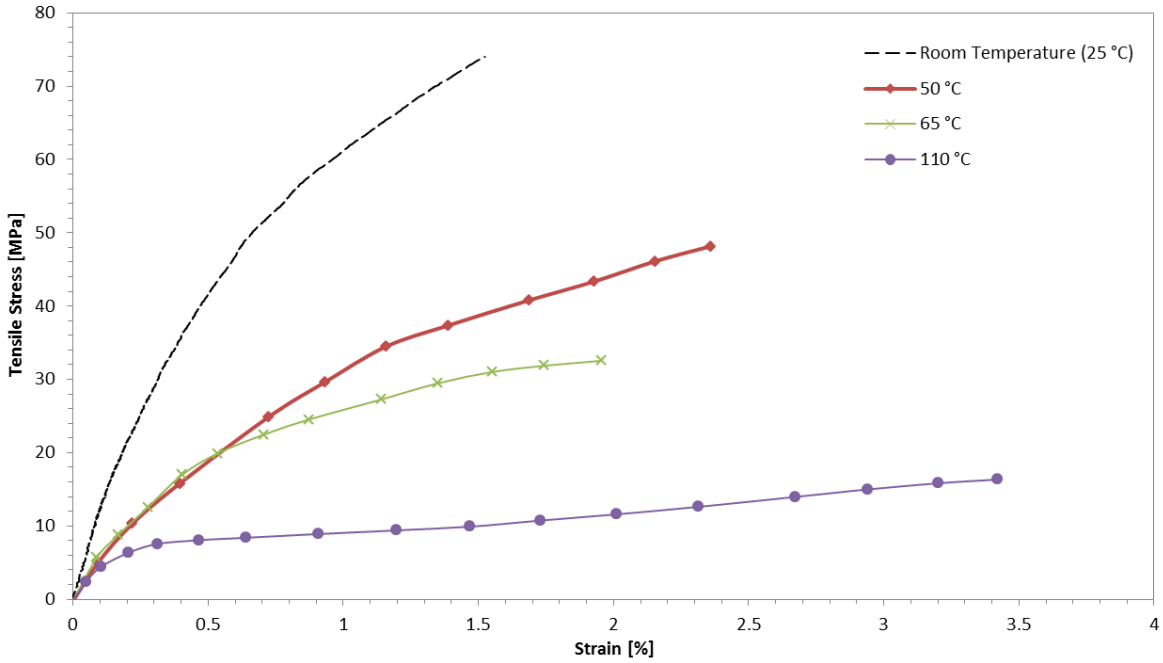
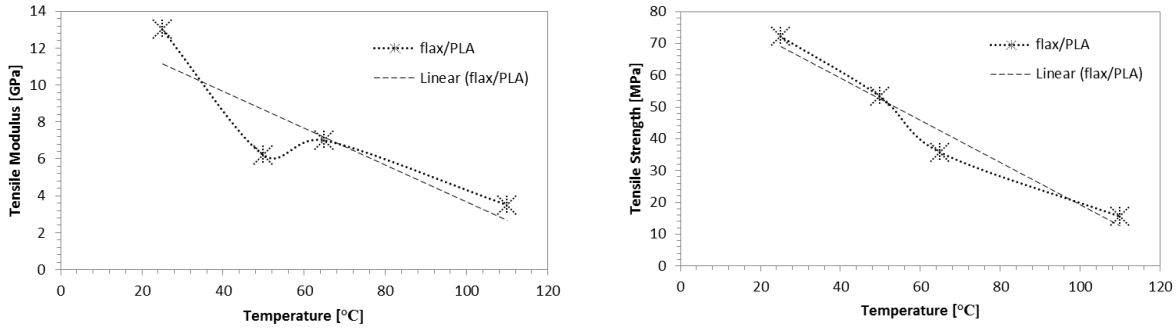


Figure 13: Stress-strain curves of flax/PLA tested in room temperature (25 °C), 50 °C, 65 °C and 110 °C



(a) (b)

Figure 14: Tensile modulus and ultimate strength of flax/PLA specimens as a function of temperature

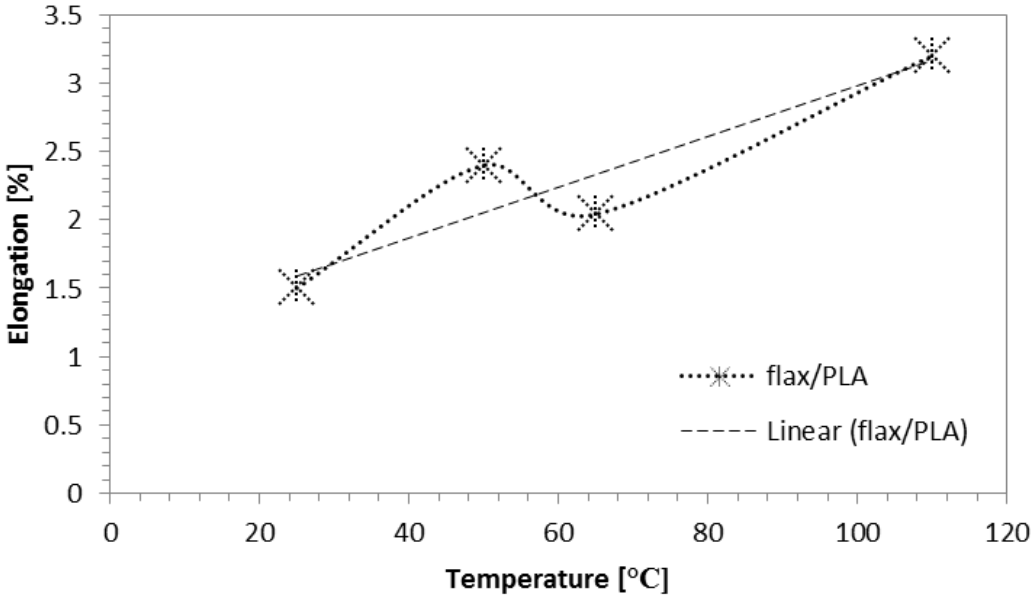


Figure 15: Elongation at break as a function of temperature

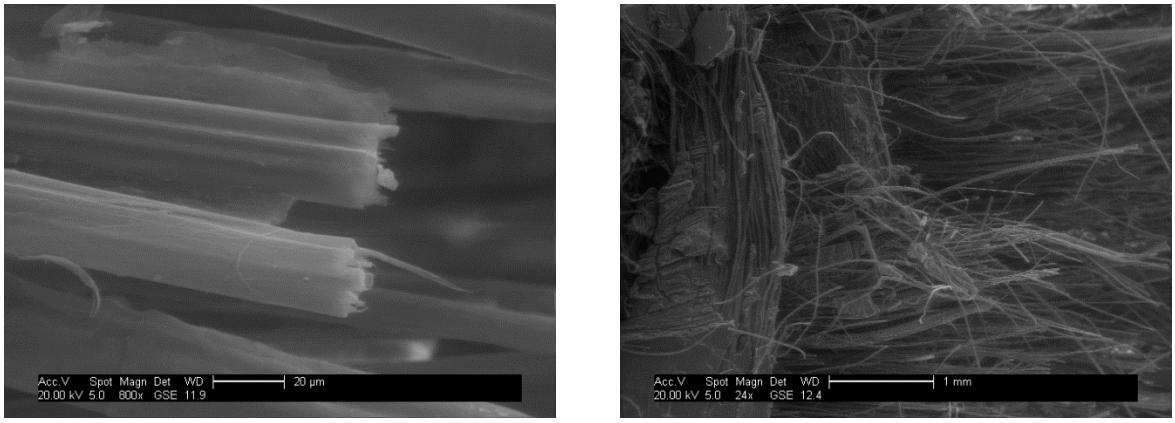


Figure 16: Detailed SEM micrograph of flax fibres after testing of flax/PLA samples at 110 °C

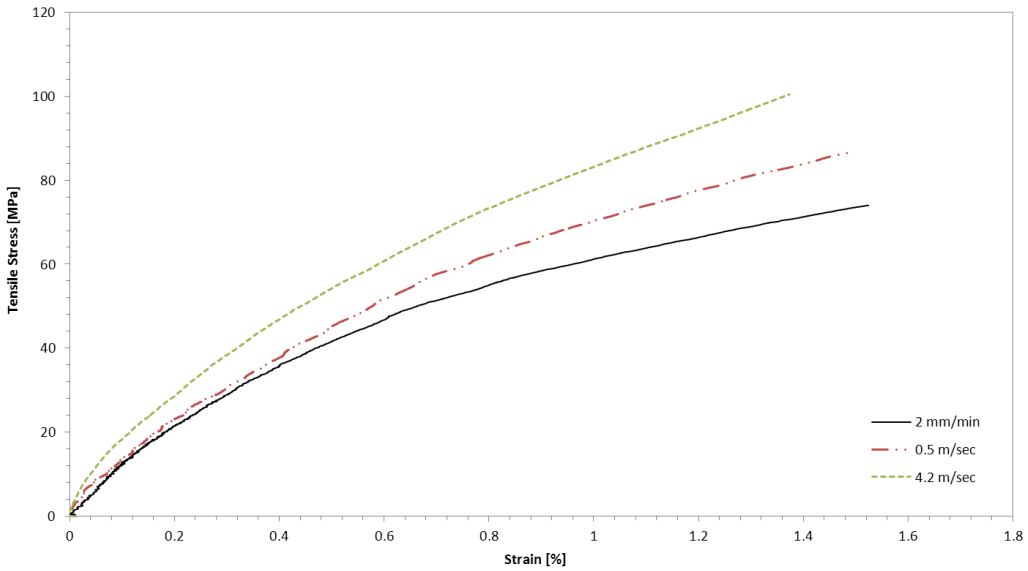


Figure17: Stress-strain curve of flax/PLA tensile specimens, tested in three different crosshead velocities.