Mechanical and thermal characterisation of poly (l-lactide) composites reinforced with hemp fibres

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Abstract. Polylactic acid (PLA) is the most promising in the bio-derived polymer’s family. But its use can be constrained by its poor mechanical properties, poor thermal stability and processing difficulties. The objective of this research is to investigate and improve mechanical and dynamic thermal properties of PLA by developing PLA composites reinforced with natural fibres (hemp). Composites were prepared by melt blending of PLA with hemp fibres. Their properties were investigated using mechanical and dynamic thermal analysis. The elastic modulus increased significantly - from 4.1 ± 0.74 to 9.32 ± 0.86 (GPA) - when the weight fraction of hemp increased from 0 to 30 (wt %). The storage modulus obtained by dynamic mechanical analysis increased from 2.20 to 4.58 (GPA) for the same change in the volume fraction of hemp. FE simulation of tensile testing and DMA were carried out to investigate the effect of strain rate and temperature on the observed properties respectively. The model was developed in the commercially available code MSC Marc mentate. The model validated all experimental results.

1. Introduction
The growing usage of synthetic polymers during the last decade has led to apprehension about the environmental impact caused by plastic waste, which has been a widespread concern. The ecological aspect of both production and disposal of standard oil-based plastics is presently of concern worldwide. This has driven the search for alternatives that are bio-derived and eco-friendly. In order to be a competitive alternative, bio-plastics must have the same desirable properties as obtained in conventional plastics.

Poly (lactic acid) (PLA) is chemically synthesized from lactic acid derived from corn starch [1], the most commonly used aliphatic polyesters exhibiting comparable properties to conventional plastics derived from corn starch [2, 3].

PLA has a poor mechanical and thermal properties which restricting its widespread applications. Shortcomings in mechanical properties of PLA may be overcome and sustained by several means like reinforcement and blending. For example, PLA has been blended with poly(caprolactone) (PCL) to increase its flexibility [4, 5] and with poly (hydroxybutyrate) (PHB) to improve tensile properties and

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biodegradability [6]. There is much interest in PLA nanocomposites because of the potential of montmorillonite nanofillers to improve the mechanical, barrier and biodegradation properties of PLA [7-10]. Most recently PLA – mineral filler composites are in focus to increase the heat distortion temperature (HDT) [11].

Natural fibres reinforced polymer composites have been remained a centre of attention for academics and industrial research for the last decade or so. Automotive, construction and decking industry have shown their interests in natural fibre polymer composites due their competitive advantages, such as low cost, high strength –to- weight ratio, recyclability and low density when compared to synthetic fibres reinforced composites. [12]

This research investigates the development of PLA composites reinforced with natural fibres (hemp). Composites have been processed and the effects of hemp content on the mechanical and thermo-mechanical properties of PLA-hemp composites have been studied [13].

2. Experimental

2.1. Materials
General purpose Polylactic acid (PLA), a trade name is HM_{1011}, was supplied by Hycaill Company, Netherlands. HM_{1011} is completely amorphous. The polymer was supplied in the form of granules with specific gravity of 1.24 g/cm³ and melting range 150 – 175 °C. The glass transition (T_g) range is 55 – 65 °C supplied by the manufacturer. Vegetable based dry retted hemp of variable dimensions was supplied by Hempcore Technology Ltd UK in the chopped form.

2.2. Composite preparation
Dried PLA is melt blended with chopped hemp fibres in different ratios of 90/10, 80/20, 70/30 (weight %). Mixing of PLA with hemp was carried out in Haake OS-Polylab rheomix at 170 °C for 10 minutes with constant rotor speed of 60 rpm. For each run, total mass (PLA + Hemp) was about 58 (g) with 70 (%) filling capacity of the Haake Polylab rheometer. Samples for tensile and dynamic mechanical analysis of the Composites were compression moulded at 180°C for three minutes at 10~12 Tons pressure followed by quenching for three minutes at the same pressure level. This was carried out in 20 Ton laboratory hot press.

2.3. Tensile testing
The tensile testing of the composites was performed using Tinius Olsen H50 KS with a clip-on extensometer, used to measure the modulus more precisely. The tensile machine was equipped with a load cell of 5kN. Compression moulded dumbbell – shape tensile specimens (width ~10mm, thickness ~ 2mm, length ~30 mm) were extended at a crosshead speed of 10 mm / min.

2.4. Dynamic Mechanical Thermal Analysis (DMTA)
The viscoelastic properties of the PLA/Hemp composites were investigated using dynamic mechanical analysis (DMA). DMA Q800 apparatus (TA Instrument Inc, USA) was used to measure the storage modulus, loss modulus and Tan Delta (Tan δ) of each composite sample as a function of temperature. All samples were tested in the flexure (dual-cantilever bending) mode. The rectangular specimens (width 12mm, thickness 3mm, length 64mm) were heated at a constant rate of 3/min from room temperature to 140 and tested at a frequency of 1Hz.
3. FEA Simulation

Finite element simulations of tensile testing and DMTA of PLA/HEMP composites were carried out using commercially available code MSC Marc/Mentat. A schematic of the specimens used in the FE simulation of PLA/Hemp composite material for both tensile testing and DMA is shown in Figure 1. Eight nodes 3D element (element type 7) were used to model specimens. The tensile specimen was discretised to 5600 elements with number of element of 70, 10 and 8 in X-axis, Y-axis and Z-axis, respectively, whereas in DMA simulation, the specimen was discretised to 4608 element with 64, 12 and 8 number of elements in X-axis, Y-axis and Z-axis, respectively. In tensile testing simulations, the left hand side of the specimen was kept fixed, restricting the movement of nodes in all three directions, whereas, the right hand side of the specimen was allowed to move in the x-direction. The overall length of the specimen was 90 mm, width of 20 mm and thickness of 2 mm. The material data used in the simulations were achieved from a tensile testing of PLA/Hemp composites. The ambient temperature is selected as 20°C for the specimen. The number of simulation steps was kept at 500 with a total time of 40 Sec. For material modelling of tensile specimen, the response of specimen measured in tensile testing was incorporated to the model. The data obtained from the machine was in the form of Force (N) Vs. Elongation (mm), which was converted into the Stress (MPa) Vs Strain (%) at the end to perform the simulation.

In DMA simulation, the two ends of the specimen were fixed and a fluctuating displacement was applied to the through the centre region of the specimen. The new deflection of the specimen was resembled to the double cantilever beam. The fluctuating load applied to the two rigid surfaces glued to the specimen at the centre point has amplitude of 50 µm and frequency of 1 Hz. The load was

![Figure 1. Schematic of the specimens used in the FE simulations](image)
4. Results and discussions

4.1. Tensile testing

Table 1 presents summary of the effect of different contents of reinforcement on tensile properties of PLA. It is clearly evident that incorporation of the hemp fibre brought a stiffening effect into the PLA-hemp composites and causing a significant improvement in the elastic modulus of the PLA. The elastic modulus increased from $4.1 \pm 0.3$ to $9.3 \pm 0.62$ (GPa) when the contents of hemp fibre increased from 0 to 30 (wt %). It was also observed that tensile strength is gradually increased with increasing contents of hemp fibre, but overall the tensile strength of the composites decreased as compared to pure PLA. The same kind of behaviour for PLA- hemp composites also reported by Nina Graupner [14]. He observed that the incorporation of hemp fibre increases the young’s modulus and reported the increase in tensile strength in machine direction while decrease in cross direction. Robert Masirek et al. [13] have also reported a decrease in tensile strength of the amorphous PLA-hemp composites and improvement in tensile modulus is observed. From the table it is also clear that elongation to break is also affected with hemp fibres. Sawpan et al. [14] have also studied the properties of PLA- hemp composites and reported a good adhesion between the fibres and matrix. They also reported that the as PLA and hemp fibres both are brittle, so that the higher amount of fibre loading in composites can cause the reduction in strain failure as shown in table 1.

| PLA / Hemp ( wt %) | Tensile Strength ( MPa ) | Tensile Modulus ( GPa ) | Elongation @ break ( % ) |
|--------------------|--------------------------|-------------------------|-------------------------|
| 100/0              | $43 \pm 1.3$             | $4.1 \pm 0.28$          | $4.1 \pm 0.6$           |
| 90/10              | $24 \pm 1.5$             | $4.8 \pm 0.34$          | $2.0 \pm 0.7$           |
| 80/20              | $30 \pm 0.8$             | $6.9 \pm 0.43$          | $2.0 \pm 0.5$           |
| 70/30              | $38 \pm 1.7$             | $9.3 \pm 0.62$          | $1.0 \pm 0.5$           |

4.2. Morphological analysis

Morphology of hemp fibre is investigated using a field emission gun (FEG) scanning electron microscope (SEM), LEO 1530 VP prior to incorporate in the PLA. Figure 2 (a) shows the morphology of the pure chopped hemp fibres. It is clear from the figure that the hemp fibre has damage marks on the surface. The plants have natural waterways for food and water transportation to different parts of the plants, therefore the internal structure of the hemp fibre indicates hollow structure. Figure 2 (b) & (c) shows the SEM analysis of the fracture surface of the tensile samples for PLA- chopped hemp composites. It is observed from fractured surface morphology that hemp fibre is not properly dispersed in the matrix and some fibre lumps are observed. Some of the fibre pull out is also observed shows the weak mechanical interface. It is also observed that the structure of the fibre within the composites remained hollow and it seems that PLA did not able to penetrate effectively into the fibre structure,
thus resulting a hollow structure in the composites. The creation of the hollow structure in the composites could be one the reason for reduce tensile strength of the composites with incorporation of the chopped fibres into the matrix.

4.3. Dynamic mechanical thermal analysis

In DMA analysis a sinusoidal stress is applied to the materials and the viscoelastic properties of the materials is measured under periodic deformation. The sinusoidal wave is applied in a periodic motion and the amplitude of the stress and resulting strain is used to measure the energy absorbed by the elastic portion (storage modulus, $E'$), energy dissipated by the viscous portion (loss modulus, $E''$) and the loss factor (tan $\delta$) as a function of temperature. Figure 3(a) shows the dynamic mechanical spectra for storage modulus as a function of fibre loadings and indicates that the storage modulus increases relative to the amount of fibre loading. Table 2 summarizes the effect of hemp fibre contents on storage modulus at various temperatures. It is observed that the storage modulus of the composite increased with the increasing contents of the hemp. Storage modulus increased from 2.28 to 4.6 (GPa), when the contents of hemp increased from 0 to 30 (wt %) at 30 °C. Improvement in the storage modulus relative to fibre loadings is a reconfirming the tensile test results. Figure 3 also shows that the storage moduli of the PLA and PLA/hemp composites remain almost constant at temperatures below the glass transition temperature (up to about 60 °C) and then drop at the Tg, but seen increasing again.
around 90 °C due to stabilizing capability of the hemp fibres which implies that the reinforcement can be useful to increase heat distortion temperature (HDT).

The Figure 4 shows the damping factors (tan δ) for PLA and PLA-hemp filler composites as a function of temperature. The oscillation frequency sweep was set at 1Hz with a temperature ramp of 3 °C/min. Damping (tan δ) is highly sensitive to the structural transformation of the polymers. It was observed that incorporation of hemp fibre caused reduction in the area under the tan-delta curve thus reducing its damping capability of the composites. Also the peak of the tan delta curve lies in the same temperature range, suggesting that the glass transition temperature of the composites remains unchanged.

![Figure 3](image.png)

**Figure 3.** Storage modulus of PLA and PLA – chopped Hemp composites as a function of temperature

**Table 2.** Glass transtition temperature ($T_g$) and storage modulus of PLA and composites

| PLA / Hemp | Storage Modulus (30 °C) | Storage Modulus (40 °C) |
|------------|-------------------------|-------------------------|
| 100 / 0    | 2.28                    | 2.18                    |
| 90 / 10    | 3.72                    | 3.63                    |
| 80 / 20    | 3.60                    | 3.52                    |
| 70 / 30    | 4.60                    | 4.55                    |

**4.4. Simulation analysis**

Figure 5 shows the stress-strain curves of PLA/Hemp composites. The stress and strain levels were observed at the centre point of the specimen. A significant increase in stiffness of a hemp fibre composite was observed in the analysis. A close agreement between experimental and numerical results was achieved in the analysis. Incorporation of content of hemp fibres reduced the tensile
strength of PLA/Hemp composites. However, an increase in tensile strength was observed with increasing level of hemp content in PLA composites. The model was simulated for different content of hemp in PLA composites and the deformation process in tensile tests was observed (see Figure 6 & 7). An inhomogeneous deformation in the specimen behaviour was observed at the start tensile testing in the FE simulations. The simulation was carried out for lower strain rate level and no significant changes in the deformation behaviour of the specimens were observed. The model was used to verify the experimental results and good agreement between experimental and numerical results were observed.

![Figure 4](image)

**Figure 4.** Damping factors (tan $\delta$) of PLA and PLA / hemp composites as a function of temperature.

A DMA simulation of the developed PLA composites was carried out and response of the studied materials was observed at various temperatures as shown in Figure 8. A nearly linear increased in plastic deformation was observed in PLA/Hemp composites. The data were used to calculate the Storage modulus of the composites at various temperatures. The Modulus is the ratio of periodic stress to periodic strain i.e. \( E' = \text{stress} / \text{strain} \) and the measure of the energy absorbed by the elastic contents in the sample i.e. storage modulus \( (E = E' \cos \delta) \) and the measured of the energy dissipated i.e. loss modulus can be calculated using \( (E'' = E' \sin \delta) \) where the tan delta is \( \tan \delta = E'' / E' \), where $\delta$ is the phase difference between stress - strain and equal to $0^\circ < \delta < 90^\circ$.

![Figure 5](image)

**Figure 5.** Stress strain curves of pure PLA and its composites obtained from experiments and simulation tests.
It is observed that experimental results have good agreement with numerical results obtained from the simulation for the dynamic mechanical spectra as shown in Figure 8. The differences in calculated magnitudes for storage moduli between experimental and FE simulation, can be subjected to assumption incorporated in the FE simulations and the expressed chemical and physical differences among the fibres type, that are, shape and hardness of the fibres, surface area of the fibres and orientation of the fibres.

![Stress distribution in the specimens](image)

**Figure 6.** Stress distribution in the specimens

![Calculated plastic strain level in tensile testing](image)

**Figure 7.** Calculated plastic strain level in tensile testing

5. **Conclusion**
The PLA – hemp composites were developed and analysed using standard tensile and thermo mechanical techniques to investigate their mechanical and visoelastic properties. The reinforcement fibres increased the mechanical stiffness and caused to reduce the tensile strength. The storage modulus is evidently increased with fibres loading in the composites reinforcing the tensile properties. In order to compare the experimental results, the FE simulation models were developed for tensile and DMA analysis. A close agreement was observed between the experimental and simulation results.
Further studies are required to understand the structural properties of biocomposites.

**Figure 8.** Storage moduli obtained from FE simulation of PLA and PLA-hemp composites.

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