Poly(lactic acid)-Hemp-Nanosilica Hybrid Composites: Thermomechanical, Thermal Behavior and Morphological Properties

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ABSTRACT
PLA-hemp-nanosilica composites were prepared by a film stacking method, using hot compaction in a heated press with interspersed layers of hemp fibre. Dynamic mechanical properties measured with modulated force thermomechanometry (mf-TM) showed that the storage modulus increased with increase in filler loading due to increasing restriction to mobility of polymer molecule. The loss modulus and tan(δ) in contrast showed an opposite trend. Thermal property of the composites was assessed using differential scanning calorimetry (DSC). DSC results were determined with increasing scanning rate, the temperature of a low melting peak increased. Double melting behaviour appeared in the heating curve when using a slower scanning rate. Nano-silica promoted small and imperfect crystals that changed successively into more stable crystals through a melt-recrystallization process.

Keywords-biopolymer, crystallization, hybrid composite, multiple melting, thermomechanical.

I. INTRODUCTION
Poly(lactic acid) (PLA) is a commercial, biocompatible thermoplastic derived from natural resources by enzyme treatment of corn followed by polymerization, with wide applications in agriculture, medical devices, packaging and textiles. PLA possesses reasonably good mechanical and optical properties however low toughness and thermal stability of PLA limit its applications. Some of its physical properties, such as its toughness, crystallization rate and gas barrier properties, are still not satisfactory for certain processing and application. Consequently, there is a sustained interest to enhance these properties. The incorporation of fillers such as natural fibres and inorganic fillers from various sources into polymer matrix has been a well-accepted process to enhance mechanical and thermal properties.

Major drawbacks associated with the use of natural fibres as reinforcement in polymers include the poor wetting and the very weak interface which commonly occur between the fibres and most of the polymers used as matrix. The incompatibility of natural fibres with polymer matrix is responsible for poor interfacial of fiber/matrix adhesion hence reduce the mechanical properties of the composites. Better interfaces bonding for natural fiber composites can be achieved either by fiber and matrix modification with physical /chemical treatments or by the use of interfacial additives. PLA has been plasticized, blended with related polymers [1, 2] and used to prepare composites reinforced with natural fibres such as flax fibre, kenaf, silkworm, ramie and sugar beet pulp to improved the physical, mechanical properties and thermal behaviour of PLA-fibre composite [3-8]. Nanofillers also have been widely used to enhance
PLA composites on mechanical and physical properties which is influence the crystallization and morphological properties. Much research has been performed to alter PLA composite properties with inorganic fillers such as montmorillonite clay, silica, carbon black and talc as reinforcing agents [9-15].

Thermomechanical properties of PLA-silica by melt blending found that the tensile strength and modulus value of the composites enhanced by incorporation of nanoparticles. The silica nanoparticles were uniformly distributed in the PLA matrix for filler contents below 5.0 % w/w, whereas some aggregates were detected with further increasing filler concentration [11]. Another study reported that a uniform dispersion of silica in PLA was achieved for filler contents below 5.0 % w/w with addition of a high surface area (200 m² g⁻¹) nanosilica prepared by melt blending. The thermomechanical properties of the nano-composites improved because of their degree of dispersion and polymer-filler interaction [14].

Many authors [16-18] have reported that fiber-matrix interfacial compatibility influences the mechanical properties of PLA composites. A stronger fiber/matrix interface which improved the mechanical properties has been found with alkali treated hemp fibre [16]. Composites of hemp fibre reinforced PLA prepared by batch mixing were investigated by Masirek et al. [17]. The mechanical properties, thermal stability, degradation behavior and morphology of PLA-hemp composites were found strongly affected by the preparation condition and the hemp content in the composites. Mechanical tests showed that PLA composites reinforced with 20 % w/w hemp fibre increased the modulus of elasticity (reaching 5.2 GPa) of the composites. Other research investigated by Hu and Lim [18] found that 40 % volume fraction of alkali treated fiber gave the best mechanical properties and better adhesion for hemp fiber reinforced PLA composites fabricated using hot compression moulding.

The melting behaviour including multiple melting for many semicrystalline polymers has been reported [12-14, 19-23]. Double melting behaviour of pure PLA was observed during heating of non-isothermally crystallized pure PLA. This behaviour was explained by a melt-recrystallization model [14, 23]. Except for studies on multiple melting of pure PLA, the multiple melting of PLA composites with natural fibres and inorganic fillers has been less studied in recent years. The double melting behaviour of poly(lactic acid) filled with modified carbon black (PLA-MCB) composite was attributed to the melting of two populations of lamella that secondary crystallization was produced by small lamellae at low temperature and a primary crystallization process was formed from the major crystals at higher melting temperature [12]. The double melting peak of PLA-bamboo fibre-talc composites (PLA-BF-talc) studied at various heating rates noticed that the main melting temperature of the composites increased with the increasing of heating rate [13].

The aim of this paper was to prepare natural fibre (hemp fibre) and inorganic filler (nano-silica) hybrid composites using a film stacking method. This research investigated changes in mechanical properties and morphology that nano-silica imparted on the hemp fibre reinforced PLA. The double melting behaviour of PLA composites has been studied systematically.

II. EXPERIMENTAL

2.1 Materials
Poly(lactic acid) (PLA 2002D, extrusion grade) was obtained in pellet form from Natureworks Co., Minnetonka, USA. Hemp Fibre was purchased from Hemp Store Auckland, New Zealand. Fumed silica Cab-O-Sil M5 (200 m² g⁻¹ average surface area), was purchased from Cabot Corporation USA. Chloroform (purity 99.0-99.4 %, lab grade) was obtained from Merck KGaA, Darmstadt, Germany.

2.2 Composite preparation
PLA pellet, hemp fibre and fumed silica were dried in an oven at 60 °C for 24 h to remove moisture. PLA pellet (30 g) was dissolved in 300 mL of chloroform for 24 h followed by stirring for another 5 h to obtain PLA solution. Three layers of PLA-hemp composite (PH) was prepared by using a film stacking method, solvent was evaporated, then the composite was consolidated by compression moulding at 180 °C for 10 min under a load of 2.4 MPa and 30 s at 12.1 MPa. The nano-silica particles were dispersed in the matrix PLA phase to enhance properties between fibres. Composites with 2.5, 5.0, 7.5 and 10.0 % w/w of silica nanoparticles were separated by ultrasonication during dispersion in a PLA solution in chloroform. The sonicated PLA-silica dispersion was added to a woven hemp fibre mat designated as PLA-hemp-nanosilica (PSH2.5, PSH5.0, PSH7.5 and PSH10.0) composites.

2.3 Characterization
The characterization aimed to obtain information on mechanical properties, thermal behaviour, crystalline structure and surface morphology of PH and PSH composites. The thermo-mechanical properties was carried
out with modulated force thermomechanometry (mf-TM) using a Perkin-Elmer Diamond DMA (20 x 10 x 2 mm in tensile mode at 1 Hz with 10 µm deformation, heated from 30 to 190 °C at 2.0 K-min\(^{-1}\)). Thermal behaviour was performed with differential scanning calorimetry (DSC) using Perkin-Elmer Pyris 1 DSC, calibrated with indium according to the procedure for standard DSC.

Crystallization and melting curves were obtained by heating about 5 mg mass of composites in a sealed aluminum pan. Prior to cooling scan, composites was first heated to 180 °C and held in the molten state for 2 min to remove the thermal history. The second heating scan was obtained as a melting data. The measurement was carried out at a scanning rate of 2.0 K-min\(^{-1}\), 10.0 K-min\(^{-1}\) and 20.0 K-min\(^{-1}\) using N\(_2\) as the purging gas. The heat flow data from DSC scans were used to calculate the cold crystallization temperature (T\(_{cc}\)), enthalpy of crystallization (\(\Delta H_{cc}\)), melting temperature (T\(_m\)) and enthalpy of fusion (\(\Delta H_m\)).

Wide-angle X-ray scattering (WAXS) was done by using a Bruker Nanostar (Ni-filtered CuK\(\alpha\) radiation source with wavelength = 0.1542 nm, generated at 40 kV and 35 mA) and environmental scanning electron microscopy (ESEM) was used for morphology study.

### III. RESULTS AND CONCLUSION

#### 3.1 The thermomechanical properties

Fig. 1 displays the dynamic storage modulus and loss modulus for PLA-hemp (PH) and PLA-hemp-nanosilica composites (PSH2.5, PSH5.0, PSH7.5 and PSH10.0) as a function of temperature. Table 1 summarizes the data for dynamic mechanical properties of PH and PSH composites at ambient temperature.

The storage modulus (\(E'\)) decreased gradually upon heating from ambient temperature and rapidly dropped in the glass transition region around 60 °C due to softening of composites. This accompanied with the appearance of maximum loss modulus (\(E''\)) peak within the same transition region. The temperature position of this maximum peak determines the glass transition temperature (\(T_g\)) of PLA composites. As the content of silica increases, the \(T_g\) is increase with highest \(T_g\) for PSH7.5 at 59.0 °C compared with 57.4 °C for PSH2.5 and 57.0 °C for PH composite. Mathew et al. [24] discussed the shift to higher temperature usually indicates restricted molecule movement because of better interaction between the fibre and polymer matrix. In addition, an increase in \(E'\) monitored in the temperature region from 80 to 110 °C reflected an increase in the structural stiffness due to post-\(T_g\) cold crystallization, which is in agreement with \(E''\) shown in Fig. 1.

As shown in Table 1, the addition of nanosilica in the PLA matrix resulted in a significant change in \(E'\). The \(E'\) of PLA composites was increased by 10.23 % from 10.75 GPa (PH) to 11.85 GPa with addition of 2.5 % w/w nanosilica (PSH2.5) in PLA matrix.

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Storage Modulus /GPa</th>
<th>Loss Modulus /GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>120</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>150</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>180</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1. Dynamic mechanical properties of PH and PSH composites measured with Diamond DMA.
Further increases in $E'$ were observed with increasing nanosilica loading due to restriction movement of the PLA macromolecules. Beyond 5.0 % w/w filler loading the $E'$ increased linearly, though decreased in value with filler loading higher than 7.5 % w/w which consider as maximum improvement of the $E'$. The increased of storage modulus indicating better interfacial bonding between hemp fibres and PLA matrix. The same behaviour was observed in the preparation of PLA and silica with a melt blending study. Research found that fumed silica with high surface area (200 m$^2$/g) provided the highest thermo-mechanical improvement with a good distribution for filler contents below 5.0 % w/w obtained by melt-blowing [14].

### 3.2 Thermal behaviour

Fig. 2 shows the second DSC heating scans, melt-crystallized non-isothermally at scanning rate of 10.0 K-min$^{-1}$ for PLA-hemp composites (PH). There are three transitions indicating glass transition ($T_g$), cold crystallization temperature ($T_c$) and melting temperature ($T_m$) of the composites.

![DSC curve](image)

Fig. 2. Non-isothermal DSC curve of PLA-hemp composite (PH) at 10.0 K-min$^{-1}$ scanning rate.

Crystallization of PLA composites on cooling was negligible, whereas it crystallizes on heating producing a crystalline phase, through a cold crystallization process, which melts with two peaks or double melting endotherms ($T_{m1}$ and $T_{m2}$). Double melting peak or endotherms was observed at low temperature of about 150 °C and higher melting peaks at 160 °C.

The crystallization and melting behaviour of PH and PSH composites studied with non-isothermal DSC at a scanning rate of 10.0 K-min$^{-1}$ are summarized in Table 2. The degree of crystallinity ($\chi_c$) of PH and PSH composites was calculated using equation 1:

$$\chi_c = \frac{\Delta H_m - \Delta H_{mc}}{\Delta H_m} \times 100\%$$

where $H_m$ is the melting enthalpy (J/g) that was calculated from the fusion peak in DSC curve, $H_{mc}$ is the cold crystallization enthalpy of the PLA composites and $H_m^*$ is the enthalpy of completely crystalline PLA taken as 93.1 J/g [25].

### Table 2. The non-isothermal DSC data of PH and PSH composites at scanning rate of 10.0 K-min$^{-1}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\chi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>116.90</td>
<td>7.007</td>
<td>152.17</td>
<td>159.81</td>
<td>6.932</td>
<td>0.02</td>
</tr>
<tr>
<td>PSH2.5</td>
<td>122.03</td>
<td>6.485</td>
<td>154.16</td>
<td>160.16</td>
<td>6.504</td>
<td>0.05</td>
</tr>
<tr>
<td>PSH5.0</td>
<td>122.20</td>
<td>5.825</td>
<td>155.08</td>
<td>160.66</td>
<td>6.826</td>
<td>1.07</td>
</tr>
<tr>
<td>PSH7.5</td>
<td>124.94</td>
<td>4.799</td>
<td>155.70</td>
<td>160.84</td>
<td>6.220</td>
<td>1.52</td>
</tr>
<tr>
<td>PSH10.0</td>
<td>120.67</td>
<td>3.489</td>
<td>153.83</td>
<td>158.79</td>
<td>4.141</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 2 demonstrated that the addition of hemp fibre in combination with nanosilica slightly increased the $T_c$ and $T_m$ of PSH composites. The addition of 2.5 % w/w nanosilica into PLA matrix leads to an increase of $T_c$ of about 5.0 °C as observed for PSH2.5. Further increase of $T_c$ was observed at 7.5 % w/w filler loading which considered as maximum increment. Beyond 7.5 % w/w reduced the $T_c$ of PSH composites. This result indicated that the well dispersed nanosilica in PSH7.5 acted as effective nucleation agents in PLA matrix. However, a much smaller crystallization enthalpy ($\Delta H_c$) of PSH7.5 was obtained because of its restricted chain mobility in forming crystalline lamellar.

As shown in Table 2, in presence of nanosilica, the melting peak at low temperature ($T_{m1}$) of PSH2.5 composites shifted approximately 2.0 °C towards higher temperature compared with $T_{m1}$ for PH composites. However, nanosilica did not significantly alter the melting peak at high temperature ($T_{m2}$) of PSH composites which $T_{m2}$ was observed around 159-160 °C for all composites. Overall, the
cold-crystallization temperature ($T_{cc}$) of PSH composites increased at low silica loading (2.5-7.5 % w/w) and reduced in enthalpy of crystallization ($\Delta H_{cc}$) resulted in increased $\chi_c$. This result might be attributed to the nucleating activity of nanosilica in PLA matrix.

This DSC data agree well with a previous study, and similar observations have been reported [14]. The addition of 5.0 % w/w in PLA prior to mixing using melt-blending revealed double melting behaviour at temperatures of around 150 °C and $T_{cc}$ at 124 °C with 1.0 % crystallinity. In addition, the decreases of $\Delta H_{cc}$ and enthalpy of melting ($\Delta H_m$) resulted the increases of $T_{cc}$ suggest a decrease of the extent and kinetics of crystallization of a PLA matrix due to highly restricted segmental motions at the organic-inorganic interface [26].

For brevity only multiple melting behaviour of PH and PSH7.5 composites are discussed in this article to study the effect of scanning rate on melting endotherms of PLA composites. Melting behavior of PLA composites by non-isothermal DSC and modulated temperature DSC has been discussed in other article [27, 28]. Fig. 3 displays the melting endotherms of PH composite melt-crystallized non-isothermally at scanning rate of 2.0 K-min$^{-1}$, 10.0 K-min$^{-1}$ and 20.0 K-min$^{-1}$. The melting endotherms for PSH7.5 composite, is displayed in Fig. 4.

As shown, the slow heating reveals a double melting endotherm for both PH and PSH7.5 that is characteristic of melting-recrystallization and remelting (rrr) during the heating scan. Small or imperfect crystals were developed when crystallization was conducted at low scanning rates and low values of crystallinity were attained. The imperfect crystals lead to rearrangement and recrystallization much easier during heating process. Thus, the large reorganization of the crystal phase resulted in multiple-melting behaviour. Conversely, rapid scanning rates eliminated recrystallization resulting in a single melting peak on heating curve. A rapid scanning rate at 20.0 K-min$^{-1}$ caused the chain segments of PLA to move more freely. There are no new crystals formed during the heating process probably due to hemp and silica having less or no effect on the chain segment movement of PLA within the composites at rapid scanning rate.

Fig. 4. Non-isothermal DSC of PLA-hemp-nanosilica composites (PSH7.5) at 2.0 K-min$^{-1}$, 10.0 K-min$^{-1}$ and 20.0 K-min$^{-1}$ scanning rate.

Similar observations of double melting endotherm were observed in PLA-BF and PLA-BF-talc at slow heating rates (2.5-10.0 K-min$^{-1}$). Research found that the peak area of the double melting was dependent on the heating rate. The lower melting peak increased with increasing the heating rate whereas the higher melting peak decreased [13].

Wide-angle X-ray scattering images of PH and PSH composites are displayed in Fig. 5. The constant equatorial distribution of scattering intensity in rings corresponding to different crystalline reflection of PH and PSH composites indicates a perfectly random orientation of crystallites. PLA shows an amorphous nature.
Fig. 5. WAXS scattering image of PLA-hemp (PH) and PLA-hemp-nanosilica (PSH) composites.

The wide-angle X-ray 2θ charts give an insight into the crystalline structure of the composites shows in Fig. 6. As shown in Fig. 6, the diffraction peaks observed at 2θ = 16.0°, 20.0° and 22.5° that corresponding to the following crystal planes; 110, 203 and 205 for α-form of PLA (pseudo-orthorhombic) [12, 24, 29]. No systematic changes in diffraction peak positions are identified indicating that no other crystalline structure exists except the imperfectly crystalline α'-form.

Fig. 6. The 2θ scattering intensity of PLA-hemp (PH) and PLA-hemp-nanosilica (PSH) composites.

The reason that new crystal modification has not been discovered might be that nucleating the agent, nanosilica, enhanced the nucleation density and made the crystals in an imperfect α'-form. Thus the multiple melting peaks should be due to melting of different populations of lamellar crystals or through a process of mrr. The WAXS results are in agreement with the mechanical properties and DSC results discussed earlier. This result demonstrates that there is a first order transition of the two phases (α'-to-α) in this temperature range [24].

3.3 Morphological study

Fig. 7 shows the surface morphology of PH and PSH composites at 100X magnification. Fig. 8 displays the morphology of PH and PSH composites at higher magnification (3000X). SEM images revealed a uniform and effective dispersion of nano-filler where it is not possible to detect any aggregated silica particles in the PSH composite even at 7.5 % w/w filler loading indicating a high level of dispersion and distribution as well as adhesion to the polymer matrix, which is responsible for the improvement of mechanical and thermal properties of PLA composites. Some small residual aggregates of nanosilica were observed with the higher 10.0 % w/w silica loading.

Fig. 7. SEM images (100X) of PLA-hemp (PH) and PLA-hemp-nanosilica composites (PSH).

Fig. 8. SEM images (3000X) of PLA-hemp (PH) and PLA-hemp-nanosilica composites (PSH).
IV. CONCLUSION

Hybrid PLA-hemp-nanosilica composites were prepared with a film stacking method. The composites exhibited reinforcement due primarily to the high aspect ratio hemp fibres, secondary reinforcement and restriction of mobility of the PLA matrix due to silica nanoparticles. The nanosilica introduced crystal nucleation of PLA. PLA crystals formed under the cooling conditions used showed the phenomena of melting-recrystallization-remelting, which was confirmed by varying heating rates used for crystallization and melting. The increases in storage modulus were evidence of a nanosilica contribution in PLA matrix inducing reinforcement as detected by the thermomechanical properties. The hybrid nanocomposites presented an improvement of thermomechanical properties because of good dispersion, a combination of nano-particles and high aspect ratio fibres and effective polymer filler interaction. The thermomechanical, thermal behavior and morphological performance of the composites demonstrated that the biocomposites produced are suitable for structural application where renewable resource and high performance are required.

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