DYNAMIC MECHANICAL PROPERTIES AND MELTING BEHAVIOUR OF POLY(LACTIC ACID)–HEMP–NANOSILICA HYBRID COMPOSITES

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Abstract
Modulated temperature thermomechanometry (mT-TM) was used to determine the dynamic mechanical properties of the PLA composites across a broad temperature range. The storage and loss modulus increased with nanosilica addition, while the damping factor decreased respectively. Differential scanning calorimetry (DSC) results confirmed that the cold crystallization enthalpy gradually decreased that corresponded to an increase in filler content. Melting behaviour of PLA composites was obtained by using DSC and modulated temperature differential scanning calorimetry (mT-DSC). The crystallization and melting behaviour of poly(lactic acid)–hemp–nanosilica hybrid composites was studied in the range of 60–170 °C at various heating rates of non-isothermal DSC. Double melting endotherms were explained by a process of partial melting, recrystallization and remelting (mrr).

1 Introduction

Poly(lactic acid) (PLA) is a commercially bio-based polymer prepared from renewable resources. PLA has superior optical properties and is regarded as one of the promising bio-polymer with large market potential. The poor thermal stability and mechanical properties limit its applications. The physical and mechanical properties of PLA could be enhanced by incorporation of fillers, such as natural fibres and inorganic fillers might lead to change in PLA crystallization and melting behaviour. Double-melting behaviour including multiple melting behaviour has been observed for many semicrystalline polymers and their multiple melting behaviour has also been reported [1-3]. The main model of double-melting behaviour is a melt-recrystallization model. Yasuniwa et al. [4] reported the double melting behaviour of pure PLA during differential scanning calorimetry (DSC) heating of non-isothermal crystallized pure PLA by using the melt-recrystallization model to explain the double-melting behaviour of pure PLA. Except the studies on the multiple melting behaviours of pure PLA, the multiple melting behaviours of PLA composites with natural fibers or inorganic fillers have been less studied in recent years. Su et al. studied the multiple melting behaviour of poly(lactic acid) filled with modified carbon black (PLA–MCB) [5]. The double melting behaviour of 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 primary crystallization process was formed from the major crystals at higher melting temperature. Double-melting behaviour of bamboo fiber–talc–poly(lactic acid) composites studied with DSC at various cooling heating rate have been reported [6]. The double melting

peak occurred during heating process after slow cooling rate. This research noticed that the main melting temperature of the composites increased with the increasing of heating rate. In this paper, the natural fiber (hemp) and inorganic filler (silica) were prepared, the dynamic mechanical properties and double melting behaviour have been studied carefully. The aim is to optimize the mechanical properties and clarify the non-isothermal DSC and mT-DSC effect on double melting behaviour of the PLA composites.

2 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, was purchased from Cabot Corporation USA. Chloroform (purity 99.0-99.4 %, laboratory grade) was obtained from Merck KGaA, Darmstadt, Germany.

2.2 Composite preparation

The nanosilica was dispersed in the matrix PLA phase to enhance properties between fibres. Nanosilica particles of 8–12 nm exist as aggregates of about 20 particles fused together during high temperature furnace nebulation. The silica aggregates then form larger agglomerates that were separated by ultrasonication during dispersion in a PLA solution in chloroform. The sonicated PLA–silica dispersion was added to a woven hemp fiber mat. This hybrid composite was designated as PLA-hemp (PH) and PLA-hemp-silica (PH-S) composite as shown in Table 1. Three layers of PH and PH-S composite 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 t and 30 s at 10 t.

Composite	PLA [%·w/w]	Silica [%·w/w]
PH	100.0	0.0
PH-S2.5	97.5	2.5
PH-S5.0	95.0	5.0
PH-S7.5	92.5	7.5
PH-S10.0	90.0	10.0

Table 1. Identification of abbreviations for PLA-hemp composites and its nanocomposites.

2.3 Characterization

The dynamic mechanical properties were determined via 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 30 to 190 °C at 2.0 K·min^{-1}). The thermal analysis was performed using a 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 aluminium pan. Prior to a cooling scan, composites were 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}, 5.0 K·min^{-1} and 10.0 K·min^{-1} using N$_2$ as the purging gas. The heat flow data form DSC scans were used to calculate the cold crystallization temperature *(T_{cc})*, enthalpy of crystallization (*ΔH_{cc})*, melting temperature *(T_m)* and enthalpy of fusion (*ΔH_m*). Modulated temperature DSC (mT-DSC) was used to clarify the melting behaviour of PH and PH-S composites. mT-DSC melting scans were obtained by using a heat-cool modulation from 30 to 180 °C, at an average heating rate of 2.0 K·min^{-1} with a period of 60 s and modulation amplitude of 1 °C. The heat flow data from

the mT-DSC scans were used to analyze the total heat capacity ($C_{p,total}$), storage heat capacity ($C_{p'}$) and loss heat capacity ($C_{p''}$). The T_{cc}, ΔH_{cc}, T_m and ΔH_m *for both* composites were obtained from $C_{p,total}$ curve allowing comparison with conventional DSC data.

3 Result and Discussions

3.1 Dynamic Mechanical Analysis

Figure 1 shows the dynamic storage modulus for PLA-hemp (PH) and PLA-hemp-nanosilica (PH-S2.5, PH-S5.0, PH-S7.5 and PH-S10.0) composites as a function of temperature. The addition of nanosilica in PLA matrix and in combination of hemp had strong influence on the storage modulus. The storage modulus of PH composite increased by addition of nanosilica indicating better interfacial bonding between hemp fibers and PLA matrix. The highest modulus is represented by PH-S7.5, followed by PH-S5.0 and PH-S2.5. The storage modulus at 30 °C, was increased by 14 % from 1.74 GPa to 1.98 GPa with the addition of 2.5 %·w/w of silica. Further increase in storage modulus up to 19 % was observed with increasing 7.5 %·w/w silica loading. The increase in the storage modulus was attributed to the reinforcement effect in the PLA composites imparted by silica that allow better stress transfer from the PLA matrix to the hemp fibres. These effects are related to the improvement of the thermo-mechanical stability in PLA composites. The same behaviour was observed in the preparation of PLA and silica with melt-blending study [7].
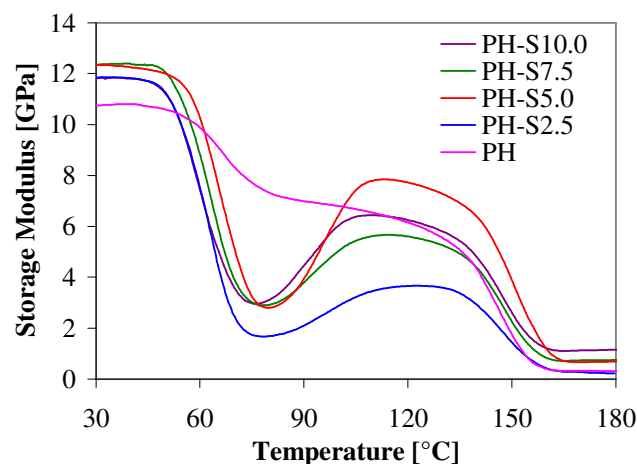

Figure 1. Storage modulus of PLA-hemp composites and its nanocomposites.

Refer to Figure 1, the storage modulus shows a sharp decrease around 60 °C, and then increases at 100 °C in agreement with loss modulus for PH and all PH-S composites shown in Figure 2. A decreasing trend was observed with the increasing temperature due to softening of polymer. The increase of modulus could also be linked to the cold crystallization of the PLA composites. The glass transition temperature (T_g) was derived from the loss modulus curves to study the effect of hemp fibre-PLA matrix on mobility of polymer chain. The T_g of PLA composites slightly shift to higher temperature with addition of silica. As the content of silica increases, the T_g is increase with highest T_g for PH-S7.5 at 59.0 °C compared with 57.4 °C for PH-S2.5 and 57.0 °C for PH composite. Mathew et al. [8] discussed the shift to higher temperature usually indicates restricted molecule movement because of better interaction between the fibre and polymer matrix. Besides, the α-relaxation involves the movement of polymer chains. The presence of crystalline structures or reinforcement could also act as a physical crosslink, decrease the mobility of rigid amorphous phase and consequently increase the composite stiffness.

The damping factor or tan δ peak intensity indicates the number of polymer chains involved in the relation process as shown in Figure 2. The tan δ peak for PH and all PH-S composites was observed at 100 °C, in agreement with cold crystallization shown in the loss modulus curve. The melting peak of PH and PH-S composites were observed in a temperature range 150 to 170 °C. These results indicate that mechanical properties show a better thermal stability in PLA-hemp composites with addition of silica.
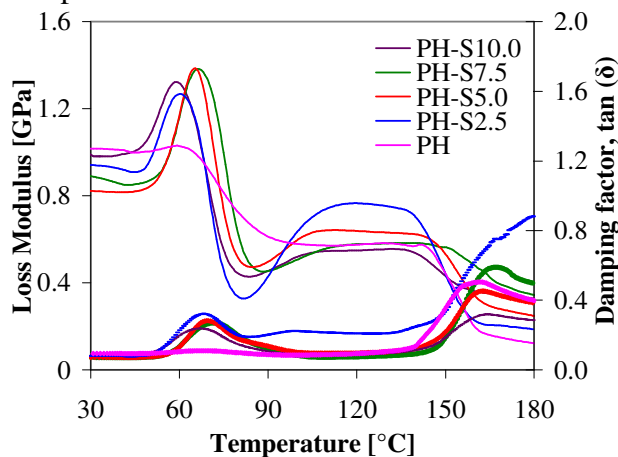

Figure 2. Loss modulus and damping factor of PLA-hemp composites and its nanocomposites.

3.2 Cold Crystallization and Melting Behaviour of PLA-hemp Composite

The non-isothermal crystallization and melting curve from second heating cycles at a scanning rate of 10.0 K·min⁻¹ for PH and all PH-S composites are illustrated in Figure 3. Double melting endotherms were detected at low temperature about 150 °C and high melting peaks at 160 °C for PH and all PH-S composites. As the nanofiller increases, the melting peak at 150 °C increased and the remelting peak at higher temperature decreased. It continued to decrease when more than 7.5 %·w/w of nanosilica added. The contribution of nanosilica alters the endotherm peak temperature of PLA composites. It is observed that the peak of melting temperature (T_m) increased by about 3.5 °C for nanocomposites containing 7.5 %·w/w nanosilica (PH-S7.5). This result is explained by melt recrystallization and remelting process. Other research has been linked this process with the existence of two different crystal structures; α-form (*pseudo-orthorhombic*) melts at higher temperature and β-form (*orthorhombic*), known as imperfect crystal melts at lower temperature within melting temperature range [7].
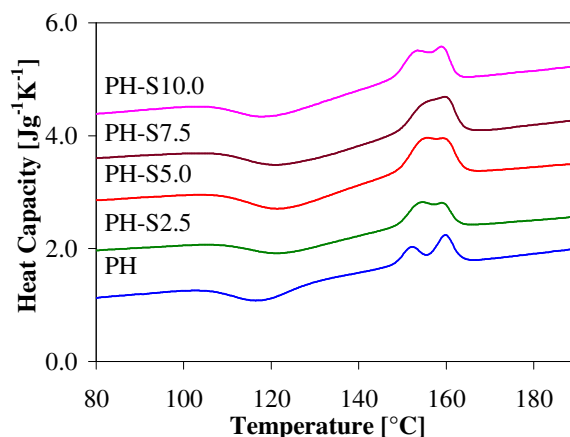

Figure 3. Non-isothermal curves of PLA-hemp composites and it nanocomposites.

Table 2 displays the thermal properties of PH and all PH-S composites. The T_{cc} of PH composite was detected at 117 °C. The introduction of nanosilica into the PLA matrix leads to an increase of the T_{cc}. The T_{cc} shifted to higher temperature as the content of nanosilica continued to increase, then decrease when more than 7.5 %·w/w added. This result can be explained by the agglomeration of the nanosilica. When more nanosilica was added, more aggregates remained. In general, larger aggregates contributed to the crystallization of PLA. This was confirmed by the gradually decrease of ΔH_{cc} (as shown in DMA properties in Figure 1 and 2) that corresponded to an increase in filler content. The incorporation of nanosilica into PLA matrix shows a positive impact on the thermal properties hence improved the mechanical properties.

Composite	T_{cc} [°C]	ΔH_{cc} [Jg^{-1}]	T_m [°C]	ΔH_m [Jg^{-1}]
PH	116.90	7.007	152.43	6.932
PH-S2.5	122.03	6.515	154.16	6.414
PH-S5.0	122.20	5.825	155.08	6.826
PH-S7.5	124.94	4.799	155.89	6.220
PH-S10.0	120.67	7.631	153.83	5.111

Table 2. Thermal Properties of PLA-hemp composites and it nanocomposites.

Upon addition of nanosilica, the spherulites of the polymer became smaller and offer opportunities to induce more polymer chain to crystallize, promotes a faster crystal growth, thus result in an enhancement of the crystallization process of PLA matrix. When these nanosilica were well dispersed in the PLA matrix, the number was large, even at a filler content of 2.5 %·w/w, which was enough to form nucleating sites and promote the growth of PLA crystals. However, high filler content of 10.0 %·w/w nanosilica might retard the chain mobility of PLA matrix and reduce the nucleating efficient of crystallization.

3.2.1 Dependence of Melting Endotherms on Heating Scan
Figure 4 displays the subsequent melting endotherms of PH and PH-S composites with 7.5 %·w/w filler, melt-crystallized non-isothermally at slow scanning rate of 5.0 K·min^{-1}. The slower scanning rate of 2.0 K·min^{-1} is displayed in Figure 5 to investigate the effect of scanning rate on double melting peak of PLA composites.
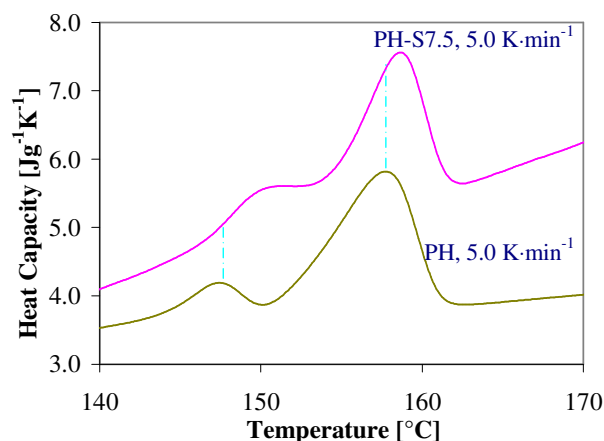

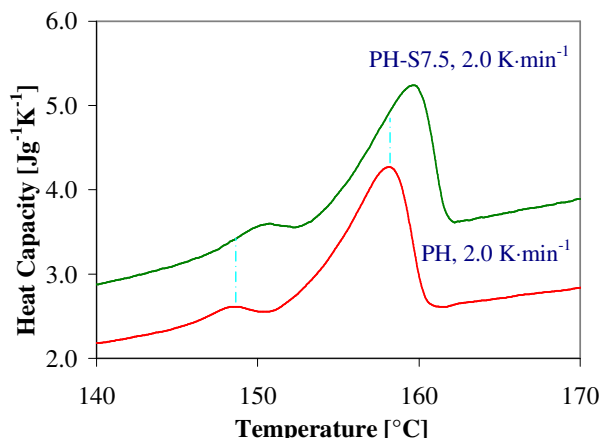**Figure 4.** Non-isothermal DSC for PH and PH-S7.5 at scanning rate 5.0 K·min^{-1}.

Figure 5. Non-isothermal DSC for PH and PH-S7.5 at scanning rate 2.0 K·min^{-1}.

As shown in Figure 4 and 5, double melting peak are observed for both composites. The introduction of nanosilica leads to a shift of both lower and higher melting peaks to higher temperature. With a slow scanning rate of 5 K·min^{-1}, the melting peak at low temperature reduced then increased the remelting peak at higher temperature. As the scanning rate goes to the slowest scan, the double melting peak became sharper with more polymers at melting peak change to remelting peak due to more polymer can recrystallize. In addition, the onset temperature for melting peak shifted slightly to higher temperature. The lower the heating rate, the longer time available for the polymer chain to reorganize which leads to more perfect crystal. Thus the positions of these peaks are expected to shift to higher temperature if they result from a continuous melting recrystallization of existing crystals.

Composite	T_{cc} [°C]	ΔH_{cc} [Jg^{-1}]	T_{m1} [°C]	T_{m2} [°C]	$\Delta H_{m1,2}$ [Jg^{-1}]
PH 2 K·min^{-1}	96.3	5.22	148.1	158.1	7.21
PH-S7.5 2 K·min^{-1}	97.4	10.37	150.5	159.6	10.67
PH 5 K·min^{-1}	101.3	12.70	147.5	157.8	16.20
PH-S7.5 5 K·min^{-1}	106.6	9.36	149.9	158.9	9.86

Table 3. Thermal properties of non-isothermal DSC of PH and PH-S7.5 composites.

Table 3 displays the thermal properties of PH and PH-S7.5 composites. Non-isothermal at 2.0 K·min^{-1} of PH composite shows the T_{cc} at 96 °C. The introduction of nanosilica into the PLA matrix leads to an increase of T_{cc} of about 5 °C as observed for non-isothermal at 5.0 K·min^{-1}. The well dispersed nanosilica in PH-S7.5 acted as an effective nucleation agent in the PLA matrix, as evidenced by small changes in the T_{cc} compared with PH composite. However, a much smaller crystallization enthalpy of PH-S7.5 was obtained because of its restricted chain mobility in forming crystalline lamellar.

3.2.2 Dependence of Melting Endotherms on DSC Method
To further substantiate the origin of double melting endotherms, another technique mT-DSC was used. The heat flow curve generated from mT-DSC for PH composite is given in Figure 6. The oscillation of heat flow curves is apparent as the temperature increases overall throughout the entire scan. The melting transition is interpreted and data from the mT-DSC scans was used to obtain the $C_{p,total}$, $C_{p'}$, and $C_{p''}$ as shown in Figures 7 and 8. Double melting endotherms are clearly observed for PH and PH-S7.5 composite in $C_{p,total}$ curve.
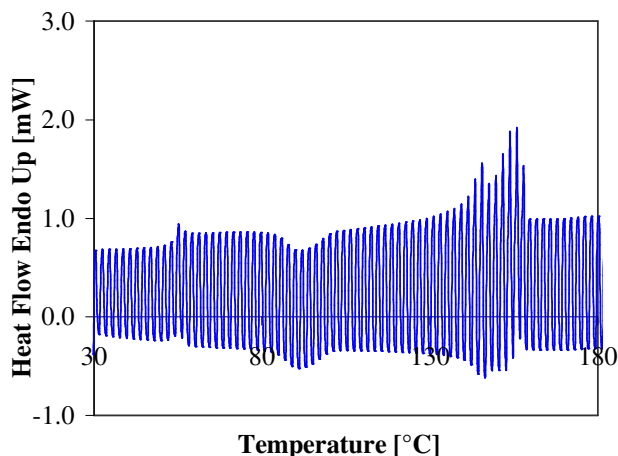
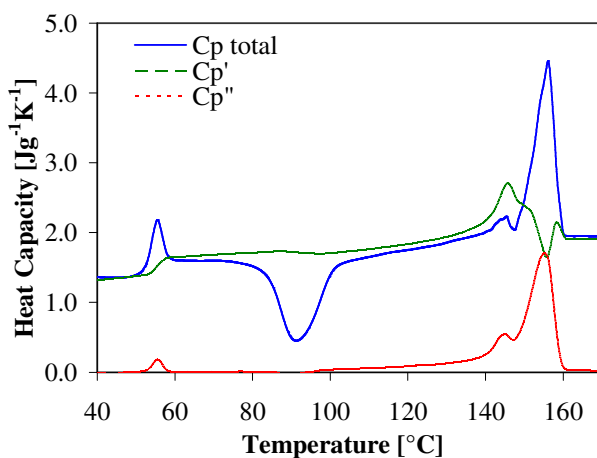**Figure 6.** Heat flow curve from mT-DSC of PLA-hemp composites (PH).

Figure 7. Heat Isothermal mT-DSC curves of PLA-hemp composites (PH).
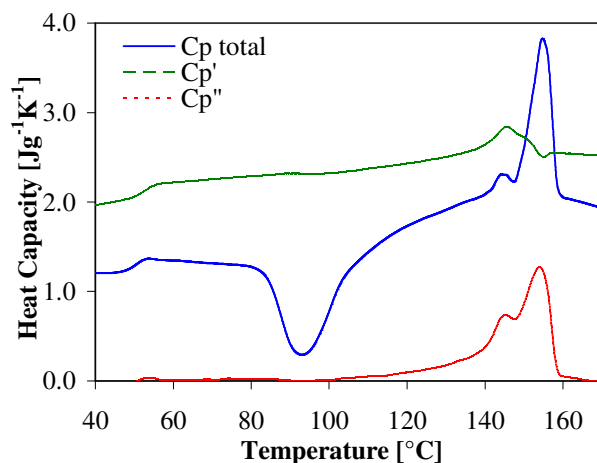

Figure 8. Heat isothermal mT-DSC curves of PLA-hemp-silica composites (PH-S7.5).

The thermal properties of PH and PH-S7.5 composites from mT-DSC data are displayed in Table 4. The T_{cc} of PH composite is 92 °C lower than non-isothermal DSC. The mT-DSC curve and data in Table 4 shows lower double melting endotherms for both PH and PH-S7.5 composites compared with melting endotherms on non-isothermal DSC due to crystals have more time to reorganize into more stable structures.

Composite	T_{cc} [°C]	ΔH_{cc} [Jg^{-1}]	T_{m1} [°C]	T_{m2} [°C]	$\Delta H_{m1,2}$ [Jg^{-1}]
PH mT-DSC	91.7	16.36	145.0	155.9	18.62
PH-S7.5 mT-DSC	94.3	12.29	146.1	156.2	13.51

Table 4. Thermal properties of mT-DSC of PH and PH-S7.5 composites.

The mT-DSC technique provided a high crystallinity, with formation of small crystals. Some of the crystals had a tendency to reorganize into more stable structures during a heating scan in the melting temperature range. As demonstrated in Figure 7 and 8, the *Cp'* represent a reversing process of PLA composites. The *Cp'* curve clearly shows the recrystallization and remelting process where PLA composites initially melted from 120 to 150 °C then recrystallize at 150 to 158 °C, then finally the composited remelted. The *Cp"* represents non-reversing process of PH and PH-S7.5 composites that completely undergo a melting process in the melting temperature range. The *Cp'* curve reveals that double melting endotherms for PH and PH-S composites as the process of melting, recrystallization and remelting (mrr). It was reported that the thermal history of poly(3-hydroxybutyrate) had a similar melting behaviour [3].

4 Conclusion

PLA is a unique biodegradable polymer with promising applications, and this improvement is highly desirable. Therefore, film stacking of PLA-silica matrix with hemp fibers can be considered as a possible way to improve the mechanical and thermal properties of PLA based composites. Nanosilica acted as a nucleating agent in the PLA matrix, and, therefore, accelerated the crystallization of PLA. The mT-DSC revealed that during heating, crystal rearrangement occurred at temperatures far below the melting range. Hemp fiber promoted recrystallization in the melting temperature range and silica promoted forming of small crystals or imperfect crystals in PLA composite. The crystallization enthalpy was reduced by addition of nanosilica due to restricted chain mobility in forming crystalline lamellae, explained by the process of melting, recrystallization and remelting.

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