



Non-isothermal Crystallization of Poly(lactic acid)-Hemp-Silica Nanocomposites Plasticized with Tributyl Citrate

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Non-isothermal crystallization of PLA composites consisting of hemp fibres and nanosilica was studied by differential scanning calorimetry at various scanning rates. The crystallization peak of plasticized PLA composites increased 6-18 °C compared with plasticized PLA. Hemp fibres promoted imperfect crystals that recrystallize in the melting temperature range and nanosilica acted as a nucleating agent in the PLA composites, enhancing the crystallization rate of the PLA.

1. Introduction

Poly(lactic acid)(PLA) is a semi-crystalline polymer and its physical and mechanical properties largely depend on the degree of crystallinity and crystallization rate. In amorphous form, application of PLA is limited by low glass transition temperature (T_g) and at temperatures greater than T_g , the crystalline form offers useful mechanical and physical properties. Generally addition of filler and plasticizer provides effective nucleation and mechanical reinforcement in polymer composites that induced nucleation for crystallization of PLA matrix, accelerating the overall crystallization process. Nucleation agents such as talc [1], silica [2], and carbon black [3] intensified the crystallization by dense heterogeneous nucleation on the surface of additive particles. Meanwhile addition of plasticizer such as citrate esters [4], effectively reduce T_g and increase the chain mobility of PLA.

The aim was to prepare hybrid PLA composites containing micro-sized hemp fibres and nano-silica particles, measure crystallization and melting of the PLA matrix and interpret using kinetic model. Non-isothermal crystallization is a practical method to investigate the crystallization behaviour of PLA because polymers are usually processed under non-isothermal environments. Non-isothermal crystallization kinetics of PLA composites using Avrami model is used in this paper to evaluate the nucleation ability and crystal growth rate due to hemp fibres, nanosilica and the contribution of tributyl citrate (TBC) plasticizer in the PLA composites.

2. Composite preparation

2.1 Materials and Preparation: Poly(lactic acid) (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. PLA composites with and without TBC (10 %-w/w of total composite) were prepared by solution casting followed by a film stacking method. A pre-determined amount of filler (2.5 %-w/w nanosilica) was added and well dispersed in PLA solution in chloroform by ultrasonication for 30-45 min. The sonicated PLA-silica dispersion was added to three layers woven hemp fibre mat. Solvent was evaporated, then the composite was consolidated by compression moulding at 180 °C for 10 min under a pressure of 2.4 MPa and 30 s at 12.1 MPa. Neat PLA and plasticized PLA were similarly prepared for comparison.



2.2 Characterization: Non-isothermal crystallization kinetics was performed with a Perkin Elmer Pyris 1 differential scanning calorimetry (DSC), calibrated with indium according to the recommended procedure. Crystallization curves were obtained by heating about 8 mg mass of composites in a sealed aluminum pan. The measurement was carried out at various scanning rates (1, 2 and 10 K·min⁻¹) using N₂ as the purging gas. Prior to a cooling scan, composites were first heated to 180 °C and held in the molten state for 2 min to remove any thermal history.

3. Results and Discussion

3.1 Non-isothermal Crystallization and Melting Behaviour

The action of hemp and nanosilica with and without TBC as a plasticizer on crystallization and melting behaviour of PLA composites was quantitatively analysed through non-isothermal DSC. Table 1 shows the thermal properties for PLA and PLA-silica (PS), PLA-hemp (PH), PLA-hemp-silica (PHS) and PLA, PS, PH, PHS plasticized with TBC known as (pPLA, pPS, pPH and pPHS) at selected scanning rates of 2.0 K·min⁻¹.

Table1: Thermal properties of PLA composite with and without plasticizer.

Composite	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	Composite	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)
PLA	93.5	no peak	150.5	pPLA	80.9	no peak	150.4	81.2
PS	88.4	no peak	151.1	pPS	no peak	no peak	150.9	87.4
PH	99.8	149.1	159.3	pPH	no peak	140.1	153.7	96.0
PHS	98.1	150.1	160.3	pPHS	no peak	138.7	151.6	99.1

Crystallization of neat PLA and PLA composites on cooling, under cooling rate used, was negligible, whereas PLA crystallizes on heating above T_g producing a crystalline phase, through a cold crystallization process, as shown in Fig. 1a.

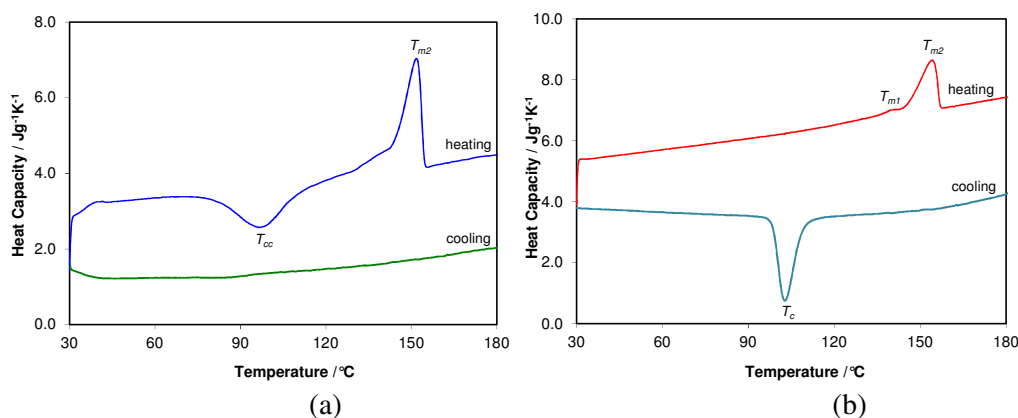


Fig 1. Non-isothermal DSC curve of (a) PLA and (b) pPH at scanning rates of 2.0 K·min⁻¹.

The addition of 2.5 %·w/w nanosilica in PLA matrix (PS) reduced the cold crystallization temperature (T_{cc}) and slightly increased melting temperature (T_{m2}). This result revealed that nanosilica acted as an effective nucleating in the PLA matrix and it modified the morphology and the physical properties of PLA composites. However, T_{cc} and T_{m2} for PLA reinforced with hemp fibres (PH) and a combination of hemp and nanosilica in PLA composites (PHS) were higher than neat PLA because the hemp fibres restricted mobility of PLA in the composites and created imperfect crystals, which melt with two peaks or a double melting endotherm. The double melting peak indicates less perfect crystals melting at lower temperature (T_{m1}) and recrystallizing to more perfect crystals and then melting again at higher temperature (T_{m2}). An introduction of hemp fibres and nanosilica in PLA composites lead to



an increase of T_{cc} and T_{m2} of about 5.0 °C and 9.0 °C, respectively. As expected, the addition of TBC in PLA matrix reduced the T_{cc} of neat PLA and all PLA composites. TBC induced a crystallization peak (T_c) on cooling (Fig. 1b) that enhanced the nucleating ability of the fillers and chain mobility in PLA composites.

Non-isothermal crystallization kinetics was used to further analyse the nucleation activity of PLA composites with addition of TBC. The crystallinity $\chi(T)$ of PLA composites at temperature T was obtained by exploiting data from DSC curves as in equation 1,

$$\chi(T) = \int_{T_o}^T \left(\frac{dH}{dT} \right) dT \Bigg/ \int_{T_o}^{\infty} \left(\frac{dH}{dT} \right) dT \quad (1)$$

where, $T_o = T_{onset}$, $T_{\infty} = T_{end}$ of the crystallization and dH = enthalpy of crystallization.

Equation 1 was transformed to $\chi(t)$ using a relationship between crystallization time t and temperature T in a non-isothermal crystallization process as in equation 2:

$$t = (T_o - T) / \beta, \quad T = \text{temperature at the crystallization time } t, \quad \beta = \text{cooling rate.} \quad (2)$$

Hence, the fractional of crystallization of PLA composites are obtained from equation 3,

$$\chi(t) = \int_0^t \left(\frac{dH}{dt} \right) dt \Bigg/ \int_0^{\infty} \left(\frac{dH}{dt} \right) dt \quad (3)$$

Fig. 2 represents the fractional degree of crystallinity, $\chi(t)$ of pPLA, pPS, pPH and pPHS composites as a function of time t at various scanning rate. Data was obtained from crystallization on cooling, as shown in Figure 1b (example of pPH at 2.0 K·min⁻¹). The half-time of crystallization ($t_{0.5}$) was directly obtained from a plot of $\chi(t)$ against t , which indicates the change in time from the onset of crystallization to the period when the $\chi(t)$ is 50 %. Results show that the $t_{0.5}$ of pPLA composites was higher than pPS, pPH and pPHS for all scanning rates. The addition of filler increased the crystallization rate indicating that the addition of plasticizer and nucleating agents enhanced the transportation ability of polymer chains.

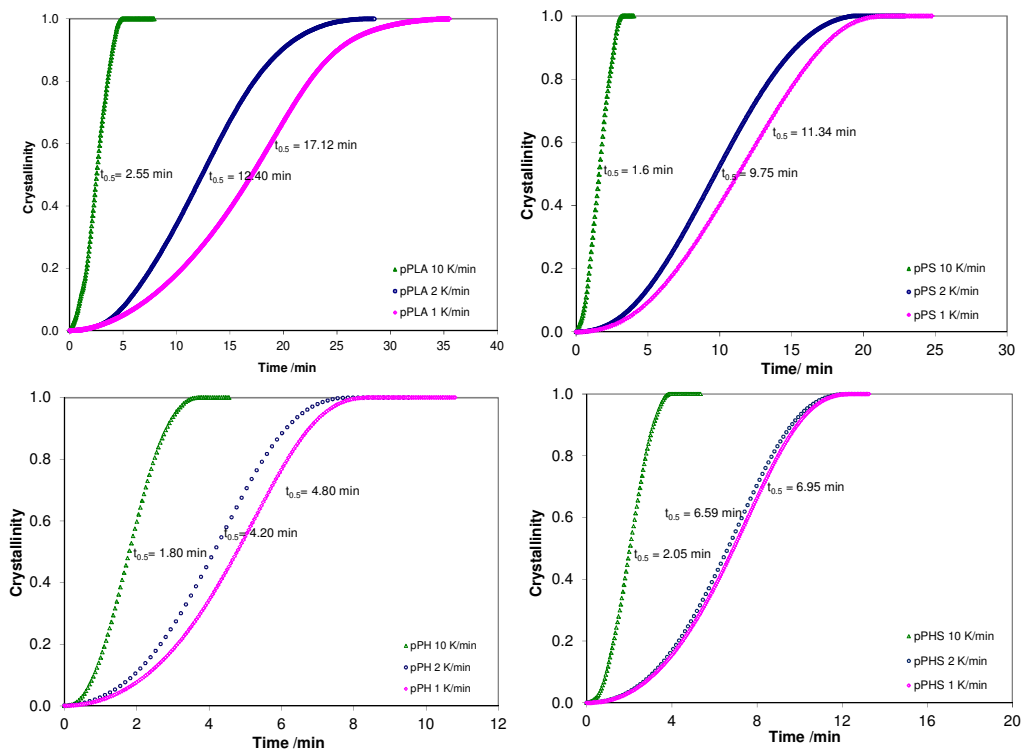


Fig 2. Plot of $\chi(t)$ against crystallization time at various scanning rate for pPLA, pPS, pPH and pPHS.



In addition to the $t_{0.5}$, kinetic rate coefficients based on Avrami model was used to characterize non-isothermal crystallization kinetics of plasticized PLA composites. Avrami equation explores the primary stage of non-isothermal crystallization, according to which the crystallinity, $\chi(t)$ dependent on crystallization time t as in equation 5,

$$1 - \chi(t) = \exp[-kt^n] \quad (5)$$

$$\log[-\ln(1 - \chi(t))] = \log k + n \log t \quad (6)$$

where, k = crystallization rate coefficient and n represents nucleation and growth geometry.

Fig. 3 shows a plot of $\log[-\ln(1 - \chi(t))]$ against $\log t$ for pPLA, pPS, pPH and pPHS at various scanning rates. The Avrami exponent n was obtained from the slope and the intercept gave the crystallization rate constant k .

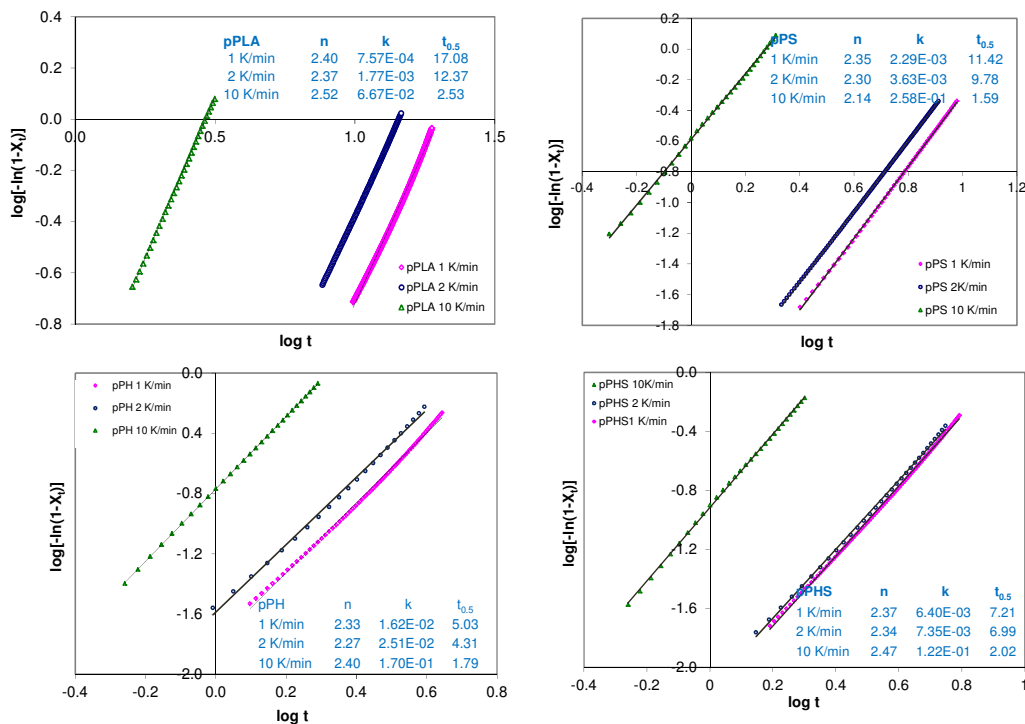


Fig. 3 $\log[-\ln(1 - \chi(t))]$ against $\log t$ curve of pPLA, pPS, pPH and pPHS at various scanning rates.

Referring to Fig. 3, a linear relationship was obtained for all composites indicating that the Avrami equation is valid to analyse the non-isothermal crystallization of PLA composites. Results showed that nucleating agents in PLA composites enhanced the crystallization rate of PLA composites. The predicted $t_{0.5}$ by the Avrami fit of all PLA composites are in good agreement with experimental values for at least 50% conversion of crystalline state.

4. Conclusion

Hemp fibres promoted imperfect crystals revealed by double melting endotherms that undergo rearrangement and recrystallization through a partial melting, recrystallization and remelting (mrr) process. Hemp and nanosilica acted as nucleating agents that enhanced the nucleation and crystallization rate of PLA composites and increased overall crystallinity.

References

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