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Thermal and Morphological Properties of Poly (lactic acid)/Nanocellulose Nanocomposites

R.Z. Khoo, H. Ismail, W.S. Chow*

*School of Materials and Mineral Resources Engineering,
Engineering Campus, Universiti Sains Malaysia, Nibong Tebal 14300 Penang, Malaysia.

Abstract

In this study, cellulose nanocrystals (CNC) were synthesized by acid hydrolysis of microcrystalline cellulose (MCC) powder. The morphology of MCC and CNC was examined using energy filtered transmission electron microscopy (EFTEM). Further, poly (lactic acid) (PLA)/CNC nanocomposite was prepared using solution casting technique. The thermal properties (i.e., glass transition temperature, melting temperature, degree of crystallinity, thermal decomposition) of the PLA/CNC nanocomposites were characterized using differential scanning calorimeter (DSC) and thermogravimetry analyzer (TGA). EFTEM studies showed that the CNC exhibited needle-like structure (approximately 10-20 nm in width and 250-300 nm in length), which is a typical measurements found in wood based nanocellulose. DSC analysis showed that CNC (up to 5wt%) is capable of acting as nucleating agent for PLA. TGA analysis showed that the of decomposition temperatures PLA/CNC nanocomposites were higher than that of pure PLA.

Keywords: Polylactic acid; Microcrystalline cellulose; Nanocellulose; Nanocomposites

* Corresponding author. Tel.: +604-5996160; fax: +604-5941011.
E-mail address: shyang@usm.my

Nomenclature	
CNC	Cellulose Nanocrystals
DSC	Differential Scanning Calorimetry
EFTEM	Energy Filtered Transmission Electron Microscope
MCC	Microcrystalline Cellulose
NC	Nanocellulose
PLA	Poly(Lactic Acid)

1. Introduction

Biopolymers have been attracting many researches and development works due to their fascinating properties such as biodegradability and biocompatibility. As a result, biopolymers have been regarded as an ideal candidate for replacement of conventional petroleum based plastics. Nanoscaled materials which were produced from biological origin were found to be suitable as a filler material in polymer matrix.[1, 2]

The term nanocellulose is often related to cellulosic materials having at least one dimension in nanometers. In nanometer scale, nanocellulose (NC) provides a wide range of possible properties to be explored where some material properties are affected by laws of atomic physics rather than following the behaviour of traditional bulk materials.[3] Nanocellulose (NC) can be further categorized into three subcategories based on cellulose source and on the production methods, which are cellulose nanocrystals (CNC), nanofibrillated cellulose and bacterial nanocelullose.[4]

CNCs are rod-like cellulose crystals with 10-120 nm in width and several hundred nanometers in length. CNCs are highly crystalline. Through strong acid hydrolysis, they are produced from biological sources like bleached wood pulp, cotton, manila, tunicin, bacteria, etc. Nanocellulose components and most amorphous cellulose from source materials were removed in the acid treatment, hence producing high purity cellulose crystals[5].

Nanocellulose had been extensively used as filler to improve strength of materials due to their high aspect ratio[6]. Examples of nanocellulose composites that have been produced are polyurethane/pineapple leaf nanofibrils composites[7], polyvinyl alcohol/curava nanofibers composites[8] and thermoplastic starch/cotton nanofibers composites[9]. Generally, nanocellulose is able to act as value added reinforcement material in polymer matrices due to its superior mechanical and thermal properties.[10]

Poly (lactic acid) (PLA) is part of the aliphatic polyesters family, usually produced from α-hydroxy acids, consists of polyglycolic acid or polymandelic acid. PLA can be produced from renewable resources, has recently gained growing attention due to its biodegradability, biocompatibility, transparency, high modulus and strength. PLA is one of the most anticipated biopolymer that provides high potential for commercial major scale production of renewable packaging. Since then, organic filler materials have been chosen to be added to PLA matrix in order to produce new materials. Incorporation of nanocellulose into PLA matrix presents a novel approach in the fabrication of next generation polymer materials.[11-14]

The objective of this study was to produce CNC using micro-crystalline cellulose (MCC) by acid hydrolysis method. PLA/CNC nanocomposites were prepared by solution casting technique. Solution casting method is hypothesized to be able to provide more homogenous distribution of CNC in PLA matrix compared to melt blending.[15] The effects of CNC loading on the thermal properties (i.e., glass transition temperature, melting temperature, degree of crystallinity, degradation temperature) of PLA were studied. The ability of CNC as nucleating agent for PLA and also its effect on PLA thermal stability were evaluated.

2. Experimental design

2.1. Materials

Poly (lactic acid) PLA, (Ingeo[TM] 3051D) was purchased from NatureWorks LLC®, USA. The specific gravity and melt flow index of the PLA are 1.25 and 25 g/10min (2.16 kg load, 210ºC), respectively. The glass transition

temperature (T_g) and melting temperature (T_m) of PLA are approximately 60ºC and 155ºC, respectively. PLA pellets were dried in an oven at 80ºC for 24h. Microcrystalline cellulose powder (MCC) was supplied by Sigma-Aldrich, USA. MCC was used as starting material for the preparation of CNC.

2.2. Cellulose nanocrystal synthesis and characterization

5g MCC powders were acid hydrolyzed for 5h using sulfuric acid (H_2SO_4) at 60% (w/v). Next, 500ml distilled water were added to quench the process. The hydrolyzed cellulose was then centrifuged at 3500 rpm for at least 5 times wash until the solution turns turbid. The generated aqueous suspension of CNC was ultrasonicated for 5 minutes before being stored in refrigerator. The morphology of CNC was examined using energy filtered transmission electron microscope (EFTEM, Libra 120-Carl Zeiss, USA).

2.3. PLA/CNC nanocomposites preparation

Prior to solution casting, CNC were dried for 24 h in ambient temperature. CNC were then dissolved in chloroform. At the same time, PLA was dissolved in chloroform in another beaker. After CNC and PLA were completely dissolved, both solutions were mixed together and poured onto Petri dishes. The PLA/CNC was then dried for 24 h under room temperature. Solution cast film samples of PLA with 1, 2 and 5 wt% CNC contents were prepared as described above. Table 1 shows the material designation and composition of PLA/CNC nancomposites. Figure 1 shows the CNC extraction process and the solution casting process of PLA/CNC nanocomposites.

Table 1. Material designation and composition for PLA/CNC composites.

Material designation	Composition	
	PLA (wt%)	CNC (wt%)
PLA	100	-
PLA/CNC-1	99	1
PLA/CNC-2	98	2
PLA/CNC-5	95	5

2.4. DSC measurements

Differential scanning calorimeter (TA instruments, model: DSC 200, USA) was used to evaluate the thermal behaviour of PLA/CNC nanocomposites. The specimens were scanned from 30ºC to 190ºC at a heating rate of 10ºC/min. The glass transition temperature (T_g), melting temperature (T_m) and cold-crystallization temperature (T_{cc}) were determined. The degree of crystanility (χ_c) of PLA/CNC nanocomposites was calculated using Equation 1.

$$X_c = \frac{\Delta H_m}{\Delta H_f \times W_{PLA}} \times 100\%$$

(1)

where χ_c is degree of crystallinity; ΔH_m is the heat of fusion of the sample; ΔH_f corresponds to the heat of fusion of 100% crystalline material, and W_{PLA} is the net weight fraction of the PLA. The heat of fusion of 100% crystalline PLA (ΔH_f) is approximately 93.6 J/g[11].

2.5. TGA measurements

Thermogravimetric Analyzer (Mettler Toledo, model: TGA/DSC 1, USA) was used to evaluate the thermal decomposition of PLA/CNC nanocomposites. The specimens were heated from 30ºC to 600ºC at a heating rate of 10ºC/min under nitrogen atmosphere.
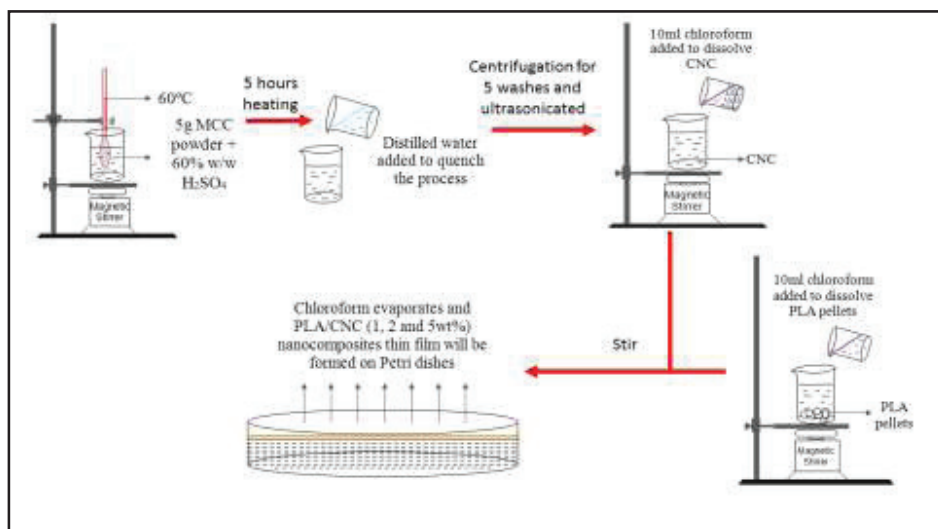
Fig. 1. CNC extraction and solution casting process of PLA/CNC nanocomposites thin film.

3. Results and discussion

3.1 Morphological characterization of MCC and CNC

Figure 2a shows the TEM micrograph of the MCC powder prior to acid hydrolysis. Most of the MCC powder are irregular shaped-like particles consists of up to 200 nm in width and 400 nm in length. From Figure 2b it can be seen that the CNC exhibited rod-like structure, at 10-20 nm in width and 250-300 nm in length, which is the typical measurements found in wood based nanocellulose.[16] When acid hydrolysis takes place, amorphous portions of the long chain cellulose are preferably hydrolyzed, while the crystalline regions having higher resistance to acid attack, hence producing rod-like particles, CNC in nanoscale region.[17] Based on these findings, it is clear that acid hydrolysis can effectively reduce a large amount of fiber sizes (from micron-size to nano-size), which is in agreement with previous findings by other authors. On top of that, it can be seen that the cellulose rods were agglomerated in some places while in some other regions they are separated. Generally, during drying of cellulose, molecular contact between CNCs increases due to forces resulting from removal of water and high temperature. Hence, drying process of CNCs are regarded as one of the most important and challenging steps in order to fully utilise this material in producing reliable products.[18]
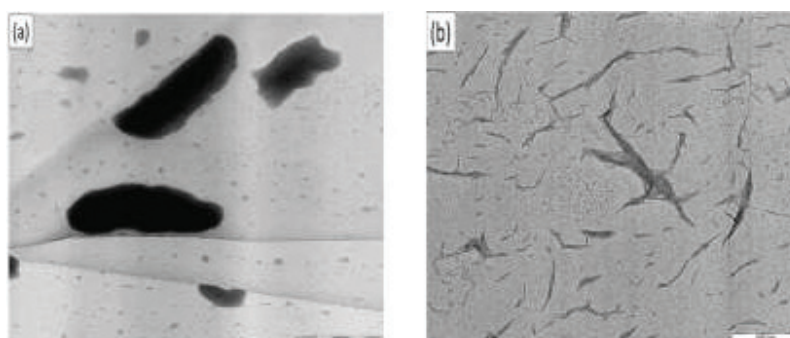

Fig. 2. TEM micrograph taken from (a) MCC; (b) CNC.

3.2. Thermal characterization of PLA/CNC nanocomposites

3.2.1. Differential Scanning Calorimetry (DSC)

Thermal characteristics (e.g. T_g, T_c, T_m) of PLA and PLA/CNC nanocomposites are summarized in Table 3. Based on Table 3, no significant changes of glass transition temperature of the PLA and PLA/CNC nanocomposites were observed. Glass transition temperature (T_g) is commonly identified as a complex phenomenon that relies on several factors such as intermolecular interaction, chain flexibility and molecular weight of the material itself.[19] It is expected that the T_g of PLA is not much affected by the addition of CNC. Similar findings were reported by Liu et al[20] where they incorporated 2.5 to 5.0 wt% of flax cellulose into PLA. The T_g of PLA/flax cellulose is similar to that of pure PLA.

It should be mentioned that cold-crystallization temperature (T_{cc}) of PLA and PLA/CNC nanocomposites is hardly observable. This indicates that the material is highly crystalline after the solution casting technique. From Table 3, it can be seen that the degree of crystallization (X_c) of PLA was affected by the CNC loading. At 5 wt% CNCs, higher crystallinity (34.5%) were obtained compared to neat PLA (30.9%), which could be due to presence of CNCs that accelerates the crystallization of PLA. This phenomenon can be ascribed to the anchoring effect of the cellulosic nanofillers, likely to be acting as a nucleating agent.[21-22] According to Du et al[23], cellulose in PLA can act as heterogeneous nucleus and promote PLA chains crystallization at lower temperature. Nevertheless, it can be seen that the χ_c of PLA/CNC-1 and PLA/CNC-2 is slightly lower than that of PLA. This can be due to insufficient amount of nanofillers to act as nucleating agent[24].

Table 2. Thermal characteristics of PLA and PLA/CNC nanocomposites.

Materials designation	Thermal characteristics			
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
PLA	58.5	149.9	29.1	30.9
PLA/CNC-1	59.1	151.8	23.3	27.7
PLA/CNC-2	59.4	149.7	21.2	29.1
PLA/CNC-5	58.1	144.4	23.0	34.5

3.2.2. Thermogravimetric Analysis (TGA)

TGA is an important analysis used to investigate thermal decomposition of polymeric materials. The weight loss of a substance due to formation of volatile product after degradation is monitored as a function of temperature or time. The TGA results of PLA and PLA/CNC nanocomposites are summarized in Table 4. Note that T_{10} is the corresponding temperature at which weight loss of material is 10%. The T_d referred to end decomposition temperature whereas T_{max} is the temperature taken from DTG curves (maximum peak). From Table 4, it can be seen that the T_{10} and T_d of PLA was increased as the increasing loading of CNC. This indicates that CNC increases the thermal stability of PLA and slows down the rate of thermal degradation.[25] Similar finding was reported by Mandal and Chakrabarty[26] on the polyvinyl alcohol/nanocellulose composites.

Table 3. TGA results for PLA and PLA/CNC composites.

Material designation	T_{10} (°C)	T_d (°C)	T_{max} (°C)
PLA	324.0	353.0	338.0
PLA/CNC-1	328.0	361.0	349.0
PLA/CNC-2	332.0	373.0	358.7
PLA/CNC-5	332.0	376.0	358.9

4. Conclusions

Cellulose nanocrystals (CNC) were successfully synthesized by acid hydrolysis of microcrystalline cellulose (MCC) powder. Most of the MCC powder are irregular shaped-like particles consists of up to 400 nm in length and 200 nm in diameter. On the other hand, the synthesized CNC exhibited rod-like structure (approximately 8 nm in width and 250nm in length) which is the typical measurements found in wood based nanocellulose. Adding CNC into PLA did not change the T_g and T_m, however, it is worth to note that the CNC is able to act as nucleating agent for PLA (at 5wt% CNC loading). Besides that, presence of CNC also favours improvements in the thermal stability of PLA.

Acknowledgements

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