

INFLUENCE OF DIFFERENT ORGANO-MODIFIED NANOCCLAYS ON THE MECHANICAL AND THERMAL PROPERTIES OF BIODEGRADABLE POLY-LACTIC ACID (PLA)

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Abstract

PLA/nanoclay composites with various weight percentage of nanoclay were prepared by solvent casting method. Three commercially available organo-modified nanoclays were used to assess the mechanical properties of PLA/nanoclay composites. Thermal characteristics were determined using DSC. It was observed that there is an optimal concentration of nanoclay beyond which the mechanical properties will deteriorate. It was found that different organo-modified nanoclays exert critical influences over the properties of the nanocomposites.

1 Introduction

1.1 Background

In recent years, the development of composites from renewable polymers with eco-friendly reinforcing agents has attracted great interest in addressing anticipated fossil resources depletion and a decrease of usable landfill areas. Renewable biodegradable polymers are the most promising candidates in this endeavour due to their biodegradability, compostability and reproducibility from alternative resources with lower energy consumption [1, 2].

Biodegradable polymers produced from renewable resources have created much attention and interest in packaging industries to develop new materials to meet sustainability goals. Polylactic acid (PLA) has been popular in recent years as a renewable resource to replace petroleum-based polymers. It has been widely used for various biomedical applications due to its biodegradability, biocompatibility and high stiffness. However, poor toughness and the high cost of PLA compared to petroleum-based polymers had restricted its potential widespread application.

The use of nano-sized inorganic fillers had been intensively studied as they often exhibit remarkably improved mechanical properties and functional properties compared to virgin polymers or conventional composites with macro- or micro-sized fillers [3]. Nanocomposites with surface-modified inorganic nano-fillers exhibit superior improvements in mechanical properties, thermal stability, gas barrier properties and crystallization behaviour due to better

interaction of the inorganic filler with the polymer matrix [4-7]. Challenges still exist in getting a homogenous dispersion of nanoscale inorganic fillers within the polymer matrix that would result in improved properties that suit different industrial applications. In this work, commercially available nanoclays were used to improve the mechanical properties of PLA. Thermal and mechanical properties were evaluated to investigate their reinforcement effects in PLA.

2 Experimental

2.1 Materials

A commercially available PLA (3001D) was purchased from NatureWorks LLC. This PLA contains mainly L-lactic acid with 1.4±0.2% of D-lactic acid and a density of 1.24g/cm³. Nanoclays used in this study were Cloisite 15A, 25A and 30B supplied by Southern Clay Products. The nanoclays are natural montmorillonite modified with quaternary ammonium salt. Fig.1 shows their respectively organic modifiers. They are chemically bonded with dehydrogenated tallow and tallow which consists of ~65% of C18, ~30% of C16 and ~5% of C14.

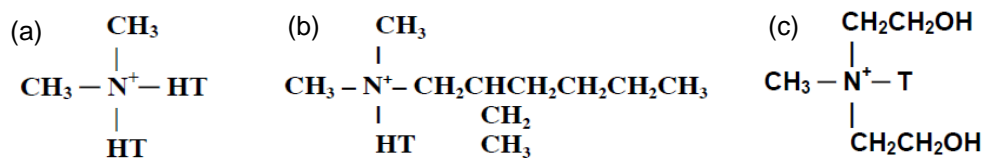


Figure 1. Organo-modified nanoclays from Southern Clay (a) Cloisite 15A (b) Cloisite 25A (c) Cloisite 30B

2.2 Preparation of PLA\Nanoclay composites

PLA and PLA\nanoclay composites with 1 and 5wt% of nanoclay were prepared using solvent casting method. The solution was sonicated and degassed before casting into films.

2.3 Materials Characterization

2.3.1 X-ray Diffraction Analysis (XRD)

The crystallinity of PLA and PLA\nanoclay composites were evaluated via XRD scanning from 10° to 25° with scanning speed of 0.01steps per second using a PANalytical X'Pert PRO XRD machine. The operating condition to perform all scanning was set at 40KV, 30mA with Cu K α radiation ($\lambda=0.154\text{nm}$).

2.3.2 Differential Scanning Calorimetry (DSC)

A Netzsch DSC 204 F1 Phoenix instrument was used to analyse both pure PLA and PLA\nanoclay composites. Sample mass of about 3-4mg were used in the measurements. The samples were heated from room temperature to 180°C at a heating rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_{cc}) of pure PLA and nanocomposites were obtained. Percentage of crystallinity (%X_c) of pure PLA and nanocomposite can be calculated by taking into account their filler content, %X_c = ($\Delta H_m - \Delta H_c$)/ ΔH_{m0} (1-f)·100. ΔH_c , ΔH_m , ΔH_{m0} are the enthalpies of crystallization, melting and melting of PLA with 100% crystallinity ($\Delta H_{m0}=93\text{J/g}$), respectively; while f refers to the weight fraction of nanoclay.

2.3.3 Mechanical Testing

The tensile properties of all samples were obtained using a Shimadzu universal testing machine. The samples were cut into rectangular strips with dimensions of 5mm (width) X

70mm (length). The samples were tested at a cross head speed of 50mm/min with initial grip separation of 50mm. At least five samples were tested for each formulation.

3 Results and Discussion

3.1 X-ray Diffraction Analysis (XRD)

X-ray diffraction analysis is a rapid and efficient characterization technique to study the crystallinity of PLA and PLA/nanoclay composites. Fig.2 shows high angle XRD diffractograms for pure PLA and PLA/nanoclay composites at 1 and 5wt% of Cloisite 15A, 25A and 30B.

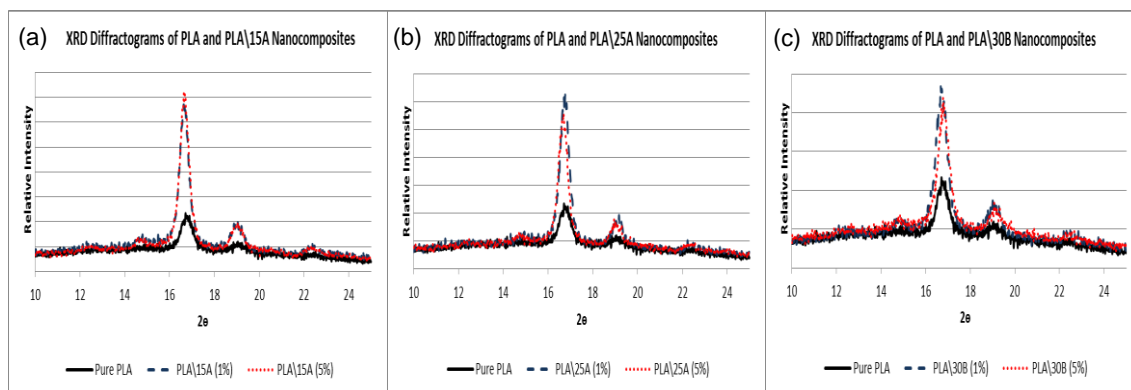


Figure 2. XRD diffractograms for (a) PLA/15A (b) PLA/25A (c) PLA/30B nanocomposites.

Crystallinity of PLA generally increased after incorporation of different nanoclays, as shown in Fig.2. This implies that nanoclay may act as nucleating agent to promote formation of more crystalline structures and hence increases the crystallinity of nanocomposite [8]. Fig.2 has also shown that the crystallinity of nanocomposite was not greatly affected even at higher nanoclay loadings. However at higher nanoclay loadings, the crystallinity of PLA could possibly be affected if nanoclay exceeds certain level which may reduce the size of crystalline structure [8].

3.2 Differential Scanning Calorimetry (DSC)

Thermal characteristic of PLA and PLA nanocomposites such as glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_{cc}) were measured using DSC. DSC thermographs of PLA and PLA with 5wt% of Cloisite 15A, 25A and 30B were plotted and shown in Fig.3 to study the effect of different organo-modifiers.

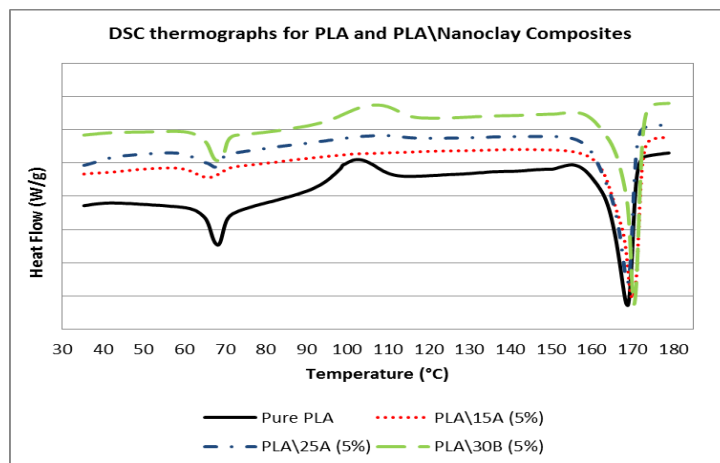


Figure 3. DSC thermographs for PLA and PLA with 5wt% of Cloisite 15A, 25A and 30B.

The T_g of PLA does not vary significantly with incorporation of nanoclay. However, T_g for 5wt% of Cloisite 15A and 25A samples was observed to have shifted slightly to lower temperature. The T_m of PLA and PLA nanocomposites remain around 169°C to 170°C upon incorporation of nanoclay.

Fig.3 shows the area under the cold crystallization peak (T_{cc}) reduced with incorporation of nanoclay. The cold crystallization temperature (T_{cc}) of PLA nanocomposites was observed to have increased compared to pure PLA. The most common observation is the nucleating effect of nanoclay which provides larger number of nucleation sites and allows the polymer to crystallize at much higher temperatures [5].

In this study, crystallinity of PLA increased with addition of nanoclay. This was also observed in high angle XRD scanning as shown in Fig.2, which revealed the crystallinity of PLA increased after incorporation of nanoclay. The increase of crystallinity might be due to the nucleating effect of nanoclay which promotes the formation of more crystalline structures.

3.3 Tensile Properties

Tensile properties of PLA\15A, PLA\25A and PLA\30B nanocomposites are shown in Figs. 4(a) to 4(c). It can be observed that the Young's Modulus of PLA improved by the addition of Cloisite15A and 30B. The Young's Modulus increased 7.55% by adding 5wt% of Cloisite 15A and 9.79% by adding 1wt% of Cloisite 30B, respectively.

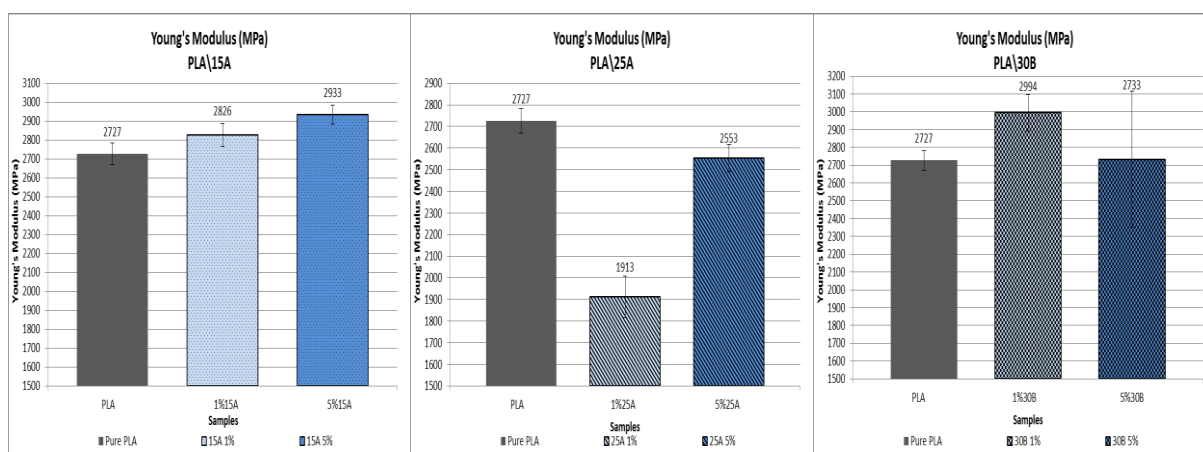


Figure 4. Comparison on Young's Modulus (MPa) for PLA and PLA nanocomposites, (a) PLA\15A (b) PLA\25A and (c) PLA\30B.

The addition of 1wt% of Cloisite 30B has shown greater improvement in Young's Modulus as compared to Cloisite 15A and 25A. This may suggest the diols present in Cloisite 30B may have played an important role in favoring the enthalpy interaction with the C=O bonds present in the PLA backbone [4, 9]. Fig.4 (b) also shows that the incorporation of Cloisite 25A has a detrimental effect on the mechanical properties of PLA although the Young's Modulus of PLA\25A increased with increasing Cloisite 25A content.

The Young's Modulus of all samples generally increases with low nanoclay content but may reach a peak as the nanoclay content is increased, see Fig.4(c). This might be due agglomeration of nanoclay may happen at high nanoclay content and these may result in stress concentration within the polymer matrix and pre-mature failure of the samples [5]. Based on this study, the optimum nanoclay formulation with enhanced Young's Modulus was obtained at 1wt% of 30B. Young's Modulus of nanocomposite may have deteriorated at

higher nanoclay content due to agglomeration of nanoclay [5]. It was found that the presence of hydroxyl groups in the organo-modifier resulted in better compatibility with the ester group to achieve better mechanical properties as compared to organo-modifier with larger d-spacing and longer oligomer [10]. Tensile fracture surfaces of nanocomposites will be examined under SEM to gain better understanding of the causes of materials failure.

4 Conclusion

XRD analysis revealed crystallinity of PLA increases with the addition of nanoclay regardless of the type of nanoclay used. DSC results ascertained that the crystallization kinetics of PLA changes after incorporation of nanoclay. T_g and T_m of PLA do not vary significantly with addition of nanoclay. At higher nanoclay loadings, T_g was observed to have shifted to slightly lower temperature for 5wt% of Cloisite 15A and 25A sample. Sample 1wt% of Cloisite 30B showed improvements in Young's Modulus over pure PLA. Cloisite 30B may have better interaction and compatibility with PLA due to its polar character.

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