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Mechanical and thermal properties of melt processed PLA/organoclay nanocomposites

Norazura Ibrahim¹, Margaret Jollands² and Rajarathinam Parthasarathy²

¹Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia.

²Rheology and Materials Processing Centre, School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne, Australia.

E-mail: norazura.ibrahim@gmail.com

Abstract. Polylactic acid (PLA) and organically modified layered silicates (organoclay) with concentrations of 2-10 wt% were prepared by melt intercalation technique. The effects of organoclay on the mechanical and thermal properties of PLA were studied. Tensile properties were evaluated using an Instron Universal Tester. Modulated differential scanning calorimetry (MDSC) and Thermogravimetric analyses (TGA) were performed to study the thermal behaviour of the prepared composites. The nanocomposites exhibited superior improvement of practical materials properties such as Young's modulus and thermal stability, as compared to the neat PLA. The Young's modulus drastically increased, whereas tensile strength and elongation at break decreased. The maximum degradation temperature of the hybrid increased linearly with an increasing amount of organoclay. However, MDSC has determined that the glass transition, cold crystallisation, and melting point temperatures were not significantly influenced by the presence of organoclay.

1. Introduction

Polylactic acid (PLA) has received increased interest in the last decade because of emergence of more environmentally aware consumers and increased price of crude oil. PLA is mainly used in applications such as plastic bags for household waste, disposable cups, and plates, as its degradability is a marketing advantage. PLA has higher modulus and strength [1], but lower toughness and thermal stability [2], as well as higher price, which limits its current commercial usage. Additives are commonly used to improve performance of plastics. This study focuses on the use of fillers to improve PLA properties.

A promising approach to improving properties is to prepare nanocomposites by adding montmorillonite (MMT) clay in the polymer matrix. Advantages include: (1) MMT can improve physical as well as mechanical properties; (2) the filler loadings are relatively low so the melt processing conditions do not need to be changed and (3) the final product cost may be reduced [1]. However, improvement in the nanocomposite's properties depends on several factors, including MMT concentration as well as degree of its dispersion [3]. Dispersion is controlled by the processing conditions as well as compatibility of MMT and polymer.

Several studies of PLA/organoclay nanocomposites prepared by melt intercalation technique have been reported [4-6]. However, these reports did not include how the melt processing conditions were chosen. In our recent paper [7], we described how the optimum processing conditions for processing PLA/MMT nanocomposites by melt intercalation can be identified using experimental design. In this



paper, properties of PLA/MMT nanocomposites prepared at the optimum processing conditions were reported, and the effects of filler level on mechanical and thermal properties were examined. The level of filler was varied to determine if there is an optimum level.

2. Experiment

2.1. Materials

NatureWorks® PLA polymer 7000D was used in this study. The MMT nanoclay Cloisite® 30B from Southern Clay Products was used as filler. This is a natural montmorillonite modified with a quaternary ammonium salt. PLA pellets and clays were dried to remove volatiles in a vacuum oven at 90 °C for 24 hours prior to processing.

2.2. Preparation of the nanocomposites

PLA pellets and various amounts of MMT were melt blended in a counter rotating Haake Rheomix 600. The processing conditions were set at the following temperature, rotor speed, and mixing time: 175 °C and 100 rpm for 7 min. Samples were made with seven different clay loadings (from 2 to 10 wt%). The pure PLA sample was also processed in a mixer. Specimens for property testing were obtained by compression molding. These were produced from warm melt from the mixer placed in a suitable mould in a hot-plate hydraulic press. The press platens were set at 190 °C and samples were pressed for 3 minutes and allowed to cool to ambient temperature under pressure (10 kN). All samples were then stored in a desiccator prior to testing.

2.3. Characterisation

An Instron model 4465 Universal Testing Frame and a load cell of 10 kN was used to measure tensile properties. The test was conducted at a constant rate crosshead speed of 5 mm/min at room temperature per ASTM D638 standard.

Thermal analysis was performed using a modulated differential scanning calorimeter (MDSC, TA2920) with an RCS unit, from TA Instruments. Sample and reference chamber with an empty pan were heated from -20 to 220 °C at heating rate of 2 °C/min with a heating/cooling cycle of the modulation period of 40 s and the amplitude of ± 0.5 °C. After heating up to 220 °C, the PLA samples were isothermally held for 5 min to eliminate the previous heat history and subsequently cooled down to -20 °C at a cooling rate of 2 °C/min. A second heating scan at 2 °C/min was also performed. The data analysis reported here is from the second heating cycle. The degree of crystallinity was calculated by considering a melting enthalpy of 93.6 J/g for 100 % crystalline PLA. All the data were recorded using TA Instrument Control software installed with the equipment.

The thermal stability was investigated using a Thermogravimetric Analyzer (Perkin Elmer STA6000). Samples of 10-20 mg were heated with a heating rate of 10 °C/min from room temperature to 600 °C both in oxidizing (air) and inert (nitrogen) atmosphere. The resulting thermograms were processed using Pyris Version 11. Each sample was run in duplicates.

3. Results and discussion

3.1. Mechanical characterisation

The tensile results of neat PLA and PLA nanocomposites are presented in Figure 1 and summarised in Table 1. Values reported here are the averages of four specimens for each sample. The modulus of the nanocomposites increased monotonically with increasing clay content, by as much as 54 % for the 10 wt% sample, which is a very significant improvement.

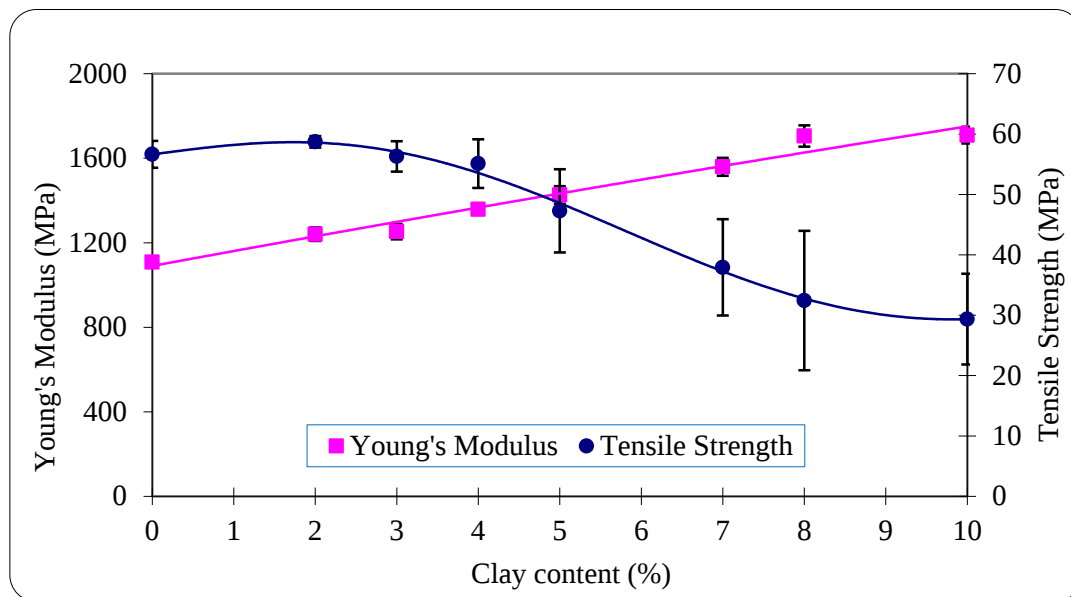


Figure 1. Tensile properties of PLA nanocomposites as a function of clay loading

Table 1. Tensile properties of PLA nanocomposites at various clay loadings

Samples	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PLA-30B-0	1110	57	7.0
PLA-30B-2.00	1240 (+12 %)	59 (4 %)	9.6
PLA-30B-3.25	1250 (+13 %)	56 (-1 %)	7.0
PLA-30B-4.50	1360 (+23 %)	55 (-3 %)	6.3
PLA-30B-5.75	1430 (+29 %)	47 (-17 %)	4.5
PLA-30B-7.00	1560 (+41 %)	38 (-35 %)	3.5
PLA-30B-8.25	1710 (+54 %)	32 (-42 %)	2.5
PLA-30B-10.00	1710 (+54 %)	29 (-47 %)	2.3

There are only a few published results on tensile (tension) properties of PLA/organoclay nanocomposites [8]. Most studies on the mechanical properties of PLA/organoclay nanocomposites were reported using dynamic mechanical analysis [9, 10]. Nevertheless, two studies did report improved tensile properties of the PLA nanocomposites. Thellen et al. [8] reported the increase in the modulus of blown film PLA nanocomposites with 5 wt% MMT was 30 to 40 %. Li et al. [11] also reported that adding 5 wt% MMT, Cloisite® 20A, or Cloisite® 30B, to PLA increased the modulus by 15% and 21 %, respectively. The nanoclay acts as a mechanical reinforcement of the polymer at a nanoscale molecular level and thus gives a higher modulus value [12].

The tensile strength and elongation of the nanocomposite increased slightly at low levels of clay content (between 2 and 4 wt%), and decreased almost linearly with increases in the clay content. Alexandre and Dubois [13] reported increased Young's modulus, but lowered tensile strength and elongation at break. Increased tensile strength was reported only for systems where strong polymer/organoclay interaction occurred [14, 15]. In this study this indicates the clay is dispersed uniformly at low concentrations (between 2 and 4 wt%) with a high surface attraction between the clay and the polymer matrix. Above this concentration, the attractive force between the clay and the polymer matrix was disturbed by the tactoid form of the clay. This corresponds to passing through the percolation threshold region, estimated at 4.2 wt% clay loading [16]. According to Chang et al., [17], strength and elongation decrease if agglomerates are present.

3.2. Thermal characterisation

Table 2 shows that the T_g of PLA decreased by 1-2 °C with the addition of the organoclay, which is not significant compared with the measured SD (0.7 °C). The T_g depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction, and steric effects [18, 19]. The drop in T_g could be due to a number of reasons such as clay aggregates, interphase regions, and adhesion problems at the clay-matrix interface at elevated temperatures [20].

Table 2. Thermal properties of PLA nanocomposites at various clay loadings

Samples	T_g (°C)	T_{cc} (°C)	ΔH_c (J/g)	χ_c (%)	T_m (°C)	ΔH_m (J/g)
PLA-30B-0	61.9	120.6	25.2	26.9	151.0	21.5
PLA-30B-2.00	61.2	121.0	27.1	29.5	151.2	23.6
PLA-30B-3.25	61.0	114.6	28.3	31.3	155.1	23.3
PLA-30B-4.50	60.6	114.2	28.4	31.8	154.9	23.1
PLA-30B-5.75	60.8	116.5	28.2	32.0	155.0	23.2
PLA-30B-7.00	60.2	116.7	28.5	32.7	155.1	23.1
PLA-30B-8.25	60.0	115.2	28.3	33.0	155.0	23.1
PLA-30B-10.00	59.9	113.6	26.8	31.8	155.0	22.7

T_g , glass transition temperature; T_{cc} , cold crystallisation temperature; ΔH_c , enthalpy of crystallisation; χ_c , degree of crystallinity; T_m , melting temperature; ΔH_m , enthalpy of fusion. T_{cc} and T_m are taken at the peak maximum of the crystallisation and melting peaks.

Paul et al. [21] reported increasing filler content did not significantly influence the T_g or T_m of PLA Cloisite® 30B nanocomposites. Because of the creation of aggregates, the increase of the nanofiller content did not lead to an extra increase of the total nanofiller surface area, and hence there was no effect on T_g and T_m . MMT nanoparticles have a great tendency to create aggregates because of their larger surface area [22].

PLA sample had a melting point at about 151 °C and a heat of fusion of 21.5 J/g. The incorporation of MMT clays led to an increase by 4 °C at 3.25 wt% of clay loading. Thereafter the T_m did not change significantly. Most studies [4, 21] reported that the incorporation of MMT clays did not significantly change the melting point of the materials.

Table 2 also shows that the cold crystallisation temperature, T_{cc} , of the PLA nanocomposites was significantly reduced by the addition of organoclay. The T_{cc} of PLA-30B-10.00 nanocomposites was 7 °C lower than neat PLA. Similar observations were reported by Lee et al. [12] and Day et al. [23]. Both stated that clay nanoparticles can act as effective nucleating sites for crystallisation in PLA. This was attributed to the nucleating effect of the nanosized clay. The large surface area facilitates the PLA crystallisation process, thus, T_{cc} decreases with the addition of nanoclays [12].

From Table 2, it can also be seen that the χ_c of PLA nanocomposites increased significantly (by ± 2.2 SD) in the presence of organoclay up to around 8.25 wt%. Above 8.25 wt%, χ_c decreased. This indicates that the clay had a nucleation effect at lower clay loadings [24]. The nucleation efficiency will be the highest below the percolation threshold. Thereafter the rate of increase of nucleation due to the presence of fillers reduces, finally becoming very low at very high clay loadings [25]. This behaviour is attributed to the creation of larger agglomerates above the percolation threshold, and hence a reduction in the number of available nucleation sites. It can be said that a small amount of nucleating agent helps form polymer crystals while a larger amount hinders the ordered arrangement of molecular chains resulting in low crystallinity [26].

Of these thermal properties, crystallisation is the most important from both scientific and commercial viewpoints, because many mechanical properties of PLA are significantly influenced by its crystallinity [27]. The higher modulus at higher clay loadings is consistent with the higher

crystallinity. The higher modulus of the nanocomposites is generally attributed to the reinforcement effect of the filler, but may also indicate that the crystallinity is higher [28].

3.3. Thermogravimetric analysis

In general, the addition of a filler can improve the thermal stability of the filled polymer composite systems. As inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components into organic materials can improve their thermal stabilities. Many studies have reported that polymer/MMT composites have higher thermal stability than that of the neat polymer matrix [22, 29].

Table 3 summarises the maximum degradation temperatures. The degradation temperature was higher in all nanocomposites than in PLA. The shift was more pronounced for the nanocomposites with higher filler content. This suggests that the introduction of nanofillers increases the thermal stability of PLA [29]. The increase in thermal stability could be caused by an ablative reassembling of the silicate layers, which may occur on the surface of the nanocomposites, creating a protective barrier. The increase in the thermal stability has also been attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix [30]. This is a common behaviour observed for nanocomposites and is partly responsible for their flame-retardant properties that are usually improved as well as their thermal stability [13].

Table 3. Thermal degradation behaviour of PLA nanocomposites at various clay loadings

System	Onset degradation temperature (°C)	Maximum degradation temperature (°C)	Residue (wt %) at 600 °C
PLA-30B-0	341	357	1.0
PLA-30B-2	342	359	3.4
PLA-30B-3.25	340	362	3.5
PLA-30B-4.50	341	363	5.2
PLA-30B-5.75	343	365	5.7
PLA-30B-7.00	343	369	7.2
PLA-30B-8.25	342	368	8.7
PLA-30B-10.00	342	370	9.1

The thermal properties of PLA are significantly influenced by the addition of the organoclay Cloisite® 30B. The results suggest the nanocomposites have a degree of dispersion, but the dispersion decreases as the filler level increases. PLA nanocomposites containing a few percent of Cloisite® 30B are more thermally stable than neat PLA. The role of the organoclay in the nanocomposite acts as a heat barrier, which enhances the overall thermal stability of the system. The superior performance in this study of nanocomposites samples compared with PLA suggests that the optimised processing condition meets this requirement.

4. Conclusions

PLA/organoclay nanocomposites were prepared at optimum processing conditions with varying levels of organically modified MMT (from 2 to 10 wt%). Mechanical properties showed a large increase of Young's modulus compared with the unfilled control PLA (up to 54 %). However, the tensile strength was reduced, by up to 50 %. As for thermal analysis, increasing clay loading decreased the glass transition slightly and increased crystallinity: this suggests that modified MMT is a nucleating agent for PLA. Thermal analysis showed that at higher clay loading thermal stability improved significantly. Investigations of the nanocomposite morphology (transmission electron microscopy and small-angle X-ray scattering) will be reported in a forthcoming article.

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