Morphology and mechanical properties of polylactide/montmorillonite composites

N Ibrahim1*, M Jollands2 and R 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.

*norazura.ibrahim@gmail.com

Abstract. In this study, polylactide (PLA)/montmorillonite (MMT) composites were prepared by melt intercalation technique. Three types of MMT, Cloisite® 30B, Cloisite® Na+ and Cloisite® Ca++DEV were used as fillers. The morphology and mechanical properties of the composite materials were investigated and compared with unfilled PLA, keeping the same thermomechanical history. The morphology of the composite materials was evaluated by small-angle x-ray scattering (SAXS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the tensile properties of these composites were measured by an Instron universal testing machine. The morphology observations showed that the good affinity between the organo-modified clay (Cloisite® 30B) and the PLA was sufficient to form intercalated structure in the nanocomposite. Cloisite® Na+ and Cloisite® Ca++ DEV clays exhibited a modest improvement of the Young’s modulus of about 18 % and 17 % respectively, due to poor dispersion in the PLA matrix as well as poor polymer–filler interactions compared to Cloisite® 30B. Compared to those of pure PLA, the PLA/Cloisite® 30B composites showed notable improvement of the Young’s modulus of about 54 %.

1. Introduction
Polylactide (PLA) is a biodegradable and biocompatible polymer which has proved itself to be a promising alternative for petroleum-based polymers [1]. PLA is different than most thermoplastic polymers in that it is derived from renewable resources, eco-friendly with interesting physical characteristics [2, 3]. Its properties can be further enhanced by simply blending in the molten state with selected additives [4]. All of these features make PLA an attractive alternative to nondegradable petroleum-based plastics [5].

The use of organo-modified montmorillonite (MMT) or nanoclay to strengthen polymer-based composites has given academic and industrial sectors considerable attention because of the addition of small amounts of nanoclay that could substantially improve the mechanical properties of pristine polymers [6-8]. Nanoclay is abundant and much cheaper than other nanomaterials, partly because the basic materials come from natural sources that are easily accessible [9]. For this reason, clay and layered silicate fillers have been extensively researched and there is now a broad variety of understanding about their use in polymer composites [10-12]. Although clay has several engaging properties, its application
are restricted as the clay dispersion could not simply be achieved due to its tendency to form large aggregates [13].

The field of polymer nanocomposites based on layered silicates, such as MMT, has led to growing interests. Some research reports on PLA microcomposites based on natural MMT have been published in recent years [14, 15]. However, most of the previous works done have neglected to study the mechanical properties of PLA microcomposites extensively, thus, a comparison with this study is not possible. The properties of PLA/MMT nanocomposites prepared under optimum processing conditions have been reported in our recent paper [16] and the effects of filler loading on mechanical and thermal properties have been investigated. In this paper, PLA/MMT nanocomposites and microcomposites were prepared at optimum processing conditions. The role of MMT in terms of its structure-property relationship of PLA/MMT nanocomposites and microcomposites was investigated by examining their morphology and mechanical properties.

2. Methodology
2.1 Materials
NatureWorks® PLA polymer 7000D, a commercial product of NatureWorks LLC was used in this study. It is designed for injection-stretch blow moulding applications. Cloisite® 30B is commercially available and was supplied by Southern Clay Products was used to form the nanocomposites. Cloisite® 30B is a montmorillonite modified with bis-(2-hydroxyethyl) methyl tallowalkyl ammonium cations. Two types of natural MMT (unmodified), Cloisite® Na⁺ and Cloisite® Ca²⁺DEV were loaded with PLA-based microcomposites. Grade Cloisite® Na⁺ is dispersible in water, while grade Cloisite® Ca²⁺DEV is not dispersible. All MMT powder were oven-dried at 60 °C for at least 24 hours before use.

2.2 Preparation of the composites
PLA pellets and various quantities of MMT were mixed in Haake Rheomix 600 under optimum processing conditions [16]. The processing conditions were set at the following temperature, rotor speed, and mixing time: 175 °C and 100 rpm for 7 min. The unfilled PLA sample was also processed in a mixer. Compression moulding was used to obtain specimens for mechanical testing. Pressure platens were set at 190 °C and samples were pressed for 3 minutes, allowing cooling at ambient temperature under pressure (10 kN). Before the testing, all samples were stored in a desiccator.

2.3 Characterisation
2.3.1 Morphology Properties
Small-angle x-ray scattering (SAXS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to study the morphology of PLA/MMT composites. SAXS was used to study the quantitative evaluation of the morphology of PLA/MMT composites. The experiments were performed using a Nanostar Bruker AXS device. The x-ray source (CuKα radiation, wavelength λ = 1.54 Å) was generated using an applied voltage of 40 kV and a filament current of 35 mA. Bragg’s law (λ = 2d/sin θ) was used to compute the d-spacing. Measurements ranging from 20 = 0.6 to 14 ° were performed.

The morphology of fracture surfaces from the tensile tests of the composites were studied at room temperature. A 30 kV accelerating voltage FEI Quanta 200 SEM was used for observation of the fracture surfaces of composites. The surfaces of the sample were mounted on aluminium stubs and gold-coated to avoid charging with a sputter coater. Perpendicular to the fractured surface, the samples were viewed.

TEM images were obtained with a digital camera Gatan ORIUSTM SC1000 using a JEOL 2100 electron microscope. Most of the measurements were performed using a 200 kV accelerating voltage, while the exposure times varied between 1 and 6 seconds. Samples for TEM were cut with a diamond knife at room temperature to give 75 nm nominal thickness sections. Sections were collected on copper grids coated with formvar and carbon. Due to some constraints, only a few samples were taken for measurements. Several images of different magnifications were taken to ensure that analysis was based on a representative sample region.
2.3.2 Mechanical Properties
For measuring tensile properties, an Instron model 4465 Universal Testing Frame and a load cell of 10 kN were used. The test was carried out at a constant rate of 5 mm/min at room temperature in accordance with the ASTM D638 standard. Samples were dried 24 hours prior to testing in an oven at 50 °C. For each sample, the property values reported here represent an average of the test results ran on four specimens.

3. Result and Discussion
3.1 Morphology properties
In this section, the neat PLA was compared with PLA composites at 3.25 wt % MMT loading. In order to completely wet the polymer and intercalate the clay or organoclay tactoids, it is imperative that the polymer and clay or organoclay surface polarities be matched [17]. Polar interactions are also critical to the formation of intercalated or exfoliated nanocomposites through the intercalation of polymer melt [18].

The SAXS diffractograms of all samples are presented for the range of 2θ between 0.6 ° and 14 ° as shown in Figure 1. There was an intense peak of Cloisite® 30B while Cloisite® Na+ and Cloisite® Ca++ had weak peaks. The diffraction peak was shifted to lower angles for the PLA-30B-3.25, indicating that the d-spacing had increased and suggesting the formation of disordered intercalated structure. Due to the dilution of the filler in the polymer, the diffraction peak was also much weaker. The SAXS pattern of PLA-Na-3.25 and PLA-Ca-3.25 did not show any peaks corresponding to either the Cloisite® Na+ or Cloisite® Ca++ or a possible intercalation. This was attributed to concealment of the small peaks by the broad PLA peak. Further studies were conducted using SEM and TEM to confirm the PLA/MMT hybrid nanostructure and to verify SAXS findings.

![Figure 1. SAXS diffractograms of neat PLA, Cloisite® 30B, Cloisite® Na+, Cloisite® Ca++ and the corresponding of their nano and microcomposites.](image)

SEM images of the neat PLA and PLA composite are shown in Figure 2 at 800x magnification at 3.25 wt % MMT load. When comparing nanocomposite and microcomposites micrographs, nanocomposite at 3.25 wt % Cloisite® 30B had a lower agglomeration than microcomposites with the same clay content. Figure 2 (b) reveals that a good degree of dispersion of Cloisite® 30B in the PLA was obtained as less aggregates could be observed in the micron range in the sample, in agreement with SAXS data. Whereas in the case of PLA microcomposites, aggregates of about 7-20 μm were distributed in the polymer matrix (circles in the Figure 2 (c) and (d)). This has been attributed to poor natural MMT dispersion. Although the SAXS patterns may not be considered as the most confirmatory measure for
describe the degree of intercalation or exfoliation of the clay layers in the polymer matrix, they certainly are very useful to make qualitative observations. It is best described by TEM in the next section to justify that the degree of agglomeration in this microcomposite samples was much higher than nanocomposite samples.

Figure 2. SEM micrographs of samples at 800× magnification.

Figure 3 (a)-(c) shows TEM micrographs of PLA composites at 3.25 wt % MMT loading at 30,000× magnification. The dark areas represent the clay and the gray/white areas correspond to the polymer matrix. It can be seen in Figure 3(a) that the nanocomposite PLA-30B-3.25 yielded at most a mixture of intercalated/exfoliated structures. The observation from SAXS previously is consistent with TEM images which represents an intercalated/exfoliated nanocomposite. This may be due to the organic modification of MMT which provides the possibility for PLA chains to diffuse between the layers during processing [19]. Figure 3 (b) and (c) illustrate that the natural clay in PLA-Na-3.25 and PLA-Ca-3.25 microcomposite exists as aggregates and the dispersion is not uniform. It is clear that the nature of the filler influenced the overall morphology. The mixing of PLA with modified clay led to the formation of a nanocomposite material with characteristic intercalated peaks in SAXS and high aspect ratio of tactoids or exfoliated layers in TEM. Mixing PLA with unmodified clay did not result in the formation of a nanocomposite material, as no shift in the characteristic peak of clay was observed in SAXS, large aggregates and agglomerates in TEM and SEM were observed. This highlights the importance of using multiple techniques to characterize the morphology of the composite. The melt processing of PLA and unmodified MMT, as revealed by SAXS, SEM and TEM, results in the formation of conventional
composites due to their hydrophobicity in the composites system. As the filler level increased, the number of agglomerates increased.

![TEM micrographs of samples at 30,000x magnification.](image)

**Figure 3.** TEM micrographs of samples at 30,000x magnification.

### 3.2 Mechanical properties

Figure 4-Figure 6 show the tensile properties of neat PLA and PLA composites. It was found that with increasing clay content, the Young’s modulus of the composites increased monotonically. At 10 wt %, for PLA-30B, the increase in stiffness was around 54 % compared to the neat PLA sample, which is a major improvement. This significant improvement in the modulus is consistent with the nanocomposites' intercalated structure and a high level of polymer-silicate interaction leading to large mechanical reinforcement. These findings are consistent with previous studies [20, 21], which reported similar enhancement in terms of stiffness with incorporation of MMT. Jiang et al. [21] also reported that the improvement in stiffness was due to the reinforcement effect of the rigid inorganic MMT which constrains the molecular motion of PLA chains.

Adding unmodified clay gave the Young's modulus of PLA a modest improvement. PLA-Na and PLA-Ca improved modulus by 18 % and 17 %, respectively at the same 10 wt % filler load. The inferior performance of the micro filler was attributed to the low interaction between the low aspect ratio microparticles and the surrounding polymer matrix, as well as aggregate and/or agglomerate development as demonstrated by SEM and TEM. According to Folkes [22], mechanical reinforcement of composites with poor polymer-filler interaction is achieved by friction between the polymer and the filler due to shrinkage on cooling.
The tensile strength (Figure 5) and extension (Figure 6) decreased with the introduction of more inorganic phase and high aspect ratio filler as opposed to the results of the Young's modulus. The nanocomposite PLA-30B had much better tensile strength and elongation than the microcomposites at low filler loadings. However, the nanocomposite performance was lower than the microcomposite samples when the filler level was further increased. Many studies of polymer/organoclay nanocomposites showed an increase in Young's modulus but reduced tensile strength and elongation at break [23]. For PLA-30B, a very significant reduction in tensile strength was observed, especially above 5 wt %. The tensile strength decreased about 47 % at 10 wt % of clay loading compared to just 15 % for PLA-Na and 13 % for PLA-Ca. This indicates that the organoclay is dispersed uniformly with a high surface attraction between the clay and the polymer matrix at low clay loadings (between 2 and 4 wt %). The attractive force between the clay and the polymer matrix was disturbed above this concentration by the tactoid form of the clay. Agglomerates act as material flaws, which triggered brittle response and early material failure in the tensile testing. These results are in good agreement with the results published earlier [24]. Tensile strength and elongation at break are very sensitive to agglomerate presence, so these results are consistent with the results of SEM and TEM.

![Young's modulus of PLA composites with different percentage of clay loading.](image)

**Figure 4.** Young's modulus of PLA composites with different percentage of clay loading.

![Tensile strength of PLA composites with different percentage of clay loading.](image)

**Figure 5.** Tensile strength of PLA composites with different percentage of clay loading.
Figure 6. Extension of PLA composites with different percentage of clay loading.

4. Conclusions
The nature of the filler influences the PLA properties. The MMT's organic modification enhances the neat PLA's morphology and Young's modulus composites by enhancing the compatibility between PLA and clay, resulting in a composite with higher properties to those of neat matrix. The nanoscopic dimensions result in some interrelated features that distinguish between nanocomposites and microcomposites. By adding only a small amount of organoclay (10 wt %), the Young's modulus of PLA was significantly enhanced. Better compatibility led to better dispersion and stronger interactions between polymer filler. However, the tensile strength and the elongation at break of the nanocomposite performance was lower than the microcomposite samples when the filler level was further increased (above 5 wt %).

Acknowledgments
The author gratefully acknowledges the Ministry of Higher Education Malaysia (MOHE) and Universiti Teknologi MARA for the scholarship support.

References
[1] Mohanty A K Misra M and Drzal L T 2002 Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world J. Polym. Environ. 10, p. 19-26.
[2] Dorgan J R Lehermeier H J Palade L I and Cicero J 2001 Polylactides: properties and prospects of an environmentally benign plastic from renewable resources Macromol. Symp. 175, p. 55-56.
[3] Sinha Ray S Maiti P Okamoto M Yamada K and Ueda K 2002 New polylactide/layered silicate nanocomposites. 1. Preparation, characterization, and properties Macromolecules 35, p. 3104-3110.
[4] Pluta M Jeszka J K and Boiteux G 2007 Polylactide/montmorillonite nanocomposites: Structure, dielectric, viscoelastic and thermal properties Eur. Polym. J. 43, p. 2819-2835.
[5] Sinclair R G 1996 The case for polyactic acid as a commodity packaging plastic. J. Macromol. Sci. Part A 33, p. 585-597.
[6] Tseng C R We J Y Lee H Y and Chang F C 2001 Preparation and crystallization behavior of syndiotactic polystyrene-clay nanocomposites Polym. 42, p. 10063-10070.
[7] Vaia R A Ishii H and Giannelis E P 1993 Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. Chem. Mater. 5, p. 1694-1696.
[8] Okamoto M Morita S and Kotaka T. 2001 Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites Polym. 42, p. 2685-2688.
[9] Markarian J 2005 Automotive and packaging offer growth opportunities for nanocomposites. Plastics Add. Compound. 7, p. 18-21.
[10] Lan T Kaviratna P D and Pinnavaia T J 1995 Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. Chem. Mater. 7, p. 2144-2150.
[11] Ogawa M and Kuroda K 1997 Preparation of inorganic–organic nanocomposites through intercalation of organoammonium ions into layered silicates Bulletin Chem. Soc. Japan 70, p. 2593-2618.
[12] Theng B K G 1974 The Chemistry Of Clay-Organic Reactions Wiley, New York.
[13] Muzny C D Butler B D Hanley H J M Tsvetkov F and Peiffer D G 1996 Clay platelet dispersion in a polymer matrix Mater. Letters 28, p. 379-384.
[14] Pluta M Galeski A Alexandre M Paul M A and Dubois P 2002 Polylactide/montmorillonite nanocomposites and microcomposites prepared by melt blending: Structure and some physical properties J. App. Polym. Sci. 86, p. 1497-1506.
[15] Paul M-A Alexandre M Degee P Henrist C Rulmont A and Dubois P 2003 New nanocomposite materials based on plasticized poly(L-lactide) and organo-modified montmorillonites: thermal and morphological study Polym. 44, p. 443-450.
[16] Ibrahim N Jollands M and Parthasarathy R 2016 Optimising processing conditions of PLA nanocomposites using response surface methodology Pertanika J. Sci. Technol. 25, p. 63-72.
[17] LeBaron P C Wang Z and Pinnavaia T J 1999 Polymer-layered silicate nanocomposites: an overview App. Clay Sci. 15, p. 11-29.
[18] Vaia R A and Giannelis E P 1997 Polymer melt intercalation in organically-modified layered silicates: model predictions and experiment Macromolecules 30, p. 8000-8009.
[19] Shyang C W and Kuen L S 2008 Flexural, morphological and thermal properties of poly(lactic acid)/ organo-montmorillonite nanocomposites Polym. Comp. 16, p. 263-270.
[20] Lee J H Park T G Park H S Lee D S Lee Y K Yoon S C and Nam J D 2003 Thermal and mechanical characteristics of poly(L-lactic acid) nanocomposite scaffold Biomater. 24, p. 2773-2778.
[21] Jiang L Zhang J and Wolcott M P 2007 Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms. Polym. 48, p. 7632-7644.
[22] Folkes M 1982 Short Fiber Reinforced Thermoplastics John Wiley & Sons, Inc., New York, NY.
[23] Alexandre M and Dubois P 2000 Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials Mater. Sci. Eng. 28, p. 1-63.
[24] Rhim J W Hong S I and Ha C S 2009 Tensile, water vapor barrier and antimicrobial properties of PLA/nano clay composite films. Food Sci. Technol. 42, p. 612-617.