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Processing, Morphological, Thermal and Absorption Behavior of PLA/Thermoplastic Starch/Montmorillonite Nanocomposites

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***Abstract*—**Thermoplastic starch, polylactic acid glycerol and maleic anhydride (MA) were compounded with natural montmorillonite (MMT) through a twin screw extruder to investigate the effects of different loading of MMT on structure, thermal and absorption behavior of the nanocomposites. X-ray diffraction analysis (XRD) showed that sample with MMT loading 4phr exhibited exfoliated structure while sample that contained MMT 8 phr exhibited intercalated structure. FESEM images showed big lump when MMT loading was at 8 phr. The thermal properties were characterized by using differential scanning calorimeter (DSC). The results showed that MMT increased melting temperature and crystallization temperature of matrix but reduction in glass transition temperature was observed Meanwhile the addition of MMT has improved the water barrier property. The nanosize MMT particle is also able to block a tortuous pathway for water to enter the starch chain, thus reducing the water uptake and improved the physical barrier of nanocomposite.

***Keywords*—**Montmorillonite, Nanocomposite, Polylactic acid, Starch.

I. Introduction

IN recent years, plastics made from natural resources and biodegradable materials such as starch, poly lactic acid (PLA) and poly-3-hydroxybutyrate (PHB) have received great attention [1]-[2]-[3]. But some biodegradable polymer materials, exhibit problems in processing and mechanical properties that could be reduced by blending two or more polymers [4]. PLA is aliphatic linear thermoplastic polyester which its biocompability, biodegradability and mechanical properties make it attractive for disposable and biodegradable plastic substituent with various applications in tissue engineering, drug delivery, food packaging and bottle containers [5]-[6]. However some drawbacks of PLA such as high cost, slow rate of degradation, high permeability to oxygen, water vapor and carbon dioxide, poor thermal stability and inherent brittleness can limit its applications in many areas like packaging and agriculture films [7]-[8]. PLA is degraded by simple hydrolysis of the ester bond and does not require the presence of transienzymes to catalyze this hydrolysis. The rate of degrada tion is dependent on the size and shape of the article, theisomer ratio, and the temperature of hydrolysis [9]. The preparation of PLA/starch composites resulting in reducing the overall cost dramatically, improving the thermal properties and enhancing the biodegradability of blends [2]-[10]-[11]. A major problem of this blend is incompatibility of the hydrophilic starch with the hydrophobic PLA that makes a weak adhesion between these two components. This resulted in poor mechanical properties of final blends [19]. To overcome this problem and to improve the interfacial adhesion of blend, reactive compatibilization with Maleic Anhydride was studied. [11]. Glycerol, formamide and water are used separately or combined as plasticizer [12]. During glatinization the crystalline structure of native starch is destroyed in presence of plasticizer, final product is called thermoplastic starch(TPS) which has low oxygen permeability, so it can be used as a good barrier for oxygen in biodegradable packaging applications. TPS is a hydrophilic material and must be blended with other polymers to produce materials that suitable for many applications [13].

Meanwhile, poor mechanical and barrier properties of biopolymer-based food packaging are improved by using of layered silicates or nanoclays for producing nanocomposites. Saponite, hectorite and montmorillonite (MMT) are different clays that are used in polymer layered silicate (PLS). These clays are naturally abundant, economical and environmentally friendly [14]. Polymer-Clay Nanocomposite, PCN is a class of clay filled polymer that has high application in food packaging industries. Several properties of PCN can be improved in comparison with neat polymer counterparts. Some of these improvements include: increase in heat resistance and flame retardancy, reduction in weight, superior mechanical strength, improved barrier properties against moisture and volatiles, ultraviolet, oxygen and carbon dioxide [15]. However, type of polymer and nanoclay and the extent of dispersion of nano particle in the polymer matrix would give major impact to the properties.

II. Experimental

A. Materials

Injection grade of PLA was obtained from Innovative Pultrusion Sdn. Bhd. Tapioca starch was supplied by Thye Huat Chan Sdn Bhd. Maleic anhydride was purchased by MERCK with 95% purity while glycerol with 99.5 % purity was used obtained from Texchem Sdn Bhd. Pristine MMT Cloisite Na^+ (Nanomer 1.42E) was provided by Nanocor Inc., USA.

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B. Processing

During gelatinization method, tapioca starch and glycerol, were mixed together to provide thermoplastic starch then montmorillonite was added to this mixture in the feed hopper of the twin screw extruder. Polylactic acid, maleic anhydride was pre-mixing with high speed mixer according to formulations shown in Table I. Later, the mixture containing of PLA was added at the middle of extruder by a single screw extruder as a side feeder. All the materials compounded in the counter-rotating twin-screw extruder (with L/D= 30 and D=25mm) at 180^{0}C with the screw speed of 60 rpm. The barrels temperatures were maintained at 180^{0}C [28]. The strand shape extrudates were cooled and pelletized prior to dried in an oven at 50-60^{0}C for 8 hours to remove any moisture. Later, the resin was hot pressed at 170^{0}C into 3mm thin sheets. The process configuration is shown in Fig. 1.

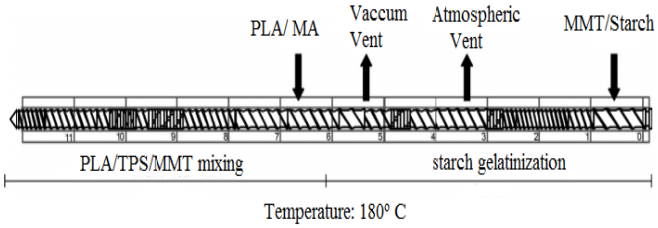


Fig. 1 Twin screw extruder process configuration

TABLE I
FORMULATION OF SAMPLES

sample	PLA (wt%)	Starch (wt%)	Glycerol (wt%)	MA[1] (wt%)	MMT (phr)
A	58	28	12	2	0
B	58	28	12	2	4
C	58	28	12	2	8

[1]: Maleic Anhydride

C. Testing and Characterization

Field Emission Scanning Electron Microscope (FESM) with a Carls Zeiss Supra 35 Vp and EHT= 8-10 kV was used to study the morphology of nanocomposites. Fractured surface of samples were coated via Gold-Plutonium to examine under electron beam. X-ray diffraction analysis (XRD) was performed with a Siemens 500 X-ray diffractometer by using Cu-WL anode in 2-Theta range between 1° to 10° and the voltage of 40 kv. The structure of MMT in matrix was the main interest. The interlayer spacing of nanoclay (*d-spacing*) was calculated by using Bragg Equation as follows:

$$\lambda = 2d \sin \theta \quad (1)$$

where, θ is diffraction angle and λ is the wavelength.

Thermal behavior of the nanocomposites were examined by Perkin-Elmer differential calorimeter (DSC) under nitrogen purge and the samples weight was about 10-12 mg. the heating rate was 10˚C per minute in a range of room temperature (about 24˚C) to 200˚C with the heating-cooling cycle.

For the water absorption test, the specimens were dried at 50^{0}C in an oven for 20 hours. The specimens were weighed (W_c) prior to submerged in distilled water at 24°± 2 ˚C for 2,4,6,4,8 and 24 hours[22]. The specimens were taken out of water and softly blotted with tissue paper to remove excess water. The samples then instantly weighed (W_w) and the percentage of water uptake (W_f) was calculated as follows:

$$\%W_f = \frac{W_w - W_c}{W_c} \text{ x } 100\% \quad (2)$$

III. Results and Discussion

A. Structural Characterization

The structural characterization of MMT in PLA/starch matrix was studied with XRD analysis. A single peak at 2θ of 7.0^0, corresponding to an interlayer spacing of 1.26 nm was obtained for pristine NA-MMT as shown in Figure 2. These findings are in agreement with Rezaie and Haddadi [17] which obtained an interlayer spacing of *d*=1.12 nm and 2θ value of 7.9^0. The diffraction peak of pristine MMT was completely disappeared when MMT content was increased at 4 phr (for sample B). This may indicate an exfoliated structure of MMT in PLA/starch matrix. Further increased the MMT content to 8 phr (sample C) had shifted the diffraction peak of pristine MMT peak from 7^0 to lower values of 5.7^0 (*d* spacing=1.52nm). This finding was corresponding to the intercalation structure of MMT in PLA/starch matrix due to insufficient polymer chains introduced into MMT galleries resulting in the layers being intercalated [18].

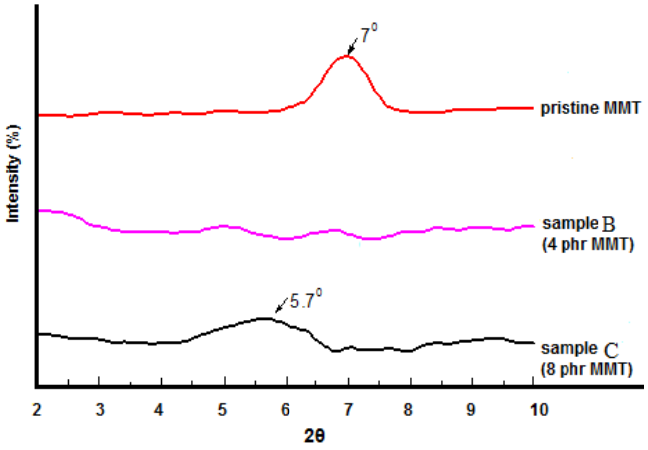


Fig. 2 XRD pattern for pristine MMT and nanocomposites

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B. Morphology of Samples

The morphologies of the samples were analyzed by FESEM and the images are presented in Fig. 3-5. From Fig. 3, it can be seen that the starch granule was uniformly distributed within the PLA matrix with the aid of maleic anhydride (MA) as a compatibilizer. Chow et al [15] found that MMT was dispersed uniformly throughout polystyrene (PS) matrix due to its finer particle size and the MMT was intercalated within PS matrix. In our case, a finer and a smoother surface of sample B (4 phr of MMT) was due to the exfoliated structure of MMT with PLA/starch matrix, which was confirmed with the findings from XRD analysis. In sample B with 4 phr loading of MMT the starch granules slightly protrude from the matrix without affected the continuity of PLA matrix (Fig. 4). The roughest surface with 8 phr MMT was exhibited by sample E (Fig. 5). The size of starch granule became irregular and bigger than the other samples. The MMT particles agglomerated thus affecting the continuity of PLA/starch matrix. The same findings were reported by Majdzadeh-Ardakani et al [16]. They found that at lower MMT loading, the silicate layers of MMT were expanded and evenly dispersed in the thermoplastic starch in nanometer sizes, so that they can impart the reinforcing effect into the matrix. However, by increasing the clay content has led to agglomeration of MMT in starch matrix.

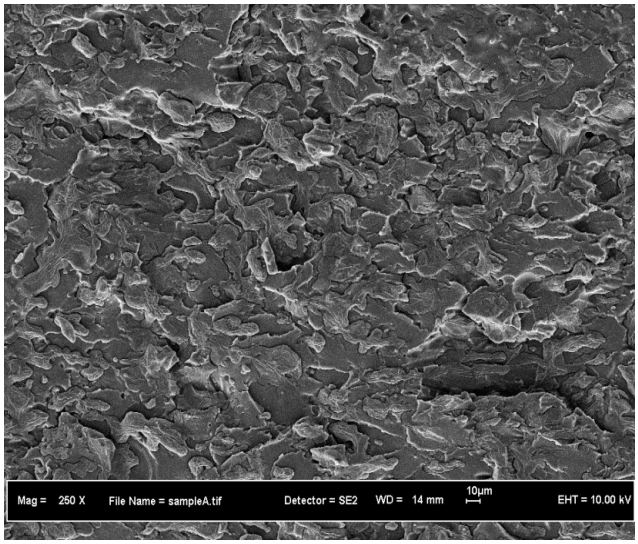


Fig. 3 FESEM image for the sample without MMT content

C. Differential Scanning Calorimetry

The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) become the main interest. The formation of exothermic crystallization peak of PLA can be seen at the off-set point of 102^0C. This was in agreement with other investigations that have been done byFukushima et al [22], Balakrishnan et al [21] who all reported appearance of crystallization peak of PLA, upon heating in their studies. The DSC testing was running with a heat-cool cycle mode. However, the cooling stage was not

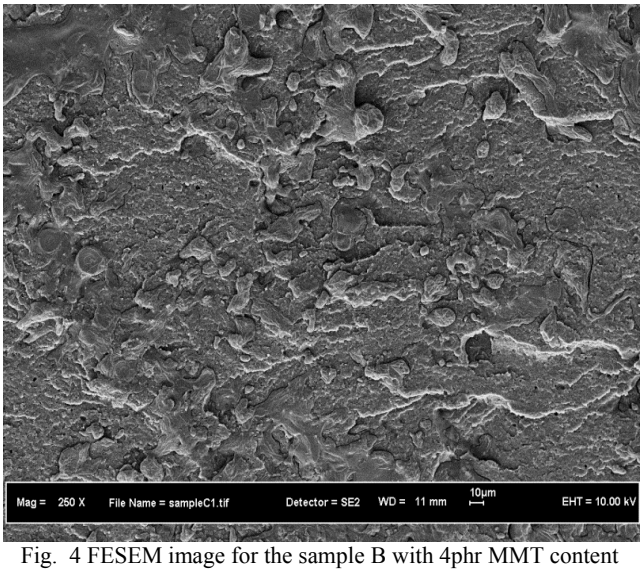


Fig. 4 FESEM image for the sample B with 4phr MMT content

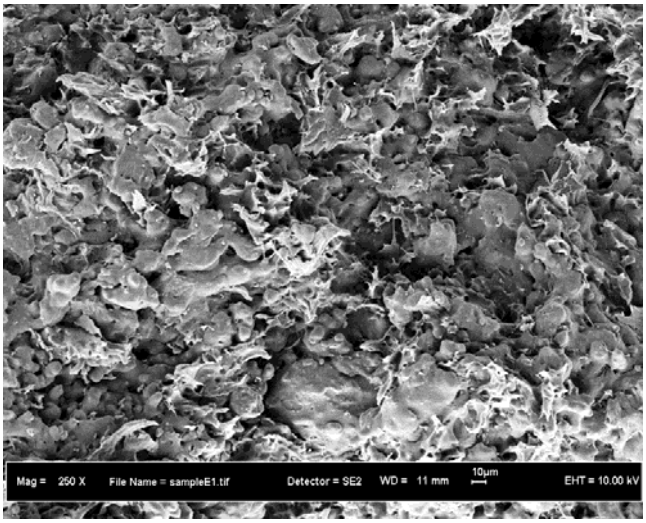


Fig. 5 shows the plots of thermograms of all samples

included in Fig. 6 due to difficulty to see T_c peaks of PLA. This was due to the distinctive characteristic of PLA which has a very slow crystallization rate during cooling [23]. Therefore, only the heating stage of DSC thermogram was considered. Value of Tg depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction and steric effects. The T_g of PLA (59ºC) was reduce to 55^0C with the incorporation of thermoplastic starch (sample A). This emphasized that the chain mobility of PLA has been increased; owing to the plasticizing effect brought gelatinized starch with glycerol [20].

The reduction of Tg affected other two temperatures i.e. Tm and Tc. The addition of starch into sample A has decreased the Tm value from 152^0C to 146^0C, while Tc was reduced from 102^0C to 86^0C.

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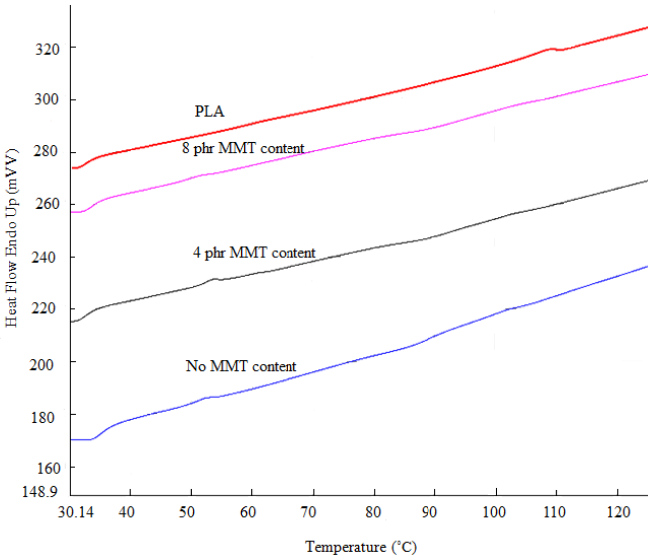


Fig. 6 DSC result in heating rate for Polylactic acid, and three samples

TABLE II
RESULTS OF DSC TEST

Sample	T_g (^{0}C)	T_m (^{0}C)	T_c (^{0}C)
Pure PLA	59	152	102
Sample A (without MMT)	55	146	86
Sample B (4wt% MMT)	54	147	89
Sample C (8wt% MMT)	52	147	90

However, the addition of MMT into PLA/starch matrix gave insignificant effects to Tg, Tm and Tc of samples. All MMT-containing samples have nearly the same values of each temperature with variations of about 2-3%. Pluta et al [24] reported a small reduction of Tg of PLA was observed (from 54^{0}C to 53.2^{0}C) with 3 wt% MMT loading. Ray et al [25] and Lee at al [20] also found small reduction in Tg with the addition of MMT. Question arises either these temperatures were largely influenced by starch alone or with minor contribution from MMT. Siew et al [26] claimed that nanosized MMT particles have capability of plasticizing the PLA/starch matrix, thus reducing Tg of the system. However, results tabulated in Table II show that MMT has little effect on Tg, Tm and Tc.

D. Water Absorption

Poly lactic acid is a hydrophobic polymer while tapioca starch and MMT are hydrophilic materials. So, a portion of water absorption is related to starch that is a hydrophilic polysaccharide. The percentage of water absorption for various samples in different timescales is observed in Fig. 7 and Table III. All the samples have an ascending trend in eight early hours of submerging in distilled water but they are different values that the lowest value is related to sample C

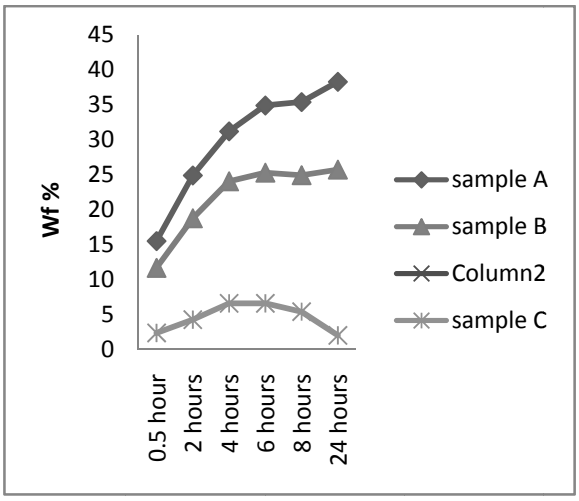


Fig. 7 Water absorption values in various submerging times

TABLE III
PERCENTAGE OF WATER ABSORPTION WITHIN 24 HOURS

Time	Water Absorbtion%		
	Sample A	Sample B	Sample C
0.5 hour	15.5	11.5	2.5
2 hours	25	18.5	4.0
4 hours	31	24	6.5
6 hours	35	25	6.5
8 hours	35.5	25	5.5
24 hours	38	25.5	2.0

with 8 phr of MMT loading and the highest one belongs to sample A without MMT content. It can be deduced that the addition of MMT diminished the water absorption of the nanocomposites. Water absorption of starch is due to capability of water molecules to penetrate through the starch network. The diffusion of water in starch is attributed to the nature of the polymer which shows strong interaction with water. Meanwhile, lower absorption of MMT-containing were due to the role of MMT as physical barrier in the nanocomposites, MMT is able to reduce the accessibility of water molecules to the starch chain by blocking a tortuous pathway for water to enter the nanocomposite [27]. Although MMT is hydrophilic in nature, the amount of water absorbed in lower compared to the starch itself [29]. The percentage of water intake for sample B (4phr of MMT) was proportional against time probably due to small amount of MMT to block the water pathway. In contrast, sample C (8 phr MMT loading) showed the reciprocal relationship after 6 hours as the water intake decreased against time. Higher loading of MMT was capable of being physical barrier to the water pathway to enter the starch network.

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IV. Conclusion

Na-MMT clay was successfully incorporated into PLA/TPS blends via a twin screw extruder to produce PLA/starch/MMT nanocomposites. It was found that MMT loading affected the MMT structure in matrix and morphological properties. From the XRD analysis, the diffraction peak of pristine MMT at 7^0 was disappeared when 4 phr MMT was added into the PLA/starch blend. This was corresponded to an exfoliated structure of MMT in the matrix. However, at 8phr MMTloading, the diffraction peak was shifted to lower values at 5.7^0 which corresponded to the intercalated MMT structure. These structural effects were manifested in FESEM images. Sample B with 4 phr MMT content showed smooth surface and the MMT particles were uniformly distributed throughout the matrix. Further addition of MMT has caused the agglomeration of MMT particles, thus resulting coarse and rough surface. DSC results revealed that, the melting temperature of PLA/starch (Tm) was not significantly affected by the addition of MMT. Reduction in Tg was observed with increasing the content of MMT in nanocomposites that is because of increasing the flexibility of polymer chains. Meanwhile, physical barriers of samples were improved with addition of MMT. From the water absorption test, the percentage of water uptake was reduced about 95% relative to sample A (without MMT) when 8phr MMT was added into the sample. This was due to a tortuous pathway for water to enter the starch chain was blocked by MMT particles, thus reducing the amount of water absorbed by the sample. Higher MMT content improved the physical barrier property of sample.

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