Effect of Organoclay Incorporation on Mechanical, Barrier and Thermal Properties and Anti-bacterial Performance of PLA and PLA Composites with Triclosan and Wood Flour

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SUMMARY

Polylactic acid (PLA) is a biodegradable polymer which has a wide range of applications; in this work, all PLA based composites formulations were compounded by twin screw extruder and testing specimens were produced. This article focuses on determinations of mechanical, antibacterial, thermal and barrier properties of PLA composites. It was found that only the tensile modulus of PLA composites increased while the others decreased when 10% wood was loaded. The effect of Triclosan and Cloisite[®] 30B compounding did not change the mechanical properties and glass transition temperature. However, by the presence of wood and Cloisite[®] 30B, T_m values of the composites exhibited double peak characteristic which was related to an increase in crystallinity level. Antibacterial activity of the PLA composites was improved with the Cloisite[®] 30B content, and this was attributed to cationic bactericide quaternary ammonium group between the silicates layers. Hydrophobic material Triclosan obviously changed water vapor permeability (WVP) of the PLA from 8.24 x 10⁻¹¹ to at 7.26 x 10⁻¹¹ g.mm/mm².h.Pa for triclosan/PLA specimens. All PLA composites samples with 0.5% clay content showed a significant increase in oxygen barrier property.

1. INTRODUCTION

Currently, demand for plastic industry is rising in many applications, such as, plastic bag, food packaging, electronic and automotive. Among these applications, plastic packaging has good production value as well as profit. Most of plastics being used are from non-renewable sources, but lower than 10% of plastics were recovered in USA¹. Now, it is time to produce biodegradable packaging materials for environmental and health concerns. Thus, biodegradable plastics have become more attractive for many researchers²⁻⁶. Polylactic acid or polylactide (PLA) is a biodegradable, thermoplastic, and aliphatic polyester derived from renewable resources, such as, corn starch which has a wide range of food packaging applications.

For such applications, PLA products need to be highly hygienic or have antimicrobial properties. An extensive way to access active PLA packaging product is incorporation of antimicrobial agents with PLA. Biodegradable reinforcing materials, such as, wood flour, are extensively used for producing wood polymer composites (WPC) due to its several advantages (reduce polymer matrix used, increase modulus, lower density and cost²). Addition of wood makes PLA more environmentally friendly and wood/PLA packaging products are hygienic and has efficiency to inhibition of bacterial growth during their service, and they should be quickly biodegradable after service life. Recently, Prapruddivongs and Sombatsompop³ studied the effect of Triclosan loading on antibacterial property of wood/PLA composites using plate count agar (PCA) technique and found that, Triclosan had ability to kill or retard *Escherichia coli* (*E.coli*) growth rate up to 83.40 and 96.78% for neat PLA and 10% wood/ PLA, respectively. This exhibited a good alternative for PLA packaging applications.

Barrier property is one of important properties for food packaging because good barrier property can potentially extend food quality and shelf life⁴. PLA is an appropriate candidate for packaging end-use application and has limitations in gas barrier property which should be improved⁵. This drawback can be enhanced by general technique copolymerization, blending and filling techniques. But, the filler incorporation, especially organoclay into the PLA matrix, has the most attention because of cost-saving and good barrier property⁶. These clay/ polymer composites have strong barrier properties because the clay layers retard the diffusing molecule pathway

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due to tortuosity. Clays are essentially impermeable inorganic crystals, gas molecules have to permeate around the crystals instead of permeation in a straight line path which takes longer mean path and time for gas absorption though these clay/polymer composites⁷.

Cloisite[®] 30B is an organo-modified montmorillonite having two hydroxyl groups, and the reaction between hydroxyl groups of Cloisite® 30B and PLA makes this clay more compatibility for producing PLA-clay composites8. Moreover Cloisite® 30B could also reduce permeability of PLA¹⁰ and also showed a bacteriostatic function against Listeria monocytogenes¹¹. There are three main techniques that can be used for composites preparation, including in-situ polymerization, solution intercalation and melt intercalation. The melt intercalation is preferred for industrial applications because of the absence of solvent and compatibility with current processing techniques9. Three types of composites derived from interaction between clays and polymers are immiscible, intercalated, and exfoliated. These factors can be characterized by X-ray diffraction (XRD).

The main objectives of this study are to prepare Triclosan/organoclay/PLA and Triclosan/organoclay/wood/PLA composites through melt blending and to understand the effects of organoclay loading on barrier-mechanical and antibacterial properties.

2. EXPERIMENTAL

2.1 Materials and Chemicals

PLA (2003 D- NatureWorks, USA) with of specific gravity of 1.24 and MFI of 5-7 g/10 min used as matrix material. Triclosan (2,4,4'-trichloro-2'-hydroxydiphenylether)(Koventure Co. Ltd., Thailand) with melting temperature of 56-58 °C and a decomposition temperature of 280 °C was selected as antibacterial agent. Wood flour with an average particle range of 100-300 µm was used and supplied by V.P. Wood Co., Ltd., Bangkok, Thailand. Amino-silane N-2-(Aminoethyl)-3aminopropyltrimethoxysilane (KBM 603, Shin-Etsu Chemical Co. Ltd., Japan) was used as chemical coupling agent to improve compatibility between the PLA and wood. Organomodified clay Cloisite 30B (Southern Clay Products Inc., USA) was used for improving barrier property. Gramnegative *Escherichia coli (E. coli,* ATCC 25922) was used as testing bacteria.

2.2 Composite Specimen Preparation

Wood flour was treated with 1.0% silane coupling agent Amino-silane KBM 603 and then dried in an 80 °C oven 3 days. Dried PLA at 70 °C overnight was then mixed with the treated wood, Triclosan and Cloisite® 30B using a high speed mixer. The PLA and PLA composite formulations including their designations are given in Table 1. Compounding of the mixture was carried out using a twin screw extruder at 180 °C (Polylab-Rheomex CTW 100P, Haake, Germany). The extrusion was done under 50 rpm screw rotating speed and temperatures used from feed to die zones were 170, 180, 180, 180 and 170 °C, respectively. The extrudate dried at 70 °C overnight after pelletised, was then compression molded (at 160 °C and 150 kg/cm²) to film thickness of 1 and 0.5 mm for antibacterial and permeability tests, respectively. There are two steps involved in preparing the sample. First, the pellets were

Sample code	Ingredient and content					
	PLA (P, wt%)	Cloisite® 30B (C, wt%)	Triclosan (T, wt%)	Wood flour (W, wt%)		
Р	100.0	-	-	-		
0.5CP	99.5	0.5	-	-		
1CP	99.0	1.0	-	-		
2CP	98.0	2.0	-	-		
TP	98.5	-	1.5	-		
0.5CTP	98.0	0.5	1.5	-		
1CTP	97.5	1.0	1.5	-		
2CTP	96.5	2.0	1.5	-		
WP	90.0	-	-	10.0		
0.5CWP	89.5	0.5	-	10.0		
1CWP	89.0	1	-	10.0		
2CWP	88.0	2	-	10.0		
TWP	88.5	-	1.5	10.0		
0.5CTWP	88.0	0.5	1.5	10.0		
1CTWP	87.5	1.0	1.5	10.0		
2CTWP	86.5	2.0	1.5	10.0		

Table 1. PLA composite formulations

preheated for 5 min and then held at the compression pressure for 3 min before cooling down to room temperature.

2.3 Mechanical Properties

The mechanical properties (Young's modulus, tensile strength and elongation at break) were studied using a universal testing machine using ASTM D638-8. The notched Charpy impact strength was determined by an impact testing machine using ASTM D6110-10.

2.4 Antibacterial Activity Evaluations

Antibacterial evaluation was performed by plate count agar (PCA) method in accordance with ASTM E2149 (2001). In this test, two film samples of 2.5 x 5cm² were placed in the flasks containing 50 ml of diluted E. coli inoculums with optical density (OD) of 0.1. Then, flasks were placed on a reciprocal shaker at 37 ± 0.5 °C at a shaking rate of 100 rpm. The contact times used were 0, 60, 120, 180 and 240 min, respectively. The contact time is the time in which testing samples had been shaken in the flasks filled with diluted *E. coli* inoculums (OD = 0.1). The bacterial solution of 100 µL was placed and spread on agar in sterilized petri dishes. The sterilized petri dishes were kept in an incubator for 24 h at 37 ± 0.5 °C. The antibacterial evaluation was determined by counting the living cell bacteria colonies and more details can be found elsewhere³.

2.5 Water Vapor Permeability

Water vapor permeability (WVP) was determined through ASTM E96/ E96M-12. The film specimens were put on the cup filled 10g of silica gel. The cup (including film and silica gel) was placed in an environmental chamber using 39 °C with 90% RH. The silica gels were weighed after 1 week. WVP was calculated by using the standard water permeability Equation (1):

$$WVP = \frac{(permeance \times t)}{\Delta p} \tag{(}$$

where permeance is the rate of water vapor transmission (g/mm²h), t is the average film thickness (mm) and Δp is the vapor pressure difference between both sides of film (Pa).

2.6 Oxygen Permeability

To determine oxygen permeability of PLA composite films, an oxygen permeability test equipment OX-Tran model 2/10 (Mocon Co. Ltd., USA) was used. The experiment was performed in a stainless steel chamber. Oxygen and nitrogen were used as the test and purge gas. 0.5 mm thick films were placed in the chamber which permeated oxygen passing each film over a certain period detected by oxygen sensor. To ensure no leaked gas, O-ring and silicone grease were applied between the films and chamber wall. Each film was examined using two steps, the first step was to check the leak checking between the film and chamber wall while second step was to determine amount of oxygen passing the PLA film during test (each step was done by 10 cycles with took 45 min each).

2.7 Characterizations

Differential scanning calorimetry (DSC; TA Instruments Q1000, USA) was used to study the thermal behavior of the samples, including glass transition temperature (T_g), melting temperature (T_m) and percentage of crystallinity (X_c). The tests were performed in temperature range of 30 to 200 °C before cooled down to 30 °C, re-heated again to 200 °C and finally cooled down to 10 °C/min with nitrogen.

X-ray diffraction (XRD) patterns of PLA composites were collected from a Rigaku X-ray diffractometer, (CuK_{α} radiation, 30 kV, 10 mA) using step size of 0.02° and 4.0° min⁻¹. The basal spacing (d 0 0 1) was obtained from Bragg's equation as given in Equation (2):

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

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

Figures 1a-d shows the mechanical properties of PLA and 10% wood/ PLA composites with and without 1.5% Triclosan filled with different concentrations of Cloisite® 30B. It was observed that the mechanical properties (Young's modulus, Elongation at break and impact strength) of PLA and PLA based composite as a function of Cloisite[®] 30B did not change significantly with clay content. For example, the modulus of the neat PLA changed from 3.80 GPa to 3.89, 3.88 and 3.93 GPa whereas elongation at break changed from 2.87% to 2.32, 2.71 and 2.51% when 0.5, 1 and 2% clay were added, respectively. However, tensile strength was found to drop. Tensile strength of neat PLA decreased from 62.36 MPa to 56.13, 55.16 and 52.55MPa with 0.5, 1 and 2% clay loaded, respectively. In general, tensile strength of organoclay/ polymer composites has been found to increase with clay content, however, a drop in tensile strength property of the clay/polymer composites was also found by some authors^{14,15}. The reason of this difference is still unclear. However, Zaidi et al. suggest that the decreasing phenomena could be considered as a result of the delamination between the polymer matrix and silicate interlayer¹⁴. For the wood/PLA specimens, the higher rigidity of 10% wood was found to increase the modulus of the PLA. The lesser rigidities thermoplastics often underwent this effect^{12,13}. On the other hand, tensile strength, elongation at break and impact strength decreased with the addition of 10% wood. For example, tensile strength, elongation at break and impact strength of the neat PLA decreased from 60.36 MPa, 2.87% and 31.76J/M to 49.23 MPa, 1.54% and 29.64J/M, respectively. The drop in the mechanical properties was due to weak compatibility between the wood and PLA^{16,17} while the effect of Triclosan compounding did not show definite trend because of small amount of the Triclosan loaded.



Figure 1a. Mechanical properties of PLA and PLA based composites (solid line and dashed line are PLA and wood/PLA composites, respectively) :(a) Young's modulus

Figure 1b. Mechanical properties of PLA and PLA based composites (solid line and dashed line are PLA and wood/PLA composites, respectively): (b) tensile strength





Figure 1c. Mechanical properties of PLA and PLA based composites (solid line and dashed line are PLA and wood/PLA composites, respectively): (c) elongation at break

3.2 Thermal Property and Clay Dispersion Analysis

The glass transition (T_{σ}) , melting (T_{m}) temperatures and the percentage of crystallinity (X) of PLA and PLA/ composites are given in Table 2. The T_a values of the PLA, CP and WP were around 60 °C. It can be seen that the addition of clay and Triclosan did not affect the T_g values for all loadings used. On the contrary, T values of the PLA were affected obviously by the presence of wood and Cloisite® 30B. The T_m peak of the PLA based composites shows a double melting peak (figures not shown) resulting in two T_values which paid responsibility to crystallinity level of the composites to be increased. The T_m of the neat PLA was split from 153.0 to 143.4 (T_{m1}) and $155.2(T_{m2})$ and $148.5(T_{m1})$ and $157.8(T_{m^2})$ when 0.5% clay and 10% wood were compound, respectively. The percentage of crystallinity of the PLA specimens increased when wood and Cloisite® 30B were filled especially, at 10% wood loading. The nucleating agent wood18 increased the crystallinity level of PLA up to 37.49% and 39.45% for WP and TWP, respectively. Similar to wood fiber, Cloisite® 30B also increase amount of crystalline of the PLA significantly. The percentage of crystallinity increased with the 0.5% clay and then started to drop when 1% and 2% clay were added. The crystallinity percentage of the neat PLA changed from 20.3% to 29.7%, 15.5% and 22.5% by 0.5%, 1% and 2% clay addition, respectively.

Figures 2a-b shows XRD patterns of pureCloisite[®] 30B,PLA and 10% wood/ PLA with different concentrations of clay. In general, if there is no clay platelets separation (immiscible), the XRD pattern of the composites would show the same as observed from the clay powder. For the complete dispersion of clay (exfoliation), no X-ray peak scan is exhibited because the distances between platelets would be larger than the limitation of wide angle X-ray can detect. In the case

where an "intercalation" occur the peak shifts of lower 2θ or larger d-spacing will exhibit, showing that the platelets have expanded¹⁹. The characteristic peak of Cloisite® 30B occurred at 20 = 4.78° with the layer distance of d $(0\ 0\ 1) = 18.54$ Å. But, in this work, no X-ray peaks were shown for all composite samples, meaning that there were no immiscible composites that occurred. For 1.0% and 2.0% Cloisite® 30B loadings, the specific peak of 1 and 2%wt. CP shifted to lower angle from $2\theta = 4.78^{\circ}$ to 2.02 and 2.26° at d spacing (0 0 1) values of 43.85 and 39.20Å, respectively. The peak of WP added with 2% Cloisite® 30B also shifted to lower angle at $2\theta = 2.22^{\circ}$ d spacing (0 0 1) value of 39.90Å. These indicated that the intercalation dispersion had exhibited for 1CP, 2CP and 2CWP samples, except for 1CWP sample. For 0.5% Cloisite® 30B loading for PLA, there were no X-ray peak was given for both PLA and WP composites (Figures 2a and **b**) while the crystallinity level of these specimens raised up from 20.3 to 29.7 and 39.35% for 0.5CP and 0.5CWP, respectively (Table 2). This indicated that 0.5% Cloisite® 30B exhibited the exfoliation dispersion which provided more surface area and facilitated nanoparticles to act as nucleating agent for PLA. The similar phenomena also was found by Das K. et al.20. In the case of 1CWP, there was no Cloisite® 30B characteristic peak while the percentage of crystallinity dropped from 37.49% to 26.86%, suggesting that this was not the exfoliation dispersion. It was postulated that the influence of high dosage of wood as compared with Cloisite® 30B content disturbed the detection of XRD scan which resulted in the disappearance of the occurrence of intercalated characteristic peak.

3.3 Antibacterial Property

The quantitative antibacterial evaluations for PLA, 1.5% Triclosan/ PLA with and without 10% wood at the different concentrations of Cloisite[®] Figure 1d. Mechanical properties of PLA and PLA based composites (solid line and dashed line are PLA and wood/PLA composites, respectively): (d) impact strength



Table 2. Thermal properties of PLA and PLA based composites

Sample code	Glass transition temperature	Melting t	emperature T _m)	Percent of crystallinity (%X _c)		
	(T _g)	T _{m1}	T _{m2}			
PLA	60.4	153.0		20.30		
0.5CP	60.2	143.4 155.2		29.70		
1CP	60.6	143.3	155.6	15.50		
2CP	61.0	150.9	160.5	22.30		
ТР	59.8	151.1		17.32		
0.5CTP	59.8	148.6	155.2	27.17		
1CTP	59.8	149.4	159.5	27.94		
2CTP	59.9	150.2	159.9	22.22		
WP	60.6	148.5	157.8	37.49		
0.5CWP	60.6	148.6	158.0	39.35		
1CWP	60.3	149.5	158.2	26.86		
2CWP	59.1	147.8	157.4	27.95		
TWP	59.0	147.5	157.1	39.45		
0.5CTWP	58.7	146.9	156.9	32.44		
1CTWP	58.1	146.3	156.4	24.38		
2CTWP	58.2	146.6	156.3	20.90		

30B are given in the **Figures 3a-d**. For all control samples, *E. coli* grew up continuously when contact time was increased. The *E. coli* grown up behavior for pure PLA sample (**Figure 3a**) was similar to the control. This reveals that the neat PLA did not disturb the growth of bacteria. But, the growth rate was noticed to be slower for Cloisite[®] 30B added specimens, indicating that the clay could inhibit the bacterial growth rate. The antibacterial activity of organoclay Cloisite[®] 30B was caused by the operation of quaternary ammonium groups between the silicates layers which are extensively used as cationic bactericide to prohibit the microorganism growth²¹.

Figure 2a. XRD patterns of Cloisite[®] 30B and PLA based composite with Cloisite[®] 30B loading of 0.5–2% wt: (a) Cloisite[®] 30B /PLA composites



Figure 2b. XRD patterns of Cloisite[®] 30B and PLA based composite with Cloisite[®] 30B loading of 0.5–2% wt: (b) Cloisite[®] 30B /10% wood/ PLA composites







The viable cell count of E. coli in comparison with the control sample for 60 - 240 min. contact time decreased obviously when the clay content was increased (Figure 3b). This means that both Triclosan and Cloisite® 30B could be active to kill or retard the E. coli under the testing conditions. The addition of 10% wood affected the bacterial inhibition of Cloisite® 30B (Figure 3c) in CP samples. The changes in E. coli viable cell count were not significant in comparison with the control, even when 2% clay was added. But, the E. coli colony forming unit of CTP by the presence of 10% wood did not affect significantly (Figure 3d). The E. coli viable cell count of CTWP decreased with the Cloisite[®] 30B content and contact time. In comparison between Figures 3c and 3d, at 240 minute contact time, the E. coli viable cell count of control samples of CWP (Figure 3c) and CTWP (Figure 3d) were about 8.4 and 8.5 log (cfu/ml) while the viable cell count of the same samples were changed to around 8.1 and 7.4 log (cfu/ml) when 2% clay were compounded, suggesting that the wood could affect the antibacterial activity of the Cloisite® 30B but could not affect the antibacterial efficiency of the Triclosan. In order to understand antibacterial performance, the viable cell count was changed to percent bacteria reduction.

Table 3 shows percentage of bacterial reductions at different contact times for PLA, 10% wood/PLA and 1.5% Triclosan/10% wood composites with Cloisite® 30B loadings of 0.5-2.0 wt%. It can be seen that both neat PLA and WP did not show antibacterial performance, but when the clay was added, the antibacterial performance has been improved greatly with PLA up to 78.85% for 2% clay at 240 min. contact time while the best antibacterial performance of the WP was 52.79% for 1 % clay added at 240 minutes of contact time. For PLA and WP compounded with 1.5% Triclosan, it was clear that the Triclosan was active

under the testing conditions, moreover TWP showed the better antibacterial activity than the TP. This could be due to the fact that wood could act as the antibacterial promoter for the Triclosan/ PLA composites by interrupting the interaction between the Triclosan and PLA and absorbs more water molecules to leave Triclosan to be free and easy to migrate out of the polymer matrix³. However, at the presence of Cloisite[®] 30B, the antimicrobial result of TWP was slightly worse than that of TP. Antibacterial result of 2CTP and 2CTWP at 240 min. contact time were 92.14% and 97.22, respectively. The wood particles could play a vital role in obstructing the quaternary ammonium groups of Cloisite® 30B to move to the PLA surface and kill the bacteria, resulting in the drop in antibacterial performance of the WP and TWP in a presence of clay.

3.4 Water Vapor Permeability (WVP)

The effect of Cloisite® 30B loading on the WVP of the PLA and PLA based composites are shown in Figure 4. At 0% clay, the PLA had the most WVP at 8.24 x 10⁻¹¹ g.mm/mm².h.Pa while 1.5% Triclosan/PLA had lowest WVP at 7.26 x 10⁻¹¹ g.mm/mm².h.Pa. From previous work³, it was found that the water contact angle of the pure PLA increased from 58.6° to 68.8° when 1.5% Triclosan was added. This indicated that the Triclosan made the PLA to be more hydrophobicity and harder for water molecules to penetrate. It was interesting to note that the highly hydrophilic wood also reduced the WVP property of the PLA. This is because the wood particles increase the crystallinity of PLA from 20.3% to about 40%. The more crystalline and denser polymer structures lead to the lesser water penetration into the polymer surface. WVP of all testing formulations decreased with the Cloisite[®] 30B loading. For example, WVP of TWP changed from 7.7 x 10⁻¹¹ g.mm/mm².h.Pa to 6.69 and 6.46 x 10⁻¹¹ g.mm/mm².h.Pa when 0.5 and 2% clay





Figure 3c. Viable cell count of E.coli with 0.5-2% wt Cloisite[®] 30B loading for 0-240 min. contact time: (c) Cloisite[®] 30B / 10% wood flour/PLA composites







Sample code	Contact time			Percentage of bacterial reduction (%)						
	(min.)	0.0%C		0.5%C		1.0%C		2.0%C		
		0%W	10%W	0%W	10%W	0%W	10%W	0%W	10%W	
Р	60	7.46	0.00	38.80	6.06	47.76	22.72	37.31	36.36	
	120	10.46	0.00	40.70	15.00	48.84	25.00	67.44	40.13	
	180	0.00	25.59	37.66	35.56	71.42	31.11	77.27	38.89	
	240	0.38	0.00	50.77	33.48	73.07	52.79	78.85	44.26	
TP	60	87.69	58.90	87.66	54.79	86.15	54.79	83.07	61.64	
	120	66.39	77.78	63.03	83.70	87.39	85.18	98.32	87.41	
	180	74.00	93.06	90.50	91.20	96.00	90.13	97.50	92.13	
	240	80.56	90.94	86.11	92.15	94.44	93.35	97.22	92.14	

Table 3. Percentage of bacterial reductions at different contact times for PLA, 10% wood/PLA and 1.5% Triclosan/10% wood/PLA composites with Cloisite® 30B loadings of 0.0-2.0 wt.%



were added, respectively. Improving of water vapor permeability of the clay/ PLA composites could be attributed to the impermeable clay silicate layer distributed in the polymer matrix¹¹. These clay/polymer composites usually have strong barrier properties because the clay layers retard the diffusing molecule pathway due to tortuosity. Clays are essentially impermeable inorganic crystals, gas molecules have to permeate around the crystals instead of permeation in a straight line path which takes longer mean path and time for gas absorption though these clay/ polymer composites²². Thus, the water molecules have to take longer time to go through these silicate layers resulting in the improved WVP.

3.5 Oxygen Permeability

The oxygen permeability results of tested films are shown in Figure 5. Oxygen permeability of the PLA decreased when Triclosan, wood flour and Cloisite® 30B were added. The oxygen permeability value of the pure PLA was 9.36 cc.mm/m².day but decreased to 8.47, 8.74 and 7.18 cc. mm/m².day for TP, WP and TWP, respectively. TWP had less oxygen permeability value than WP, TP and neat PLA by 1.56, 1.29 and 2.18 cc. mm/m².day, respectively. Hence, the better dispersion of chemical components showed the better films barrier property. This also indicated that all the materials blended affected







the oxygen permeability of PLA films by obstruction of oxygen molecules to penetrate through the surface of PLA films. When considered the Cloisite® 30B content, the oxygen permeability was found to decrease with the clay loading. The barrier property of all films increased reasonably when Cloisite® 30B was added as compared with the films without Cloisite® 30B especially, 0.5CWP due to the exfoliated dispersion as discussed in X-ray diffraction pattern. However, the oxygen barrier properties slightly performed with the higher clay loading due to the more impermeable silicate layer content dispersed in the polymer matrix.

4. CONCLUSIONS

Mechanical, antibacterial, thermal and barrier properties of Triclosan, wood and Cloisite® 30B compounded with PLA have been determined and discussed. The addition of 10% wood changed the mechanical properties by increasing in Young's modulus and decreasing in tensile strength, elongation at break and impact strength while the mechanical properties did not change significantly with the Triclosan and clay loaded samples. T_a vales of the composites were not affected by the addition of clay and Triclosan. On the contrary, T_m values of the composites showed double peak characters when wood and Cloisite® 30B were added. X-ray diffraction (XRD) showed an exfoliation characteristic for 0.5CP with and without 10% wood resulting in higher crystallinity levels from 37.49% and 20.30% to 39.35% and 29.70%, respectively. The barrier property of all composite films increased reasonably when Cloisite® 30B was added as compared with the films without Cloisite[®] 30B, especially 0.5CWP as a result of the exfoliate dispersion. Antibacterial activities of the PLA composites were found to improve with the Cloisite® 30B content that might be attributed to cationic bactericide quaternary ammonium groups between the silicates layers.

ACKNOWLEDGMENTS

The authors would like to thank the Office of the Higher Education Commission (OHEC) under the National Research University Program, and the Thailand Research Fund (TRF Research Senior Scholar; RTA5580009) for financial co-support throughout this work.

REFERENCES

- EPA., Municipal solid waste in the United States, 2005 facts and figures. Washington, DC: Environmental Protection Agency, 2005,1.
- Thwe M.M. and Liao K., Effect of environmental aging on the mechanical properties of bambooglass fiber reinforced polymer matrix hybrid composites. *Compos. Part A- Appls.*, 33 (2002) 43.
- Prapruddivongs C. and Sombatsompop N., Roles and evidence of wood flour as an antibacterial promoter for triclosanfilled poly(lactic acid). *Compos. Part B-Eng.*, 43 (2012) 2730.
- Duncan T.V., Applications of nanotechnology in food packaging and food safety: Barrier materials antimicrobials and sensors. J. Colloid. Interf. Sci., 363 (2011) 1.
- Koh C.H., Park S.J., Jeog M.A., Hwang H.Y., Hong T.Y., Ha Y.S. and Nam Y.S., Preparation and gas permeation properties of biodegradable polymer/layered silicate nanocomposite membranes. *Desalination*, 233 (2008) 201.
- Fukushima K., Tabuani D. and Camino G., Nanocomposites of PLA and PCL based onmontmorillonite and sepiolite. *Mater. Sci. Eng. C*, 29 (2009) 1433.
- Adame D. and Beall W.G., Direct measurement of the constrained polymer region in polyamide/clay. *Appl. Clay Sci.*, 42 (2009) 545.
- Krikorian V. and Pochan D.J., Poly (L-lactic acid)/layered silicate nanocomposite: fabrication, characterization and properties. *Chem. Mater.*, **15** (2003) 4317.
- 9. Chen G.X. and Yoon J.S., Clay functionalization and organization

for delamination of the silicate tactoids in poly(L-lactide) matrix. *Macromol. Rapid Commun.*, **26** (2005) 899.

- Najafi N., Heuzey M.C. and Carreau PJ., Polylactide (PLA)clay nanocomposites prepared by melt compounding in the presence of a chain extender. *Compos. Sci. Technol.*, **72** (2012) 608.
- Rhim W.J., Hong, I.S. and Ha S.C., Tensile, water vapor barrier and antimicrobial properties of PLA/ nanoclay composite films. *Food Sci. Technol.*, 42 (2009) 612.
- Faruk O. and Matuana L.M., Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Comp. Sci. Technol.*, 68 (2008) 2073.
- Bledzki A. and Faruk O., Injection moulded microcellular wood fibre– polypropylene composites. *Compos. A*, **37** (2006) 1358.
- Zaidi L., Bruzaud S. and Bourmaud A., Me'de'ric P, Kaci M, Grohens Y. Relationship between structure and rheological, mechanical and thermal properties of polylactide/ cloisite 30B nanocomposites. J. Appl. Polym. Sci., 116 (2010) 1357.
- 15. Meng Q.K., Hetzer M. and Kee D.D., PLA/clay/wood nanocomposites: nanoclay effects on mechanical and thermal properties. J. Compos. Mater., **45** (2010) 1145.
- Sykacek E., Schlager W. and Mundigler N., Compatibility of softwood slour and commercial biopolymers in injection molding. *Polym. Compos.*, **31** (2010) 443.
- Lee S.Y., Kang I.A., Doh G.H., Yoon H.G., Park B.D. and Wu Q., Thermal and mechanical properties of wood flour/talc-filled polylactic acid composites: Effect of filler content and coupling treatment. *J. Therm. Compos. Mater.*, **21** (2008) 209.
- Pilla S., Gong S., O'Neill E., Rowell MR. and Krzysik A.M., Polylactide-pine wood flour composites. *Polym. Eng. Sci.*, 48 (2008) 578.
- Paul D.R. and Robeson, L.M., Polymer nanotechnology: Nanocomposites. *Polymer*, 49 (2008) 3187.

- Das K., Ray D., Banerjee I., Bandyopadhyay N.R., Sengupta S., Mohanty A.K. and Misra M., Crystalline morphology of PLA/ Clay nanocomposite films and its correlation with other properties. J. Appl. Polym. Sci., 118 (2011)143.
- Hong S.I. and Rhim J.W., Antimicrobial activity of organically modified nano-clays. *J. Nanosci. Nanotechn.*, 8 (2008) 5818.
- Bharadwaj R.K., Mehrabi A.R., Hamilton, C., Trujillo, C., Murga, M., Fan, R. and Chavira, A., Thompson AK. Structure-property relationships in cross-linked polyester–clay nanocomposites. *Polymer*, 13 (2002) 3699.

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