

## **PLA-NANOCOMPOSITE FILM FOR PACKAGING APPLICATIONS**

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### **Abstract:**

**Poly(lactic acid) or PLA is one of the well-known biodegradable polymer derived from renewable resources such as corn starch, tapioca starch, and sugar cane. PLA is the most extensively utilized biodegradable polyester with potential to replace conventional petrochemical-based polymers. However, PLA has some drawbacks such as brittleness, poor gas barrier etc. Nanocomposite polymers have increased interest due to their characteristics, especially in mechanical and thermal properties. The objectives of this research are to prepare PLA formulations using three different PLAs. The formula giving high gloss coating film were selected to prepare nanocomposite film by incorporated with different amount of various types of organoclays. The physical properties of the PLA coating films were studied and it was found that the PLA 7000D with 0.1% of closite-30B provided decent viscosity for coating process. In addition, the composite coating films showed good physical properties such as high gloss, good adhesion, good hardness. There is a possibility of using the obtained formulation as a paper coating film.**

### **1. Introduction**

Paper packaging industry is one of growing industries due to the increasing of demands for packaging products in the market. In addition, market competition that highlight to the outlook of the packages to enhance the image of the products and attract consumers to buy products [1]. Paper coating is a process to apply a coating film onto paper to impart certain qualities to the paper, including weight, surface gloss, smoothness and protection. The coating materials widely used are thin laminated-plastic films or liquid polymeric coat. Those materials are not biodegradable and cause problems in raising the amount of non-degradable packaging wastes.

The environmental concerns over non-biodegradable petrochemical-based plastic packaging materials has raised interest in the use of biodegradable alternatives, such as polylactides or poly(lactic acid) (PLA), originating from renewable sources [2-3]. Poly(lactic acid) (PLA) is one of the most promising materials since it is thermoplastic, bio-degradable, biocompatible with high-strength, high-modulus and good processability [4]. PLA is a linear aliphatic thermoplastic polyester produced either by the polycondensation of lactic acid or by the ring opening polymerization of lactide. Lactide is a cyclic dimer prepared by the controlled polymerization of lactic acid, which is obtained from the fermentation of renewable sugar feedstock, such as corn or sugar beets.

However, PLA has some disadvantage properties such as brittleness, low thermal stability, medium gas barrier properties and low solvent resistance. This causes PLA is not commonly used for food packaging applications [5]. The nanoscale distribution of nanoclays (such as montmorillonite, saponite or hectorite), with a high aspect ratio (100–1500) and extremely high surface-to-volume ratio (700–800 m<sup>2</sup>/g) established significant improvement to the polymer matrix in terms of mechanical, gas barrier, and optical properties at low filler content [6]. To exploit the enhanced properties of such nanocomposite, various studies have been performed on the preparation of PLA-based nanocomposites [7-8]

The main objectives of this study were to prepare PLA/organoclay composite films and to investigate the effects of type and amount of nanoclay addition toward the physical properties as well as a potential of the PLA/organoclay composite films in the application of paper coating film packaging.

## **2. Materials and Methods**

### *2.1 Materials*

Three types of Poly-L-lactide (PLA) which are; PLA2000D, PLA4042D and PLA7000D were purchased from BC Polymer Marketing Company, Bangkok, Thailand. Three types of nanoclays were purchased from Southern Clay Products Inc., Texas, USA. Chloroform and Toluene were purchased from ACI labscan. Ethyl Acetate was purchased from Lab scan Analytical Sciences.

### *2.2 Preparation of films*

A 15% stock solution of PLA was prepared by completely dissolving PLA in chloroform at 40 °C. 100 grams of each PLA stock solution was taken and diluted with toluene or ethyl acetate. The obtained PLA solution were used to coat onto the Lenetta chart (back&white paper). Gloss and viscosity were determined. The formula, providing an appropriate viscosity and high gloss of coated paper, was selected to prepare nanocomposite coating films. In this study, PLA7000D:toluene in the ratio of 100:50 imparted the highest gloss film and suitable viscosity for paper coating application.

### *2.3 Preparation of nanocomposite films*

Nanocomposite films were prepared by incorporated PLA7000D:Toluene(100:50) solution with three different amounts of various types of organoclays, as shown in Table 1. Organoclay was incorporated into the formula by using homogenizer for 2 minutes then coated onto the Lenetta chart using 100 micrometre coating applicator. Physical properties of nanocomposite dried films were investigated.

Type of organoclay	Amount of organoclay (%) in PLA7000D formula		
	Cloisite 15A	0.025	0.050
Cloisite 20A	0.025	0.050	0.100
Cloisite 30B	0.025	0.050	0.100

**Table 1:** Formulations of PLA7000D/organoclay composite films

#### 2.4 Testing procedures

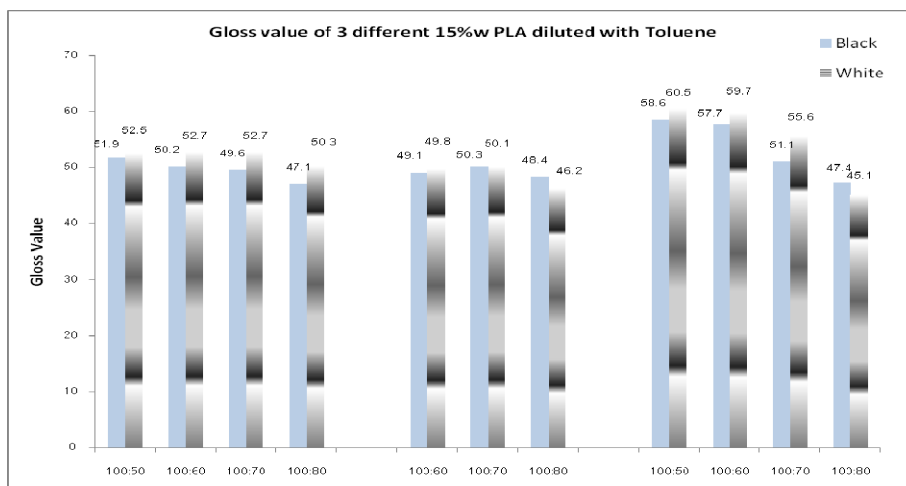
Viscosity of solutions was tested using Brookfield viscometer (RV spindle 4 @ 20 rpm). Gloss, Adhesion, Hardness, Blocking resistance and Water vapor transmission rate were investigated to confirm the possibility of using PLA solution in paper packaging coatings. X-Ray diffraction was used to study the crystal structure of nanocomposite films.

#### 2.5 Scale up

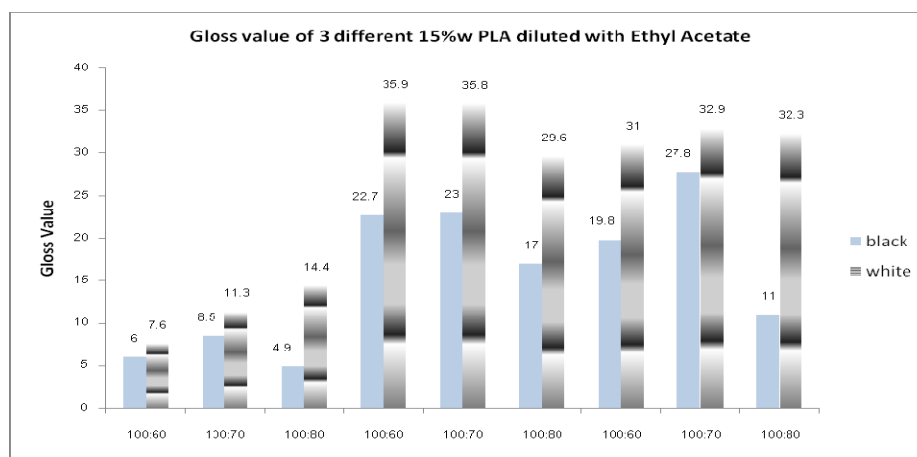
The formula, providing an appropriate physical properties for paper coating application, was selected to scale up and coat onto the sample paper for food packaging. In this study, PLA7000D:Toluene(100:50) solution incorporated with Cloisite 30B at 0.1% imparted the highest hardness and adhesion values and suitable WVTR for food paper coating application. Physical properties such as Gloss, Adhesion, Hardness and Blocking resistance of nanocomposite film were investigated compared with neat PLA film.

### 3. Results and Discussion

From the preparation of three different PLA films, PLA7000D diluted with toluene in the ratio 100:50 provided the highest gloss compared with other PLA:toluene and PLA:ethyl acetate ratios as shown in figure 1. PLA7000D solution diluted with toluene in the ratio of 100:50 was suitable (around 700-900 cps) to coat paper and was chosen to prepare nanocomposite film by incorporated with different amounts of various types of organoclays. PLA7000D solution diluted with toluene in the ratio of 100:50 was incorporated with three different contents of organoclays, Cloisite 15A, Closite 20A and Closite 30B. The viscosity of each modified PLA solution were taken. The results showed that Cloisite 15A imparted slightly increase in viscosity. Meanwhile, Closite 20A and Closite 30B showed no significant in increasing the viscosity as the content of organoclays increased. The PLA solution modified with Cloisite 15A presented the highest viscosity relative to ones modified with Closite 20A and 30B as shown in Figure 2. However, all of the modified PLAs with organoclays provided decent viscosity for coating process.

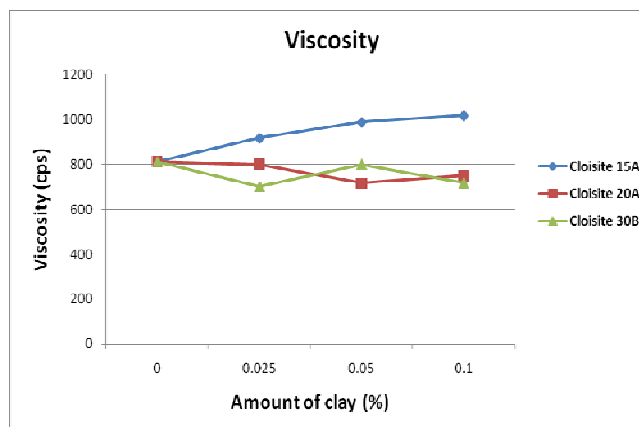


A	PLA4042D : Toluene	PLA2000D : Toluene	PLA7000D : Toluene
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B	PLA4042D : EA	PLA2000D : EA	PLA7000D : EA
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**Figure 1.** Gloss value at 60 degree of PLA films where PLAs formulars were diluted with Toluene (A) and with Ethyl Acetate (B).



**Figure 2.** Viscosity of PLA7000D/organoclay composite films.

Physical properties such as glossiness of dried coating nanocomposite films was investigated. The results are shown in Figure 3. All modified PLA dried composite films did not show significant different in gloss. They were varied in the range from 49 to 58.9. The PLA solution modified with Cloisite 20A at 0.05% by weight showed the highest gloss value (58.9) while Cloisite 30B at 0.1% gave the lowest (49). In addition, gloss value of film which measured from white part (recoated) has tended to be higher than black part (non-coated).

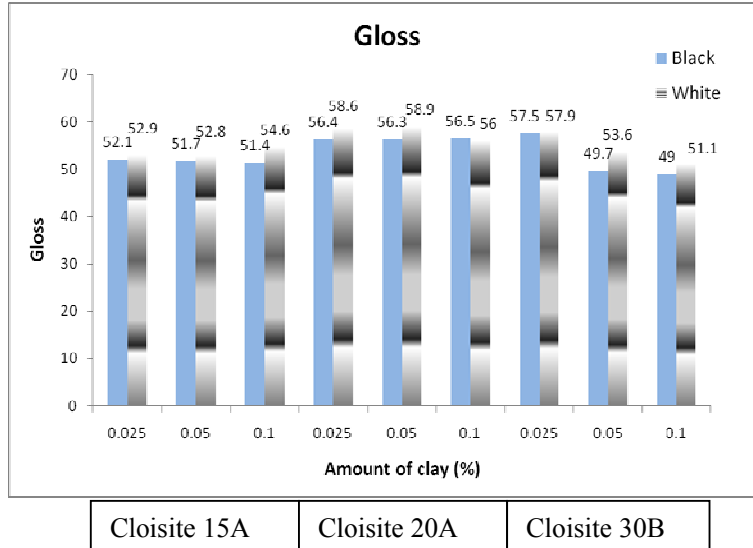
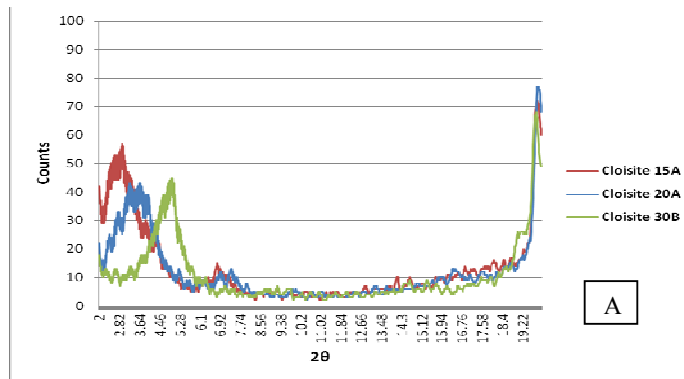
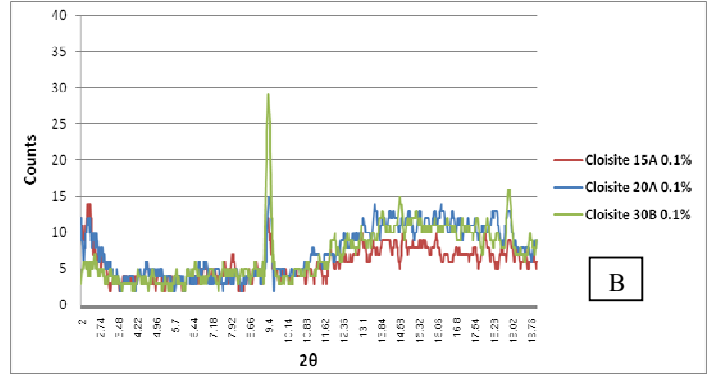


Figure 3. Gloss value of PLA nanocomposite films.

X-ray diffraction measurement results of the three different types of organoclays are shown in Figure 4 (A). The XRD patterns of the three different types of organoclays showed the increasing of the layers distance because the peaks at  $2\theta$  were less than 7 degrees compared with unmodified clay which peak appeared at  $2\theta$  equal to 7 degrees. The XRD patterns of Cloisite 30B showed no peak of remained unmodified clay at  $2\theta$  equal to 7 degrees while there was a peak at  $2\theta$  equal to 7 degrees in XRD patterns of Cloisite 15A and Cloisite 20A. This confirmed that Cloisite 30B was more completely modified than the others. However, calculated interspacing of layer of Cloisite 15A (3.01 nm) and Cloisite 20A (2.42 nm) were slightly higher than Cloisite 30B (1.79 nm).

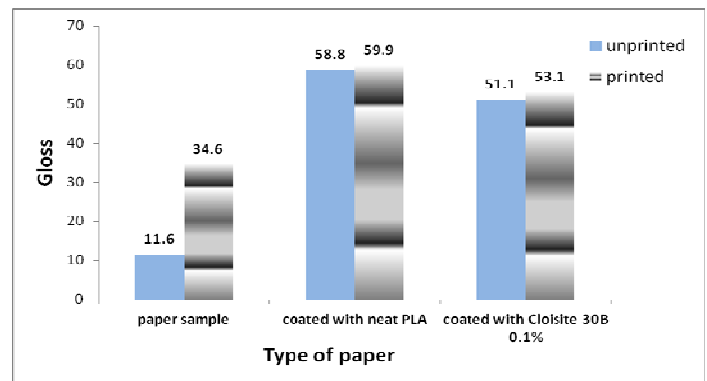




**Figure 4.** XRD patterns of three different types of organoclays (A) and XRD patterns of PLA7000D/ organoclay nanocomposite films incorporated with three different types of organoclays at 0.10% concentration (B)

X-ray diffraction measurement results of the dried coating nanocomposite films of PLA 7000D incorporated with organoclays were investigated. The XRD patterns results are shown in Figure 4(B). It showed that there are no peak of unmodified clays ( $2\theta = 7$  degree) in the film with all three types of organoclays. However, the XRD profile of PLA composite films with 0.1% Cloisite 30B showed that the 2 theta peak at 2.30 degree of the d-spacing of 3.85 nm disappeared. This means the organoclay structure in the PLA matrix changed to exfoliated structure. Meanwhile, the 2 theta peaks in XRD profiles of PLA composite films with 0.1% Cloisite 15A and 20A remained. This means the nanocomposite films with 0.1% Cloisite 15A and 20A showed intercalation structure.

Physical properties such as hardness, adhesion and blocking resistance of dried coating nanocomposite films was investigated. The results showed that hardness and adhesion values increased with increasing the amount of organoclays and Cloisite 30B demonstrated the highest values for both hardness and adhesion. WVTR of nanocomposite films decreased with increasing the amount of organoclays and the different type of organoclays at the same was not showed a significant different in WVTR. Nanocomposite films presented the lower WVTR compared with neat PLA film. All of the nanocomposite films presented good blocking resistance property due to there was no coated papers stuck together when peeling force was applied.



**Figure 5.** Gloss value of a coated and uncoated paper.

Sample paper for food packaging were coated with PLA7000D:Toluene(100:50) solution incorporated with Cloisite 30B at 0.1% for scale up and physical properties such as Gloss, Adhesion, Hardness and Blocking resistance of nanocomposite film were investigated compared with neat PLA film.

Gloss value of the nanocomposite film and neat PLA film coated on the sample papers were higher than uncoated sample paper as shown in Figure 5. In addition, gloss value of neat PLA film was higher than nanocomposite film. However, after coating the two part of paper (white part and color part) with both formular, gloss value of the white part (unprinted) and color part (printed) increased to similar value confirming that coated sample paper with both formulas improved the glossiness of the packaging and also enhanced the value of the products.

Physical properties such as hardness, adhesion and blocking resistance of nanocomposite film and neat PLA film were investigated. The results showed that adhesion value of nanocomposite film was higher than that of neat PLA film. Besides, the white part (uncoated) tend to be higher adhesion than that of the color part (recoated) for both formulars. All of the nanocomposite films presented good hardness and blocking resistance properties due to there was no coated papers stuck together when peeling force was applied. The results revealed that the modified PLA nanocomposite film was suitable for paper coating packaging compared with neat PLA films.

#### **4. Conclusions**

Nanocomposite films were prepared by incorporated PLA with different amount of various types of organoclays. PLA 7000D with 0.1% by weight of Cloisite 30B provided decent viscosity and physical properties for coating process. In addition, the composite coating films showed good physical properties such as high gloss, good adhesion, good hardness and lower WVTR through the film compared with neat PLA coating film. Paper coating film properties can be improved by choosing the proper type of nanoclay and its optimum concentration. The increased gloss, hardness and adhesion properties suggest a great potential of the PLA/organoclay composite films in the application of paper coating film packaging.

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