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*Original Article*

# Poly (lactic acid) organoclay nano composites for paper coating applications

Tatcha Sonjui[1] and Nantana Jiratumnukul[1,2]*

[1] *Department of Materials Science, Faculty of Science,*

[2] *Research Unit of Advanced Ceramic and Polymeric Materials, National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok, 10330 Thailand.*

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**Abstract**

Poly(lactic acid) or PLA is a well-known biodegradable polymer derived from renewable resources such as corn strach, tapioca strach, 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 and poor gas barrier properties. Nano composite polymers have experience and increasing interest due to their characteristics, especially in mechanical and thermal properties. The objectives of this research were to prepare PLA formulations using three different PLAs. The formulas giving high gloss coating film were selected to prepare nano composite 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%w/w of Cloisite 30B provided decent viscosity for coating process. In addition, the nano composite coating films showed good physical properties such as high gloss, good adhesion, and good hardness. There is a possibility of using the obtained formulation as a paper coating film.

**Keywords:** poly(lactic acid), composite film, coating, biodegradable polymer, packaging

## 1. Introduction

The paper packaging industry is one of the growing industries due to an increasing demand for packaging products in the market. In addition, market competition often forces companies, especially in market of consumer products, to enhance the packaging in order to improve the image of their products and by this attract more consumers to buy them (Kirwan, 2005). Paper coating, which is one way to enhance the packaging, is a process where a coating film is applied 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 therefore cause problems due to the increasing 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 (Petersen *et al.*, 1999), such as polylactides or poly(lactic acid) (PLA), originating from renewable sources (Zaidi *et al.*, 2010). Poly(lactic acid) (PLA) is one of the most promising material since it is thermoplastic, biodegradable, biocompatible with a high strength and modulus and possesses good processability (Drumright *et al.*, 2000). 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 disadvantages related to its properties such as brittleness, low thermal stability,

* Corresponding author.
Email address: nantanaj@gmail.com

medium gas barrier properties, and low solvent resistance. For these reasons PLA is not commonly used for food packaging applications (Weber *et al.*, 2002). The nano scale distribution of nano clays (such as montmorillonite, saponite or hectorite), with a high aspect ratio (100–1,500) and extremely high surface-to-volume ratio (700–800 $m^2/g$) established signicant improvements to the polymer matrix in terms of mechanical, gas barrier, and optical properties at low filler content (Alexandre and Dubois, 2000). To exploit the enhanced properties of such nano composites, various studies have been performed on the preparation of PLA-based nano composites (Sinha Ray and Bousmina, 2005).

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

## 2. Materials and Methods

### 2.1 Materials and chemicals

Three types of poly-L-lactide (PLA), PLA2000D, PLA4042D, and PLA7000D, were purchased from BC Polymer Marketing Company, Bangkok, Thailand. Three types of organoclays including three organically modified montmorillonite clays (Cloisite 15A, Cloisite 20A, and Cloisite 30B) were purchased from Southern Clay Products Inc., Texas, U.S.A. Chloroform and toluene were purchased from RCI Labscan. Ethyl Acetate was purchased from Lab-Scan Analytical Sciences.

### 2.2 Preparation of films

A 15%w/w 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 to adjust viscosity. The obtained PLA solution was used to coat the Leneta chart (black & white paper) via a 100 micron-applicator. Gloss and viscosity were determined. The formula, providing an appropriate viscosity and high gloss of coated paper, was selected to prepare nano composite coating films. In this study, PLA 7000D: toluene in the ratio of 100:50 imparted the highest gloss film and suitable viscosity for paper coating application.

### 2.3 Preparation of nano composite films

Nano composite 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 two minutes then coated onto the Leneta chart using a 100 micron-coating applicator. Physical properties of nano composite dried films were investigated.

### 2.4 Testing procedures

Viscosity of solutions was tested using a Brookfield viscometer (RV spindle 3 @ 20 rpm). Gloss, adhesion, hardness, blocking resistance, and water vapor transmission rate (WVTR) were investigated to confirm the possibility of using PLA solution in paper packaging coatings. The crystal structure of the organoclay nanoparticles and their PLA nano composite films were carried out by XRD (Bruker, D8-Advance), using $CuK_\alpha$ radiation ($\lambda = 0.1542$ nm) with Ni filtered at 40 kV and 30 mA. The relative intensity was recorded in scattering range ($2\theta$) of 2-20°.

### 2.5 Scale-up

The formula, which was providing the appropriate physical properties for paper coating application, was selected to scale-up and coated onto the sample paper for food packaging. In this study, PLA7000D:toluene (100:50) solution incorporated with Cloisite 30B at 0.1%w/w 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 nano composite films were investigated compared with neat PLA films.

## 3. Results and Discussion

Three different PLA solutions with various diluent ratios were prepared and the gloss and viscosity of dried films was taken. It was found that viscosity of PLA4042D solution diluted with toluene and ethyl acetate in the ratio of 100:50 and PLA7000D solution diluted with toluene in the ratio of 100:50 were suitable to coat paper (suitable viscosity is around 700-900 cps) as shown in Table 2. However, PLA7000D diluted with toluene in the ratio 100:50 provided the highest gloss compared with other PLA:toluene and

Table 1. Formulations of PLA7000D/organoclay nano composite films.

| Type of organoclay | Amount of organoclay (%w/w) in PLA7000D formula | | |
|---|---|---|---|
| Cloisite 15A | 0.025 | 0.05 | 0.1 |
| Cloisite 20A | 0.025 | 0.05 | 0.1 |
| Cloisite 30B | 0.025 | 0.05 | 0.1 |

Table 2. Viscosity of PLAs solutions.

| 15%w/w stock solution of PLA: diluent Toluene (TE) Ethyl Acetate (EA) | Viscosity (Brookfield RV Spindle 3 @ 20 rpm) (cps) | | |
|---|---|---|---|
| | PLA4042D | PLA2002D | PLA7000D |
| 100:0 | 14,400 | 5,442 | 5,525 |
| 100:50TE | 825 | - | 812 |
| 100:60TE | 621 | 325 | 575 |
| 100:70TE | 575 | 238 | 225 |
| 100:80TE | 379 | 178 | 175 |
| 100:60EA | 825 | 300 | 333 |
| 100:70EA | 517 | 203 | 200 |
| 100:80EA | 400 | 150 | 150 |

PLA:ethyl acetate ratios as shown in Figure 1. Therefore, PLA7000D diluted with toluene in the ratio 100:50 condition was chosen to prepare nano composite films 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, Cloisite 20A, and Cloisite 30B. The viscosity of each PLA solution incorporated with organoclay was taken. The results showed that Cloisite 15A imparted slightly increase in viscosity. Meanwhile, Cloisite 20A and Cloisite 30B showed no significant increase in the viscosity as the content of organoclays increased. The PLA solution incorporated with Cloisite 15A presented the highest viscosity relative to ones incorporated with Cloisite 20A and 30B as shown in Figure 2. However, all of the PLAs incorporated with organoclays provided decent viscosity for coating process.

Physical properties such as gloss of dried coating nano composite films were investigated. The results are shown in Figure 3. All dried nano composite films incorporated with organoclays did not show significant differences in gloss. They were varied in the range from 49.0 to 58.9. The PLA solution incorporated with Cloisite 20A at 0.05% w/w showed the highest gloss value (58.9), while Cloisite 30B at 0.1% gave the lowest (49.0). In addition, gloss value of film which measured from the white part (non-coated) has tended to be higher than black part (recoated).

X-ray diffraction measurement results of the three different types of organoclays are shown in Figure 4 (top). The XRD patterns of the three different types of organoclays showed an increase of the layer distance because the peaks at 2θ were less than 7 degree compared with unmodified organoclay, where the peaks appeared at 2θ equal to 7 degree (Rhim *et al.*, 2009). The XRD patterns of Cloisite 30B showed no peak of any remaining unmodified organoclay at 2θ equal to 7 degree, while there was a peak at 2θ equal to 7 degree in XRD patterns of Cloisite 15A and Cloisite 20A. This confirmed that Cloisite 30B was completely modified in comparison to the other montmorillonite clays. 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).

X-ray diffraction measurement results of the dried coating nano composite films of PLA 7000D incorporated with organoclays were investigated. The XRD patterns results are shown in Figure 4 (bottom). It shows that there are no peaks of unmodified organoclays (2θ = 7 degree) in the film with all three types of organoclays. However, the XRD profile of PLA nano composite films with 0.1%w/w Cloisite 30B showed that the 2θ peak at 4.60 degree related to a

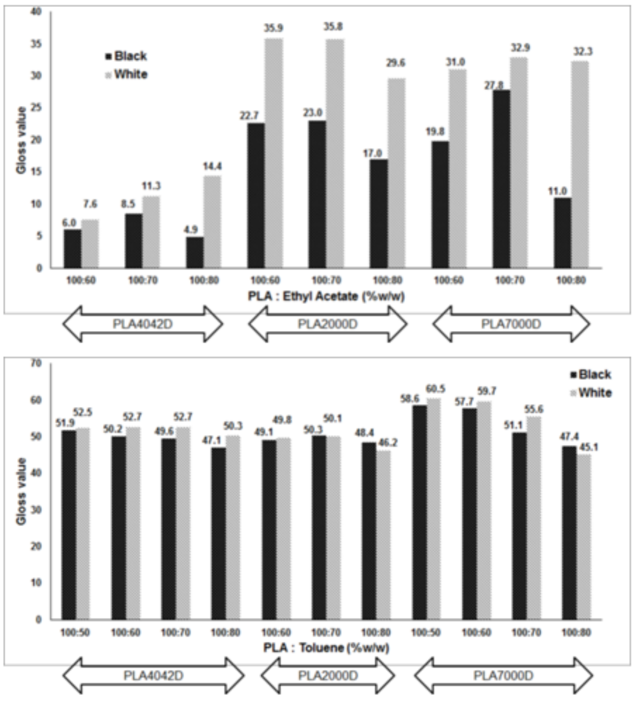



Figure 1. Gloss value at 60 degree of three difference PLA films where PLAs formulas were diluted with toluene (top) and with ethyl acetate (bottom).

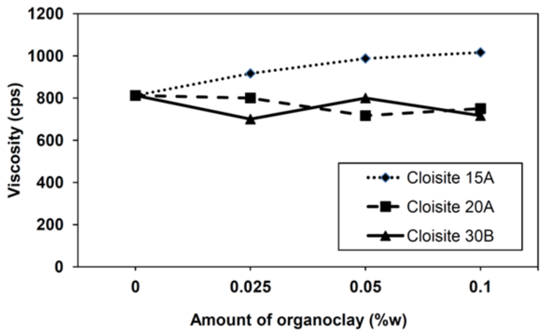



Figure 2. Viscosity of PLA7000D/organoclay nano composite lms incorporated with three different concentrations and types of organoclays.

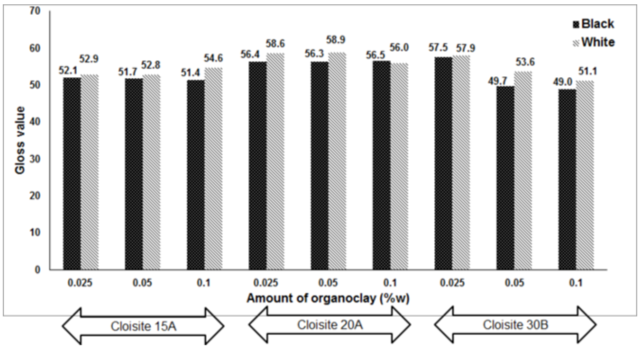



Figure 3. Gloss value of PLA7000D/organoclay nano composite films incorporated with three different concentrations and types of organoclays.

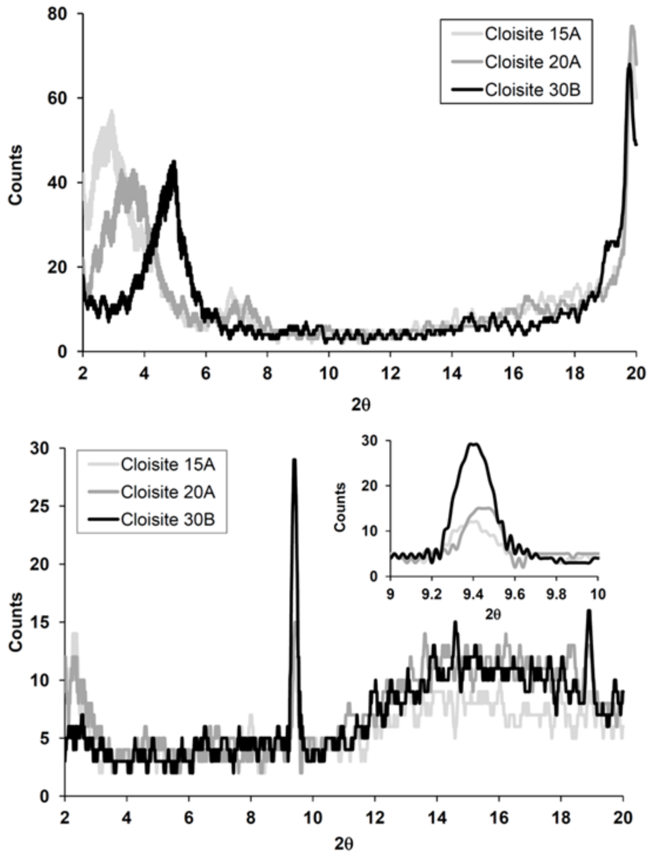



Figure 4. XRD patterns of three different types of organoclays (top) and XRD patterns of PLA7000D/organoclay nano composite films incorporated with three different types of organoclays at 0.10% concentration (bottom).

d-spacing of 3.85 nm has disappeared. This means that the organoclay structure in the PLA matrix changed to an exfoliated structure. Meanwhile, the 2θ peaks in XRD profiles of PLA nano composite films with 0.1%w/w Cloisite 15A and 20A at 2.30 degree remained. This means the nano composite films with 0.1%w/w Cloisite 15A and 20A showed intercalation structures.

Physical properties such as hardness, adhesion and blocking resistance of dried coating nano composite films were investigated and shown in Table 3. The results showed

Table 3. Physical property testing results for PLA7000D dried coating nano composite films coated onto the Leneta chart with three different amounts of various types of organoclays.

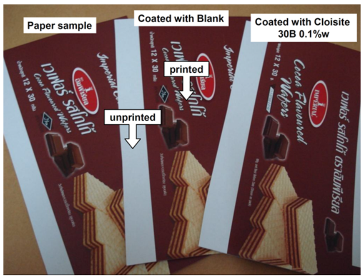
| Organoclays | Adhesion (cross cut) | | Hardness (g) | |
|---|---|---|---|---|
| | recoated | non-coated | recoated | non-coated |
| Blank | 0B | 0B | 190 | >1,000 |
| 15A 0.025% | 0B | 0B | 240 | >1,000 |
| 15A 0.05% | 0B | 0B | 270 | >1,000 |
| 15A 0.1% | 0B | 0B | 360 | >1,000 |
| 20A 0.025% | 0B | 0B | 240 | >1,000 |
| 20A 0.05% | 0B | 0B | 310 | >1,000 |
| 20A 0.1% | 0B | 0B | 470 | >1,000 |
| 30B 0.025% | 0B | 0B | 320 | >1,000 |
| 30B 0.05% | 0B | 1B | 350 | >1,000 |
| 30B 0.1% | 0B | 4B | 520 | >1,000 |

Table 4. Water vapor transmission rate (WVTR) testing results for PLA7000D dried nano composite films with organoclays.

| Organoclays | WVTR (g/$m^2$ day) |
|---|---|
| Blank | 715 |
| 30B 0.025% | 670 |
| 30B 0.05% | 636 |
| 30B 0.1% | 613 |
| 15A 0.1% | 584 |
| 20A 0.1% | 600 |

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 testing results are shown in Table 4. It was found that WVTR of nano composite films decreased with increasing amount of organoclays, and the different types of organoclays at the same ratio did not show a significant difference in WVTR. All of the prepared nano composite films presented a lower WVTR compared with neat PLA film (blank). Moreover, all nano composite films presented exhibit good blocking resistance properties as there were no coated papers stuck together when a peeling force was applied.

Sample papers for food packaging were coated using PLA7000D:toluene (100:50) solution incorporated with Cloisite 30B at 0.1%w/w for scale-up and physical properties such as gloss, adhesion, hardness, and blocking resistance of nano composite film were investigated compared with neat PLA films.



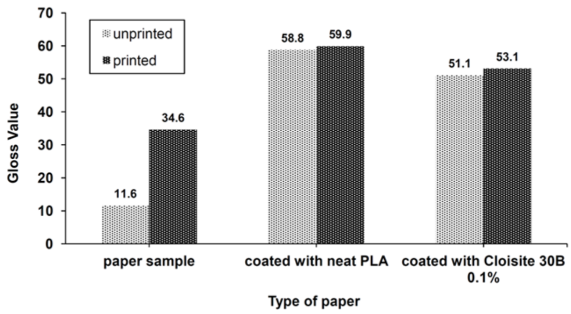




Figure 5. Sample paper for food packaging used in this study (top) and gloss value of a coated and uncoated paper (bottom).

Gloss value of the nano composite film and neat PLA film coated on the sample papers were higher than uncoated sample papers as shown in Figure 5 (top) and (bottom). In addition, gloss value of neat PLA film was slightly higher than that of nano compsite film. However, after coating the two parts of the paper (white and color part) with both formulas, gloss value of the white part (unprinted) increased from 11.6 for uncoated sample papers to 58.8 and 51.1 for neat PLA films and nano composite films, respectively, while the color part (printed) also increased from 34.6 for uncoated sample papers to 59.9 and 53.1 for neat PLA films and nano composite films, respectively. These results confirmed that coating the sample papers with both formulas can improve the gloss value of the packaging and also enhance the value of the products.

Physical properties such as hardness, adhesion, and blocking resistance of nano composite film and neat PLA film were investigated. The results showed that the adhesion value of nano composite films was higher than that of neat PLA films and that the white part (uncoated) has tended to show higher adhesion than the color part (recoated) for both formulas. All of the nano composite films presented good hardness and blocking resistance properties as no coated papers stuck together when a peeling force was applied. The results revealed that the PLA nano composite films incorporated with organoclays were suitable for paper coating packaging compared with neat PLA films.

## 3. Conclusions

Nano composite films were prepared by incorporated PLA with different amounts of various types of organoclays. PLA7000D solution with 0.1%w/w 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 throughout the films compared with neat PLA coating films. Paper coating film properties can be improved by choosing the proper type of organoclay 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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