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# Poly(lactic acid)/Wood Flour/Montmorillonite Nanocomposites (II) : Thermal properties*1

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## ABSTRACT

This study investigates the thermal properties of nanocomposites prepared from poly(lactic acid) (PLA), wood flour (WF) and montmorillonite (MMT) by melt compounding with a twin screw extruder. In order to enhance the mechanical properties of PLA/WF composites, maleic anhydride grafted PLA (MAPLA) is synthesized as a compatibilizer. MAPLA prepared in the laboratory is characterized using FR-IR. From SEM microphotographs, the presence of MAPLA has a positive effect on the mechanical properties of WF-reinforced PLA composites. The addition of WF/MAPLA into neat PLA increased the glass transition temperature ($T_g$). The addition of 1 to 5 wt% MMT into PLA/WF/MAPLA composite decreases the $T_g$. The cold crystallization temperature ($T_{cc}$) was decreased by the addition of MMT. The MMT could act as effective nucleating sites of PLA crystallization. The thermal stability evaluated by thermogravimetric analysis (TGA) is improved with the contents of MMT up to 3 wt%.

*Keywords* : thermal properties, PLA, wood flour, TGA, DSC

## 1. INTRODUCTION

The utilization of lignocellulosics and polymers from renewable resources has recently attracted increasing attention, due to environmental concerns and the depletion of petroleum resources[1-4]. Polymers from renewable resources can be classified into natural polymers such as starch[5-7], protein and cellulose[8-10], and synthetic polymers[11-13]. The development of synthetic polymers using monomers from natural resources provides a new direction for the development of biodegradable polymers.

One of the most promising biodegradable polymers is poly(lactic acid) (PLA), which can be derived from renewable resources, because of its desired mechanical strength, thermal plasticity, and biocompatibility[13,14]. The PLA has been used for many applications including grocery and composting bags, automobile panels, textiles, and bio-absorbable medical materials [15,16]. The high bulk density of wood flour

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(WF), as well as its low cost and availability, makes it attractive to composite manufacturers and users[17].

Montmorillonite (MMT) is hydrous alumino-silicate clay composed of unitsmade up of two silica tetrahedral sheets with a central alumina octahedral sheet so that the oxygen ions of octahedral sheet do also belong to the tetrahedral sheet. The structure of montmorillonite has been established by Hendricks[18]. From electron microscopy[19], it is basically composed of aggregates, whose size range: 0.1～10 μm, that is made up by association of a number of primary particle, which, in turn, are composed of a number of super-imposed lamellae. The height of the primary particle is 80～100 Å, and the diameter is 300 Å, and the thickness of the lamella is 9.6～10 Å. Thus, each primary particle contains approximately 8 lamella or 16 planes.

The combination of WF and thermoplastic polymers presents a number of problems[20]. However, incompatibility between the fiber and matrix causes a poor interfacial adhesion between hydrophilic wood and the hydrophobic plastic matrix, therefore resulting in poor ability to transfer stress from the matrix to the fiber reducing mechanical strengths and ductility[21].

In this study investigates the physical properties of the PLA/WF/MAPLA composites filled with organically modified MMT was investigated. In order to enhance the mechanical properties of PLA/WF composites, MAPLA was synthesized as a compatibilizer. The thermal properties of the resultant composites were characterized by differential scanning calorimetr (DSC) and thermogravimetric analysis (TGA).

# 2. EXPERIMENTAL

## 2.1. Materials

The polylactic acid (PLA) was supplied by NatureWorks of USA. Its molecular weight (Mw) is 159,000 g/mol and melt flow index is 10～30 g/10 min. Maleic anhydride was purchased from Sigma-Aldrich (USA). 2,5-Dimethyl-2,5-di-(tert-butylperoxy) hexane organic peroxide (Luperox 101) was provided by SEKI ARKEMA Co., LTD. Organically modified montmorillonite (MMT, Cloisite 30B) was obtained from Southern Clay Products Co. and used as received without further purification. The chemical structure of the MMT is shown in Fig. 1. The organic modifier for clay 30B is methyl tallow bis-2-hydroxyethyl quaternary ammonium ion (65% C18, 30% C16, 5% C14). The wood flour used in this study was obtained from J.Retenmaier & Sohn Co., Germany and Its particle size is 80～100 mesh (70～150 μm).

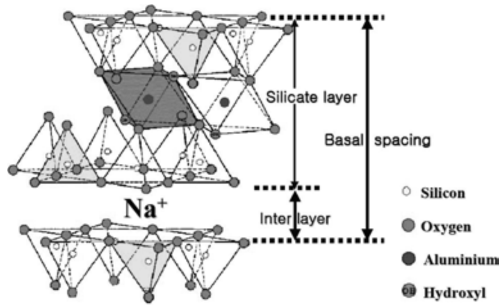



Fig. 1. Structures of layered materials.

## 2.2. MAPLA Preparation

The MAPLA was prepared by using a twin-screw extruder (19 mm diameter screw and L/D = 40, Bautek Co, Korea). The PLA, 10 phr MAH and 4 phr peroxide were premixed in a rotating mixer before being added into the hopper of the extruder. The temperature of the extruder were set as 160 to 180°C from feeding to barrel zones. MAPLA was purified by dissolving in chloroform and precipitated by adding a large amount of n-pentane. The precipitate was filtrated by using 0.2 μm membrane filter.

The sample were dried in the vacuum oven at 60°C for 24 h.

## 2.3. Composite Preparations

Before preparing composites, the raw materials were dried in a vacuum oven at 60°C for 24 h. Compounding was carried out through a melt mixing method by using the twin screw extruder. The temperature of the extruder were set as 190 to 210°C from feeding to barrel zones, respectively. The screw speed of the extruder was set at 100~150 rpm. The products were dried in a vacuum oven at 60°C for at least 24 h.

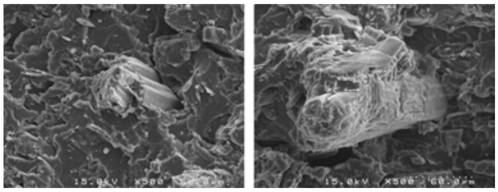
## 2.4. DSC and TGA

The morphology of the PLA/WF composites was obtained by scanning electron microscopy (model: HITACHI S-4200) at an accelerated voltage of 15 kV after silver coating. The crystalline melting and recrystallization behavior was measured by a differential scanning calorimetry (TA Instruments DSC 2910) at a heating rate of 10°C/min in $N_2$ atmosphere. The change in weight of sample due to decomposition was measured by using a thermogravimetric analyzer (TGA) on a TA Instruments TGA-2050. Analysis was done under an $N_2$ atmosphere from room temperature to 700°C at a heating rate of 10°C/min.

# 3. RESULTS and DISCUSSION

## 3.1. SEM Photographs of Composites

Fig. 2 shows the SEM images of PLA/WF (70/30 wt%) composites with and without MAPLA. As shown in Fig. 2(a), the gaps between PLA and WF for the fractured composites without MAPLA is observed indicating poor internal bonding. This is related to the lower mechanical properties of the composites. The addition of MAPLA facilitates the affinity between PLA and WF resulting in stronger adhesion and the phase boundary is unconspicuous in Fig. 2(b). Hence, the presence of MAPLA has a positive effect on the mechanical properties of WF-reinforced PLA composites in comparison with composites made without MAPLA.



(a) (b)

Fig. 2. SEM morphology of the PLA/WF composites; (a) without MAPLA, (b) with 2 wt% MAPLA.

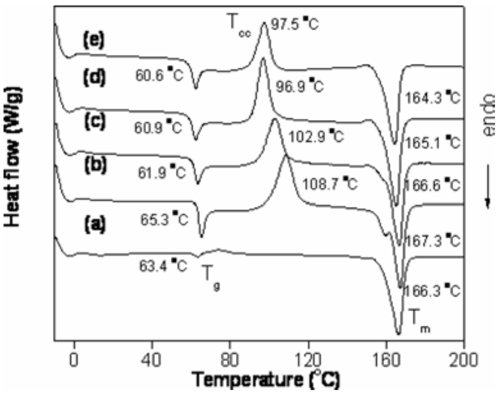



Fig. 3. DSC thermograms of neat PLA and PLA composites; (a) neat PLA, (b) PLA/WF/MAPLA (68/30/2), (c) PLA/WF/MMT/MAPLA (67/30/1/2 wt%), (d) PLA/WF/MMT/MAPLA (65/30/3/2 wt%), (e) PLA/WF/MMT/MAPLA (63/30/5/2 wt%).

## 3.2. DSC Analysis

The DSC thermograms of neat PLA and PLA composites are shown in Fig. 3. The glass transition temperature ($T_g$) of neat PLA is 63.4°C. The glass transition temperature of PLA/WF/

MAPLA (68/30/2 wt%) was increased from 63.4°C to 65.3°C. This indicates that a weak interaction, possibly some hydrogen bonding, might have existed between WF and PLA because of the carbonyl groups in the PLA and hydroxyl groups in the WF. The addition of MMT into PLA/WF/MAPLA composite as the function of the MMT contents from 1 to 5 wt% decreases the $T_g$. The $T_g$ depends primarily on chain intermolecular attraction, molecular weight, branching and steric effects[22]. In this study of nanocomposite system, the intermolecular attractions of PLA segments seem to be interrupted by the charged MMT, and subsequently the PLA backbone chains additionally gain the segmental mobility. It can also be addressed that the MMT may provide steric factors that seemingly increase the chain mobility of PLA backbones.

In DSC thermograms of neat PLA, there is no cold crystallization temperature ($T_{cc}$) peak. This result implies that the neat PLA heated from -10°C to 200°C at a heating rate 10°C/min remain amorphous. However, the cold crystallization temperature of PLA composites filled with MMT was observed with the peak temperature. The $T_{cc}$ was decreased by the addition of MMT. The nano sized layered silicates of MMT provide large surface area due to their aspect ratio and thus it is reasonable to consider that the MMT could act as effective nucleating sites of PLA crystallization. The increased nucleating sites are likely to facilitate the PLA crystallization process in the PLA nanocomposite system, and thus the $T_{cc}$ is decreased by the addition of MMT[23]. In Fig. 3, it can be seen that the melting temperature ($T_m$) of PLA/WF/MMT/MAPLA composites are lower than that of PLA/WF/MAPLA composite because the incorporated MMT increases the number of small crystallites and subsequently lowers the overall crystallinity of the PLA.

Table 1. Thermal properties of PLA composite reinforced with WF

| Sample (PLA/WF/MMT/MAPLA) | $T_D^i$ (°C) | $DT_p$ (°C) |
|---|---|---|
| 100 | 333.3 | 353.2 |
| 70/30 | 304.5 | 353.2 |
| 68/30/0/2 | 308.4 | 348.6 |
| 67/30/1/2 | 309.0 | 360.1 |
| 65/30/3/2 | 313.3 | 364.2 |
| 63/30/5/2 | 308.8 | 365.3 |

$T_D^i$ : initial decomposition temperature at 5% weight loss

$DT_p$ : thermal peak temperature

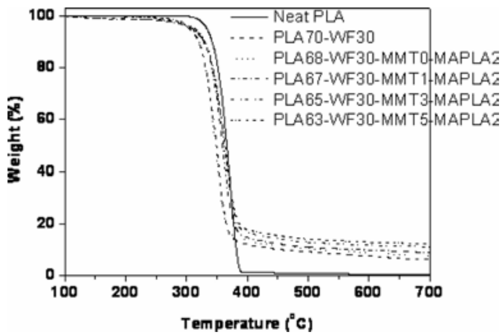



Fig. 4. TGA thermograms of neat PLA and PLA composites.

## 3.3. TGA Analysis

Fig. 4 shows the thermal decomposition of neat PLA and PLA composites. The addition of WF decreases the decomposition temperature of PLA composites compared to neat PLA. Table 1 shows the initial decomposition temperature ($T_D^i$) at a weight loss of 5% and derivative thermogravimetry ($DT_p$) of PLA composites. The $DT_p$ was obtained from the differentiation of weight change by temperature. The $T_D^i$ of neat PLA decreases from 333.3°C to 304.5°C with the addition of 30 wt% WF. It can be seen that the thermal stability of WF is lower than that of PLA. The $T_D^i$ of PLA/WF/MAPLA composite at

2 wt% MAPLA level was increased by about 4°C compared to PLA/WF (70/30 wt%) composite, but the $DT_p$ was decreased by 4.6°C.

The addition of MMT increases the thermal stability of WF reinforced PLA composistes. The initial decomposition temperature of PLA/WF/MMT/MAPLA (65/30/3/2 wt%) composite was increased by 4.9°C compared to PLA/WF/MAPLA (68/30/2 wt%) composite. The $DT_p$ was also increased by 15.6°C. However, the addition of 5 wt% MMT into PLA/WF/MAPLA composite showed no more increase in thermal stability. The increase in the $T_D^i$ is attributed to the hindered diffusion of volatile decomposition products caused by the silicate layers. It is generally believed that the introduction inorganic components in to organic materials can improve their thermal stabilities.

## 4. CONCLUSIONS

This study investigates the thermal properties of composites prepared from PLA, WF and MMT by melt compounding. In order to enhance the interfacial adhesion between hydrophilic WF and hydrophobic PLA that maleic anhydride grafted PLA (MAPLA) was synthesized and used as a compatibilizer. From SEM microphotographs, the presence of MAPLA has a positive effect on the mechanical properties of WF-reinforced PLA composites in comparison with composites made without MAPLA. The addition of WF/MAPLA into neat PLA increased the $T_g$. The addition of MMT into PLA/WF/MAPLA composite as the function of the MMT contents from 1 to 5 wt% decreases the $T_g$. The $T_{cc}$ of PLA composites filled with MMT was observed with the peak temperature. The $T_{cc}$ was decreased by the addition of MMT. The MMT could act as effective nucleating sites of PLA crystallization. The thermal stability was improved by the addition of 3 wt% MMT, while at the loading level of 5 wt%, the initial decomposition temperature was decreased by about 4.5°C. The addition of MMT effectively improves the thermal stability of the PLA composites.

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