

Characterization and Properties of Composites of Woodflour and Polylactic Acid*¹

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ABSTRACT

Modification of polylactic acid (PLA) and 10% maleic anhydride (MAH) with 15% dicumyl peroxide (DCP) based on MAH weight was conducted in the kneader at 160°C and 30~70 rpm, for 15 min. The resulting MAH-modified PLA (PLA-MA) was then evaluated as a compatibilizer for PLA- wood flour (WF) composites. The FTIR and ¹H-NMR analysis gave evidence of PLA-MA formation. After kneading and reacting with MAH and DCP, the number (Mn) and the weight average (Mw) molecular weights of PLA decreased as compared to the original PLA. The presence of WF in the composites decreased the tensile strength and several other physical properties. The higher the WF loading resulted in the greater the reduction of tensile strength. An addition of 10% PLA-MA as a compatibilizer to the composites improved the tensile strength and several other physical properties, increased the flow temperature, and decreased the melt viscosity. The improved composite revealed 1.42 times increased in tensile strength but not over PLA alone, and absorbed considerably less water compared to those of the composites free-compatibilizer.

Keywords : wood flour, polylactic acid, composites, compatibilizer

1. INTRODUCTION

Since the environmentally-sound management and wise usage of natural renewable resources for production of industrial and consumer materials and energy were pronounced in the 1990's, a great deal attention has been focused on research and the production of biodegradable and

recyclable products. Wood plastic composites (WPCs) are a new group of materials that are generating interest in many applications. Up to now, the matrices commonly used in WPCs are polyolefin resins (i.e., polyethylene/PE, polypropylene/PP, polyvinyl chloride/PVC and polystyrene/PS). These resins are non-biodegradable but recyclable. In this context, preparation of

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composites from biodegradable polymers and woody fillers has become an interesting approach for the development of new biodegradable composite products.

PLA has been known as a polyester for fibers. PLA has been regarded as a good potential for biodegradable packaging and consumer goods because of the very good thermoplastic behavior, such as mechanical strength, transparency, compostability, and safety. PLA is degraded in compost and hydrolyzed in an alkaline solution. Furthermore, PLA has glass transition temperature of T_g about 60°C. Therefore, it is a good barrier material for solvents, flavors, and aromas, and a medium barrier for permanent gases. When it is incinerated, the heat of combustion is half or less compared to conventional plastics, such as polystyrene and polyethylene. The raw material, lactic acid is produced by fermentation of carbohydrates from renewable resources such as corn (Sinclair, 1996; Whiteman *et al.*, 2002). Recent advances in the production process of PLA, together with improvements of its properties as a material have also opened up a promising market outlook in the sector of fibers and nonwovens, films, thermoformed and injection molded articles (Lunt and Shafer, 2000).

Many attempts have been made to use cellulose as reinforcement in polyester composites. However, it was found that the interfacial bonding between fiber and matrix was weak and after contact with water and subsequent drying, the fiber was not bonded at all due to the compatibility problem between hydrophilic cellulose fibers and hydrophobic thermoplastics (Flodin and Zadorecki, 1986). Therefore, to obtain polymer-woody filler composites with high strength and quality by improving the adhesion between the woody filler and the matrix polymer, a modified polymer grafted with a small amount of monomer has often been used. Parti-

cularly, MAH is considerably well utilized as a modifier. Rennecker (2004) had reviewed number of literatures to show specific anhydrides allowed the esterification of wood surfaces for different matrices, i.e., acetic anhydride for cellulose acetate butyrate (Glasser *et al.*, 1999), phthalic anhydride for polystyrene (Maldas and Kokta, 1990), maleic anhydride grafted polypropylene (MAPP) for polypropylene (Kishi *et al.*, 1989; Han, 1990; Felix and Gatenholm, 1991; Kazayawako *et al.*, 1999; Albano *et al.*, 2001; and Van De Velde and Kieken, 2001), maleic anhydride grafted styrene-ethylene-butylene-styrene (Hedenberg and Gatenholm, 1995 and Oksman *et al.*, 1998), maleic anhydride grafted polyethylene for polyethylene (Kim *et al.*, 1997), and maleic anhydride grafted *trans*-1,4-isoprene rubber for *trans*-1,4-isoprene rubber (Febrianto *et al.*, 1999 and 2001).

The conceptual idea of the present work is to apply analogous reactions as described on the publications (Kishi *et al.*, 1989; Han, 1990; Febrianto *et al.*, 1999) to modify PLA with MAH in the presence of peroxide in the kneader under certain time, rate of rotation and temperature. The resulting product, MAH modified PLA (PLA-MA), was analyzed to prove the occurrence of grafting and then evaluated as a compatibilizer for PLA-WF composites. The effect of WF content and PLA/PLA-MA ratio on the mechanical, physical and flow properties were evaluated.

2. MATERIALS and METHODS

2.1. Materials

PLA used was LACTY which was supplied by Mitsui chemical co., and Shimadzu co., respectively. DCP was purchased from Nacalai tesque Inc. Other chemical reagents such as *n*-pentane (EP), benzyl amine (GR), and MAH

were purchased from Nacalai tesque inc., while chloroform and acetone were purchased from Wakenyaku co. All these polymers and solvents were used as received. WF (cellulosin, 150 mesh pass) was used as filler, which was supplied by Hitachi Chemical Co., Ltd.

2.2. Preparation of PLA-MA

PLA and 10% MAH were reactively blended in the melt state in the kneader (Toyo Seiki Labo-Plastomill LPM 18-125). When PLA and MAH were homogeneously mixed (torque value stable) DCP initiator was added. The amount of initiator was 15% based on the MAH weight. The reaction conditions were 160°C and 30~70 rpm, for 15 min.

2.3. Purification of PLA-MA

Approximately 0.2 g of PLA-MA was dissolved in 170 mL chloroform and stirred overnight. The PLA-MA (chloroform solution) was then re-precipitated in n-pentane. The precipitate was filtrated by using a 0.2 µm membrane filter. The samples were washed with n-pentane, filtered again, and dried in the vacuum oven at 60°C for 24 hours.

2.4. Reaction of PLA-MA with Benzyl Amine

For obtaining the better proof of grafting reaction, approximately 0.5 g of PLA-MA was dissolved in 50 mL chloroform in a 200 mL erlenmeyer flask and then benzyl amine was added to the solution. The reaction was conducted in the water bath at 40°C for 2 hours. The sample was concentrated and re-precipitated in n-pentane. The precipitate was filtrated with a 0.2 µm membrane filter. The sample was washed with n-pentane, filtrated again, and dried in vacuum oven at 60°C for 24 hours.

2.5. FTIR Measurement

Samples from three kinds of PLA-MA sampling conditions (before purification, after purification and after reaction with benzyl amine) were prepared for FTIR measurement. The samples were dissolved in 0.5% chloroform and injected to the cell (fixed thickness cell p/n 202-32002). Shimadzu FTIR spectrometer FTIR 8600PC equipment was used with the measurement conditions as followed: the analysis precision was 4 cm⁻¹; the measurement range was 4600~400 cm⁻¹; the integration time was 40 times; the mirror speed was slow; and gain was auto.

2.6. NMR Measurement

Proton nuclear magnetic resonance (¹H NMR) spectroscopy (Bruker ARX 300) was used for the analysis of sample's chemical structures. The measurement conditions were as followed: the solvent was chloroform; the amount of injected sample was 50 mg; the internal standard was TMS; the measurement temperature was 300 K; the integration time was 8~16 times; and the false delay was 2 seconds.

2.7. Determination of Molecular Weight by Gel Permeation Chromatography (GPC)

The number (M_n) and weight average (M_w) molecular weights of pure PLA, PLA after kneading and PLA-MA were evaluated by The GPC (GPC-900, Nihon-bunko co., Japan). The conditions of analyzing were as followed: the column used was TSK-GEL GMH_{HR}-H with the size of 7.8 mm ID X 300 mm; the flow speed was 1.0 mL/min.; the mobile phase solvent was chloroform; the injection volume and concentration were 100 µL, 1, and 0.5%; the column temperature was 40°C; the detector was RI; and the standard was polystyrene.

2.8. Compounding PLA, PLA-MA, and WF

Compounding PLA and WF as well as PLA, PLA-MA and WF were carried out by using a kneader at 180°C and 30~90 rpm, 10 min. That is, a prescribed amount of PLA with or without PLA-MA was placed into the kneader, thermostated at 180°C and 30 rpm for 2 min. The WF was added subsequently in 3 min. The rate of rotation was increased to 90 rpm and mixing was continued for 5 min. The content of filler was varied from 0 to 60% (i.e., 0, 10, 20, 30, 40, 50, and 60%). The amount of matrix and WF were 24 grams, being enough to fill up the mixing chamber and causing torque while kneading.

2.9. Preparation of Composite Sheet

Compounded samples were molded into sheet by hot pressing with hot press (Toyo Seiki 10 t bench) for the preparation of test specimens. The prescribed amount of compounded samples (5~7 grams) were placed between a pair of terephthalate sheet with 0.3 mm thick space bad. The temperature of the hot press was 200°C, and the samples were subjected to 0~50 and 150 kgf/cm² pressure for 2 and 0.5 min, respectively. After subsequent cold pressing at the same pressure for 30 sec, the sheets were then cooled at room temperature.

2.10. Tensile Test

Strip samples 80.0 × 5.0 × 0.3 mm were prepared from composite sheets. Tensile tests were made on these strip samples with a Shimadzu Autograph DCS-R-500. Test specimens with a span length of 40 mm were tested at a cross head speed of 10 mm/min after conditioning at 20°C and 60% R.H. The average values of tensile strength, breaking elongation,

and Young's modulus with ten replications were reported.

2.11. Water Absorption and Thickness Swelling Tests

Square samples of 50.0 × 50.0 × 0.3 mm size were prepared from the composite sheets. Water absorption and thickness swelling tests were made on these square samples in three replications. The samples were dried overnight in the vacuum oven at the temperature of 60°C and then stored in a desiccator. The weight and thickness (W1 and D1) of the samples were measured after conditioning at 20°C and 60% R.H. Subsequently, the samples were dipped for 24 hours to water that had been conditioned at a room adjusted to 20°C, 60% R.H. for 48 hours. Then, the samples were wiped, and the weight and the thickness (W2 and D2) were measured. Finally, the samples were dried in the 60°C oven in vacuo to obtain the constant weight (W3). Water absorption and thickness swelling were calculated as shown in the following Eq. (1. and 2).

$$\text{Water absorption} = \frac{W2 - W3}{W1} \times 100\% \quad (1)$$

$$\text{Thickness swelling} = \frac{D2 - D1}{D1} \times 100\% \quad (2)$$

2.12. Melt Viscosity and Flow Temperature Tests

The melt viscosity and the flow temperature of the composites were measured by a flow tester (Shimadzu CFT-500 C). Approximately 1.0~1.2 grams of the kneaded samples after being dried in 60°C oven in *vacuo* for 48 hours were prepared for each test. In this test, the flow temperature of the samples was determined automatically when the melts were extruded through the pinhole of a die fitted at

the bottom of the cell. The diameter of die and its length-to-diameter (L/D) ratio used were 1 mm and 10, respectively. The measurements were performed in a temperature range from 50 to 300°C with a temperature rise rate of 10°C/min under a constant stress of 1.225×10^7 Pa after preheating time of 120 s. The apparent melt viscosity of the sample was automatically calculated as a ratio of shear stress to shear rate.

3. RESULTS and DISCUSSION

3.1. FTIR and NMR Analysis of PLA-MA

The FTIR and $^1\text{H-NMR}$ spectra of PLA, PLA and 10% MAH, and PLA-MA prepared from PLA with 10% MAH and 15% DCP based on MAH weight before and after purification, and PLA-MA with benzyl amine are presented in Figs. 1 and 2. In the FTIR spectra of PLA and 10% MAH, and PLA-MA (before purification) the peak at around 700 cm^{-1} corresponds to C=C of MAH, and the small peak at 1850 cm^{-1} is characteristic for C=O of MAH (Fig. 2). In the spectrum of PLA-MA after purification in which unreacted of MAH was removed, the peak at around 700 cm^{-1} disappears, while the peak at 1850 cm^{-1} becomes smaller but still exists. Furthermore, benzyl amine reacts on the maleoyl group of PLA-MA, so if the addition occurs, the peaks from amino group at around 3500 and 3411 cm^{-1} , and benzene ring at around 1618, 1589, and 690 cm^{-1} exist. In the spectrum of PLA-MA with benzyl amine, the peak at around 690 cm^{-1} can be seen, but it is not reliable owing to much noise.

For a better proof of the grafting, the proton NMR was used. The $^1\text{H-NMR}$ spectra of PLA and 10% MAH, PLA-MA before and after purification, and PLA-MA with benzyl amine are shown in Fig. 3 (A, B, C, and D). The

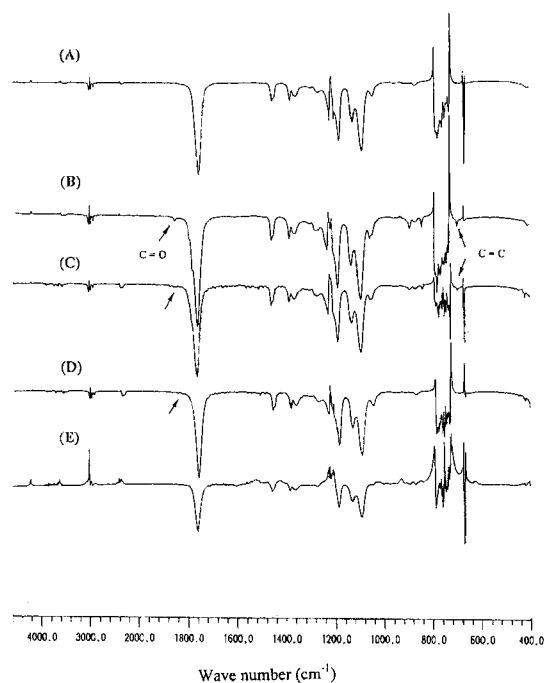


Fig. 1. Infra red spectra of related samples (A: PLA; B: PLA and 10% MAH; C: PLA-MA before purification; D: PLA-MA after purification; E: PLA-MA with benzyl amine).

signal around 1.5~1.6 ppm corresponds to the methyl proton of PLA side chain. The signals at 5.2 ppm, 7.0 ppm, and 7.2 ppm correspond to methine proton of PLA side chain, C=C proton of MAH, and the solvent, respectively. After kneading (reaction), the integral value of MAH proton decreases due to the opening of the C=C bonds to form the C-C bonds. After purification, the free un-reacted MAH was completely extracted results in the peak of the proton on the C=C bonds have not existed in the spectra of this sample (Fig. 3C). On the other hand, in the spectra of the PLA-MA reacted with benzyl amine, it is expected that the benzene ring signal is present at around 7.3 ppm, but the signal overlaps with solvent peaks. However, by magnifying the signal, it was found that the peak area is obviously bigger

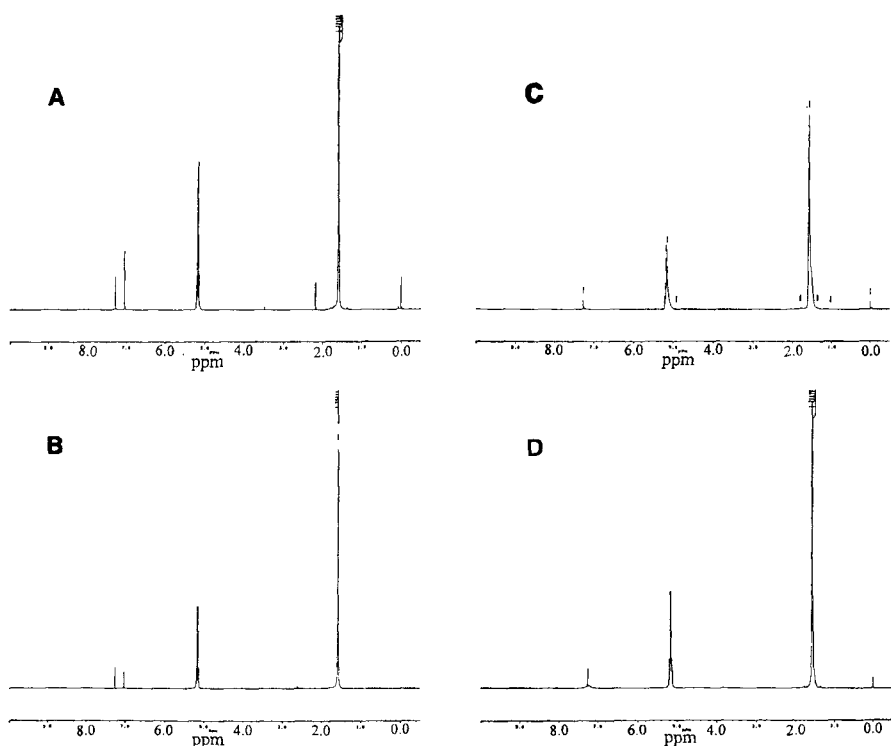


Fig. 2. ¹H-NMR spectra of PLA and 10% MAH (A), PLA-MA before and after purification (B and C) and PLA-MA with benzyl amine (D).

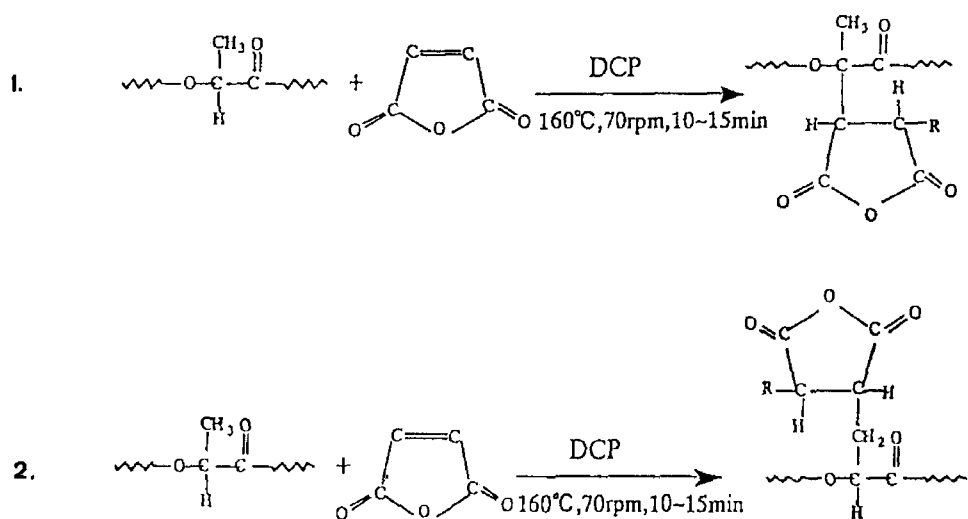


Fig. 3. Proposed reaction mechanisms between PLA and MAH in the presence of DCP.

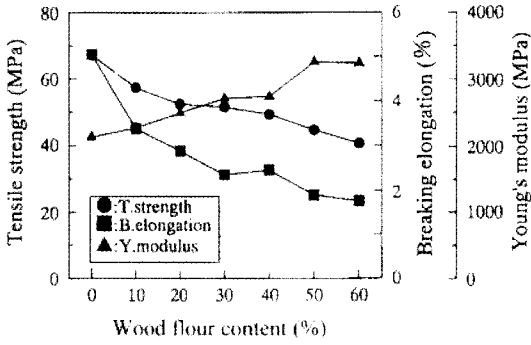


Fig. 4. Relationship between WF content and tensile properties of PLA-WF composites.

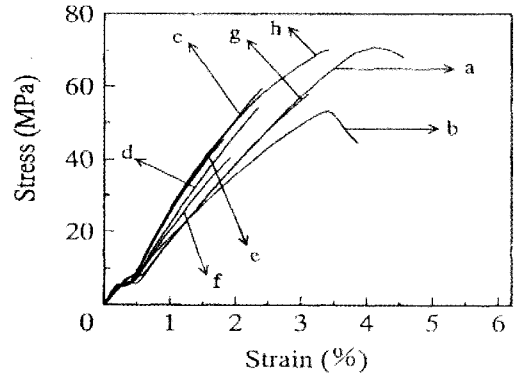


Fig. 7. Characteristic stress-strain curve for PLA, PLA-MA films, PLA/WF and PLA/PLA-MA/WF composites (a: PLA; b: PLA-MA; c: PLA/WF (90/10); d: PLA/WF (70/30); e: PLA/WF (50/50); f: PLA-MA/WF (50/50); g: PLA/PLA-MA/WF (45/5/50); and h: PLA/PLA-MA/WF (40/10/50).

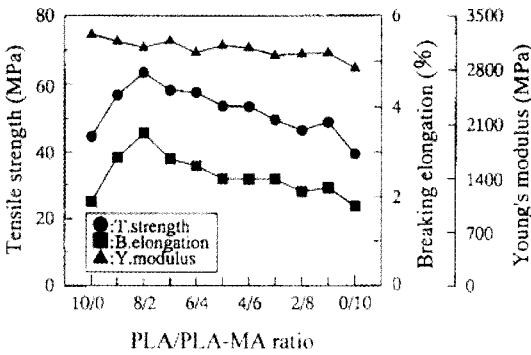


Fig. 5. Relationship between PLA/PLA-MA ratio and tensile properties of composites.

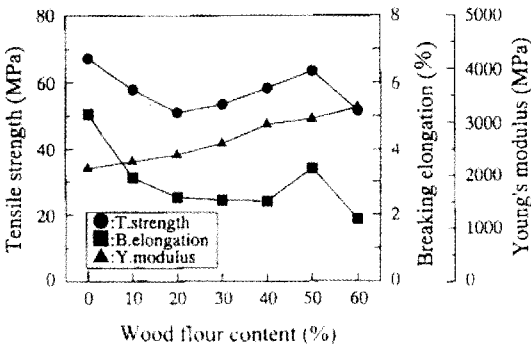


Fig. 6. Relationship between WF content and tensile properties of composites (PLA: PLA-MA = 4: 1).

3.2. Tensile Properties of PLA/WF or PLA/MPLA-MA/WF Composites

Keeping the kneading conditions at 180C and 30~90 rpm, for 10 min, the ratios of filler content in PLA and WF composites and PLA-MA content in PLA/PLA-MA/WF composites were changed. The tensile strength, the breaking elongation and the Young's modulus obtained from the stress-strain curves are shown in Figs. 4, 5, 6 and 7.

For understanding the stiffness and the strength of short-fiber reinforced thermoplastics between the non polar PLA and polar WF, several factors are very influential. These are dispersion, adhesion, fiber breakage and agglomeration, fiber distribution and orientation, the volume/weight fraction of the fibers, micro-structure etc. Fig. 4 exhibited that the tensile strength, breaking elongation, and Young's modulus of WF and PLA composites were significantly influenced by WF loadings. Tensile strength and breaking elongation of WF and PLA composites were found to decrease stea-

rather than the solvent peak. From the above results, it can be confirmed that part of MAH has been grafted to the chain of PLA. The possible reaction mechanisms of PLA and MAH in the presence of DCP are shown in Fig. 3.

dily with WF loading. It was observed that the tensile strength and breaking elongation of PLA and WF composites were 67.30~40.76 MPa and 5.1~1.8% at a WF loading of 0~60%. Conversely, the Young's modulus value increase linearly with increasing the WF loading. The Young's modulus value was increased from 2100 MPa to around 3250 MPa when WF loading was increased from 0 to 60%. These are a common observation with almost all filled polymer systems (Kishi *et al.*, 1989; Zaini *et al.*, 1996; Febrianto *et al.*, 1999; and Sombatsompop *et al.*, 2005). Reduction in breaking elongation and tensile strength were probably caused by a number of reasons including: (i) poor dispersion of the fibers in the matrix; (ii) moisture pick up, (iii) increases of interfacial defect or debonding between PLA and WF. As for the first reason, WF fibers tended to cling together, due to strong interfiber hydrogen bonding, and resisted dispersion of the individual fiber as the fiber content was increased. In the second case, since the WF is hydrophilic in nature and was chemically untreated (in this part of the experiment), the fibers may have picked up moisture during storage, processing, and testing. It was thought in this work that the moisture may have interfered with the adsorption effects by reducing the effect of physical bonding and potentially acting as a lubricant between the fiber surface and PLA phases. The last reason for interfacial defects and debonding between PLA matrix and WF filler was due to WF is polar and hydrophilic material, while PLA is non polar and hydrophobic which are not compatible each other, thus blending both materials resulted poor adhesion at interface. On the other hand, substantial improvement of the Young's modulus was found as the WF

added. This is probably caused by the fact that the WF is more rigid than PLA matrix polymer.

On the contrary, when only 10% PLA-MA compatibilizer was added to the PLA and WF composite, the tensile properties, particularly tensile strength of the composites, increased phenomenally. The 10% of PLA-MA amount was the maximum limit of PLA-MA addition (Fig. 5). The composites with 10% PLA-MA, 40% PLA, and 50% WF had a tensile strength value 1.42 times greater than that of the composites composed of 50% PLA and 50% WF, and about 0.94 times as compared to pure PLA. From these observations, the reason for the positive role of PLA-MA addition is apparent and attributable to the enhanced formation of PLA-MA (MAH-modified PLA) and acting as a compatibilizer in the composites. It was reported that addition small amount of MAPP onto WF and PP composites (Kishi *et al.*, 1989; Han, 1990; and Sombatsompop, 2005), MTIR (maleic anhydride modified *trans*-1,4-isoprene rubber) onto *trans*-1,4-isoprene rubber (TIR) and WF composites (Febrianto *et al.*, 1999) greatly enhanced the tensile properties of the composites. Furthermore, the possible reason for its negative role when the PLA-MA was added to PLA and WF composites higher than 10% presumably due to 1) the increased occurrence of low molecular weight substances within the composites with excess addition of PLA-MA (un-reacted MAH in the PLA-MA remained and its reactants with other additives); 2) the degradation of WF and PLA resulting from kneading and molding at high temperature in the presence of excess acidic MAH. It is also clear from Fig. 5, that the tensile strength of PLA-MA film is smaller than that for the PLA film. One of the reasons for this presumably

due a lower molecular weight of PLA-MA compared to PLA film (Table 1).

Tensile properties of the composites composed of PLA, PLA-MA, and various WF contents (0~60%) with the weight ratio of PLA to PLA-MA used was 4:1 was also prepared and evaluated. The tensile strength, breaking elongation, and Young's modulus of the composites gave almost similar trend. They increased with increasing the WF from 20 to 50%. The effect of PLA-MA compatibilizer was greater in the composites having more WF content up to 63.55 MPa for 50% WF loading (Fig. 6). Typical comparative stress versus strain curves of PLA, PLA-MA, WF and PLA with or without PLA-MA compatibilizer under various WF contents are shown in Fig. 7, where a decrease in failure strain was observed with an increase in WF content due to restrictions posed by the WF. However, addition of the PLA-MA compatibilizer to the composites helped in stress transferring from the matrix to fiber, and shifted the mechanical characteristics of the system towards a stiffer and stronger material with decreased elongation. It is known that the strength of the short fiber composites is dependent on the transferal of load from the matrix to the fibers. Well developed interactions between the stronger cellulose fibers and the plastic phase are, thus, required for this type of mechanical behavior which suggests that PLA-MA promotes adhesion between the fibers and the plastic components.

Based on these findings, it can be therefore concluded that the improved mechanical properties of the composites presumably resulted from the esterification between anhydride groups of PLA-MA and -OH groups of WF. This grafting may improved the adhesion between WF and PLA-MA.

Table 1. The number (Mn) and weight average (Mw) molecular weights of PLA and PLA-MA

Sample	Mn ($\times 10^4$)	Mw ($\times 10^4$)
PLA (pure)	10.74	19.58
PLA-MA	3.35	9.32
PLA (15 min. kneading)	2.54	7.71

3.3. Water Absorption and Thickness Swelling of the Composites

The effects of WF filler content with and without PLA-MA compatibilizer addition on several physical properties (i.e. water absorption and thickness swelling) of composites composed of 50% WF, 40~50% PLA, 0~10% PLA-MA were presented in Fig. 8.

It is obvious that the water absorption and thickness swelling values of composites of WF and PLA much affected by WF content and PLA-MA addition. The absorption of water by PLA or PLA-MA, which is hydrophobic in nature, is negligible. As a result, the increase in water absorption and thickness swelling values are proportional to the WF content in the composites due its hydrophilic material (Fig. 8). Use of PLA-MA compatibilizer, however, decreased the water absorption and the thickness swelling at the same WF loading, which might be attributed to some of the hydrophilic OH-groups reacting with acid anhydride to form ester linkages when kneading at 180°C for 10 min, followed by hot-pressed at 200°C for 2.5 min and thereby giving lower water absorption and thickness swelling values. Similar results had been investigated by Febrianto *et al.*, (2006) using MAH in the WF-recycled polypropylene (RPP) composite, and Febrianto *et al.*, (1999) using MTIR in the WF-TIR composites.

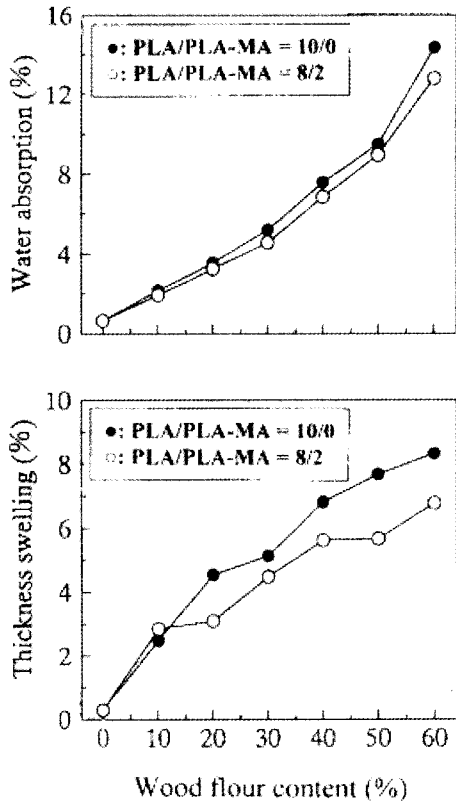


Fig. 8. Relationships between WF content and water absorption and thickness swelling of PLA/WF and PLA/PLA-MA/WF composites.

3.4. Flow Temperature and Melt Viscosity of the Composites

The flow temperature and melt viscosity of composites obtained from various amounts of WF and PLA-MA are presented in Figs. 9 and 10. The flow temperature and melt viscosity of the composites increased as the WF content increases (Fig. 9). On the other hand, due to kneading at temperature as high as 180°C, a reaction of MAH and PLA in the presence of DCP resulted in a decrease in molecular weight (Table 1). This fact might be due to the depolymerization (chain scission) of the polymer. As a result, the viscosities of the composites are lowered especially at lower filler-loading com-

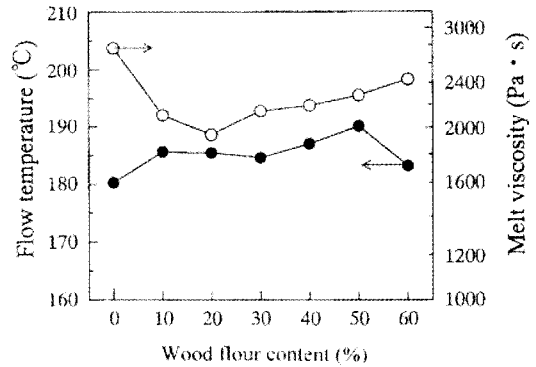


Fig. 9. Relationships between WF content and flow temperature and melt viscosity of the PLA-WF composites.

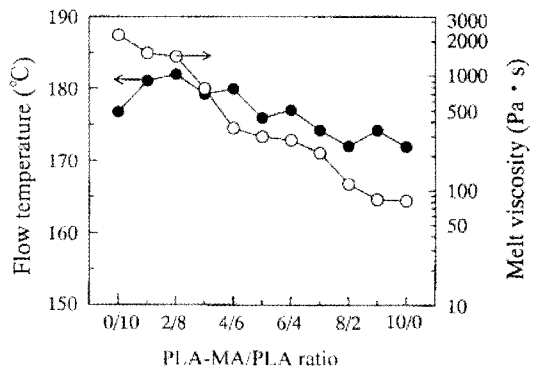


Fig. 10. Relationships between PLA-MA/PLA ratio and flow temperature and melt viscosity of composites.

posites. Addition of PLA-MA to the composites significantly decreased the melt viscosity of the composites (Fig. 10). The higher the amount of PLA-MA introduced, the more was the melt viscosity reduced. On the contrary, the flow temperature of the composites is not so much affected by the addition of PLA-MA.

4. CONCLUSION

PLA-MA can be prepared satisfactory through mechanical blending PLA and MAH in the presence of DCP in the kneader at 160°C and 30~70 rpm, for 15 min. The FTIR and

¹H-NMR gave evidence of PLA-MA formation. After kneading and reacting with MAH and DCP, the number (Mn) and the weight average (Mw) molecular weights of PLA decreased as compared to the original PLA. The presence of WF in the composites decreased the physical and mechanical properties of composites. An addition of 10% PLA-MA as a compatibilizer improved tensile strength, breaking elongation, Young's modulus, water absorption and thickness swelling, and increased flow temperature and decreased melt viscosity of the composites. The improved composite consist of 50% WF, 40% PLA, and 10% PLA-MA had 1.42 times increased in tensile strength but not over PLA alone, and absorbed considerably less water compared to those of the composites not having a compatibilizer.

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