COMPOSITE OF WOODFLOUR AND POLY LACTIC ACID IV®: Processing Conditions for Production of Composites

(*Komposit dari Serbuk Kayu dan Asam Polilaktat IV : Kondisi proses untuk produksi komposit*)

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ABSTRAK

Sifat mekanis dan sifat pengaliran komposit *Poly Lactic Acid* dengan serbuk kayu dievaluasi pada berbagai proses pembuatan, berbagai kadar *modifier (maleic anhydride/MAH)* dan radikal inisiator (*Dicumyl peroxide/DCP)*. Pada proses dua tahap, MPLA dipersiapkan lebih dahulu, kemudian ditambahkan pada pengisi (WF) dan matrik (PLA) saat pencampuran. Pada proses kontinyu, PLA dimasukkan kedalam alat pencampur (*kneader*), dikuti dengan MAH, inisiator dan bahan pengisi secara beurutan. Pada proses satu tahap, semua bahan baku (PLA, WF, MAH dan DCP) diaduk manual, kemudian dimasukkan ke dalam mesin pencampur. Suhu, waktu dan laju rotasi pencampuran berturut-turut dalam pembuatan komposit PLA dengan serbuk kayu adalah 180 C, 15 min., dan 30~90 rpm. Kekuatan tarik, elongasi patah dan modulus young's komposit yang dibuat melalui proses dua tahap lebih tinggi dari proses kontinyu dan atau proses satu tahap. Urutannya adalah sebagai berikut: proses dua tahap > proses kontinyu> proses satu tahap. Jumlah optimum dari *modifier* MAH dan radikal inisiator DCP berturut-turut adalah 5% (berdasarkan berat matriks), dan 15% (berdasarkan berat MAH). Viscositas leleh dan suhu pengaliran komposit cenderung menurun dengan penambahan baik MAH maupun DCP.

Keywords: processing method, kneading condition, modifier, initiator, flow behavior, tensile properties

INTRODUCTION

In our previous publications (Febrianto *et al.*, 2002a; 2002b, and 2002c) the modification of PLA and 10% MAH with 15% DCP was conducted in the kneader at 160°C, 30~70 rpm, for 15 min. The resulting MAH-modified PLA, so called MPLA, was then evaluated as a compatibilizer for PLA-WF composites. The FTIR and ^{1}H-NMR analysis gave evidence of MPLA 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 worsened the tensile strength and several other physical properties. An addition of 10% MPLA as a com-

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patibilizer 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 not having a compatibilizer. Through FTIR measurement it was proved that grafting by esterification had been attained between the OH-groups of WF and acid anhydride groups of MPLA during kneading at 180°C, 30-90 rpm for 10 min. Furthermore, by titration analysis, the MAH content of MPLA prepared from 10~20% MAH with 0.3~15% DCP was 0.83~1.66%. The tensile strength varied with the amount of MAH content.

It was observed that the composites of PLA-WF, with or without MPLA compatibilizer, were easily degraded by termites (*Coptotermes formasanus*) and bacteria (*Baccilus sp.*) but they were hardly attacked at all by the brown-rot (*Tyromyces palustris*) and white-rot (*Coriolus versicolor*) fungi within the experimental conditions adopted. The tensile properties of the composites varied with the filler types. The tensile properties of the composites with cellulose powder (CP) based filler are greater than those with WF and CS (corn starch) based fillers. The order is CP>WF>CS. The scanning electron microscopy (SEM) showed that addition of MPLA compatibilizer to the composites improved the dispersion and the adhesion of the filler and the matrix. It was found that after immersion in cold water for 24 hours and drying at 60°C for 7 days or 105° C for 3 days, the tensile properties of the composites based on CP and WF fillers were unchanged. The composites based on CP and WF fillers were more resistant to water than the CS-filled composite. After storage in a room adjusted to 20° C and 60 % R.H. for 3 months, the moisture content (MC) of the composites with CP/WF/CS fillers was less than 6%. The CP and WF-filled composites with MPLA compatibilizer tended to give lower MC than compatibilizer-free composites.

The mechanical properties of composites are considered to be affected by processing method and kneading conditions (such as mixing temperature, mixing time, and rate of rotation) (Febrianto *et.al.*, 2001; Sean *et.al.*, 1991; and Takase and Shiraishi, 1989). In the earlier part, MPLA was prepared in advance and added to the PLA and fillers (CP/WF/CS) while kneading. This process may be referred to *two step* process. However, if the process completed in *one step* or *continuously*, it may be termed a shortened or simplified. In the present study, in order to standardize the process, the way and the conditions of processing of composites were investigated. The effect of concentration of radical initiator (DCP) and modifier (MAH) on tensile and flow properties were explored.

MATERIALS AND METHODS

Materials

PLA used was LACTY # 9000 which was supplied by Shimadzu co., with Mn and Mw based on GPC analysis were 7.12 x 10^4 and 13.68 x 10^4, respectively. DCP, 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. The fillers used were CP and WF.

Methods

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

Compounding the Composites. The methods of processing composites were as follows:

1. ***Two-step process***: MPLA was prepared in advance and added to the filler and PLA. This mixture was placed into a kneader which had been preheated to 180 °C and was rotated at 30 rpm for 5 min. After charging, the rate of rotation was increased to 90 rpm and kneading was continued for 5 min. (Fig. 1).
2. ***Continuous process***: PLA was placed into a kneader at 160~210° C at 30 rpm, for 1-2 min. After charging of the PLA, MAH and radical initiator were added into the molten PLA. After further reaction for 1 min, the filler was added within 3-4 min. The rate of rotation was increased to 50~110 rpm and kneading was continued for 4~14 min. (Fig. 2).
3. ***One-step process***: Total 24 grams of PLA, WF, MAH, and DCP were hand-mixed. This mixture was placed into a kneader, which had been preheated to 180°C and was rotated at 30 rpm within 5 min. After charging, the rate of rotation was increased to 90 rpm and kneading was continued for 10 min. (Fig.3)

Preparation of Composite Sheet. Kneaded samples were molded into sheet by hot pressing with Toyo seiki 10 t bench hot press for testing. The prescribed amount of kneaded samples (5~7 grams) were placed between a pair of terepthalate sheet with 0.3 mm thick spacer. The temperature of the hot press was 200°C, and the sample were subjected to 0~50 and 150 kgf/cm^2 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.

Tensile Test. Strip samples 80.0 x 5.0 x 0.3 mm were prepared from composite sheets. Tensile tests were made on these strip samples with a Shimadzu Autograph DCS-R-500. The measurements were made with a span length of 40 mm and cross head speed of 10 mm/min in a room adjusted to 20°C and 60% R.H. The average values of tensile strength, breaking elongation, and Young's modulus were obtained automatically from ten repeated measurements.

Viscosity Measurement. A flow tester (Shimadzu CFT-500 C) was used for the melt viscosity measurement. Approximately 1~1.2 g of the kneaded samples after being dried at room temperature in *vaccuo* for 48 hours were prepared for measurement, being made at 200°C under a constant load of 100 kgf.

Flow Test. Thermal flow temperature of the blended samples was measured by the flow tester. The measurement was made at constant heating rate of 10° C/min and under compresive load of 100 kgf.

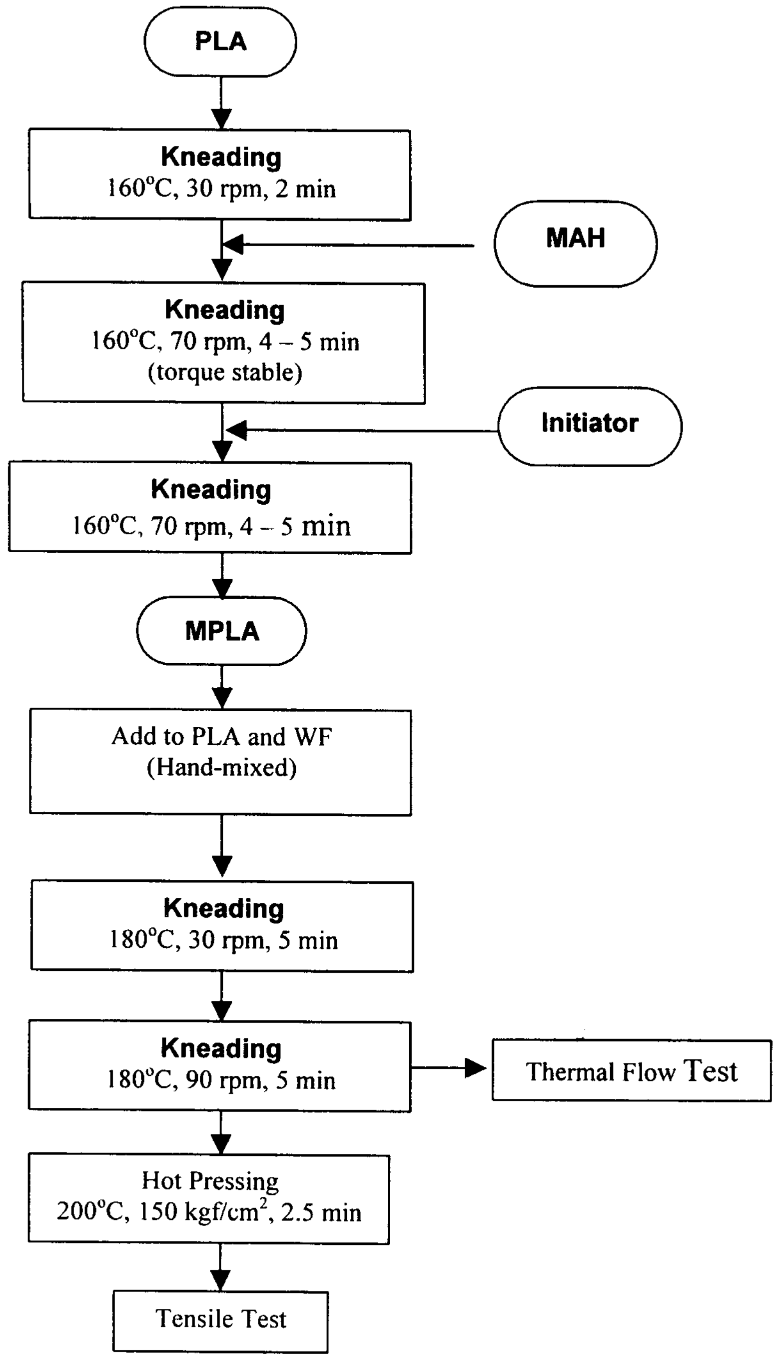

Figure 1. Flow chart of two-step processing method

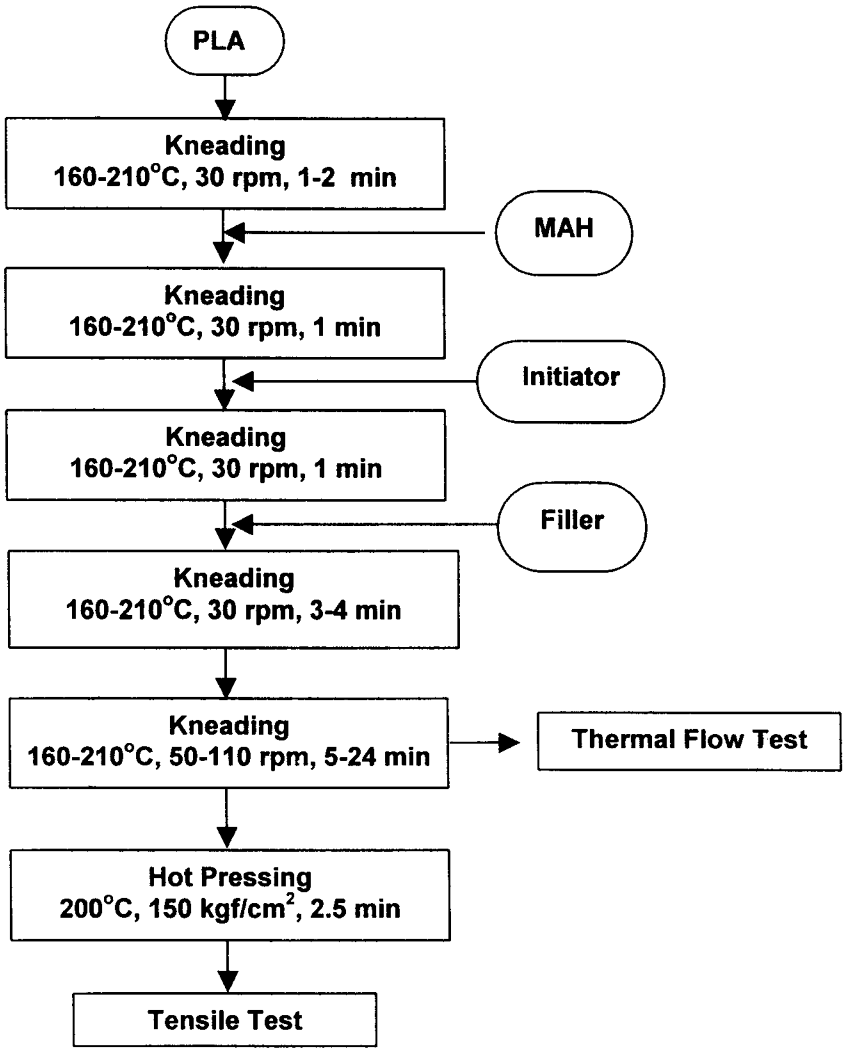

Figure 2. Flow chart of continuous processing method.

RESULTS AND DISCUSSION

Tensile and Flow Properties of Composites Prepared Using Continuous Process

In our previous publications (Febrianto *et.al.*, 2002a; Febrianto *et.al.*, 2002b; and Febrianto *et.al.*, 2002c) the composites were prepared using two-step process. It is quite possible that the tensile properties of composites vary with different process. Therefore, the tensile properties of composites were studied under various process and mixing conditions. In this part, the tensile properties of composites were evaluated using continuous process under various mixing conditions, and various concentration of modifier (MAH) and initiator (DCP).

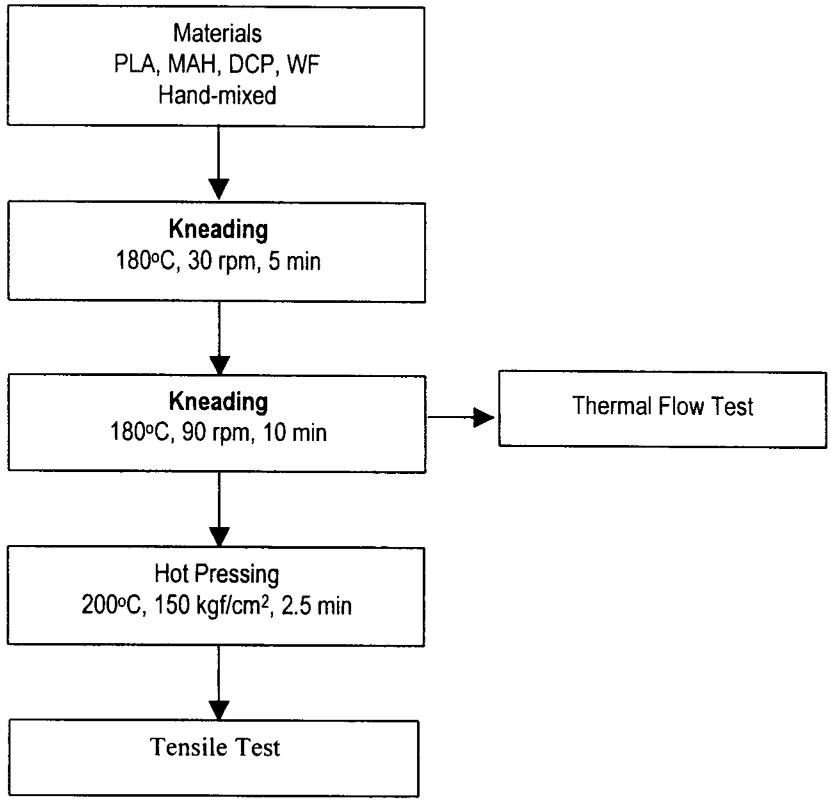

Figure 3. Flow chart of one-step processing method.

Effect of Mixing Temperature on Tensile Properties of Composites

Figure 4. shows the tensile properties of composites containing 50% PLA, 50% CP, 5% (based on PLA weight) MAH and 15 % DCP (based on MAH weight) under various kneading temperatures ranging from 160° C to 210° C. The rate of rotation and the kneading time were fixed at 90 rpm, and 15 min, respectively.

It is clear that the tensile strength, breaking elongation, and Young's modulus of composites increase with the rise in temperature and then decrease, showing maximum improvement at 180° C. In fact, in short-fiber composites, the fiber aspect ratio, the quality of dispersion, and the interface between fiber and polymer control directly the performance of the composites (Febrianto *et al.*, 2001; Han and Shiraishi, 1990, 1991; Raj and Kokta, 1991; Takase and Shiraishi, 1989; Sean *et.al.*, 199; Sapieha *et.al.*, 1989). At low temperature, e.g. below 180° C, the viscosity as well as the shear stress of the mixture is high and this causes the breakdown of the fibers during mixing. However, the decrease of strength at mixing temperatures above 180° C can be explained by the thermal degradation of the cellulose fibers. In fact, we observed that the color of the mixture became darker with the increase of the mixing temperature.

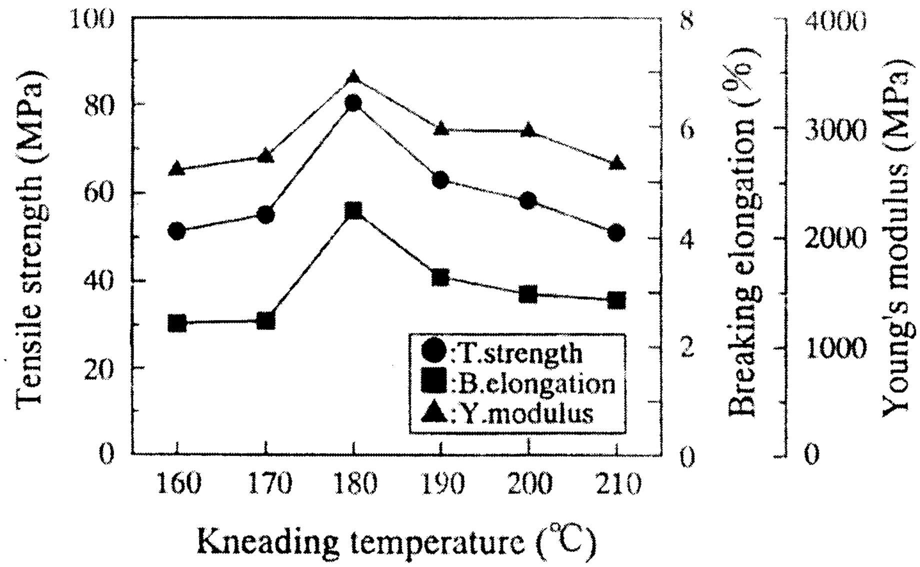

Figure 4. Effect of kneading temperature on tensile properties of composites.

Effect of Mixing Time on Tensile Properties of Composites

Figure 5 reveals the tensile properties of composites containing 50% PLA, 50% CP, 5% MAH and 15% DCP under various kneading times ranging from 10 to 30 min. All other kneading parameters (i.e., rate of rotation and mixing temperature) which affected the tensile properties of the composites remained constant at 90 rpm, and 180° C.

The tensile strength, the breaking elongation, and the Young's modulus increase with mixing time initially, but they decrease with increased mixing time up to 15 min. The quality of dispersion control the performance of short-fiber composites (Febrianto *et.al.*, 2001; Han and Shiraishi, 1990, 1991; Raj and Kokta, 1991; Takase and Shiraishi, 1989; Sean *et.al.*, 199; Sapieha *et.al.*, 1989). In the case of PLA-CP composites in the presence of MAH and DCP, an increase in mixing time from 10 to 15 min. provides improved dispersion for the mixture. In order to maximize the tensile properties and to avoid the possible damage to cellulose fibers, 15 min. was found to be the preferred mixing time.

Effect of Rate of Rotation on Tensile Properties of Composites

Keeping the mixing temperature and mixing time at 180° C and 15 min, respectively, the rate of rotation of the kneader was varied from 30~110 rpm. The results on tensile strength, breaking elongation, and Young's modulus are shown in Fig. 6.

At the initial level, increasing the rate of rotation from 30 to 50 rpm resulting in almost similar value of the tensile strength. The tensile strength increases with increasing the rate of rotation to 90 rpm and decreases up to this point. These facts

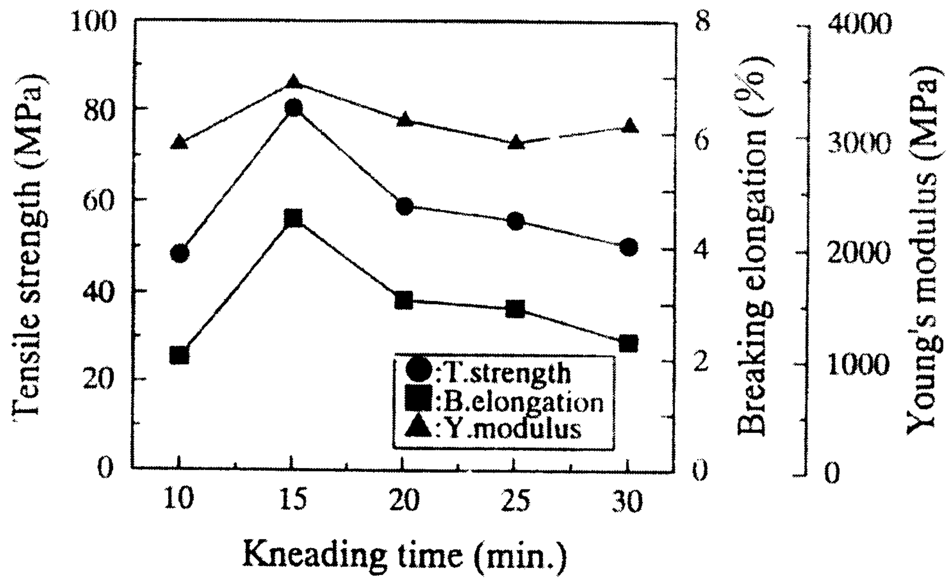

Figure 5. Effect of kneading time on tensile properties of composites.

show that the dispersion of the fibers within the composites and the adhesion between the matrix and the fiber fillers can be enhanced by a higher rate of rotation.

Effect of MAH Concentration on the Tensile and Flow Properties of Composites

In the previous experiment the amount of MAH used was 5 parts of the matrix, and CP was used as a filler. In this experiment, the amount of MAH was varied from 0~20 parts of matrix, and WF was used as a filler. The effect of added amount of MAH on the tensile and flow properties of composites comprised of 100 parts of PLA, 100 parts WF, 15 parts of DCP (based on MAH weight) were investigated. The kneading temperature, kneading time, and the rate of rotation of the kneader were set at 180° C, 30~90 rpm, for 15 min., respectively. The results are presented in Table 1.

The tensile strength and the breaking elongation of composites both increased with increases in the MAH content, yielding a maximum at its 5 parts addition and the value decreased with further addition. Almost similar phenomena occurred with the Young's modulus. Addition of MAH up to 5 parts results in the highest Young's modulus value and remain constant with further addition. The reasons for positive role of MAH addition is apparent and attributable to the formation of MPLA. The negative role by contrast which appeared when excess MAH was used, is not so clear and is difficult to understand. Possible reasons for this are (1) the reduction of initiator caused by possible reaction with excess MAH; (2) The degradation of WF and PLA resulting from kneading and molding at high temperature in the presence of excess acidic MAH (Febrianto *et al.*, 2001; Takase and Shiraishi, 1989).

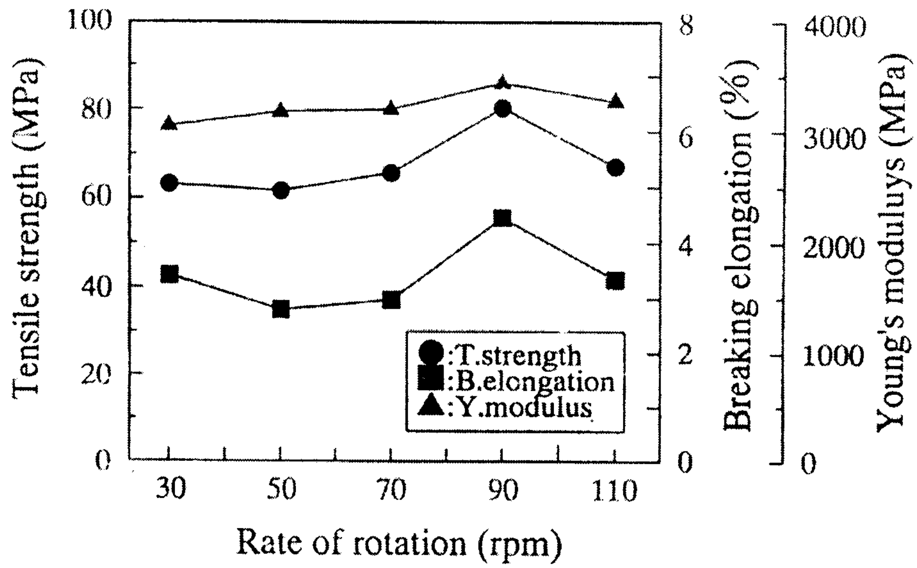

Figure 6. The effect of the rate of rotation on tensile properties of composites.

Table 1. Tensile and flow properties of PLA-WF-MA-DCP composites prepared using the *Continuous process* under various MAH concentration

MAH Content (%)	TS (MPa)	BE (%)	YM (x10^{-3} MPa)	MV (Pa.S)	FT (°C)
0	41.33	1.64	3.000	347.7	165
1	47.77	1.85	3.229	136.7	165
3	53.22	2.10	3.101	125.6	165
5	65.16	3.30	3.211	126.1	165
10	50.54	1.98	3.080	101.1	165
15	42.66	1.76	2.975	87.5	160
20	37.68	1.56	29.08	45.2	160

Note : TS : Tensile Strength; BE : Breaking Elongation; YM : Young's Modulus; MV : Melt Viscosity; FT : Flow Temperature.

Conversely, the melt viscosity and flow temperature of the composites were found decrease with the addition of MAH. The higher the amount of MAH added, the lower is the melt viscosity and the flow temperature of composites (Table 1). These facts might be due to the depolymerization (chain scission) of the matrix as a result of the MAH addition (Febrianto *et al.*, 2001; Takase and Shiraishi, 1989).

Effect of DCP Concentration on the Tensile and Flow Properties of Composites

The effect of the added amount of DCP radical initiator on the tensile properties and flow properties of the composites comprised of 100 parts of PLA, 100 parts

CP, 5 parts of MAH were studied. The DCP varied from 0~25 parts (based on MAH weight). The kneading temperature, kneading time, and the rate of rotation of the kneader were set at 180° C, 30~90 rpm, for 15 min., respectively. The results are shown in Table 2.

The tensile strength, the breaking elongation, and the Young's modulus of composites increased with increases in DCP concentration, yielding a maximum at 15 parts addition and decreasing with further addition. This can be explained in the following way. First, the increase in the concentration of the radical initiator increases the formation of PLA macro radical. This results in the enhancement of the strength of the composites because of the MAH addition to the PLA molecules. This also results in lowering the molecular weight of PLA, consequently, in a decrease of the strength of composites. Consequently, maximum strength of composite appears when the amount of initiator DCP is optimal.

On the other hand, the melt viscosity of the composites decreased with increases in the radical initiator content. An increase in the concentration of the initiator increases the formation of radicals on PLA chains. resulting in the degradation of PLA matrix. The flow temperature of the composite remained constant with addition of radical initiator.

Table 2. Tensile and flow properties of PLA-CP-MA-DCP composites prepared using the *Continuous* process under various DCP concentration.

DCPContent (%)	TS (MPa)	BE (%)	YM ($\times 10^{-3}$ MPa)	MV (Pa.S)	FT (°C)
0	45.47	1.87	2.949	945.6	165
5	58.95	2.75	2.899	5.218	165
10	61.49	2.98	3.101	5.416	165
15	80.43	4.49	3.450	286.5	165
20	66.10	2.97	3.220	343.5	165
25	65.28	2.88	3.150	361.1	160

Note: TS : Tensile Strength; BE : Breaking Elongation; YM : Young's Modulus; MV : Melt Viscosity; FT : Flow Temperature.

Table 3. Tensile and flow properties of PLA-WF-MA-DCP composites prepared using the *One-Step* process under various MAH concentration

MAH Content (%)	TS (MPa)	BE (%)	YM ($\times 10^{-3}$ MPa)	MV (Pa.S)	FT (°C)
0	41.33	1.64	3.199	348	165
1	40.97	1.93	2.909	332	170
3	57.06	2.51	3.163	192	160
5	57.93	2.83	3.342	111	165
10	53.54	2.44	3.152	76.5	165
15	50.83	2.37	3.073	35.3	160

Note: TS : Tensile Strength; BE : Breaking Elongation; YM : Young's Modulus; MV : Melt Viscosity; FT : Flow Temperature.

Tensile and Flow Properties of Composites Prepared Using One-Step Process

In the previous experiments, it was demonstrated that MAH can be easily reacted with PLA in the presence of an initiator (DCP) forming an ester linkage with woody filler in its composites. In this experiment, the PLA, WF, MAH, and DCP were simply blended in *one-step* process. The MAH content was varied from 0~15%. DCP used was 15% based on MAH weight. The kneading condition were adopted from the best kneading conditions that have been proved in the previous experiments, that are, 180° C, 30~90 rpm, 15 min. The tensile and flow properties of composites were examined and data was presented in Table 3.

The tensile strength, the breaking elongation, and the Young's modulus of composites increased with increases in the MAH content, yielding a maximum at its 5 parts addition and the value decreased with further addition. Once more, it is stipulated that MAH can be easily grafted with PLA in the presence of initiator DCP and then forming ester linkage with woody filler materials in its composite. The tensile strength, the breaking elongation, and the Young's modulus of composite prepared using one-step process were a little lower compared to the composites prepared using the *continuous* process and *two-step* process. As a whole a summary data of tensile properties of composites of WF and PLA prepared using the *two-step* process, the *continuous* process, and the *one-step* process is presented in Table 4.

The melt viscosity of the composites was found decrease with the addition of MAH. The higher the amount of MAH added, the lower is the melt viscosity of composites These facts might be due to the depolymerization (chain scission) of the matrix as a result of the MAH addition (Febrianto *et.al*, 2001; Takase and Shiraishi, 1989). The flow temperature of the composites remained unchanged with addition of MAH up to 10%. Beyond this point, the flow temperature decreased with an increased of MAH concentration.

CONCLUSION

The optimum kneading temperature, kneading time and the rate of rotation for the production of the composites were 180° C, 15 min, 30 ~90 rpm, respectively.

The tensile strength, the breaking elongation and the Young's modulus of composites using the *Two-Step* process were higher than those of the *Continuous* or *One-Step* process. The order was as follows: *Two-Step* process > *Continuous* process > *One-Step* process.

Table 4. Tensile properties of PLA-WF composites prepared using various processing methods

Properties	PLA film	Control*	Processing Methods		
			Two-step process**	*Continuous* process***	*One-step* process****
T. Strength (MPa)	73.87	41.33	68.70	65.16	57.93
B. Elongation (%)	5.41	1.64	3.11	3.30	2.83
Y. Modulus (x 10^{-3} MPa)	2.19	3.20	3.57	3.91	3.34

Note : PLA: Lacty # 9000; MPLA was prepared from PLA and 10% MAH with 15% DCP (based on MAH weight); Kneading: 180°C, 30~90 rpm, 10 min (*two-step* process), 15 min (control, *continuous* and *one-step* process); Hot-pressing: 200° C,2.5 min, 150 kgf/cm^2; *: PLA/WF: 50/50; **: PLA/MPLA/WF: 40/10/50; *** and ****: PLA/MAH(DCP)/WF: 50/5(15)/50.

The optimum amount of MAH modifier and radical DCP initiator were 5% (based on matrix weight), and 15% (based on MAH weight), respectively.

The melt viscosity and the flow temperature of the composites tend to decrease with addition of both MAH and DCP.

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