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COMPOSITE OF WOODFLOUR AND POLY LACTIC ACID V: Properties of Poly Lactic Acid Composites with Wood in Relation to Fiber Pretreatment Technique and Processing Condition

(Komposit Tepung Kayu dan Asam Polilaktat V: Sifat-sifat Komposit Asam Polilaktat dengan Kayu Dalam Hubungannya dengan Teknik Praperlakuan Serat Kayu dan Kondisi Proses)

Fauzi Febrianto, Mariko Yoshioka, Yuko Nagai, and Nobuo Shiraishi

ABSTRAK

Sifat mekanis komposit Poly Lactic Acid (PLA) dengan pengisi cellulose powder (CP), refiner ground pulp (RGP), dan wood flour (WF) yang diberi perlakuan pendahuluan encapsulation dan asetilasi di evaluasi. Pemberian perlakuan pendahuluan berupa encapsulation pada bahan pengisi sebelum proses pencampuran komposit meningkatkan kekuatan tarik, elongasi patah, modulus Young, viskositas leleh dan laju pengaliran komposit yang dihasilkan. Urutan peningkatan adalah CP>RGP>WF. Komposit terbaik yang dihasilkan adalah komposit yang terbuat dari 50% PLA dan 50% encapsulated CP (ECP) dengan kekuatan tarik 1,21 kali dibandingkan komposit tanpa perlakuan pendahuluan encapsulation. Suhu, waktu dan laju rotasi optimum untuk pencampuran bahan komposit adalah 180 °C, 15 min., dan 30-90 rpm. Perlakuan pendahuluan asetilasi pada WF menghasilkan komposit yang lebih baik sifat mekanisnya dibandingkan PLA-WF tanpa asetilasi.

Keywords: PLA, CP, RGP, WF, encapsulation, acetylation and processing conditions

INTRODUCTION

In our previous publication (Febrianto et al., 2002) the physical and mechanical properties of composite of PLA-WF with or without MPLA compatibilizer are much affected by processing conditions. It was observed that the tensile strength, breaking elongation, and Young's modulus of composites using the Two-step process were higher than those of the the Continous process or One-step process. The order was as follows: Two-step process > Continous process > One-step

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2 Department of Forest Products Technology, Faculty of Forestry Bogor Agricultural University. P.O.BOX 168 Bogor 16001 West Java, INDONESIA. Center for Life Sciences Study, Bogor Agricultural University. Gedung PAU 3rd Floor, Kampus IPB Darmaga Bogor 16680, INDONESIA.
3 Faculty of Agriculture, Kyoto University, Kyoto 606-8502, JAPAN
process. Furthermore, the properties of composite also can be improve through chemical modification of the matrix and or the filler (Maldas et al., 1989; Hans, 1990; Raj and Kokta, 1991).

There are several methods that can be used to enhance the interfacial reaction between the lignocellulose and thermoplastics. The use of dispersing and coupling agents, pretreatment of fibers by encapsulation, or grafting and coating fibers with chemicals have all been shown to result in improvement of interfacial adhesion between the composite components. In this paper, the tensile and the flow properties of PLA composites with various types and concentration of fillers (CP, WF, and RGP) were investigated under some pre-treatment techniques (i.e., encapsulation, and acetylation) and processing conditions.

**MATERIALS AND METHODS**

**Encapsulation of Fibers with PLA**

An equivalent of 25 g of dry fibers (CP, RGP, WF) were first dispersed in 2000 ml of acetone. The solution of water-acetone was removed from fibers by filtration. The fibers were then re-dispersed in 1200 ml of the same solvent and added to a solution containing 25 g of PLA (LACTY with Mn and Mw of 10.74 x 10^4 and 19.58 x 10^4, respectively) in 300 ml chloroform. The resulting mixture was mixed using mechanical stirrer for 15 min. The solvent in the mixture (acetone and chloroform) were evaporated by stirring under heating (60°C) in the fume hood. Finally, the encapsulated fibers were left overnight in a vacuum oven at 60°C (Fig. 1).

Figure 1. Flow chart of fibers encapsulation

**Acetylation of Wood Flour**

One hundred parts of dry WF and 100 parts of acetic acid were dispersed in the 500 ml three neck round flask at 40°C for 30 min. After that, 250 parts of acetic anhydride, 375 parts of acetic acid and 1.0 part of sulfuric acid were added to the flask. Acetylation was carried out for 60 min. with temperature using from 40-77°C, followed by constant temperature of 77°C for 12 min. To eliminate by-products, 10 parts of magnesium acetate (20%aq.) and 240 parts of distilled water were added and the process was carried out in the reactor at 0-150°C for 60 min. and allowed at 150°C for 50 min. The products were then precipitated with dilute acetic acid, filtrated and washed with distilled water. Finally, the acetylated WF was left overnight in a
vacuum oven at 60°C (Fig.2). In the acetylation of wood flour - PLA composites experiment, the amount of filler varied from 10-50%.

**Compounding the Composites**

Compounding PLA with acetylated WF or encapsulated CP, RGP, and WF were carried out by using a kneader. The compounding temperature, rate of rotation and time used were 180°C, 30-90 rpm, 15 min., respectively. That is, a prescribed amount of PLA with acetylated WF or encapsulated CP, RGP, WF was placed into a kneader, thermostated at 180°C, 30 rpm for 5 min. The rate of rotation was increased to 90 rpm and mixing was continued for 10 min. The amount of PLA and fillers were 24 grams, being enough to fill up the mixing chamber and causing torque while kneading. In the encapsulation fibers with PLA experiment, the amount of filler varied from 10-50%.

**Preparation of Composite Sheet**

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

**Tensile Test**

Strips samples 80.0 x 5.0 x 0.3 mm were prepared from composite sheets. Tensile tests were made on these strip samples with 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% RH. The average values of tensile strength, breaking elongation, and Young’s modulus were obtained automatically from ten repeated measurements.

**The Melt Viscosity and the Flow Temperature Tests**

The melt viscosity and the flow temperature of the composites were measured by a flow tester (Shimadzu CFT-500C). Approximately 1.0-1.2 grams of kneaded samples after being dried in 60°C oven in vacuum for 48 hours were prepared for each test. In this test, the flow temperature of the sample was determined automatically when the melts were extruded through the pin hole of a die fitted at the bottom of the cell. The diameter of die and its length-to-diameter ratio (L/D) used were 1 mm and 10, respectively. The measurement 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 x 10⁷ Pa after preheating time of 120 sec. The apparent melt viscosity of the sample was automatically calculated as a ratio of shear stress to shear rate.
Figure 2. Flow chart of wood flour acetylation
RESULTS AND DISCUSSION

The Tensile and Flow Properties of PLA-Encapsulated Fibers Composites under various Filler Types and Concentration

In order to verify the observed dependence of the tensile properties on fiber concentration, the variation of the tensile properties as a function of fiber concentration is presented in Fig. 3.

The tensile strength, breaking elongation, and Young’s modulus of composites containing encapsulated fibers are greatly different compared to those of control (non-encapsulated fibers) composites. Tensile properties, particularly tensile strength and Young’s modulus increased for all types of fillers. The order the increase was as followed: ECP (encapsulated CP)>ERGP (encapsulated RGP)>EWF (encapsulated WF). The difference in strength values obtained can be presumably attributed to the difference in properties among CP, RGP and WF. WF is a composite material mostly composed of cellulose (40-50%), hemi-cellulose (20-30%) and lignin (20-30%) with small quantities of inorganic compound and extractives. CP consists simply of D-glucose units linked by the 1,4-β-glicoside bond. Several thousand glucose units are linked to form one large molecule, and different molecule can then interact to form a large aggregate structure held together by hydrogen bond (MC Murry, 1992). Hence, filler with a higher degree of polymerization can result in greatly strengthened composites. In the case of ECP, tensile strength remained nearly constant after 10% filler loading, while Young’s modulus increased continuously with increasing fiber concentration. Conversely, tensile strength of the ERGP and EWF composites slightly decreased with the rise of fiber concentration. The Young’s modulus-valued unchanged with the rise of fiber concentration. Poor adhesion between non-encapsulated fibers and polymer is responsible for inferior strength results when compared to the results of encap-

Figure 3. Effect of type and concentration of fillers on tensile properties of encapsulated fiber composites.
sulated fiber-filled composites. Encapsulation of the fibers can protect the fiber-fiber contact during composites manufacture and promote high fiber-matrix adhesion resulting in improvement of the tensile properties (Maldas et al., 1989; Maldas and Kota, 1990; Raj and Kota, 1991).

The results of the melt viscosity measurement (Fig. 4) reveal that encapsulation of the fibers increases the melt viscosity of the composites. It is an additional indication that encapsulation of the fibers enhances the adhesion between the fibers and the matrix. The melt viscosity also increases with an increase in fillers content, particularly of the encapsulated composites. The higher the filler loading, the greater is the melt viscosity. The flow temperature of the composites is affected to a great extent by filler content rather than filler coating (Fig. 5). For all cases, it can be said that composite with higher filler loading tend to result in higher flow temperature.

Effect of Processing Conditions on The Tensile Properties of Encapsulated Fibers Composites

The effect of mixing time. The effect of mixing time on tensile properties of the encapsulated CP composites was studied in the range of 10-20 min. The mixing temperature and the rate of rotation were fixed at 180° C and 30-90 rpm. The results are presented in Fig. 6. Figure 6 shows that the tensile strength and the breaking elongation increase with mixing time initially up to 15 min. mixing time, and they decrease beyond this point. The highest tensile strength and breaking elongation values were 70.81 MPa and 5.32%, respectively. In the previous publications (Febrianto et al., 2002a), it has already explained that the quality of dispersion control the performance of short-fiber composites (Sean et al., 1991; Febrianto et al., 2001). Increased mixing time up to 15 min. provides improved dispersion. The Young’s modulus of the composites decreases with mixing time increasing beyond 10 min, and it remains constant afterwards. In order to maximize the tensile properties and to avoid possible damage to the cellulose fibers, 15 min was found to be the preferred mixing time.

Figure 4. Effect of type and concentration of fillers on melt viscosity of encapsulated fiber composites.

Figure 5. Effect of type and concentration of fillers on flow temperature of encapsulated fiber composites.
The effect of mixing temperature. The effect of mixing temperature on the tensile properties was observed in the range of 170-210°C. The mixing time and the rate of rotation were set at 15 min and 30-90 rpm. The tensile properties obtained are shown in Fig. 7. Figure 7 reveals that the tensile strength of the composites increases with a rise in temperature before it decreases, showing maximum improvement at 180°C. At a lower temperature, e.g. 170°C, the viscosity as well as the shear stress of the mixture is very high and this causes fibers breakdown during mixing. However, the decrease in strength at a mixing temperature above 180°C can be explained by thermal fiber degradation (Sapienha et al., 1989; Febrianto et al., 2001). In fact, it was observed that the color of the mixture became darker with an increase in mixing temperature. The mixing temperature has no effect on the Young's modulus of the composites, but it causes a lightly decrease in the breaking elongation of the composites.

The effect of the rate of rotation. The effect of the rate of rotation on the tensile properties of the composites was evaluated in the range of 30-110 rpm. The mixing time and mixing temperature were set at 15 min and 180°C. The results are shown in Fig. 8. Figure 8 exhibits that the tensile strength of the composites is not affected by rate of rotation. Increasing the rate of rotation from 30 to 90 rpm results in almost the same tensile strength. On the other hand, the breaking elongation first slightly improved with the rate of rotation rising from 30 to 90 rpm before decreasing. As the breaking elongation improves, the Young's modulus of the composites slightly decreases. Based on this result and related to other processing parameters (mixing time and mixing temperature), the homogenous dispersion of the fibers in the matrix in this experiment has been achieved at 180°C, 15 min and 90 rpm. The tensile strength, the breaking elongation, and Young's modulus values are 70.81 MPa, 5.32%, and 2.314 x 10^3 MPa, respectively.
The Tensile and Flow Properties of PLA-Acetylated WF Composites under Various Filler Concentration

HPLC (Shimadzu LC-10A series equipped with SPD-10A UV-vis detector) was used to measure the acetyl content of the acetylated WF. The acetyl content was found to be 23.4% by weight. The tensile test samples were made from directly compounded products of acetylated WF with PLA composites. In this case, acetylated WF was used in various proportions. For comparison, the composites composed of PLA with various proportions of WF were also prepared. The tensile strength and breaking elongation values decreased with increases in WF content, either in the PLA-WF composites or in PLA-acetylated WF composites. WF is hydrophilic and polar materials while PLA is hydrophobic and non-polar. The strength of the composites decreases due to inability of the WF to support stresses transferred from the polymer matrix. The breaking elongation decreases with increasing WF content. This is a common observation with almost all filled polymer systems. Reduction in elongation is due to the decreased deformability of a rigid interphase between the WF and the matrix material (Kishi et.al., 1989; Zaini et.al., 1996; Febrianto et.al., 1999). However, in both composites, the Young's modulus values were found to increase with increases in the WF content. This is also a common phenomenon, i.e. WF addition results in greater modulus. Although, the rate of decrease for both composites is almost the same, the PLA-acetylated WF provides the stronger composites than unacetylated WF-PLA composites (Fig. 9).

Figure 8. Effect of rate of rotation on tensile properties of encapsulated CP composites

Figure 9. Effect of type and concentration of fillers on tensile properties of PLA-acetylated WF and PLA-WF composites.
CONCLUSION

Pretreatment of fibers by encapsulation prior to kneading improved the tensile strength, the breaking elongation, and the Young’s modulus, increased the melt viscosity and the flow temperature of the composites based on CP, RGP, and WF fillers. The increased were in the order of: CP>RGP>WF. The best composite consisted of 50% PLA and 50% encapsulated, and this was 1.21 times as strong as the control CP composite. The optimum kneading conditions for preparing the encapsulated fibers composites were 180 C, 15 min, and 30-90 rpm.

The acetylation of WF resulted in related composites with higher mechanical properties than unacetylated WF composites.

REFERENCES


