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Synthesis of Oligoesters Plastic Film from Polylactic Acid with Mono Ester Plasticizer of Wood Flour and Rice Bran and its Hydro Degradation

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Abstract

Composites of polylactic acid (PLA) with mono ester plasticizer (MEP) from wood flour and rice bran were prepared to evaluate the effect of MEP filler content on the mechanical, functional, thermal, and morphological properties of the composites and its degradation. The SEM study provided evidence that there was sufficient interfacial adhesion between the PLA matrix and the MEP from wood flour and rice bran filler. This was likely a result of mechanical interlocking among them. An addition of 10 and 30% MEP from wood flour or rice bran resulted in an improvement of strain and tensile properties of the composite. The composites of PLA and MEP from wood flour and rice bran experienced degradation through hydrolysis of regions that have crystalline structure.

Keywords: polylactic acid, fiber, cellulose, wood flour, rice bran

Abstrak

Komposit dari polylactic acid (PLA) dan mono ester plasticizer (MEP) dari tepung kayu dan bekatul disiapkan untuk mengevaluasi pengaruh jenis bahan isian MEP terhadap sifat mekanis, fungsi, sifat termal, dan morfologis komposit tersebut beserta reaksi degradasinya. Hasil analisis dengan SEM menunjukkan bahwa terdapat *interfacial adhesion* yang cukup besar antara matriks PLA dan MEP dari tepung kayu dan bekatul, yang dapat disebabkan oleh *mechanical interlocking* antara keduanya. Penambahan 10 dan 30% MEP tepung kayu dan bekatul menyebabkan perbaikan regangan (*strain*) dan tegangan tarik (*tensile*). Komposit PLA dan MEP dari tepung kayu dan bekatul mengalami degradasi dengan hidrolisis pada bagian yang berstruktur kristal.

Kata kunci: polylactic acid, serat, selulosa, tepung kayu, bekatul

Introduction

Plasticizers are widely used in polymer industry as additives to increase the mobility of polymer chains. The plasticizers occupy the intermolecular spaces between polymer chains. They reduce intermolecular interactions between polymer chains, thus, increasing the free volume and reducing the energy required for molecular motion. The plasticizers should also reduce the glass transition temperature of the material to under room or other temperature that results in a flexible material (Sejidov et al., 2005; Wypych, 2004). This leads to a decrease in intermolecular forces along polymer chains that improves the flexibility and chain mobility, decreases brittleness (Bordes et al., 2009; Guilbert et al., 1996; Markarian, 2008). The chemical structure, composition, molecular weight and functional groups of the plasticizer affect degree of plasticity (Moreno, 1992).

Changing in type and amount of a plasticizer will affect the properties of the film (Cao et al., 2009; Rahman, 2004). Effective plasticization and compatibility between plasticizer and polymer are determined by various parameters such as polarity, hydrogen bonding, dielectric constant and solubility parameters (Choi et al., 2004; van Oosterhout and Gilbert, 2003). Optimum stirring rate could uptake the insoluble plasticizer and cause better dispersion for the polymer (Bodmcier and Paeratakul, 1997). Glycols is the most liquefaction reagent that can give products rich in hydroxyl groups (Kobayashi et al., 2004; Krz'an et al., 2005; Zhang et al., 2009).

For many applications, natural fibers provide reinforcement properties at lower cost, lower density, but higher strength and stiffness (Smita et al., 2006). The hydrophilic nature of natural fibers influences the overall mechanical properties, as well as other physical properties of the fiber (Wuppertal, 1981). Natural fibers wood flour and rice bran contain cellulose, hemicellulose, and lignin. Cellulose is a linear polymer consisting of D-anhydro-glucose

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repeating units linked by 1,4-b-D-glycosidic linkages (Nevell and Zeronian, 1985), while hemicellulose contains several different sugar units that exhibit a considerable degree of chain branching containing pendant side groups giving rise to its non crystalline nature. Each repeating unit contains three hydroxyl groups and has ability to form hydrogen bond that plays a major role in directing the crystalline. Lignin is a highly cross-linked, three-dimensional aromatic polymer consisting of phenylpropane units linked together by C-C or other bonds. Hydrogen bonds among the macromolecules of the wood polymers within cellulose, the hemicellulose and the lignin are built by a large amount of the hydroxyl groups (-OH). Wood flour and rice bran, as fiber, can be liquefied by depolymerization of wood in a liquid reagent under elevated temperatures combined with solubilization (Balat, 2008; Behrendt, 2008; Bouvier et al., 1988). With the liquefaction process, the fibers are broken down into macrostructure that converts them into low molecular weight components and increases hydrogen/carbon ratio. Mono ester plasticizer can be synthesized from glycerol, diethylene glycol, p-toluene-sulphonic acid and dibutyl tin (IV) oxide and hexanoic acid. Biopolymer-based films plasticizers can be divided into water soluble and water insoluble (Smita et al., 2006). The type and the amount of plasticizer strongly affect dispersion of the polymeric film formation (Johnson et al., 1991).

Poly lactide has high strength, thermal plasticity, and biocompatibility (Tadashi and Masayuki, 2008). However, some physical properties of poly lactide such as brittleness limit its application (Cohn and Salamon, 2005). Poly lactide can be broke down thermally by hydrolysis. Hydrolysis degradation of the ester bonds results in monomers and the process depends on the molecular weight and the crystallinity of the polymer. The crystallinity plays an important role in the polymer hydrolysis where slow degradation occurs for crystalline poly lactide but fast for amorphous of poly lactide (Tsuji dan Ikada, 1997). The mode of scission in the hydrolysis of biodegradable polymers could be completely random regarding the backbone bonds. The hydrolytic degradation in aqueous solution proceeds through random cleavage of the ester bonds. The hydrolytic degradation is controlled by the amount of absorbed water, the diffusion coefficient of chain fragments within the polymer and the solubility of degradation

products (Schliecker et al., 2003). The mechanism of degradation of solid polymer matrix can proceed in surface and bulk (Siepmann et al., 1998). As we found from previous results, poly lactide with liquefied wood flours and rice bran, as additives, lead to more water uptake concerning to a higher degree of crystallinity within the composite films.

The purpose of this research project was to prepare and analyze MEP from liquefied wood flour and rice bran, and to evaluate its dispersion to poly lactic acid matrix in a composite.

Experimental

Materials

Poly lactide materials were bought from Natural Work. Glycerol, diethylene glycol, p-toluenesulphonic acid, dioxane, hexanoic acid (HA), suberic acid (SA) and di-n-butyl tin oxide, chloroform (Aldrich) were commercially provided. The fiber fillers rice bran and wood flour were collected from local sources.

Films Preparation

1. Liquefaction of wood flour and rice bran

Polyol mixture of glycerol (240 g) and diethylene glycol (60 g), p-toluene-sulphonic acid (9 g) were placed into a three-necked glass reactor equipped with a mechanical stirrer. The mixture is heated with a constant stirring to 160°C. The wood flour or rice bran (100 g) was added gradually and the temperature was raised to 180°C. The liquefaction reaction was carried out for 120 min. The degree of liquefaction was evaluated by determining the residue after dilution of the sample with dioxane and water (4:1 v/v). The diluted sample was then filtered using Whatman fast flow filter paper. The residue on the filter paper was dried in an oven at 120°C to get a constant weight. The residue ratio was calculated as the weight percentage based on the starting wood material.

2. Synthesis of ester plasticizers of wood flour and rice bran

Dibutyl tin (IV) oxide, hexanoic acid (adipic acid or suberic acid) and liquefied wood flour or rice bran were added into a round-bottomed reaction vessel. The reaction vessel was put into a silicone oil bath, and the temperature was raised to 150°C for 2 hours. Then the system is cooled down under nitrogen. The reaction vessel was connected to a distillation system with the

temperature of 180°C for 7 hours. Products were washed out from the reaction vessel, precipitated and then separated by funnel separator.

3. Poly lactide and MEP of Wood Flour and Rice Bran Film Preparation

4.5 mg poly lactide with 0.5 mg MEP of wood flour or rice bran and 3.5 mg poly lactide with 1.5 mg MEP of wood flour or rice bran are mixed and made into solution in 75 ml chloroform solvent in an erlenmeyer. The solution was heated in a hot plate Haake Rheocard 600 at 45°C for 1 hour. The film forming solution was spread onto a petridish and allowed to air-dry at room temperature overnight.

4. Hydrolytic Degradation

Pure poly lactide 5 mg, PLA with 10% and 30% MEP from wood flour and rice bran were each hydrolyzed at 37°C and 60°C, for 7 days, 28 days, 56 and 84 days. Approximately 15 mg of PLA film was putted in 5 ml of LC-MS water. Afterward, 12 samples of each material in each temperature were taken out (3 samples of each material, each aging time, and each temperature). Poly lactide composite films were taken out from the water, wiped with Kleenex and weighted the wet weight. The films were put in a vacuum oven for 1 week and weighted to get the dry weight. The wet weight and dry weight were used to calculate the mass loss.

$$\text{Mass loss} = [(\text{wet weight} - \text{dry weight}) / \text{wet weight}] \times 100 \%$$

Characterization

1. Scanning Electron Microscopy (SEM)

SEM analysis was performed with Hitachi S-4800, which is a versatile platform comprising high resolution performance. Film pieces were mounted on metal studs and sputter-coated with gold-palladium using a Cressington 208HR sputter coater. All samples were examined using an accelerating voltage of 0.6 - 2.0 kV.

2. Fourier Transform Infrared Spectrometry (FTIR)

The FTIR spectra of the films were recorded with an IR spectrometer (Perkin Elmer Spectrum 200) in the wavenumber range of 4000-500 cm^{-1} .

3. Mechanical Properties

Mechanical properties such as tensile strength, percentage elongation at break, and modulus value were measured using an Instron Universal testing machine (Model 5566), equipped with pneumatic clamps. The tests were performed with 500 N load cell with the cross head speed of 4 mm/min. The software program used was Bluehill. Prior to tensile test, all the samples were conditioned at 50% relative humidity and 23°C. Before conducting test, five specimens with a rectangular shape (80.5 mm^2) were prepared by using EP 04/80 (Elastocon AB, Sweden).

Results and discussion

Hydrolytic degradation

Figure 1 and 2 show that the hydrolyzed chains were fragmented to form lower molecular weight products that are more soluble causing faster erosion and higher weight loss. The decrease in mass percent during 28 day period is due to the steady loss of low molecular weight chain fragments that are produced from hydrolysis of the PLA with MEP of wood flour and rice bran backbone. Poly lactide with MEP of wood flour and rice bran samples at 37°C and 60°C turned to whitish, due to crystallization.

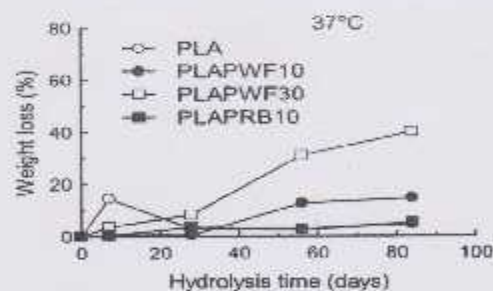


Figure 1. Weight loss vs hydrolysis time poly lactide with MEP from wood flour and MEP of rice bran at 37°C.

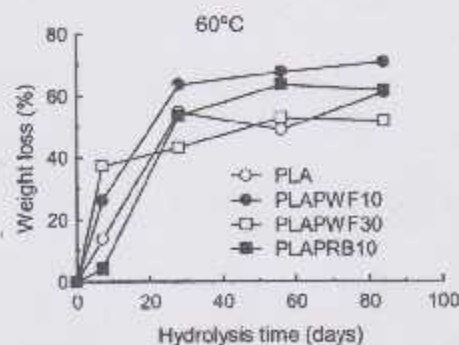


Figure 2. Weight loss vs hydrolysis time poly lactide with MEP from wood flour and MEP of rice bran at 60°C.

Figure 1 also shows that at 37°C first cracks started to appear after 28 days and after 56 days samples collapsed into several pieces. Meanwhile, as shown in Figure 2, at 60°C the samples had already started to crack in the first week and lost their weight. As degradation proceeds, number of carboxylic acid chain ends increases during the autocatalysed ester hydrolysis. Initially, hydrolysis of ester bonds occurs homogeneously through the matrix and water diffuses into the amorphous regions resulting in random hydrolytic scission of ester bonds. Before PLA with MEP of wood flour and rice bran are fully degraded, the soluble oligomers which are close to the surface can be leached out, whereas the core of the polylactide composite remains entrapped. As shown in Figure 1 the highest weight loss was achieved at 37°C (polylactide with 30% wood flour MEP especially after 28 days), while the lowest weight loss was the polylactide with 10% rice bran MEP (its weight loss remained constant since 0 - 80 days of degradations). Compared with Figure 2, it was found that at 60°C the weight loss of mostly all polylactid with monoester plasticizer with wood flour or rice brand increased drastically starting from 0 to 28 days. High temperatures seem to increase hydrolysis degradation.

Scanning Electron Microscopy (SEM)

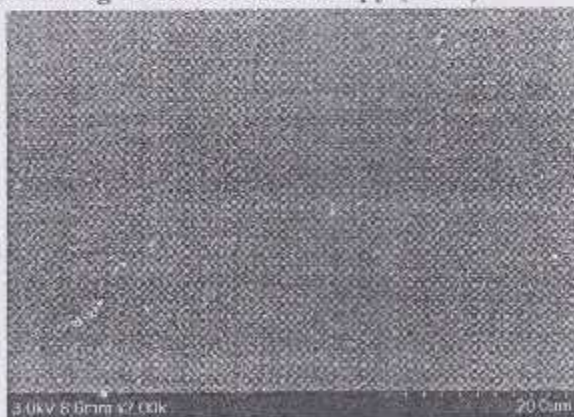


Figure 3. SEM of pure polylactide.



Figure 4. SEM of polylactide with 30% wood flour MEP



Figure 5. SEM polylactide with 30% rice brand MEP

Polylactide with monoester plasticizer wood flour and rice bran film before hydrolysis shows spherulitic morphology. The inherent polar and hydrophilic nature of lignocellulosic fibers and the non-polar characteristics of most thermoplastics results in compounding difficulties leading to nonuniform dispersion of fibers within the matrix, which impairs the efficiency of the composite. Crystalline and amorphous regions were found within the spherulite, meanwhile free amorphous region between the spherulites.

The fiber breakage indicates good interfacial adhesion between PLA and MEP from wood flour and rice bran. Some fiber fractures and fiber splitting can be seen, which demonstrate a strong fiber matrix adhesion. The interface between PLA with MEP from wood flour and rice bran particle is well formed. Macromolecules are very easy to form strong hydrogen bonds because the surface has plenty hydroxyl groups.

Surface changes

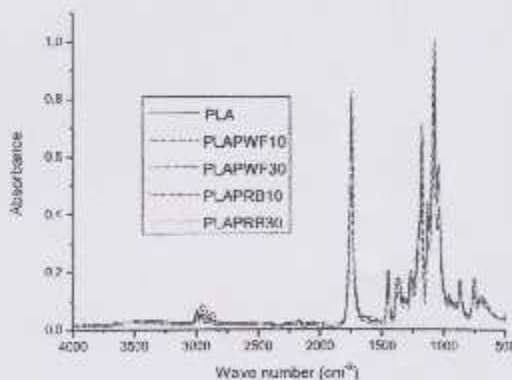


Figure 6. FTIR polylactide with MEP of wood flour and rice bran fillers

By adding of MEP from wood flour and rice bran to polylactide, the crystalline peak of PLA at 754 cm⁻¹ was shifted to a decreased intensity with respect to the amorphous peak at 866 cm⁻¹ and 870 cm⁻¹, suggesting a reduction in the

crystallinity of polylactide. The interaction between the carbonyl groups of PLA and hydroxyl groups of MEP from wood flour and rice bran through hydrogen bonding was indicated by the peak at $1746\text{--}1747\text{ cm}^{-1}$. The peaks at 1747 cm^{-1} , 1746 cm^{-1} , 1455 cm^{-1} , and 1451 cm^{-1} were related to the characteristic of wood flour and rice bran MEP. The peak at 1267 cm^{-1} was due to the -OH plane deformation, might be related to the phenol-lignin complex which is retained in the residue. Compared with the spectrum of neat PLA, the spectrum of the composite containing of wood flour fiber and rice bran shows the presence of OH groups at 2955 cm^{-1} and 2944 cm^{-1} .

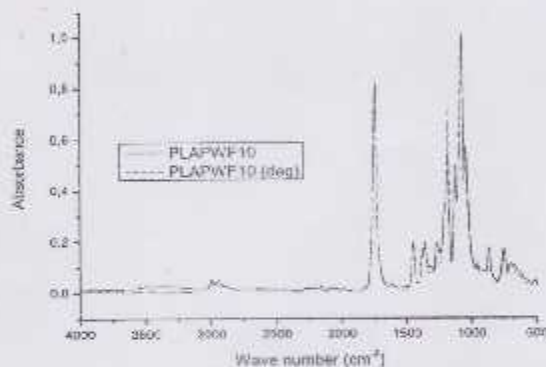


Figure 7. FTIR spectra of hydrolysis degradation of polylactide and polylactide with 10% MEP from wood flour before and after degradation 28 days, 370°C

Figure 7 shows FTIR spectra of hydro-degradation of polylactide with monoester plasticizer wood flour or rice bran. The carbon acetyl hydrogen stretching vibration absorbance intensity ratio at 2995 cm^{-1} decreased upon water. The small band at 1746 cm^{-1} is attributed to carbonyl groups of uronic acids from hemicellulosic contaminants, which are rapidly removed by hydrolysis.

Mechanical

Strength at break of polylactide with 10% and 30% MEP from wood flour decreases as compared to pure polylactide (31.37 Mpa), polylactide with 10% MEP from wood flour (15.84 Mpa) and polylactide with 30% MEP from wood flour (10.37) indicating an efficient stress transfer between polylactide and wood flour. Strong adhesion of the MEP from wood flour with polylactide interface is necessary for an effective stress transfer and load distribution throughout the interface which shows a more resilient matrix. MEP from wood flour and rice

bran fiber contents led to the formation of fiber that compromised the ultimate strength of composites. The percentage of load carried by the fibers becomes higher for a higher ratio of elastic modulus of fibers and matrix. The addition of MEP from rice bran by 10% improved the modulus from pure PLA 31.37 MPa to 42.06 MPa, while adding of MEP from rice bran by 30% had relatively the same modulus as that of pure polylactide (31.22 Mpa).

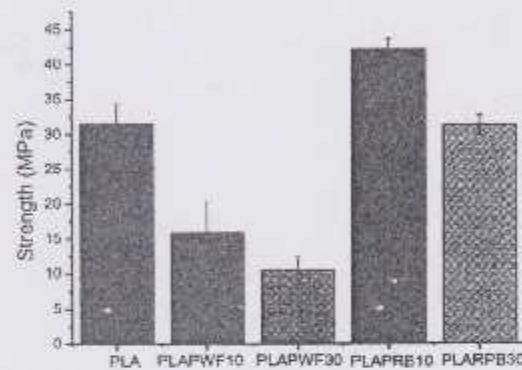


Figure 8. Tensile strength PLA with 10% and 30% MEP from wood flour and rice bran filler

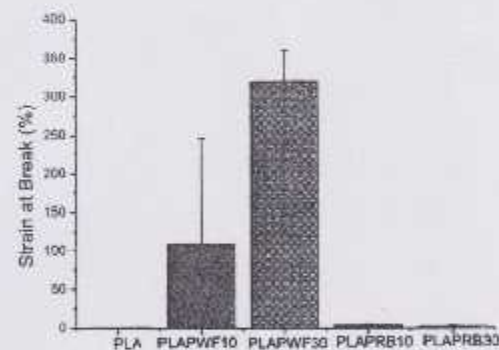


Figure 9. Strain at break polylactide with 10% and 30% wood flour and rice bran MEP fillers

The MEPs from wood flour cause a dramatic increase in elongation at break i.e 108.88% and 319.13% for polylactide with 10% and 30% wood flour MEPs, respectively, compared to that of pure polylactide that has 1.44% elongation. The adding of MEP from wood flour results in high mechanical strength of composites with a strong fiber matrix interface, and uniform distribution of fiber, which enables stress transfer from the matrix to the fiber, obtaining full mechanical advantages of fibers. The effects of

MEP were to inhibit polylactide crystallization and enhance the plasticizer effect, increase molecular mobility of starch chain, promote the interaction between polylactide and wood flour, and increase elongation at break. The adding of MEP from rice bran also increases strain at break polylactide, but the increase is not drastically as that of 10% rice bran MEP (3.820%) and 30% rice bran MEP (2.376%).

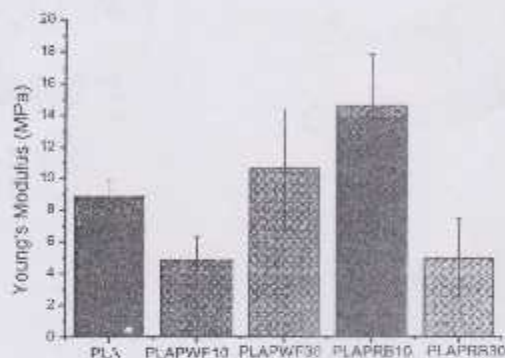


Figure 10. Young's modulus polylactide with MEP of wood flour and rice bran filler 10% and 30%.

MEP from wood flour and rice bran improve the interfacial matrix fiber bonding resulting in the enhancement of tensile properties of the composites. The Young's modulus of the natural fiber reinforced polymer composites increases with increasing fiber loading. The tensile strength of the natural fiber reinforced polymer composites increases with fiber content up to a maximum or optimum value, then the value will drop.

Adding of MEP from wood flour by 10% and rice bran by 30% decreases Young Modulus (4.880 Mpa) and (4.936 Mpa) compared with neat PLA (8.818 Mpa) causing the film matrix to become less dense and facilitating the movements of the polymer chain under stress, consequently improving the flexibility. However, it increases the tensile stress of polylactide with 30% MEP from wood flour (10.583 Mpa) and 10% MEP from rice bran (14.565 Mpa), which increases stiffness.

Conclusions

The addition of MEP from wood flour and rice bran resulted in an increase in the tensile strength, in comparison with pure polylactide, which showed a more resilient matrix, higher mechanical strength. The effect of fiber content

in MEP on the properties of polylactide natural fiber reinforced composites is particularly significant, due to interaction between the carbonyl groups of PLA and hydroxyl groups of wood flour. SEM images showed indication of good interfacial adhesion.

During hydrolytic degradation process and morphological changes of polylactide during the degradation, water penetrated into polylactide leading to hydrolytic cleavage of ester bonds. Degradation rate constants were higher for amorphous polylactide and MEP of wood flour and rice bran as a result of increasing permeation through the amorphous domains. Faster hydrolysis induced by the increase of crystallinity polylactide with MEP of wood flour and rice bran.

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