

Compatibilization of Amylopectin-grafted-Poly (Hexyl Methacrylate) in Polyblend

A.S.Handayani^{*a,b}, A.R.Putra^a, M. Chalid^a, E. Budianto^c, D. Priadi^a.

^aDepartment of Metallurgical and Materials Engineering-University of Indonesia, Jakarta, Indonesia

^bDepartment of Chemical Engineering- Institute Technology of Indonesia-Tangerang Selatan, Indonesia

^cDepartment Chemistry, Faculty of Mathematic and Natural Science, University of Indonesia Depok, Indonesia

Abstract: Amylopectin-grafted-Poly (Hexyl Methacrylate) is one of the copolymer modifications based on natural polymers with synthetic polymers, which can be used to reduce fossil feedstock. Polypropylene (PP) based composites containing chicken feather fibers (CFF) were successfully prepared by simple blending procedure. Maleic anhydride-grafted-PP and amylopectin-grafted-poly (hexyl methacrylate) was used as compatibilizer to promote dispersion of CFF. To investigate the compatibilizer effect, the result was characterized by using FT-IR and FE-SEM. The resulting PP-based composites were characterized in term of morphology, thermal stability and mechanical behavior. The result shows that the PP/CFF/PP-g-MA has less aggregation and more hydrophobic compare to the PP/CFF/PP-g-MA. However, PP/CFF/PP-g-MA has lower stability than PP/CFF/PP-g-MA.

Keywords: Ap-g-PHMA, Chicken Feather Fiber, Impact Polypropylene (iPP), PP-g-MA, Rheomix.

1. INTRODUCTION

The replacement of fossil feedstock with renewable biomass is a major effort of modern plastic industry. Natural polymers are special class of material among the polymers based on natural resources [1]. Modification of both (fossil feedstock and natural polymers) have been found for a variety of applications, including for aerospace, leisure, construction, sport, packaging and automotive industries, especially for the last mentioned application [2]. The modification of polymers by blending can be done with several approaches to ensure that the interaction between the components is adaptable. Some studies have shown that the use of commercial polymers is immiscible and need compatibilization to achieve properties required for specific application [3].

^{*}This document is a collaborative effort

*Corresponding author

Email addresses: aniek.sri@ui.ac.id (A.S. Handayani)

andri.rahma@ui.ac.id (A.R. Putra)

chalid@metal.ui.ac.id (M. Chalid)

emilb@ui.ac.id (E. Budianto)

dedi@eng.ui.ac.id (D. Priadi)

The modification of polymers by blending has some approach to ensure that the interaction between the components mixed well. Some studies have shown that the use of commercial polymers is immiscible and need compatible agent to achieve required properties for specific application [3]. A large number of the commercial polymer blends are available and many of them contained compatible agent. Improving the biodegradability of hybrid bio composite based on iPP and CFF by blending technique, has several disadvantages about immiscibility of each other component. A number of papers on blending biopolymers have been published, however none of those paper not using compatible agent, such as, PP/ground chicken quill [4], PLA/starch [3], Feather fibers and cellulose fiber/PP matrix composites [5], wool keratin/polypropylene [6], cassava starch/kenaf bio composites [7].

Polymer composites in this paper, have the incompatibility between the hydrophilic natural fibers with a hydrophobic matrix of polypropylene (PP). This leads to undesirable properties of the composite. Therefore it is necessary to modify the surface of the fiber by using chemical modification to improve the adhesion between the fiber and the matrix. Interfacial activity in heterogeneous polymer blends is the role of Compatibilizer [4], these effects usually associated with an increased interface adhesion and dispersion of particles leading to improve the mechanical properties. On the other hand, one of many advantages of using compatible agent is that it can reduce the usage of iPP.

Chicken feather fibers (CFF) have a unique structure and properties not found in natural or synthetic fibers. Although CFF cannot be processed like wool or silk fibers because of complex protein structures in feathers, the secondary structure of the feather like barbs have suitable structures and properties for use as a natural protein fiber. They have good properties such as low density, good compressibility and resilience, the ability to damp the sound, warmth retention and morphology typical feather barb structure makes them unique fiber [3].

PP-grafted-maleic anhydride (PP-g-MA) is the most popular third component that is added to aid both adhesion and mixing in PP/polyamide system [7]. In PP/PA blend, the PP-g-MA compatibilizer preferentially resides at the interface of PP/PA and improves interfacial adhesion through the chemical linkage of the anhydride groups with the polyamide end groups [5]. Ap-g-PHMA is synthesized by atom transfer radical polymerization, it is a modification of the natural polymer and synthetic polymer. Ap-g-PHMA was having hydrophilic and hydrophobic functional groups that were believed to be miscible with PP and CFF. Between PP and CFF, there is an incompatibility issue between hydrophilic and hydrophobic fiber. The purpose of this study was to compare the performance of Ap-g-PHMA and PP-g-MA as compatibilizer of PP / CFF blends. The success modification of Ap-g-PHMA was done in the previous research. Incorporation of PP/CFF blends were characterized by FE-SEM, FTIR and tensile test. The thermal stability of polymers blends were extensively characterized by Scanning Thermal analyzer (STA).

2. EXPERIMENTAL PROCEDURE

Synthesis of Amylopectin-g-Poly (hexyl methacrylate) as a compatibilizer

Amylopectin macro-initiator was obtained by reacting amylopectin with EBiB (Ap-EBiB) as previous described [10] [15]. In a typical copolymerization ([DMF] : [H₂O] = 50 : 50 (v/v) at 30°C, [HMA] = 1mmol L⁻¹, [Ap-EBiB] : [HMA] : [CuCl] : [CuCl₂] = 100 : 1 : 1 : 0.8, ratio of [bpy]/([CuCl]+[CuCl₂]) = 2.5, 9.390g of Ap-EBiB (100mmol of EBiB initiating groups)) was dissolved in 30ml of water and 20ml of DMF in an autoclave and degassed by purging with Nitrogen. An amount of 5.91ml (1mmol) of degassed HMA was then added. A Cu-bpy stock solution in water was prepared by adding 4ml of degassed water to 2.2 mg (1 mmol) of CuCl, 2.1 mg (1mmol) of CuCl₂ and 14.05 mg (4.5mmol) of bpy under nitrogen. A 2ml then freshly prepared CuCl-CuCl₂-bpy stock solution was added to the autoclave. The polymerization was stopped by bubbling with air and the product isolated by extensive dialysis against distilled water and lyophilization.

Composites Preparation

Composites of iPP, PP-g-MA, Ap-g-PHMA and CFF were prepared by melt-blending. A weight ratio percentage of iPP/CFF is 60:40; iPP/CFF/PP-g-MA is 56.6:37.7:5.6 and IPP/CFF/Ap-g-PHMA is 60.25:38.15:1.6. The third compositions were processed at the same condition (170°C, 120 rpm and 15 minutes rotation time). The CFF that were used is light chicken feather without pretreatment. The samples

were molded in a hot-press equipment at 180°C for 3 minutes. After this period a pressure of 50 bars was applied for 2 minutes. And then the press plates were quickly cooled to room temperature.

Characterization

Composites Analysis

The Fourier Transforms Infrared (FTIR) analysis of iPP/CFF/PP-g-MA, iPP/CFF/Ap-g-PHMA and iPP/CFF were performed using a Perkin-Elmer FTIR spectrometer (Spectrum 2000 series, resolution 2.0 cm⁻¹, 100 scans) having diamond ATR (Attenuated Total Reflection) device between 4000-5000 cm⁻¹. High-resolution imaging of the composites morphology was achieved using QUANTA 200 FEG-scanning electron microscope (FE-SEM).

Thermal analysis of composites were performed with a scanning thermal analysis instrument. Sample (10.0 mg, dry weight) was loaded in aluminum pans and the moisture level adjusted to 10% by adding deionized water. Samples were scanned from 30 °C to 400 °C, at a heating rate of 10 °C/min. While sealed empty pans were used as reference. The onset temperature (To), peak temperature (Tp), conclusion temperature (Tc) and the enthalpy of gelatinization were recorded.

The tensile properties of the specimens were determined using a universal testing machine (Instron, model 3367, 30 kN load, 12.5 mm/min crosshead speed and gauge length 100 mm). The same instrument was used to measure the flexural properties of the specimens. A support fixture with cylindrical surfaces with a span of 50.8 mm was used for the flexural tests. A minimum of five samples of each composite is tested to take the average results with the standard deviation.

3. RESULT AND DISCUSSION

Molecular Analysis

The chicken feather has both hydrophobic and hygroscopic characteristic with approximately ratio will be 60:40. Cysteine in the keratin (8.87%) has S-H groups that causes the S-S bonding. The high content of cysteine makes the keratin stable by forming network structure. Chemical structure of Ap-g-PHMA that is composed of amylopectin with hydroxyl groups causes hygroscopic properties, while collaboration with PHMA causes hydrophobic properties. Chemical structure of PP-g-MA has a long chain that is hydrophobic and PP MA hydrophilic. These shows that the short chain of MA facilitates miscibility of both components.

The infrared spectra of PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA are presented in Fig.1. In the spectrum of PP/CFF, several absorbance can be distinct at 1168, and 1001.7 cm⁻¹, which are due to C-O and C-C bond stretching. The band stretch around 3377, and 3387 cm⁻¹ is assigned to hydrogen bonded OH on the CFF molecules. There are several additional characteristics absorption bands at 1376 cm⁻¹ (-CH stretching from PP), 1457 cm⁻¹ (-CH₂ or CH₃), 1544 cm⁻¹ (-NH bending for β-sheet at CFF), 1647 cm⁻¹ was assigned to the C=O amide I with α-helix conformation of CFF and 2871-2951 cm⁻¹ were assigned to iPP. Compared to PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA have some new band (see Fig.1.) at 1759 cm⁻¹ assigned to carbonyl C=O stretch for Ap-g-PHMA, and at the band 3752 cm⁻¹ does not appear on the PP / CFF / PP - g - MA.

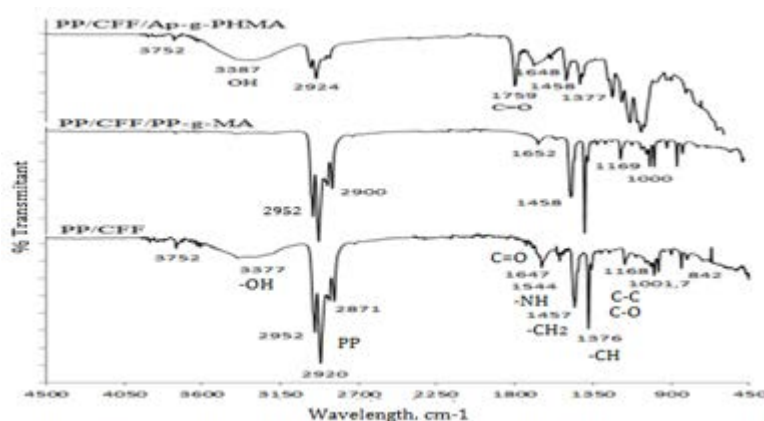


Figure 1. Comparison of FT-IR Spectra for PP/CFF, PP/CFF/MA-g-PP and PP/CFF/Ap-g-PHMA

Mechanical Behavior

The PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA adhesion in the prepared composites was evaluated by a SEM investigation. Fig. 2 displays representative micrographs of the composites. The CFF appears to be separated from one to another and homogeneously distributed within the PP, however their adhesion to the matrix remains unsatisfactory. Fig. 2B shows that pulled-out fibers left large voids, cavities and imprints on the polymer fracture surface. The use of PP-g-MA as compatible agent has better compatibility to PP/CFF compared with Ap-g-PHMA, it significantly improves adhesion. As illustrated in Fig. 2A, the cavities and imprints are still evident. The major component in CFF has some hydrophobic side chain and no hydroxyl group [4], except for serine, the amino acid is found in all components of the CFF. Therefore, compatible agent is required to increase the hydroxyl groups that are more environmental friendly in PP/CFF poly blends. PP-g-MA has both these (hydrophilic and hydrophobic) properties, and has short chain hydroxyl group of MA, therefore it is easy for holding hydrophilic CFF chain and the other hand holding hydrophobic CFF chain.

In the PP/CFF/Ap-g-PHMA sample, fewer voids and cavities around the fibers were observed. Fig. 2C indicates an enhancement on PP/CFF/Ap-g-PHMA adhesion. This picture shows that the mixture looks compatible but rigid, it indicates that it was physically looks compatible, but the tensile strength showed a decline. This is due to the number of hydroxyl groups on amylopectin, as an example; for every each glucose unit has three hydroxyl groups, if substitution occurs just in one primary hydroxyl group, then the number of OH groups to be 2 times the amount of glucose in amylopectin. While PHMA has hydrophilic long chain and will also be easier to hold the CFF compared with PP. this leads to reduced mechanical strength of the composites.

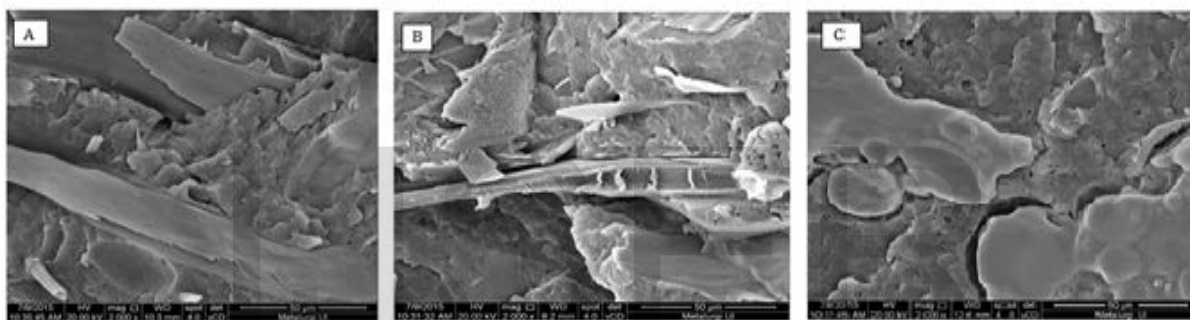


Figure 2. Morphology of PP/CFF/PP-g-MA (A), PP/CFF (B) and PP/CFF/Ap-g-PHMA (C).

Mechanical Properties is one of the most important parameter that is used to evaluate polymers blends. Fig. 4 and Fig. 5 show the effect of temperature on the tensile stress and ultimate tensile stress of the PP/CFF/PP-g-MA composites. It has been explained earlier that the Ap-g-PHMA gives the rigid polyblend due to the number of hydroxyl groups of amylopectin and possessed thereby reducing the tensile strength of PP/CFF/Ap-g-PHMA. In the other hand, the chain length of hexyl methacrylate causes the compounds become easier to join with the amino acid at the CFF than with the PP. Therefore the interaction between PP and CFF with compatible agent Ap-g-PHMA becomes more brittle. This proves that the use of natural recourses will increase its biodegradability properties and lower mechanical properties.

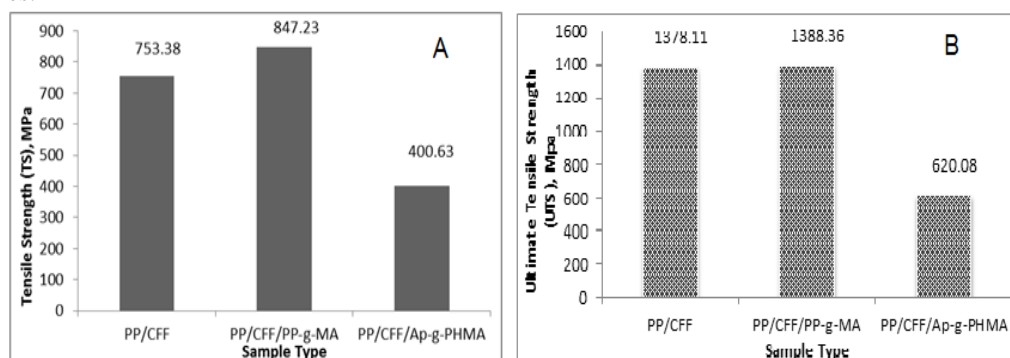


Figure 3. Tensile strength of PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA with PP/CFF/Compatible agent composition is 60:37:3 (A), Ultimate Tensile Strength (UTS) of PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA (B)

Thermal Behavior

Thermo-gravimetric analysis (TGA) is a standard technique to determine the composition or thermal stability of materials with heating rate of 10°C/minute. The sample was heated from 30°C to 750°C to determine the complete thermal degradation of polymers-blend. All samples were prepared in nitrogen atmosphere with flowing rate of 60 ml/min. Three samples were conducted for these experiments.

The initial decomposition temperature (IDT) of PP/CFF in the Fig.6 was 240°C. The IDT of PP/CFF/PP-g-MA was 259.85°C and IDT of PP/CFF/Ap-g-PHMA was 218°C. The decrease of IDT is because of the decomposition of pure amylopectin around 120° C with the composition of the composite in approximately 3% and 37% CFF composition. The TGA curve of PP/CFF has a rapid weight loss in the range temperature of 240 – 472°C, similar with PP/CFF/PP-g-MA. Refer to TGA curve for PP/CFF, PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA are almost in range of 240-472°C, the total weight loss for each samples is difference. The total weight loss of PP/CFF/PP-g-MA is the highest and PP/CFF/Ap-g-PHMA is the lowest. Under nitrogen atmosphere, the residual weight should be related to the amount of carbon in the composites. Which is 9.92% for PP/CFF/Ap-g-PHMA, 3.24% for PP/CFF and 3.26% for PP/CFF/PP-g-MA. The total weight loss of PP/CFF is higher than PP/CFF/PP-g-MA and PP/CFF/Ap-g-PHMA composites. It might be due to the incorporation of PP/CFF with PP-g-MA which stabilize the composite at high temperature. The composites of PP/CFF/Ap-g-PHMA was stabilized at temperature with 240-432°C, and the PP/CFF/Ap-g-MA will be stabilized at high temperature about 279-472°C.

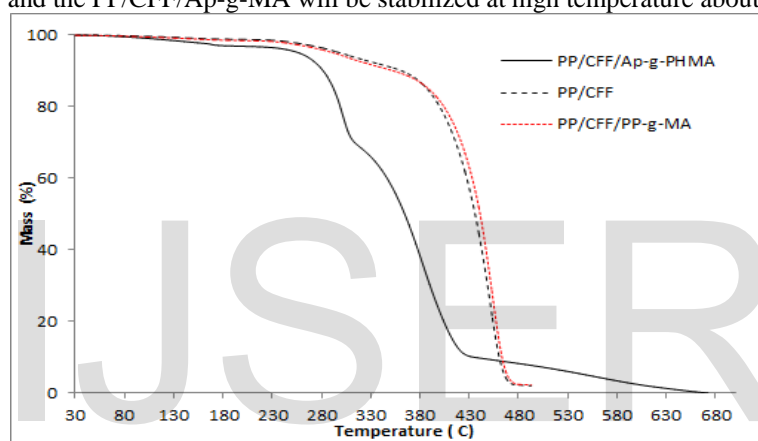


Figure 4. TGA curve of PP/CFF/Ap-g-PHMA, PP/CFF and PP/CFF/PP-g-MA

4. Conclusions

In this study, the compatibility of PP-g-MA and Ap-g-PHMA has been proven to improve dispersion, interfacial, adhesion and tensile strength in a mixture. The PP/CFF/PP-g-MA mixture has better interfacial adhesion, it was evidenced by scanning electron microscope. The addition of PP-g-MA for incompatible mixture improves the homogeneity of CFF phase dispersed in PP matrix with a reduction in interfacial tension. The tensile strength of the incompatible mixture is lower than the compatible mixture due to poor adhesion between the phases. However, there are still improvements on adhesion by the adding of PP-g-MA and Ap-g-PHMA. Tensile strength of PP/CFF increased with the addition of PP-g-MA in range of 279-472°C and decreased with the addition of Ap-g-PHMA in range of 272-432°C.

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