Utilization of amylopectin-grafted-poly(hexyl methacrylate) as bio-compatible agent for polypropylene/starch polymers blend

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Abstract. PP film/starch blend at different ratio of composition and various amount of Amylopectin-grafted-Poly (Hexyl methacrylate) (Ap-g-PHMA) as bio compatible agent were prepared by blending method. In this study PP/starch blends were obtain 0.6% and 1% Ap-g-PHMA were processed in Rheomix. The structure characteristic, melt flow index (MFI) and thermal properties of the films product were characterized by Fourier Transform Infra-Red Spectroscopy (FTIR), Simultaneous Thermal Analysis (STA). The experimental result indicated that addition of Ap-g-PHMA to the PP/starch blend resulting in increased of MFI values more than three times, raised of starch content in PP matrix, and reduced crystallinity degree.

1. Introduction

Starch is one of the highest natural polymers that have some advantages such as edible, biodegradable, low cost, abundance in nature and renewable [1-3]. Starch has been widely used in various applications, including medicine, agriculture, textile, and especially for packaging. However, if it is compared to conventional synthetic plastic, starch has weakness, owing to its strong hydrophilic character, poor mechanical property and low thermal stability [3]. To improve its mechanical properties, starch has been incorporated with polymer synthetic such as polypropylene (PP). It has been known that PP is hydrophobic synthetic polymer with excellent film forming abilities, good mechanical and barrier properties, but poor adhesive and not biodegradable [4]. To overcome the disadvantages of starch and PP, several methods have been used. Blending PP to biodegradable polymer such as starch as low price material, reduce the final product price and raise the biodegradation rate [5]. Previous study has shown that blending of thermoplastic starch and Poly Lactic Acid (PLA) with no compatible agent lead to phase separation [6]. The addition of maleic anhydride (MA) as compatibilizer agent improves interfacial adhesion between starch and PLA resulting in improvement of thermal and mechanical properties of the blending [7]. Many compatible agents have been used in synthetic polymer productions or research. Among these materials, maleic anhydride-grafted-poly propylene (MAPP) is one of the most popular used. Utilization MAPP as compatible agent raised interface bonding strength, flexural modulus and other mechanical properties [8]. The objective of this research was developing PP film/starch matrix that compatible with Ap-g-
PHMA by melting compounding to improve its performance. This paper presents the impact of the Ap-g-PHMA as compatible agent and the influence of starch content in the PP film matrix. These composites specimen were characterized using Fourier Transform Infra-Red Spectroscopy (FTIR), thermal behavior by Simultaneous Thermal Analysis (STA) and analyze the Melt Flow Index (MFI).

2. Experiment

2.1. Materials

Natural starch, 2, 2'-Bipyridine (bpy) (with 99 % purity) and Dimethyl Sulfoxide (DMSO) (with purity of 99.9%) were purchased from Sigma-Aldrich. Ethyl α-bromoisobutyrate, EBiB (with purity of 99 %), amylopectin (α-1, 4-glucan with α-1,6-cross-linking; one terminal group per 25 glucose units) and Hexyl Methacrylate (HMA) were also purchased from Sigma-Aldrich. CuCl (I) and CuCl (II) with purity 99.9% were purchased from Merck. Di Methyl Formamide (DMF) (at 99.9% purity) and Tetra Hydro Furan (THF with 99.9% purity) as solvent were purchased from Merck. Polypropylene film with MFI 10 g/10 min was supplied from Chandra Asri Petrochemical (CPAC-Indonesia).

2.2. Synthesis of Amylopectin Macro-Initiator (Ap-EBiB)

Amylopectin macro-initiator (Ap-EBiB) was prepared by combining amylopectin to EBiB as described in previous study [8].

2.3. Synthesis of Compatibilizer Amylopectin-Graft-PHMA (Ap-g-PHMA)

Copolymerization of Ap-g-PHMA was carried out as described in previous study [2]. Hence Ap-EBiB was reacted to [HMA] and (BPy/CuCl+CuCl₂) as ATRP catalyst system in mixed media reaction (DMF: H2O). Starch was dried in the oven at 105°C for 24 h to achieve its moisture content less than 5%. Then starch was compounded into a polypropylene film in the Minilab II Haake™ Rheomix CTW 5 conical that equipped with twin-screw extruder (Thermo Scientific Haake GmbH, Karlsruhe, Germany), a barrel temperature of 170 to 190°C from the feeding zone to the dead zone, respectively. Two levels of load was prepared for all materials. Starch was blend to PP film with a weight ratio of 40 and 50 % and was added to compatible agents at 0.6 and 1 phr respectively. Samples were compounded in specimens test by injection molded using a 5-ton Battlefield BA 200CD Plus machine, with a UNILOG 4000 control system (closed-loop control). A mold from Master mold Inc, having cavities for tensile specimen according to ASTM D638 was used.
2.4. Characterization

The Fourier transforms infrared (FTIR) analyses of Starch and PP/Starch/Ap-g-PHMA were performed using a Perkin-Elmer FTIR spectrometer (Spectrum 2000 series, resolution 2.0 cm, 100 scans) having diamond ATR device (attenuated total reflection) between 4000-500 cm\(^{-1}\). Thermal analyses of composites were performed with a simultaneous thermal analysis. Sample (10.0 mg, dry weight) was loaded in aluminum pans and the moisture level was adjusted to 10% by adding deionized water. Samples were scanned from 30 to 500\(^\circ\)C, at heating rate of 10\(^\circ\)/min, and a sealed empty pan was used as reference. Melt Flow Index (MFI) samples were measured using Zwick Melt Indexer with ASTM D.1238 as standard method.

3. Result and Discussion

Figure 1 shows the FTIR spectra of starch (a) that contain a broad band at 1007 cm\(^{-1}\), which is related to CH\(_2\)OH groups, and band of 1157 cm\(^{-1}\) which is typical of C-O-C group. The FTIR spectrum of PP/Starch/Ap-g-PHMA film (b, c) demonstrated characteristic peaks of PP, starch and Ap-g-PHMA. The peak at 1751 cm\(^{-1}\) is the characteristic of Ap-g-PHMA carbonyl stretching band (C=O), also at peaks 1661 cm\(^{-1}\) and 1657 cm\(^{-1}\) indicated of carbonyl stretching band. The spectrum that showed at peak 1462 cm\(^{-1}\) and 1377 cm\(^{-1}\), respectively are attributed to C-OH stretching recorded as well as the change of starch. Other peaks at 1156 - 1176 cm\(^{-1}\) are typical of C-O-C group. The peaks at 1000-1007 cm\(^{-1}\) are the characteristic of CH\(_2\)OH [9].

The thermal properties, such as glass transition temperature (Tg), melting temperature (Tm) and heat of fusion \(\Delta H_f\) are presented in the DSC curves in Figure 2 and 3. This figures show the DSC curves of
PP/starch/Ap-g-PHMA (60/40 at 0.6 and 1 phr respectively) and PP/starch/Ap-g-PHMA (50/50 at 0.6 and 1 phr respectively). The peak around 161.81°C corresponds to melting temperature of PP/starch/Ap-g-PHMA (60/40 at 0.6 phr), while peaks around 159.08°C, 160.58°C and 160.6°C correspond to melting point of PP/starch/Ap-g-PHMA ratio of 60/40 at 1 phr, 50/50 at 0.6 phr and 50/50 at 1 phr, respectively. The degradation temperature of pure starch is around 120°C, while PP melting point is 173°C, so the melting point of the blends situated in between these two temperatures. The increase of starch weight in the blend, reduce the melting point of the components.

Result of all composites thermal properties determination is summarized in Table 1. The higher level of coupling agent used, the lower of melting temperature (Tm) appeared. It is reduced to -0.9°C for ratio of 50/50, and -0.45°C for ratio of 60/40. In addition, the increased of fibers/PP ratio at lower levels of coupling agent causes a slight increase in melting temperature (+0.14°C at 0.6 phr). However, utilization of coupling agent at about 1%, slightly lower the melting temperature (-0.31°C). Usage of
Ap-g-PHMA as a coupling agent in PP/starch blends normally reduce the melting temperature (Tm) of pure PP. Since the melting temperature of starch is about 120°C and the Ap-g-PHMA melting temperature about 140.75°C, so that Tm composites definitely less than that of pure PP [2]. This indicates that Ap-g-PHMA compound influences the dispersion of starch in PP matrix, and enhance miscibility mixture as described by Simmons et al., (2013) [10].

Table 1. Thermal Properties of PP/starch/ Ap-g-PHMA blends.

| Samples | Tg (°C) | Tm (°C) | Tc (°C) | \( \Delta H_f \) (J/gr) | Xc |
|---------|---------|---------|---------|-----------------|-----|
| PP : 100 | -20.00 | 173.00 | 110.00 | 207.10 | - |
| PP/starch/ Ap-g-PHMA : 50/50/0.6 | 63.94 | 160.58 | 117.1 | 1.81 | 17 |
| PP/starch/ Ap-g-PHMA : 50/50/1 | 64.37 | 160.60 | 117.3 | 1.89 | 18.25 |
| PP/starch/ Ap-g-PHMA : 60/40/0.6 | 64.70 | 161.81 | 112.5 | 2.53 | 22.77 |
| PP/starch/ Ap-g-PHMA : 60/40/1 | 65.14 | 159.08 | 118.3 | 3.08 | 24.80 |

From Table 1, it can be seen that PP blends with starch, increased glass transition temperature from -20°C to 64°C. The effect of Ap-g-PHMA as a coupling agent (at 0.6 and 1%) increase glass transition temperature around 0.67% at ratio of 50/50 and 0.68 % at ratio of 60/40. This result in accordance with the changes in molecular mobility which is the amorphous fraction is located between crystalline lamellae. This case normally is categorized as semi crystalline material relative to an amorphous situation. Hamma et al., (2015) demonstrated that utilization of DSC on PP, at different degree of crystallinity, showed that almost all samples have Tg above Tg PE. This is indicated that the sample have semi crystalline properties. Crystallinity can be determined from calorimetric differential curve based on [11].

Table 1 shows also that with the increasing starch content at low level of Ap-g-PHMA, enhanced the crystallization temperature (Tc) from 112.5 to 117.1°C (4.08%). In contrast, at high level of Ap-g-PHMA, at the same condition of starch composition, the crystallization temperature decreased from 118.3 to 117.3°C (0.84%). Experimental result indicated that the higher of starch content in composites the higher crystallization temperature, but, reduced the degree of crystallinity. Based on Gonzales et.al., (2009) studied, it was confirmed that composites of PP/cassava starch below 30 phr increased degree of crystallinity, but crystallization temperature remain stable. According to them, the filler particles gave a nucleating effect that influences the growth of PP’s spherulites. In this study, increasing starch content in PP matrix decreased degree of crystallinity, but increased crystallization temperature. Based on the thermal behavior, the composite in this experiment is categorized as semi crystalline as they have Tg, Tm and Tc [10].

Figure 4 shows the TGA curves of all samples. It is showed that an initial weight loss at 120 and 170°C corresponds to evaporation of water and dehydration of amylopectin [8]. While the weight loss
step in the second range (266 – 320°C) was attributed to the degradation of starch compounds including degradation of glycoside ring [11]. The last degradation step is related to decomposition of PP matrix contained in Ap-g-PHMA at maximum temperature in the range of 400-460°C. Filler content in PP matrix lead reduction in chain mobility in the boundary layers [12]. The degradation process of the starch is highly complex. Starch structure need to be broken so that the amyllose and amylopectin can be degraded. Starch is much easily degraded than PP, since it has carbon-oxygen bonds.

Figure 4 indicates also a residue that does not relate to PP. According to Gonzalez (2009), PP degrades through chain rupture, so it can be assumed that this residue relates to crosslink structure that is exist in starch granules. Due to highly hygroscopic in nature, it is impossible to eliminate all the water content in the blends, since water induces the increase in granule and swelling size [13-15].

![Figure 4. TGA-curves of PP/starch/Ap-g-PHMA 50/50/0.6 ( ), 60/40/06 ( ); 50/50/1 ( ) and 60/40/1 ( )](image)

The melt flow index (MFI) is a measure of viscosity inversion. Increase the MFI value by adding starch content, reduce its viscosity [16]. The MFI is used also as a measurement of the uniformity of flow rate of thermoplastic material. It is a practical method that widely used to relate the molecular weight and viscosity of polymer compounds.

| Samples             | Ap-g-PHMA (phr) | MFI values (g/10 min) |
|---------------------|-----------------|-----------------------|
| PP film             | -               | 10                    |
| PP/starch, 60/40    | 0.6             | 36±1.16               |
| PP/starch, 60/40    | 1.0             | 63±1.62               |
| PP/starch, 50/50    | 0.6             | 33±0.49               |
| PP/starch, 50/50    | 1.0             | 57±0.47               |
Table 2 shows the MFI value at different compositions of PP /starch in polypropylene matrix. At all level of Ap-g-PHMA as compatible agent, the MFI value reduced with increasing the starch content. However, by adding the compatible agent content at same ratio of PP/starch, increase the MFI value until almost twice. In contrast, previous studied done by Suttivunarubet et al. (2016), utilized PP/starch/PP-g-MA at 30% starch content, demonstrated that compatible agent give low MFI. It was stated that compatibilization of starch in that mixture has poor dispersion, and incapable to widely disperse into the PP matrix [17, 18]

4. Conclusion
The addition of Ap-g-PHMA enhanced the MFI of PP/starch.Ap-g-PHMA blend. The MFI of pure PP film is 10 gr/10 min while its value of PP/starch/PP-g-PHMA at 50/50 (0.6 phr) is 33±0.49 gr/10 min. It is recommended that these blends could be used as good interfacial adhesion and compatible material. The weight loss effect of Ap-g-PHMA is lower in PP/starch blends (60/40, 1 phr and 50/50, 0.6 phr) than that of in (60/40 0.6 phr and 50/50, 1phr). In all samples showed similar thermal properties pattern such as Tg, Tc and Tm. Hence indicated that PP/starch blends build semi crystalline material. Based on the TGA studies, starch produces a long-term effect on degradation process of PP, as the Ap-g-PHMA added as compatible agent, the decomposition temperature of the mixture raised.

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