Mechanical properties and crystallinity of linier low density polyethylene based biocomposite film

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ABSTRACT

Cassava starch filled linear low-density polyethylene (LLDPE) films are made in order to make plastics which environmentally friendly. The use of compatibilizer ethylene - acrylic ester - maleic anhydride polymerized is needed to obtain a compatible mixture of starch which is hydrophilic and LLDPE which is hydrophobic. In this study LLDPE films obtained were tested for tensile strength and elongation before and after accelerated aging and density. Melt flow index (MFI) of the film was also measured to determine the rheological properties. Crystallinity has been done by an X-Ray diffraction. The results showed that the addition of thermoplastic starch tended to reduce the tensile strength, elongation, and MFI values but increase the density of LLDPE films. The aging process at a temperature of $70\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 168 hours ± 2 hours tends to increase the tensile strength but decrease the extension of the break.

Keywords: biocomposite film, cassava starch, crystallinity, LLDPE, mechanical properties

INTRODUCTION

The development of biodegradable plastics from natural polymers is emerging due to problems associated with non-biodegradable plastics wastes all over the world. To this end, one of prospective materials that have been widely investigated is cassava starch. Although prospective in terms of biodegradability, low-cost, and abundant availability, cassava starch is brittle and difficult to process. Addition of plasticizer is, in general, needed to reduce its brittleness. One of common plasticizers is a mixture of water and glycerol (Adamu *et al.*, 2017; Lutfi *et al.*, 2017; Mendes *et al.*, 2016). Cassava starch can be co-compounded with synthetic polymer and enhance the (partial) biodegradability of the final compound. Co-compounding between starch and polyolefin has been reported in literature. Wan *et al.* (2014) and Obasi and Igwe (2014) reported the development starch/polypropylene-based plastics. Tanetrungroj and Prachayawarakorn (2015) and Nguyen *et al.* (2016) reported the co-compounding between starch and low-density polyethylene. In general, the starch composition in the co-compound is less than 50%. Another prospective polyolefin for the development of biodegradable plastics is linier low-density polyethylene (LLDPE). LLDPE is a synthetic polymer that is generally used for packaging due to its flexibility and elasticity, allowing the preparation of thinner plastics film compared to other polyolefins. LLDPE is chemical resistant, transparent, and inexpensive, however, it is non-biodegradable. Co-compounding between LLDPE and cassava starch results in biodegradable plastics composite

(Nguyen *et al.*, 2016). Due to polarity difference, LLDPE and starch are not miscible. Maleic anhydride grafted polyethylene (PE-g-MA) has been widely used as compatibilizer for starch and polyethylene co-compounds (Samper *et al.*, 2015; Sabetzadeh *et al.*, 2015; Oragwu, 2016).

In the present work, LLDPE is co-compounded with cassava starch, using ethylene acrylic ester maleic anhydride terpolymer as compatibilizer. The starch was hydrolyzed to break the branched amylopectins that are responsible for the inflexibility and brittleness of the starch-based products. We have previously reported the biodegradability of identical co-compound, in which the product was exposed to microorganisms-containing media at ambient temperature (Nurhajati *et al.*, 2018). Different from the previous publication, here we report the physical properties, i.e. density, melt flow index, and crystallinity, of the co-compounds as a function of starch content, as well as the stability of the co-compound at elevated temperature ($70\text{ }^{\circ}\text{C}$).

MATERIALS AND METHOD

Materials

Identical materials as reported in our previous publication (Nurhajati *et al.*, 2019) were used. LLDPE resin Asrene UF 1810T (extrusion grade, density 0.921 g/cm^3 , and melt index 1 g/10 min ($190\text{ }^{\circ}\text{C}/2.16\text{ kg}$)) was purchased from PT Chandra Asri. Orang Tani® cassava starch powder was used for preparing thermoplastic starch (TPS) formulations. Compatibilizer Lotrader

4210 and antioksidan Songnox 1010 were purchased from PT Bunga Permata and PT. Intera Lestari Polimer, respectively. Aquadest, stearic acid, and glycerol were purchased from Bratachem.

Experimental equipment

Internal mixer Haake Rheomix was used for co-compounding process, hydraulic press was used for preparing plastics film, Universal Testing Machine (UTM) Tinius Olsen-H25K was used for the determination of tensile strength before and after stability test at elevated temperature. Densimeter EW-200SG Mirage, melt flow indexer (MFI) Tinius Olsen-MP 1200, and X-ray diffraction (XRD) Rigaku miniflex 600 were used for the determination of density, melt flow index, and crystallinity of the co-compound, respectively.

Methods

Prior to mixing with LLDPE, a homogenized mixture of 10% water, 20% glycerol, and 70% starch was prepared. The starch was then co-compounded with LLDPE with varying composition of 30, 40, 50, 60, 70 phr. In addition, 5 phr Lotader 4210 as a compatibilizer was added. The starch/LLDPE film was then prepared using hydraulic press at 150 °C and 150 kg/cm². The mixing and co-compounding process was performed in an internal mixer (Haake Rheomix) at 130°C and 40 rpm for 15 min (Nurhajati *et al.*, 2019).

Physical properties testing

Physical properties that include density (ISO 1183-1:2012, method A), melt flow index (ASTM D1238, at 2.16 kg and 190°C), and crystallinity of the resulting starch/LLDPE film were then measured. The crystallinity was measured using X-ray diffractometer, at $2\theta = 0-70^\circ$, 40 kV, 20 mA, and degree per minute. Crystallinity degree (X_c) was determined according to:

$$X_c = \frac{\text{Crystalline area} \times 100\%}{\text{Total area (crystalline + amorphous)}} \quad (1)$$

Stability of the film upon exposure to high temperature (70 °C ± 2 °C) was performed in an oven for 168 ± 2 h. The tensile strength and elongation at break of the film before

and after exposure to the aging treatment were measured according to SNI ISO 11193.2:2010 to determine the film stability. Tensile strength and elongation at break measurements refers to ASTM D 882.

RESULTS AND DISCUSSION

Starch/LLDPE Film Density, Melt Flow Index, and Crystallinity

Figure 1 shows the density of starch/LLDPE film and melt flow index as a function of starch content. It is shown that the film density increases with increasing starch content in the film. This result is expected, because starch (1.5 g/cm³) possesses higher density than LLDPE (0.921 g/cm³). Similar results were reported by Kormin *et al.* (2017) and Nurhajati *et al.* (2019).

In contrast to the density profile, figure 1(b) and table 1 shows a decrease in MFI and degrees of crystallinity as starch content increases. MFI determines the flowability of a polymer material. In this study, MFI test was performed at 190 °C and 2.16 kg. Addition of 30 and 70 phr starch decreases the film's MFI by a factor of 26% and 93%, respectively. In general, higher density leads to higher viscosity and lower flowability, as shown in figure 1(a) and (b). Similar results have been reported by Oduola and Akpeji (2015) on cassava starch/polypropylene (PP), Kormin *et al.* (2017) on starch/LLDPE, Atli *et al.* (2018) on sawdust/Bioplast GS 2189, and Zhang (2018) on polylactic acid (PLA)/polyolefin elastomer (POE)/modified starch mixture.

The resulting diffractogram pattern is diffraction peaks with varying intensities. Each peak has a different high intensity. Polymers can contain crystalline regions mixed with amorphous regions. X-ray diffractograms of crystalline polymers produce sharp peaks, whereas amorphous polymers tend to produce widening peaks. In general, the polymeric material is semicrystalline, which means it has both an amorphous and crystalline part. The XRD test results related to peaks at 2-theta and the intensity for LLDPE film results are presented in Figure 2.

In Figure 2, LLDPE films without starch appear 2 dominant peaks at 2-theta = 21.76° and 24.14° and a peak that widens at 2θ = 19.46°. This is similar to Kim and Lee

Figure 1. Starch/LLDPE film density (a) and melt flow index (b) as a function of starch content.

(2017) (21.6° and 24.0), and Wang *et al.* (2019) (20.94° and 23°). Starch containing plasticizers have 5 main peaks at 2-theta = 15.22°, 17.2°, 18°, 20.4°, and 23.1°. This result is similar to Lomeli *et al.* (2014) (15.2°, 17.2°, 18.1°, 20.1° and 23.1°) and Ajiya *et al.* (2018) (15°, 17°-19°, 24°).

LLDPE film with 30 phr starch content has two main peaks at 2-theta = 21.8° and 24.08°. The addition of tapioca starch 50 phr shows a mixed pattern with two main peaks at 2-theta = 21.74°, and 23.82° (Figure 2d). The addition of tapioca starch 70 phr shows a mixed pattern with two main peaks at 2-theta = 21.96° and 24.44°. The addition of starch causes a decrease in intensity. Figure 2 shows that the LLDPE component causes the main peak intensity in the diffractogram, even though the LLDPE component is incorporated into the composite less than starch (Figure 2e)). This is in line with the results of research by Tanetrungroj and Prachayawarakorn (2015).

Tensile Strength and Elongation at Break

Mechanical stability upon exposure to elevated temperature (i.e. accelerated aging) is one of quality standards for plastics-based glove products. In this study, the tensile strength and elongation at break were measured

at elevated temperature $70 \pm 2^{\circ}\text{C}$ for 168 ± 2 h. Figure 3 shows the tensile strength and elongation at break as function of starch content. It is seen from figure 3(a) that tensile strength (TS) before thermal aging decreases with increasing starch content in the composite film. After thermal aging, TS decreases with increasing starch content up to 70 phr. Further increase in starch content increases the TS. On the other hand, elongation at break (EB) data in figure 3(b) shows decrease of EB values with increasing starch content, both before and after thermal aging. After 40 phr, however, the EB value plateaus for the samples after aging.

The decreasing trend of TS as a function of starch content in figure 3(a) indicates low interfacial adhesion between the LLDPE matrix with the starch molecules. Agglomerates of ungelatinized starch molecules that are not fully covered by the LLDPE matrix can also worsen the interfacial adhesion, leading to low mechanical properties of the composite. The weak interfacial adhesion also contributes to the decrease in EB values, as observed in figure 3(b). It is also known that brittleness is one of the main drawbacks in starch-containing materials. In principle, starch is polysaccharide consisting of amylose (linier chains) and amylopectin (branched chains).

Figure 2. XRD diffractogram from LLDPE film (a), Starch containing additives (b), LLDPE films on various amounts of starch (c. 30 phr, d. 50 phr, e. 70 phr).

Figure 3. The effect of starch content to (a) tensile strength and (b) elongation at break of LLDPE/starch film.

Table 1. Degrees of crystallinity.

Sample	Crystallinity (%)
LLDPE	0.53
Starch containing additives	39.19
LLDPE films on 30% of starch	30.21
LLDPE films on 50% of starch	27.12
LLDPE films on 70% of starch	13.02

The reason for brittleness of starch has been explained elsewhere. Similar results were reported by Yamak (2016) and Sanyang *et al.* (2015).

Thermal aging of the starch/LLDPE film at $70 \pm 2^\circ\text{C}$ for 168 ± 2 h changes the TS and EB trends as described in the previous paragraph. Exposure to high temperature might modify the water content, molecular arrangement, and gelatinization state of the starch molecules inside the film, leading to more crosslinking and stronger interfacial adhesion between the polymer chains. Both factors lead to higher TS and lower EB values, as observed in figure 3(b). Similar results were reported by Pg Adnan and Arshad (2017). Based on the standard and the experimental results shown in figure 3, starch/LLDPE film with starch content ≤ 20 phr is the most suitable material for the particular application.

CONCLUSION

The addition of thermoplastic starch tended to reduce the tensile strength, elongation, and MFI values but increase the density of LLDPE films. The aging process at a temperature of $70^\circ\text{C} \pm 2^\circ\text{C}$ for 168 hours ± 2 hours tends to increase the tensile strength but decrease the extension of the break.

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