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Bio-plastic composite characteristics of the modified cassava starch-glucomannan in variations of types and amount of fillers

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Abstract

The aim of this research was to investigate the effect of variations in filler types, the amount of fillers and their interactions on the characteristics of bio-plastic composites from modified cassava starch-glucomannan, and determine the type and amount of fillers that produce the best bio-plastic composite characteristics of modified cassava starch-glucomannan. This research applied a randomized block design with factorial experiments using two factors consisted of the type of filler (ZnO, CMC and chitosan) and the amount of fillers (0, 0.2, 0.4, 0.6, 0.8 and 1.0 g), with the total of 18 combination treatments. Each combination treatment was grouped into 4 based on the processing time of making bio-plastic composites. The variables observed were tensile strength, elongation at break, Young's modulus, swelling, degradation time of bio-plastic composites, surface profiles using scanning electron microscopy (SEM) and functional groups using FTIR spectrometers. The results showed that the type, the amount of fillers and their interactions had a very significant effect on tensile strength, elongation, Young's modulus, swelling, and degradation time of bio-plastic composites from modified glucomannan cassava starch. Bio-plastic composites from modified cassava-glucomannan starch using ZnO with the addition of 0.6-1.0 g had the best characteristics compared to others with tensile strength values reaching 2012.45-2022.23 MPa, elongation at break 8.12-8.65 %, Young's modulus 23.265.32-24,904.31 MPa, swelling 9.52-9.72 %, and degradation time of 6.25 days. Transverse surface profiles showed a smooth wave surface, there were not any holes or pores and visible fibers, while longitudinal surface profiles showed a fewer holes or pores and more smooth surface with not too high waves. In addition, these bio-plastic composites contained functional groups (O-H) and (C-H).

Key words: Bio-plastic composites, modified cassava starch, glucomannan, fillers

Introduction

Bio-plastic or its composite from raw materials of starch and glucomannan had been widely developed, but the quality was still very low. Harsojuwono and Arnata (2016) made bio-plastic from modified cassava starch used concentration of 6 % and the plasticizer glycerol of 1 %, resulting products with a tensile strength of 930 MPa, elongation at break of 18.75 %, and Young's modulus of 4960 MPa. Meanwhile, Harsojuwono *et al.* (2017) made bio-plastic composites from modified cassava starch and dried at 50 °C for 5 hours with hot air debit of 5±1 m^3/minute, resulting product that had a tensile strength of 1057.40 MPa, elongation at break of 15.95 %, Young's modulus of 6629.47 MPa, swelling of 9.91 % and the degradation time of 7 days, respectively. Harsojuwono *et al.* (2018) developed bio-plastic of modified cassava starch and used treatment of gelatinization temperature at 75±1 °C and pH 5, resulting product that had a tensile strength of 1657.43 MPa, the elongation at break of 10.32 %, Young's modulus of 16060.37 MPa, swelling of 9 % and degradation time of 7.33 days. Furthermore, Harsojuwono *et al.* (2019) developed a bio-plastics composite from modified cassava starch and glucomannan on the ratio of 3:1 and used 1 % acetic acid solution. The resulting product had a tensile strength of 1997.40 MPa, elongation at break of 8.90 %, Young's modulus of 22442.70 MPa, swelling of 10.40 % and degradation time of 6.33 days. Meanwhile, according to Aveorus (2009), the International Plastic Standard (ASTM 5336) showed the characteristics of tensile strength for PLA plastics from Japan reaching 2050 MPa and PCL plastics from the UK reaching 190 MPa, elongation at break for PLA plastics from Japan reaching 9 % and PCL plastic from the UK reaching > 500 %. This showed that bio-plastic or bio-plastic composites developed from cassava starch and glucomannan did not meet the International Standards.

It was necessary to optimize the other factors that influenced the characteristics of bio-plastics composite, including application of filler materials, both in the type and the volume added. According to Melani *et al.* (2017), filler is a material used to strengthen the physical and mechanical properties of a composite based on the principle of adhesion. Researchers have tried several filler materials to increase quality of bio-plastic composites. Rahmatunisa (2015) showed that the biodegradable tapioca styrofoam that uses ZnO as filler and ethylene glycol as plasticizer could result the packaging materials for dry products. According to Hardjono *et al.* (2016), bio-plastics from *kepok* banana peel that used citric acid and $CaCO_3$ filler of 0.4 % w/w had a tensile strength of 4.202 MPa. This value was higher than bio-plastics of *kepok* banana peel that used 0.4 % CMC filler w/w with a tensile strength of 4.032 MPa. Conversely, the degradation ability of bio-plastics of *kepok* banana peel with the addition of $CaCO_3$ filler of 0.4 % w/w was less than bio-plastics with the addition of CMC filler of 0.4 % w/w. Khalistyawati *et al.* (2016) showed that bio-plastics composites made of modified starch: (corn husk: PLA) at a ratio of 70: (15:15), added with 4.5 % ZnO filler and 30 % glycerol plasticizer, had tensile strength of 8.55 MPa and an elongation at break of 49.17 %. These values were in accordance to the bioplastic criteria of SNI 7818: 2014. However, the edible film from carrageenan and modified starch with addition of nanochitosan filler at 1 % v/v had a thickness of 0.065 mm and a transparency level of 82.56, meet that of the Chromameter Standard for bioplastic (Rochima *et al.,* 2018). Prasetyo *et al.* (2013) showed that addition of a silane coupling agent from 0 to 1.5 % in a polyester-cantula composite with 3D fiber webbing increased impact resistance, bending and tensile strength. Addition of 1.5 % silane coupling agent caused the composite had an impact resistance of 92.4 %, bending of 9.6 % and tensile strength of 30,990 MPa, which was higher than without silane coupling agent. Kartika (2017) showed that bio-composite from mango seed starch using ZnO hybrid of 3 %, clay of 6 % and glycerol of 25 % had a tensile strength of 6.053 MPa, elongation at break of 58.148 %, density of 1.338 g/cm^3 and water absorption of 27.845 %, respectively. Melani *et al.* (2017) showed that making bio-plastics from taro yam starch using melt intercalation method with addition of clay filler of 4 % and sorbitol of 25 %, stirred for 40 minutes and dried at 45 °C for 5 hours, resulted bioplastics with tensile strength of 89.33 MPa, the degradation residual weight of 52 %. Their study indicated that the resulted bioplastics had the quality that meet with the Indonesian National Standard (SNI).

Above mentioned studies confirmed that the amount of fillers in the manufacture of bio-plastics or bio-plastics composites could improve their quality. Variation of types and amount of filler material has different impact on the characteristics of bio-plastic and it’s composite. Limited research has been done on the application of filler materials in bio-plastic composites manufacture from modified cassava starch-glucomannan. In this regard, it was necessary to study the type and amount of appropriate fillers in the manufacture of bio-plastic composites from the modified cassava starch-glucomannan as its composite characteristics are not according to International Plastic Standards. The research was aimed at investigating the effect of filler type, amount of fillers and their interaction on the characteristics of bio-plastic composites from the modified cassava starch-glucomannan, and determine the type and amount of fillers that produce the best characteristics of bio-plastic composites from modified cassava starch-glucomannan.

Materials and methods

Material: Modified cassava starch (Indo Food Chem.), glucomannan and chitosan (CV Nura Jaya), acetic acid (CH_3COOH), glycerol, ZnO, CMC, chitosan and aquadest (CV Brathacem) were used. The research tools consisted of water bath, drying oven, teflon molder of 20 cm, and plastic mechanical test equipment namely Autograph-Sidmazu based on ASTM D638, scanning electron microscope (SEM) and FTIR spectrometer.

Research design: This research used a randomized block design with factorial experiments using two factors. The first factor was a type of filler with 3 levels, namely ZnO, CMC and chitosan. The second factor was the amount of fillers with 6 levels, namely 0, 0.2, 0.4, 0.6, 0.8 and 1.0 g. So there were 18 treatment combinations. Each treatment combination was grouped into 4 replicates based on the time of the bio-plastic composite manufacturing process, so that there were 72 experimental units.

Making bio-plastic composites from the modified cassava starch-glucomannan: Preparing the research materials that covered: filler material according to treatment, modified cassava starch and glucomannan on ratio of 3:1 with a total weight of 6 g, 93 g of 1 % acetic acid solution, 1 g glycerol. Furthermore, mixed the fillers material with types and amount according to treatment with 93 g of 1 % acetic acid solution and stirred for 10 minutes. That mixture was added to modified cassava starch and glucomannan, and stirred again for 10 minutes. After that, it was added 1 g glycerol then stirred and heated at 75±1 °C in the water bath until gel formation. The gel was molded with a teflon molder which had 20 cm diameter after this dried in the drying oven at 60 °C for 5 hours. Bio-plastic composites formed were cooled at room temperature then removed from teflon molder after 24 hours.

The variables observed were tensile strength, elongation at break and Young’ Modulus (ASTM D638), swelling (Harsojuwono and Arnata, 2016), biodegradation time (ISO 17556), surface profile of bio-plastics composite using scanning electron microscope (SEM) (Harsojuwono *et al.,* 2017) and functional groups with FTIR spectrometers (Gable, 2014).

Data analysis: The data were analyzed using ANOVA and means were compared by applying Duncan’s multiple comparison test. SPSS 25 was used for data analysis.

Results

The tensile strength, elongation at break and Young’s modulus: The analysis of variance showed that the filler type, amount of fillers and their interactions had a very significant effect to tensile strength, elongation at break and Young’s modulus of bio-plastic composites from modified cassava starch-glucomannan. The value of the tensile strength was between 1476.87-2022.23 MPa, elongation at break was between 8.12-12.76 % and Young’s modulus was between 11.574.22- 24.904.31 MPa, as shown in Table 1.

Table 1 showed that the bio-plastic composite from modified cassava starch-glucomannan using ZnO filler (0.6-1.0 g) had a high tensile strength (2012.45-2022.23 MPa), but it was not significantly different from that of the bio-plastic composites from modified cassava starch-glucomannan using CMC filler (0.4-0.8 g). Table 1 also show that the bio-plastic composite from modified cassava starch-glucomannan using chitosan filler (1.0 g) had the largest value of elongation at break (12.67 %) which was not significantly different from the elongation at break (11.65 %) of the bio-plastic composite from modified cassava starch-glucomannan with addition of 0.8 g chitosan filler. Bio-plastic composite from modified cassava starch-glucomannan on the addition of ZnO between 0.6-1.0 g and CMC between 0.4-0.6 g, had low value of elongation at break (8.12-8.82 %). This value was not significantly different from the elongation at break value (8.91 %) of bio-plastic composite from modified cassava starch-glucomannan with addition of 0.8 g CMC filler. Furthermore, the study also found that the bio-plastic composite from modified

Table 1. Mean of tensile strength, elongation at break and Young's modulus of bio-plastic composites from modified cassava starch-glucomannan in treatment of type and addition of fillers

Type and addition of fillers	Mean of tensile strength (MPa)	Mean of elongation at break (%)	Mean of Young' modulus (MPa)
ZnO (0 g)	1996.64b	9.35b	21,354.44b
ZnO (0.2 g)	1998.78b	9.21b	21,702.28b
ZnO (0.4 g)	2001.13b	9.01b	22,210.10b
ZnO (0.6 g)	2022.23a	8.12c	24,904.31a
ZnO (0.8 g)	2017.45a	8.15c	24,753.99a
ZnO (1.0 g)	2012.45a	8.65c	23,265.32a
CMC (0 g)	1993.86b	9.33b	22,080.40b
CMC (0.2 g)	1995.76b	9.01b	22,150.50b
CMC (0.4 g)	1999.79ab	8.76c	22,828.65ab
CMC (0.6 g)	2001.45ab	8.82c	22,692.18ab
CMC (0.8 g)	2000.02ab	8.91bc	22,446.91b
CMC (1.0 g)	1997.56b	9.21b	21,689.03b
Chitosan (0 g)	1998.12b	9.27b	22,275.59b
Chitosan (0.2 g)	1867.78c	9.13b	20,457.61bc
Chitosan (0.4 g)	1754.9d	9.67b	18,147.88c
Chitosan (0.6 g)	1623.67e	10.23b	15,871.65d
Chitosan (0.8 g)	1577.89f	11.65ab	13,544.12e
Chitosan (1.0 g)	1476.87g	12.76a	11,574.22f

The same notation behind the mean in the same column denote no significant difference at *P*=0.05.

Table 2. The mean of swelling and degradation time of bio-plastic composites from modified cassava starch-glucomannan in treatment of type and addition of fillers

Type and addition of filler	Mean of swelling (%)	Mean of degradation time (day)
ZnO (0 g)	10.40c	6.50b
ZnO (0.2 g)	9.98c	6.50b
ZnO (0.4 g)	9.81c	6.25b
ZnO (0.6 g)	9.72c	6.25b
ZnO (0.8 g)	9.65c	6.25b
ZnO (1.0 g)	9.52c	6.25b
CMC (0 g)	10.36c	6.50b
CMC (0.2 g)	69.58b	6.50b
CMC (0.4 g)	79.98ab	6.50b
CMC (0.6 g)	90.15a	6.25b
CMC (0.8 g)	102.02a	6.25b
CMC (1.0 g)	119.76a	6.25b
Chitosan (0 g)	10.39c	6.50b
Chitosan (0.2 g)	11.78c	7.25ab
Chitosan (0.4 g)	12.49c	7.50ab
Chitosan (0.6 g)	13.67c	7.75a
Chitosan (0.8 g)	14.79c	8.25a
Chitosan (1.0 g)	16.68c	9.25a

The same notation behind the mean in the same column denote no significant difference at *P*=0.05.

cassava starch-glucomannan with addition of ZnO filler (0.6-1.0 g) had a high Young's modulus (23,265.32-24,904.31 MPa). However, this was not significantly different with that of bio-plastic composites from modified cassava starch-glucomannan with addition of MC fillers (0.4-0.6 g). Bio-plastic composite of modified cassava starch-glucomannan which used chitosan filler had the lowest Young's modulus of 11,574.22 MPa. Bio-plastics composite from modified cassava starch-glucomannan with ZnO fillers (0.6-1.0 g) had higher Young's modulus (23,265.32-24,904.31 MPa) than the research result of Harsojuwono *et al.* (2019). Harsojuwono *et al.* (2019) reported that bio-plastics composites from modified cassava starch-glucomannan with ratio of 3:1 which used acetic acid solution of 1 % had the Young's modulus of 22,442.70 MPa.

The swelling and biodegradability: The analysis of variance showed that the filler type, the amount of fillers and their interactions had a very significant effect on swelling and the degradation time of bio-plastic composites from modified cassava starch-glucomannan. The value of swelling was between 9.52-119.76 % and degradation time was between 6.25-9.25 days, as shown in Table 2.

Table 2 showed that the bio-plastic composite from modified cassava starch-glucomannan which used CMC filler (0.6-1.0 g) had a high swelling value (90.15-119.76 %) and was not significantly different from swelling value (79.98 %) of the bio-plastic composite from modified cassava starch-glucomannan by using CMC fillers (0.4 g), but significantly different with bio-plastic composites from modified cassava starch-glucomannan using ZnO and chitosan fillers. Table 2 also showed that the bio-plastic composite from modified cassava starch-glucomannan using chitosan filler (0.6-1.0 g) had the longest degradation time (7.75-9.25 days) and was not significantly different from the degradation time (7.25-7.50 days) of the bio-plastic composite from modified cassava starch-glucomannan using chitosan filler (0.2-0.4 g), but it was significantly different from the others which had a degradation time between 6.25-6.50 days.

Surface profiles: The transverse surface profile of the bio-plastic composite from modified cassava starch-glucomannan without filler is shown in Fig. 1a, while that using ZnO filler is shown in Fig. 1b. The transverse surface profile of the bio-plastic composite from modified cassava starch-glucomannan using acetic acid solution by Harsojuwono *et al.* (2019) is shown in Fig. 2 for comparison.

Fig. 1a showed that the transverse surface profile of a bio-plastic composite from modified cassava starch-glucomannan with no filler appeared to have holes (pores) on one side. While, Fig. 1b showed the transverse surface profile of the bio-plastic composite from modified cassava starch-glucomannan which used ZnO filler. The longitudinal surface profile of the bio-plastic composite from modified cassava starch-glucomannan without filler is shown in Fig. 3a, while those using ZnO fillers is shown in Fig. 3b. Fig. 4 showed the comparison of the research result of Harsojuwono *et al.* (2019).

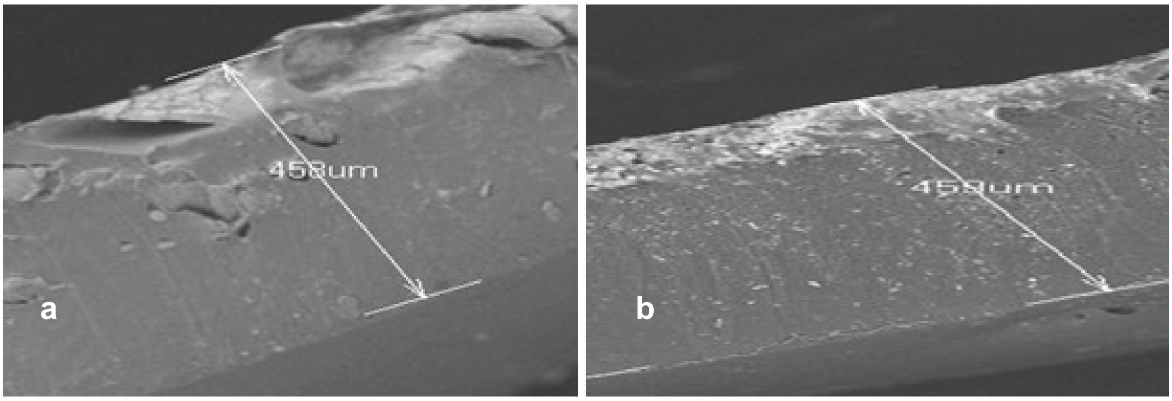

Fig. 1. The transverse surface profile of the bio-plastic composite from modified cassava starch- glucomannan (a) no filler, (b) using ZnO filler

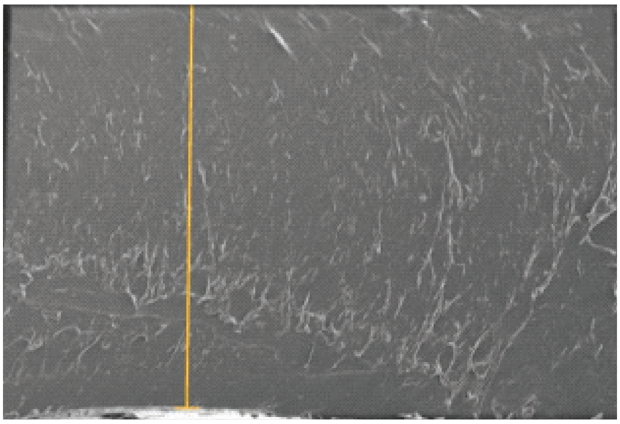

Fig. 2. The transverse surface profile of the bio-plastic composite from modified cassava starch- glucomannan using acetic acid solution of 1 % (Harsojuwono *et al.,* 2019)

Fig. 3a depicts the longitudinal surface profile of bio-plastic composites from modified cassava starch-glucomannan without filler. The Fig. 3a show large or small holes (pores) which are evenly distributed on the surface, while Fig. 3b show that bio-plastic composite from modified cassava starch-glucomannan using ZnO has fewer holes or pores and more smooth surface with not too high waves.

The functional group: The existence of functional groups in bio-plastics was highly dependent on the components that made up the bio-plastics, including the form of their composites. Fig. 5 showed that bio-plastic composites from modified cassava starch-glucomannan without filler, had more wave numbers than wave numbers in Fig. 6 which is a spectra of bio-plastic composites from modified cassava starch-glucomannan using ZnO fillers. However, when it was compared with wave numbers

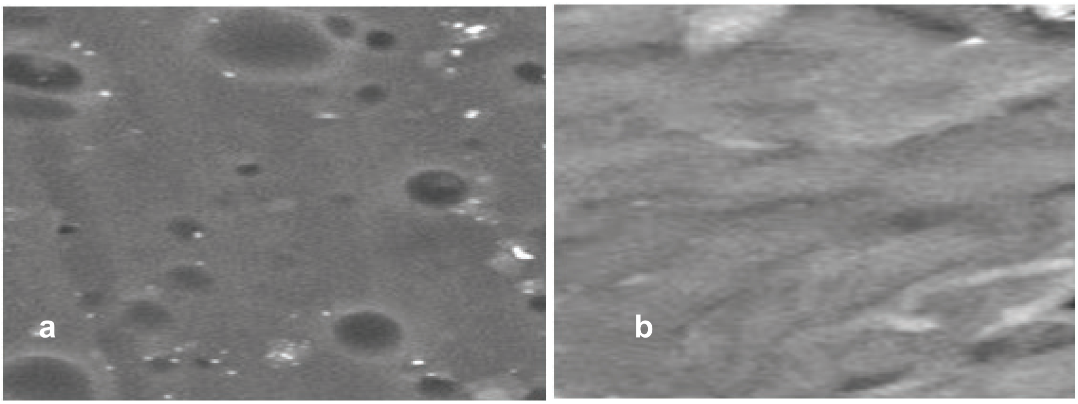

Fig. 3. The longitudinal surface profile of bio-plastic composite from modified cassava starch -glucomannan (a) no filler, b) using ZnO filler

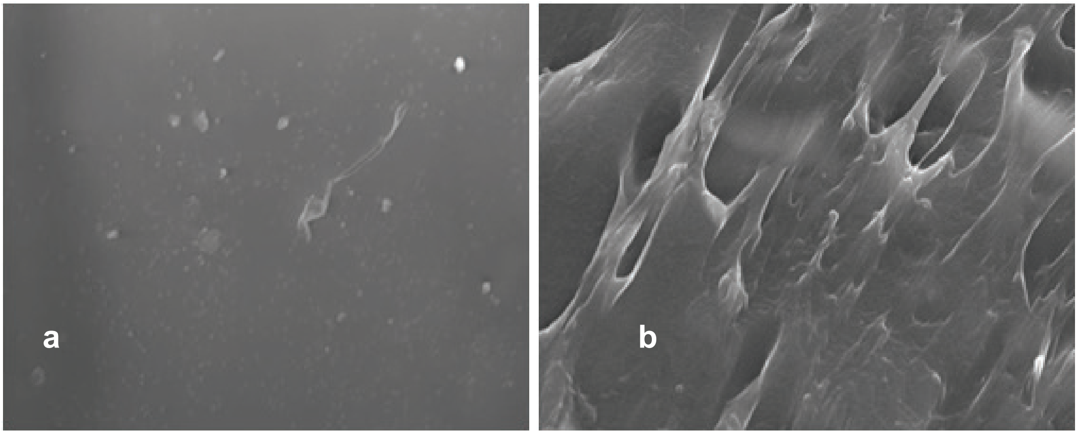

Fig. 4. The longitudinal surface profile (a) bio-plastics cassava starch using ZnO nano filler (Harunsyah *et al.*, 2017) (b) bio-plastic composite from modified cassava starch-glucomannan using acetic acid solution of 1 % (Harsojuwono *et al.,* 2019)

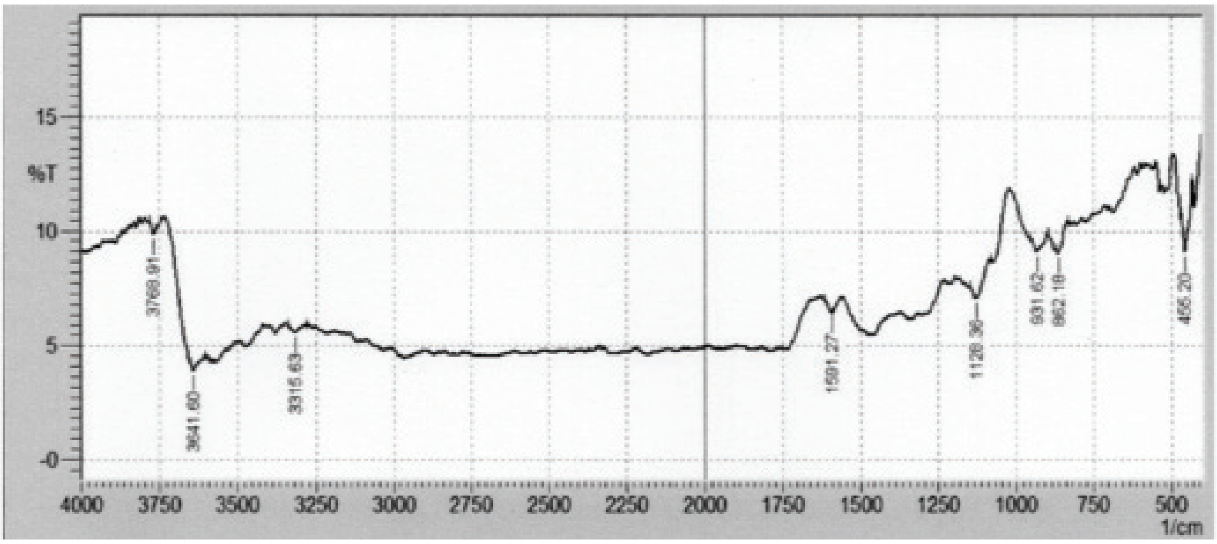

Fig. 5. The wave numbers spectra of bio-plastic composite from modified cassava starch - glucomaman without filler

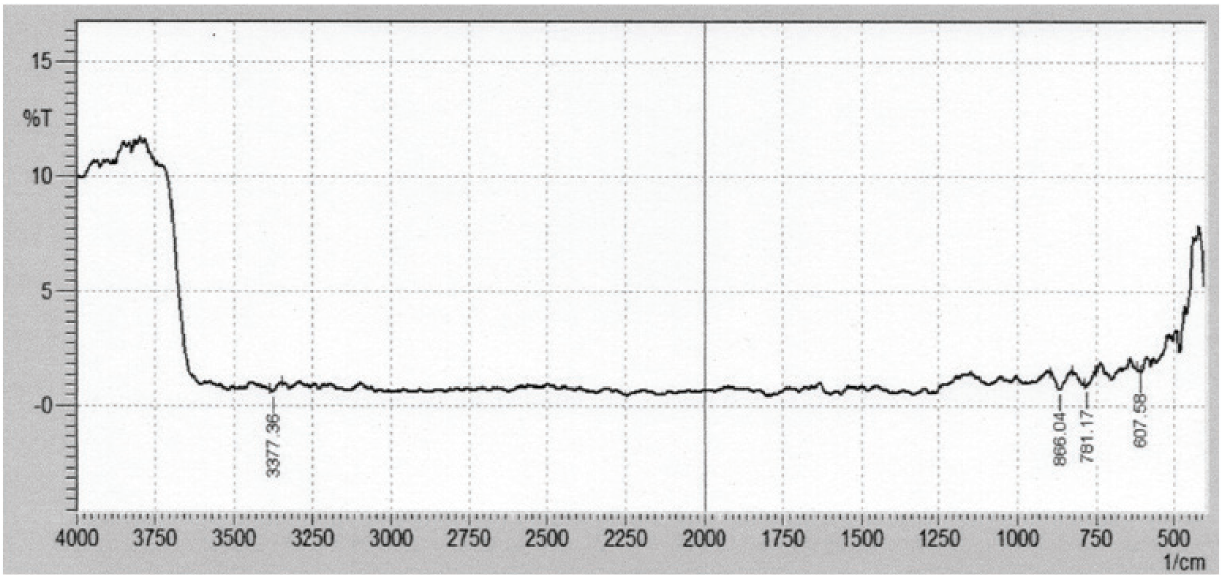

Fig. 6. The wave numbers spectra of bio-plastic composite from modified cassava starch-glucomaman that using ZnO filler

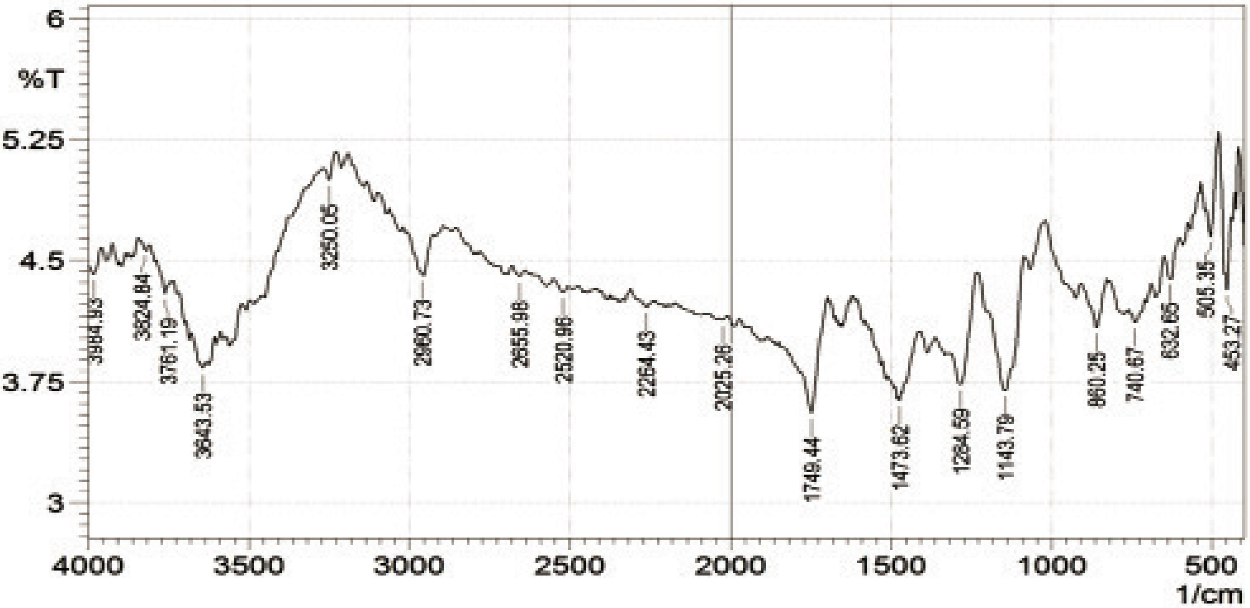

Fig. 7. The wave numbers spectra of bio-plastic composite from modified cassava starch-glucomannan that using acetic acid solution of 1 % (Harsojuwono *et al.,* 2019)

Table 3. The wave numbers and functional groups in bio-plastic composites from modified cassava starch-glucomannan without fillers and using ZnO fillers

Area standard of wave numbers* (cm^{-1})	Wave numbers of bio-plastic composite without filler (cm^{-1})	Functional group in the bio-plastic composite without filler	Wave numbers of bio-plastic composite with using ZnO filler (cm^{-1})	Functional group in the bio-plastic composite with using ZnO filler
3700 - 3800	3768.91	O-H		
3100 - 3700	3641.60 and 3315.63	O-H	3377.36	O-H
1500 - 1600	1591.27	C=C		
1050 - 1300	1128.36	C-O		
675 - 995	931.62	C-H	866.04, 781.17, 607.58	C-H
600 - 900	862.18	C-H		
< 600	455.20	—(CH_2)n		

*Gable (2014)

spectra of a bio-plastic composite from modified cassava starch-glucomannan where acetic acid solution of 1 % was used both bio-plastic composite had a fewer wave numbers as shown in Fig. 7 (Harsojuwono *et al.*, 2019).

Discussion

The tensile strength, elongation at break and Young's modulus: The result of tensile strength was in accordance with Mousa *et al.* (2014) who explained that the high hydroxyl group content of cellulose derivatives including CMC caused poor compatibility of natural fillers because of it's hydrophilic nature. However, the lowest tensile strength value (1476.87 MPa) was shown by bio-plastic composites from modified cassava starch-glucomannan using chitosan fillers on the addition of 1 g. The overall results mentioned above were still higher than the research results of Khalistyawati *et al.* (2016) which showed that bio-plastics composites with a ratio of modified starch: (corn husk:PLA) = 70:(15:15), using ZnO (4.5 %) and glycerol (30 %) had a tensile strength value of 8.55 MPa. The results were also higher than the research results of Kartika (2017) where bio-composite from mango seed starch using hybrid ZnO of 3 %, clay of 6 % and glycerol of 25 %, had a tensile strength value of 6.053 MPa. According to Kasmuri and Zait (2018), the addition of filler from eggshells (source of minerals) increased the tensile strength of bio-plastic starch by 4.94 %, compared to the addition of chitosan which was only able to increase it by 1.28 %. But, it was further explained that the amount of fillers on the starch-based bio-plastics would improve the performance of bio-plastics. Bio-plastic composites from the modified cassava starch-glucomannan using fillers or without fillers, only qualified to SNI plastic standards with tensile strength values of 24.7- 302 MPa (Nurlita *et al.*, 2017), ISO 527/1B International Standards with values of 35.95 MPa and PCL from the United Kingdom with values of 190 MPa but it did not qualify to international plastic standards (ASTM 5336) for PLA plastics from Japan with values of 2050 MPa (Averous, 2009). However, the value of elongation at break was still lower than the elongation at break (49.17 %) of bio-plastic composite from the mixture of modified starch, corn husk and PLA with the ratio of 70: (15:15), using ZnO (4.5 %) and glycerol (30 %) (Khalistyawati *et al.*, 2016). This bio-plastic composite that was studied by Khalistyawati *et al.* (2016) was according to the SNI 7818: 2014 criteria. Kartika (2017) reported that bio-composite from mango seed starch which used hybrid ZnO filler of 3 %, clay of 6 % and glycerol of 25 %, had an elongation at break of 58.148 %. The elongation at break of bio-plastic composite from modified cassava starch-glucomannan with or without fillers, both were not yet qualified for SNI (21-220 %), but some of them fulfilled the PLA plastic standard from Japan which set the maximum elongation at break of 9 %. All of the bio-plastic composites from modified cassava starch-glucomannan had qualified the international plastic standard (ASTM5336) which set the elongation at break smaller than 500 % for PCL plastic from the UK. Related to the value of elongation at break, the information of the addition of ZnO filler evidently suitable of the opinion of Harunsyah *et al.* (2017), who explained that increasing concentration of ZnO caused an increase in the tensile strength but it decreased the elongation at break. The point was the increasing ZnO concentration caused the increasing Young's modulus value. This happens because the Young's modulus was directly proportional to the tensile strength but inversely proportional to elongation at break. Bio-plastic composites from modified cassava starch-glucomannan which used fillers or without fillers, both of them had qualified the Young's modulus of international plastic standards ISO 527/1B with a minimum value of 6019 MPa.

Swelling and degradation time: In general, swelling value of the bio-plastic composite from modified cassava starch-glucomannan using CMC was higher than swelling value of the bio-plastic composite from modified cassava starch-glucomannan using the fillers of ZnO and chitosan. According to Sapei *et al.* (2017), the addition of ZnO significantly decreased ability of swelling of bio-plastic composites. Swelling value of the bio-plastic composite from modified cassava starch-glucomannan using the fillers of ZnO and chitosan was in the range of 9.52-16.68 %, which was similar to the results of Harsojuwono *et al.* (2019), which showed that composite bio-plastics with a ratio of modified cassava starch with glucomannan = 3:1 using 1 % acetic acid solution, had swelling value of 10.40 %. Swelling characteristics of bio-plastic composites from modified cassava starch-glucomannan using fillers or without fillers still did not qualified to International Plastic Standards (EN 317) which determined a maximum swelling value of 1.44 %. Related to the degradation time, these results were similar to the research results of Harsojuwono *et al.* (2019) which showed that bio-plastics composites from modified cassava starch-glucomannan on the ratio of 3:1 with addition of 1 % acetic acid solution, had a degradation time of 6.33 days. Meanwhile, bio-plastic composites from modified cassava starch-glucomannan using filler chitosan had a longer degradation time due to the presence of anti-microbial properties of chitosan. This was in accordance with Sapei *et al.* (2015) and Rochima *et al.* (2018) who explained that higher concentration of chitosan may lead to a longer degradation time of bio-plastic composites. This study showed that the degradation time of bio-plastic composites from modified cassava starch-glucomannan with filler or without filler was meeting the international plastic standards (ASTM5336) value of 60 days.

The surface profile of bio-plastic composites: The transverse surface profile showed a smooth wave surface, there were not any holes or pores and visible fibers. This was different from the research results of Harsojuwono *et al.* (2019), as seen in Fig. 2, which showed that there were a few holes in the part of edges and very clearly visible fine fibers. This difference was in accordance with Jamnongkan *et al.* (2018), who explained that using ZnO fillers or the other additive would affect the morphology or appearance of a bio-composite profile. However, this longitudinal surface was similar to the research results of Harunsyah *et al.* (2017) where surface profile of bio-plastics using ZnO as filler showed that the longitudinal surface of the bio-plastic was not porous and smooth, there were no cracks or air bubbles (Fig. 4a). But this was very different from the research results of Harsojuwono *et al.* (2019) which showed a large fiber clumps with sharp bumps and large pores that were evenly distributed throughout the surface (Fig. 4b).

The functional group: The functional groups contained in bio-plastic composites from modified cassava starch-glucomannan without filler include (O-H), (C = C), (C-O), (C-H) and -(CH2) n while bio-plastic composites using ZnO fillers had functional groups O-H and C-H as shown in Table 3. The table show that there were differences in the composition of functional groups between bio-plastic composites without fillers from those using ZnO fillers. This was different from Harunsyah *et al.* (2017), who explained that the addition of ZnO did not change the composition of functional groups of bio-plastic composite. However, Harsojuwono *et al.* (2019) explained that there were changed composition of the functional groups contained in bio-plastic composites from modified cassava starch-glucomannan if given different treatment such as treatment of acetic acid solution of 1 % that caused bio-plastic composite had a functional group (O-H), (C-H), (C-N), (C-O), (C-C), (C = O), (N-H),-(CH2)n and (C = C).

The results showed that the type and the amount of filler affected the tensile strength, elongation at break, Young's modulus, swelling and time of degradation of bio-plastic composites of modified cassava starch-glucomannan significantly. Bio-plastic composite of modified cassava starch-glucomannan which used ZnO (0.6-1.0 g) had better characteristics than the others with tensile strength value of 2012.45-2022.23 MPa, elongation at break of 8.12-8.65 %, Young's modulus of 23,265.32-24,904.31 MPa, swelling of 9.52-9.72 %, degradation time of 6.25 days. Transverse surface profiles showed a smooth wave surface, there were not any holes or pores and visible fibers, while longitudinal surface profiles showed a fewer holes or pores and more smooth surface with not too high waves. In addition, these bio-plastic composites contained functional groups (O-H) and (C-H). Bio-plastic composites from modified cassava starch-glucomannan with or without fillers meets the plastic tensile strength requirements of the Indonesian National Standard (SNI), ISO 527 / 1B International Standards, and PCL standards from the UK, but it does not meet the requirements for international plastic standards (ASTM 5336) for PLA plastics from Japan. All of them have elongation at break that meet the requirements of international plastic standards (ASTM5336) for PCL plastics from the UK and have Young's modulus that meets international plastic standards ISO 527 / 1B. The degradation time qualifies for international plastic standards (ASTM5336) from Japanese PLA plastics and PCL from the UK, but the swelling does not qualify for International Plastic Standards (EN 317).

In order to improve the properties of bio-plastic composite from the main raw material of glucomannan and modified cassava starch, further research is needed on other factors such as the addition of thermoplastic forming agents to improve the characteristics of bio-thermoplastic composites as per international standards.

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