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The Surface Profile and Functional Group of Bio-Plastic Composites in Variations of Ratio of Starch, Glucomannan and Carrageenan.

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ABSTRACT

The objectives of the study were to identify the surface profiles and functional groups of bio-plastic composites made from starch, glucomannan and carrageenan. The study used an exploratory method, which was carried out by making a mixed bio-plastic composite of starch, glucomannan and carrageenan. The obtained composites were observed surface profiles on the transverse and longitudinal sides using Scan Electron Microscope (SEM), and identified functional groups on polymers formed by using FTIR spectrometers. The results show that the profile of the bio-plastic composite surface on the longitudinal view indicates the presence of webs with air cavities. The webs and air cavities grew larger as changes in the ratio of starch, glucomannan and carrageenan compounds from the starting ratio (6: 0: 0), to (1: 2.5: 2.5). Meanwhile, in the ratio (0: 3: 3) it appears that there are pores between air cavities. The profile of the bio-plastic composite surface at the transverse position indicates one layer in the ratio of starch, glucomannan and carrageenan = (6: 0: 0) turns into two layers with the top layer forming clumps and waves, while the bottom is flat and smooth. Next turns flat and smooth at the top and starts to tear at the bottom, as the ratio changes from (6: 0: 0) until to (1: 2.5: 2.5). Meanwhile, in the ratio (0: 3: 3) clearly visible the large pores at the upper layer. The thickness of the upper layers changes with changes in starch, glucomannan and carrageenan ratios of the composite of bio-plastics. Each of the upper thickness of the composite in the ratio (6: 0: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), (2: 2: 2), (1 : 2.5: 2.5) and (0: 3: 3) are 379, 296, 222, 219, 217, 200, 200 µm. Bio-plastic composites with mixed ratio of starch, glucomannan and carrageenan (6: 0: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), containing the OH, CH, CO (1: 2.5: 2.5) and (0: 3: 3) containing the OH, CH, CO, (CH2) n, C = C and C=O.

Keywords: bio-plastic composite, ratio of starch, glucomannan and carrageenan, surface profile and functional group

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INTRODUCTION

Bio-plastics are developed with the aim of replacing synthetic plastics that cause environmental pollution due to difficult degraded. Efforts that have been made in the manufacture of bio-plastics, among others using natural materials such as plant and animal materials. Currently, natural biological materials that potential as raw materials are starch, glucomannan and carrageenan. Starch from cassava is the most potential material as bio-plastic raw material (Firdaus and Anwar, 2004). In addition, starch from cassava has been produced on an industrial scale (Kumoro and Purbasari, 2014). Meanwhile, glucomannan is also guaranteed its availability because the source of its raw material is tuber porang have been cultivated on large scale in tropical forests (Mulyadi et al, 2017) and carrageenan can be obtained from seaweed Eucheuma cottonii which has also been cultured and produced in industrial scale (Widyastuti, 2010).

The bio-plastic development efforts of each of the above materials are remarkable. Several studies have been conducted to make bio-plastics of starch, glucomannan and carrageenan individually, but the results have not given maximum results in terms of their physical or mechanical properties as well as the surface profile and functional groups in the polymer formed. In order to improve its characteristics in order to meet national and international standards, it is incorporated some natural polymer raw materials to form composites.

The formation of bio-plastic composites from a mixture of starch, glucomannan and carrageenan is not widely known. Harsojuwono et al (2016) developed only bio-plastics from modified cassava starch with the results showing gel tissues with air cavities on a longitudinal surface profile. While it appears transversely displays a layered arrangement in a vertical direction with a thickness of 380 microns, while the magnification of 2500 times looks wave forms in the vertical direction. Al-Hassan and Norziah (2012) showing the presence of cavities between tissues on the longitudinal surface profile of edible films derived from starch and gelatin composites. Mulyadi et al (2017) just showed a composite of glucomannan and Carboxy Methyl Cellulose affecting its mechanical characteristics. Meanwhile, Martins et al (2012) showed the existence of fine pores on edible film made from raw carrageenan and soybean gum. Ariska and Suyatno (2015) showed a widening of the peak on edible film composite of carrageenan and banana tuber starch which has a wave number of 3456.9 cm-1, with a higher intensity than starch and carrageenan individually. The above information has not yet informed the bio-plastic composite characteristics of a mixture of starch, glucomannan and carrageenan. Therefore, the purpose of this study was to identify the characteristics of bio-plastic composites, especially the surface profiles and functional groups made of mixed of starch, glucomannan and carrageenan in different ratios.

MATERIALS AND METHODS

Materials

The main tool used between water bath, teflon, automatic cabinet dryer, SEM (Scan Electron Microscope) and FTIR (Fourier Transform Infra Red) spectrometer. Materials of study include starch, glucomannan, carrageenan, aquades, 25% acetic acid solution and glycerol.

Implementation of research

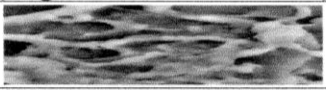
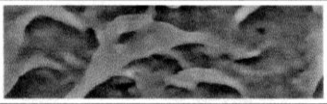
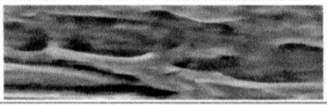
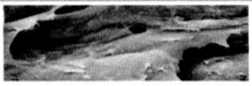
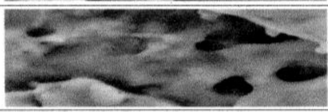
The explorative method used in this study and begins with the manufacture of bio-plastic composites of starch, glucomannan and carrageenan. The formed bio-plastic composites are identified surface profiles and functional groups. Bio-plastic composites are prepared as follows: Starch, glucomannan and carrageenan with a ratio (6: 0: 0); (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), (2: 2: 2), (1: 2.5: 2.5) and (0: 3: 3) each weighing 6 g mixed aquades 100 g, 0.2 g of 25% acetic acid and stirred for 10 minutes with a spatula in a beaker glass, after which the plasticizer added 1 g glycerol. The mixture is stirred again with a spatula for 10 minutes to keep the mixture homogeneous. Next, the mixture is heated and stirred in a water bath at a temperature of 70 ° C to form a gel. The formed gel is then printed on Teflon with a diameter of 20 cm. After that it is dried on an automatic cabinet dryer with a hot air rate of 5 + 0.1 m3 / min at a temperature of 50^{o}C for 5 hours. The formed bio-plastic is lifted slowly and cooled to room temperature for 24 hours and ready to be identified. The identification of the surface profile of the bio-plastic composites was performed on the transverse and longitudinal sides by using SEM, while the identification of functional groups was performed using an FTIR spectrometer.

RESULTS AND DISCUSSION

Bio-plastic composite surface profile on longitudinal position

The bio-plastic composites of starch, glucomannan and carrageenan produce surface profiles in longitudinal position as shown in Table 1. Table 1 shows the various profiles of the bio-plastic composite surfaces of mixed of starch, glucomannan and carrageenan with different ratio. The profile of the bio-plastic composite surface (magnification 3000 times) in the ratio of starch, glucomannan and carrageenan = 6: 0: 0 indicates the presence of webs with closer airspaces than composites with mixed ratio (5: 0.5: 0.5), (4 : 1: 1), (3: 1.5: 1.5), (2: 2: 2), and (1: 2.5: 2.5). The lower the ratio of starch to glucomannan and carrageenan, the more visible the air cavities are getting wider. This occurs until to the ratio of starch, glucomannan and carrageenan = 1: 2.5: 2. This profile is different when compared to the composite surface profile with the ratio of starch, glucomannan and carrageenan = 0: 3: 3. In the ratio of starch, glucomannan and carrageenan = 0: 3: 3, the profile of the bio-plastic composite surface indicates the presence of thick webs with air cavities accompanied by a considerable pore. These webs indicate the presence of cross linking that occurs in the formation of bio-plastic composites. According to Anonymous (2003) Cross link occurs because two molecules or more in the granule are connected by the hydroxyl group (-OH) (Anonymous, 2003). The profile of the bio-plastic composite surface on starch ratio: glucomannan: carrageenan = 6: 0: 0 shows a surface profile similar to edible film composite of starch and gelatin of Al-Hassan and Norziah (2012) research results. Meanwhile, the bio-plastic composite in starch ratio: glucomannan: carrageenan = 1: 2.5: 2.5 shows a longitudinal surface profile similar to the carrageenan composite surface profile with nanocrystalline cellulose of Zarina and Ahmad (2015) studies, as shown in Table 1.

Table 1: The profile of the surface on longitudinal position in variations ratio of starch, glucomannan and carrageenan from bio-plastic composite

Ratio of Starch : glucomannan : carrageenan	Surface profile on longitudinal position (magnification of 3000 times)	Reference of surface profile on longitudinal position
6 : 0 : 0		 (Al-Hassan and Norziah, 2012
5 : 0.5 : 0.5		
4 : 1 : 1		
3 : 1.5 : 1.5		
2 : 2 : 2		
1 : 2.5 : 2.5		 (Zarina and Ahmad, 2015)
0 : 3 : 3		

Bio-plastic Composite Surface Profiles on Transverse Position

The bio-plastic composites of starch, glucomannan and carrageenan produce surface profiles in the transverse position as shown in Table 2. Table 2 indicates the existence of different surface profiles at the transverse position. There are consist of one layer and some are divided into two layers. The thickness of the coating changes with the changing ratio of starch, glucomannan and carrageenan in the formation of bio-plastic composites. Bio-plastic composites in the ratio of starch, glucomannan and carrageenan = 6: 0: 0 indicate the presence of webs forming clumps with a layered arrangement in the vertical direction with a thickness of 379 μm in a single layer at 180 times magnification. This is different when compared to other bio-plastic composites with the ratio of starch, glucomannan and carrageenan (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), (2: 2: 2), (1: 2.5: 2.5) and (0: 3: 3), which shows a surface profile with two layers. In addition, bio-plastic composites with starch, glucomannan and carrageenan (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), (2: 2: 2), (1: 2.5: 2.5) and (0: 3: 3) indicate the presence of surface degradation in sequence. Initially in the ratio of starch, glucomannan and carrageenan (5: 0.5: 0.5), the upper surface profile shaped rough webs with a thickness of 296 μm while the bottom looks flat and smooth. It undergoes changes to be shape wavy with the form of a finer web with 222 μm thickness at the top layer and remains flat and smooth on the bottom of bio-plastic composite in the ratio of starch, glucomannan and carrageenan (4: 1: 1). Furthermore, in the ratio of starch, glucomannan and carrageenan (3: 1.5: 1.5), the wave-shaped surface profile is increasingly lost although there are still visible thin-thick divides with 219 μm thickness at the top, but the bottom remains flat and smooth. In the subsequent degradation of the mixture of starch, glucomannan and carrageenan = 2: 2: 2, the upper surface profile has no visible barriers that are clear only in the form of irregular lines with a thickness of 217 μm, while the bottom begin appear horizontal lines. The apparent profile changes occurred in the ratio of starch, glucomannan and carrageenan = 1: 2.5: 2.5, i.e. appear tearing of the bottom while the top was flat and smooth with a thickness of 200 μm. Meanwhile, bio-plastic composites in the ratio of starch, glucomannan and carrageenan = 0: 3: 3, indicate a large hole in the upper surface profile with a thickness of 214 μm, while the bottom appears flat and smooth. The above-mentioned changes occur because of the influence of bonding ability among composite polymers. The composite properties are determined by material composition, geometry (particle size, distribution and orientation) and the concentration of the material (Teresa, 2008). The bio-plastic composites in the ratio of starch, glucomannan and carrageenan (5: 0.5: 0.5) and (4: 1: 1) yield profile on transverse position similar to research result of Al-Hassan and Norziah (2012) about composite of edible films from starch and gelatin, as shown in Table 2. Meanwhile, bio-plastic composites in the ratio of starch, glucomannan and carrageenan (1: 2.5: 2.5) show a transverse surface profile similar to the composite profile of carrageenan and crystalline cellulose of Zarina and Ahmad (2015), as seen in Table 2.

Functional Group Profile

This bio-plastic composite is composed of the main ingredients of starch, glucomannan and carrageenan which belong to the polysaccharide class as well as the glycerol plasticizer and the pH regulator in the form of acetic acid. The formation of bio-plastic composites with starch, glucomannan and carrageenan materials undergoing plasticization in the presence of glycerol in certain acidity conditions (certain pH) will cause changes in functional groups of each component due to the polymerization reaction (Averous, 2004). The result of the reading with FTIR spectrophotometer, is obtained the wave numbers as shown in Table 3.

According to Anonymous (2012), the absorption peaks at the wave number around 3200 - 3500 cm^{-1} indicate the presence of hydroxyl (O-H) which binds to hydrogen. While the wave numbers between 2850 - 2970 cm^{-1} indicate alkenes (C-H), wave numbers of 2750-2850 cm^{-1} indicate aldehydes (C-H), spectrum of 2500-2700 cm^{-1} indicate hydrogen bonds of carboxylic acids, and 2100-2260 cm^{-1} denotes the presence of alkenes (C = C). Wave number of 2000 - 2300 cm^{-1} show ester functional groups and 1650 - 2000 cm^{-1} indicates the presence of simple aromatic compounds. Meanwhile, according to Anonymous (2013), at the wave numbers of 1630 - 1690 cm^{-1} there is a functional group C = O and the aromatic ring is present at a moderate to strong intensity uptake near the 1500 cm^{-1} waves as well as at the absorption peaks around the wave number of 3000 - 3100; 1550 - 1600 and 600 - 900 cm^{-1}. In the wave number of 1000 - 1300 cm^{-1} indicates the presence of carboxyl group (C-O), the wave number 675 - 995 cm^{-1} shows the presence of the alkenes function group (C = C) while it is below 700 cm^{-1} indicating other hydrocarbon compounds such as - (CH2) n (Thu, 2015).

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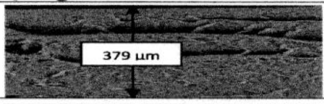
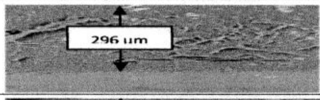
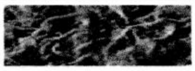
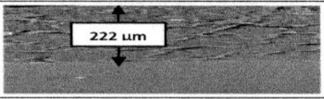
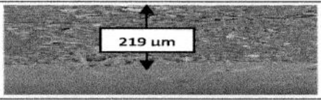
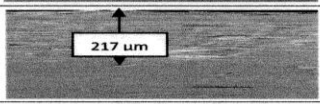
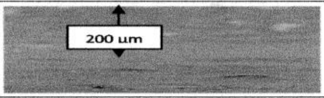
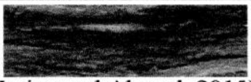
Table 2: The profile of the surface on transverse position in variations ratio of starch, glucomannan and carrageenan from the bio-plastic composite

Ratio of Starch : glucomannan : carrageenan	Surface profile on transverse position (Magnification of 180 times)	Reference of surface profile on transverse position
6 : 0 : 0		
5 : 0.5 : 0.5		 (Al-Hassan and Norziah, 2012)
4 : 1 : 1		
3 : 1.5 : 1.5		
2 : 2 : 2		
1 : 2.5 : 2.5		 (Zarina and Ahmad, 2015)
0 : 3 : 3		

Based on the above description by classifying the numbers of waves present in the spectrum (Table 3), the OH, CH, CO, (CH2) n, C = C function groups are present in the bio-plastic composites by the ratio of starch, glucomannan and carrageenan (6: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5). Meanwhile, the functional groups of O-H, C-H, C-O, (CH2) n, C = C and C = O are present in the bio-plastic composites with the ratio of starch, glucomannan and carrageenan (2: 2: 2) mixtures (1: 2.5: 2.5) and (0: 3: 3). It appears that one functional group C = O is not present in a bio-plastic composite with a ratio of a mixture of starch, glucomannan and carrageenan (6: 0: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5). This may be influenced by a lower carrageenan ratio in bio-plastic composites with a ratio of starch, glucomannan and carrageen mixture (6: 0: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5) than the ratio of starch, glucomannan and carrageenan (2: 2: 2), (1: 2.5: 2.5) and (0: 3: 3). The results of Brigida et al., (2010); Noranizan and Ahmad (2012); Safinas et al (2013) showed that the composite of carrageenan and nanocrystalline cellulose have a wave number between 3,300 to 3,200 cm^{-1} indicating the presence of an O-H functional group, the ~ 2900 cm^{-1} wave number indicating the presence of C-H and the wave number 1603-1690 cm^{-1} shows the presence of carbonyl functional groups (C = O).

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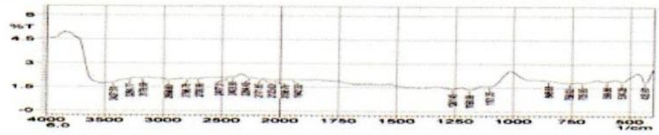
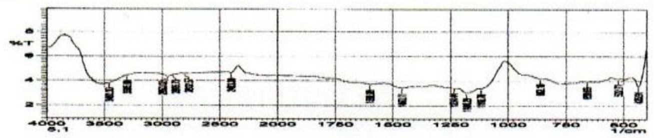
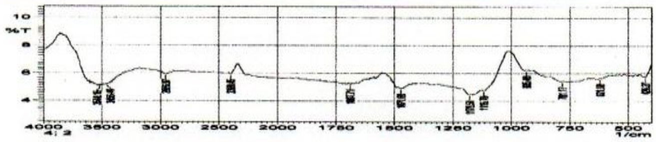
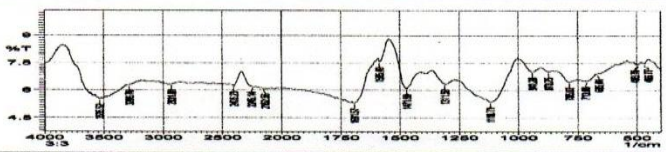
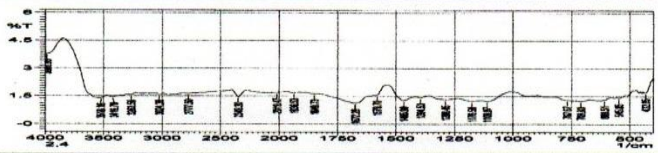
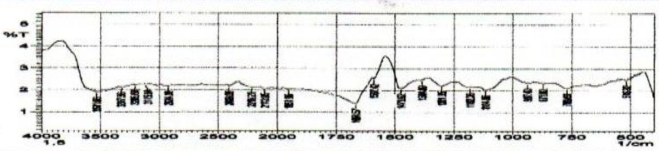
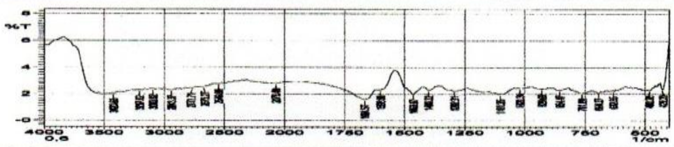
Table 3: The wave numbers and functional groups in variations ratio of starch, glucomannan and carrageenan from the bio-plastic composite

Ratio of starch : glucomannan : carrageenan	The wave numbers	Functional groups of bio-plastic composite
6 : 0 : 0		O-H, C-H, C-O, (CH2)n, C=C
5 : 0.5 : 0.5		O-H, C-H, C-O, (CH2)n, C=C
4 : 1 : 1		O-H, C-H, C-O, (CH2)n, C=C
3 : 1.5 : 1.5		O-H, C-H, C-O, (CH2)n, C=C
2 : 2 : 2		O-H, C-H, C-O, (CH2)n, C=C, C=O
1 : 2.5 : 2.5		O-H, C-H, C-O, (CH2)n, C=C, C=O
0 : 3 : 3		O-H, C-H, C-O, (CH2)n, C=C, C=O

CONCLUSION

The profile of the bio-plastic composite surface at longitudinal position indicates the presence of webs with air cavities. The webs and air cavities are further enlarged as changes in the ratio of starch, glucomannan and carrageenan mixture of bio-plastic composites ranging from the ratio (6: 0: 0), to (1: 2.5: 2.5). Meanwhile, in the ratio (0: 3: 3) it appears that there are pores between air cavities. The profile of the bio-plastic composite surface at the transverse position indicates the layer change, initially a one layer in the ratio of starch, glucomannan and carrageenan = (6: 0: 0) turns into two layers with the top layer forming a lumps and the waves and the bottom. flat and smooth, which then turns flat and smooth in the top layer and starts to tear at the bottom, in accordance with the ratio changes from (6: 0: 0) to (1: 2.5: 2.5). Meanwhile, in the ratio of starch, glucomannan and carrageenan = 0: 3: 3, clearly visible large pores in the upper layer. The thickness of the upper layers changes with changes in the ratio of starch, glucomannan and carrageenan as the composer of bio-plastics composite. Each thickness for the bio-plastic composite at the ratio (6: 0: 0), (5: 0.5:

0.5), (4: 1: 1), (3: 1.5: 1.5), (2: 2: 2), (1 : 2.5: 2.5) and (0: 3: 3) are 379, 296, 222, 219, 217, 200, 200 µm. Bio-plastic composites with mixed ratio of starch, glucomannan and carrageenan (6: 0: 0), (5: 0.5: 0.5), (4: 1: 1), (3: 1.5: 1.5), contain the functional groups of O-H, C-H, C-O, (CH2)n, C=C, meanwhile the ratio of starch, glucomannan and carrageenan (2: 2: 2), (1: 2.5: 2.5) and (0: 3: 3) contain the functional groups of OH, CH, C-O, (CH 2) n, C = C, and C = O.

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