Modification of Sorghum Starch-Cellulose Bioplastics with Sorghum Stalks Filler

Modifikasi Bioplastik dari Pati Sorgum dan Selulosa dengan Pengisi Batang Sorgum

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Abstract

This study evaluated the modification of bioplastics production by various ratios of sorghum starch and cellulose from red seaweed *eucheuma spinossum*, and the use of glycerol as plasticizer and sorghum stalks as filler. Solid-liquid matrix transition should be far over the operating temperature of gelatinization and extracted at 95°C in order to avoid the loss of conductivity. The analyzed variables were starch and cellulose seaweed *eucheuma spinossum* and the addition of variation of filler. Sorghum stalk addition expected to affect the mechanical and physical properties of bioplastics. A thin sheet of plastic (plastic film) was obtained as results that have been tested mechanically to obtain the best condition for the formulation of starch-cellulose 8.5:1.5 (g/g). From the result of morphological studies, the fillers in the mixture composites were more randomly in each product and the addition of filler can increase mechanical properties of bioplastics. Chemical modification had a major effect on the mechanical properties. The phenomena of degradation and thermo-plasticization were visible by chemical changes observed in FTIR spectrum results.

Keywords: bioplastics, sorghums starch, cellulose, filler.

Abstrak

Penelitian ini mengevaluasi modifikasi produksi bioplastik dengan beragam rasio pati sorgum dan selulosa dari rumput laut *eucheuma spinosum*, penggunaan gliserol sebagai *plasticizer* dan batang sorgum sebagai pengisi. Transisi matriks padat-cair harus jauh di atas suhu operasi gelatinisasi dan diekstraksi pada 95°C untuk menghindari hilangnya konduktivitas. Variabel yang dianalisis adalah pati dan selulosa rumput laut *eucheuma spinosum* dan penambahan pengisi batang sorgum, diduga dapat mempengaruhi sifat mekanik dan fisik bioplastik. Lembaran tipis plastik (film plastik) diperoleh sebagai hasil yang telah diuji mekanik untuk mendapatkan kondisi terbaik pati-selulosa 8,5: 1,5 (g/g). Berdasarkan hasil uji morfologi, pengisi dalam komposit campuran lebih acak pada setiap produk, dan penambahan pengisi dapat meningkatkan sifat mekanik bioplastik. Modifikasi kimia berpengaruh besar pada sifat mekanik. Fenomena degradasi dan thermoplastisasi terlihat pada perubahan kimia yang dapat diamati pada spektrum hasil uji FTIR.

Kata Kunci: bioplastik, pati sorgum, selulosa, pengisi.

1. Introduction

The interest in developing biodegradable plastic from renewable resources arise as effort to decrease the problem caused by the generation of synthetic plastic and depletion of oil reserves (De Santiago, *et al*. 2015). Plastic is a synthetic polymer from petroleum which is in limited number and cannot be renewed. The use of plastic cause the plastic wastes, which are difficult to be handled and become an environmental problem. Plastics such as polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) are synthetic plastics which cannot be degraded by microorganisms in environment because of the inability of enzyme to degrade the petrochemicals polymer. So the innovation by creating environmentally friendly plastic (biodegradable plastic) which are closer to LDPE (Low Density Polyethylene) plastic characteristics is needed. LDPE, one of the most widely used packaging plastic, is the worst offender by being highly resistant to degradation. Starches such as corn, wheat, rice and banana has been added into LDPE to make it biodegradable (Gupta and Sharma, 2010).

This research used sorghum starch as bioplastics or biodegradable plastic material.

Starch is very compatible source for the development of bioplastics. It is one of the lowest-cost biodegradable materials currently available in the global market. Granules diameter of starch are ranging from 1 to 100 mm and can present different regular or irregular shapes. Starch granules are partially crystalline and are composed mainly of two glucopyranose homopolymers: amylose and amylopectin (Moran, *et al*. 2013).

Packaging technology made of bioplastics is one of the efforts to decrease the use of non-degradable plastic. As an agricultural country which is rich of natural resources (products), Indonesia is very potential to produce biopolymers from a large variety of materials, so that the biodegradable plastic packaging technology has good prospects (Darni, 2011). Development biodegradable material plastic using renewable natural materials (renewable resource) are expected (Handayani and Wijayanti, 2015). If starch is combined with the fillers to form a bio-composite, the presence of filler material will affect the properties of the composites formed (Bayandori, *et al*., 2009). This study aims to modify the bioplastics production by using various ratios of sorghum starch and cellulose from red seaweed *eucheuma spinossum*, and the usage of glycerol as plasticizer and sorghum stalks as filler to increase its mechanical properties.

2. Experimental Section

2.1 Materials

Materials used are Sorghum seeds (from traditional market) and sorghum stalks (BPPT South Lampung, Indonesia), *eucheuma spinossum* (from seaweed farmer), caustic soda flake (china, 5H3/Y26/S/15 CN/370307 PI: 001 99%), H_2O_2 (Merck For Analysis ISO 1.07209.10001 6%), distilled water (for TDS 0-2 ppm pH 5,5-7, SNI), and glycerol (Merck For Analysis ACS, Reag. Ph Eur 1.04092.1000)

2.2 Instrumentation

The instrument which used are water and a magnetic stirrer, drying oven, thermometer, digital weighing-machine, desiccators, Universal Testing Machine Autograph AGS-500D Shimadzu and Scanning Electron Microscopy (SEM) use ZEIZZ EVO MA 10.

2.3. Extraction of Cellulose.

Seaweed *eucheuma spinossum* weighed as much as 30 g then placed in a measuring cup

800 mL. Then material was mixed with NaOH solution which concentration is 40%. Comparison of materials and NaOH solution was 1:8 (wt/v). The result of residue then added with 6% of H_2O_2 concentrate solution and passed over at room temperature for 3 hours while stirring occasionally. Comparison residue and H_2O_2 solution was 1: 8 (wt/v).

2.4. Preparation of Filler

Sorghum stalks are dry and then attenuate it using hammer mill, hammer rod mill measuring the output of 2-5 cm. Sorghum stalks that have became small-sized must be put back into the disk to change into a powder and extracted the cellulose content. Then sorghum powder is sieved using a sieve size 63 μm.

2.5. Bioplastics Synthesis

The bioplastics procedure was based on Weiping Ban methods (Ban, *et al*. 2006). The ratio of starch-cellulose was 5.5:4.5; with a variation of 0.25 g filler. 600 mL solution placed on a hot plate stirrer was proceeding at 95°C as gelatinization temperature. Then a mixture of sorghum starch-cellulose was added with glycerol 25% and mixed for 35 minutes. 25 mL solution is poured into petri dish then dry it in an oven with the temperature of 60°C for 8 hours. Then the mold was raised and put into desiccator for 48 hours. Furthermore, bioplastics were stored in a zip lock bag and ready for the analysis process. These steps were repeated for a variety of starch: cellulose 6.5: 3.5; 7.5: 2.5; 8.5: 1.5; 9.5: 0.5; 10: 0 (g/g) with filler addition 0.5 g and 1 g. The density was tested by dividing mass with volume, so that the density values obtained (g/mL) each sample. Water uptake was tested by weighing the initial and final weight of the bioplastic that has been put into the water. Water uptake values was obtained by dividing the final weight of bioplastic mass with its initial then multiplied by 100%.

3. Result And Discussion

3.1 Mechanical Properties of Bioplastics

Bioplastics produced in this research getting lightly browned, because the effect of the addition of filler. Bioplastics after drying process can be seen in Figure 1. Percent extension shows the elasticity of bioplastics when pulled until break. The effect of starch-cellulose ratio on the value of strain and filler can be seen in Figure 2. Gelatinization at 95°C was occured because solid-liquid matrix

transition should be far over the operating temperature of the fuel cell 80-100°C in order avoid the loss of conductivity (Kim, *et al*. 2009). On heating of starch granules in water, swelling takes places, and affecting in collapse and rupturing of the amylose and amylopectin. The ruptured amylopectin has low affinity towards interaction, gives weak cohesive, and flexible amylopectin films. The highest strain of bioplastics product achieved on starch: cellulose ratio 5.5:4.5 (g/g) with 0.25 g filler.

Figure 1. Bioplastics starch: cellulose ratio 5.5:4.5 (g/g) and 0.25 g of filler.

Strain value decreased by 0.5 g of filler addition and increased at 1 g. The maximum strain achieved at the filler addition in ratio of 0.25 g of starch: cellulose 5.5: 4.5 (g/g). The maximum tensile strength at 0.5 g filler with starch: cellulose ratio 10: 0 (g/g). While the maximum strain achieved on the ratio of starch: cellulose 9.5: 0.5 (g/g) with value 29.28%, 23.05%, 24.19%. Previous research (Darni, *et al*. 2015) shows the greatest strain 18.82% on the ratio value of starch: chitosan 8.5: 1.5 to 0.25 g filler. Our previous research (Darni, *et al*. 2014) showed that the highest strain achieved with the starch and cellulose

ratio is 6.5:3.5 by 25% weight glycerol concentration. In this research without increasing the filler addition, we found the value of the strain is 24.5%. It means that the combination of filler and cellulose make the value of bioplastics strain increase. Therefore, the filler give positive effect to the mechanical properties of bioplastics.

Figure 3 shows the value of the higher bioplastics stress in the addition of 0.25 g filler. Stress values increased with 0.5 g filler but at 1 g the stress was decline. The maximum stress was achieved at 0.25 g filler addition and starch: cellulose ratio 8.5: 1.5 (g/g). The addition of 1 g filler, produces the maximum extension at a ratio of starch: cellulose 10: 0 (g/g). The extension of the value contained in the addition of 0.5 g filler with a ratio of 10: 0 (g/g). Each value is 5790.9 kPa, 7000 kPa, and 5539.1 kPa.

Each decrease in Young's modulus and strength there is an increase of filler in the starch film. But, a decrease in the value of tensile strength is related to the empty space that occurs because of the bond between polysaccharide terminated by glycerol. Thus causing the bonds between the molecules in the film bioplastics weakened (Septiosari, *et al*. 2014).

Figure 4 shows the maximum value of Young's modulus is at the ratio of starch: cellulose 5.5:4.5 (g/g) and 0.25 g filler variations. While the value of the largest Young modulus filler at 0.5 g and 1 g are 46566.8 KPa at a ratio of starch: cellulose 5.5: 4.5 (g/g) and 29076.8 KPa at a ratio of starch: cellulose 10:00 (g/g).
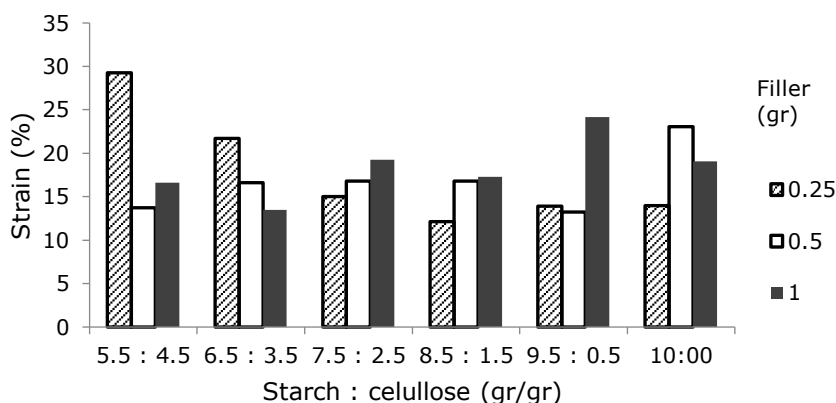

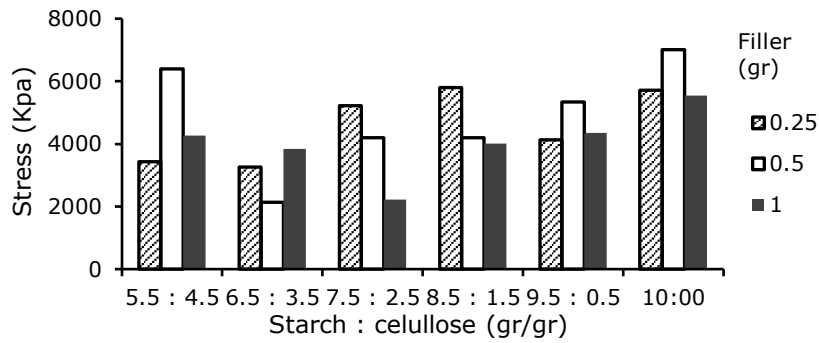**Figure 2**. Effect of Starch: Cellulose Ratio(g/g) and Filler Against The Strain of Bioplastics

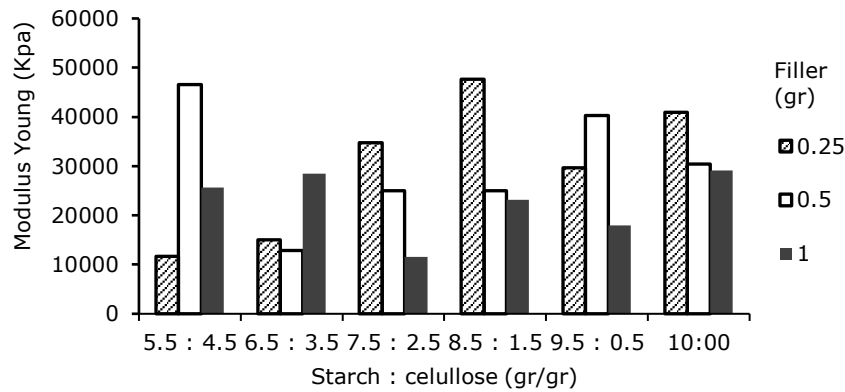**Figure 3.** Effect of Starch: Cellulose Ratio (g/g) and Filler against the Tensile Strength

Figure 4. Effect of Starch:Cellulose Ratio (g/g) and Filler Against Young's Modulus of Bioplastics
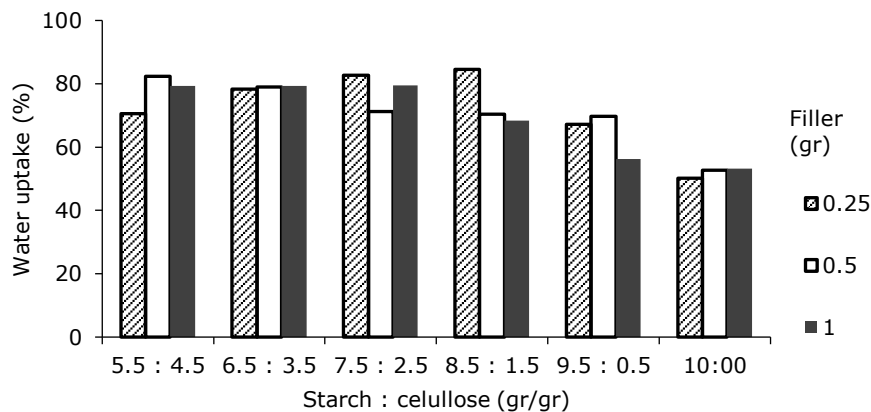

Figure 5. Effect of Starch:Cellulose Ratio (g/g) and Filler Against The Water Uptake Test of Bioplastics

It proves that the Young's modulus values decreased with no filler addition. Best Young modulus value is at 0.25 g filler variation. Moreover, separation phase of starch component could be occured simultaneously with polyol crystallization resulting in increased crystallinity of starch. Crystallization of starch components occurs during film formation, increasing Young's modulus and tensile strength (Krogars, 2003). The mechanical strength improved by given the addition of filler in the sample of bioplastics. Hydrogen bonds are formed to make the longer chain, resulting in increased elongation at adding filler in the sample. The value of Young's modulus HDPE standards is 10.3 to 206.7 MPa.

3.2 Effect of starch: cellulose ratio to the physical properties of bioplastics.

The physical properties are properties that can be seen as the results and be the subject to investigated. Water absorption can be seen in Figure 5. Figure 5 shows the lowest water

uptake test is at the ratio of starch: cellulose 10: 0 (g / g) at each the higher the
variation filler 0.25 g, 0.5 g and 1 g. This showed that the more addition of cellulose, the more water uptake percentage. This phenomenon was caused by the hydrophilic nature of cellulose. The results of water uptake test are 50.12%, 52.67%, and 53.24% with bioplastics samples with the addition of filler water uptake properties. Density may be defined as the mass per unit volume of material. Density is the physical properties of a polymer. In Figure 6 the highest density seen in the ratio of starch: cellulose 10:0 (g/g) 0.25 g filler is of 0.99 g / mL, 1.2 g.mL at the ratio of starch: cellulose 10:0 (g/g) filler 0.5 g, and 1.0 g / mL at the ratio of starch: cellulose 10:0 (g/g) filler 1 g. The maximum density is at 0.5 g filler with less variation ratio of starch: cellulose 10:00 (g/g). By the sample of bioplastics density test there are various factors influencing the density of a sample of bioplastics.

3.3 FTIR analysis of functional groups

FTIR analysis aim to determine the functional groups present in the bioplastics. FTIR spectroscopy is the technique widely used to study the interaction mechanisms involved in mixture. If an organic compound is irradiated with infrared rays having a certain frequency, then the frequency will be absorbed by these compounds. The number of absorbed frequencies. measured as percent of transmittance (% T).

Figure 7a shows the spectrum stretching vibration-OH (alcohol) at wave number 3408.22 cm^{-1}, C-H stretch at 2927.94 cm^{-1}, C=O (carbonyl) stretch at 1643.35 cm^{-1}, C-H bending at 1411.89 and 1240.23 cm^{-1}, Spectrum 7b shows the vibration OH at 3381.21 cm^{-1}, C-H stretching at 2931.80 cm^{-1}, C-H bending at 1411.89 and 1240.23 cm^{-1}. Figure 7c shows stretching vibration OH at wave number 3408 cm^{-1}, stretching vibration C-H at 2929.87 cm^{-1}, buckling vibration C-H at 1411.89 and 1240.23 cm^{-1} (Boulder, 2002). On this picture there is a change incorporation of functional groups with differences ratio of starch and cellulose which can be seen from the change in the width of the peak in the wave number area ~3300 cm^{-1} although there was insignificant change.
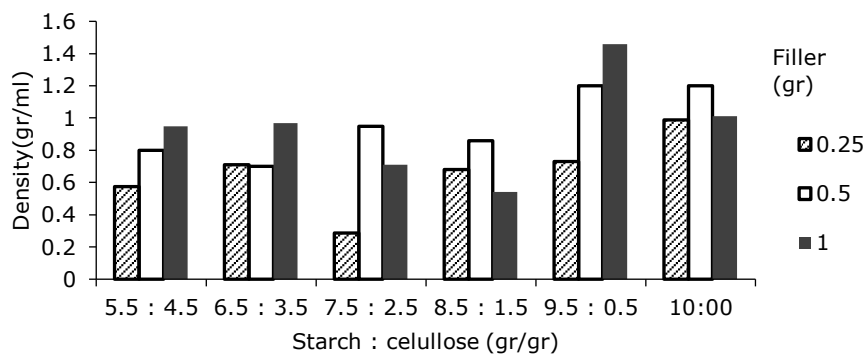

Figure 6. Effect of Starch:Cellulose Ratio (g/g) and Filler Against Density of Bioplastics
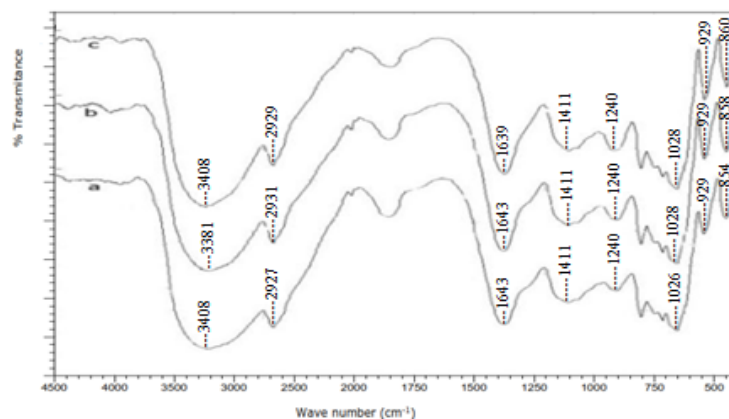

Figure 7. FTIR spectra of bioplastics with Starch:Cellulose, a) 8.5:1.5 (g/g), b) 9.5: 0.5 (g/g), c) 10:0 (g/g) filler 0.25g
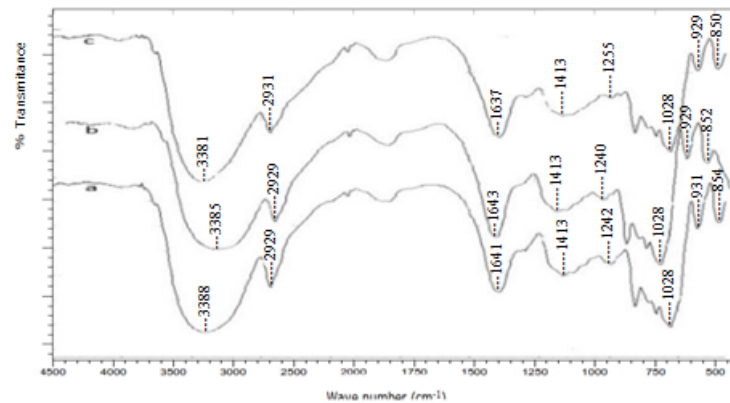
Figure 8. FTIR spectra of bioplastics with Starch:Cellulose, a) 8.5:1.5 (g/g), b) 9.5: 0.5 (g/g), c) 10:0 (g/g) filler 0.5g
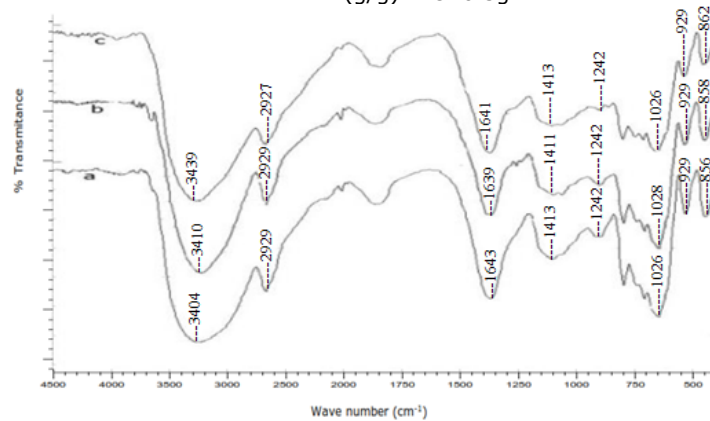

Figure 9. FTIR spectra of bioplastics with Starch:Cellulose, ratio a)8.5:1.5 (g/g), b) 9.5:0.5 (g/g), c)10:0 (g/g) filler 1 g.
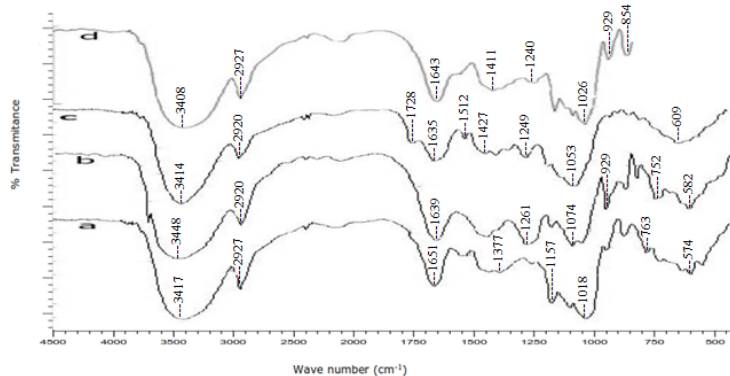

Figure 10. FTIR spectra of (a) Sorghum stalks, (b) cellulose seaweed *Eucheuma spinosum*, (c) sorghum starch and (d) starch:cellulose ratio 8.5:1.5 (g/g) 0.25 g filler.

Figure 8a shows there are stretching vibration C=O at wave number 3381.21 cm^{-1}, C-H stretching at 2931.80 cm^{-1}, C=O stretching at 1637.56 cm^{-1}, and C-O-C stretch at 1028.06 cm^{-1}. Figure 8b shows stretching vibration OH at 3385.07 cm^{-1}, C-H stretching at 2929.87 cm^{-1}, C=O stretching at 1643.35 cm^{-1}, and C-O-C stretching at 1028.06 cm^{-1}. While Figure 7c shows OH at wave number 3388.93 cm^{-1}, C-H stretching at 2929.87 cm^{-1}, C=O stretching at 1641.42 cm^{-1}, and C-O bond stretching of C-O-H group at 1026.13 cm^{-1}.

The incorporation of this result does not change significantly with the functional groups of 0.5 g filler. But there are some OH functional groups replaced by other groups, hydrogen atom is replaced by amylopectin cellulose. The changes are not significant because H atoms are replaced in relatively small amounts. But the change can be seen from the reduction in the width of the spectrum in the area of wave number ~3300 cm-1 (Boulder, 2002).

Figure 9a shows the results of ratios spectrum starch: cellulose 8.5:1.5 (g/g) include O-H stretching at wave number 3404.36 cm^{-1}, C-H stretching at 2929.87 cm^{-1}, C=O stretching at 1643.35 cm^{-1}, and C-O-C stretching at 1026.13 cm^{-1}. Figure 9b shows the results of spectrum ratio of starch: cellulose 9.5:0.5(g/g) include OH 3410.15 cm^{-1}, C-H stretch at 2929.87 cm^{-1}, C=O stretch at 1639.49 cm$^{-1,}$ and C-O-C stretch at 1026.06 cm^{-1}.

Figure 9c shows the results of spectrum ratio of starch: cellulose 10: 0 (g/g) include OH stretch at 3439.08 cm^{-1}, C-H stretch at 2927.94 cm^{-1}, C=O stretch at 1641.42 cm$^{-1,}$ and C-O bond stretching of C-O-H group at 2931.80 cm^{-1}, C=O stretching at 1637.56 cm^{-1}, and C-O-C stretch at 1028.06 cm^{-1}.. On this image the merger does not change very significant in the ratio of functional groups with each starch and cellulose with filler 1 g. It shows that the ratio at 1 g filler addition does not give a significant impact on the bioplastics result.

Figure 10a shows the result of trunk sorghum include OH stretch at 3417.86 cm^{-1}, C-H stretch at 2927.94 cm^{-1}, C=O stretch at 1651.07 cm$^{-1,}$ and C-O-C stretch at 1018.41 cm^{-1}. Picture 10b shows the result of cellulose seaweed *Eucheuma spinossum* include OH stretch at 3448.72 cm^{-1}, C-H stretch at 2920.23 cm^{-1}, C=O stretch at 1639.49 cm$^{-1,}$ and C-O-C stretch at 1072.42 cm^{-1}.

Figure 10 is a combination of the specific functional group contained in each constituent of bioplastics. In the joint formed by the starch modification process called grafting or transplantation, the change of OH- functional groups break up and replaced by groups of glycerol and filler. Based on the overall IR data, there was no new functional group formed at various ratios of starch and cellulose with a variety of increased filler. Variation of mass ratio of starch: cellulose only affects the physical properties of bioplastics produced.

According to the literatures (Yang, *et al*. 2006), there was typical crystallinity in the native starch just like line a Figure 10c, but for the EPTPS (TPS was plasticized by ethylene bisformamide), A-Style crystallinity disappeared and V$_H$- style crystallinity (the crystallinity between plasticizer and Starch) was formed by the induction of the thermal process. During the thermoplastic process, the strong action between hydroxyl groups of starch molecules was substituted by hydrogen

bonds formed between plasticizers and starch.

3.4 SEM

Bioplastics film morphology is visibly uneven as seen on Figure 11, this is due to lack of homogeneous solution of bioplastics produced (Jones, *et al*. 2013). Different starch content with high amylose will produce homogeneous plastic film and higher amylopectin will improve the phase separation. This happens because only amylose soluble in water. Then amylopectin forms agglomerates resulting in less homogeneous bioplastics.
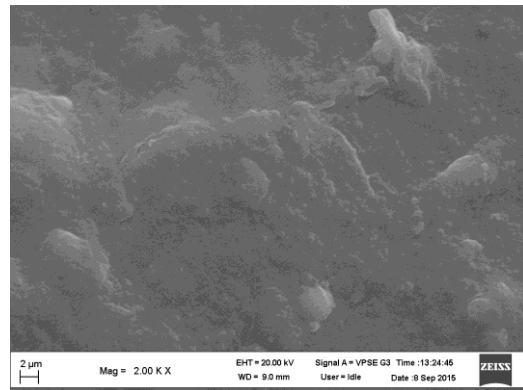

Figure 11. Surface morphology of bioplastics from starch: cellulose 8.5: 1.5 (g/g) 0.25 g filler the surface of bioplastics (magnification 20.000x),
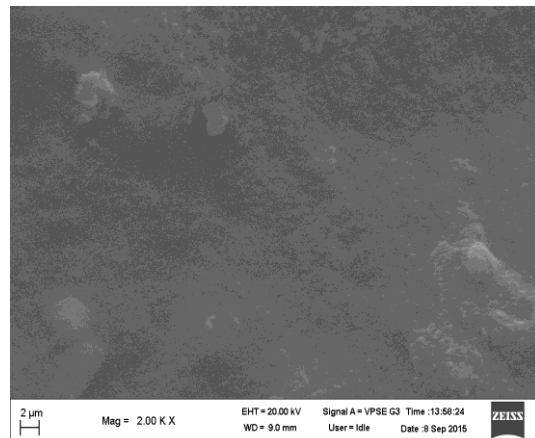

Figure 12. Surface morphology of bioplastics from starch: cellulose 8.5: 1.5 (g/g) 0,5 g filler bioplastics surface magnification (20.000x).

Judging from the structure, the cellulose has many hydroxyl groups that can form hydrogen bonds with water. And cellulose in fact is insoluble in water and other solvents. The reason is the high rigidity of the chain and the chain intermolecular forces due to hydrogen bonding between hydroxyl groups on adjacent chains. This is occur because of

the size of amylopectin is still too big. Amylopectin is still large in size resulting in not meeting the particle amylopectin starch matrix, this can be seen on Figure 12, the surface of each sample of the white color is not spread evenly or do not dissolve completely in the sample of bioplastics.

4. Conclusion

Based on the research results can be concluded that the addition of filler in the ratio of starch: cellulose has significant changes in the mechanical properties of bioplastics. The addition of filler into the bioplastics sample can improve physical and mechanical properties of bioplastics. Bioplastics characteristics contained in the starch : cellulose ratio 8.5: 1.5 (g/g) with a value of 5790.9kPa, an extension value 12.15%, Young's modulus 47661.8 kPa, and bioplastics density of 0.68 g/mL.

5. Acknowledgements

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