Plagiarism Checker X Originality Report

Similarity Found: 29%

Date: Saturday, August 15, 2020
Statistics: 899 words Plagiarized / 3082 Total words
Remarks: Medium Plagiarism Detected - Your Document needs Selective Improvement.

__ Synthesis of Modified Thermoplastic Starch (TPS) Using In-Situ Technique 1Rozanna Dewi, 2Harry Agusnar, 2Basuki Wirjosentono, 2Halimah, 3Medyan Riza 1Universitas Malikussaleh/Lhokseumawe, Aceh, Indonesia 2Universitas Sumatera Utara/Medan, Sumatera Utara, Indonesia 3Universitas Syiah Kuala/Banda Aceh, Aceh, Indonesia ARTICLEINFO ABSTRACT Article history: Received 30 September 2014 Received in revised form 17 November 2014 Accepted 25 November 2014 Available online 6 December 2014 Keywords: © 2014 AENSI Publisher All rights reserved.

__ INTRODUCTION Starch has been broadly utilized as crude material for biodegradable plastic because of its biodegradability, sustainably and accessible in immense amount. Plastic arranged from starch containing low measures of water is regularly fragile. To diminish the weakness, starch was plasticized with hydrophilic plasticizers, for example, glycerol and liquefied for getting ready thermoplastic starch (TPS).

Subsequent to maturing at encompassing conditions for a while, glycerol-plasticized TPS demonstrated a fragile conduct because of movement of glycerol from starch network because of it collaborates with starch by non-covalent hydrogen holding, bringing about stage detachment. One powerful method of forestalling movement of plasticizers is to join or connection adaptable effect modifier to starch with covalent bonds which will bring about adjusted starch with malleable property1.

Inside the current accessible modifiers, isocyanate bunches have high action to respond with the hydroxyl gathering of starch. Therefore, polyurethane prepolymer (PUP) bearing isocyanate bunches has frequently been utilized to harden starch. Adaptable polyol delicate portions in polyurethane (PU) connected to starch through urethane linkage have worked as effect modifier.

It is fundamental to adjust starch utilizing PUP in a naturally benevolent manner for getting ready bendable thermoplastic starch1. Asia is the world's biggest customer of plastic which assimilates about 30% of plastic utilization on the planet followed by the Americas, Europe and different nations with the goal that consistently around 100 million tons of plastic is created on the planet for use in different mechanical areas and the trash delivered in any case is like the plastic delivered each year2.

Alongside the expanded mindfulness for ecological protection, needs of biodegradable plastic materials has expanded from year to year. In 1999, biodegradable plastic creation just 2500 tons, which is 1/10.000 of the all out creation of engineered plastic material. In 2010, the creation of biodegradable plastics is anticipated to arrive at 1.2 million tons, or 1/10 of the complete creation of plastic materials2.

Biodegradable plastics industry will form into a significant industry later on with the goal that we have to deliver plastic materials that have prevalent qualities and can be debased naturally. In this study, we need to incorporate changed thermoplastic sago starch (TPS) on the condition of in – situ by responding sago starch with MDI and castor oil at the same time, coming about the development of more homogenous and better size polyurethane prepolymer (PUP), just as the adjustment response not just happen on the outside of the PUP particles yet in addition into the mass stage (inward piece of the molecule).

The shaping system and the structure just as mechanical properties of adjusted TPS were concentrated through FTIR, SEM and ductile test. Castor oil is utilized on the grounds that it is gotten from vegetable oil which can be sustainably and natural cordial. Warm trademark and biodegradability level of changed TPS were estimated and will be distributed soon.

The virtue of this investigation separated from in-situ process which gives more bit of leeway then the regular one is sago starch as crude material of TPS has not yet used maximally in Indonesia while the creation is still high. The capacity is change recently, from the primary food in the eastern of Indonesia to become farming grub.

In this way this investigation will improve the estimation of sago. The past investigation has been finished by utilizing corn as the starch source. In any case, corn is as yet utilized as one of the fundamental hotspot for the primary food with constrained creation and the cost is high in Indonesia, so it is viewed as not an attainable asset at the moment.

Experimental: Materials: Sago Starch, Castor oil, 4,4'-methylenedi-p-phenyl diisocyanate (MDI), sorbitol and glycerol plasticizer is used without any further pretreatment. Synthesis of Modified TPS: Sago 23.7 g were weighed and put into a 500 ml Erlenmeyer flask and added to 162.7 ml on water. Sago is heated and stirred until cooked to become gel at gelatinization temperature 70 ° C for about 30 minutes.

After the gel is almost formed, castor oil reacted with MDI in the ratio according to the table below and pour directly into the sago gelatinization. The mixture was stirred vigorously for a few minutes and poured into sago gelatin that has been prepared. Erlenmeyer containing sago gelatin is also added with sorbitol 7% (14 grams). The mixture was then printed on a sheet of glass to avoid very fast hardening occurred.

Film layer were left for 24 hours in ambient conditions to be dried, thus easily to be removed from the casting glass. After drying the film is released from the casting sheet glass and cut according to the testing requirements. Table 1: The weight ratio of each component Sampel _Modification Formula _ _ _Sago (g) _Water (g) _Sorbitol 7 % (g) _Castor Oil (g) _MDI (g) _ _Sago Starch (PS) _31 _155 _14 _0 _0 _ _PUP _0 _0 _14 _15 _13 _ _TPS 10 _31 _155 _14 _2 _1 _ _TPS 20 _31 _155 _14 _3 _2 _ _TPS 30 _31 _155 _14 _4 _3 _ _TPS 40 _31 _155 _14 _5 _4 _ _TPS 50 _23,7 _162,7 _14 _6 _5 _ _ Analysis Conducted: The testing performing were Fourier Transform Infrared (FTIR) and Scanning Electron

Microscopy (SEM) for structure and morphology analysis, and tensile and elongation test for mechanical analysis.

RESULT AND DISCUSSION Structure Analysis: After the modified thermoplastic starch is formed, several tests were conducted to determine the in -situ optimization process of gelatinised sago starch with MDI and castor oil, homogenization and refining PUP (Polyurethane Prepolymer) filler particle size in the modified Thermoplastic Starch (TPS), chemistry and interaction of modified TPS, and characterization of TPS mechanical properties.

FTIR analysis on PUP and modified TPS was conducted to study the structure of the components. It can be seen in Figure 1 for PUP, the C = O of ester group occurred at 1700 cm-1. Range catchment area for the ester group is 1690-1760 cm-1, this is almost the same as the results of previous studies conducted1, where transmission C = O of ester group obtained in the 1704-1744 cm-1. OH group wavelength of polyol was shown at 3000 cm-1, and it is in line with value obtained in reference (3000 – 3500 cm-1).

Meanwhile for the C-O, it was appeared at wavelength of 1250 cm-1, also in line with the reference (1080-1300 cm-1).

4000 _3500 _3000 _2500 _2000 _1500 _1000

Wavenumber cm-1 C:\Program _ Files\OPUS_65\MEAS\PUP.0 _ PUP _ Instrument _ type and / _ or accessory _ 29/01/2014 _ _Page 1/1 Fig.

1: Fourier Transform Infrared (FTIR) test for PUP Figure 2 shown FTIR analyses for modified TPS 3. Ester group C=O occurred at 1700 cm-1 and OH group of polyol occurred at 3000 cm-1 wavelength, same result as FTIR test for PUP. The ester C-O found at 1250 cm-1 wavelength. If we compare the FTIR result for PUP and modified TPS 3, wavelength profile for both is almost similar.

This indicated that urethane linkage structure for both sample is similar due to the influence of castor oil and MDI linkage. The urethane linkage is not disturbing starch matrix, thus it is compatible with castor oil and MDI. Hence, polyurethane of modified TPS 3 is cross link to starch matrix by urethane linkage.

4000 _3500 _3000 _2500 _2000 _1500 _1000

Wavenumber cm-1 Page 1/1 Fig.

2: Fourier Transform Infrared (FTIR) test for modified TPS 3

4000 _ 3500 _ 3000 _ 2500 _ 2000 _ 1500 _ 1000

Wavenumber cm-1 Page 1/1 Fig. 3: Fourier Transform Infrared (FTIR) test for modified TPS 3, extracted with water solvent.

4000 _3500 _3000 _2500 _2000 _1500 _1000

Wavenumber cm-1 Page 1/1 Fig. 4: Fourier Transform Infrared (FTIR) test for modified TPS 3, extracted with toluene solvent Figure 3 and 4 show FTIR test for modified TPS extracted with water and toluene solvents. It can be seen that OH group of polyol is occurred at wavelength of 3200 cm-1.

Ester amine group C-O is present at 1000 cm-1 (reference wavelength for ester C-O is 1180-1360 cm-1). This phenomenon is indicating water and toluene solvent only dissolve unreacted castor oil and MDI but cannot dissolve the cross link developed between castor oil, MDI and starch matrix. The formation of modified TPS consists of several steps.

The first step is involving plasticizing of starch by water through de-structuration process (Figure 5.a). Starch macromolecule become flexible and resulting formation of thermoplastic starch (Figure 5.b). Water is one kind of effective chain extender and cross-linker to prepare waterborne poliurethane microparticle.

Thus, PUP synthesized from castor oil and MDI (figure 5.c) reacted with water to develop cross linking waterborne polyurethane microparticle during the vigorous mixing take place. PUP was formed in-situ during the mixing process.

The surface of PUP microparticle consist of NCO group, lead to the development of multifunctional microparticle (Figure 5.d). High content of NCO microparticle improved probability and efficiency of PUP link to the starch matrix and consequently will improve reaction yield. Fig. 5: Formation of modified TPS scheme Figure 6 shows morphology of modified TPS.

The network mechanism between PUP and starch matrix is developed through urethane linkages. The compatibility between hydrophobic PUP and hydrophilic starch improved effectively due to the presence of this urethane linkage. Similar finding was also obtained using corn starch and PUP form castor oil1.

However, methodology on preparing PUP is different, where the PUP is synthesized outside by reacting castor oil and MDI before added to the mixing reactor consist of gelatin starch. Fig. 6: Modified TPS morphology structure. Morphology Analysis: Figure 7 shows that the TPS 3 surface is rough due to micro phase separation in the TPS.

A continuous section consists of starch matrix as the majority with least amount of PUP occurred. Some PU micro particles dispersed in the continuous starch matrix through cross link bonding. The particle size of the polyurethane prepolymer is very small, which is about 2 µm.

Suitability between the hydrophobic polymer and hydrophilic polymer is usually not good due to lack of adhesion interface. However, in this study interface between the PUP and the starch matrix is continuous and dense and well bonded to the starch matrix which shows good conformity between the hydrophobic PU and hydrophilic starch.

In addition, if associated with FTIR results above, then good conformity has contributed to the development of urethane network (urethane linkage) between the PUP and the starch matrix. Figure 8 show the SEM analysis for PUP, where there is no continuous

Advances in Environmental Biology, 8(18) Special 2014, Pages: 26-33 part as well as no dispersed part occurred and this show the morphology different between PUP and modified TPS. / / Fig.

7: SEM image for modified TPS 3 SEM results for modified TPS showed inflation in the sample during the test. This happened because the high amount of light energy and the amount of magnification provided at the scanning time of the sample causing inflammation of the sample into white areas and some cracks seen.

However, under the pressure of inflammation, the interface between the matrix and the PU dispersion of white starch still look tight and dense, which shows that there is good conformity between starch matrix and micro particles PUP. Fig. 8: SEM Image for PUP SEM image for cross-section of modified TPS 3 is shown in Figure 9 below. The cross-section part is formed as the result of tensile test conducted.

The SEM image showed rough surface and irregular form. PUP microparticles are very difficult to be detached from starch and hardly visible pores left vacant by PU microparticles can be seen. This indicates that the PU microparticles bound to the starch matrix through cross-link bonding and the interface between the polymer through urethane linkage is very strong. Fig.

9: SEM image for cross-section of modified TPS 3

Advances in Environmental Biology, 8(18) Special 2014, Pages: 26-33 Cross-section of modified TPS 3 immersed with solvents toluene and water for 24 hours was done and the image shown in Figure 10 and Figure 11. Figure 10 showed almost no PU micro particles are extracted out of the starch matrix, which states that the PU micro particles bound to the starch matrix through cross-link bonding and interface between the polymer is very strong through the urethane linkage.

Figure 11 showed the same thing, starch matrix is not soluble when extracted in water. This result indicates that the starch matrix resistance to water increased when compared to the raw starch. Fig. 10: SEM image for cross cutting of modified TPS 3 extracted with Toluene Fig.

11: SEM image for cross cutting of modified TPS 3 extracted with Water Mechanical Analysis: Tensile strength is the maximum attraction before the final break. This test intended to see the changes that occur in the mechanical strength of plastic. Tensile strength testing performed using Universal Testing Machines Electronic System based on the standard ASTM D638, 1991.

Tensile Strength data testing results can be seen in Table 2 below. Tensile strength obtained at Plastic Starch (PS) is 0,26 kgf/cm2, for modified Thermoplastic Starch (TPS 1 - TPS 5) is 0,40-0,66 kgf/cm2, while the tensile strength for PUP obtained is 1,27 kgf/cm2.

Table 2: Tensile strength and elongation at break of different composition of modified TPS Sample _Tensile Test (kgf x cm2) _Elongation (%) _Water absorption (%) _ _PUP _1,27 _125 _10 _ _PS _0,26 _100 _75 _ _TPS 1 _0,40 _115 _25 _ _TPS 2 _0,58 _117,5 _23 _ _TPS 3 _0,66 _119 _20 _ _TPS 4 _0,55 _119,5 _18 _ _TPS 5 _0,47 _119,5 _17 _ _ Tensile strength of plastic films is strongly influenced by the content of plasticizer added because it can increase flexibility.

The addition of PUP has also led to increased flexibility of modified TPS due to the cross linking between the PUP and the starch matrix thereby increasing the molecular weight of the starch and increased elongation of modified TPS. This is because the castor oil was added as materials for PUP which acts

Advances in Environmental Biology, 8(18) Special 2014, Pages: 26-33 as an impact modifier, causing increased elongation and lower tensile strength properties.

Therefore, the tensile strength properties of modified TPS sheet is influenced by the balance of the increase in molecular weight and starch content of castor oil3. Elongation is the maximum length change before the film broken. Per cent elongation test result data can be seen in Table 2. The elongation value obtained for Plastic Starch (PS) is 100%, for modified Thermoplastic Starch (TPS 1 – TPS 5) is 115% - 119.5%, while the PUP pure elongation obtained a value of 125%.

From these data it can be seen that the higher content of PUP added has made the elongation value of modified TPS is increasing. This is happened due to the presence of polyols in PUP led to increasing flexibility of modified TPS4. Additionally, the flexibility of modified TPS was caused also by the addition of sorbitol plasticizer.

In our previous reserach, we have compared the used of two plasticizer types which are glicerol and sorbitol and we found that sorbitol improved TPS flexibility better than glicerol. One of the properties of conventional plastics is impermeable to liquids. Water absorption is the amount of water absorbed by the plastic film in per cent after a test sample immersed in water at room temperature for 24 hours.

The water fills the empty spaces in the plastic film. The lower the per cent of water absorption obtained the better the quality of the plastic. From Table 2 it can be seen that the value of water absorption results for plastic starch (PS) is 75% and modified Thermoplastic Starch (TPS 1-5) ranged from 17-25%, while the Polyurethane Prepolymer (PUP) is only able to absorb water 10%.

Water absorption decreases with increasing addition of PUP and plasticizer on modified TPS which increases the adhesive properties between molecules so that the amount of water bound to the polysaccharide compound will decrease causing water levels lower absorbed, due to the less pores in the plastic. The water content in modified TPS decreases with increasing PUP which indicates that the modified PUP has increased hydrophobicity of the starch so that the plastic material produced absorb less water1.

Conclusion: From FTIR and SEM analysis conducted, it can be concluded that modified TPS was successfully prepared using in-situ technic. The existence of the cross link and urethane linkage between starch matrix and PUP has been shown to be consistence with previous researches conducted and also in line with other reference figure. PUP is also compatible with starch matrix as shown by SEM image through tight and dense phase.

When immersed in water and toluene solvent, almost no PU microparticles are extracted out of the starch matrix, which states that the PU microparticles bind to the starch matrix through cross-link bonding and interface between the polymer is very strong through the urethane linkage. PU microparticles acted as an impact modifier for the modified TPS and consequently improved the toughness of TPS.

Tensile strength decreases with increasing content of PUP into modified TPS. Per cent elongation increases with increasing content of PUP in modified TPS. Meanwhile, the higher content of PUP has reduced the water content absorbed. Modified TPS 3 has higher tensile test with reasonable elongation at break and water absorption, thus this variation can be used for further research for process optimization. REFERENCES Qiangxian Wu, Zhengshun Wu, Huafeng Tian, Yu Zhang, and Shuilian Cai. 2008.

Strcture and Properties of Tough Thermoplastic Strach Modified with polyurethane microparticles. Ind. Eng. Chem, 47: 9896- 9902. Dayanti, R., 2006. Pengaruh Jenis dan Konsentrasi Plasticizer serta Nisbah Pati dengan Air Terhadap Sifat Fisik Edible Film Pati Sagu (Metroxylon sp). USK. Banda Aceh. Yoshang Lu, Lan Tighzert, Patrice Dole, and Damien Erre. 2005.

Preparation and Properties of starch termoplastic modified with waterborne polyurethane from renewable resources, Polymer, 5: 9863-9870. Xiaohua Kong dan Suresh S. Narine, 2007. Physical properties of polyurethane plastic sheets produced from Poliol from Canola oil, Biomacromolecules, 8: 2203-220.

INTERNET SOURCES:

1% - http://phys.lsu.edu/~fmoxley/JCP.pdf
<1% - http://www.aensiweb.com/old/aeb/Special%2010/15-19.pdf
21% - http://www.aensiweb.com/old/aeb/Special%2010/26-33.pdf
<1% - http://ijirse.in/docs/ican14/ican43.pdf
<1% - https://www.researchgate.net/publication/238360581_Characterization_of_the_PolYurethane_foam_using_alginic_acid_as_a_polyol
<1% - https://www.mdpi.com/2079-6412/9/6/401/pdf
<1% - https://www.researchgate.net/publication/231389778_Structure_and_Properties_of_Tough_Thermoplastic_Starch_Modified_with_Polyurethane_Microparticles
<1% - https://www.technology.matthey.com/article/63/4/299-310/
1% - https://iopscience.iop.org/article/10.1088/1755-1315/365/1/012052/pdf
<1% -

http://www.pertanika.upm.edu.my/Pertanika%20PAPERS/JST%20Vol.%2027%20(3)%20Jul.%202019/28%20JST(S)-0516-2019.pdf
<1% - https://www.sciencedirect.com/science/article/pii/S0950061820318018
<1% - https://www.researchgate.net/publication/334526915_Effect_of_pine_resin_derivatives_on_the_structural_thermal_and_mechanical_properties_of_Mater-Bi_type_bioplastic
<1% - https://iopscience.iop.org/article/10.1088/1742-6596/1167/1/012048/pdf
<1% - https://www.researchgate.net/publication/263776011_Intumescent_Flame_Retardant_PolyurethaneStarch_Composites_Thermal_Mechanical_and_Rheological_Properties
<1% - https://www.researchgate.net/publication/241649116_Effects_of_Radiation_and_Thermal_Cycling_on_Teflon_R_FEP
<1% - https://www.sciencedirect.com/science/article/pii/S0950061819303964
<1% - https://www.researchgate.net/publication/265645479_Preparation_and_performance_evaluation_of_castor_oil-based_polyurethane_prepolymerpolylactide_blends
<1% - http://archive.org/stream/jstor-25129918/25129918_djvu.txt
<1% - https://www.researchgate.net/publication/259158640_Effects_of_hygrothermal_aging_on_glass-fibre_reinforced_polymer_laminates_and_adhesive_of_FRP_composite_bridge_Moisture_diffusion_characteristics
<1% - https://www.sciencedirect.com/science/article/pii/S0144861716312103
<1% - https://www.researchgate.net/publication/264729677_Thermoplastic_starch_modified_with_polyurethane_microparticles_Effects_of_hydrophilicity_of_polyurethane_prepolymer
1% - https://pubs.acs.org/doi/10.1021/bm050804c
1% - https://www.emerald.com/insight/content/doi/10.1108/978-1-78756-793-1-00033/full/html
<1% - https://pubs.acs.org/doi/abs/10.1021/ma035385v
<1% - https://pubs.acs.org/doi/10.1021/bm049512m