Synthesis of Modified Thermoplastic Starch (TPS) Using In-Situ Technique

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ABSTRACT

A demand of practical and consumptive lifestyle has encouraged increasing used of plastic each year and consequently has produced significant number of waste. It is important to develop a user friendly plastic but having competitive strength with a conventional plastic. Modified Thermoplastic Starch (TPS) is prepared from local resource Sago which is available abundantly in Indonesia and does not have a proper value. Polyurethane Prepolymer (PUP) was synthesized and mixed reactively with Sago using in situ model in an intensive mixer to prepare modified TPS. The variations of PUP in the TPS are used to see their influence on the reaction occurred as well as on the characteristic of the modified TPS produced. Several tests have shown forming mechanism and characteristic of modified TPS such as Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and tensile test. PUP and sago matrix was cross link through urethane linkage and found out to be compatible together with tight and dense phase. PU Micro particles acted as an impact modifier for the modified TPS and consequently improved the toughness of TPS. TPS 3 has higher tensile test with reasonable elongation at break and water absorption.

INTRODUCTION

Starch has been widely used as raw material for biodegradable plastic due to its biodegradability, renewably and available in huge quantity. Plastic prepared from starch containing low amounts of water is often brittle. To reduce the brittleness, starch was plasticized with hydrophilic plasticizers such as glycerol and melted for preparing thermoplastic starch (TPS). After aging at ambient conditions for several months, glycerol-plasticized TPS showed a brittle behaviour due to migration of glycerol from starch matrix due to it interacts with starch by non-covalent hydrogen bonding, resulting in phase separation. One effective way of preventing migration of plasticizers is to graft or link flexible impact modifier to starch with covalent bonds which will result in modified starch with ductile property.

Within the current available modifiers, isocyanate groups have high activity to react with the hydroxyl group of starch. Thus, polyurethane prepolymer (PUP) bearing isocyanate groups has often been used to toughen starch. Flexible polyol soft segments in polyurethane (PU) linked to starch through urethane linkage have functioned as impact modifier. It is essential to modify starch using PUP in an environmentally friendly way for preparing ductile thermoplastic starch.

Asia is the world's largest consumer of plastic which absorbs about 30% of plastic consumption in the world followed by the Americas, Europe and other countries so that every year about 100 million tonnes of plastic is produced in the world for use in various industrial sectors and the garbage produced anyway is similar to the plastic produced each year. Along with the increased awareness for environmental conservation, needs of biodegradable plastic materials has increased from year to year. In 1999, biodegradable plastic production only 2500 tons, which is 1/10.000 of the total production of synthetic plastic material. In 2010, the production of biodegradable plastics is projected to reach 1.2 million tons, or 1/10 of the total production of plastic materials. Biodegradable plastics industry will develop into a major industry in the future so that we need to produce plastic materials that have superior characteristics and can be degraded by nature.

In this study, we want to synthesize modified thermoplastic sago starch (TPS) on the state of in –situ by reacting sago starch with MDI and castor oil simultaneously, resulting the formation of more homogenous and

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finer size polyurethane prepolymer (PUP), as well as the modification reaction not only occur on the surface of the PUP particles but also into the bulk phase (inner part of the particle). The forming mechanism and the structure as well as mechanical properties of modified TPS were studied through FTIR, SEM and tensile test. Castor oil is used because it is derived from vegetable oil which can be renewably and environmental friendly. Thermal characteristic and biodegradability level of modified TPS were measured and will be published soon.

The virtue of this study apart from in-situ process which provides more advantage then the conventional one is sago starch as raw material of TPS has not yet utilized maximally in Indonesia while the production is still high. The function is change lately, from the main food in the eastern of Indonesia to become husbandry fodder. Thus this study will enhance the value of sago. The previous study has been done by using corn as the starch source. However, corn is still used as one of the main source for the main food with limited production and the price is high in Indonesia, so it is seen as not a feasible resource at the moment.

**Experimental:**

**Materials:**

Sago Starch, Castor oil, 4,4'-methylene-di-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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modification Formula</th>
<th>Sago (g)</th>
<th>Water (g)</th>
<th>Sorbitol 7% (g)</th>
<th>Castor Oil (g)</th>
<th>MDI (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sago Starch (PS)</td>
<td>10</td>
<td>31</td>
<td>155</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PUP</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>TPS 10</td>
<td>12</td>
<td>31</td>
<td>155</td>
<td>14</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>TPS 20</td>
<td>13</td>
<td>31</td>
<td>155</td>
<td>14</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>TPS 30</td>
<td>14</td>
<td>31</td>
<td>155</td>
<td>14</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>TPS 40</td>
<td>15</td>
<td>31</td>
<td>155</td>
<td>14</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>TPS 50</td>
<td>16</td>
<td>23.7</td>
<td>162.7</td>
<td>14</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

**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 conducted, where transmission C = O of ester group obtained in the 1704-1744 cm^{-1}. OH group wavelength of polylol 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}).
**Fig. 1:** Fourier Transform Infrared (FTIR) test for PUP

Figure 2 shows 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 crosslink to starch matrix by urethane linkage.

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

![Diagram](image)

**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 oil. 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.

![Diagram](image)

**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
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**
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>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Test (kgf x cm²)</th>
<th>Elongation (%)</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUP</td>
<td>1.27</td>
<td>125</td>
<td>10</td>
</tr>
<tr>
<td>PS</td>
<td>0.26</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>TPS 1</td>
<td>0.40</td>
<td>115</td>
<td>25</td>
</tr>
<tr>
<td>TPS 2</td>
<td>0.58</td>
<td>117.5</td>
<td>23</td>
</tr>
<tr>
<td>TPS 3</td>
<td>0.66</td>
<td>119</td>
<td>20</td>
</tr>
<tr>
<td>TPS 4</td>
<td>0.55</td>
<td>119.5</td>
<td>18</td>
</tr>
<tr>
<td>TPS 5</td>
<td>0.47</td>
<td>119.5</td>
<td>17</td>
</tr>
</tbody>
</table>

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
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 TPS. 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