Thermal Behavior of Modified Thermoplastic Starch (TPS) Synthesized from Sago (*Metroxylon Sagu*) with Diphenylmethane Diisocyanate and Castor Oil

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Abstract

Purpose – The purpose of this research is to synthesize modified thermoplastic sago starch (TPS) through in-situ mechanism by reacting sago starch with diphenylmethanediisocyanate (MDI) and castor oil simultaneously, resulting in a more homogenous and finer-sized polyurethane prepolymer (PUP).

Design/Methodology/Approach – The methods used were Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) for thermal characterization and stability of PUP, modified TPS non-extracted and extracted with toluene and water.

Findings – TGA test results presented shows that PUP begins to decompose thermally at a temperature of 300–500 °C. Weight loss occurs rapidly between these temperatures and is completely discharged at a temperature of 500°C, which is called weight loss transition.

Research Limitations/Implications – When extracted with toluene and a water solvent, the melting point and latent heat of fusion slightly decreased; however, it is still higher than the original value of sago. In terms of thermal stability, modified TPS decomposes and loses weight at 150–200 °C in small quantities, continues with weight loss rapidly, and is completely discharged at 500°C. The thermal stability is considered high; thus, modified TPS application can be varied.

Practical Implications – DSC analysis and TGA shows that modified TPS has good thermal characteristics and thermal stability. Modified TPS has a melting point of 104.69°C, and the latent heat of

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fusion (ΔH) is 234.27 J/g. This value is close to the PUP melting point and latent heat of fusion, which reveals the formation of cross-link between the starch and PUP.

Keywords Sago, modified thermoplastic starch (TPS), castor oil, Methylene Diphenylene Diisocyanate, (MDI), thermal characteristics

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1. Introduction

The basic materials used today for plastic are polypropylene and polyethylene. The waste produced is high and harmful for the environment since it cannot be degraded naturally. Eventhough the plastic waste can be recycled, and public discussion associated with the level of safety and health for the user, especially since the issuance of Peraturan Kepala Badan Pengawasan Obat dan Makanan RI No. HK 00.05.55.6497 Tentang Bahan Kemasan Pangan (Head of Drug and Food Control Body Regulation on Food Packaging Materials) on 2008, which prohibits using of recycled plastics for food packaging (Pudjiastuti *et al.*, 2012). Asia is the world's largest consumer of plastic; it absorbs about 30% of global plastic consumption, and about 100 million tonnes of plastic is produced in the world for various industrial sectors (Dayanti, 2006). Along with the increased awareness for environmental conservation, the need for biodegradable plastic materials has increased. In 2010, the production of biodegradable plastics was projected to reach 1.2 million tons (Dayanti, 2006).

Starch has been widely used as raw material for biodegradable plastic due to its biodegradability, renewably, and availability. Plastic prepared from starch, with its low amounts of water, is brittle. To reduce the brittleness, starch is plasticized with hydrophilic plasticizers, such as glycerol, and is melted for preparing thermoplastic starch (TPS). After several months, glycerol-plasticized TPS becomes brittle because glycerol migration from starch matrix interacts with starch by non-covalent hydrogen bonding leading to phase separation. Grafting a flexible impact modifier to the matrix starch with the covalent bonds can prevent it (Wu *et al.*, 2008). With the current available modifiers, isocyanate groups have high activity to react with the hydroxyl group of starch. Polyurethane prepolymer (PUP) is used to toughen starch. Polyol soft segments in polyurethane (PU) is linked to starch matrix by urethane linkage and plays a role as an impact modifier. Protection of the environment can be done by using polyol from renewable materials, such as vegetable oil (Lu *et al.*, 2005). Among many types of plant oils, castor oil has three hydroxyl groups and is a candidate to synthesize poliueratan (Carme Coll *et al.*, 2008).

Ferrer *et al.* (2007) has characterized the polyurethane network synthesized from vegetable-based polyol and compared it to polyurethane network from petroleum-based. Polyurethane network can be synthesized fromvegetable-based polyol and petroleum-basedpolyol. The purpose is similar, to react with isocyanate and form polyurethane. The different is only on the biodegradability of polyurethane formed, where the vegetable based polyol will make the Polyurethane biodegradable in nature (Ferrer *et al.*, 2007). Wu et al. (2008) has conducted a research on synthesizing modified TPS using corn starch with PUP from diphenyl methanediisocyanate (MDI) and polyols produced from castor oil. This modification produces micro particle fillers, e.g., polyurethane prepolymer (PUP) and will consequently resulting micro composite sago starch material. The process Wu conducted strengthened thermoplastic corn starch using PUP that binds to the starch matrix through the urethane bond. In this case, the PUP mixed into the starch matrix as filler after synthesized separately and already forming micro particle PUP (Wu *et al.*, 2008).

In this study, we want to synthesize modified TPS through an in-situ mechanism by reacting sago starch with MDI and castor oil simultaneously, resulting in a more homogenous and finer-sized polyurethane prepolymer (PUP). Modified TPS structure, forming mechanism, properties, and biodegradability have been published previously (Dewi *et al.*, 2014). The thermal behaviours of modified TPS were characterised through DSC analysis and TGA, and the result will be discussed in this paper.

2. Experimental

2.1. Materials

Sago Starch, Castor oil, DiphenylmethaneDiisocyanate, sorbitol, and glycerol plasticizer.

2.2. Synthesis of modified TPS

Sago (31 g) was put into an Erlenmeyer flask and mixed with 155 ml of 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 (4 g) and MDI (3 g) are poured directly and blended together with vigorously mixing for a few minutes. Sorbitol 7% (14 g) is also added. The mixture is poured onto a sheet of glass for thin printing. Film was dried in ambient conditions for 24 h. After this, it was removed from its casting and cut to fit the testing requirements. As a comparison, polyurethane prepolymer (PUP) was also produced by reacting castor oil (15 g) and MDI (13 g). Once the mixture is homogenous, it is printed and dried to form the PUP film.

2.3. Analysis conducted

The tests used were Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) for thermal characterization and stability of PUP, modified. TPS non-extracted and extracted with toluene and water are the type or variant of samples tested with DSC and TGA..

3. Result and discussion

The melting point is a condition where the sample temperatures increases, so the sample state change from solid into liquid. In contrast to metals, plastics generally do not consist of a specific melting point. The value of melting point is needed to determine the product's process and application conditions. The plastic would be good as packaging material or not and survive at a certain temperature in accordance with the plastic durability to be determined with thermal stability analysis. DSC analysis was conducted for the sample PUP, modified TPS, modified TPS extracted with toluene and water. Images of DSC test results are shown by Figures 1–3.

The DSC for the PUP test result showed a melting point of 105.55 °C and a latent heat of fusion (ΔH) is 224.38 J/g; for the modified TPS, the melting point is 104.69 °C and the ΔH is 234.27 J/g. The modified TPS melting point was obtained almost in the same way as the PUP which indicates the development of cross-link between starch and PUP, when compared to the sago starch which is only about 70 °C. The addition of starch matrix into the PUP increased the melting point of the modified TPS and proved the occurrence of cross-links. The higher melting point indicates a growing number of cross-links occurred. It is influenced by hydrogen bonds contained in plastic. More hydrogen bonds in film mean the higher melting point will be due to energy required to break bonds.

The melting temperature and latent heat of modified TPS extracted with toluene and water decreased. Modified TPS extracted with toluene showed a melting point of 98.23 °C

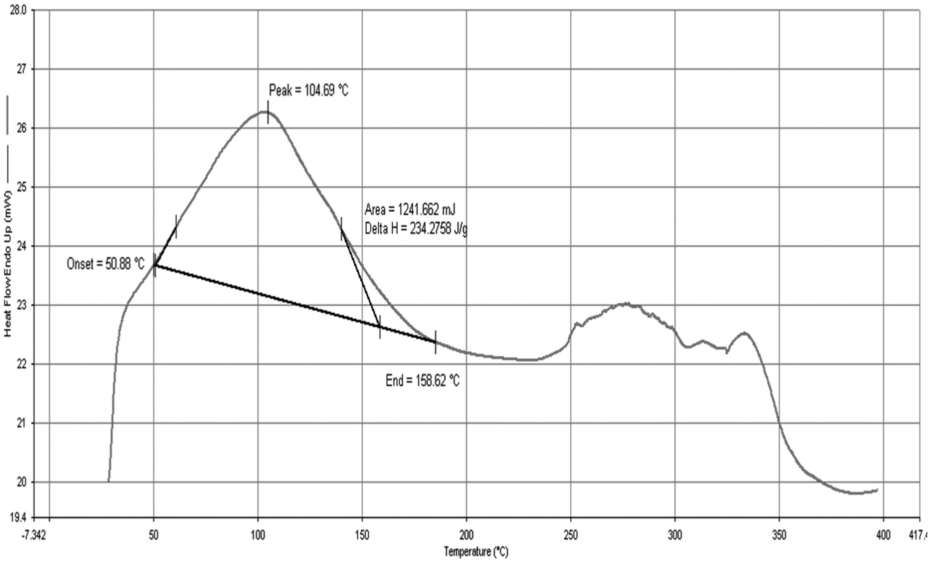

Figure 1.
DSC Analysis Modified TPS

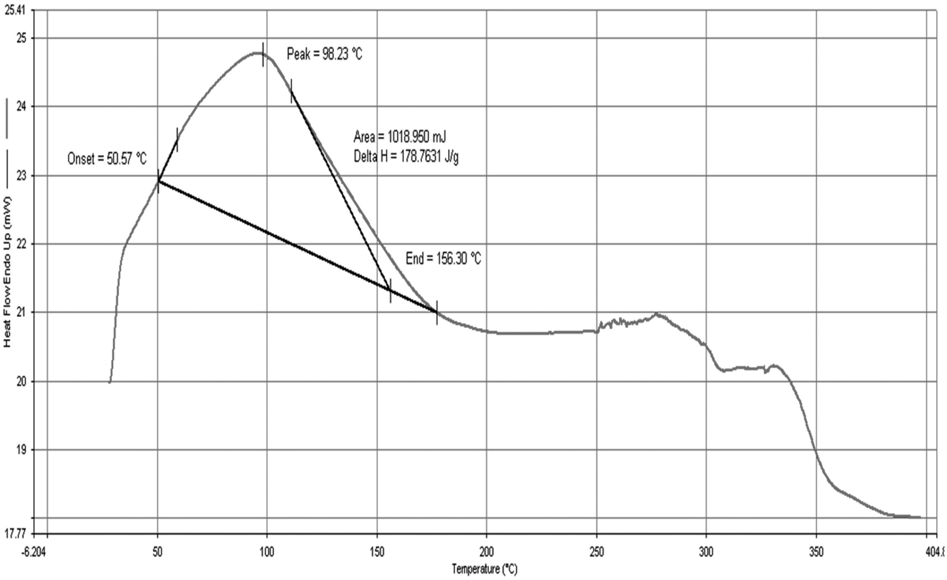

Figure 2.
DSC Analysis for Modified TPS Extracted with Toluene

and a Δ*H* of 178.76 J/g; for TPS extracted with water, the melting point is 74.86 °C and the Δ*H* is 87.74 J/g. The decrease in the melting point and Δ*H* is due to a certain partial amount of castor oil and MDI dissolved in the toluene and due to sago starch dissolved in water solvent.

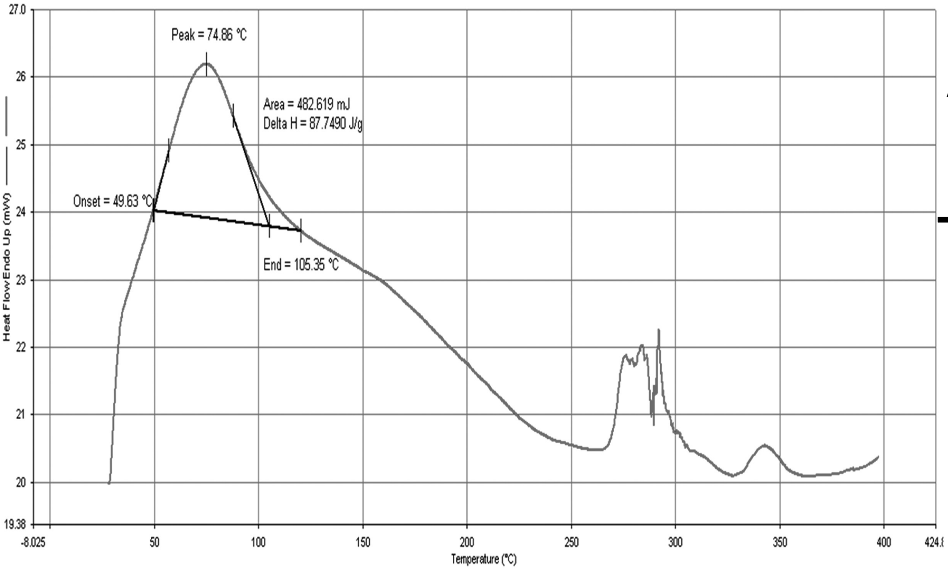

Figure 3.
DSC Analysis for Modified TPS Extracted with Water

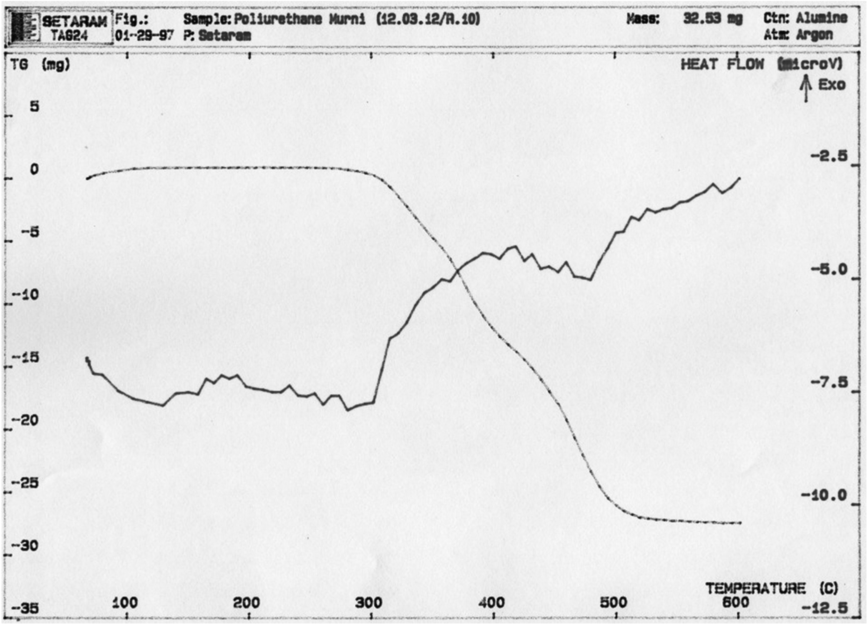

Figure 4.
Thermal Decomposition of PUP

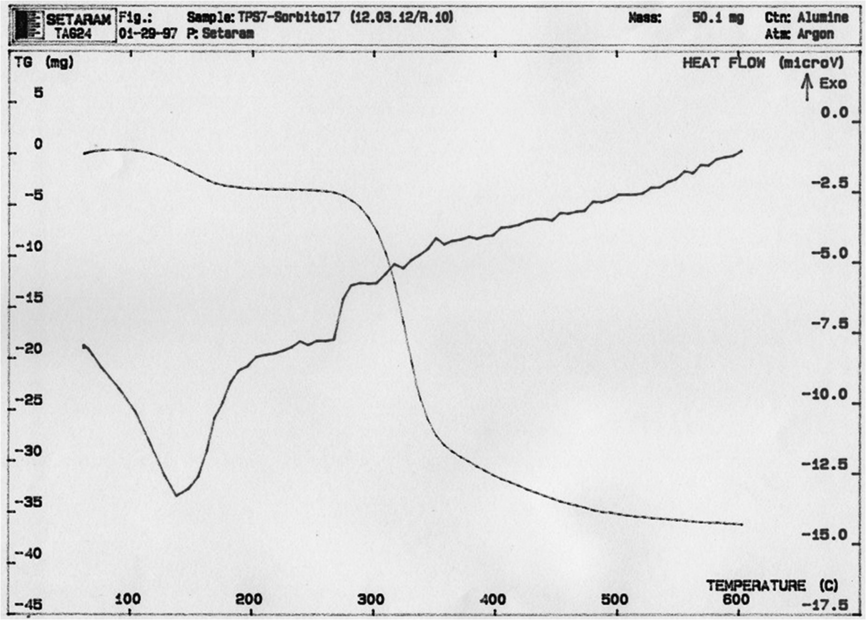

Figure 5.
Thermal Decomposition of Modified TPS

In term of thermal stability, TGA test results showed that PUP decomposes thermally at a temperature of 300–500 °C as show n in Figure 4. Weight loss occurs rapidly between these temperatures and is completely discharged at a temperature of 500 °C, which is called weig ht loss transition (Figure 5). The modified TPS decomposes and loses weight at 150–200 °C in small quantities, continues with weight loss steeply, and is completely discharged at 500 ° C. Modified TPS loses weight faster than PUP because of the weight loss occurring in the first transition phase, which means the starch component has lower thermal stability compared with PUP. Considering the high temperature range where the modified TPS decomposed until it is fully decomposed, the application of modified TPS can be varied within that temperature range. Having said this, there is a need to combine thermal behavior with the mechanical characteristic that has been published previously to fit the best application (Rozanna *et al.*, 2014).

4. Conclusion

From DSC analysis and TGA conducted, modified TPS has good thermal characteristics and thermal stability. Modified TPS has a melting point of 104.69 °C, and the ΔH is 234.27 J/g. This value is close to the PUP melting point and the ΔH, which reveal the formation of cross-link between starch and PUP. When extracted with toluene and water solvent, the melting point and ΔH slightly decreased; however, it is still higher than the original value of sago. In term of thermal stability, modified TPS decomposes and loses weight at 150–200 °C in small quantities, continues with weight loss rapidly, and is completely discharged at 500 °C. The thermal stability is considered high; thus, the modified TPS application can be varied.

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