

Improved Mechanical and Thermal Properties of Modified Thermoplastic Starch (TPS) from Sago by using Chitosan

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ABSTRACT

The use of starch as bioplastic has been widely studied; however, the quality needs to be improved before it can substitute the commercial plastic. Sago is one of starch sources that can be used for this purpose and is available in considerable amounts in Indonesia. Previous research to synthesize a modified sago starch thermoplastics (TPS) *in-situ* by reacting plasticized starch with diphenylmethane diisocyanate (MDI) and castor oil; simultaneously to produce polyurethane prepolymer (PUP) in more homogeneous phase and smaller size has been successfully done. At this phase, chitosan of 0.5, 1, 1.5, 2 and 2.5 gram was added into the compound and acted as filler to improve the mechanical and thermal properties of TPS. The chitosan was first diluted into acetate acid and mixed rigorously with the starch and PUP. Sorbitol was added as plasticizer. The modified TPS-chitosan was then characterized mechanically, thermally, and biodegradability. The results

of this study showed that the optimum mechanical properties of modified TPS were obtained with an addition of 1 gram chitosan; tensile strength and elongation were 200.04 MPa and 24.96 % respectively. Thermal Gravimetric Analysis showed that modified TPS-chitosan had a good thermal stability and could only be degraded at high temperature of 534°C. DSC result showed that modified TPS-chitosan had a high melting point of 385.41°C and ΔH 152.61 J/g. This value is higher than melting point of TPS alone which is 104.69°C. Modified

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TPS-chitosan was degraded earlier than TPS which was 19 days in nature compared to 2-4 months. Overall, mechanical and thermal properties of modified TPS are improved with the addition of chitosan.

Keywords: Biodegradability, chitosan, mechanical properties, Modified Thermoplastic Starch (TPS), sago, thermal characteristics

INTRODUCTION

Basic material used to produce plastic is polypropylene and polyethylene. The waste produced is very high and therefore increases the cost to recycle the material. Recycled plastic still has a lot of controversy associated with the level of safety and health impact to the user. The regulation by Head of Drug and Indonesian Food Control Body Regulation on Food Packaging Materials No. HK 00.05.55.6497 regarding food packaging material dated on August 20, 2007 has entered into force in August 2008 which prohibit the use of recycled plastics (Pudjiastuti & Listyarini, 2012)

Biodegradable plastics industry will develop into a major industry in the future so that it is important to produce plastic materials that have superior characteristics and can be degraded by nature. Starch has been widely used as raw material for biodegradable plastic due to its biodegradability, renewability and availability in huge quantity. However, plastic prepared from starch cannot compete with the conventional plastic in term of its mechanical and thermal properties. Therefore, the bioplastic needs to be modified to improve its mechanical and thermal properties. Wu et al. (2008), synthesized modified thermoplastic starch (TPS) using corn starch with polyurethane prepolymer (PUP) from diphenylmethane diisocyanates (MDI) and polyols derived from castor oil. This modification produces micro particles fillers (PUP). Protection of the environment can be realized when the polyol replaced with renewable materials, such as vegetable oil (Lu et al., 2005). Among many types of plant oils, castor oil has three hydroxyl groups, thus is a good candidate to synthesize poliuretan due to its ability to improve the mechanical properties or durability against water (Ferrer et al., 2008)

Rozanna et al. (2014) had synthesized modified thermoplastic sago starch (TPS) through *in-situ* mechanism by reacting sago starch with MDI and castor oil simultaneously, resulting the formation of more homogenous and finer size polyurethane prepolymer (PUP), as well as the modification reaction that occurred not only on the surface of the PUP particles but also in the bulk phase. The virtue of this study apart from *in-situ* process which provided more advantage than the conventional method was sago starch. as a raw material of TPS which is still not being maximally utilized in Indonesia despite of its high production. The function of sago starch has changed lately from main food in the eastern of Indonesia into

a husbandry fodder. The mechanical and thermal properties of modified TPS is better than bioplastic; however, it is still not competitive compared to conventional plastic.

Through this research, the mechanical and thermal properties of modified TPS are being improved by adding chitosan into the mixture. Chitosan has been known as a material that can improve the mechanical properties of plastic and can reduce its ability to absorb water. The modified TPS-chitosan is expected to have a competitive mechanical property like the conventional one as well as zero waste to the environment.

MATERIALS AND METHODS

Materials

Sago starch, Castor oil, 4, 4'-methylenedi-*p*-phenyl diisocyanate (MDI), chitosan, acetic acid (2%), and sorbitol plasticizer were used without any further pretreatment.

Synthesis of Modified TPS-Chitosan

Chitosan with five different weights as mentioned in the Table 1 were diluted with acetic acid (2%) and added into a 15.5g of sago in 500ml Erlenmeyer flask. The mixture was heated and stirred at a temperature of 70°C for about 30 minutes to form a gel. Subsequently, castor oil and MDI were poured directly into the sago gelatinization to form the polyurethane prepolymer (PUP). The mixture was stirred vigorously for a few minutes and sorbitol was added as plasticizer. The mixture was then printed on a sheet of glass and dried at ambient temperature for 24 hours. Sago starch plastic (PS) and PUP-chitosan were synthesized for comparison.

Table 1
Composition in five samples of modified TPS - chitosan

No.	Sample	Sago starch (g)	Chitosan (g)	MDI (ml)	Castor oil (g)	Sorbitol (g)
1	TPS - Chitosan 1	15.5	0.5	1	2	7
2	TPS - Chitosan 2	15.5	1	2	3	7
3	TPS - Chitosan 3	15.5	1.5	3	4	7
4	TPS - Chitosan 4	15.5	2	4	5	7
5	TPS - Chitosan 5	15.5	2.5	5	6	7

Analysis Conducted

A tensile strength test was performed to test the mechanical properties of the modified TPS-chitosan. Whereas the thermal characteristic, stability and biodegradability rate of the modified TPS-chitosan were measured by using a Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

RESULTS AND DISCUSSIONS

Mechanical Properties

Tensile strength is the measurement of the force required to pull something to the point where it breaks. The tensile strength for the modified TPS-chitosan was performed by using Universal Testing Machines Electronic System based on the standard ASTM D638, 1991. The tensile strength for each sample is recorded in Table 2.

Table 2
Tensile strength for each sample

No	Sample	Tensile strength		Elongation (%)
		(Kgf/mm ²)	(MPa)	
1	TPS - Chitosan 1	13.30	130.41	15.08
2	TPS - Chitosan 2	20.40	200.04	24.96
3	TPS - Chitosan 3	8.50	83.35	21.32
4	TPS - Chitosan 4	9.40	92.17	19.76
5	TPS - Chitosan 5	8.50	83.35	11.84
6	Bioplastic sago + Sorbitol	0.26	0.03	57.00
7	PUP + Chitosan	15.20	149.05	13.40

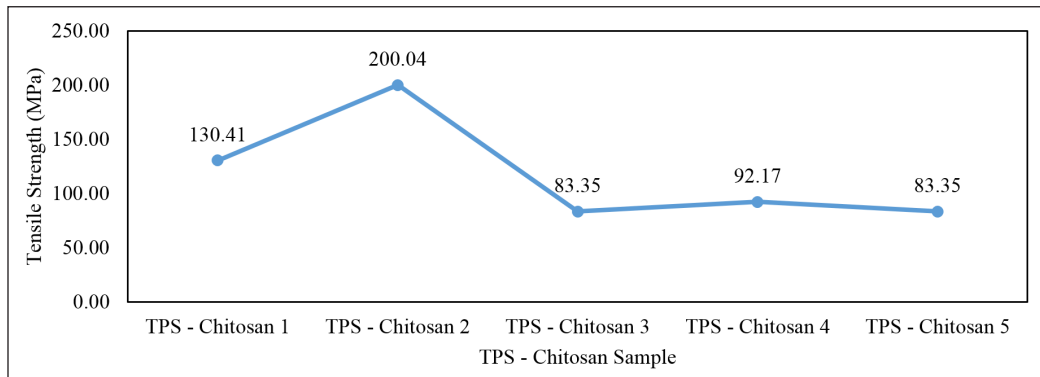


Figure 1. Tensile strength for various TPS - Chitosan sample

As illustrated in Figure 1, the addition of 0.5 g and 1 g of chitosan has increased the tensile strength to 13.30 kgf/mm² (130.41Mpa) and 20.40 kgf/mm² (200.04 Mpa) respectively. Reversely, the addition of 1.5g, 2.0g and 2.5g of chitosan has reduced the tensile strength to 8.50 kgf/mm² (83.35 Mpa), 9.40 kgf/mm² (92.17 Mpa), and 8.50 kgf/mm² (83.35 Mpa) respectively. The tensile strength of modified TPS - chitosan obtained for all five samples have managed to exceed the Moderate Class Plastic mechanical properties of 1-10 MPa. Previous research conducted by Rozanna et al. (2014) also revealed that the tensile strength for TPS without chitosan was only 0.40-0.47 kgf/mm², while the tensile strength of pure PUP was 1.72 kgf/mm². This is because the higher the concentration of

chitosan, the more hydrogen bonds formed in the TPS-chitosan. Therefore, chemical bond grows stronger and difficult to break as it requires energy to break the bond. However, this only occurs within a range of concentration of chitosan. In this case, the addition of 0.5 g and 1g of chitosan has increased the tensile strength, while addition of 1.5 g, 2.0 g and 2.5 g of chitosan has reduced the tensile strength. Therefore, the best conditions for TPS-chitosan printing occur on the addition of chitosan 0.5 g and 1 g. The result obtained was similar to research done by Hartatik. Hartatik et al. (2014) studied that the addition of chitosan of 1% and 2% into cassava starch increased the value of tensile strength of bioplastics, while the addition of chitosan of 3% and 5% decreased it. (Hartatik et al., 2014). The more chitosan added, the tensile strength of bioplastics will decrease further as the bioplastics become fragile (Hartatik et al., 2014).

Tensile strength of TPS-chitosan was also influenced by PUP reacted *in-situ* from MDI and castor oil. It had also led to an increased flexibility of modified TPS-chitosan due to the presence of cross linking between the PUP and the starch matrix which subsequently had increased the molecular weight of the starch and elongation of modified TPS. This is because the castor oil added as materials for PUP acts as an impact modifier that increased the elongation and lowered the tensile strength properties. Therefore, the tensile strength properties of modified TPS sheet was influenced by the balanced increase in molecular weight and starch content of castor oil (Wu et al., 2008). Data in Table 2 show that the tensile strength of bioplastic made up of sago only is lower (0.26 kgf/mm²) than bioplastic made up from the combination of TPS-chitosan (15.20 kgf/mm²). Additionally, the plasticizer added had also contributed to the increased flexibility.

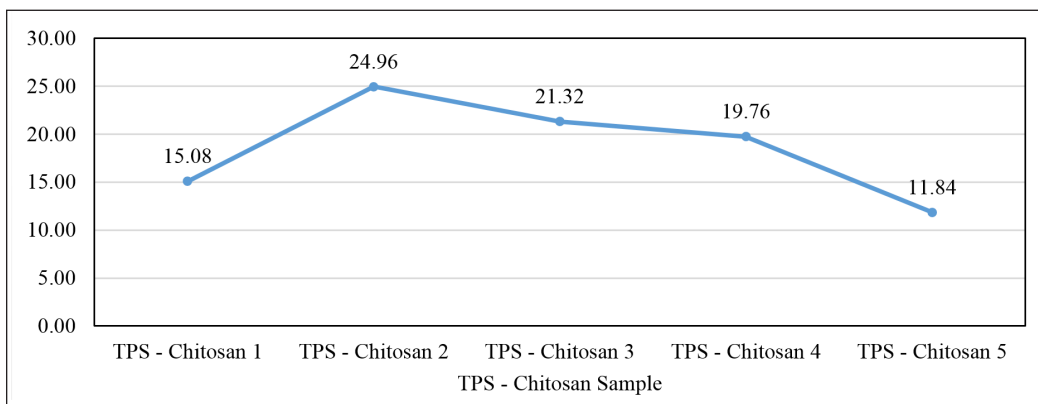


Figure 2. Elongation for various TPS-chitosan samples

Elongation demonstrates a flexibility/elasticity of a film by measuring the maximum length it can reach before breaks. The elongation of TPS-chitosan was influenced by the amount of chitosan added as shown in Figure 2. Higher concentration of chitosan will

reduce the elongation of TPS-chitosan due to the lower distance of its intermolecular bond. Elongation of all TPS-chitosan sample has fulfilled the moderate properties group which was 10-20%. The moderate properties group in plastic refer to the plastic with medium elongation capability. Elongation of a plastic is determined by its application, thus it has to be adjusted accordingly. Previous research done for TPS (15.5 g) without chitosan has shown that the elongation was 15-19.5 % while for PS (Plastic starch made from sago and plasticizer only) the elongation was 10 %.

Polyol derived from castor oil used to form PUP has improved the flexibility of TPS (Rozanna et al., 2014). Research done by Wu et al. (2008) on corn TPS had shown that PUP would improved the tensile and elongation of TPS at certain level; however, after optimum figure, the tensile strength would decrease (Wu et al., 2008).

Thermal Characteristics

Melting Point. Melting point is the temperature at which a substance change from solid to liquid state. The thermal stability analysis help to determine if a specific plastic is good for packaging and can survive a certain temperature depends on its durability. Differential Scanning Calorimetry (DSC) test was performed for TPS – Chitosan 1 and TPS – Chitosan 2 to test its thermal stability.

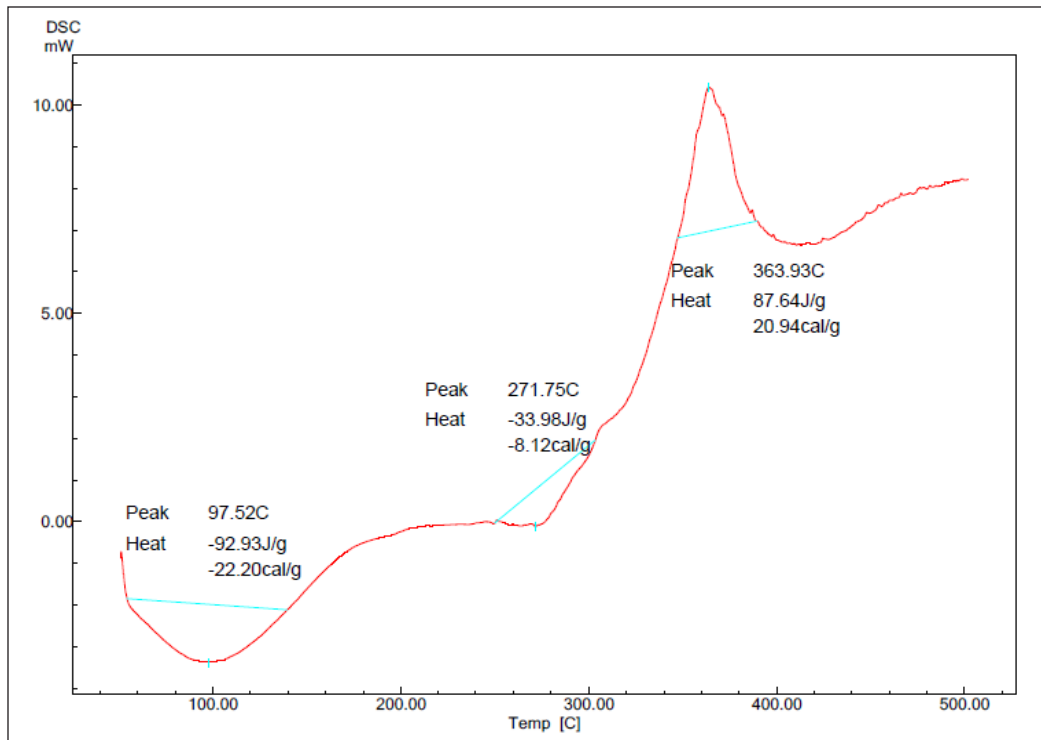


Figure 3. DSC for modified TPS-chitosan 1

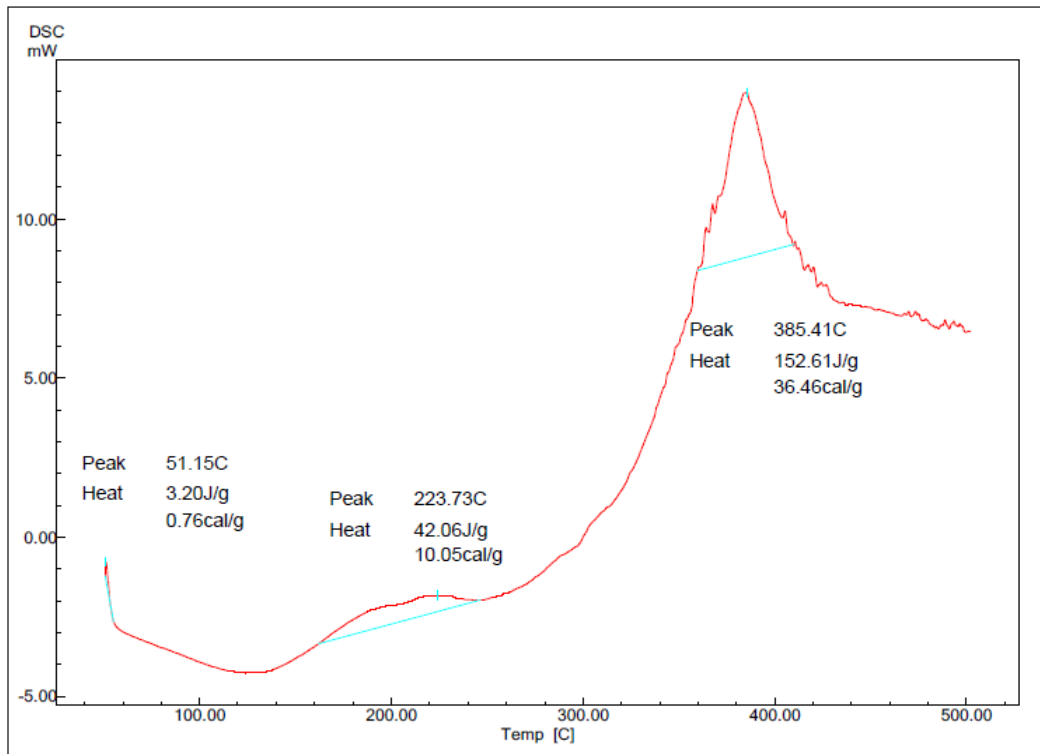


Figure 4. DSC for modified TPS-chitosan 2

Figure 3 and 4 above show the DSC test result for modified TPS - Chitosan 1 and TPS - Chitosan 2. The melting point was 363.93°C and 385.41°C; and the latent heat of fusion (ΔH) was 87.64 J/g and 152.61 J/g, respectively. The result shows an increase in chitosan concentration has increased the melting point. Melting point of modified TPS - Chitosan mixture was higher than in TPS only was due to cross link formed between TPS and chitosan. Addition of chitosan into the mixture had improved the melting point. The higher melting point showed that more cross links occurred and the higher the tensile strength. Rozanna et al. (2014) found that melting point of PUP was 105.55°C and ΔH was 224.38 J/g, while for TPS only, its melting point was 104.69°C and ΔH was 234.27 J/g.

Another means to determine thermal characteristic of TPS-chitosan was through Thermal Gravimetric Analysis (TGA). Figure 5 below shows the result of TGA performed on TPS - Chitosan 1. TPS-chitosan 1 started to lose weight at 6th minute and 165°C, and was fully decomposed at 24th minute and 534°C. Drastic weight lost took place at 11th minute and 271°C until 16th minute and 375°C. The result for TPS-chitosan 1 and 2 was almost similar. Previous study done by Rozanna et al. (2014) showed that the PUP began to decompose at temperature of 300 - 500°C. Meanwhile, TPS started to decompose at 150 - 200°C in small quantities, continued with weight loss steeply and completely discharged

at temperature of 500°C. Modified TPS-chitosan lost weight faster than PUP at the first transition because starch had a lower thermal stability compared to PUP. Meanwhile, TPS-chitosan showed higher temperature to decompose compared to TPS only.

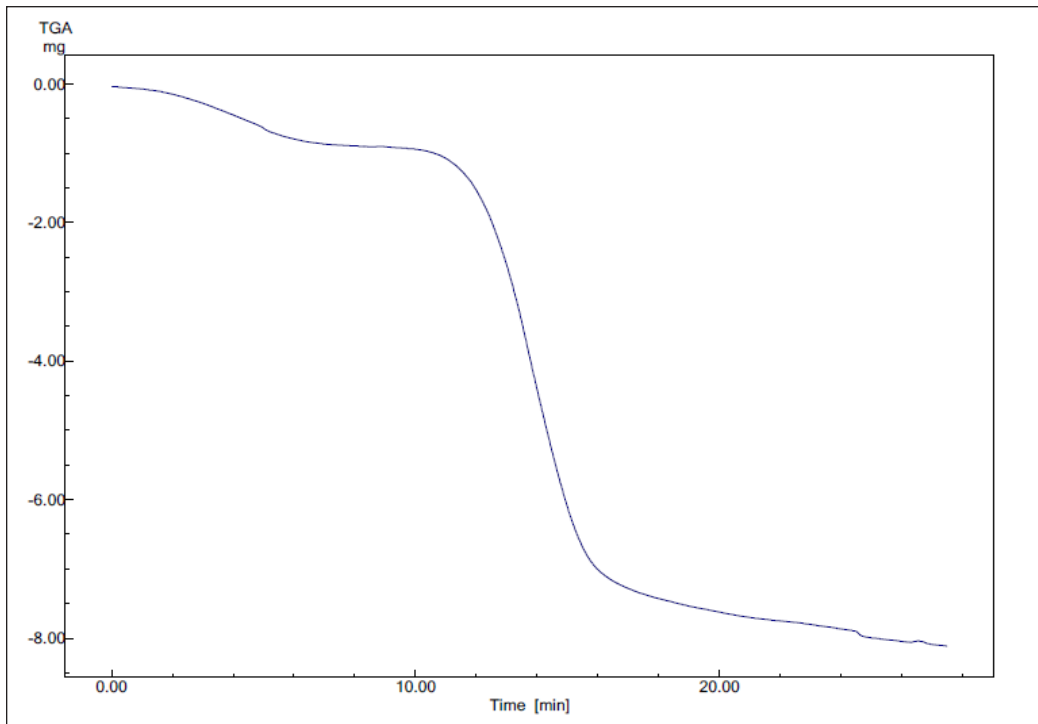


Figure 5. TGA for modified TPS-chitosan 1

Biodegradability

As shown in Figure 6, biodegradability rate of TPS-chitosan at various composition was affected by composition of MDI and chitosan. High amount of MDI and chitosan in the mixture has led to lower rate of biodegradability. Starch is a natural polymer that can be easily degraded in nature, while chitosan has slower rate of degradation. Rate of biodegradability of polymer depends on its structure. Since crystallinity of chitosan was higher than starch, hence higher concentration of chitosan in the mixture reduced TPS-chitosan rate of biodegradability.

A hundred percent weight loss occurred in 19 days for all TPS-chitosan, except TPS-chitosan 4 and 5. The biodegradability rate was higher compared to the previous research, where TPS was degraded at 10-16 weeks depending on PUP concentration (Rozanna et al., 2014). This was due to weather condition where the samples was buried in a rainy season; therefore, the soil moisture has increased. Hartatik et al. (2014) also revealed a similar finding that after 15 days buried almost 75% of bioplastic had degraded from cassava-chitosan. This shows that higher amount of chitosan in the mixture reduces the

biodegradability rate. Biodegradability of cassava-chitosan was almost fully degraded in 45 days (Lazuardi & Cahyaningrum, 2013).

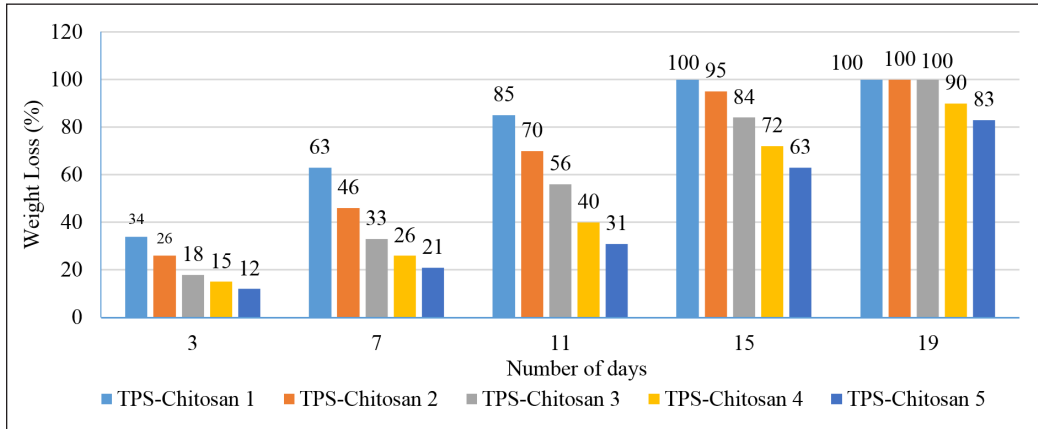


Figure 6. Biodegradability rate of various TPS-chitosan

CONCLUSION

Addition of chitosan has improved the mechanical and thermal properties of modified sago starch thermoplastics (TPS). The optimum concentration of addition of 1 g chitosan has resulted in increased tensile strength (200.04 MPa) and improved elongation (24.96%). The melting point of modified TPS - Chitosan (385.41°C and ΔH is 152.61 J/g) was higher than TPS (104.69°C and ΔH is 234.27 J/g). A modified TPS-chitosan also has a good thermal stability up to 534°C and will be degraded in nature in 19 days.

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