PREPARATION AND CHARACTERIZATION OF THERMOPLASTIC STARCH FROM PINEAPPLE STEM: EFFECT OF PLASTICIZERS

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Abstract

This work studied the effect of types and amount of plasticizers on thermoplastic starch properties from pineapple stem with good mechanical properties, water resistant and biodegradable. Three plasticizers were studied: erythritol, xylitol, and sorbitol. Thermoplastic starch film was prepared by solution casting. When glycerol was used as co plasticizer, it could improve the flexibility of thermoplastic starch. Thermal properties of thermoplastic starch film by DSC showed that when the plasticizers were added, the heat of fusion (ΔHm) was reduced. Water absorption of thermoplastic starch films are maximum in 1 hour and constant after immersed in distilled water for 3 hours. Films can maintain in their shapes at least 13 days after that they dissolved. Thermoplastic starch from pineapple stem and plasticizers i.e. sorbitol and xylitol showed no significant difference in water absorption. Thermoplastic starch films from mixed plasticizers showed more hydrophilic when compared with film from single plasticizer. Films without glycerol show high tensile strength and modulus. Thermoplastic starch film from pineapple stem is water resistant and biodegradable in water. All thermoplastic starch degraded within 30 days after biodegradability test in soil. Thermoplastic starch film made from pineapple stem is considered a naturally biodegradable plastic.

Keywords: Erythritol; Pineapple starch; Plasticizer; Sorbitol; Thermoplastic starch; Xylitol

Introduction

Nowadays, the production and use of plastic has increased dramatically both in the form of products and various packaging. Due to the lightweight properties of plastic and low cost, Thailand is the world's fifth largest waste discharger. More than half of the 8 million tons of waste that enters the ocean is plastic. Since January 2020 supermarkets and convenience stores refrain from handing out plastic bags. It is the first step towards reducing environmental waste. Reduce and stop using plastic including reusing plastic waste could be reduce plastic pollution.

But the plastics industry revealed that from the past covid situation Domestic and export plastic sales rose 40-50 percent during the lockdown period. During this situation food packaging

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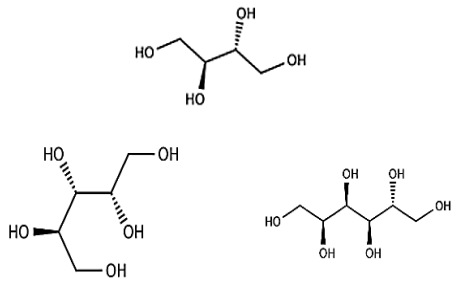


Figure 1. Chemical structure of erythritol, xylitol, and sorbitol

Figure 2. Various sizes of pineapple starch

increased up to 10 percent especially, and biodegradable food packaging increased up to 30 percent as well.

From the above problems, it was found that Thai people are increasingly interested in the use of biodegradable plastics. Researchers have therefore invented thermoplastic starch, which are biodegradable plastics. It is interesting because the main raw material for production is starch which is an easily available raw material found in Thailand. It is cheap and comes from renewable resources.

Thailand is an agricultural country with a variety of economic crops. Pineapple is one of the popular crops of Thailand that is cultivated in large numbers. After harvesting, pineapple pulp will be utilized and unused parts are bark, core, leaves, stems, roots and rhizomes. Pineapple rhizomes can be used to produce starch used in the plastics industry. In this research, the aim is studying the preparation of thermoplastic starch from pineapple stem. There was a report that in pineapple stem has high content of amylose and amylopectinas high as 34-35%w/w (Nakthong *et al*., 2017), The problem of using glycerol is film show low tensile strength. Pineapple stem was mixed with a sugar alcohol plasticizers ie. erythritol, xylitol and sorbitol. These plasticizers reduce the binding force between the molecular chains of starch, resulting in flexibility and shape changes (Pual *et al*., 2009), In addition the particle size of pineapple starch will be investigated. Therefore, the purpose of this work is to study the preparation and properties of thermoplastic starch from pineapple starch which is the waste from agriculture product in Thailand. In order to apply the starch from agricultural residues and to bring benefits in the plastics industry and to support the agricultural sector as well.

Mathematical Models

Materials

Starch from pineapple stem after removing bromelain enzyme was received from factory in Rayong. Pineapple starch was sieved into various sizes ie. 40, 60, 80, and 100 mesh. Various types of sugar alcohols were used as plasticizer including glycerol. Erythritol (Ery), xylitol (Xy) and sorbitol (Sor) from LOBA were used as received. Glycerol from KEMAUS was used as received. (Figure 1.)

Preparation of Pineapple Starch Powder

Pineapple powder was grinded with a high-speed blender**.** It was then sieved with 100, 80, 60, and 40 mesh sieve and baked in an oven at 60°C for 24 h to remove moisture**.** Then the pineapple powder was kept in a ziplock bag and stored in a desiccator**.** (Figure 2.)

Preparation of Thermoplastic Starch

Pineapple starch were prepared with various components and plasticizers as shown in Table 1. PS and erythritol, xylitol, sorbitol with various ratios ie. 80/20, 70/30 and 60/40 by weight based on 15% weight of PS in water. The solution was heated and stirred well at 80-90°C for 10-20 minutes. The homogeneous solution was then formed film by solution casting and left to cool in the fume hood. Then glycerol was added as a co plasticizer with different ratios ie. 25/5 and 15/15 by weight as shown in Table 2.

Crystal Structure by X-Ray Diffraction (XRD)

X-ray generator Cu anode, $K_{\alpha 1}$ 1.544° A by taking pineapple starch and thermoplastic starch

film with a size 2 cm. × 2 cm., scan 2θ from 5-40 degrees, step size equal to 0.01 with a scan rate of 5 seconds.

Thermal properties by Differential Scanning Calorimetry (DSC)

Pineapple starch and thermoplastic starch films approximately 5-15 mg were heated under a nitrogen gas atmosphere**.** The samples were heated from 30 to 210°C at a rate of 10°C/min, held at 210°C for 1 min, then cooled down from 210 to 30°C at a rate of 10°C/min. The samples were held at 30°C for 1 min and then reheated again with the same condition. The percentage crystallinity ($\%X_C$) has been calculated using the following equation.

$$X_{c(\%)} = \frac{\Delta H_f \times 100}{\Delta H^\circ_f} \quad (1)$$

Where ΔH°_f is heat of fusion 100% crystalline of PS (from experiment is approximately 259.05 J/g), ΔH_f is the enthalpy of melting.

Melt Flow Rate

Thermoplastic starch films were cut into small pieces approximately 6 g. Melt flow rate was tested in accordance to ASTM D1238 at 230°C. A piston press and a weight of 2.16 kg were pushing the molten thermoplastic through the die. The samples were weighed every 10 min to obtain the MFI which is measured in grams/10 minutes.

Table 1. composition and conditions for thermoplastic starch preparation

Pineapple starch (PS) and plasticizers ratio	Temperature (°C)	Time (min)
PS80 /Ery20	80	10
PS80 /Xy20	80	10
PS80 / Sor20	80	10
PS80 / Ery20	90	15
PS80 / Xy20	90	15
PS80 / Sor20	90	15
PS70 / Ery30	90	20
PS70 / Xy30	90	20
PS70 / Sor30	90	20
PS60 / Sor40	90	20
PS60 / Xy40	90	20
PS60 / Sor40	90	20

Table 2. component ratios for TPS preparation with glycerol as co plasticizer

Pineapple starch (PS) and plasticizers ratio	Temperature (°C)	Time (min)
PS70 /Ery25 / Gly5	90	20
PS70 /Xy25 / Gly5	90	20
PS70 / Sor25 /Gly5	90	20
PS70 / Ery15 / Gly15	90	20
PS70 / Xy15 / Gly15	90	20
PS70 / Sor15 /Gly15	90	20

Mechanical Properties by Tensile Testing

Mechanical properties were tested by Instrons Universal Testing by using load cell 1 kN, gauge length 57 mm and crosshead speed 5 mm/min. Thermoplastic starch films were cut into size in accordance with ASTM D638 Type I. At least 5 specimens each were tested for each sample. Tensile strength, elongation at break and modulus were reported.

Water Absorption

3 pieces of 2 cm. × 2 cm. of thermoplastic starch film were weighted and soaked in 20 mL of distilled water in a closed container. Weight was recorded before and each day after soaking, for a period of 7 days to find the percentage of water absorption. The percentage of water absorption can be calculated as show in Figure 3, by the following equation.

$$\%\, water\ absorption = \left(\frac{w_1 - w_0}{w_.}\right) \times 100 \quad (2)$$

W_1 = weight at any time
W_0 = weight at the beginning

Biodegradability Tests

Biodegradability of thermoplastic starch film (2 cm × 2 cm) was evaluated by exposing the film into compost soil; 20% water, 20% organic substance, 30% rotten leaves, 5% urea and 5% water paper at 30-45°C. Each specimen was buried 2 cm. depth from the surface and dug out of the compost soil after 1, 7, and 30 days as show in Figure 4.

The sample was washed with water and dried at room temperature. Biodegradability test was determined by measuring weight loss of the specimens (Shaw *et al*., 2006), The percentage of weight loss (W_l) was calculated as:

$$\%W_1 = \left[\frac{W_0 - W_t}{W_0}\right] \times 100 \quad (3)$$

Where W_0 is the initial mass
W_t is the remaining mass at any given time, t.

All results are the average of three specimens.

Figure 3. Optical images of TPS films of PS/Ery, PS/Xy and PS/Sor before water absorption testing

Results and Discussion

Crystal Structure by XRD

Films prepared from PS/plasicizer with ratio 70/30 at 90°C for 20 minutes show smooth and clear. XRD results in Figure 5 reveals that film from PS/Ery had a wide peak distribution pattern and a high intensity similar to that of pineapple stem powder. This indicates that erythritol slightly reduced the crystallinity of the pineapple powder or there is no interaction between erythritol and pineapple stem or no gelatinization. Sharp peaks of PS/Ery are clearly seen than that of pure PS so PS/Ery show more high crystallinity pure PS. While films from PS/Xy and PS/Sor showed a significantly lower intensity compared to the pineapple powder. This indicates that thermoplastic starch films are amorphous. It also found that the thermoplastic starch from pineapple stem has become amorphous. This is because the starch granules were destroyed by heat and shear forces (Muhammad *et al*., 2015), as well as the addition of plasticizer that penetrates the starch granules and breaks the hydrogen bonds that hold the starch molecules together.

Starch Films From Different Plasticizers

Thermal Properties by DSC

The thermal properties of pineapple starch and thermoplastic film starch were studied by DSC technique (Metler Toledo Model: DSC1). The glass transition temperature (Tg), crystallization temperature (Tc) and melting temperature (Tm) were studied as shown in Table 3, while cooling thermogram and second heating thermogram showed no change. It was found that addition of plasticizers resulted in changes at each peak during the melting temperature range of thermoplastic starch prepared from erythritol. There were two broad peaks, from 68.48°C-102.42°C and 135.42°C-197.51°C cause hydrogen bonds to the starch molecular chains with high amylose content so low absorbs water, resulting in incomplete gelatinization. It was also found that the addition of plasticizers would change the melting temperature range. The glass transition temperature (Tg) could not be observed from the thermogram. The melting temperature of thermoplastic starch was increased compared to pineapple starch. This is similar to corn starch which revealed broad endothermic peak and high enthalpy of melting (Mano et al., 2003). The film therefore has increased crystallinity due to the orderly rearrangement of amylose and amylopectin. This corresponds to the XRD effect indicating that the amylose molecule has merged with the plasticizer. When considering the effect of the sugar alcohol plasticizer, it was found that PS/Ery had a wide peak distribution pattern and a high intensity similar to that of pineapple powder. This indicates that the added erythritol reduces the crystallinity of the pineapple powder slightly. It was also reported that the maximum melting temperature range of the cornstarch composite film was found. High amylose and gelatin exhibit wide fusion peaks in relation to the crystalline fraction of amylose molecules in starch (Muhammad *et al*., 2015).

Figure 4. Images of samples for biodegradability test

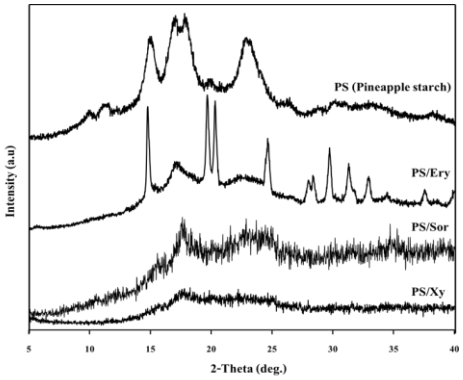


Figure 5. XRD patterns of PS and thermoplastic starch films from different plasticizers

Table 3. Melting temperature, ΔHm and percentage of crystallinity of PS and thermoplastic starch

1st Heat	Tm (°C)			ΔHm (J/g)	X_c (%)
	Onset (°C)	Peak (°C)	Endset (°C)		
PS	85.23	116.50	163.41	259.05	-
PS /Ery	66.48	97.99	102.42	62.14	23.98
	135.42	167.95	197.51	78.31	30.23
PS / Xy	168.16	174.79	207.87	80.37	31.04
PS / Sor	174.39	177.49	187.56	13.83	5.33

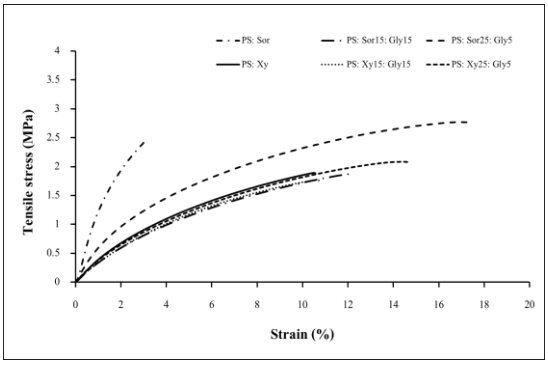
TPS of PS/Ery melting peaks were re-established in the melt temperature range of 135.42°C-197.51°C. The addition of plasticizers was also found to increase each peak during the melt temperature significantly as shown in Table 3 because the addition of plasticizer may help to arrange the molecular chains of starch to be more organized. This is consistent with the study of the effect of type and quantity of thermoplastic starch plasticizer. The glass transition temperature (Tg) was not evident in the DSC measurement, but the melting temperature was reported. It was also found that when plasticizers were added the melting temperature was increased compared to starch without adding plasticizers. (Huang *et al*., 2005; Liu *et al*., 2009)

Melt Flow Rate

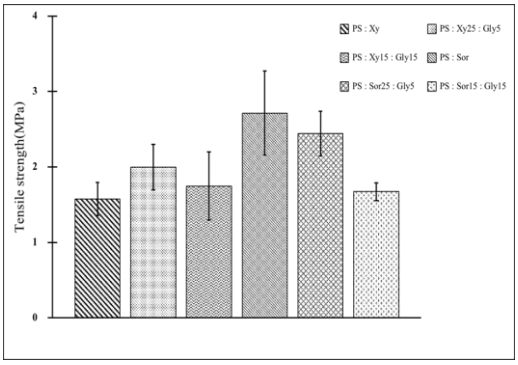
It was found that at 190°C all thermoplastic starch samples melted but did not flow. At 230°C, it was found that all samples can melt and flow. The thermoplastic starch melt flow rates of PS/Ery, PS/Xy and PS/Sor are 41.49 ± 0.14, 79.96 ± 1.81 and 63.20 ± 0.97 g/10 min, respectively. TPS of PS/Xy showed the lowest MFR this might be because this is not thermoplastic starch which is related to XRD result.

Tensile properties

From Figure. 6(a), films prepared from sorbitol only showed high tensile strength but low elongation value than film with co plasticizer. Therefore, glycerol was responsible for increasing the film flexibility. Films prepared from mixed plasticizers ie. PS/Xy25/Gly5 and PS/Xy15/Gly15 showed an increase in strength and elongation of 2 MPa, 13.43% and 1.74 MPa, 10.51%, respectively. While PS/Sor25/Gly5 and PS/Sor15/Gly15 reveal no significant change on strength as seen in Figure 6(b). Thermoplastic starch films without glycerol are hard and brittle. This is similar to the results reported by Baek et.al. (2004). Thermoplastic starch film with glycerol more than 20% by weight show sticky character, low tensile strength and a significantly lower elongation at break in Figure 6(C). Plasticizers were inserted between the polymer chains, making the film more flexible. Films containing glycerol greater than 20% by weight significantly altered the mechanical properties of the films shown in the form of highly flexible materials. Figure 6(d) reveal the high modulus of thermoplastic starch film made from plasticized with sorbitol.



(a)



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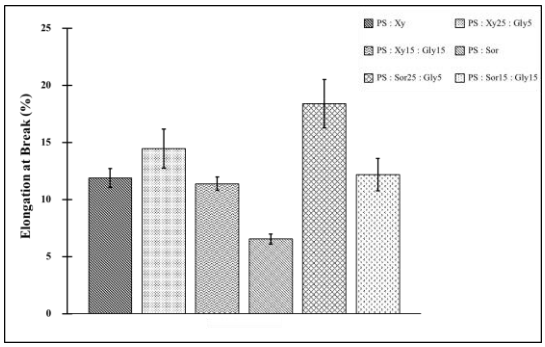
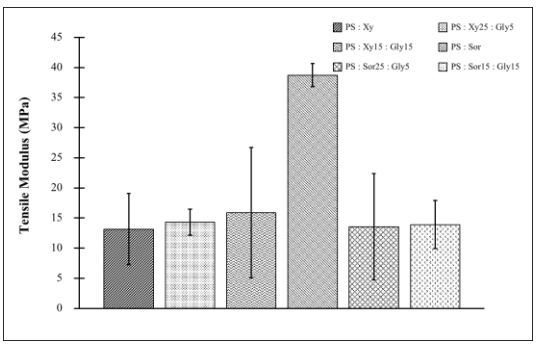


(c)



(d)

Figure 6. (a) Stress- strain curve (b) Tensile strength (c) %Elongation at break (d) Tensile modulus

Water Absorption

Water absorption of Thermoplastic starch is approximately 40-55% and remains constant since 24 hours as seen in Figure 7(a). The thermoplastic starch film using xylitol and sorbitol shows lower water absorption than the film using erythritol. Up to 168 hours, films are still remaining in their shape so thermoplastic starch from pineapple starch could be used as water-resistant film. While Figure 7(b), shows the effect of the mesh size of pineapple starch used sorbitol 30% weight. Figure 7(c), shows that when glycerol is added the film show lower water absorption. Figure 7(d), shows the effect of starch concentration in water on water absorption of film. Most of the experiments used in this work referred to 15%weight of starch.

Biodegradability Test

Soil microbial degradation behavior of thermoplastic starch film after 7 days showed darker film and higher relative humidity from 25.6% to 26.7%RH. When the humidity is high, bacteria in the soil causes the growth of microorganisms in the soil. After 30 days, it was found that the film cracked and some parts decomposed in the soil. Therefore, the thermoplastic starch film is considered a biodegradable plastic. (Figure 8.)

Conclusions

Pineapple starch can be formed into a thermoplastic starch film by heating until gelatinization. Three types of plasticizers: erythritol, xylitol, and sorbitol were used with starch which can break the bond. The hydrogen bonding with hydroxyl group of starch molecules increased the amorphous fraction. Sorbitol and xylitol could be used as plasticizers for pineapple starch like the other starch. Glycerol as co plasticizers can increase % elongation at break of TPS. After 24 h, the water absorption percentage was stable and the film can be decomposed into the soil.

Therefore, thermoplastic film starch from pineapple starch is considered to use as a biodegradable plastic.

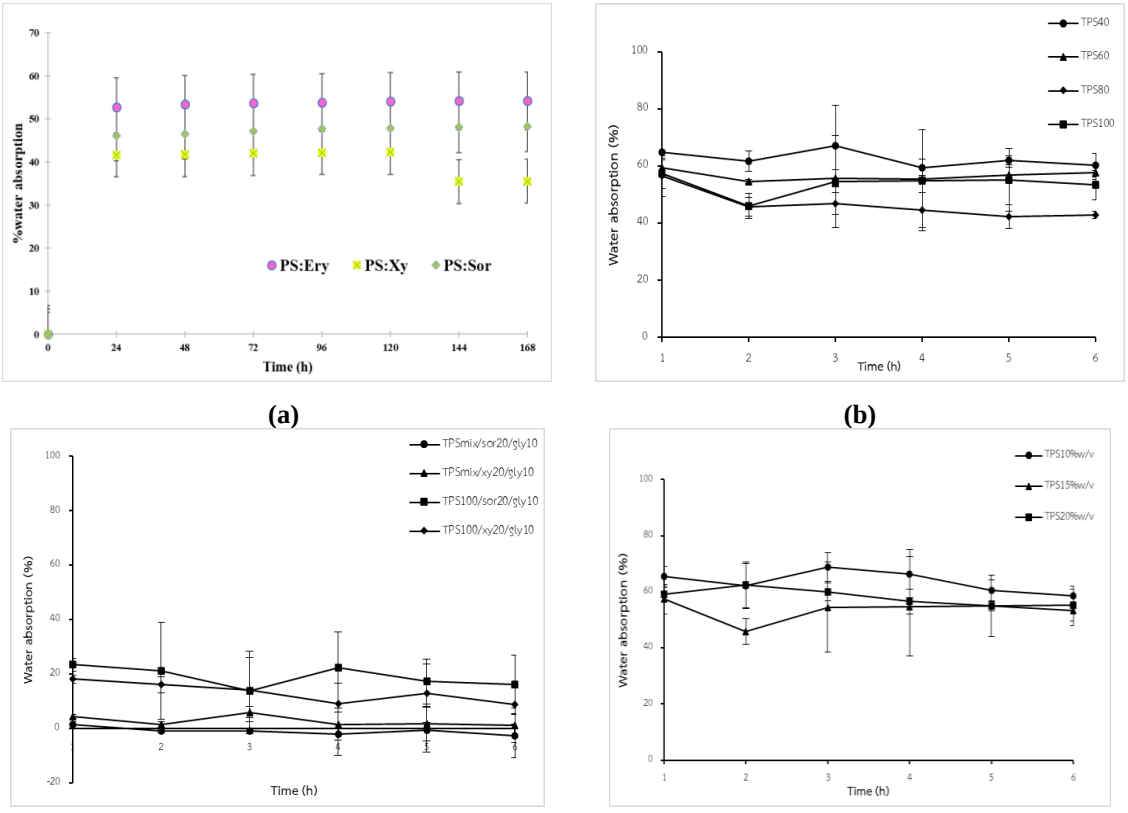
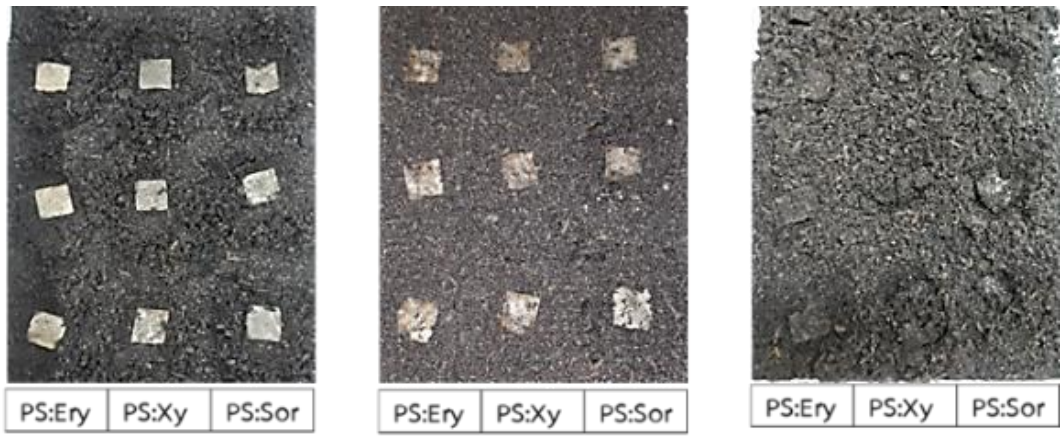


Figure 7. Water absorption (%) of thermoplastic starch films from PS70/plasicizer30 (a) differents sugar alcohols, (b) different starch sizes, (c) mesh100 and mix size of PS with co plasticizers, (d) different concentrations of PS (100mesh) in water for PS70/Sor30



Day 1 Day 7 Day 30

Figure 8. The biodegradability of film at various times

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