PROPERTIES OF THERMOPLASTIC CASSAVA STARCH MODIFIED BYPECTIN
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Abstract: This research was aimed to study on properties of thermoplastic starch (TPS) prepared from cassava starch using glycerol as a plasticizer at the ratio of starch:glycerol; 65:35. Properties of the TPS were modified by different contents of pectin. Starch and glycerol were mixed using a high-speed mixer, then compounded using an internal mixer at temperature of 140 °C and the rotor speed of 40 rpm. The specimens were shaped with compression molding and tested for mechanical and morphological properties. Different contents of pectin, i.e., 2%, 4%, 6%, 8% and 10% were added into the TPS samples. It was observed that with the incorporation of 10% pectin, the tensile strength increased from 0.53 to 1.95 MPa and Young’s modulus increased from 1.84 to 23.7 MPa. Furthermore, IR peak shift was also found for the TPS added by pectin. In addition, morphology and water uptake of the TPS were studied.

Introduction: Starch is an important productive polysaccharide in plant. Native starch commonly exists in a granular structure with about 20 - 45 % crystallinity. Under the action of high temperature and shear, starch can be processed into thermoplastic starch (TPS)1. During the thermoplastic process, water and other plasticizers play an indispensable role, because the plasticizer can form hydrogen bonds with starch.

Several starches are used for producing TPS, including rice starch2, pea starch3, corn starch4. TPS is already used in several commercial products, but intense research continues to improve its properties and widen the possible range of its applications. The main disadvantages of TPS are poor mechanical properties and high water uptake. Research is now focused on modifying the structure of starch, usually by chemical modification during process,5,6,7 and also improving by blending with other polymers.8,9 Both of these strategies are aimed at reducing its hydrophilicity and improving mechanical properties. One approach to increase mechanical properties is to use pectin. It was reported that when pectin was blended with corn starch and plasticized with glycerol, pectin-modified starch could form edible and biodegradable films which have a wide range of good mechanical properties and excellent oxygen barrier.10

The objective of this study was to modify TPS from cassava starch by using pectin. The TPS and pectin-modified TPS were characterized by function group analysis, morphology, tensile properties, and water uptake.

Methodology:
1. Materials
Cassava starch was obtained from Chaopraya Phuchrai 2999 (Kamphaengphet) Co., Ltd. (Kamphaengphet, Thailand). Glycerol (plasticizer) was obtained from Lab System Co., Ltd. (Bangkok, Thailand). Pectin was purchased from Union Chemical 1986, Co., Ltd. (Bangkok, Thailand).
2. Sample preparation
Cassava starch and glycerol were pre-mixed in closed container and kept overnight. The weight ratio of cassava starch and glycerol was maintained at 65:35. The compounding was carried out using an internal mixer. The processed samples were compressed at 140°C into 2
mm thick plates. The property modification of the TPS blend was carried using different contents of pectin, i.e., 2%, 4%, 6%, 8% and 10%.

3. Fourier transform infrared spectrophotometer, FTIR

FTIR spectra of different TPS samples were recorded on a Spectrum 2000 GX spectrometer (PerkinElmer, USA) using KBr disk technique with a resolution of 4 cm$^{-1}$ in a spectral range of 4000-600 cm$^{-1}$ using 16 scans per sample.

4. Morphology

Morphology of the blends were observed by Scanning Electron Microscope (LEO 1450 VP). The samples were broken in liquid nitrogen and then coated with thin layer of gold to prevent electrical charge during observation.

5. Tensile properties

The tensile measurements of dumbbell specimens were carried out using Universal Testing Machine operated by WINDAP software with 100 N load cell and a cross-head speed of 40 mm/min. The blends were conducted according to ASTM D 638 at the temperature of 23±1 °C and relative humidity of 60±5%.

6. Water uptake

Samples were dried at 105 °C for 2 hr and then stored at 100% relative humidity at the temperature of 30 ± 2 °C. The 100% relative humidity was obtained using saturated solution of H$_2$O. The percentage water uptake was calculated as followed:

$$\text{Water uptake} \, (\%) = \frac{W_2 - W_1}{W_1} \times 100$$  \hspace{1cm} (1)

where $W_2$ and $W_1$ were the final weight and the dried weight of the sample, respectively.

Results and discussion:

1. Fourier transform infrared spectroscopy

![Figure 1. IR spectra of the TPS samples modified by different contents of pectin](a) 0% (b) 6% and (c) 10%]

It can be seen in Figure 1(a) that the TPS exhibits IR main peak positions in the range of 3500–3250 cm$^{-1}$, 3000–2800 cm$^{-1}$, 1475–1450 cm$^{-1}$, 1275–1070 cm$^{-1}$, and 1200–1000 cm$^{-1}$, representing O–H stretching, C–H asymmetric stretching of $-\text{CH}_2-$, $-\text{CH}_2-$ deformation,
C–O–C stretching and C–O–H stretching, respectively. It can be seen in Figures 1(b) and 1(c) that the new peak at 1720 cm$^{-1}$ was found and it was assigned for C=O stretching of COOH. In addition, IR peak shift of O-H stretching was also found for the TPS added by pectin.

2. Morphology

**Figure 2.** SEM micrographs of different TPS samples modified by various contents of pectin (a) 0% (b) 6% and (c) 10%
It was found from Figure 2(a) that fractured surface of the TPS sample was smooth. In Figures 2(b) and 2(c), it was observed that pectin particles were randomly distributed in the TPS matrix and no void between two different phases was noticed, showing good phase compatibility between the starch and pectin.

3. Tensile properties

**Figure 3.** Mechanical properties of different pectin-modified TPS samples.
The effect of TPS modified by pectin on the mechanical properties is shown in Figure 3. The stress at max load (Figure 3(a)) and Young’s modulus (Figure 3(c)) of the TPS sample were approximately 0.53 MPa and 1.84 MPa, respectively. However, the stress at max load and Young’s modulus significantly increased with increasing pectin contents. The maximum stress at max load and Young’s modulus, found in the TPS blend with 10% pectin, was approximately 1.95 MPa and 23.7 MPa, respectively. This could be due to the structural similarity of cellulose between starch and pectin, leading to good compatibility between the different phases. Figure 3(b) shows the relationship between the strain at max load of the TPS with the addition of different amounts of pectin. It can be observed that pectin decreased the strain at max load of the TPS sample.

4. Water uptake

![Graph showing water uptake over time for different TPS samples.]

**Figure 4.** The relationship between water uptake and time of different TPS samples at 100% RH

The result of water uptake of different TPS specimens performed at the temperature of 30 ± 2 °C and 100% RH are shown in Figure 4. The maximum water uptake was at the range of 37-38%. It was found that water uptake of the TPS samples slightly increased with the addition of pectin. This is because pectin contains various hydrophilic functional groups compared with starch.

**Conclusions:** Different TPS samples were prepared using internal mixer and compression molding techniques. The modification of the TPS blend was carried out using different contents of pectin. It was found that the incorporation of 10% pectin into the TPS blend presented the highest stress at max load and Young’s modulus. IR peak shift was also found for the TPS modified by pectin. For morphology, pectin phase was combined with TPS phase. In addition, water uptake of the TPS sample slightly increased with the addition of pectin.

**References:**

Keyword: Thermoplastic starch, Cassava starch, Pectin, Compression molding, Mechanical Properties