# การเตรียมและสมบัติของเทอร์โมพลาสติกสตาร์ช/เคลย์ นาโนคอมพอสิท Preparation and properties of thermoplastic starch/clay nanocomposites

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# บทคัดย่อ

นาโนคอมพอสิทของเทอร์โมพลาสติกสตาร์ชที่เสริมแรงด้วยมอนต์มอริลโลไนต์สามารถเตรียมได้ด้วย กระบวนการที่ใช้แรงเฉือนต่ำ ขั้นตอนแรกเตรียมมอนต์มอริลโลไนต์ดัดแปรด้วยซอร์บิทอลเพื่อขยายช่องว่างระหว่าง ชั้นของมอนต์มอริลโลไนต์ ต่อมาเตรียมเทอร์โมพลาสติก สตาร์ชโดยการใช้ของผสมระหว่างฟอร์มาไมด์และซอร์บิทอล เป็นพลาสติไซเซอร์ ศึกษาโครงสร้างการแทรกสอดของมอนต์มอริลโลไนต์ดัดแปรด้วยเทคนิคเอ็กซ์เรย์ดิฟแฟรกชั่น (XRD) และกล้องอิเล็กตรอนแบบส่องทะลุ (TEM) จากการศึกษาเสถียรภาพทางความร้อน, การต้านทานแรงดัด โค้ง และการต้านทานแรงดึง พบว่าเมื่อเพิ่มปริมาณของมอนต์มอริลโลไนต์ดัดแปรส่งผลให้เสถียรภาพทางความร้อน, การต้านทานแรงดัดโค้ง และการต้านทานแรงดึงของเทอร์โมพลาสติกสตาร์ช เพิ่มขึ้น

# Abstract

Thermoplastic starch nanocomposites reinforced by modified-montmorillonite were prepared using the low shear process. Montmorillonite was first modified by sorbitol, increasing distance between layers. The mixture of formamide/sorbitol was used as a plasticizer for thermoplastic starch. The intercalation structure was observed by XRD and TEM. The thermal stability and flexural strength and tensile strength of thermoplastic starch was improved when the modified-montmorillonite was added

คำสำคัญ: นาโนคอมพอสิท เทอร์โมพลาสติกสตาร์ช มอนต์มอริลโลไนต์ เคลย์ Keywords: Nanocomposites, Thermoplastic Starch, Montmorillonite, Clay

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#### 1. Introduction

Nowadays, the world's annual consumption of plastic materials has increased significantly. Plastics are used in many fields such as packing industry, electrical industry, automobile industry, agricultural industry and medical industry. The considerable growth in plastic use is due to the beneficial properties of plastics. These include high resistance to chemicals, excellent thermal and electrical insulation properties, extreme durability and lighter weight than competing materials. Although plastic items lend themselves to be reused many times over, some plastic products for example plastic film representing the largest section of plastic use for food packaging become waste only a short time after use. The enormous volumes of them give the environment pollution and raise it up every year. Many researches are therefore seeking alternatives based on materials which can degrade under certain conditions or after a predetermined length of time. Starch-a biodegradable polysaccharide produced in abundance at low cost-possesses thermoplastic behavior, making it one of the most promising candidate as an alternative to traditional plastics. Starch is a complex homo-polymer composed of D-glucose units linked together in two different forms: the linear form amylose and the highly branched amylopectin. However, starch can not be used as plastic directly, because it can not be processed thermally. This is attributed to the strong interaction between the hydroxyl groups of the starch molecules. Starch must be converted to Thermoplastic Starch (TPS) for its thermal processability. Basically, TPS can be prepared by adding the plasticizer into starch. Plasticizer will form hydrogen bonding with starch, replacing interaction between starch molecules. TPS applications, however, are limited by its poor mechanical properties.

Recently, there has been research about polymer/clay nanocomposites by high shear process i.e. melt extrusion. Clay is environmentally friendly, naturally abundant and economic. Although the high aspect ratio of clay is ideal for reinforcement, the nanoclays are not easily dispersed in most polymer due to their preferred face-to-face stacking in agglomerate. Structure of montmorillonite is shown in figure 1. The replacement of the organic exchange cation in the surfactants can enlarge the galleries and induce the polymer chain into the galleries, so it can disperse well in polymer matrix. However, alkylamonium surfactant gives waste water in clay modification process. The essential raw material for a nanoclay is montmorillonite (MMT), 2-to-1 layered smectile clay with platelet structure and easily to enlarge the galleries.

The objective of our research is to develop a low shear process for modifying montmorillonite and preparing TPS/modified-montmorillonite nanocomposites.



Figure 1. Structure of Montmorillonite

### 2. Experimental

### 2.1. Materials

The following materials were used in this work:

2.1.1 Montmorillonite was supported by Mettallurg and Materials Science Research Institutes.(Bangkok, Thailand)

2.1.2 Sorbitol and formamide were purchased from Ajax Finechem.

2.1.3 Cassava starch which a food grade, was supplied by Thai-Wah Company Ltd. (Bangkok, Thailand)

#### 2.2. Modification of montmorillonite

The montmorillonite and sorbitol were weighted at a ratio of 1:2. The sorbitol was melted at 100 °C and pre-mixed with montmorillonite. The mixture of sorbitol and montmorillonite was mixed in a high speed mixer at 3000 rpm for 2 min. The melted mixture became solid after left at room temperature. This solid mixture was smashed.

# 2.3. Preparation of thermoplastic starch/modifiedmontmorillonite nanocomposite

The cassava starch, modified-montmorillonite, sorbitol and formamide were first pre-mixed manually.

These mixtures were sift by 45 mesh sieve and kept in the sealed plastic bag overnight to let molecules of formamide permeate into the cassava starch molecule. Then, thermoplastic starch/modifiedmontmorillonite nanocomposites were prepared by two roll mill (150 °C) and smashed (0.5 m.). These thermoplastic starch/modified-montmorillonite nanocomposites were stored in the sealed plastic bag. Table 1 shows the compositions of TPS/modified-MMT nanocomposites

#### 2.4. X-Ray diffraction

The distance layers of raw montmorillonite, modified-montmorillonite and thermoplastic starch/ modified-montmorillonite nanocomposites were measured by D8 Discover Brukeraxs X-Ray Diffractometer (40 kV., 40 mA.)

## 2.5. Transmittion electron microscopy

A transmittion electron microscopy (TEM) was used to determined the morphology of nanocomposites by JSM 2010 Transmittion electron microscope at acceleration voltage of 160 kV. Microtomed ultrathin film specimems with thickness 70 nm were used for TEM observation.

Table 1	The co	ompositions	of TPS	/modified-MMT	' nanocomposite
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MMT Content	MMT-sorbitol	Starch	Formamide	Sorbitol
(%)	(g)	(g)	(g)	(g)
0	0	250	50	25
1	7.5	250	50	20
3	22.5	250	50	10
5	37.5	250	50	0

#### 2.6. Thermo gravimetric Analysis (TGA)

The DSC 822e Mettler Toledo was used to study thermal stability of thermoplastic starch/ modified-montmorillonite nanocomposites under nitrogen atmosphere. The range of scanning was 50-600 °C at the heating rate was 20 °C/min.

#### 2.7. Mechanical properties

The specimens were compression molded at 155 °C and cut into 10X100 mm. Tensile stress and strain were measured using LLOYD LR100K Universal Testing Machine. The crosshead speed was 50 mm./min. Result was averaged from five measurements. According to ASTM D 790M-82, three points bending was measured using 500 Universal Testing Machine. The crosshead speed was 50 mm./min.

#### **3.** Result and discussion

## 3.1. X-Ray diffraction

XRD pattern was carried out to study the intercalation of starch and sorbitol molecule in the MMT layers. Figure 2 shows the XRD pattern of raw MMT, modified–MMT and TPS/modified–MMT containing 3% MMT. It showed that the crystal

plan (001) moved from 6.48° to 4.68°. According to Bragg's diffraction equation  $\lambda = 2d \sin \theta$ , the distance layers of MMT were enlarged from 1.28 to 1.89 nm. This is probably due to intercalation of sorbitol molecule into the MMT layers. So sorbitol could be a modifying agent of MMT. For TPS/ modified-montmorillonite nanocomposites, no crystallization peak was observed. This inferred that the crystals of MMT were exfoliated by molecule of starch. Because of polarity of sorbitol, starch molecule can intercalate into clay gallery more easily.

#### 3.2. Morphology of nanocomposites

TEM photomicrographs of TPS/modified-MMT nanocomposites (3 wt.% MMT) are shown in Figure 3. The TEM photograph reveals white areas that are the TPS phase and black areas that are the MMT layers dispersed in TPS phase. It indicated that melting TPS molecule chains intercalated in MMT layers. The nanocomposites structure was intercalated and exfoliated because the MMT layers were expanded and disorder dispersed in the TPS phase on the scale of nanometers. The TEM results correspond with the XRD patterns.



Figure 2. XRD patterns of: MMT, modified-MMT and TPS/modified-MMT nanoconposites.

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Figure 3. TEM micrograph of TPS/modified-MMT nanoconposites.

### 3.3. Thermal stability

Comparing thermal stability of organic and inorganic materials, inorganic materials had a thermal stability and thermal properties better than organic materials. Therefore, MMT that was a inorganic materials, was used. Figure 4 shows thermal stability of TPS/modified–MMT nanocomposites with various amounts of modified–MMT. These curves showed two step of decomposition. First step, called onset decomposition temperature, was a decomposition of plasticizer and second step, called endset decomposition temperature, was a decomposition of nanocomposites. Endset decomposition temperature of TPS, TPS/modified-MMT nanocomposite 1%, TPS/modified-MMT nanocomposite 3% and TPS/ modified-MMT nanocomposite 5% were 345.6, 350.06, 351.70, and 352.47 respectively. The result indicated that adding modified-MMT improved thermal stability. However, increasing amount of modified-MMT from 1 to 5 % did not further improved thermal stability.

#### 3.4. Mechanical properties

Figure 5, 6 and 7 show stress at break, elongation at break and 3 points bending of TPS/ modified–MMT with various amounts of modified– MMT. By increasing amount of modified–montmo– rillonite, stress at break and 3 points bending increased whereas elongation at break decreased. Interestingly, only little amount of modified–MMT (max. 5%wt.), tensile strength and flexural strength increased up to 92% and 40%, respectively. This may indicated that modified–MMT dispersed well in TPS matrix in nanoscale and had a good interaction with starch molecule.



Figure 4. TGA curves of TPS/modified-MMT with various amounts of modified-MMT.





Figure 5. Stress at break (MPa) of TPS/modified-MMT with various amounts of modified-MMT.







Figure 7. Three points bending (MPa) of TPS/ modified-MMT with various amounts of modified-MMT

# 4. Conclusion

In this work, a low shear process can be used to modify MMT and prepare TPS/modified-MMT nanocomposites. MMT was modified by sorbitol. Distance between layers of MMT was enlarged from 6.48° to 4.68° due to intercalation of sorbitol molecule. Thermal stability and mechanical properties of thermoplastic starch were increased by adding modified-MMT. Amount of modified-MMT had less influence on thermal stability whereas it showed strong effect on mechanical properties. Both tensile strength and flexural strength increased with increasing amount of modified-MMT.

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