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## The synthesis of Cellulose nanofibers from *Sesbania Javanica* for filler in Thermoplastic starch

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### Abstract

This research was aimed to study the synthesis of cellulose nanofibers from *Sesbania Javanica* and the effect of the cellulose nanofiber (CNF) addition on thermoplastic starch derived from tapioca flour. The mechanical properties, morphological structure and thermal stability of neat thermoplastic starch and their composites were investigated by Tensile testing, Scanning Electron Microscope (SEM) and Thermogravimetric analysis (TGA), respectively. Moreover moisture absorption was also studied. The composites with 0, 1, 2 and 3 phr of cellulose nanofibers content were prepared. Cellulose nanofibers were synthesized in the aqueous suspension (containing 8.63% of dried cellulose nanofibers). The percentage yield was found of 14.8% and the average diameter is about 100 nm. The addition of cellulose nanofibers in thermoplastic starch showed that the modulus of the composites tended to improve, however, the tensile strength did not change significantly and tended to decrease when higher cellulose nanofibers content. SEM revealed the formation of CNF aggregates in the composites, especially the content of 3.0 phr of CNF, that is why no improvement in the tensile strength of the composites. Also, the moisture absorption of the TPS/CNF composite improved with the cellulose nanofibers content.

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## 1. Introduction

In recent years, the interest in biodegradable materials (especially biodegradable polymers) has been growing greatly both in research and manufacturing since these materials can be easily degrade under well-defined environmental conditions [1], which differ from the conventional polymer derived from petroleum resources. Most conventional polymers cannot biodegrade or require for hundreds of years to decay, as the main cause of environmental concerns. Therefore the polymer researchers focus on biodegradable polymers which are polymers capable of being decomposed by bacteria or other living organisms. One of the most promising raw materials for the production of biodegradable plastics is starch, which is naturally abundant, renewable, cheap, non-toxic and biodegradable [1].

Thermoplastic starch (TPS) is one of a number of biodegradable polymers which has become increasingly attractive in recent times [2]. TPS can be prepared by starch. Starch is not a true thermoplastic but in the presence of plasticizers (water, glycerol, sorbitol, etc.) [3] with thermal and mechanical processing for disrupting of semi-crystalline starch granules and form to a continuous polymer phase [1, 4]. Generally, when the starch granules are heated, the thermal degradation occurs before melting. From this result, starch cannot be melt-processed to any products directly. Therefore, the addition of plasticizers is an important process which interacts with the hydroxyl groups of starch and then the hydrogen bonding among the starch reduces. Finally the melting temperature of starch is lower than the degradation temperature, that is why the thermoplastic starch can be melt-processed with conventional technologies used in synthetic plastics (injection-molding and extrusion). Many plasticizers used in the research such as water, glycerol or other polyols such as 1,4-butanediol (BDO), ethylene glycol (EG), propylene glycol (PG), D-sorbitol, Polyethylene glycol (PEG) or other compounds containing nitrogen such as urea, ammonium derived, amines, etc [4].

The chemical structure of starch is composed of numerous hydroxyl group (OH) which is referred to as a hydrophilic group, so the thermoplastic starch is more sensitive to water in ambient condition and lose its properties such as mechanical properties, etc. Some drawbacks of TPS can limit its applications in many areas. However, there are many ways to improve water resistance of TPS such as the selection of type and content of plasticizers and mixing with the synthetic polymers. Another one approach is the addition of reinforcing fillers which help to improve mechanical properties and also resist moisture absorption of TPS [1, 5]. Such materials are cellulose fiber, kaolin or pectin [4].

Nowadays, nano-sized cellulose fiber is one of the most interesting reinforcing fillers for improving mechanical properties and moisture absorption of TPS, since its abundance, low weight, high strength and biodegradability [6]. Furthermore it is also a polysaccharide containing repeating unit of glucose as same as the starch [5]. Nano-sized cellulose can be classified into 3 types including cellulose nanowhiskers (CNW), cellulose nanofibers (CNF) and bacterial nanocellulose (BC) [7]. Many researchers have studied the isolation of CNW from lignocellulosic material. CNW are rod-like shaped nano-sized crystals (3-10 nm in diameter and 100-300 nm in length) which can be isolated by acid hydrolysis [7]. However CNF are typically nano-sized fiber with 5–50 nm in diameter and several micrometers long [6] depend on the source and separation technique (that contain both the amorphous and crystalline phase of cellulose. In addition, CNF have specific characteristics such as the high surface area and aspect ratio [8, 9].

Sano (*Sesbania Javanica* Miq.) is a flowering plants in the Fabaceae family (commonly known as the pea family). Sano is a tropical seasonal plant which naturally grow in wet area, especially around the ditch or canal in the central region of Thailand. Therefore this study selected *Sesbania Javanica* was a starting material for the synthesis of cellulose nanofibers (CNF).

The aim of this research was to study the synthesis of cellulose nanofibers (CNF) from *Sesbania Javanica* and effect of the addition of CNF on the properties of thermoplastic starch (TPS) and their composites. Thermoplastic starch was derived from the mixture of tapioca flour and plasticizers (water and glycerol), and then melt-compounded using a twin-screw extruder. The composites with 0, 1, 2 and 3 wt.% CNF content were prepared from CNF suspension. For the characterization methods were mechanical properties, thermal properties, morphological structure and moisture absorption.

## 2. Materials and methods

### 2.1. Materials

Tapioca flour (TF) used as a starting material for thermoplastic material was supplied by E.T.C. Eaib Tong Chan. *Sesbania Javanica* stems was used as a source of lignocellulosic biomass for cellulose nanofibers. Sodium hydroxide solution was used to extract noncellulosic binding materials like hemicelluloses/lignin complexes. Sodium chlorite and glacial acetic acid were used for the delignification. Cellulase from *Aspergillus niger* was obtained from Sigma-Aldrich. Hydrogen peroxide and sodium bicarbonate act as oxidizing agent and neutralizing agent, respectively. Glycerol was used as plasticizer for thermoplastic starch preparation.

### 2.2. Preparation of cellulose fiber from *Sesbania Javanica*

*Sesbania Javanica* stems were cut into pieces and immersed in 15 wt.% sodium hydroxide solution for 48 h at ambient temperature. The chunks were then milled to short fiber and washed with tap water. The short fibers were dried at 55 °C for 48 h in dry oven. Then 30 g of dried short fiber (dry mass) were delignified by treating with 1000 mL of 1.4 wt.% sodium chlorite solution and the pH of this solution was adjusted to 3.0-4.0 using acetic acid. The mixture was kept at 70 °C for 5 h in order to dissolve lignin. The process was followed by oven-drying at 55 °C for 24 h and dried cellulose fibers were obtained.

### 2.3. Preparation of cellulose nanofibers

From the previous step, 10 g of cellulose fiber isolated from *Sesbania Javanica* stems were hydrolyzed using 400 mL of 0.25 wt.% cellulase enzyme with adjusted pH to 4.8 by 0.02 M buffer solution of acetic acid. The fibers were soaked at 50 °C for 48 h. The temperature was then set to 80°C and the fibers were soaked further for 2 h in order to stop enzyme action. The microcellulose were filtered and then soaked in 35 wt.% hydrogen peroxide solution with the ratio of 1 g of cellulose to 50 mL of hydrogen peroxide solution at 80-90 °C for 48 h. Nanofibers were obtained in the form of suspension which were then added with 0.13 g of sodium bicarbonate and the mixture become neutral. After that the suspension was washed with distilled water and centrifuged 4-5 times for washing out excess sodium bicarbonate.

### 2.4. Preparation of cellulose nanofibers filled Thermoplastic starch

For the preparation of Thermoplastic starch, 100 g of tapioca flour was first mixed with 35 g of glycerol and 40 g of distilled water, then sieved through the flour sieve and finally the homogeneous material in powdery state was obtained, so it is called “neat TPS”. In addition cellulose nanofibers filled thermoplastic starch composite (TPS/CNF), the CNF contents in composites were 1, 2 and 3 phr (dry starch basis) by addition of the appropriated amount of suspension. For neat TPS with CNF content of 1, 2 and 3 phr are abbreviated as “TPSCNF1.0”, “TPSCNF2.0” and TPSCNF3.0, respectively.

The previous mixture were melt-compounded using a co-rotating twin-screw extruder (Rheocord RC 300p and Rheomex PTW16/25D, HAAKE, Germany) with temperature profile of 90, 110, 120, 120, 120°C respectively and speed of 60 rpm. The extrudates were then compression mold into thick film with thickness of ~0.7 mm following the process: press without pressure at 120°C for 3 min, pressed with 800 psi for 5 min at 120°C and finally cooled to 85°C for 30 min under the same pressure.

### 2.5. Characterization of Composites

- **Tensile Testing** For tensile tests of the composited were performed with an Instron 5969 universal testing machine (Instron Engineering Corporation, USA) equipped with a load cell of 5 kN. For gauge length of 33 mm and crosshead speed of 50 mm min<sup>-1</sup> were used. The specimens according to the ASTM D412 Die C were cut from the compression molded films. Before testing all specimens were dried at 50 °C for 4 days in

dry oven and then kept in an airtight container with silica gel at ambient temperature until they were going to be tested. At least 5 specimens were tested for each composition.

- **Thermogravimetric analysis** TGA measurements were carried out using a Perkin Elmer analyzer model TGA7 on samples of about 5 mg. The sample was heated from 50 to 700 °C at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere with a flow rate of 30 mL min<sup>-1</sup> to prevent thermo-oxidative degradation.
- **Morphological structure** Scanning Electron microscopy (SEM), CamScan model MX2000 was used to study the morphology of CNF (the suspension was freeze-dried to obtain the dried fiber) and microstructure of fractured surfaces of the thermoplastic starch and the composites. The fractured surfaces were obtained by immersing the extrudates of each composition in liquid nitrogen and then fractured.
- **Moisture absorption** To study the effect of cellulose nanofibers (CNF) addition on moisture absorption of composites. The specimens were cut from the compression molded film and were the same size as that of tensile test. Before moisture absorption test, the specimens were dried at 60 °C in dry oven until constant weight was reached. Then the dried specimens were kept in a desiccator of 75% RH using saturated NaCl solution. At specific time intervals the specimens were removed from the desiccator and weighed until equilibrium was reached. Five specimens of each composition were tested, and the average values were reported.

### 3. Results and Discussion

#### 3.1. Cellulose nanofibers (CNF)

Cellulose in suspension was found containing 8.63% of dried cellulose nanofibers. The percentage yield was found of 14.8%. Figure 1 shows the characteristics of CNF suspension (a) and SEM micrographs of CNF (b and c). From Figure 1(b)-(c) revealed that the average diameter of cellulose nanofibers is about 100 nm. The CNF was found similar to other researches [10, 11].

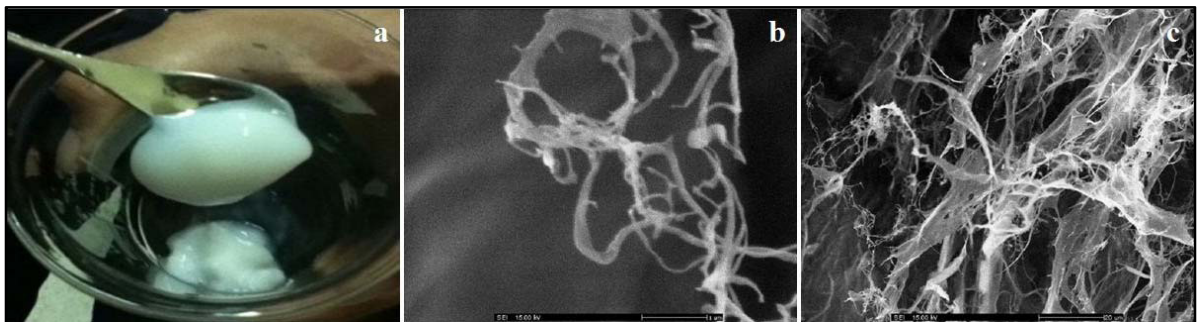


Fig. 1. (a) Suspension of CNF prepared from *Sesbania Javanica*; (b) and (c) SEM micrographs of Freeze-dried CNF.

#### 3.2. Mechanical properties

Stress-strain curves of neat TPS and their composites films are shown in Fig. 2. It is observed that the brittle behavior of the neat TPS and their composites. Young's modulus, tensile strength and elongation at break are shown in Fig. 3 with standard deviation (SD). From the results, the Young's modulus of the composites were slightly higher than neat TPS as reinforcing effect of cellulose nanofibers (CNF) [8, 12] as shown in Fig. 3(a).

The effect of cellulose nanofibers on the tensile strength is presented in Fig. 3(b). The tensile strength of neat TPS is 27.30 MPa. It can be seen that the tensile strength did not significantly different with the CNF content up to 2 phr of CNF, however, when higher CNF concentration decreased the tensile strength clearly. For this reason resulted from the aggregation of CNF with higher CNF contents. Similar result was reported by other researchers [8, 10]. Furthermore in Fig. 3(c), the elongation at break of composites, it was extremely decreased with the addition of CNF while shows brittleness to some extent.

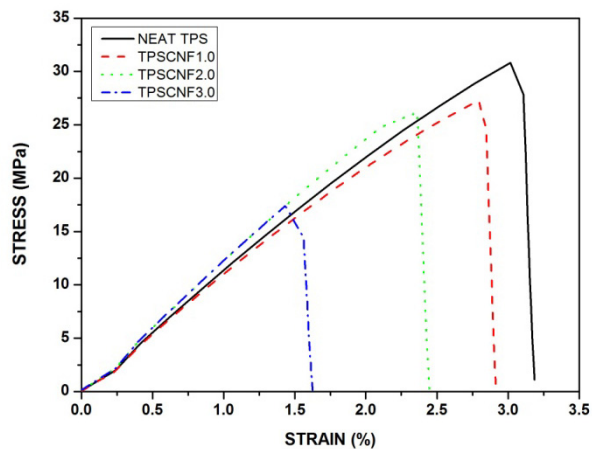
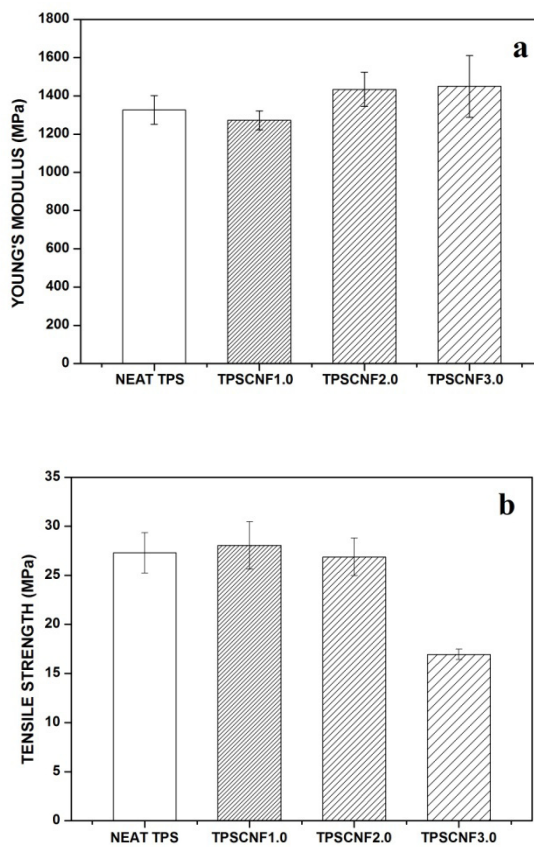


Fig. 2. Stress-Strain curves of neat TPS and their composites with various CNF contents.



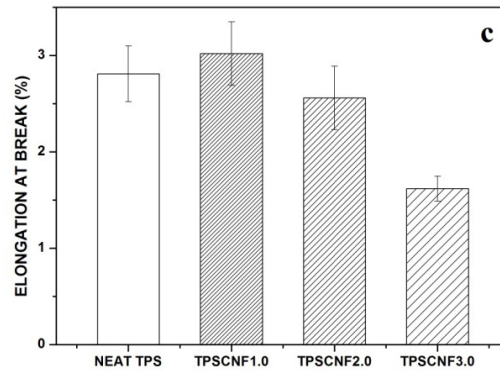


Fig. 3. (a) Young's modulus; (b) Tensile strength; and (c) Elongation at break of neat TPS and their composites with various CNF contents.

### 3.3. Thermal stability

Thermal stability of both neat TPS and their composites were characterized using thermogravimetric analysis. The TGA of the samples are shown in Fig. 4. From TGA curves showed an initial drop between 106.85 and 210°C which correspond to the vaporization and removal of bound water [13]. The results showed that the peak degradation temperature for neat TPS and their composites containing 1.0, 2.0 and 3.0 phr of CNF (dry starch basis) were 316.27, 313.56, 311.52 and 301.03 °C, respectively. It can be noted that the peak degradation temperature did not significantly different with the CNF content up to 2 phr of CNF and when higher CNF concentration decreased slightly.

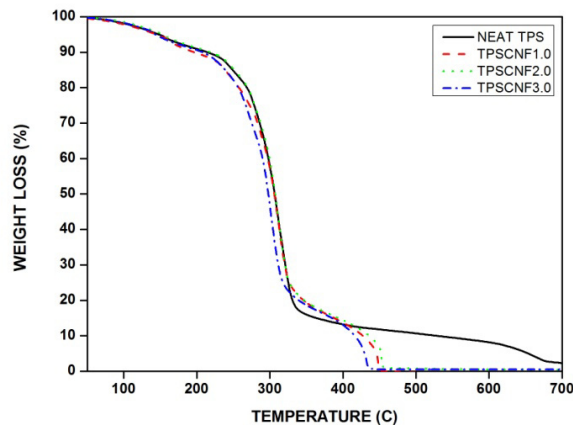


Fig. 4. TGA thermogram of neat TPS and their composites with various CNF contents.

### 3.4. Morphological structure

Fig. 5 shows the SEM micrograph of fractured surface of neat TPS (a) and their composites extrudates containing 1.0 (b), 2.0 (c) and 3.0 (d) phr of CNF (dry starch basis). The micrographs with a magnification of 500 revealed the distribution of CNF in thermoplastic starch matrix. From Fig. 5(a) it is observed that neat TPS shows a relatively smooth surface as a result of the completely gelatinization of starch. For composites with lower CNF concentration (not more than 2.0 phr) the dispersion of CNF seems to be uniform and nanofiber seem as white dots on the surface as shown in Fig 5(b)-(c). In Fig. 5(d), however, higher CNF concentration it can be seen that the dispersion of CNF

was not uniform and formed aggregates, that is why the tensile strength of the composites did not increase [8-10].

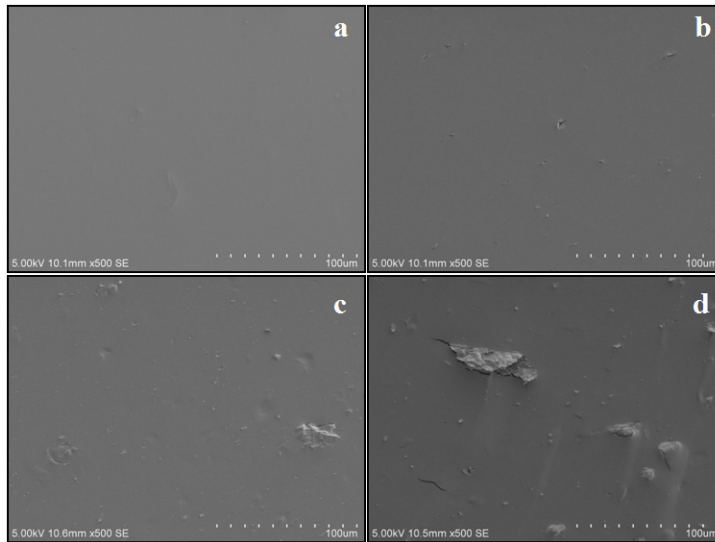


Fig. 5. SEM micrograph of neat TPS (a); and their composites with various CNF contents; (b) 1.0; (c) 2.0; and (d) 3.0 phr

### 3.5. Moisture absorption

The moisture absorption of neat TPS and their composites is shown in Fig. 6. From Fig. 6, it can be seen that all samples were reached an equilibrium moisture within 30 days. From the results it is observed that the moisture absorption curves of neat TPS and the composite containing 1.0 phr of CNF (TPSCNF1.0) did not significantly different, however, for the composites containing 2.0 and 3.0 phr of CNF (TPSCNF2.0 and TPSCNF3.0) there was significant differences between the curves. It should be noted that addition of CNF results in percentage of equilibrium moisture absorption for the composites tended to decrease as reported on other research [8, 12].

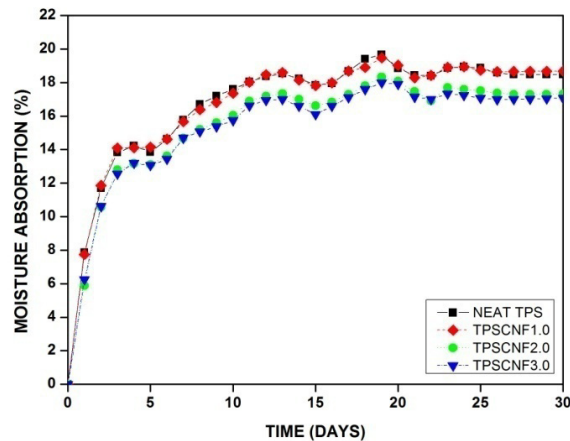


Fig. 6. Moisture absorption versus time relationships for neat TPS and their composites with various CNF contents.

#### 4. Conclusions

The aim of this research was to study the synthesis of cellulose nanofibers from *Sesbania Javanica* and the effect of the addition of cellulose nanofibers on the properties of thermoplastic starch and the composites. The prepared cellulose nanofibers were in the aqueous suspension (containing 8.63% of dried cellulose nanofibers). The percentage yield was found of 14.8%. The average diameter of cellulose nanofibers is about 100 nm from SEM observation.

Mechanical properties of thermoplastic starch and the composites showed that the modulus of the composites was increased and the moisture resistance was improved with the addition of cellulose nanofibers. The composites with higher cellulose nanofibers content, especially the content of 3.0 phr of CNF, SEM microscopy revealed the formation of cellulose nanofibers aggregates in the composites. This observation is the reason why the tensile strength of the composites did not increased.

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