DEVELOPMENT OF THERMOPLASTIC STARCH
NANOCOMPOSITES FOR WET CONDITIONS

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Abstract

The need for environmentally friendly materials for applications in packaging has never been greater. One of the challenges in packaging applications is to have a material that has the right balance of properties and cost. A new type of thermoplastic starch copolymer has been investigated for its physical properties; this thermoplastic starch copolymer was prepared by reacting starch and polyesters. This paper will discuss the investigation on the use of cassava starch and clay to further improve the formulation of thermoplastic starch copolymer. The objective of adding cassava starch is to reduce cost, whereas the objective of adding clay is to further improve the properties under wet conditions. The materials were processed using a lab-scale twin screw extruder and injection molding. Addition of Na-montmorillonite improved water resistant and mechanical properties.

1. Introduction

Starch is a widely available, low cost, and naturally renewable. In addition, starch is generated from carbon dioxide and water by photosynthesis in plant, and it is a biodegradable agro-polymer. For these reasons starch is expected as a promising alternative to petrochemical resources for packaging applications.

Starch based polymers can provide biodegradable and sustainable solutions for the products such as single use disposable packaging, consumer goods and other plastics. The general procedure to process starch based polymers involves the granular disruption by the combination of temperature, shear, and a plasticizer, which is usually water and / or glycerol. The resultant material is known as thermoplastic starch (TPS). In recent years, there are many

research related to starch-based plastics because it is compostable and in order to reduce the amount of petroleum-derived plastics in solid waste streams. However, the use of TPS is limited in industrial applications, owing to its low mechanical property and humidity.

A new type of thermoplastic starch copolymer has been developed by Polymer Specialties International Ltd., Canada. This thermoplastic starch copolymer was prepared by reactive extrusion with the addition starch, polyester (and other chemicals) in order to obtain a thermoplastic starch copolymer (WO 2013/116945 – Process for making starch-resin copolymer, Polymer Specialties International).

Preliminary work in our laboratory with this material showed some promising results with respect with resistance to water. Under wet conditions this new thermoplastics starch copolymer exhibits far better mechanical properties than regular thermoplastic starch.

In this study, we tried to further improve the formulation of thermoplastic starch copolymer (TPSC) using cassava starch and nanoclays. The objective of adding cassava starch is to reduce cost, whereas the objective of adding nanoclays is to further improve the properties such as tensile, flexural and other dynamic mechanical properties under wet conditions.

2. Material and method

2.1. Materials

Thermoplastic starch copolymer was supplied by Polymer Specialties International Ltd. (Canada), unmodified cassava starch was supplied by Bahiamido (Brazil), and glycerol (98 %) was purchased from Sigma Aldrich (USA). Two types of nanoclays were used in this study, one based on unmodified Na-montmorillonite clay (Na-MMT (Cloisite Na^+)) and organically modified montmorillonite (Cloisite 30B), both were purchased from Southern Clay (USA).

2.2. Preparation of TPSC nanocomposites

The TPSC nanocomposites were prepared in aqueous media. TPSC, cassava starch, and nanoclays were dried in a convection oven at 50 °C for 1 week prior to use. The procedure consisted of two steps. The first step was the preparation of starch nanocomposites and second was the preparation of TPSC nanocomposites.

Preparation of starch nanocomposites
For the preparation of starch nanocomposites, the 5 wt. % nanoclay and glycerol were dispersed in distilled water by sonication for overnight at room temperature. A separate mixture of 10 wt. % of cassava starch was prepared in distilled water; the suspension was heated to 80 °C with continuous stirring for 20 min to achieve gelatinization of starch. The dispersion with nanoclay and glycerol was added to the starch mixture and heated to 80 °C under continued stirring. The resulting products were left for drying overnight 50 °C in convection oven followed by drying in a vacuum oven at 50 °C for 24 h.

Preparation of TPSC nanocomposites
The TPSC nanocomposite was prepared by mixing TPSC and starch nanocomposites using a laboratory scale twin-screw extruder. Both materials were dried at 50 °C for 24 h to

minimize moisture in the extrusion process. The components were introduced in the feeding zone and allowed to melt at 150 °C and mixing speed was set at 75 rpm. Mechanical test samples were prepared by injection molding. Barrel temperature was 150 °C and the pressure was 100 psi. Two different specimen geometries (rectangular bar and dumbbell) were prepared. After injection molding, the specimens were kept in an oven 115 °C for 11 min. Then, the bars were conditioned at 23 °C at 50 % relative humidity for flexural, tensile and impact tests.

2.3. Characterizations

Mechanical properties

The mechanical properties for TPSC nanocomposites were determined from the tensile and flexural stress-strain curves following ASTM methods D1708 and D790. The average slope of the elastic region of each tensile and flexural curve was determined as the modulus of the material. The average maximum stress achieved in the tensile and flexural tests was also calculated as the yield strength of the materials. The standard deviation was calculated using the test result of 5 specimen bars. The dynamical mechanical thermal analysis were carried out with a DMTA-V (Rheometric Scientific) using a single cantilever test. The dynamic storage modulus (E') was measured as a function of temperature from 30 to 110 °C, at a constant heating rate of 3 °C / min and displacement amplitude of 0.1 %, at a frequency of 1 Hz. Samples were conditioned at different relative humidity levels (50 and 100 %) at 23 °C for different time (from 0 to 24 h).

Morphology

The surface morphology of the TPSC nanocomposites was investigated with scanning electron microscopy (SEM) analysis using a LEO1550 (Zeiss). The specimens were sputter-coated with gold prior to the experiment to avoid any charging during scanning (15 mA, 120 s). The size of features in the image (diameter) was measured using the Image J software.

Water absorption studies

For water absorption characterization studies, the samples were dried in a vacuum oven until constant weight was obtained and then placed in desiccators to cool before water absorption testing by gravimetric methods and this weight was taken as initial weight (Wi). The samples were then soaked in deionized water for different periods (0 to 30 days), after which they were blotted-dry with a lint free cloth. The increase in weight was taken as final weight (Wf). Water absorption is expressed as the increase in weight percent. The percentage of water absorption was calculated by the equation (1). In addition, the diffusion of water for period between 1 and 24 h was calculated. It is of great significance for composites because it tells how much of a liquid diffuses into a composite, how rapidly and to what extent. From the curves of water absorption as a function of time the water diffusion coefficients were calculated for each specimen. Among several authors, Fick's second law is generally considered the starting point of the mathematical description of diffusion, although it may not be obeyed by polymers or polymer composites. The Boltzmann's form of Fick's general diffusion equation used in this work.

$$\textit{Water absorption } (\%) = ((W_f - W_i) \, / \, W_i) \times 100. \tag{1}$$

3. Results and discussion

3.1. Mechanical properties

The results of flexural and tensile experiments are presented in **Table 1**. The flexural and tensile strength of TPSC decreased after addition of cassava starch without nanoclays. However, these strengths were significantly raised due to the addition of cassava starch with nanoclays. Especially by incorporation of Na-MMT, the flexural and tensile strength was significantly increased. These results suggested that the presence of an unmodified clay affected mechanical properties of TPSC matrix more significantly than the organically modified clay. The increase in properties is related to the reinforcement effect of nanoclays in the polymer matrix and it is supported by morphological analysis results. It is likely that the high interfacial surface area provided by well dispersed nanoparticles enhanced the load transfer between the polymer matrix and nanoparticles, resulting in improvement of compression-mechanical properties of composite samples. Other authors observed similar effect in other polymers.

Table 1. Mechanical properties of TPSC and TPSC-nanocomposites.

| | Starch composite (wt. %) | | | | | Mechanical properties | | | | |
	TPSC	Cassava starch	Glycerol	Cloisite 30 B	Na – MMT	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at bleak (%)
No.1	100	0	0	0	0	9.0	204.8	6.79	116.5	9.56
No.2	70	24.0	6	0	0	6.8	384.4	5.02	139.1	4.34
No.3	70	22.5	6	1.5	0	7.0	396.8	5.46	163.0	3.50
No.4	70	21.0	6	3.0	0	7.3	380.2	5.91	151.7	4.99
No.5	70	22.5	6	0	1.5	7.9	405.9	5.23	153.8	4.33
No.6	70	21.0	6	0	3.0	8.4	483.6	6.38	161.1	4.82
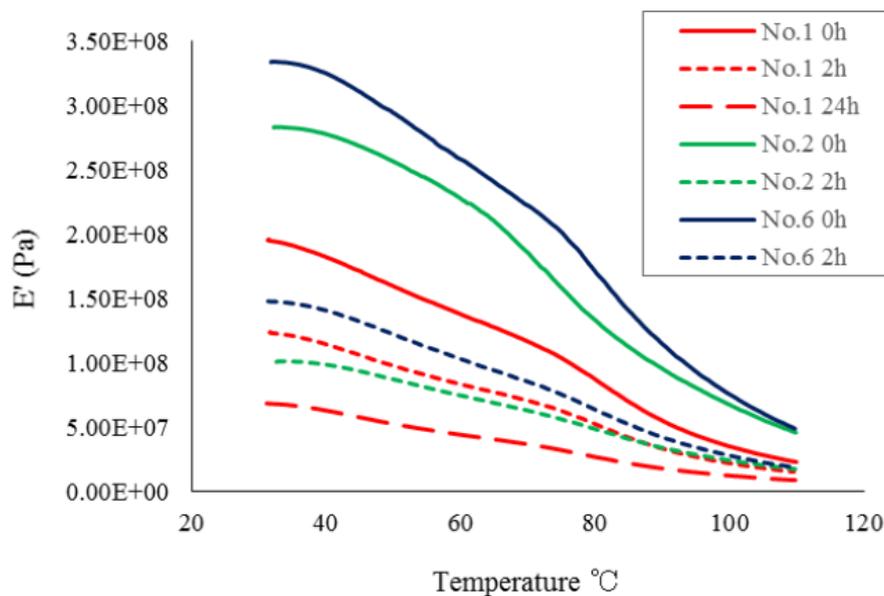
Figure 1. DMTA of TPSC and TPSC-nanocomposites.

The DMTA analysis was carried out to follow the temperature dependence of storage modulus (E') of the TPSC nanocomposites. Results are shown in **Figure 1** for samples 1, 2 and 6 for three different situations: without contact to water (labelled as 0h), immersed in water for 2 hours (labelled 2h) and immersed in water for 24 h (labelled as 24h). It was observed that in the entire range of temperature (30 to 110 °C), the addition of starch composites to the blend system extensively increased the storage modulus. For samples without contact to water (0h), the storage modulus of Na-MMT composite was higher than that of other samples. This is likely due to a better dispersion of the clay and to greater reinforcing effect of the stiffer clay silicate layers in the TPSC nanocomposites. In addition, these samples were treated in water for 2 and 24 h. After 2 h of contact to water, the storage modulus of samples which contained starch decreased. The addition of Na-MMT resulted higher modulus than other samples for the same conditions (2 h water treatment). The modulus of samples with starch was not measured after 24 h of water contact because samples were brittle.

3.2. Morphology

The SEM images from the fractured surfaces of the thermoplastic starch copolymer (TPSC) and TPSC nanocomposites with 3 wt. % of Na-MMT are shown in **Figure 2**. The images were taken with a magnification of 2000 times at the microscope to show an overview of the fractured surfaces. From **Figure 2b** it can be seen that the dispersion of starch granules with the size about 10 μm. There were some broken starch granules which have the size less than 10 μm as well. However, the location of the nanoclay was not confirmed in the TPSC nanocomposites by the SEM images.
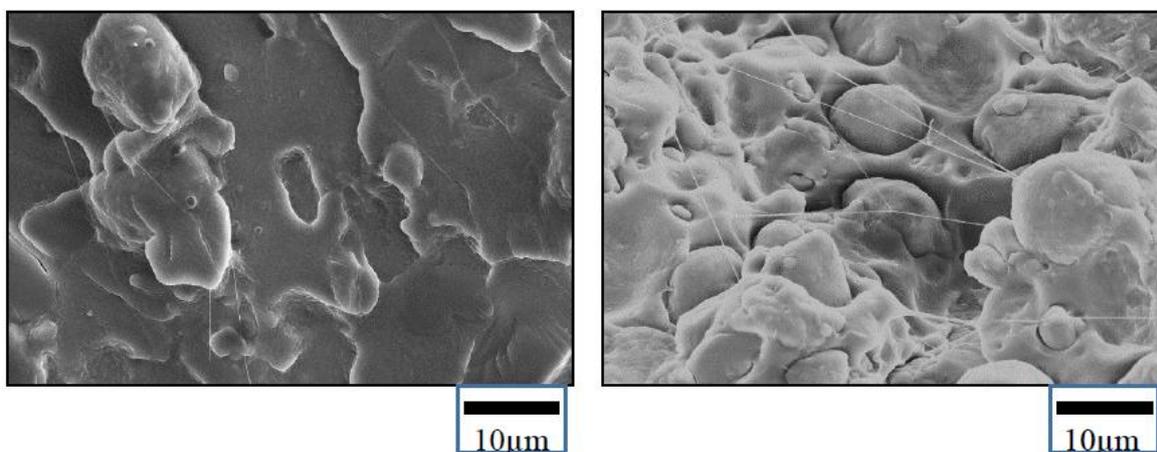
Figure 2. SEM images of TPSC (2a, left) and TPSC with 3 wt. % of Na-MMT (2b, right).

3.3 Water absorption studies

From **Table 2**, it can be seen that TPSC with starch composites showed a drastic increase in the water absorption with a value of 30.4 % for 24 h and diffusivity was higher than other samples. In addition, these samples were broken and degraded within 24 h. On the other hands, the blends with nanoclay decreased water absorption and diffusivity when compared to starch without nanoclay. Some cracks were observed in the TPSC nanocomposites, although samples were not broken completely.

Table 2. Water absorption and diffusivity of TPSC and TPSC-nanocomposites.

	Water absorption (%)									Diffusivity (mm^{2}s^{-1} × 10^8)
	0h	2h	6h	8h	24h	48h	96h	144h	168h	
No.1	0.0	1.7	3.4	4.0	7.3	9.6	11.2	10.4	10.4	0.45
No.2	0.0	6.5	15.0	18.5	30.4	–	–	–	–	6.27
No.6	0.0	4.3	8.6	9.7	18.9	21.4	19.7	19.4	20.1	2.65

4. Conclusions

New TPSC nanocomposites with nanoclay were prepared via a simple method. Mechanical properties and water resistance of the TPSC nanocomposites were measured. Addition of nanoclay improved mechanical properties and decreased water absorption. Because of its renewability, biodegradability and low cost, starch based materials became one of feasible agro-based sources that can replace petroleum based materials in packaging applications. They are in tune with the concept of sustainable development.

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