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Preparation and Characterization of Thermoplastic Starch Based On Dry Heat-Treated Cassava Starch and Glycerol

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Abstract

In the study, the plasticizing effect of glycerol in the preparation of thermoplastic starch (TPS) from dry heat treatment (DHT) cassava starch was studied. DHT cassava starch-based TPS samples were prepared by using an internal mixer with different contents of glycerol (20 wt.%, 25 wt.%, 30 wt.%, and 35 wt.%) and then were characterized by different analysis methods Thermogravimetric analysis (TGA), X-ray diffraction (XRD), and Fourier transform infrared spectrum (FTIR). The mechanical properties were also investigated. The physicochemical characteristics of TPS samples showed that the structure of starch completely changed after the plasticization process in the presence of glycerol. The plasticizing efficiency of glycerol was also evaluated through the difference in mechanical properties results. Among the samples studied, the sample with 25% plasticizer showed the best plasticizing efficiency, with a tensile strength of 13.57 MPa and an elongation at break of 54.27%.

Keywords: Cassava starch, cassava thermoplastic starch, glycerol plasticizer, plasticizing efficiency.

1. Introduction

Recent years, due to environment pollution concerns, biodegradable polymers made from renewable natural resources has gained more and more attention. Starch is considered as one of promising biopolymers for replacing petroleum-based plastics due to it renew-ability, degradability, and low cost. Starch is widely accessible in plants such as cassava, corn, potato, tubers, roots, and many more. However, it still has a limited ability to process [1]. This disadvantage can be solved by a structural modification process of starch which is called as "plasticization". Plasticization takes place at high temperature with the presence of plasticizer and results in an amorphous and homogeneous substance known as "thermoplastic starch" (TPS) [2]. TPS is low-density, flexible, and renewable, and it can be used easily with standard equipment, which is commonly used in synthetic polymer production.

In addition, the molecular structure of native starch needs to be modified due to the lack of characteristics that are needed for industrial use. Among starch modification methods, dry heat treatment (DHT) has received significant attention due to its simplicity and safety. It is a straightforward physical method that may improve starch performance because it produces no treated effluents, and the resulting products don't contain any traces of chemical components, making it a "green technology" [3]. DHT partially cleaves the glycosidic bonds in starch, changing its molecular size distribution and creating a new intermolecular packing that enhances the material properties. The use of DHT starch was expected to enhance the interaction between starch molecules and plasticizer, helping to improve some properties of TPS. However, current studies on DHT starch mainly focuses on applications in the food industry, while studies using it to manufacture TPS are limited.

Plasticizer plays a vital role in TPS production and processing. It can penetrate into starch molecules and destroy the intra- and inter- molecular hydrogen bonds between starch molecules. Glycerol is one of the most widely used plasticizers to prepare TPS [4]. It is a tiny, polar molecule with a high boiling point and vapor pressure that is harmless and able to enter the gaps between starch granules. Both amylose and amylopectin films can be plasticized with glycerol. The best elastic modulus and highest tensile strength were displayed by glycerol-plasticized starch films. Several studies worldwide have studied the plasticizing impact of glycerol on cassava starch. According to a study by Adamu [5], a glycerol content of 0–20% decreased the tensile strength but enhanced the elongation of the cassava starch-based film. Tarique [6] used glycerol with different content of 15%, 30%, and 45% to plasticize cassava starch. Results showed that the addition of glycerol plasticizer to the cassava starch film improved its overall characteristics.

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In this study, cassava starch was chosen to be used because it can be easily found in Vietnam. It's a revisable resource with an inexpensive cost, and it can become a promising green material in the future, especially for food packaging applications. The main purpose of this study is to prepare and characterize properties of DHT cassava starch-based TPS processed by the extrusion technique with the presence of glycerol plasticizer. The effects of different contents of glycerol on the properties of DHT cassava-based TPS are also evaluated.

2. Materials and Methods

2.1. Materials

Cassava starch with a starch content of at least 85%, fineness of 99%, moisture content of less than 13%, and whiteness of 99% is supplied by Phuc Thinh cassava starch factory of Vietnam. Glycerol was purchased from China with a density of 1.26 g/mL, purity of 99.5%. All other chemicals (lauric acid, and zinc stearate) were purchased from China.

2.2. Preparation of Dry Heat Treatment Cassava Starch

First, DHT cassava starch (DCS) was prepared according to Carla I.A. La Fuente's study [7]. Cassava starch was dried by heat oxidation for four hours at 130 ºC in a dryer model 101-1A, then was allowed to cool to room temperature.

2.3. Preparation of DCS-Based TPS

To enhance the penetration of plasticizer molecules into the starch chain, glycerol plasticizer was uniformly blended with DCS with the content of 20 wt.%, 25 wt.%, 30 wt.%, and 35 wt.%. The mixture was then stored at room temperature for 18 hours prior to mixing. 1.5 wt.% lauric acid and 0.2 wt.% zinc stearate were also added to the mixture. Starch is naturally hygroscopic and easily absorbs moisture from the air; therefore, in this work, lauric acid and zinc stearate were used to reduce the moisture absorption of the DCS-based TPS. The samples were then combined using a Brabender internal mixer (Germany) at 155 °C, 60 rpm, and 12 minutes of mixing time.

Following mixing, the extruded TPS samples were pressed using a Xiangying hot press (China) at 160 °C and 100 kg/cm² to create thin, 1 mm-thick plates.

The samples are labeled as TB, 20G, 25G, 30G, and 35G, respectively. The composition of samples was listed in Table 1.

Table 1. Composition of studied samples

Samples	Glycerol (%)	Starch (%)	Zinc stearate (%)	Lauric acid (%)
TB	0.00	100.00	0	0
20G	19.66	78.64	0.20	1.50
25G	24.56	73.74	0.20	1.50
30G	29.49	68.81	0.20	1.50
35G	34.40	63.90	0.20	1.50

2.3. Analytical Method

2.3.1. Mechanical properties

Tensile strength and elongation at break of the samples were measured in accordance with ASTM D638 standard using BP-1068 mechanical testing machine (BAOPIN, China), tensile speed of 50 mm/min. An average value of five tests was reported.

2.3.2. Fourier transform infrared spectrum

The Fourier transform infrared spectrometer (FTIR) (NEXUS 670) was used to record the sample's infrared spectrum in the 400–4000 cm^{-1} range. OMNIC 5a software was utilized for collecting and processing the data.

2.3.3. Thermogravimetric analysis (TGA)

The thermal stability of samples was determined by using a Netzsch thermogravimetry analysis system (model TGA209F1, Germany). The sample was put into a platinum crucible and heated from room temperature to 600 ºC at a rate of 10 ºC/min in an inert gas atmosphere (N_2).

2.3.4. X-Ray diffraction (XRD)

The X-ray diffractometer (Bruker, model D8-ADVANCE) was used to measure the crystallinity of samples at 40 kV/30 mA using Cu radiation (wavelength λ = 1.5406 Å) and a graphite crystal monochromator. The 2θ scanning range covered 10º to 50º.

3. Results and Discussion

3.1. Mechanical Properties

The tensile strength and elongation at break of samples are displayed in Table 2.

Table 2. Mechanical properties of TPS samples

Sample	Tensile strength at break (MPa)	Elongation at break (%)
20G	9.13±0.58	20.42±1.12
25G	13.57±0.65	54.27±0.96
30G	10.56±0.55	57.73±2.21
35G	8.82±0.40	62.72±1.16

The mechanical results demonstrate that the tensile strength and elongation at break increase with increasing plasticizer content, from 20% to 25%. This can be explained by the fact that the higher the content of glycerol, the higher the ability of glycerol to penetrate the starch chain; therefore, the ability to break connections between starch chains and form intermolecular hydrogen bonds between starch and glycerol increases with the increase of content of glycerol plasticizer. However, tensile strength rapidly decreases when the plasticizer percentage rises from 25% to 35 wt.%. Wenyong Liu also noted that the mechanical characteristics of cassava starch reduced when it was plasticized with glycerol, with the glycerol concentration rising from 30 wt.% to 50 wt.% [8]. This is because starch molecules and plasticizers establish hydrogen bonds, which lessen starch's strong intramolecular attraction and enhance the flexibility of the starch chains. As a result, the tensile strength and elongation at break decrease and increase, respectively.

3.2. Fourier Transform Infrared Spectrometer Spectrum

The FTIR spectra of samples are presented in Fig. 2.

The infrared spectrum of the TB sample displays characteristic peaks: the peak at approximately 3400 cm^{-1} is assigned to O-H valence vibrations (free O-H groups and intramolecular and intermolecular O-H groups); the peak at approximately 2930 cm^{-1} is assigned to the stretching vibrations of C-H bonds [9]; the peak at 1712 cm^{-1} is assigned to the stretch vibrations of C=O bonds; 1643 cm^{-1} is assigned to the bending vibrations of O-H bonds [9]; the peak at 1200 cm^{-1} is assigned to the valence vibrations of C-O groups; the peak at 999 cm^{-1} is assigned to the valence vibrations of C-O bonds in C-O-C groups; and at 920 cm^{-1} is assigned to the C-O bond in C-O-H groups. The IR spectra of the plasticized starch exhibited peaks that were similar to those of starch when glycerol plasticizer was added [10].

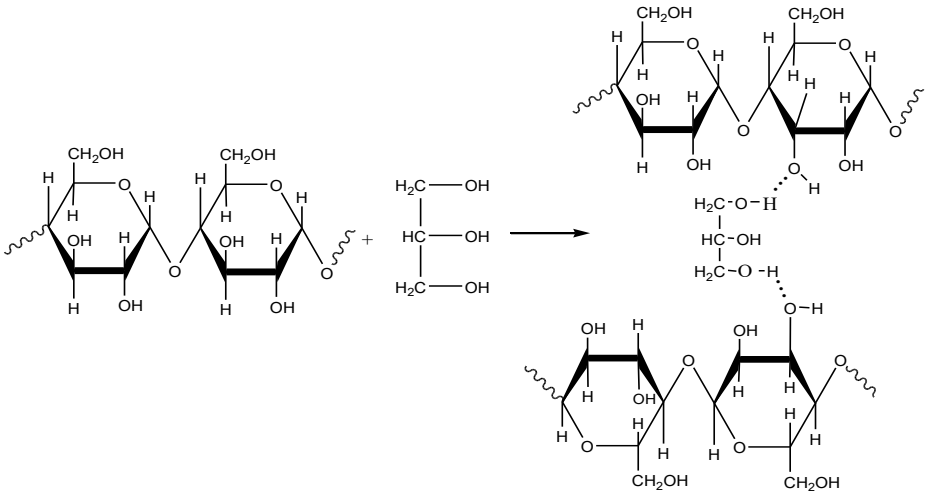

Fig. 1. Interaction of starch and glycerol

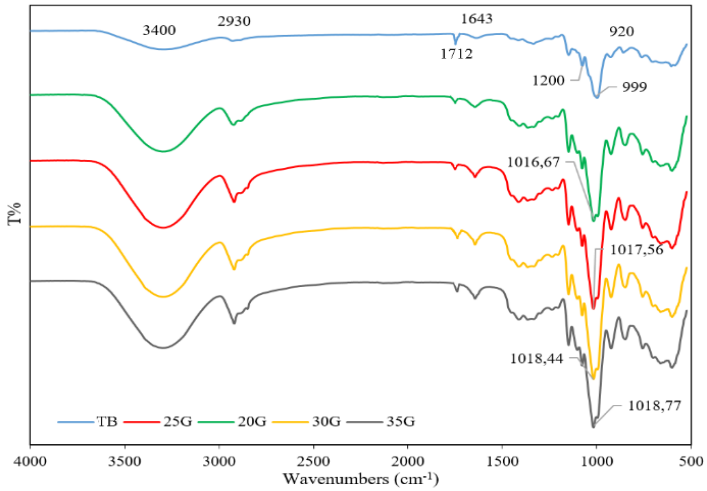

Fig. 2. FTIR spectrums of unplasticized starch (TB) and TPS samples with different content of glycerol

The plasticized starch sample did, however, have higher peak intensities than the TB sample at 3400 cm^{-1} (O-H valence vibration), 2930 cm^{-1} (C-H valence vibration), and 1643 cm^{-1} (O-H bending vibration). These peaks also increased in intensity as the glycerol content increased. Furthermore, the fingerprint region (between 1500 cm^{-1} and 500 cm^{-1}) had variations in the peak band's shape and intensity, which were brought about by the interaction of starch and glycerol. When glycerol content is 20, 25, 30, and 35%, respectively, the valence vibration of the C-O bond in the C-O-H group at peak 999 cm^{-1} (in TB) moves to higher wavenumbers, precisely 1016.67, 1017.56, 1018.44, and 1018.77 cm^{-1}. Bergo [10] also reported similar results when examining the impact of glycerol on the physical characteristics of cassava starch films.

3.3. X-Ray Diffraction

XRD was used to access the crystalline structure of TPS samples after plasticizing process. XRD diffraction pattern of samples was shown in Fig. 3.

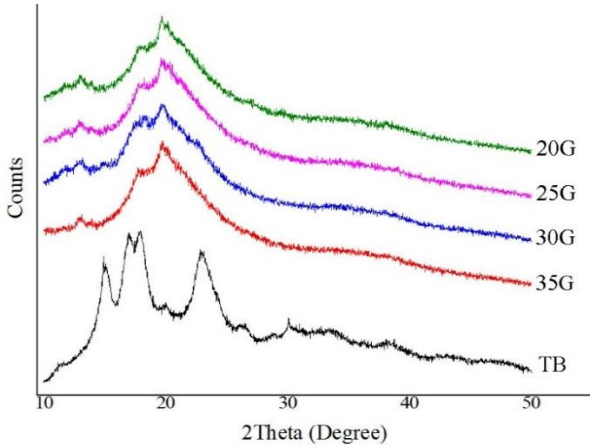

Fig. 3. XRD diffraction pattern of studied samples

Respective crystallinity of samples was listed in Table 3.

Table 3. Crystallinity of studied samples

Sample	Crystallinity (%)
TB	31,12
20G	28,75
25G	24,27
30G	22,64
35G	21,98

As can be seen in Fig. 3, the starch sample (which is labeled as TB) displayed a typical α-type X-ray pattern with a single peak at 15°, a double peak at 17° and 18°, a weak peak at 20.3°, and an obvious single peak at 23° [8]. The XRD pattern of TPS samples completely changes after plasticizing with glycerol. The appearance of a V_h-type crystallization peak can be observed with the most noticeable peak at 19.5° when compared to the original starch sample. This type of crystal structure was formed due to the interaction between the plasticizer and the amylose component in the starch during the plasticization process [11].

It is also observed that the intensity of the crystallization peaks tends to diminish as the plasticizer content increases from 20% to 35%. This corresponds to the decrease in the crystallinity of the samples which is shown in Table 3. The mechanical breakdown of molecular bonds caused by the strong shear forces in plasticization is one of factors which contributed to the decrease in crystallinity of TPS samples [12]. XRD results also show that the peak intensities of the 30G and 35G samples do not significantly differ.

3.4. Thermogravimetric Analysis

TGA was used to evaluate thermal stability of samples. TGA curves and thermogravimetric analysis data of studied samples were shown in Fig. 4 and Table 4, respectively.

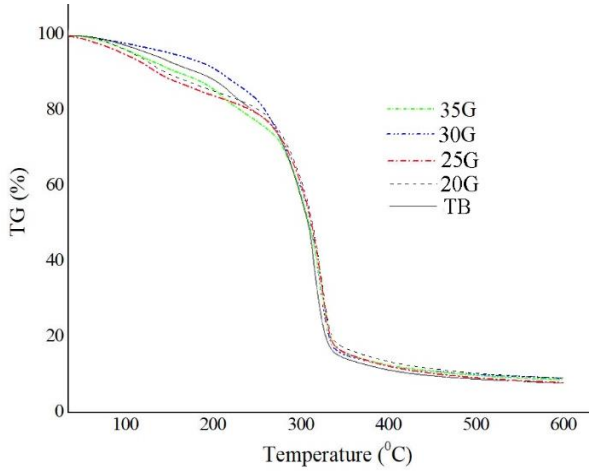

Fig. 4. TGA curves of studied samples

Table 4. Thermogravimetric analysis data of studied samples

Sample	Stage 1 (50–260 °C)		Stage 2 (260–500 °C)	
	T_{peak} (°C)	% loss of mass	T_{peak} (°C)	% loss of mass
TB	-	-	318.1	87.92
20G	213.2	21.2	314.9	70.8
25G	214.4	21.8	320.9	71.1
30G	216.8	22.6	323.7	70.6
35G	218.2	23.4	324.7	70.9

In Fig. 4, TGA curves showed that the TB sample undergoes a single stage of thermal degradation at a temperature of 318.1 °C in the absence of plasticizer. With the combination with the plasticizer glycerol, the plasticized starch samples undergo two primary stages of heat degradation: Stage 1: from 50 °C to 260 °C, the mass loss is ascribed to the evaporation of water and the dehydration reaction between the OH groups of starch and the OH groups of glycerol; stage 2: from 260 °C to 500 °C, the mass loss is ascribed to the thermal breakdown process in the range of amylose and amylopectin in starch [13, 14]. The maximal decomposition temperature of the samples increases with the increase of glycerol content, as shown in Table 4. This may be due to the plasticization process enhancing the molecular chain's flexibility [15]. The maximum decomposition temperature, however, is lower at low glycerol content (20%) than it is in the unplasticized sample. This can be explained by the incomplete plasticization process, which makes starch easily decompose at high temperatures with strong chain cleavage [13].

4. Conclusions

Here, glycerol with different content was used to plasticize the DCS. The relationship between glycerol and cassava starch in TPS was indicated by the IR spectra. The XRD spectrum was also used to assess the crystal structure of samples and confirmed that the crystallite type of starch was completely changed after the plasticization process with the presence of glycerol. The TGA data showed that the thermal properties of TPS samples differed from that of the unplasticized sample. The obtained results also demonstrated that mechanical properties and thermal stability were enhanced with the increase of glycerol content from 20% to 35%. The TPS sample with 25% content of glycerol showed the best tensile strength of 13.57 MPa. The obtained results suggested that DHT cassava starch–based TPS can be a potential material for the development of biodegradable films in the future.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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