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Thermoplastic Waxy Starch Films Processed by Extrusion and Pressing: Effect of Glycerol and Water Concentration

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Thermoplastic starch properties depends of plastification process. The aim of this study was to analyze the effect of concentration of glycerol and water on plastification, glass transition temperature (T_g) and tensile properties of thermoplastic waxy starch (TPWS). Formulations were extruded in the following concentrations of starch/glycerol/water: 70/30/0 (TPWS 0%); 70/25/5 (TPWS 5%); 70/20/10 (TPWS 10%) weight percentage. Crystalline peaks in WAXS diagrams and native grains present in SEM micrographs showed that the TPWS 0% and 5% were not sufficient to promote total plastification of the waxy starch, and TPWS 10% showed the higher starch plastification. T_g measurements by DMTA were 30 ºC to TPWS 0%, 23 ºC to TPWS 5% and 40 ºC to TPWS 10%. These results showed that glycerol and water had effect plasticizer in TPWS 5% and antiplasticizer in TPWS 10%. Mechanical tensile results showed that higher tensile strength was observed in the systems with more effective starch plastification.

Keywords: *waxy starch, plastification process, plasticizer effect, films, extrusion.*

1. Introduction

Starch is a carbohydrate present in abundance on the environment, which has advantages over others biodegradable polymers such as low cost and biologically absorbable[1]. Starch consists of two major components, the linear amylose and the highly branched amylopectin[2,3]. There are three types of starch wherein the amylose concentration ranges: native starch (15-30 wt% amylose); waxy starch (0-5 wt% amylose); and high amylose starch (35-70 wt% amylose)[2,3].

Native starch is not processible and this drawback can be resolved by plastification process[4-6]. When starch is mixed with plasticizers under shear rate and temperature between 90-180 ºC their amylose/amylopectin chains are interspersed, and the amylopectin structure original is destroyed. This material is called starch thermoplastic (TPS)[7,8].

The type and concentration of plasticizer employed has significant effect on the plastification process, glass transition temperature (T_g) and mechanical properties[6,9-12]. Theoretically, plastification process consists essentially in altering the viscosity of the system, in which the material becomes processable. Plasticizers add to the polymer affect all its plastificaton process, physical and mechanical properties. Plasticizer effect is characterized by a drop in T_g and antiplasticizer effect is characterized by a grow in T_g[13].

The most commons plasticizers utilized for starch are polyols such as glycerol. However, the addition of polyols decreases film mechanical resistance[4]. Recent study has shown it was found that plastification process of waxy starch (~99 wt% amylopectin) were more easily performed than native starch (72% amylopectin and 28% amylose)[14].

In this work, we proposed to investigate the effect of glycerol and water concentration on plastification, glass transition temperature (T_g) and tensile properties of thermoplastic waxy starch (TPWS) films processed by extrusion and pressing. Many works in the literature deal with plasticization of the waxy starch with several polyols, without focusing on the variation of the amount of water together with polyols in the plastification process, mechanical properties and plasticizer effect[15].

2. Experimental

2.1 Materials

The following materials were used: waxy corn starch (Amidex® 4001 from Ingredion® with approximately 100 wt% amilopectin ; glycerol from Nitrogenius®; distilled water;

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stearic acid (MW = 284.48 g/mol) from Vetec®; and citric acid (MW = 192.13 g/mol) from Chemco® 99.5% of purity.

2.2 Preparation of film formulations and film processing

Waxy starch was mixed with different amounts of glycerol and water. The samples compositions are shown in Table 1. It was added citric acid (1 wt%), and stearic acid (1 wt%) in all samples compositions. Citric and stearic acids were used as processing auxiliaries.

Table 1. Thermoplastic waxy starch films compositions.

Films	Waxy starch [wt%]	Glycerol [wt%]	Water [wt%]
TPWS 0%	70	30	0
TPWS 5%	70	25	5
TPWS 10%	70	20	10

The TPWS compositions were plasticized in a co-rotating twin-screw extruder (Coperion 18 mm and L/D = 40). The materials were added into the feed at screw rotation speed of 300 rpm twin screw profile of high shear. The temperature profile of the feed channel to the matrix was 110, 120, 120, 125, 130, 135, and 140 ºC. After the extrusion process pellets were obtained, which were pressed (by initial pressing of 3.0 tons, and final pressing of 5.0 tons per minute each at a temperature of 140 ºC with subsequent cooling under pressing of 5.0 tons). Films obtained with a thickness of about 200 µm are shown in Figure 1.

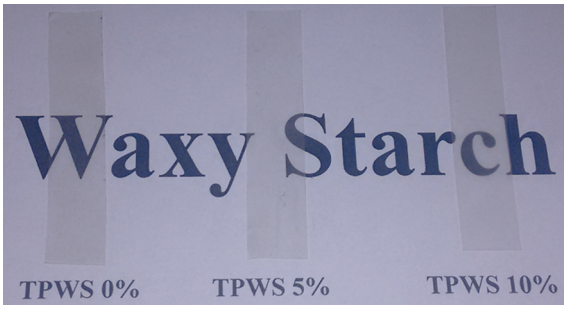

Figure 1. Films of TPWS 0%, TPWS 5%, and TPWS 10%.

2.3 Morphological analysis

The cross-section of the films obtained from cryogenic fracture was analyzed by micrographs obtained from a scanning electron microscope (SEM), model JMS 6510 (JEOL®), using an accelerating voltage of 10 kV. Samples were mounted on copper stubs, and then coated with gold.

2.4 X-ray diffraction (XRD)

The diffractograms were recorded on a LabX XRD 6000 Shimadzu® diffractometer operating at 30 kV, 30 mA and CuKα radiation (λ = 1540 Å). The samples were scanned in 2-Theta ranges varying from 10 to 40º and the scan speed employed was $0.5^{o}min^{-1}$.

2.5 Mechanical properties

Uniaxial tensile tests of films were performed in a universal testing machine EMIC® according to ASTM D 882-12[16] at a speed of 0.5 mm/min with a 10 kgf load cell at 25 ºC (± 2 ºC), 50 mm distance between the jaws, and a relative humidity (RH) of 50% (± 5%). The Young's modulus, tensile strength, and strain at break were evaluated.

2.6 Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed in a model Q800 (TA Instruments equipment®), using tension-film geometry in the range -50 ºC to 70 ºC, at the scanning rate of 2 ºC/min and constant frequency of 1 Hz. Samples were conditioned at 25 ºC and 30% RH for 48 hours. The glass transition temperature (T_g) was defined on the tan δ broad peak.

3. Results and Discussion

3.1 Morphological analysis

Figure 2 presents cross-section cryogenic fracture by SEM for TPWS 0%, 5% and 10%.

SEM micrographs showed that TPWS 0% composition exhibits some native or partly melted starch granules spread over the film indicated by white arrows (Figure 2b). The grains with diameter around one micron show that they were broken in the extrusion process. On the other hand, SEM micrographs also showed that the compositions with the addition of water exhibit less native starch granules, suggesting that water is an excellent agent for plastification (Figure 2c to 2f). Some points observed for TPWS 5% and 10% can be bubbles that caused due to presence of water.

The study about TPS films shows that the number and size of these granules grow up with increasing concentration of plasticizer such as glycerol. The complete plastification of starch under low moisture conditions in the extruder required application of a considerable amount of shear, which was not feasible in the presence of glycerol[17].

3.2 X-ray diffraction (XRD)

Figure 3 has shown X-ray diffraction patterns for waxy starch, TPWS 0%, TPWS 5%, and TPWS 10%. Waxy starch shows a typical A-type pattern, with strong reflections at 2θ about 15º and 23º, and an unresolved doublet at 17º[18]. An amorphous state was observed in the thermoplastic waxy starch film with 10% glycerol[19]. The single peak at 2θ 21º that occurs for this composition is the retrogradation of waxy starch[20]. For compositions, TPWS 0% and TPWS 5% are possible to observe

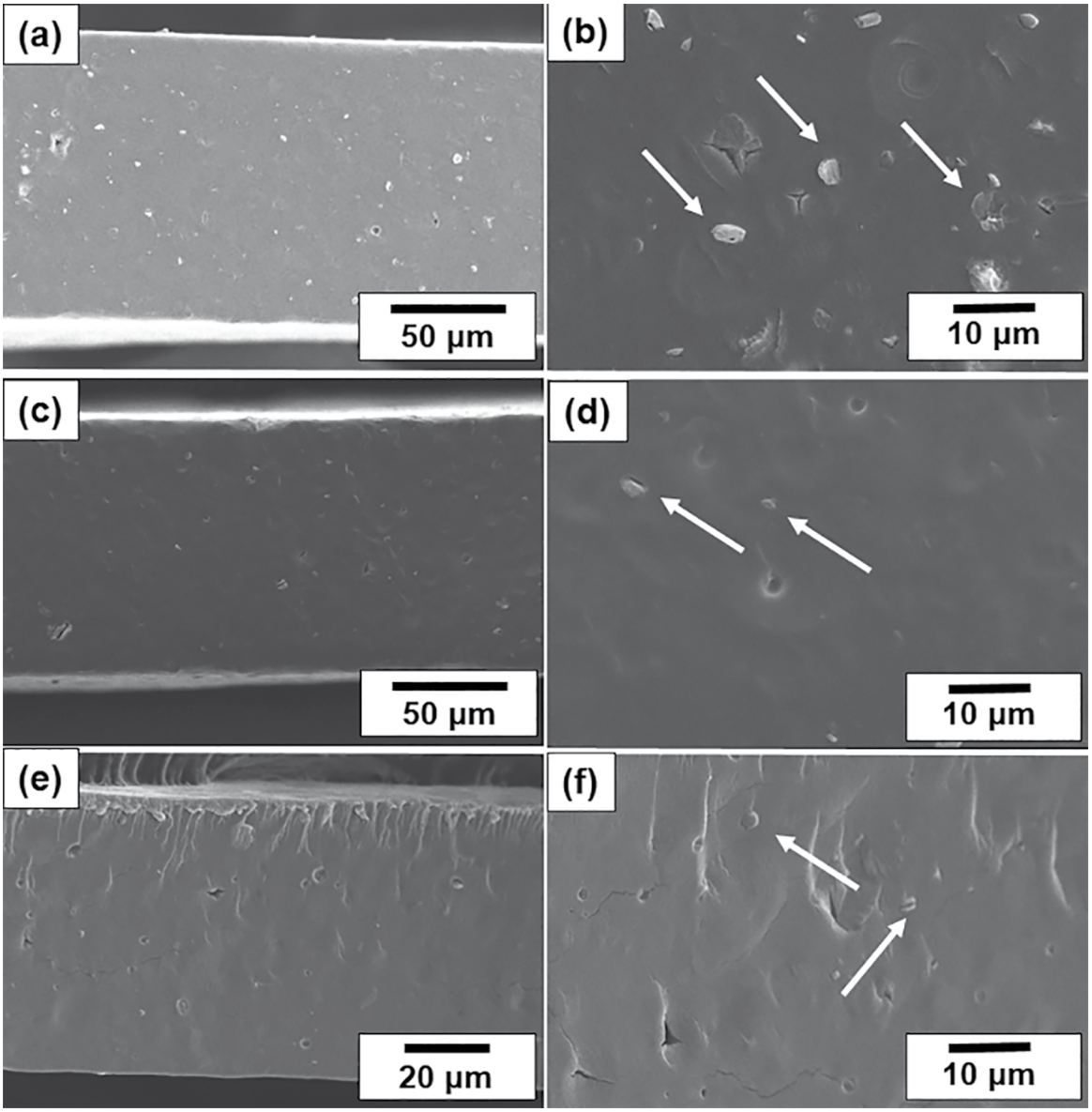

Figure 2. (a) SEM micrographs of TPWS 0%, (b) TPWS 5%, and (c) - TPWS 10%.

peaks characteristic of the waxy starch crystallinity, indicating that not occurred an efficient plastification for these compositions. The peaks characteristic of the waxy starch in the TPWS 0% and 5% compositions are according to Figure 2a and 2b, where it is possible to see the starch in the form of grains. The diffractograms prove the plastification effect of the water in the process of extrusion of the waxy starch to transform it into thermoplastic waxy starch, with less quantity of native starch grains (Figure 2c).

3.3 Dynamic mechanical thermal analysis (DMTA)

Figure 4 shows the curves of storage tensile modulus (E′) and damping factor (tan δ) versus temperature, which

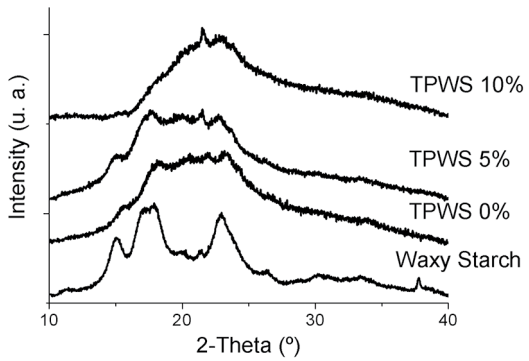

Figure 3. X-ray diffraction patterns for waxy starch, TPWS 0%, TPWS 5%, and TPWS 10%.

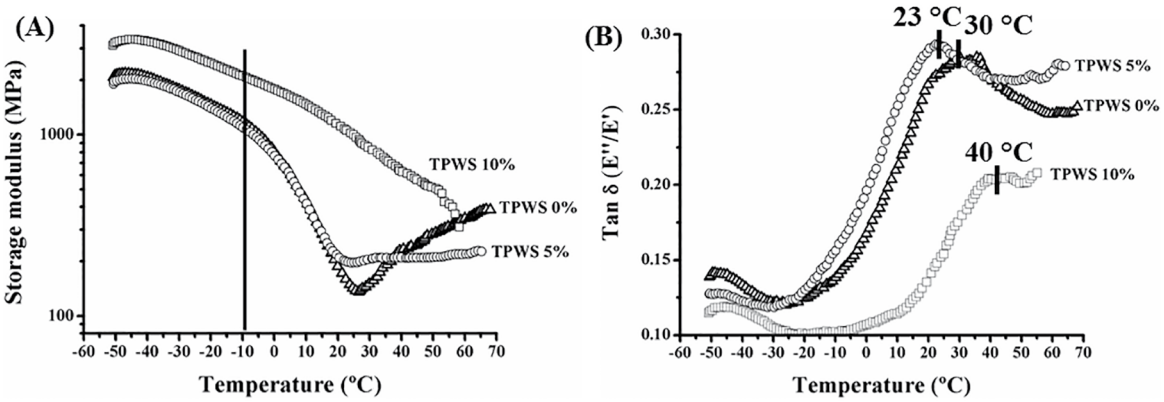

Figure 4. (a) Tensile storage modulus E′ versus temperature, and (b) Damping factor tan δ versus temperature for TPWS 0%, TPWS 5%, and TPWS 10%

the decay for E' correspond to tan δ peak. The δ peak corresponded molecular relaxation or glass transition temperature (T_g) of TPWS films that is affected by glycerol and water concentration.

T_g measurements by DMTA were 30 ºC to TPWS 0%, 23 ºC to TPWS 5% and 40 ºC to TPWS 10%. These results showed that glycerol and water had effect plasticizer in TPWS 5% and antiplasticizer in TPWS 10%.

The addition of glycerol in starch films provides more active sites by exposing its hydrophilic hydroxyl groups in which the water molecules could be adsorbed that exerted a plasticizing effect[21,22]. On the other hand, the addition of more water and removal of more glycerol causes the opposite effect, in which there is an increase in the interaction of the polymer chains, causing the antiplasticizer effect[13].

The mechanical tensile test was performed at a temperature close to the T_g of TPWS 5%, in which it is not possible to observe the mechanical tensile plasticizer and antiplasticizer effect for this composition. Black line at -10 °C on E' diagrams, we observed the smallest Young's modulus for TPWS 5%, showing the mechanical plasticizing effect for this composition[13].

3.4 Mechanical properties

Table 2 shows the results of mechanical tensile properties. The tensile strength and Young's modulus grow, while strain at rupture diminishes when add water and decrease the amount of glycerol. These results prove that the effective plastification effect with water improved the mechanical properties, as seen in SEM micrographs and WAXS diagrams.

As the mechanical test was performed below the T_g of TPWS 10% it is possible to observe the antiplasticizer effect on the mechanical properties for this composition. The phenomenon antiplasticization occurs for TPWS when the Young's modulus and tensile stress grow, while strain at rupture diminishes in relation to others compositions[13]. When there is an increase in the amount of water into the starch network, direct interactions and the proximity between starch chains were increased, thus under tensile forces, movements of starch chains were reduced, increasing T_g and Young's modulus[21-23].

Table 2. Young's modulus, tensile strength, and strain at rupture of the films.

Films	Tensile strength (MPa)	Young's modulus (MPa)	Strain at rupture (%)
TPWS 0%	5.0 (± 0.7)	218.9 (± 27.4)	0.062 (± 0.018)
TPWS 5%	7.5 (± 0.5)	360.4 (± 49.6)	0.051 (± 0.012)
TPWS 10%	9.2 (± 0.2)	704.4 (± 80.8)	0.024 (± 0.001)

4. Conclusions

We conclude that only the addition of glycerol was not effective for the total deconstruction of native starch grain and semicrystalline amylopectin structure as seen in SEM images and crystallinity peaks on WAXS diagrams. The water helped the destruction of native starch grains and semicrystalline amylopectin structure, showing an effective plastification process. Mechanical tensile results showed that higher tensile strength and Young's modulus were observed in the systems with more effective starch plastification. Glycerol and water had effect plasticizer in TPWS 5% and antiplasticizer in TPWS 10%, proving the effect of the amount of glycerol and water in T_g.

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