Relationship Between Structure and Properties of Modified Potato Starch Biodegradable Films

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ABSTRACT: Potato starch was gelatinized in the presence of water and varying amounts of glycerol at 90°C. Starch/glycerol films were prepared by casting with water. The addition of glycerol produces a decrease in the crystallinity of the starch in the films. Starch was acetylated (with acetic acid and anhydride) and maleated (with maleic anhydride). Differential scanning calorimetric analysis revealed decrease in the glass transition temperature (T_g) with the chemical modification. The starch modification on the equilibrium moisture content was determined at 25°C. The esterifications produce a decrease in the maximum moisture sorption. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4313–4319, 2006

Key words: starch; glycerol; esterification; crystallization; film biodegradable

INTRODUCTION

The development of biodegradable polymers has been accepted as one of the ways to reduce environmental problems by waste plastics. Starch is very cheap, produced in abundance, and easily available from many renewable sources. The starch is completely biodegradable at the end of its life cycle. The processing and manipulation of starch is vital for many industrial uses. Different approaches have been made to use starch for the production of tailored materials.[1–3]

Starch is a semicrystalline polymer stored in granular form as a reserve in certain plants. It is composed of repeating 1,4-α-D-glucopyranosyl units constituting amylose and amylopectin. The amylose is linear, the repeating units are linked by α (1−4) linkages, and the amylopectin has an α (1−4) linked backbone and about 5% α (1−6) linked branches. The relative amounts of amylose and amylopectin depend on the plant source and are responsible, to a large extent, for starch functional characteristics. Starch granules also contain small amounts of noncarbohydrate components such as lipids, proteins, and minerals. Potato starch granules normally contain 16–23% amylase.[1,3–5]

In native form, the starch granules are insoluble in cold water and most uses involve a heating treatment in the presence of excess of water. Below a critical temperature (about 60°C), that is, the so-called gelatinization temperature, starch granules absorb water and undergo swelling to many times their original size. This process is attributed to the diffusion of amylose outside the granule. Beyond this critical temperature, the swollen starch granules can undergo a disruption into smaller aggregates or particles and result in a gelatinized starch. The thermoplastic starch or plasticized starch is obtained after disruption and plasticization of native starch, with water and another plasticizer.[1,3–6]

Starch can be chemically modified to improve its properties, such as mechanical properties, crystallinity, and water absorption, because it is very brittle and has high water absorption. The modified starches are used in various industrial processing, that which involve heating in excess of water; one of these is the preparation of films by casting.[1–3] Fringant and coworkers demonstrated that the acetylation is an efficient chemical modification for obtaining thermoplastic starch material and for diminishing the hydrophilicity.[3,7] The starch acetate is considerably more hydrophobic than is starch and has better tensile property retention in an aqueous environment.[8]

Native starch is semicrystalline, with a crystallinity of 20−45%. Amylopectin is the main crystalline component in granular starch. The crystalline regions, consisting of double helices of the amylopectin outer chains, are arranged as their lamellar domains. Additional crystallinity may arise from cocrystallization with amylose crystallization into single-helical structure.[1,9]
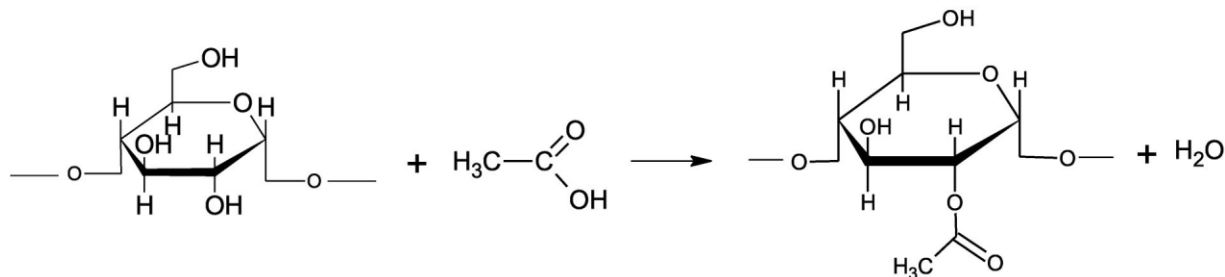
Scheme 1 Reaction of acetic acid and starch.

Numerous methods have been used in studies of crystallization in starch gels. Intensities and areas of peaks in X-ray diffraction patterns describe the starch crystallinity.[2,10,11] The bands at 1047 and 1022 cm^{-1} in FTIR were associated to the ordered and amorphous structures of starch, respectively.[12] The ratio of absorbance 1047/1022 was used to quantify the index of crystallinity.

The aim of the work is to study the modification of the chemical structure of native potato starch to obtain biodegradable starch with less equilibrium moisture content than that of the native starch. The originality of the work is based on the maleinization of starch and the comparison with other commonly used methods.

METHODS

Materials

Native Potato Starch was kindly provided by AVEBE, Argentina S. A. (Buenos Aires, Argentina). Glycerol was purchased from Aldrich.

Preparation of starch-plasticized films

Native starch (2 g) was dispersed in 30 mL of distilled water and different amounts of glycerol. The dispersion was stirred for 1 h at room temperature. Then the suspension was heated to 90°C for 15 min under con-

tinuous stirring to gelatinize the potato starch granules. The hot dispersion was poured into rectangular molds and dehydrated in a vacuum oven at 50°C to constant weight. The films were stored at room temperature in vacuum desiccators for 8 weeks in order to obtain reproducible results. The thickness of the films was 0.22 ± 0.04 mm.

Acetylating treatment of starch

During acetylation reactions, the hydroxyl groups are converted into acetyl groups. The reaction of the acetylation is given in Scheme 1.

The starch (15 g) was immersed in a solution of glacial acetic acid (80 mL), toluene (100 mL), and perchloric acid (0.5 mL) at 25°C for 4 h. After this treatment, it was washed with distilled water several times and then dried at 50°C until no weight loss occurred. The acetylated starch was stored at room temperature in vacuum desiccators. The films were prepared with 68 wt % of acetylated starch and 32 wt % of glycerol. The thickness of the films was 0.22 ± 0.04 mm.

Maleic anhydride treatment of starch

The reaction of maleic anhydride and starch is given in Scheme 2.
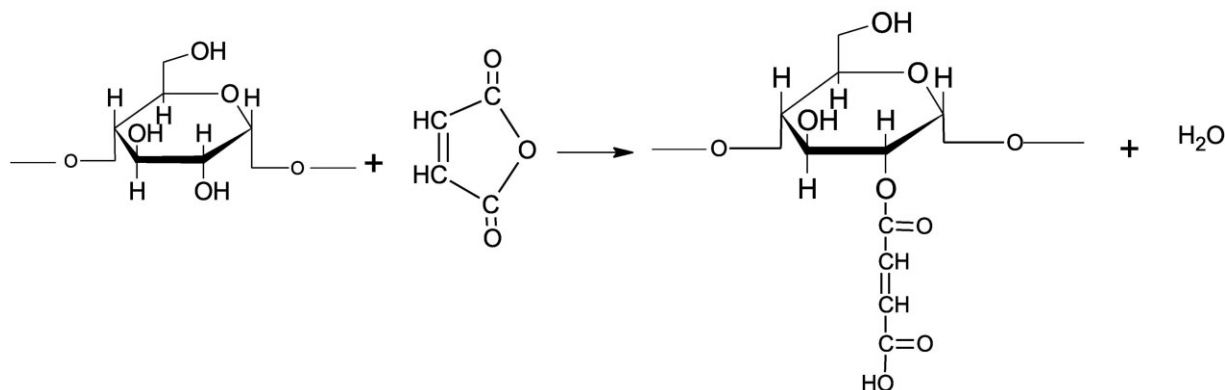
Scheme 2 Reaction of maleic anhydride and starch.

The starch (20 g) was immersed in a solution of maleic anhydride (1.6 g) (8% w/starch) with acetone (200 mL) at 25°C for 24 h, then washed several times with distilled water, and then dried at 50°C. The maleated starch was stored at room temperature in vacuum desiccators. The films were prepared with 68 wt % of maleated starch and 32 wt % of glycerol. The thickness of the films was 0.22 ± 0.04 mm.

Ester content of modified starches

The ester content of esterified starches was calculated using the techniques described by Urbanski,[13] based on saponification with an excess potassium hydroxide and back-titrated with hydrochloric acid.

Testing performed on starch and films

The specimens were investigated by X-ray scattering using a Philips Model PW 1830 X-Ray, from 5 to 60 2θ, with Cu Kα radiation, at room temperature and a scanning rate of 1°/min (RX). The crystallinity was determined dividing the crystalline area with the total (crystalline + amorphous area of starch) as previously reported.[14]

Thermal gravimetric analysis (TGA) was performed on the specimens with a Shimadzu thermal analyzer at heating rate of 10°C/min under nitrogen atmosphere. The specimen weight was in the 3–7 mg range. This test was performed to investigate thermal decomposition of the films, but it is possible that some thermal degradation occurs before the loss of weight in the specimen.

Infrared spectroscopy with Fourier transformed technique (FTIR) of specimen was obtained using a Mattson mod Genesis 2, in ATR and DRIFT, using 32 scans at 2 cm^{-1} resolution.

Glass transition temperatures were determined using a Perkin–Elmer differential scanning calorimeter (equipped with a cooling device), at a heating rate of 10°C/min under nitrogen atmosphere from −30 to 200°C. An empty pan is used as reference. The specimens were conditioned at 100°C for 15 min to eliminate any residual solvent before doing the run for determining the T_g value.

The constant relative humidity environments (rh) was generated with aqueous saturated salt solutions (with NaCl), in hermetic glass container, to make sure 75% rh (ASTM E 104–85). The powder native starch, the powder acetylated starch, and maleated starch were dried at 45°C until a constant weight (m_0). The mass was determined at different times (m_t).

To compare the behavior of the films after each treatment, before the tests, all the specimens were conditioned at 40°C until weight was constant.
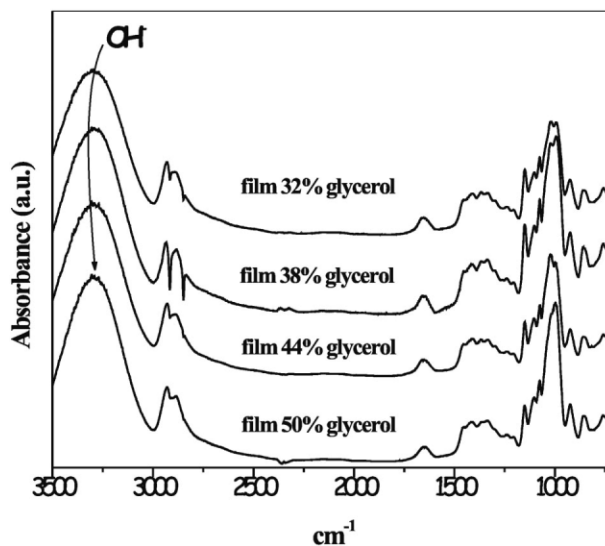

Figure 1 FTIR spectra of starch/glycerol films normalized to 2933 cm^{-1} peak height.

RESULTS AND DISCUSSION

Infrared spectroscopy of starch/glycerol films

The FTIR spectra of starch/glycerol films are given in Figure 1. Typical infrared starch spectra are obtained. All spectra showed a broad peak in the O—H stretching region at about 3200 cm^{-1}.

All spectra showed a peak in the O—H stretching region at around 3300 cm^{-1}. The spectra show peaks at 1150–950 cm^{-1}. The peak at 1150 cm^{-1} corresponds to the asymmetric vibrations of the C—O—C bridging bonds, at around 1100 cm^{-1} appear the asymmetric vibrations of the ring, and in the range 1080–960 cm^{-1} appear the stretching vibrations of the (C—O) bonds. The spectra shows peaks at 2916–2936, 2855, 1405–1465, 1245 cm^{-1} which correspond to CH$_2$ group and 2880–2900, 320 cm^{-1} which corresponds to C—H group belonging to polysaccharide molecules.

The effectiveness of chemical treatments was studied by FTIR spectroscopy. The FTIR spectra of untreated, acetylated, and maleated starches are given in Figure 2. The 2933 cm^{-1} peak corresponding to the absorption of the CH$_2$ group present in the starch does not change with the treatment. Hence, it was used as internal standard. The peak at 1740 cm^{-1} in acetylated starch, which was normalized with respect to the 2933 cm^{-1} peak, indicates the presence of an ester group (C=O stretching band). The peak at 1240 cm^{-1} in acetylated starch (which was normalized with respect to the 2933 cm^{-1} peak) indicates the presence of C=O group (C—O stretching band). These results confirm the acetylating of starch.

The peak at 1703 cm^{-1} in maleated starch (normalized with respect to the 2933 cm^{-1} peak) indicates the presence of an ester maleic group and confirms the maleinization of starch.
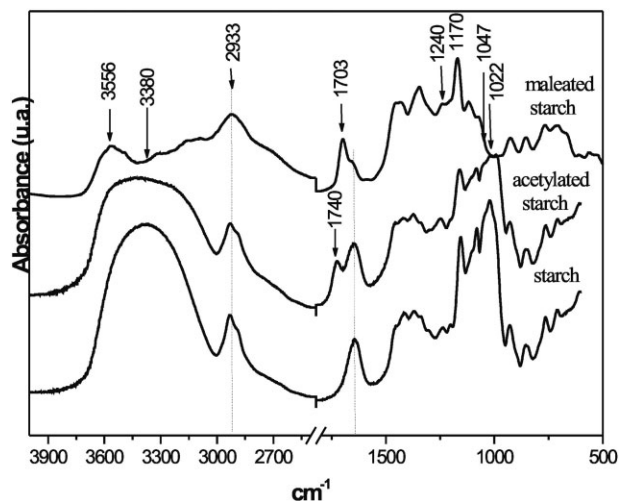
Figure 2 FTIR spectra of starch, acetylated starch, and maleated starch powders. Normalized to 2933 cm^{-1} peak height.

Figure 3 X-ray diffraction patterns for starch/glycerol films.

The bands at 1047 and 1022 cm^{-1} were associated to the ordered and amorphous structures of starch, respectively.[12] The ratio of absorbance 1047/1022 was used to quantify the index of crystallinity (Table I).
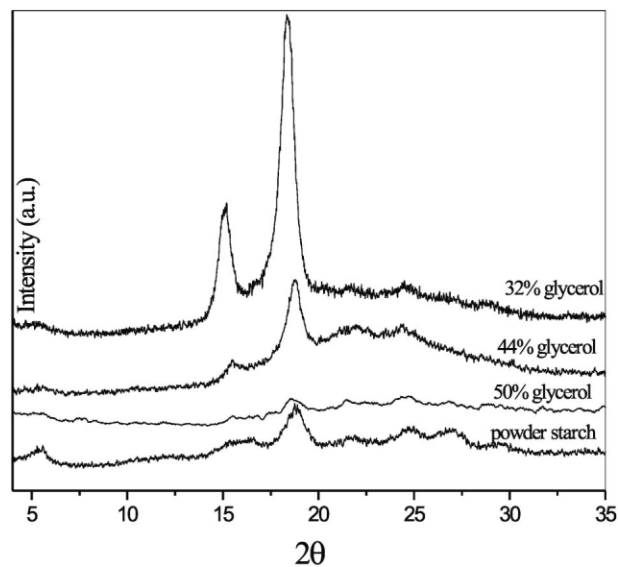
X-ray diffraction of starch

The relative crystallinity of films was investigated with X-ray diffraction. Figure 3 shows the effects of addition of glycerol. These films are of semicrystalline nature and show an X-ray scattering pattern that is characteristic for the crystalline B-type.[9,11,15]

The addition of glycerol to the starch was necessary because the film without glycerol was very brittle. The differences in relative crystallinity between the potato starch/glycerol films are presented in Table I. The final degree of crystallinity depends on the ability of the chain to form crystals, as well as on the mobility of the chain. The crystallinity of starch films decreases with glycerol content. The addition of glycerol decreases the interaction (intra and intermolecular) of the starch–starch chains, because of the strong hydrogen bonding with hydroxyl groups of starch chain and glycerol molecules; as a consequence, it decreases the crystallinity of starch in the blend.[9]

The maleinization of starch with the addition of a voluminous pendant chain produces lower relative crystallinity in powder and films, as it was confirmed by XR analysis (Tables I and II). The addition of acetic anhydride or maleic anhydride introduces more voluminous groups into the chain. This introduces further impediment of polymer chains and the movement of these chains are more restricted.[12,16–18]

The difference in crystallinity between powder and films samples is the effect of gelatinization and the presence of plasticizer. In this case, a crystalline structure reappears, which can be also associated with the B-modification. Then the morphology of native granules is unstructured, and the final crystallinity is higher.[15]

Ester content of esterifed straches

The ester content of the esterifed starches was calculated from the saponification value. Table III shows the value of ester content in acetylated and maleated starches.

TABLE I
IR Ratio of the Absorbances 1047 cm^{-1}/1022 cm^{-1} and X_c (XR) of Potato Starch/Glycerol Films

wt % starch	wt % gly	Abs 1047/abs 1022	X_c (XR)
50	50	0.73	0.19
56	44	0.85	0.29
62	38	0.89	0.34
68	32	0.93	0.37
68 (acetylated)	32	0.80	0.35
68 (maleated)	32	–	0.34

TABLE II
X_c (XR) of Powder Starch and Potato Starch/32% Glycerol Films

Starch	X_c (XR) in powder	X_c (XR) in film
Native	0.26	0.37
Acetylated	0.23	0.35
Maleated	0.20	0.34

TABLE III
Value of Ester Content in Acetylated
and Maleated Starches

| Starch	Ester content
Acetylated	2.2 mmole of acetyl/1g starch
Maleated	1.1 mmole of maleic/1g starch

Thermal decomposition of starch/glycerol films

Figure 4 shows the results of the thermal gravimetric analysis (DTG curves) of the starch films with different amounts of glycerol. The DTG curves show an initial peak about 30–150°C, which corresponds to the vaporization of water and low-molecular-weight compounds. After this peak, the curve exhibits two decomposition steps. The first peak, at about 200°C, corresponds to the decomposition of glycerol (pure glycerol was used as reference). The DTG curves of glycerol show only one peak at about 200°C. Another peak at about 300°C is due to starch decomposition. The peck at about 300°C involves elimination of polyhydroxyl groups, accompanied by depolymerization and decomposition, with final production of carbon. The peak corresponding to the starch in the films appears at less temperature, probably because of their less crystallinity (see Table II) which make easier to destroy the chain and the presence of plasticizer.

Thermal analysis was performed to determine if the chemical modification produces any change on the thermal decomposition behavior. Figure 5 shows the results of the thermal gravimetric analysis (DTG curves) of the acetylated and maleated starch. The DTG curves show an initial peak at 30–150°C, which represents the evaporation of water and low-molecular-weight compound. The curve exhibits one decomposition step, at about 300°C, which is due to starch
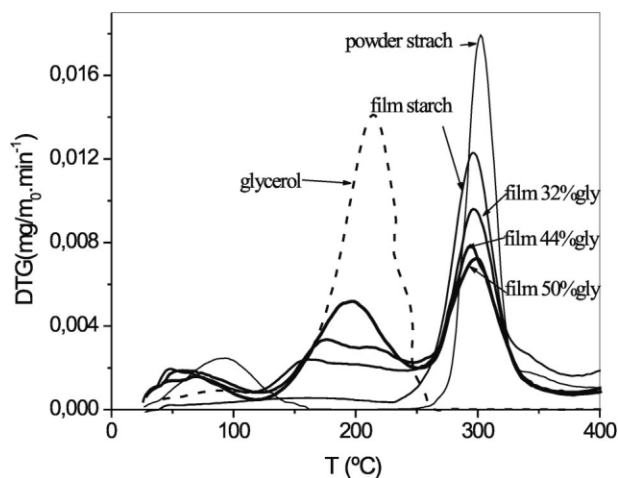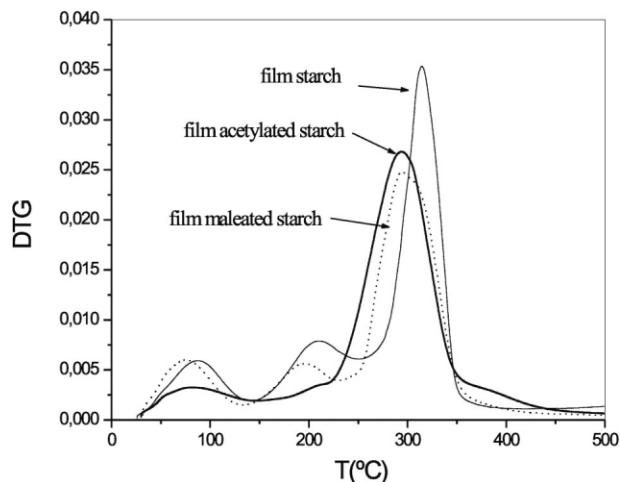
Figure 5 Dynamic TGA of starch/glycerol films and of esterified starch/glycerol films, at a heating rate of 10°C/min.

decomposition. The esterified starches are less thermally stable than native starch. The peak corresponding to the acetylated and maleated starch appears at less temperature, probably because starch chain has low O—H groups and the addition of a voluminous group at the chain which produces lower crystallinity value.

Thermal properties

The effect of glycerol and other plasticizers of starch were analyzed in a literature. The plasticization of starch by water has been demonstrated through the decrease in the T_g of native and amorphous wheat starch. The glass transition of starch is extremely sensitive to moisture. Intermolecular interactions and hydrogen bonding may play a significant role in plasticization behavior. Two glass transitions were detected in starch glycerol-water mixtures analyzed by DSC. The upper glass transition is related to a starch-rich phase and the lower one to a starch-poor glycerol-rich phase.[4] The other study, in which plasticization of starch by glycerol was investigated, a monophasic polymer-solvent system was observed.[6]

The glass transition temperatures of native and esterified starches, powder and films starches are given in Table IV. Glass transition temperature remains higher than ambient temperature.

The first T_g temperature of starch decreases with the modification, as it can be seen in the powder and film samples, because of the increase in the group pendant in the main chain, which increases the free volume.

The addition of glycerol in the films produces a plasticizing effect on the starch films, because the starch-chain mobility increases. However, maleated starch films have a higher T_g value, because the addi-

Figure 4 Dynamic TGA of starch powder and of starch/glycerol films, at a heating rate of 10°C/min (DTG curves).

TABLE IV
Glass Transition Temperatures of Powder Starch with Different Treatments and 68 wt % Starch/Glycerol Films

Starch	T_g (°C)		T_g (°C) in film	
	1st	2nd	1st	2nd
Native	100		70	108
Acetylated	69	150	50	173
Maleated	77	165	61	190

TABLE V
Equilibrium Moisture Content Average by Powder and Film Starches

Starch	%m in powder	%m in films
Native	13.7	24.6 ± 1.4
Acetylated	11.5	20.8 ± 1.2
Maleated	10.6	20.2 ± 1.3

tion of a more voluminous side group produces impediment of polymer chains, and the movement of the chains are more restricted.
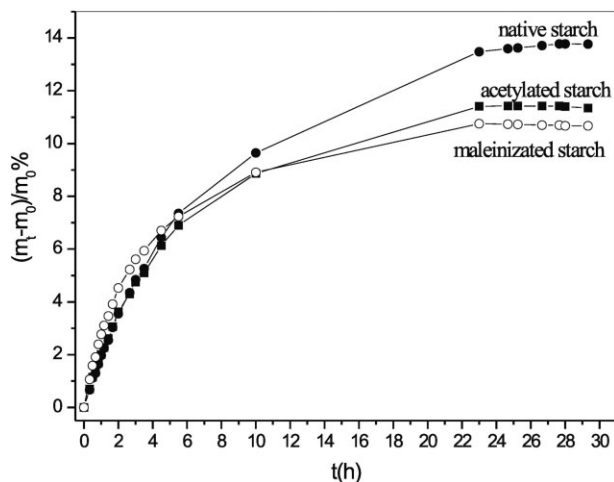
Equilibrium moisture content

The moisture content as a function of time was determined to measure the equilibrium moisture content of powder and films of native, acetylated, and maleated starches. Figure 6 shows the percentage increase in weight value (m%) of native, acetylated, and maleated powder starches at 25°C. The percentage increase in weight value (m%) was calculated as follows:

$$m\% = \frac{m_1 - m_0}{m_0} \times 100 \qquad (1)$$

where m_t is wet weight of starch at each time and m_0 is the initial weight of dry starch.

Table V shows the equilibrium moisture content average by powder and film starches.

The acetylation and maleinization produce a decrease in the maximum moisture sorption when the potato starch is in powder, before gelatination. The esterification reduces the OH^- concentration and this

reduces the maximum water sorption[18,19] producing a more hydrophobic starch.

However, the addition of glycerol and gelatinization produce higher water absorption because of greater interchain distances in the presence of glycerol. Because of the hygroscopicity of glycerol, the equilibrium moisture content usually increases. The films obtained with modified starch also absorb less water than the native film starch, as a consequence of the less hydrophilic character.[20,21]

CONCLUSIONS

The content of glycerol in the films affects the behavior of the material at room temperature. The crystallinity of potato starch/glycerol films decreases with the content of glycerol, because of the strong hydrogen bonding with chains of starch. The acetylation and maleinization of starch produces lower crystallinity; this may be expected because OH^- content decreased and the interaction between starch chains also decreased.

The DTG data indicates that the thermal decomposition occurs at a low temperature for esterified starches/glycerol films because of a less interaction between the chains of esterified starches and their low crystallinity in comparison with that of native starch.

The glass transition temperature of starch decreases with the modification because the increase in the group pendant in main chain increases the free volume. The maleated starch has a higher glass transition temperature because of the addition of more voluminous side group.

The esterification of starch reduces the water sorption with respect to that of the untreated starch, because hydrophilic character of acetylated and maleated starch is lower than the native starch.

Figure 6 Percentage increase in weight value (m%) of native, acetylated, and maleated starch powders.

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