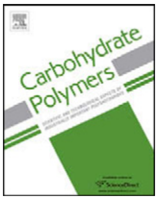
Carbohydrate Polymers 83 (2011) 354–361

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Thermal and microstructural characterization of biodegradable films prepared by extrusion–calendering process

T. Galicia-García[a,∗], F. Martínez-Bustos[a], O. Jiménez-Arevalo[b], A.B. Martínez[c], R. Ibarra-Gómez[d], M. Gaytán-Martínez[a], M. Mendoza-Duarte[d]

[a] CINVESTAV-Unidad Querétaro, Libramiento Norponiente 2000, Fracc. Real Juriquilla, Qro, CP.76001, Mexico
[b] CIATEQ, Av Retablo 150, Col. FOVISSSTE, Santiago de Querétaro, Qro CP. 76150, Mexico
[c] Centro Catalán del Plástico, Universidad Politécnica de Cataluña, Edifici Vapor Universitari, Carrier Colom, 114, 08222 Terrasa, Spain
[d] CIMAV, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Chihuahua, Mexico

ARTICLE INFO

Article history:
Received 26 February 2010
Received in revised form 1 June 2010
Accepted 26 July 2010
Available online 11 August 2010

Keywords:
Extrusion–calendering
Thermal and microstructural properties
Starch films

ABSTRACT

Native starch (corn, potato and waxy corn) and phosphorylated corn starch blended with bagasse fiber and glycerol were used for the preparation of biodegradable films. The processing extrusion variables were: feed moisture FM (18.25–20.5%), fiber content FC (0–10%) and type of starch TS (native or phosphorylated). The analysis of infrared spectroscopy showed OH and C–O bands at 2750–3250 and 550–1000 cm^{-1}, related to plasticizer–starch interactions. Films processed without fiber revealed peaks of low intensity associated to the plastizicing of starch. Differential scanning calorimeter displayed some changes in calorific capacity that could be attributed to molecular excitations and the mobility of polymeric chains (T_g) in a range of temperature between 40 and 80 °C. The dynamic mechanical analyses presented a decrease in the loss modulus at a temperature lower than 100 °C associated to a more structural mobility of bonds indicating a film with more flexibility. The thermal and microstructural characterization of films showed appropriate functional properties in the development of packing materials or flexible containers type bag.

1. Introduction

The worldwide consumption of biodegradable polymers (BPs) has increased in the last years. These natural biodegradable materials include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters) (Bernard, Gontard, & Guilbert, 1998).

Polymers are a series of viscoelastic materials. The structural and mechanical characterizations are important tools and a good example of introducing the measurement of the physical properties of industrial polymers into the research field of biodegradable polymers. Edible films or biodegradable films have a wide application in the industry market for their specified thermal and mechanical properties. Heating amorphous thermoplastic agro-polymers above the glass transition temperature, produces soft and rubbery materials, and may permit their incorporation into specific products such as packaging materials. Cooling to room temperature can reconvert rubbery products to glassy materials, giving more or less rigid forms with the desired structure (Cuq, Gontard, & Guilbert, 1997).

Starch-based biopolymers can be produced by blending or mixing as different naturals polymers as fiber. By varying the blend component and processing conditions and its miscibility with starch, the morphology and hence, the functional and structural properties can be regulated efficiently and, also, allows to design the most important mechanical and functional properties of these materials improving the efficiency of biodegradable packages. Besides, as for synthetic polymers, composition, microstructure and functional properties of films based on biopolymers determine their possible applications. In 2002, two million tons of starch were produced in the world. Because of its abundance and its renewable and environmental friendly characteristics, physically and/or chemically modified starch has been the feedstock of choice in numerous research efforts on development of biodegradable starch-based loose-fill foams and biodegradable materials.

Generally, plasticizers are used for two purposes which are to aid processing and to modify the properties of the final product. In the case of starch-based films, a plasticizer addition overcomes

---

[∗] Corresponding author. Tel.: +52 442 441 4900; fax: +52 442 441 4933.
E-mail addresses: thomhhas@yahoo.com.mx, tgalicia@qro.cinvestav.mx (T. Galicia-García).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.07.050

the film's brittleness and improves its flexibility and extensibility. Other natural polymers such as fibers of hemicellulosic materials are used as a reinforcement in biodegradable films (Mohanty, Misra, & Hinrichsen, 2002) that, because of their low specific gravity, are comparable with other synthetics fibers (Netravali, 2005, Chap. 9) as the sugar cane fiber (Fernández-Rodríguez, 2000). The skyrocketing interests on the natural fiber-reinforced composites are not only for environmental concerns but also for yielding a unique combination of high performance, reactive surface, great versatility and processing advantages at a relatively favorable cost (Bledzki & Gassan, 1999; Felix & Gatenholm, 1991; Kumar, Sairama, Rajub, & Aminabhavi, 2005). The inherent stiffness and high degree of crystallinity make the cellulose microfibers obtained from bagasse ideally suitable for reinforcing and load bearing applications in composites (Bhattacharya, Germinario, & Winter, 2008).

The use of very small asymmetric particles as a reinforcement for high performance composites and other structural materials has attracted a great deal of interest. The use of starch in the manufacture of films is associated with the originated interactions between additives (Guilbert, Gontard, & Gossis, 1996) due to formation of secondary links and a strong molecular order, with the purpose of improving their functional characteristics (Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Navarro, Martino, & Zaritzky, 1997). Most of the natural polymers present low mechanical properties in relation to synthetic materials (Fellows, 2000), for that reason, the searching of fillers, plasticizer and natural fiber sources that improve the better film properties maintaining the biodegradability of materials. In the present study, we have combined both the approaches of native or modified starch reinforced with treated fiber and the effect of extrusion–calendering process on some physical, thermal and mechanical properties of films.

2. Materials and experimental procedure

2.1. Raw materials

Waxy corn starch, corn and potato native starch food grade were acquired from Almex (Mexico D.F.). Glycerol was purchased from Sigma–Aldrich (Germany), and bagasse sugar cane was donated by Ingenio *El Modelo* (harvested 2005, Veracruz, Mexico). Phosphorylated starch was modified according to the methodology described by Paschall (1964).

2.2. Sample preparation

Bagasse sugar cane was hammer milled (Pulvex, mill) and sifted (Rotap, RX-29-Tyler Inc., USA). Fiber was conditioned in an alkaline medium to finest the fiber size. The raw material concentrations were mixed according to preliminary works (Galicia-García, Martínez-Bustos, Jiménez-Arévalo, & Aguilar-Palazuelos, 2007, Chap. 9; Galicia-García et al., 2009). The glycerol content was stayed in a continuous way (22%, w/w) (Table 1).

2.3. Preparation of pellets

An experimental laboratory single screw extruder (Cinvestav-Qro, Mexico) with an L/D ratio of 20:1, a screw compression ratio of 1:1 at 30 rpm, and a circular die with internal measurements of 3 mm diameter were used. Barrel temperatures in the feeding and final zones were kept constant at 50 °C, respectively; whereas, the barrel temperature of the second zone was 80 °C according to a preliminary test. The three heating zones were independently electrically heated, and air-cooled. Feed moisture (FM) varied from 16% to 30%, the feed rate varied according to the weight of the sample, and the screw speed was 40 rpm.

Table 1
Treatment and conditions of process used.

Samples	Variables of process		
	Feed moisture content (%)	Fiber content (%)	Type of starch
M1	18.25	0	Phosphorylated corn starch
M11	18.25	0	Native corn starch
M13	18.25	10	Native corn starch
P5	18.25	5	Native potato starch
P6	20.5	0	Native potato starch
W15	20.5	5	Waxy corn starch (high amylopectin)

M1, phosphorylated corn starch film; M11, native corn starch film without fiber; M13, native corn starch film added with fiber; P5, native potato starch film added with fiber; P6, native potato starch film without fiber; W15, waxy corn starch film added with fiber.

2.4. Extrusion–calendering process

The extrusion process was carried out with COLLIN co-extrusion equipment, model E16 T, with a relation diameter-longitude of 16/25 and a compression ratio of 1:1. Processing conditions were: (a) barrel temperatures: 60–95 °C; (b) screw speed: 13–25 rpm; (c) pressure 95–230 bar; and (d) die orifice 300 μm width. A calendering process was performed using COLLIN equipment, Model Techline CR72T, the processing conditions used were: (a) rolls speed 10–30 rpm; (b) rolls temperature: 10 °C; and (c) tension speed roll: 14–20 rpm. Samples were collected during the steady-state operation. The extrudates were stored in polyethylene bags for 12 h at 5 °C, until further analysis. Additionally, samples were dried at approximately 5% of the moisture content in a forced-air oven at 45 °C for 24 h and milled using a Brabender Quadrumat Senior Mill (Duisburg, Germany) equipped with a sieve <250 μm (60 mesh) for further analyses.

2.5. Microstructural properties

2.5.1. Infrared spectroscopy (IS)

The IS analysis is useful in discerning molecular structures, particularly in recognition of functional groups. A spectrophotometer (Spectrum GX Modelo FT-IR, Trade Perkin Elmer) was used following the methodology described by Wilson and Tapp (1999). Infrared spectra of 4000–650 cm^{-1}, were obtained. The diffuse reflectance angles were set at 5° and 32° scans were acquired per image at a resolution of 4 cm^{-1}.

2.5.2. X-ray analysis (XRA) and relative crystallinity index (RCI)

Milled and sieved samples from 7.5% to 8.5% of the moisture content, with a particle size lower than 1.19-mm, were packed onto a glass sample plate (0.5 mm deep), and mounted on a X-ray diffractometer (Rigaku Model Ultima D/Max-2100, Rigaku Denki Co. Ltd., Japón). The scans were made with a Bragg angle of 5–30° on a 2θ scale with a step-size of 0.02, operating at 30 kV and 16 mA with CuKα radiation wavelength $\lambda = 1.5406$ Å. Diffractograms were smoothed (Savistky-Golay, polynome:2, points:11) for decreasing the disturbance and for best peaks visualization. The relative crystallinity was calculated using the Herman Method, as described by Rabek (1980). The RCI was defined as the relation between the crystalline area (CA) and the total area (TA). The TA is formed by the crystalline region area (CA) and the amorphous region area (AA). The RCI was calculated as:

$$\mathrm{RCI} = \frac{\mathrm{CA}}{\mathrm{AA+CA}}$$

where RCI is the relative crystalline index. CA is the crystalline region area obtained from the curve, and AA is the amorphous region area obtained from the curve.

2.5.3. Scanning electronical microscopy (SEM)

Samples were stored with silica at 35 °C for 10 days, to remove the residual moisture. Sections were stuck to stubs, coated with an Au–Pd alloy in a high vacuum and examined using the scanning electron microscope (Philips®, model XL30 ESEM, Eindhoven, Holland), using a secondary electron detector with 15 kV of acceleration. The microphotographs were obtained using ESEM XL-30 software.

2.6. Thermal properties

2.6.1. Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC 822e, Birefrigerated, Mettler Toledo Lab Plant, Huddersfield, England) was used. Calibration was done with indium ($\Delta H_{\text{fusion}} = 28.59$ J/g, melting point $T_{\text{onset}} = 156.60$ °C). An empty pan was used as reference. The samples were heated from 30 to 220 °C at a rate of 10 °C/min. The samples were stored to relative humidity (50%) for 7 days, before determination. The principal main in these analyses was to evaluate the changes in heat flow by increasing the temperature (1 °C) of the samples (Cp), as reported by Slade and Levine (1995).

2.6.2. Dynamic mechanical analysis (DMA)

DMA is a thermoanalytical technique used to study and characterize materials. It is most useful for observing the viscoelastic nature of polymers. The dynamic mechanical measurements were conducted using a rheometric analyzer TA (TA-DMA-2980) with a film tensile clamp at a single-frequency scanning mode of 1 Hz (angular frequency $\omega = 2.2$) and a constant frequency of heating rate of 5.0 °C/min over a temperature ranging from 30 to 250 °C. The claws inside holding the probe sample were 12 mm thickness. The test dimensions of the samples were 0.5 mm × 40 mm and variable thickness was 0.28–0.35 mm. To prevent water loss during the experiment, the exposed surface of each sample was partially wrapped with aluminum foil, leaving the bottom and top in direct contact with the clamp holders. All the necessary thermal and mechanical calibrations of the instrument were performed before the experiments according to its operation manual (TA Instruments, 2004). The storage modulus (E'), loss modulus (E'') and the modulus relation with delta tangent ($\tan\delta = E''/E'$) were evaluated according to the methodology of Armelin (2002). A dynamic strain of 5 μm and amplitude of 1 μm were applied in all the DMA experiments. Before the measurements, the temperature of samples and the instrument was well equilibrated at 40.0 °C. All measurements were conducted at least in duplicate.

2.7. Analysis data

An infrared spectroscopy (IS), an X-ray diffraction (XRD), a differential scanning calorimetric (DSC), and a dynamic mechanical analysis (DMA) were obtained and evaluated (both data and graphics) using the computer interface with the Origin software (v.6.0).

3. Results and discussion

3.1. Infrared spectroscopy (IS)

The IR spectra at 4000–650 cm^{-1} were obtained for the native starch films (corn, potato, and waxy corn) and modified starch films (phosphorylated corn starch), using the extrusion–calendering process (Fig. 1). The large band at 3269–3287 cm^{-1} may be attributed to the complex vibrational stretches associated with free, inter and intramolecular-bound hydroxyl groups OH that made up the gross structure of starch and glycerol (Fang, Fowler, Tomkinson, & Hill, 2002; Pushpadass, Marx, Wehling, & Hanna, 2009; Wu, Sakabe, & Isobe, 2003; Zhang & Han, 2006). P6 and W15 films were processed at a high moisture content (20.5%) and they showed an increase in the area in relation to the other samples processed with a 18.75% moisture content, thus indicating the possible interaction between the OH groups with the starch. Pushpadass et al. (2009) and Zhang and Han (2006) reported that the depth and area of this band enlarged with an increase in the moisture and glycerol content, which meant that the effective amount of the OH groups present in the films changed considerably with the plasticizer content.

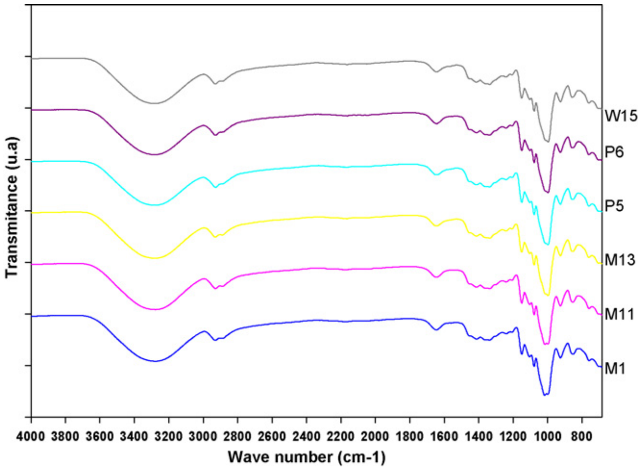


Fig. 1. Infrared spectroscopy in films obtained by the extrusion process.

The sharp peak at 2935–2918 cm^{-1} was related to the CH stretching in starch. The sharp peak at 2939 cm^{-1} is characteristic of C–H stretch. Dyer (1968) reported that the different types of vibrations of C–H linkages were localized in the area from 1900 to 3000 cm^{-1}. Aguilar-Palazuelos, Martínez-Bustos, Jiménez-Arévalo, Galicia-García, and Delgado-Rangel (2007, Chap. 10) found that the reduction in the intensity of the peaks of vibration of C–H linkages from 2800 to 2400 cm^{-1}, probably can be attributed to the possible breaking of these linkages, due to the effect of the process (extrusion, injection-moulding) in biodegradable materials of blends of corn starch–fiber–glycerol. The films prepared in this work did not show these differences, indicating that the processing conditions were less severe and did not degrade these linkages. The peaks found at 1651–1633 cm^{-1} were the δOH bend of water (water deformation band) and were representative of the bound water present in starch (Mousia, Farhat, Pearson, Chesters, & Mitchell, 2001; Pushpadass et al., 2009) and specifically at 1648 cm^{-1} water in starch and strictly bonded probably ester carbonyl (Zullo & Iannace, 2009), this behaviour was intensified in M1 sample, corroborated with the high water absorption capacity (89%).

In the vibrational range from 1417 to 1396 cm^{-1} and from 1351 to 1321 cm^{-1} there was observed a bending band attributable to a CH bending in starch. According to Pushpadass et al. (2009) this double peak is characteristic of extruded films compared with the single peak in native corn starch. Around 1020–994 and 1074–1080 cm^{-1}, they presented vibration mode characteristics of stretching C–O–C and C–O–H in the starch, this finishes that vibration presents the influence of intermolecular water content of hydrogen bonds, as well as the relation of amylose–amylopectin (Van Soest, Tournois, de Wit, & Vliegenthart, 1995) as showed in sample W15 where it is possible to observe the increment of a peak intensity, contrary to the rest of the samples.

According to Yu, Yang, Liu, and Ma (2009) and Chang, Jian, Zheng, Yu, and Mab (2010) the characteristic peaks of microcrystalline cellulose are those where the –C–O bond stretching of –C–O–H group appeared at about 1112 cm^{-1}, and the –C–O bond stretching of –C–O–C group in the anhydroglucose ring appears at about 1056 cm^{-1}. These peaks shifted to higher wavenumbers (around

1126 and 1063 cm^{-1}, respectively) in cellulose nanoparticles. This shift might be related to the weakening of the hydrogen-bond interactions among the cellulose molecules (Ma et al., 2008; Zullo & Iannace, 2009), which reported a new peak between 1015 and 1018 cm^{-1} in the thermoplastic starch suggesting that new interactions and vibration modes are occurring after thermoplasticization and the peak at 995 cm^{-1} was attributed to glycerol–starch interaction, these behaviors were observed in analyzed films. These peaks are present in our films. Below 900–750 cm^{-1}, the peaks are inside the range that corresponds to vibration modes of bonds C–C, C–O.

3.2. X-ray diffraction patterns

Native starches are biosynthetically assembled as semi-crystalline granules. The A-type structure is characteristic of a double helix in maize starch while a B-type of crystallinity is present in potato starch, while the C-type structure is more rare and is thought to be an intermediate form occurring in some plant sources such as pea starch, probably to the combination between A and B (Ratnayake, Hoover, & Warkentin, 2002; Sarko & Wu, 1978; Vermeylen, Goderis, Reynaers, & Delcour, 2004). There are also crystallinity forms induced by kneading, extrusion, compression molding, or injection molding of several native starches with glycerol as a plasticizer called V_H-, V_A-, or E_H that depend on the composition of starch, the plasticizer and the process parameters (Ma & Yu, 2004).

Fig. 2a shows the diffractograms of corn starch film without and added with fiber (M11, M13) and the films of phosphorylated corn starch (M1). The films showed the characteristic patterns type A, which are typical of cereal starch (Thomas & Atwell, 1997), with relation to data reported in the literature (Le Bail, Bizot, & Buleon, 1993).

Peaks at 2θ values ≈14.98° and 22.98° were observed in M1 films, and 2θ values ≈15.03° and 22.98° in M11 films could be associated to V_H-, V_A-, or V-glycerol crystallinity (Rappenecker & Zugenmaier, 1981). Zullo and Iannace (2009) found that in film blowing, the thermoplastic starch with glycerol the crystalline peak did not disappear. However a new crystalline structure was developed (V_H and V_A crystalline type). The morphological transition experimented by starch into the new form during processing in the presence of glycerol has been previously reported by some researchers (Bastioli, 1998; Da Róz, Carvalho, Gandini, & Curvelo, 2006; Van Soest & Essers, 1997) and also, the V_A- type crystallinity has been reported in thermoplastic starch (Dai, Chang, Peng, Yu, & Ma, 2009). According to Rappenecker and Zugenmaier (1981) and Buléon, Delage, Brisson, and Chanzy (1990), V_H led to V_A upon dehydration, conversely V_A led to V_H upon hydration. In the analyzed samples, probably after the extruded samples were exposed to the environment, the V_A type crystallinity was also changed to V_H due to hydration.

Raquez et al. (2008) reported that in the presence of plasticizers, the native starch was destructured under heating and shearing conditions, which broke the hydrogen bonds in starch, so-destroying partially its initial crystalline nature. In films M1, M11, and M13, the change of the original A-type crystallinity of starch was substituted by a B-type as reported by various authors (Da Róz et al., 2006; Galliard & Bowler, 1987; Larotonda, Matsui, Soldi, & Laurindo, 2004; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Nakano et al. (2003) reported the presence of two peaks (2θ = 37° and 53°) in phosphorylated starch prepared by a conventional process probably due to phosphate sales. However the phosphorylated films did not show these peaks, probably due to the conditions used during an extrusion–calendering process that modifies the crystalline structure. Some fragments of fiber were attached to the starch matrix decreasing in low proportion the plasticizing effect, however, improving the mechanical properties.

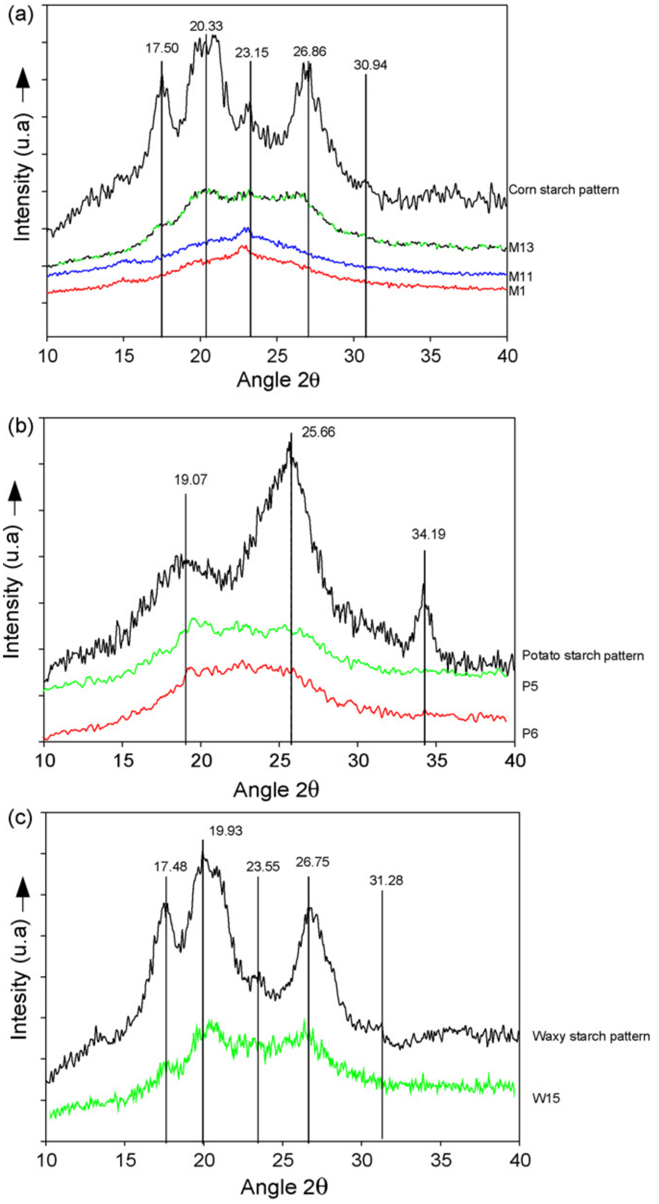


Fig. 2. X-ray diffractograms of (a) corn starch film, (b) potato starch film, (c) waxy corn starch film.

Potato starch films showed a characteristic X-ray pattern of tubers (type B) (Lineback, 1984) and related with literature values (Van Soest et al., 1996). The presence of two peaks was observed at 2θ values ≈19.73° and 25.56° in P5 film; and 19.41° and 26.12° in P6 film (Fig. 2b). The potato sample without fiber (P6) showed the presence of two peaks mainly due to the interaction between starch and a plasticizing agent that decreases the structural starch reorganization (retrogradation) (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Van Soest et al., 1996). This effect was decreased with the incorporation of fiber as observed in the P5 sample, where the diffractogram showed low intensity compared to the film fabricated with corn starch (M13); attributable to the morphology and size of potato starch granule (oval spherical, and mean size of 100 μm) (Marie-Astrid, Sandra, & Imad, 2005).

The diffractograms of waxy corn starch films (W15) showed a characteristic X-ray pattern of cereal (A-type), with three peaks at 2θ values ≈17.56°, 20.25° and 26.44° (Fig. 2c). These films did not show an increase in the structure type V characteristic of several processes of starch with high amylopectin content (Raquez et al., 2008). Two overlapped weaker peaks at about 14.8° and 16.1° in samples added with fiber can be associated with microcrystalline cellulose (Duchemin, Staiger, & Tucker, 2010; Chang et al., 2010). Also, two overlapped peaks at 20.1° and 22.4°, were ascribed to cellulose II (1–10/200) and cellulose I (200) reflection (Chang et al., 2010).

3.3. Relative crystallinity index (RCI)

RCI of corn films with and without fiber was 26.61% and 31.63%, respectively, potato 17.08% and 26.11%, respectively, and waxy corn 26.81%. The films with fiber increased the RCI in approximately 10%, to difference of without fiber samples. Aguilar-Palazuelos, Zazueta-Morales, and Martinez-Bustos (2007) found that increasing feed moisture during the extrusion of blends fiber–starch the crystallinity increased. Da Róz et al. (2006) indicated that the increase in crystallinity was probably facilitated by the progressively higher chain mobility associated with the higher corresponding plasticizer concentrations. Thermoplastic starch that is prepared by kneading, extrusion, compression molding, or injection molding of several native starches with glycerol as a plasticizer, may exhibit two types of distinguished crystallinity directly after processing. (1) Residual crystallinity: native A-, B-, or C-type crystallinity caused by an incomplete melting of starch during processing. (2) Processing-induced crystallinity: amylose V_H-, V_A-, or V-glycerol-type crystallinity, which is formed during thermo-mechanical processing (Raquez et al., 2008; Van Soest et al.,1996).

3.4. Scanning electronical microscopy (SEM)

The morphology of composites is a very important characteristic because it ultimately determines many properties of the biodegradable materials. The structure surface analysis obtained by SEM of the films showed in general, a smooth surface, typical of homogeneous amorphous material. Continuous phase formed by the plasticizer starch and fiber was observed, fact that was the foundation of preparing the films with a high performance. Similar results have been reported by various authors for thermoplastic starch (Da Róz et al., 2006; Mathew & Dufresne, 2002a; Mathew & Dufresne, 2002b). Fig. 3a illustrates the micrographs of the films at 350× magnifications. The superficial structure is free of cracks and pores that could indicate the presence of fragility and rigidity in films (López, García, & Zaritzky, 2008), the presence of creases was due to low structural order among starch chains decreasing the associations due to the plasticizing effect (Sothornvit & Krochta, 2005). During the processing of starch–fiber-plasticizing, water and glycerol disrupt inter- and intramolecular hydrogen bonds, physically is given the breaking of starch granules, making the starch become a continuous phase.

3.5. Differential scanning calorimetry (DSC)

Forssell, Mikkila, Suortti, Seppala, and Poutanen (1996) reported that it is unfeasible to detect any melting temperature for native starch, attesting for the thermal degradation of starch before it melted. All of the films processed without fiber showed an inflection of temperature at 120 °C, this could be due to the evaporation of water, the samples processed with fiber showed a different behavior where the hydrophillic nature of the fibers retards the loss of water. At 160 °C was found a second inflection of temperature associated to the initial decomposition of plasticizing (Álvarez, Vázquez, & Bernal, 2005; Wu et al., 2003) where the movement of starch chains is restricted (Xiang, Tang, Tang, & Zou, 2008) (Fig. 4a). Raquez et al. (2008) found that the melting temperature of thermoplastic starch was around 153 °C, this value was 10 °C higher than the thermoplastic films starch. This difference in melting behavior for maleated thermoplastic starch was attributed to the maleation process, which had chemically modified the whole structure of native starch backbone. A range of temperature from 20 to 100 °C showed a behavior with few changes, therefore the variation of heating capacity (ΔCp) was analyzed, that can be related to a transition of second order, where the chain segments are provided with

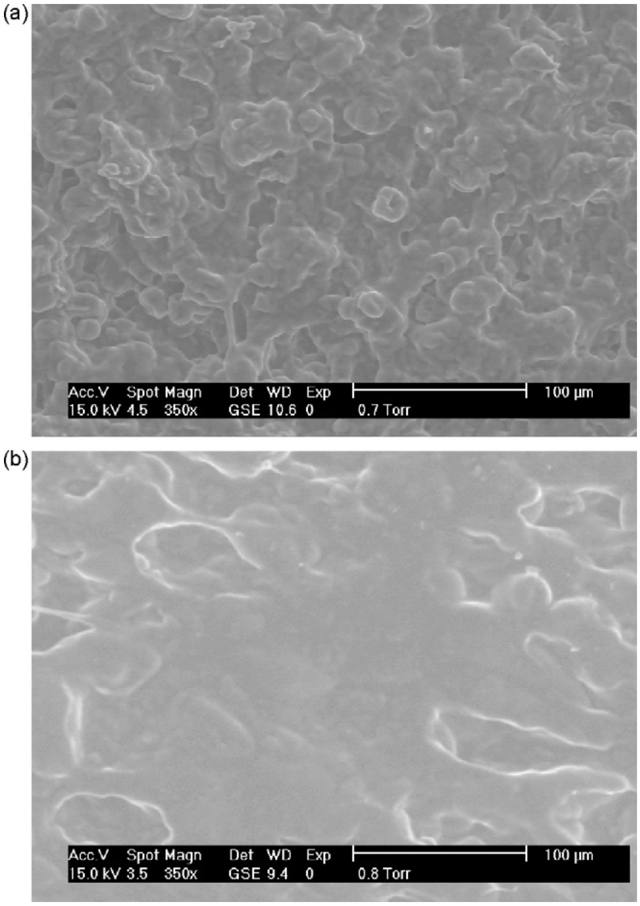


Fig. 3. Micrographs of the films: (a) superficial fields; (b) transversal fields.

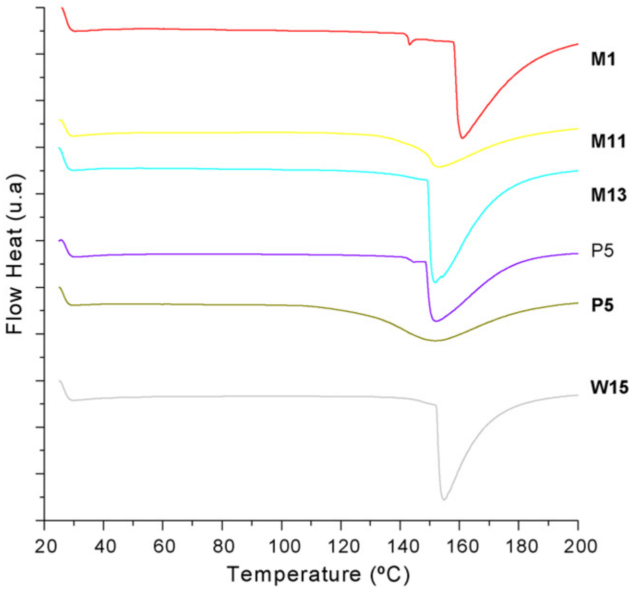


Fig. 4. DSC in films obtained by the extrusion process.

energy to confer mobility to the rotation of lateral groups around their primary links (vitreous transition, T_g) in a range from 40 to 80 °C.

3.6. Dynamic mechanical analyses (DMA)

The dynamic storage modulus (E'), loss modulus (E''), and mechanical loss tangent ($\tan\delta = E''/E'$) with the change of temperature were measured by the dynamic mechanical thermal analysis (DMTA). A decreasing E' and the increasing $\tan\delta$ indicated the elasticity of the material decreased, and the material was easier to permanently deform. The inflections in the E' and E'' temperature were accompanied by peaks in $\tan\delta$, which was the representation of a material molecular transition, such as the glass transition temperature T_g, the transition point from the glassy to a rubber state.

The T_g of dry corn starch was about 210 or 230 °C, could not be measured directly, (because it was very close to the decomposition temperature 225–250 °C) (Bikiaris et al., 1998; Huang, Yu, & Ma, 2006). Various researchers (Chen, Yu, Kealy, Chen, & Li, 2007; Laaksonen & Roos, 2000; Mano, Reis, & Cunha, 2000; Thomazine, Carvalho, & Sobral, 2005) reported that the DMA had a great functionality in measuring the viscoelastic properties of biopolymers as well as starch-based films, and the good miscibility in thermoplastic starch (Jiang, Qiao, & Sun, 2006). The moduli represent the mechanical characteristics of a starch viscoelastic system during gelatinization and retrogradation processes. The important aspect of retrogradation is the increase of storage modulus (E'), which is treated as the measurement of retrogradation.

In a range of temperature from 30 to 80 °C the material showed a decrease in the E' values, due to the fact this material was processed under mild conditions, and was further, heated again and thus, the material showed a high mobility at a structural level (unions among polymeric chains) (Yu et al., 1998) and also was soft as well as showed more elongation (ΔL) when it was subjected to traction in thermal analyses equipment (Avérous, Fringant, & Moro, 2001). Huang et al. (2006) revealed that the specific heat increments in DSC analysis of thermoplastic cornstarch biodegradable nanocomposites plasticized with urea and formamide were located at 29 °C, and those of biodegradable nanocomposites were located at 35 °C, which were basically accordant to the two transitions measured by DMTA. The decreasing in E' was found with low quantity proportion in the samples with added fiber (M13, P5 and W15) (Fig. 5a).

The E'' values in the samples M13 and W15 presented a continuous behavior, indicating that in materials added with fiber in low proportion the molecular mobility decreased due mainly to the inclusion of fiber into the starch matrix (Álvarez & Vazquez, 2004) (Fig. 5b). In the range of temperature from 90 to 150 °C the material showed an increment of E' related to lack of flexibility, this could be due to the loss of water that is trapped in the polymer starch as the plasticizing, contrary to E'' where it showed a higher dissipation energy due to an increase in the plasticizing effect in the starch matrix, together with water evaporation, this effect was more evident in the samples with fiber (3.5×10^7 a 6.5×10^7), the samples P5 showed a high value of E'' (6×10^7 MPa), this can be due to size of starch granules; potato starch had starch granules with a bigger diameter than the corn starch granules this decrease the fiber effect. Thus the resulted material showed more elasticity due to better interacting starch-plasticizing-starch (Yu et al., 1998).

The behavior of $\tan\delta$ (Fig. 5c) showed a loss of structural mobility at a small scale with an increase from 0.15 to 0.30, hence, indicating two possible discreet transitions related to material crystallization (αc). At a range of temperature from 160 to 190 °C, a drastic decrease of the E' and E'' values was experimented indicating that the mobility of the linkages was decreased, as well as the distance among polymeric chains: the flow of the samples that had fiber tends to remain at a higher temperature, probably this is due to the remainder of moisture of fiber attached in the starch matrix (Álvarez & Vazquez, 2004). Above 200 °C a stable behavior was found at low values of E', E'' and $\tan\delta$ due to the degradation of the material of most of the compounds. The $\tan\delta$ curves for all the samples showed two relaxations, which appeared, respectively, approximately between 75 and 40 °C and between 70 and 150 °C. The high temperature relaxation was attributed to the glass transition temperature of the corresponding thermoplastic starch, whereas the low temperature peak could have arisen from a plasticizer-rich phase, as already suggested by other authors (Curvelo, Carvalho, & Agnelli, 2001; Mathew & Dufresne, 2002a).

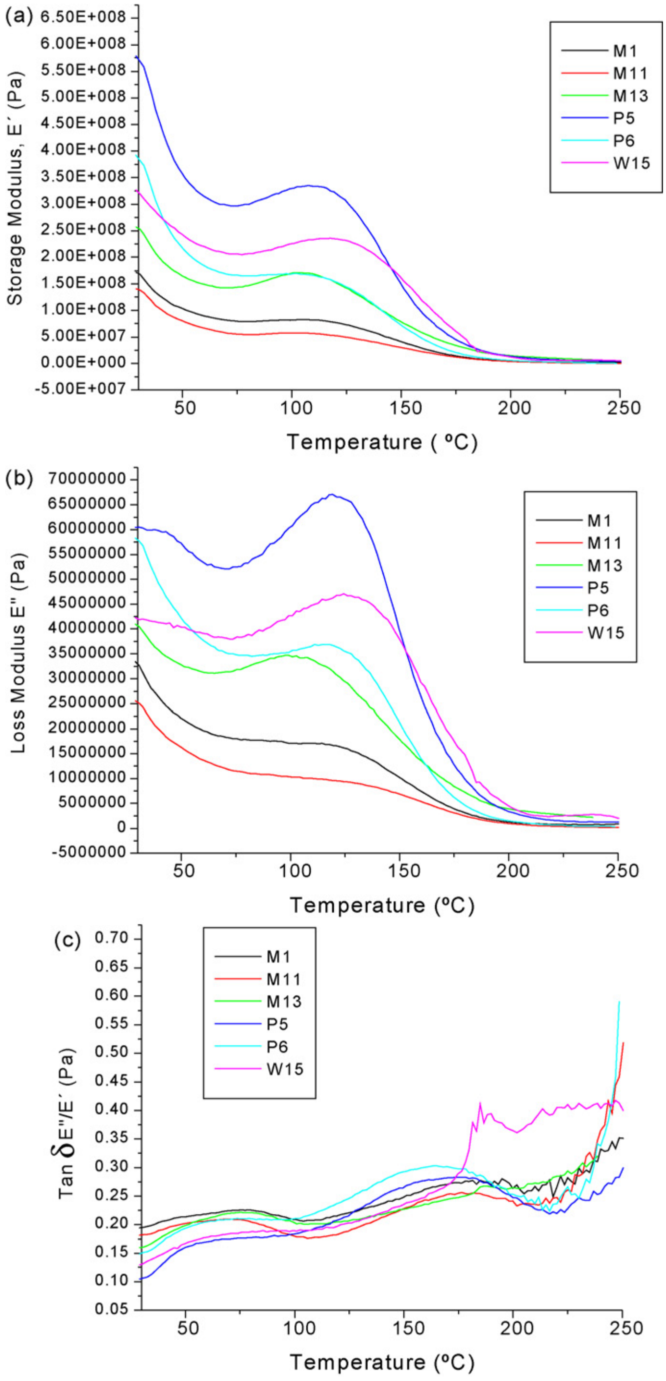


Fig. 5. Behavior of (a) storage modulus (E'), (b) loss modulus (E''), (c) $\tan\delta$ (E''/E'), with relation to temperature of extruded-calendering films.

4. Conclusions

The highest values of mechanical properties (σ_r, ε, and E) were for the films fabricated with phosphorylated or native corn starches. These properties were reinforced with the incorporation of fiber values up to 5%. Samples with fiber (M13 and P5) showed higher E values than samples without fiber (M11 and P6), this effect was more evident in potato starch than in corn starch. The films showed smaller thickness (0.02–0.04 mm). The technical data of films processed with potato starch (P5 and P6) were similar in mechanical properties to those used to fabricate commercial bags (PEBD, PEAD). The water absorption capacity analysis and disintegration index indicated the biodegradability of the films. High fiber contents impart a dark color tone to the films. These new materials acquired properties that can meet the increasing demand for biodegradable disposable plastic bags.

References

Aguilar-Palazuelos, E., Martínez-Bustos, F., Jiménez-Arévalo, O. A., Galicia-García, T., & Delgado-Rangel, J. A. (2007). Potentiality of some natural fibers and native starch for making biodegradable materials. In T. P. Klening (Ed.), *Food engineering research developments* , ISBN 1-60021-906-3 (pp. 279–294). New York: Nova Science Publishers Inc.

Aguilar-Palazuelos, E., Zazueta-Morales, J. J., & Martinez-Bustos, F. (2007). Extrudates produced from blends of native starches and natural fibers of henequen and coconut. *Starch/Stärke*, *59*, 1–10.

Álvarez, V., & Vazquez, A. (2004). Thermal degradation of cellulose derivates/starch blends and sisal fibre biocomposites. *Polymer Degradation and Stability*, *84*, 13–21.

Álvarez, V., Vázquez, A., & Bernal, C. (2005). Fracture behavior of sisal fiber–reinforced starch-based composites. *Polymer Composite*, *26*(3), 316–323.

Angellier, H., Molina-Boisseau, S., Dole, P., & Dufresne, A. (2006). Thermoplastic starch–waxy maize starch nanocrystals nanocomposites. *Biomacromolecules*, *7*, 531–539.

Armelin, E. (2002). *Síntesis y caracterización de nuevas poliesteramidas: estudio de sus propiedades*. Tesis Doctoral. Barcelona, España: Universidad Politécnica de Cataluña.

Avérous, L., Fringant, C., & Moro, L. (2001). Plasticized starch–cellulose interactions in polysaccharide composites. *Polymer*, *42*, 6565–6572.

Bastioli, C. (1998). Properties and application of Mater-Bi starch-based materials. *Polymer Degradation and Stability*, *59*, 263–272.

Bernard, C., Gontard, N., & Guilbert, S. (1998). Proteins as agricultural polymers for packaging production. *Cereal Chemistry*, *75*(1), 1–9.

Bhattacharya, D., Germinario, L. T., & Winter, W. T. (2008). Isolation, preparation and characterization of cellulose microfibers obtained from bagasse. *Carbohydrate Polymers*, *73*, 371–377.

Biliaderis, C. G., Lazaridou, A., & Arvanitoyannis, I. (1999). Glass transition and physical properties of polyol-plasticised pullulan–starch blends at low moisture. *Carbohydrate Polymers*, *40*, 29–47.

Bikiaris, D., Prinos, J., Koutsopoulos, K., Vouroutzis, N., Pavlidou, E., & Frangis, N. (1998). LDPE/plasticized starch blends containing PE-g-MA copolymer as compatibilizer. *Polymer Degradation and Stability*, *59*, 287–291.

Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, *24*(2), 221.

Buléon, A., Delage, M. M., Brisson, J., & Chanzy, H. (1990). Single crystals of V amylose complexed with isopropanol and acetone. *International Journal Biological Macromolecules*, *12*, 25–33.

Chang, P. R., Jian, R., Zheng, P., Yu, J., & Mab, X. (2010). Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites. *Carbohydrate Polymers*, *79*, 301–305.

Chen, P., Yu, L., Kealy, T., Chen, L., & Li, L. (2007). Phase transition of starch granules observed by microscope under shearless and shear conditions. *Carbohydrate Polymers*, *68*, 495–501.

Cuq, B., Gontard, N., & Guilbert, S. (1997). Thermoplastic properties of fish myofibrillar proteins: Application to the biopackaging fabrication. *Polymer*, *38*, 4071–4078.

Curvelo, A. A. S., Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch–cellulosic fibers composites: Preliminary results. *Carbohydrate Polymers*, *45*, 183–188.

Dai, H., Chang, P. R., Peng, F., Yu, J., & Ma, X. (2009). N-(2-Hydroxyethyl) formamide as a new plasticizer for thermoplastic starch. *Journal of Polymer Research*, *16*, 529–535.

Da Róz, A. L., Carvalho, A. J. F., Gandini, A., & Curvelo, A. A. S. (2006). The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydrate Polymers*, *63*, 417–424.

Duchemin, B. J. C., Staiger, M. P., & Tucker, N. (2010). Aerocellulose based on all cellulose composites. *Journal of Applied Polymer Science*, *115*(1), 216–221.

Dyer, J. R. (1968). *Application of absorption spectroscopy of organic compounds*. Englewood Cliffe, N.J.: Prentice-Hall Inc.

Fang, J. M., Fowler, P. A., Tomkinson, J., & Hill, C. A. S. (2002). The preparation and characterization of a series of chemically modified potato starches. *Carbohydrate Polymers*, *47*, 245–252.

Fernández-Rodríguez, N. (2000). *El bagazo y las fibras anuales: presente y futuro para su industrialización*. La Habana, Cuba: Congreso Iberoamericano de Investigación en Celulosa y Papel.

Fellows, M. (2000). *Tecnología del procesado de los alimentos* (2ª ed.). S.A. Zaragoza España: Ed ACRIBIA.

Felix, J. M., & Gatenholm, P. (1991). The nature of adhesion in composites of modified cellulose fibers and polypropylene. *Journal of Applied Polymer Science*, *42*, 609–620.

Forssell, P., Mikkila, J., Suortti, T., Seppala, J., & Poutanen, K. (1996). Plasticization of barley starch with glycerol and water. *Journal of Macromolecular Science—Pure and Applied Chemistry*, *A33*, 703.

Galliard, T., & Bowler, P. (1987). Morphology and composition of starch. In T. Galliard (Ed.), *Critical reports on applied chemistry, 13, starch: Properties and potentials*. Great Britain: Wiley.

Galicia-García, T., Martínez-Bustos, F., Jiménez-Arévalo, O. A., & Aguilar-Palazuelos, E. (2007). Mechanical properties of extruded biodegradable films of native starch and sugar cane fibre. In T. P. Klening (Ed.), *Food engineering research developments* , ISBN 1-60021-906-3 (pp. 263–278). New York: Nova Science Publishers Inc.

Galicia-García, T., Martínez-Bustos, F., Jiménez-Arévalo, O., Martínez-Benasat, A., Arencon, D., & Gamez, J. (2009). Caracterización microestructural de películas a base de almidón de maíz ceroso y bagazo de caña de azúcar obtenidas por el proceso de extrusión termoplástica. In *Em: Memorias de 8° Simpósio Latino Americano de Ciência de Alimentos (SLACA)* 08 a 10 de Novembro de 2009, Centro de Convenções UNICAMP, Campinas, São Paulo, Brasil.

Guilbert, S., Gontard, N., & Gossis, L. G. M. (1996). *Food Science & Technology—Lebesmittel Wissenschaft & Technologie*, *29*, 10.

Huang, M., Yu, J., & Ma, X. (2006). High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. *Carbohydrate Polymers*, *63*(3), 393–399.

Jiang, W., Qiao, X., & Sun, K. (2006). Mechanical and thermal properties of thermoplastic acetylated starch/poly(ethylene-co-vinyl alcohol) blends. *Carbohydrate Polymers*, *65*, 139–143.

Kumar, B. V. N., Sairama, M., Rajub, K. V. S. N., & Aminabhavi, T. M. (2005). Thermal, viscoelastic, solution and membrane properties of sodium alginate/hydroxyethylcellulose blends. *Carbohydrate Polymers*, *61*, 52–60.

Laaksonen, T. J., & Roos, Y. H. (2000). Thermal, dynamic-mechanical, and dielectric analysis of phase and state transitions of frozen wheat doughs. *Journal of Cereal Science*, *32*(3), 281–292.

Larotonda, F. D. S., Matsui, K. N., Soldi, V., & Laurindo, J. B. (2004). Biodegradable films made from raw and acetylated cassava starch. *Brazilian Archives of Biology Technology*, *47*(3), 477–484.

Le Bail, P., Bizot, P., & Buleon, A. (1993). B to A type phase transition in short amylose chains. *Carbohydrate Polymers*, *21*, 99–104.

Lineback, D. R. (1984). The starch granule: Organization and properties. *Bakers Digest*, *58*(29), 16–21.

López, O. V., García, M. A., & Zaritzky, N. E. (2008). Film forming capacity of chemically modified corn starches. *Carbohydrate Polymers*, *73*(1), 573–581.

Ma, X. F., Jian, R. J., Chang, P. R., & Yu, J. G. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites. *Biomacromolecules*, *9*, 3314–3320.

Ma, X., & Yu, J. (2004). The plasticizers containing amide groups for thermoplastic starch. *Carbohydrate Polymers*, *57*, 197–203.

Mano, J. F., Reis, R. L., & Cunha, A. M. (2000). Effects of moisture and degradation time over the mechanical dynamical performance of starch based biomaterials. *Journal of Applied Polymer Science*, *78*, 2345–2357.

Marie-Astrid, O., Sandra, E. H., & Imad, A. F. (2005). Comparative study of the retrogradation of intermediate water content waxy maize, wheat, and potato starches. *Journal of Agriculture and Food Chemistry*, *53*, 631–638.

Mathew, A. P., & Dufresne, A. (2002a). Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules*, *3*(5), 1101–1108.

Mathew, A. P., & Dufresne, A. (2002b). Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules*, *3*, 609–617.

Mohanty, A. K., Misra, M., & Hinrichsen, G. (2002). *Macromolecules. Materials and Engineering*, *276*, 1–24.

Mousia, Z., Farhat, I. A., Pearson, M., Chesters, M. A., & Mitchell, J. R. (2001). FTIR microspectroscopy study of composition fluctuations in extruded amylopectin–gelatin blends. *Biopolymers (Biospectroscopy)*, *62*, 208–218.

Navarro, A. S., Martino, M. N., & Zaritzky, N. E. (1997). *Journal of Food Engineering*, *34*, 411.

Netravali, A. N. (2005). Biodegradable natural fiber composites. In *Biodegradable and sustainable fibres*. Cambridge, England: Woodhead Publishing Limited.

Nakano, H., Kiso, T., Okamoto, K., Tomita, T., Manan Bin, A. M., & Kitahata, S. (2003). Synthesis of glycosyl glycerol by cyclodextrin glucanotransferases. *Journal of Bioscience and Bioengineering*, *95*(6), 583–588.

Paschall, E. F. (1964). Phosphorylation with inorganic phosphate salts. *Methods Carbohydrates. Chemistry*, *4*, 296.

Pushpadass, H., Marx, D., Wehling, R., & Hanna, M. (2009). Extrusion and characterization of starch films. *Cereal Chemistry*, *86*(1), 44–51.

Rabek, J. (1980). *Experimental methods in polymer chemistry: Application of wide-angle X-ray diffraction (WAXD) to the study of the structure of polymers*. UK: Wiley-Interscience Chichester., p. 505.

Rappenecker, G., & Zugenmaier, P. (1981). Detailed refinement of the crystal structure of Vh-amylose. *Carbohydrates Research*, *89*, 11–19.

Raquez, J.-M., Nabar, Y., Srinivasan, M., Shin, B.-Y., Narayan, R., & Dubois, P. (2008). Maleated thermoplastic starch by reactive extrusión. *Carbohydrate Polymers*, *74*, 159–169.

Ratnayake, W. S., Hoover, R., & Warkentin, T. (2002). Pea starch: Composition, structure and properties—A review. *Starch/Stärke*, *54*, 217.

Sarko, A., & Wu, H. C. H. (1978). The crystal structures of A-, B- and C polymorphs of amylose and starch. *Starch/Stärke*, *30*, 73.

Slade, L., & Levine, H. (1995). Glass transition and water food structure interactions. *Advances in Food Nutrition Research*, (38), 103–234.

Sothornvit, R., & Krochta, J. M. (2005). Plasticizer in edible films and coatings, in Innovations. In J. H. Han (Ed.), *Innovations in foods packings*. Netherlands: Amsterdan, pp. 403–428.

Thomas, D. J., & Atwell, W. A. (1997). *Starches, practical guides for the food industry*. St. Paul, MN, USA: Eagan Press.

Thomazine, M., Carvalho, R. A., & Sobral, P. I. A. (2005). Physical properties of gelatin films plasticized by blend of glycerol and sorbitol. *Journal of Food Science*, *70*(3), E172–E176.

Van Soest, J., Hulleman, S., de Wit, D., & Vliegenthart, J. (1996). Crystallinity in starch bioplastics. *Industrial Crops and Products*, *5*, 11–22.

Van Soest, J. J. G., & Essers, F. (1997). Influence of amylose–amylopectin ratio on properties of extruded starch plastic sheets. *Journal of Macromolecular Science–Pure and Applied Chemistry*, *A34*, 1665–1689.

Van Soest, J. J. G., Tournois, H., de Wit, D., & Vliegenthart, J. F. G. (1995). Short-range structure in (partially) crystalline potato starch determinated with attenuated total reflectance Fourier-transform IR spectroscopy. *Carbohydrate Research*, *279*, 201–214.

Vermeylen, R., Goderis, B., Reynaers, H., & Delcour, J. A. (2004). Amylopectin molecular structure reflected in macromolecular organization of granular starch. *Biomacromolecules*, *5*(5), 1775.

Wilson, R. H., & Tapp, H. S. (1999). Mid-infrared spectroscopy for food analysis: Recent new applications and relevant developments in sample presentation methods. *TRAC-Trends in Analytical Chemistry*, *18*(2), 85–93.

Wu, Q., Sakabe, H., & Isobe, S. (2003). Processing and properties of low cost corn gluten meal/word fiber composite. *Industrial Engineering Chemistry Research*, *42*, 6765–6773.

Xiang, H., Tang, S., Tang, H., & Zou, P. (2008). The structure and properties of a starch-based biodegradable film. *Carbohydrate Polymers*, *71*, 263–268.

Yu, J., Chen, S., Gao, J., Zheng, H., Zhang, J., & Lin, T. (1998). A study on properties of starch/glicerine blend. *Starch/Stärke*, *50*(6), 246–250.

Yu, J. G., Yang, J. W., Liu, B. X., & Ma, X. F. (2009). Preparation and characterization of glycerol plasticized-pea starch/ZnO–carboxymethylcellulose sodium nanocomposites. *Bioresource Technology*, *100*, 2832–2841.

Zhang, Y., & Han, J. (2006). Plasticization of pea starch film with monosaccharides and polyols. *Journal of Food Science*, *71*, E253–E261.

Zullo, R., & Iannace, S. (2009). The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure. *Carbohydrate Polymers*, *77*, 376–383.