Effect of Chitin Addition on Injection-Molded Thermoplastic Corn Starch

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ABSTRACT: A new type of biodegradable starch-based composites was prepared by injection-molding using glycerol and water as plasticizers. Chitin flakes, obtained from shells of *Penaeus schmitti*, were used as reinforcing phase. The effect of chitin content on the structural and tensile properties of the composite samples was examined after conditioning at 28°C and 80% relative humidity for 30 days. In general, chitin incorporation into the starch matrix resulted in materials with higher modulus and decreased elongation at break. Wide-angle X-ray diffraction and differential scanning calorimetry evidenced a significant decrease in crystallinity in the composite samples in relation to the unfilled starch material. Contact angle measurements revealed that the addition of chitin contributes to the improvement of water resistance of the composite samples when compared to injection molded starch alone. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2706–2713, 2004

Key words: biodegradable; composites; injection molding; renewable resources; thermoplastics

INTRODUCTION

Environmental pollution by synthetic polymers, owing to their high molecular weight, low surface-to-volume ratio, chemical and microbiological stability, has been recognized as the cause of growing concern. In the last 2 decades, attention has been focused on studies related to the substitution of synthetic polymers, at least in some of their applications. Biodegradable materials have been considered for various uses, from agricultural, and packaging uses to applications in the medical field.[1,2]

Starch and chitin, natural polymers obtained from renewable resources, have different properties. Starch is a major energy source in human diet, and has been used in the food industry mainly as gels. Recently, there has been increasing interest in the nonfood uses of starch, especially as a candidate to substitute polymers as a thermoplastic, because of its total biodegradability and worldwide availability at low cost. Starch can be extracted from grains, tubers, and roots as semicrystalline granules, which contain basically a mixture of the polysaccharides amylose and amylopectin, both polymers formed of α-D-glucose repeating units. Amylose is an essentially linear α-(1,4)-linked D-glucan. Amylopectin is the highly branched component of starch with α-(1,6)-linked branch points.

The granule crystallinity is associated with the short, linear chains of amylopectin, which assume double helical conformation arranged in crystalline lamellar domains.[3,4] Wide-angle X-ray diffraction studies of native starches give patterns that differ accordingly to their botanical origin: A-type from cereals and B-type from tubers. The main difference between A- and B-type crystallinities is the packing density of the double helices in the unit cell, more loosely packed in B-type starches.[5,6]

Native starch can be transformed into a thermoplastic material (TPS) through thermomechanical treatment in the presence of suitable plasticizers, such as water, glycerol, and lecithin.[7–12] The sensitivity of TPS to the humidity atmosphere has been a drawback of its commercial use, because its mechanical behavior is dependent on moisture content.

In general, physical properties of polymer materials are improved through appropriate compounding with fibers and other fillers. Cellulose microfibrils, obtained experimentally by chemical and mechanical treatments from potato pulp, have been used as a reinforcing phase in potato starch cast films.[13] Water uptake was reported to decrease with filler content. In relation to unfilled starch, composite modulus was shown to increase above T_g, even with a low filler content.

Chitin is a linear polysaccharide, composed of (1,4)-β-2-deoxy-2-acetamido-D-glucose repeating units. It is similar to cellulose from the viewpoint of both structure and abundance in nature, and is characterized by its insolubility in most common solvents. Chitin is

usually found in the supporting tissues of invertebrate animals, fungi, and bacteria.[14] In the native state, this biopolymer occurs associated with proteins, pigments, lipids, and inorganic substances, forming reinforced biocomposites.[15] Discarded crustacean exoskeletons are important source of chitin, which is found as highly crystalline microfibrils.[15,16] Chitin is a specially attractive polymer because of its potential applicability in many fields such as in separation membranes, chelating agents, cosmetics, and biodegradable and biomedical materials.[17] Chitin may be considered a relatively expensive biopolymer. However, its abundance in nature and the development of optimized methods of extraction justify the generalized use of this polymer.[18]

In the present work, plasticized corn starch/chitin composites were obtained by injection molding with the objective to obtain biodegradable thermoplastic starch with improved resistance to humidity as well as good mechanical and thermal properties. Chitin from *Penaeus schmitti* shells was used as flakes. The results of tensile tests, wide-angle X-ray diffraction, differential scanning calorimetry, and contact angle measurements were evaluated as a function of chitin composition.

EXPERIMENTAL

Materials

Corn starch, composed of 26–30% amylose and 74–70% amylopectin, and with less than 0.5% gluten was supplied by Corn Products Brazil (São Paulo, Brazil). Corn starch was dispersed in distilled and deionized water under vigorous stirring for 4 h. The dispersion was filtered and the recovered solid was dried in an oven at 50°C to constant weight (48 h), and milled. The water content of purified starch was determined by difference analysis as 4%, after 15 days at ambient conditions.

The chitin sample was isolated from shells of adult *Penaeus schmitti*, after demineralization and deproteinization. For demineralization, shells were treated with 0.6 *N* HCl for 24 h and washed with water until reaching neutral pH. For deproteinization, the resulting material was treated with 1.25 *N* NaOH at 95°C for 2 h. The material was thoroughly washed in distilled water to neutral pH and dried in an oven at 50°C. Residual pigments were removed by immersing the sample successively in ethyl alcohol and acetone baths for 3–4 days. Final drying was achieved at 50°C to constant weight. Chitin films were milled in a P1003 Primotécnica mill (Mauá, Brazil). The resulting flakes, on average 1 mm in size, were stored in a closed vessel before use. The water content of the flakes was determined by difference analysis as 2%, after 15 days at ambient conditions.

Glycerol, NaOH, HCl, acetone, and ethyl alcohol were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil) and were used as received.

Methods

Preparation of plasticized mixtures

To obtain homogeneous mixtures, to a constant weight of starch, glycerol (15 wt %), water (15 wt %), and chitin were mixed in a blender for 10 min. The chitin content was varied between 0 and 30 wt % (based on starch dry weight). The mixtures were stored in polyethylene bags before processing.

Injection molding

The plasticized mixtures were injection molded into ASTM D638-72 Type I specimens, approximately 2 mm thick, using a PicBoy 15/42 Petersen Irmãos Machine (São Paulo, Brazil), provided with three electrically heating zones, maintained at 130, 130, and 145°C from feed zone to die end. The mixtures were manually fed into the machine and the injection pressure was kept at 113 bar. The injection mold was cooled at 30–40°C by a refrigeration system and kept closed at 1275 bar. Plasticized starch was processed under the same conditions.

Conditioning

Injection-molded samples were stored at 28°C and 80% relative humidity for at least 30 days, provided by a glycerol/water solution, measured by a hygrometer, before being subjected to tests. After conditioning, unfilled starch and starch/chitin composite samples were weighed and dried in an oven at 110°C to constant weight (~18 h), left to cool in a desiccator with silica gel, and weighed. The water content was determined by difference analysis.

Wide-angle X-ray diffraction

The wide-angle X-ray diffraction diagrams of corn starch, chitin flakes, injection-molded unfilled starch, and starch/chitin composite samples were obtained with a Miniflex diffractometer (Rigaku Corporation, Osaka, Japan) operating at CuKα wavelength of 1.542 Å. Samples were exposed to the X-ray beam generated at 40 kV and 50 mA. Scattered radiation was detected at ambient temperature in the angular region (2θ) of 2 to 40° at a rate of 2° (2θ) per min and a step size of 0.1° (2θ). Diffractogram baselines were corrected by drawing a straight line at 5° (2θ). Relative crystallinity was determined by dividing the area of the diffraction peak at approximately 17° (2θ) by the total area.[19]

Differential scanning calorimetry

The differential scanning calorimetry (DSC) analyses were carried out on a Perkin-Elmer DSC-7 apparatus (Norwalk, CT). Calibration was performed with indium (AH_{fusion} = 28.6 J/g, T_o = 156.6°C). Closed stainless steel cups with approximately 15 mg of previously conditioned sample were used with an empty cup as reference. Injection-molded starch and starch/chitin composite samples could not be ground or milled under available conditions, and carefully sliced pieces were used. DSC scans were obtained by heating from −10 to 200°C, cooling to −10°C at 200°C/min, remaining at −10°C for 10 min, and reheating from −10 to 200°C with heating rates of 10, 30, and 50°C/min.

Tensile tests

Tensile properties were evaluated according to the ASTM D638-72 method on type I specimens, after conditioning at 28°C and 80% relative humidity for 30 days and equilibration at 25°C for 24 h, using a Instron Universal Testing Machine model 4204 (Canton, USA) equipped with a load cell of 1 kN at a crosshead rate of 5 mm/min. At least five bars were measured for each sample and the median values were taken.

Contact angle measurements

Contact angle measurements were performed with a NRL automated goniometer (Fostec Inc., Auburn, NY). A water droplet was dropped on the surface of a small sample cut from a dumbbell specimen prepared by injection. The evolution of the droplet shape was followed by a video camera; an image analysis software was used to determine the contact angle evolution.

RESULTS AND DISCUSSION

After processing and conditioning at 28°C and 80% relative humidity for 30 days, the equilibrium water content of the injection molded samples ranged from 11 to 13 wt % (based on total weight). This result indicates that there was significant volatilization from the samples during processing. The specimens were 2 mm thick, which could explain the low water uptake during conditioning, slightly dependent on the chitin composition. According to some authors, 0.3 mm thick thermoplastic starch samples, obtained by extruding potato starch/glycerol/water mixtures at 100 : 25 : 22 composition, presented approximately 13–15% water content, after storage at 61% relative humidity for several weeks.[20] The mechanical properties of starch-based thermoplastics are known to vary according to the plasticizer content (water included).[21–23] In the
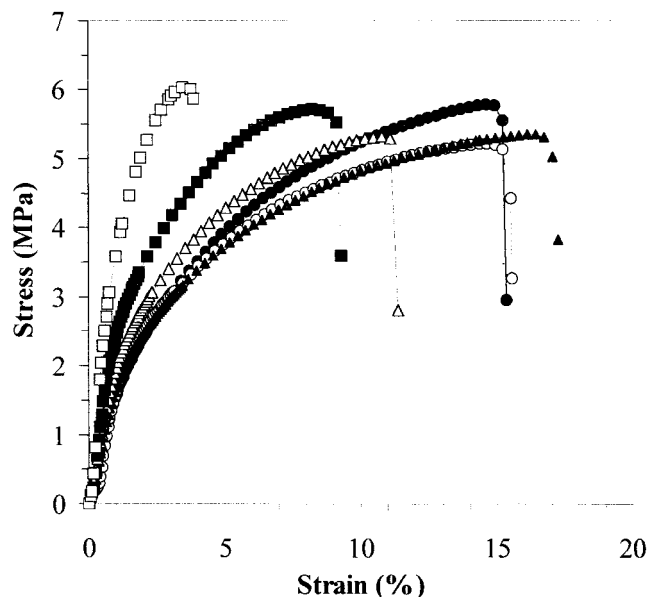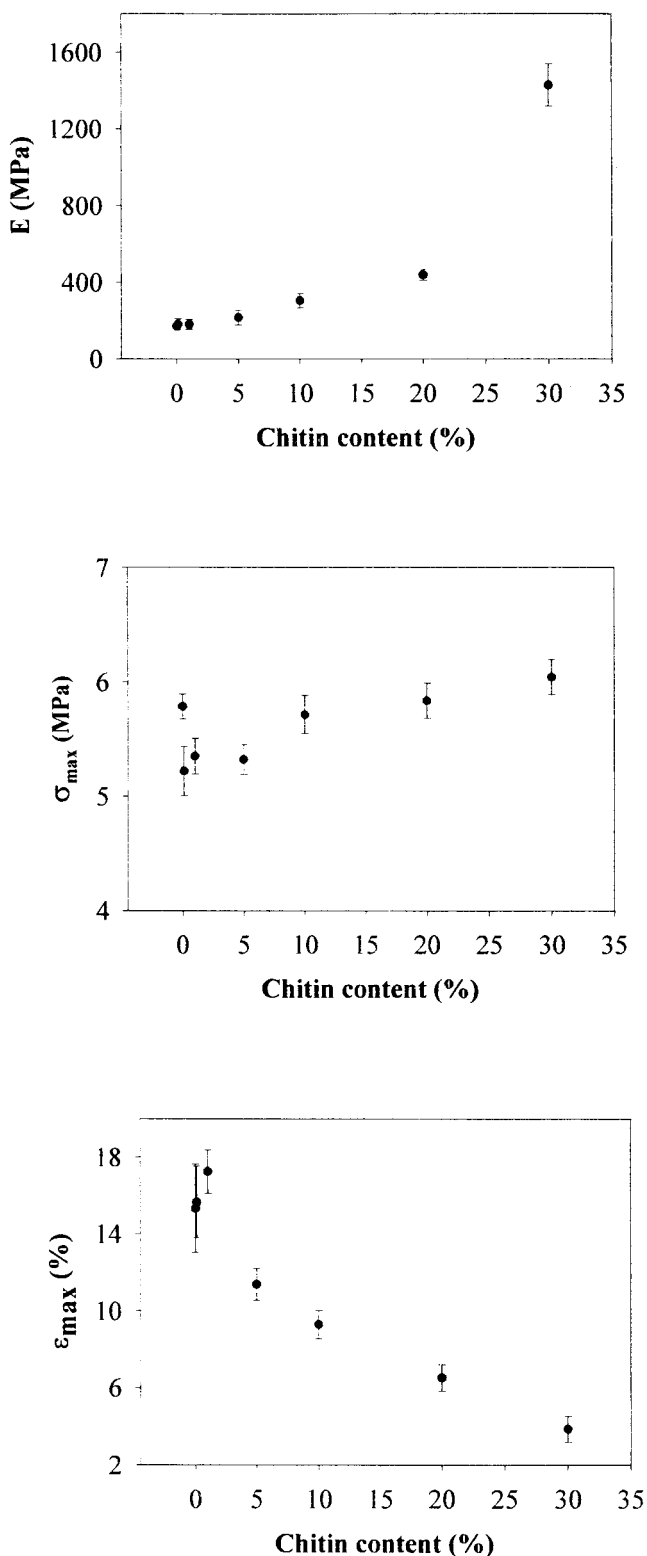

Figure 1 Stress–strain curves obtained for injection-molded glycerol/water plasticized starch (●) and some starch/chitin composites as a function of chitin content: (○) 0.1, (▲) 1, (△) 5, (+) 10, (□) 30 wt %.

present case, the small difference in water content favors a better comparison of the properties of thermoplastic starch and starch/chitin composites in relation to chitin composition.

Figure 1 shows stress–strain curves obtained for injection-molded starch and some starch/chitin composites as a function of chitin composition after conditioning for 30 days. The influence of chitin content may be visualized in Figure 2(a)–(c). Addition of chitin to starch was expected to cause three main changes compared with thermoplastic starch alone; an increase in Young's modulus (E) and stress at break (σ_{max}), and a decrease in percentage elongation at break (ε_{max}). For σ_{max}, two distinct forms of behavior were observed. When the chitin content was less than 10 wt %, a decrease in σ_{max} in relation to starch alone was observed. Higher values of σ_{max} were achieved for chitin compositions higher than 10 wt %. The variation of ε_{max} follows an increase with chitin content up to 1 wt %, when a maximum is observed; for 5 wt % and higher chitin contents, a decrease in ε_{max} is observed. Contrarily, addition of chitin to starch shows a nearly steady increase in E up to 20 wt % chitin, and the highest value of E is observed when 30 wt % chitin is added. It is difficult to compare the present results with those published in the literature, because in most cases tensile tests have been carried out with thin films.
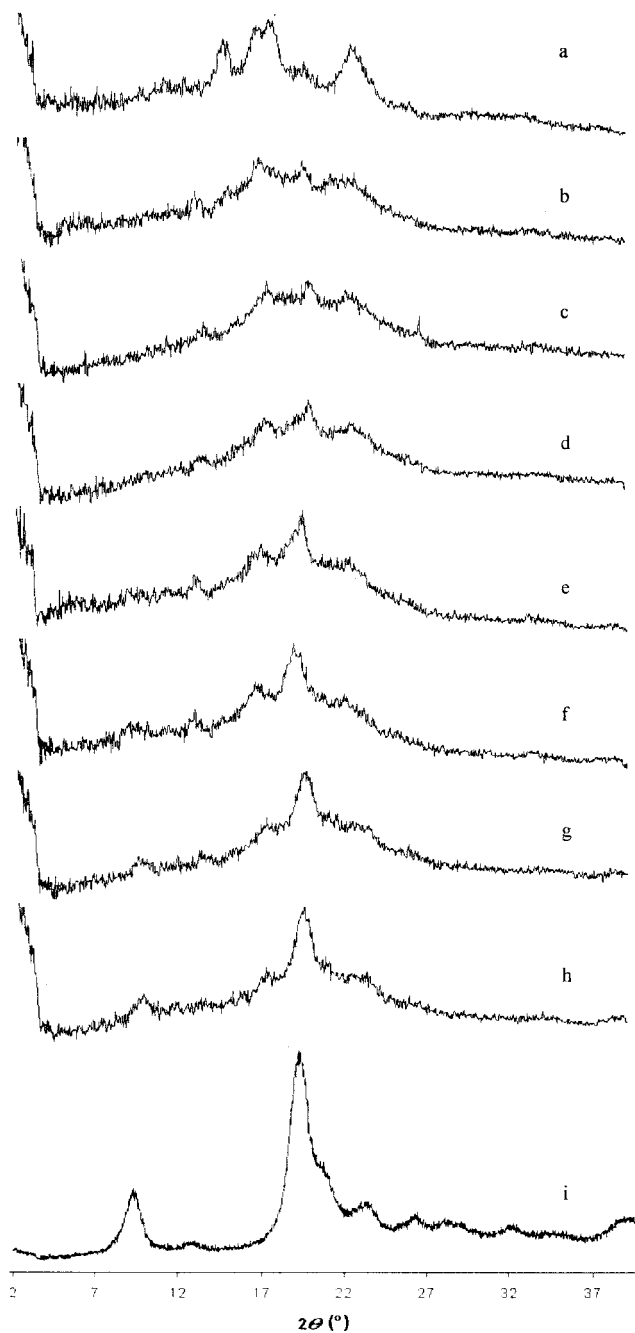
Wide-angle X-ray diffraction patterns of native corn starch, unfilled thermoplastic starch, and of starch/chitin composites conditioned at 28°C and 80% relative humidity at least for 30 days are presented in

Figure 2 Tensile properties of injection-molded glycerol/water plasticized starch and starch/chitin composites as a function of chitin content: (a) Young's modulus, E, (b) stress at break, σ_{max}, (c) percentage elongation at break, ε_{max}.

Figure 3. The typical A-type crystallinity pattern of native starch with peaks (2θ) at 15.0°, 17.2°, 18.0°, and 23.2° (trace a) has been lost during injection molding

at 130–145°C for unfilled starch. Four ill-defined diffraction peaks with angular locations at $2\theta = 13.2°$, 17.3°, 20.1°, and 22.5° are observed for unfilled starch (trace b). This pattern is characteristic of starch B-type crystallinity.[24] This crystalline structure results from spontaneous recrystallization or retrogradation of starch molecules after melting or gelatinization, and has been detected in food and in thermoplastic mate-

Figure 3 Wide-angle X-ray diffractograms of native corn starch (a), chitin film (i), injection-molded glycerol/water plasticized starch (b), and starch/chitin composites with varied chitin contents: (c) 0.5, (d) 1, (e) 5, (f) 10, (g) 20, (h) 30 wt %.

Chitin content (wt %)	Relative crystallinity (%)
0	15.5
0.5	13.8
1	11.3
5	10.2
10	9.3
20	9.0
30	8.9

rials. The degree of crystallinity of potato starch cast films was shown to depend on temperature, relative humidity conditions and period of time that elapses during film formation.[25] B-type crystallinity was shown to occur in compression-molded glycerol-plasticized starches and to vary in amount by changing processing parameters, such as temperature and water content. The total amount of B-type crystallinity was considered as a summation of residual amylopectin crystallinity, recrystallization of amylose and amylopectin, and partial cocrystallization of both polymers.[24]

As a reference, the X-ray diffraction pattern recorded for the chitin sample was included in Figure 3 as trace i. Chitin displays two crystalline peaks with high intensity at $2\theta = 9.5°$ and $2\theta = 19.4°$, also present in chitin films of other source.[26] These peaks appear in the diffractograms of the various starch/chitin composites (traces c–h) balanced by the corresponding composition. It is worth mentioning that, while the intensity of the chitin peaks increases with its composition in the composites, the most intense peak related to starch B-type crystallinity at approximately $2\theta = 17°$ is reduced.

Table I shows the relative B-type crystallinity determined for unfilled starch and starch/chitin composites. The addition of small amounts of chitin promoted a significant decrease in relative crystallinity. This effect was leveled off around 9% when higher amounts of chitin were added to the composites.

Differential scanning calorimetry (DSC) was used to gain additional information on the new materials prepared by injection molding and conditioned for 30 days. Figure 4 shows DSC spectra, first, and second scans, obtained at a heating rate of 30°C/min, for unfilled starch. In general, powdered samples allow to achieve better contact and heat transfer from sample cups. In the present case, because the samples could not be ground or milled, a higher heating rate than the 10°C/min rate normally found in the literature was preferred to better visualize the transitions. In the first

scan, a glass transition (T_g) is observed as an increment in the heat capacity at approximately 41°C. In the second heating scan, T_g decreased to 33°C. The decline in T_g detected in the second scan for potato starch films was attributed to differences in "order" in the amorphous glassy phase.[25]

An endothermic transition is observed in both spectra of Figure 4 at around 113°C, with a slight decrease in peak temperature in the second scan. For compression molded normal corn starch and high-amylose corn starches, conditioned for 2 weeks at 60% RH and with a water content of 11–13%, no T_g or melting endotherm were observed in the temperature range of −10 to 150°C, and the T_g was supposed to be below 20°C.[27] Melting endotherms at 110–120°C have been previously reported for potato starch films,[25,28] and potato amylose/amylopectin mixed films without glycerol,[28] and for injection-molded corn starch/synthetic polymer materials.[29] The endotherm, which presented increasing enthalpy with increasing crystallinity,[25] appeared only in the first DSC scan, and was related to the melting of cocrystallized amylose and amylopectin and of crystallized amylopectin alone.[28] The different experimental conditions used in the present work may have had some effect on the appearance of the melting endotherm in the second scan. Indeed, the enthalpy of this transition decreased from 1.234 J/g in the first scan to 0.569 J/g in the second scan.

The melting of amylose–lipid complexes was also related to this endothermic transition detected after hydration of compression-molded normal corn starch and high-amylose corn starches; these complexes would be recrystallized during slow cooling of the
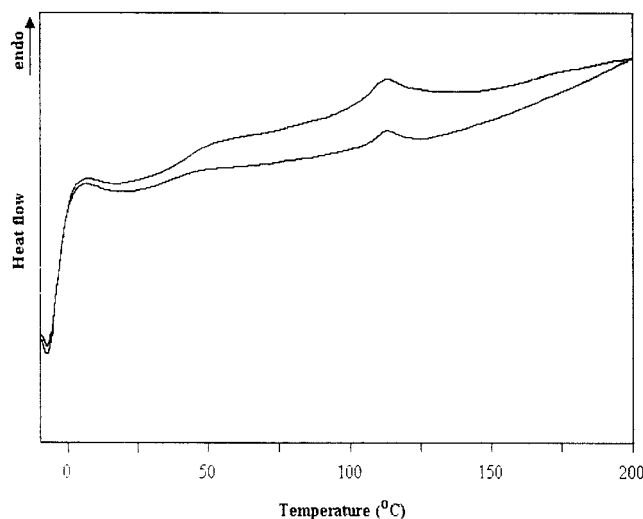
Figure 4 DSC thermograms obtained at a heating rate of 30°C/min for injection-molded glycerol/water plasticized starch after conditioning at 28°C and 80% relative humidity for 30 days: top, first heating scan; bottom, second heating scan.
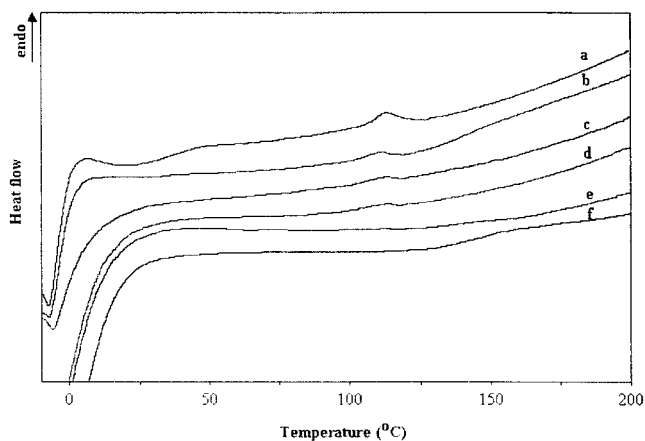
Figure 5 DSC thermograms obtained at a heating rate of 30°C/min for injection-molded glycerol/water plasticized starch and starch/chitin composites after conditioning at 28°C and 80% relative humidity for 30 days as a function of chitin content; traces (a) unfilled thermoplastic starch, (b) 0.1, (c) 0.5, (d) 1, (e) 3, (f) 5 wt %.
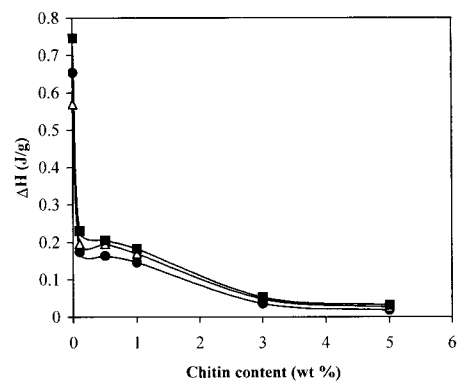

Figure 6 Variation of enthalpy related to the melting endotherm for injection-molded glycerol/water plasticized starch and starch/chitin composites as a function of chitin content, determined with different heating rates; (●) 10°C/min, (△) 30°C/min, (■) 50°C/min.

samples after processing.[27] Melting temperatures above 130°C were observed for films of glycerol plasticized waxy corn starch alone and filled with cellulose whiskers at moisture contents higher than 35%. The endothermic transition was also ascribed to the melting of water-induced crystalline amylopectin. The temperature of the peak was shown to increase with the water content.[30]

In the present case, the rapid crystalline formation, supported by the appearance of the melting endotherm in the second heating scan, suggests that amylose is the starch component involved in the retrogradation phenomenon detected by DSC.

Figure 5 shows DSC thermograms and second heating scans of some injection-molded starch/chitin composites obtained at a heating rate of 30°C/min. The DSC trace of unfilled starch (DSC trace a) was included for comparison. No T_g could be detected for

starch/chitin composites at temperatures below the melting endotherm. As can be observed for the samples with chitin contents in the range 1 to 5 wt % (DSC traces d–f), 10 min did not seem sufficient to cool the starch/chitin composites down to −10°C. The slow response of the materials might have also contributed to make T_g difficult to be observed, even when a 10°C/min heating rate was used (DSC scans not shown). On the contrary, for the starch/chitin composite sample with 5 wt % chitin, an increment in heating capacity at approximately 144°C may be attributed to T_g. However, other experiments are necessary to obtain reliable information on T_g of the composite samples.

Following the behavior of the unfilled starch matrix, a melting endotherm is observed for starch/chitin composites at low loading levels of chitin up to 5 wt %. As the chitin content is increased from 0.1 to 5 wt %, the peak temperature of this transition is slightly increased, while the enthalpy is decreased, according to the data collected in Table II for 10, 30, and 50°C/min heating rates. Magnification of the DSC curves for the

TABLE II
Peak Temperature and Enthalpy of the Melting Endotherm Observed for Injection-Molded Glycerol/Water Plasticized Starch and Starch/Chitin Composites after Conditioning at 28°C and 80% Relative Humidity for at Least 30 days

Chitin content (wt %)	Heating rate					
	10°C/min		30°C/min		50°C/min	
	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)
0	103	0.654	113	0.569	119	0.746
0.1	105	0.174	109	0.196	114	0.231
0.5	108	0.164	113	0.195	119	0.206
1	108	0.146	114	0.169	120	0.182
3	109	0.036	115	0.048	122	0.053
5	111	0.018	117	0.026	124	0.032

TABLE III
Contact Angle Measurements of Injection-Molded Glycerol/Water Plasticized Starch and Starch/Chitin Composites, after Conditioning at 28°C and 80% Relative Humidity for at Least 30 days

Chitin content (wt %)	Initial value (°)	Slope at the origin (°/s)
0	64	−0.67
0.1	69	−0.30
0.5	75	−0.50
3	93	−0.60
5	89	−0.23
10	90	−0.20
20	91	−0.17
30	80	−0.17

composite samples with 3 and 5 wt % chitin (DSC traces e and f) allowed the determination of the corresponding enthalpies. The decrease in crystallinity of injection molded starch-based materials, as the chitin content is increased up to 5 wt % (Fig. 6) is supported by X-ray diffraction results. At higher loading levels of chitin, the melting endotherm was not observed, even in the first heating scan. The results suggest that the addition of chitin lowers amylose molecular motion, resulting in the progressive decreasing of the retrogradation phenomenon.

The data obtained from measurements of contact angle of water carried out on surfaces of unfilled starch and starch/chitin composites are presented in Table III. Starch-based materials absorb water very rapidly, due to the high hydrophilic nature of the matrix and commonly used plasticizers. Glycerol and sorbitol composition were shown to influence the equilibrium moisture content, as well as the storage time necessary to reach this equilibrium.[20,31] According to Table III, the lowest initial value of the contact angle just after deposition of the droplet and the highest slope at the origin were obtained for the unfilled thermoplastic starch. For the starch/chitin composites, the initial values of contact angle of water were higher and the values determined for the slope at the origin were lower than for the unfilled sample. This result indicates that the addition of chitin contributes to diminish the hydrophilic character of the composites.

It was pointed out that a high contact angle is due to the preferred orientation of hydrophobic moieties at the air–polymer interface, which implies that the equilibrium surface properties are dictated by the surface configuration (spatial arrangement of atoms and ligands at the top surface), that changes as the water drop is placed on it.[32,33] In the present case, a linear dependence of the contact angle on the chitin content was not obtained, probably because the surface state is a complex function of surface configuration, temperature, relative humidity, adsorbed substance, and also physical roughness.[33] Indeed, this latter characteristic may vary as the chitin composition is changed.

Figure 7 shows the evolution of contact angle with time for unfilled starch and starch/chitin composites. Following the first 30 s of fast water absorption, a significant decrease in rate is observed. After 60 s, the unfilled starch sample maintains the higher water absorption rate. As chitin is added, the evolution of the contact angle with time is slower, which shows a certain improvement of water resistance of the composite samples in relation to unfilled thermoplastic starch.

CONCLUSIONS

Thermoplastic corn starch composites, containing chitin flakes as the reinforcing phase and plasticized
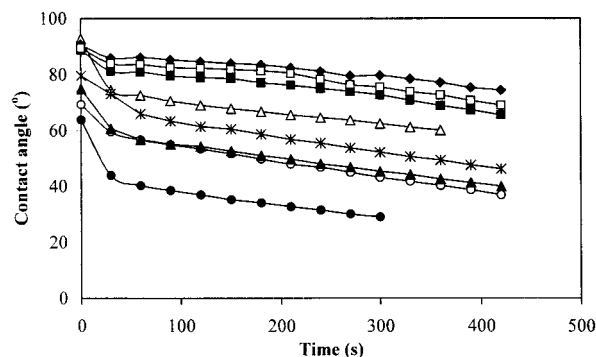
Figure 7 Evolution of contact angle of water for injection-molded glycerol/water plasticized starch (●) and some starch/chitin composites with varied chitin contents: (○) 0.1, (▲) 0.5, (△) 3, (+) 5, (◆) 20, (*) 30 wt %.

with glycerol and water, were obtained by injection molding and conditioned at 28°C and 80% RH for at least 30 days. Chitin flakes were obtained from shells of *Penaeus schmitti* after demineralization and deproteinization, followed by treatment with organic solvents. The composite samples showed higher values of Young's modulus than the unfilled starch matrix. The relative B-type crystallinity, measured by wide-angle X-ray diffraction, and the short-term retrogradation of amylose, evidenced by differential scanning calorimetry, were shown to decrease as the chitin content was increased. Results of contact angle measurements revealed an improvement of water resistance of the composite samples up to 20 wt % in relation to unfilled starch. The results may be ascribed to the intrinsic rigidity and less hydrophilic character of the chitin macromolecule. Considering the highly moist conditions under which the samples have been kept, it can be affirmed that the addition of 0.1 to 10 wt % chitin contributed to improve the properties of starch-based composite materials.

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