Available online at www.sciencedirect.com
SCIENCE DIRECT®

Carbohydrate Polymers 57 (2004) 401–413

ELSEVIER

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Extrusion of pectin and glycerol with various combinations of orange albedo and starch☆

Marshall L. Fishman*, David R. Coffin, Charles I. Onwulata, Richard P. Konstance

*Crop Conversion Science and Engineering Research Unit, US Department of Agriculture, Agricultural Research Service,
Eastern Regional Research Center, 600 East Mermaid Lane, Wyndmoor, PA 19038, USA*

Received 20 February 2004; revised 20 May 2004; accepted 21 May 2004

## Abstract

Microstructural and mechanical properties of extruded pectin and glycerol films with various combinations of orange albedo and starch were determined by universal mechanical testing (UMT), dynamic mechanical analysis (DMA), optical microscopy (OM) and scanning electron microscopy (SEM). A glass transition and a second order transition attributed to the onset of translational motion of the pectin molecules was observed in all films. Observation by OM suggested that extrusion in the presence of dilute HCl was more effective in disintegrating albedo than either water or dilute citric acid. UMT, DMA and SEM analysis revealed that extruded pectin/albedo/starch/glycerol films provided better mechanical properties than pectin/albedo/glycerol films and were comparable in mechanical properties to extruded pectin/starch/glycerol films.
Published by Elsevier Ltd.

*Keywords:* Pectin/albedo; Pectin/albedo/starch blends; Glycerol plasticization; Mechanical; Microstructural properties

## 1. Introduction

Our interest in value added agricultural commodities has led us to look for new uses for pectin, and for cost effective processes to utilize it. Pectin is a co-product of fruit juice, sunflower oil, and sugar beet production. It is a structural component of cell walls, consisting primarily of partially methyl esterified poly ($\alpha(1 \rightarrow 4)$galacturonic acid) containing rhamnose inserts in the backbone with neutral sugar side chains.

We have shown previously that pectin blended with high amylose starch and glycerol will form edible biodegradable films with a wide range of mechanical properties (Coffin & Fishman, 1993; Coffin, Fishman, & Cooke, 1995; Fishman & Coffin, 1995; Fishman, Coffin, Unruh, & Ly, 1996). These films were also shown to have excellent oxygen barrier properties (Coffin & Fishman, 1994). Blends of pectin with poly(vinyl alcohol) have also been shown to have a wide range of excellent mechanical properties (Coffin, Fishman, & Ly, 1996; Fishman & Coffin, 1998).

These studies all focused on solution cast films of various compositions. Films were cast from relatively dilute (5–8 wt%) aqueous solutions and allowed to dry at room temperature. This is an excellent laboratory method for film preparation, but extrusion is a less expensive manufacturing process. Extrusion is a widely used method for manufacturing a broad range of films, including almost all of the most widely used thermoplastics. In addition, many biopolymers have been successfully extruded (Otey, Mark, Mehltretter, & Russell, 1974; Otey, Westhoff, & Doane, 1980; Willett, Millard, & Jasberg, 1997).

We have shown previously that blends of pectin, high amylose starch, and glycerol can be successfully extruded using a twin screw extruder (Fishman, Coffin, Konstance, & Onwulata, 2000). The blends were co-extruded with water in order to obtain a material which could be handled easily, and compressed into samples suitable for mechanical testing and scanning electron microscopy analysis. These materials were found to have properties which compared favorably with those found for solution cast pectin/starch/glycerol (PSG) films.

---

☆ Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

* Corresponding author. Tel.: +1-215-233-6450; fax: +1-215-233-6406.
*E-mail address:* mfishman@errc.ars.usda.gov (M.L. Fishman).

0144-8617/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2004.05.014

Whereas extrusion is certainly a more cost efficient process for film manufacture than solution casting, the high cost of pectin itself is a major factor in the expense of the films made from it. The albedo of citrus fruits consists of nearly 50% pectin (Fishman, Chau, Hoagland, & Ayyad, 2000). It is, moreover, very inexpensive, and currently the only appreciable use for it is as animal feed. The great majority of the available material comes from oranges. Thus orange albedo is both inexpensive and has a high pectin content. Commercial pectins are produced primarily from lemon and lime peels by hot aqueous acid extraction (May, 1995).

Previously, Thibault et al. have shown that the amount of water-soluble pectins extracted from lemon peels significantly increased after extrusion in a twin screw extruder (Ralet, Axelos, & Thibault, 1994; Ralet & Thibault, 1994). The same effect also had been observed with the extraction of pectins in sugar beet pulp (Ralet, Thibault, & Della Valle, 1991). Hwang et al. have shown that extrusion also increased the yield of water soluble polysaccharides, primarily pectin, from apple pomace (Hwang, Kim, & Kim, 1998).

Thus, based on the pectin content of albedo, we decided to test the hypothesis that extruding albedo under acid conditions would extract sufficient pectin from the albedo to obtain a free standing film comparable to a PSG film. It is well known that lowering the pH of an extraction solution, if done appropriately, will increase the amount of pectin obtained. In addition to extracting pectin, the processing of albedo by extrusion under acid conditions was expected to have a second beneficial effect. Namely, to reduce the particle size of the albedo which was initially fed into the extruder. It was expected that a reduction in particle size would allow the remaining albedo to reinforce the film. Thus the albedo could potentially act as both a reinforcing filler and as a film forming material.

In this paper we describe the extrusion of pectin/albedo/glycerol and pectin/high amylose starch/albedo/glycerol blends into films, and some of their mechanical and microstructural properties. We compare properties of films extruded with and without albedo. We also compare extruded films to solution cast films of comparable compositions. The effects of the various processing parameters on the properties are evaluated.

## 2. Experimental procedures

### 2.1. Materials

The pectin used in these studies was MexPec 1400, supplied by the Grindsted Division of Danisco-Cultor (Kansas City, KS). It is a citrus pectin with a degree of methylation of 71%. Starch in granule form was Amylogel 03003 (formerly Amylomaize VII) supplied by Cerestar Corp. of Hammond, IN. Reagent grade glycerol and citric acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Reagent grade hydrochloric acid was purchased from J.T. Baker. All of these materials were used as received with no further purification. Local tap water was used in all of the extrusion runs. Deionized water was used for preparation of laboratory samples.

Frozen orange albedo from Holly Hills Co. was supplied by Dr Karel Grohmann of the USDA Florida Citrus Laboratory in Winter Haven, FL. Remaining pulp and flavedo were removed from the albedo while it was still in a wet state. The albedo was then dried in a Labconco Lyph-Lok 6 freeze dry system or a Buff-Tex vacuum tray drier. The dried albedo was ground to a fine powder by passing it twice through a 7.5 in. Wiley mill equipped with a 1 mm screen, and then stored in a plastic bucket covered with a lid.

### 2.2. Extrusion

A variety of blends were extruded using a Werner&Pfleiderer ZSK30 twin screw extruder (Krupp, Werner&Pfleiderer Co., Ramsey, NJ). These included blends of pectin, orange albedo, and glycerol; pectin, high amylose starch, orange albedo, and glycerol, and a pectin/high amylose starch/glycerol control.

Materials were made by blending the dry ingredients together in a plastic bucket, followed by slowly adding this pre-mix to the glycerol with mixing in the bowl of a model C-100-T Hobart mixer (Hobart Mfg. Co., Troy, OH). After it was sufficiently blended, the mixture was allowed to stand overnight in a plastic bucket covered with a lid. Then the mixture was ground to a powder in a commercial Waring food processor.

The blends were measured into the extruder barrel using a series 6300 digital feeder, type 35 twin screw volumetric feeder (K-tron Corp., Pitman, NJ). Feed rates were determined for each blend by weighing the amount of blend transported from the hopper to the barrel over a fixed time interval.

The extrusions were carried out in a manner essentially identical to the methods we used previously for the extrusion of pectin/starch/glycerol blends using a 1.5 mm × 35 mm exit slit die (Fishman et al., 2000). Raw material feed rates and other process conditions are given in Table 1. The temperature profiles used are given in Table 2. These were initially based on the optimum conditions used in our previous work. It was found with the albedo, however, that it was necessary to keep the barrel temperatures at or below 100 °C in order to avoid spitting through the die at the end of the barrel. These lower temperatures did not appear to cause any problems in the extrusion. Some of the trials were run using a water feed into the extruder as we have done previously. However, since one of the objectives of this study was to determine the effect of the presence of acid in the feed on the properties of the final product, some of the trials were run using a feed of pH 4 citric acid, and some were run using a feed of hydrochloric acid (pH 2.1) in place of the water. The citric acid solution had a concentration of 0.0016 wt% (0.00008 M), while the hydrochloric acid solution had

Table 1
Extrusion feed conditions

| Sample | Temp. profile | P/A/S/G ratio | Solids feed (g/min) | Water feed (ml/min) | pH |
|---|---|---|---|---|---|
| 1-1 | 1 | 70/0/0/30 | 26.7 | 40.0 | NA |
| 1-2 | 1 | | 26.7 | 33.8 | NA |
| 1-3 | 1 | | 26.7 | 33.8 | 4.0 |
| 1-4 | 1 | | 26.7 | 40.0 | 4.0 |
| 2-1 | 1 | 50/20/0/30 | 26.7 | 40.0 | NA |
| 2-2 | 1 | | 26.7 | 46.3 | NA |
| 2-3 | 1 | | 26.7 | 46.3 | 4.0 |
| 2-4 | 1 | | 26.7 | 40.0 | 4.0 |
| 3-1 | 1 | 35/35/0/30 | 20.7 | 38.8 | NA |
| 3-2 | 1 | | 20.7 | 40.0 | NA |
| 3-3 | 1 | | 20.7 | 40.0 | 4.0 |
| 3-4 | 1 | | 20.7 | 33.8 | 4.0 |
| 3-5 | 1 | | 26.7 | 33.8 | 4.0 |
| 3-6 | 1 | | 26.7 | 40.0 | 4.0 |
| 3-7 | 1 | | 26.7 | 40.0 | NA |
| 4-1 | 1 | 20/50/0/30 | 26.7 | 40.0 | NA |
| 4-2 | 1 | | 26.7 | 33.8 | NA |
| 4-3 | 1 | | 26.7 | 33.8 | 4.0 |
| 4-4 | 1 | | 26.7 | 40.0 | 4.0 |
| 5-1 | 1 | 70/0/0/30 | 26.7 | 40.0 | 2.1 |
| 5-2 | 1 | 50/20/0/30 | 26.7 | 40.0 | 2.1 |
| 5-3 | 1 | 35/35/0/30 | 26.7 | 40.0 | 2.1 |
| 6-1 | 2 | 39/0/31/30 | 26.7 | 40.0 | NA |
| 7-1 | 1 | 39/10/21/30 | 26.7 | 40.0 | NA |
| 7-2 | 1 | | 26.7 | 40.0 | 2.1 |
| 7-3 | 1 | 39/21/10/30 | 26.7 | 40.0 | 2.1 |
| 7-4 | 1 | | 26.7 | 40.0 | NA |

a concentration of 0.037 wt% (0.01 M). The pH values were determined with a pH meter. Initially pH was limited to 4 because of concerns about the pH resistance of the extruder barrel. Later it was determined that pH 2 was acceptable for the short time period of runs used in these trials.

The product was obtained as slabs exiting from the die, and was collected in approximately 6–8 in. strips. These were stored in Zip-Loc® bags in a refrigerator. In order to obtain samples thin enough to be used for tensile and dynamic mechanical testing these were compression molded using a Carver press. This was done by placing a 1.5–2 in. piece of the extrudate between two sheets (approx. 6 in. × 6 in.) of Saran Wrap® and then compressing it with a pressure of about 5000 pounds. One of the pieces of Saran Wrap® was removed and the sample was allowed to air dry with the supporting plastic film being constrained. After air drying overnight, the samples were then vacuum dried for 6–8 h at room temperature.

### 2.3. Film preparation

Redissolved films of pectin, starch, albedo, and glycerol were made by mixing 2.5 g of dried and ground extrudate into 35 ml of HPLC grade water. The mixtures were allowed to stir until all of the soluble material present went into solution. The mixtures were spread onto polycarbonate plates using a film spreader in the same manner as we prepared cast films in previous work (Coffin & Fishman, 1994). The samples were allowed to air dry overnight and then vacuum dried at room temperature for at least 30 min. The films were stored in polyethylene bags.

Cast films made from pectin, albedo and glycerol were prepared using microwave pretreatment of the albedo. For each film, a total of 2.0 g of pectin, albedo, and glycerol were used. The albedo was mixed with 25 ml of dilute citric acid or hydrochloric acid solution, and then heated for 3 or 4 min in a CEM MDS2000 microwave oven with a power of 630 watts (CEM Corp., Matthews, NC). After removal from the oven, the albedo/liquid mixture was poured into a 50 ml beaker containing the glycerol, and the pectin was added with stirring. After the pectin was completely dissolved, the film was cast on a polycarbonate plate using our usual procedure (Coffin & Fishman, 1994). It was then air-dried overnight, and then vacuum dried at room temperature for at least 30 min. The films were stored in polyethylene bags.

### 2.4. Mechanical properties

Dynamic mechanical properties were determined using a Rheometric Scientific RSA II Solids Analyzer (Rheometric Scientific, Piscataway, NJ) equipped with Orchestrator 6.5.7 software. Samples were cut 1.5 in. (38.1 mm) long and 5–7 mm wide. Sample thicknesses ranged from 0.1 to 0.4 mm. Testing was done as described previously (Coffin & Fishman, 1994).

Tensile properties were measured using an Instron model 1122 tensile tester. Samples were cut to a width of 5 mm, and a gage length of 25 mm was used. Samples were conditioned overnight in a desiccator held at a relative humidity of 51% using a saturated sodium bisulfate solution. Testing was conducted at an extension rate of 10 mm/min. Data were collected and analyzed using SMS

Table 2
Extrusion temperature profiles

| Temp. profile | Zone | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 1 | 35 | 35 | 50 | 75 | 95 | 100 | 100 | 90 | 80 |
| 2 | 35 | 35 | 50 | 75 | 110 | 120 | 100 | 100 | 90 |

TestWorks 3.1 software. The parameters investigated were tensile strength, elongation to break, and initial modulus.

### 2.5. Microscopy

Sample preparation for scanning electron microscopy (SEM) consisted of soaking rectangular strips (ca. 0.5 cm × 2 cm) in absolute ethanol for 24 h, immersing them in liquid nitrogen, and cooling for 5 min. Fractures were induced by manually bending strips held by fine forceps at the ends under liquid nitrogen. Fragments of the strips with fractures occurring normal to the long axis were thawed by immersion in absolute ethanol for 5 min, then critical point dried from carbon dioxide. Dried strip fragments were mounted on specimen stubs with fracture faces oriented up using colloidal silver adhesive (Electron Microscopy Sciences, Ft. Washington, PA) and coated with a thin layer of gold by DC sputtering. Digital images of fracture faces were collected using an Imix workstation (Princeton Gamma-TECH, Princeton, NJ) integrated with a JSM840A scanning electron microscope (JEOL USA Peabody, MA) operated in the secondary electron imaging mode.

## 3. Results and discussion

Pectin/albedo/glycerol blends containing 30% glycerol were extruded using water, pH 4 citric acid solution, and pH 2.1 hydrochloric acid, as the processing liquids. Samples of each extrudate were compression molded as described in the experimental section, and their tensile properties were determined (Table 3). Comparisons were made to determine the effects of material composition and process variables

Table 3
Tensile properties

| Sample | P/A/S/G ratio w/w/w/w | pH | Tens. strength (MPa) | Elong. break (%) | Init. modulus (MPa) |
|---|---|---|---|---|---|
| 1-1 | 70/0/0/30 | NA | 11.1 (2.4) | 14.7 (4.6) | 200.3 (79.1) |
| 1-2 | | NA | 9.2 (2.1) | 7.2 (3.9) | 278.7 (40.8) |
| 1-3 | | 4.0 | 12.9 (1.4) | 23.2 (4.1) | 185.1 (29.3) |
| 1-4 | | 4.0 | 6.3 (1.5) | 6.2 (1.9) | 139.7 (34.4) |
| Average | | | 9.9 (2.4) | 12.8 (6.8) | 201.0 (50.1) |
| 2-1 | 50/20/0/30 | NA | 3.4 (1.3) | 10.9 (5.1) | 55.7 (9.1) |
| 2-2 | | NA | 5.3 (1.4) | 23.7 (4.9) | 41.8 (8.5) |
| 2-3 | | 4.0 | 4.8 (0.4) | 17.9 (2.5) | 52.5 (7.3) |
| 2-4 | | 4.0 | 5.1 (1.1) | 12.6 (2.9) | 69.9 (12.4) |
| Average | | | 4.7 (0.7) | 16.3 (5.0) | 55.0 (10.0) |
| 3-1 | 35/35/0/30 | NA | 2.9 (0.6) | 13.0 (2.1) | 39.9 (5.4) |
| 3-2 | | NA | 2.7 (0.7) | 8.5 (3.0) | 45.3 (10.1) |
| 3-3 | | 4.0 | 3.8 (1.0) | 16.5 (4.8) | 44.3 (3.8) |
| 3-4 | | 4.0 | 3.5 (1.0) | 15.9 (6.6) | 39.7 (8.7) |
| 3-5 | | 4.0 | 5.6 (0.6) | 28.7 (1.9) | 37.2 (6.0) |
| 3-6 | | 4.0 | 4.4 (0.7) | 23.5 (4.0) | 30.3 (4.2) |
| 3-7 | | NA | 2.8 (0.5) | 18.6 (3.2) | 25.5 (3.2) |
| Average | | | 3.7 (1.0) | 17.8 (6.2) | 37.4 (6.7) |
| 4-1 | 20/50/0/30 | NA | 2.0 (0.3) | 18.8 (4.0) | 13.4 (1.3) |
| 4-2 | | NA | 2.0 (0.3) | 15.9 (1.7) | 17.7 (2.4) |
| 4-3 | | 4.0 | 2.5 (0.7) | 19.0 (5.4) | 18.5 (2.4) |
| 4-4 | | 4.0 | 2.2 (0.2) | 13.7 (1.0) | 25.9 (3.1) |
| Average | | | 2.2 (0.2) | 16.9 (2.2) | 18.9 (4.5) |
| 5-1 | 70/0/0/30 | 2.1 | 12.6 (0.9) | 27.1 (3.3) | 161.9 (13.0) |
| 5-2 | 50/20/0/30 | 2.1 | 7.3 (0.7) | 36.1 (4.5) | 40.4 (6.7) |
| 5-3 | 35/35/0/30 | 2.1 | 1.9 (0.9) | 19.8 (5.5) | 14.2 (4.9) |
| 6-1 | 39/0/31/30 | NA | 4.8 (1.2) | 21.6 (6.1) | 52.3 (4.5) |
| 7-1 | 39/10/21/30 | NA | 5.1 (1.4) | 20.3 (7.4) | 44.7 (5.6) |
| 7-2 | | 2.1 | 7.9 (1.1) | 24.5 (5.4) | 78.3 (21.4) |
| 7-3 | 39/21/10/30 | 2.1 | 6.8 (1.1) | 25.3 (2.9) | 65.8 (8.0) |
| 7-4 | | NA | 6.8 (1.2) | 22.0 (4.8) | 84.8 (17.6) |

values in parentheses are standard deviations.

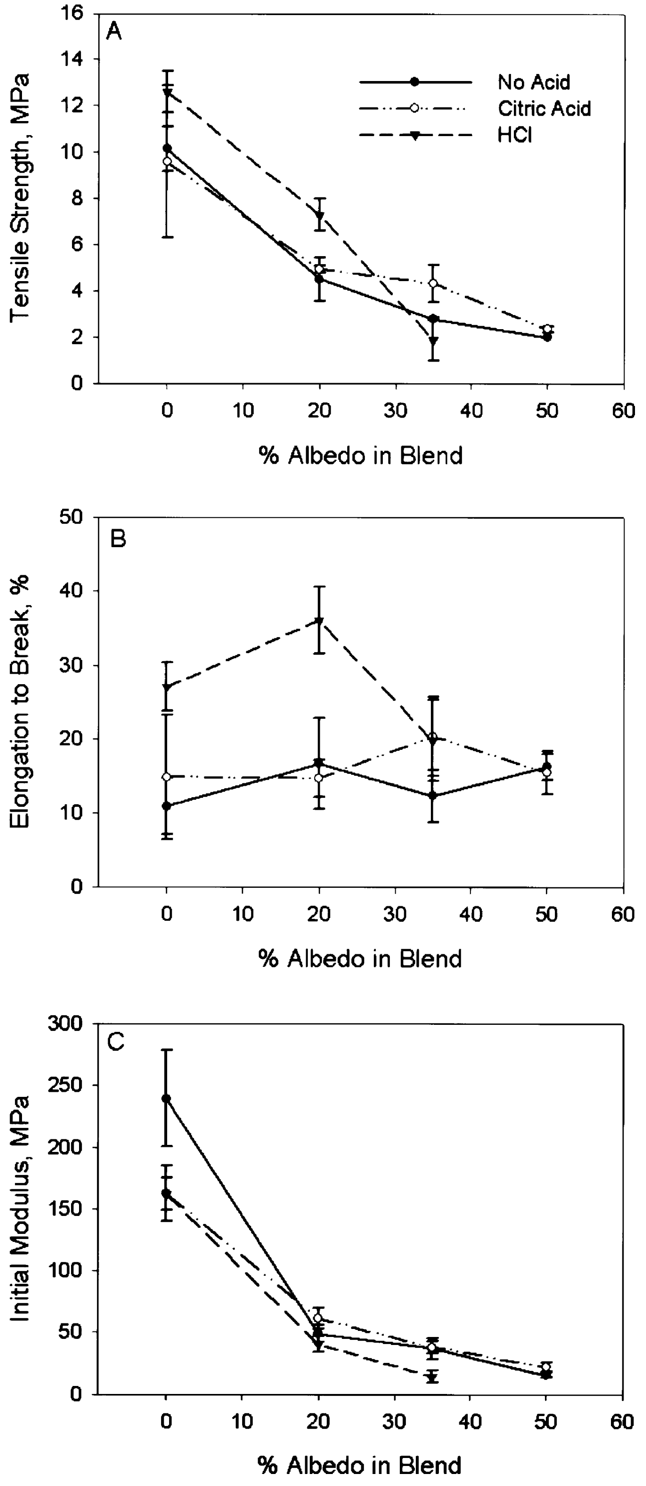

Fig. 1. Effect of albedo level and acid type used in processing on the tensile properties of compression molded films made from extruded pectin/albedo/glycerol blends.

(water and solids feed rates) on the mechanical properties. The effects of albedo level on tensile properties of all three acid conditions (no acid, NA; citric acid, pH 4 and HCl, pH 2.1) are shown in Fig. 1. The data in Fig. 1 essentially summarizes the tensile data for samples 1–5 in Table 3. Since there was generally little effect of the liquid/solids ratio observed, the values at the different liquid/solids ratios were averaged for this plot.

Tensile strength (TS) (see Fig. 1A) and initial modulus (IM) (see Fig. 1C) decreased with increasing percentage of albedo in the blend. This occurred regardless of whether or not water, citric acid solution, or hydrochloric acid solution was used as the liquid processing component in the extrusion. The drop off in TS was significant when as little as 28% of the pectin in a 70/30 pectin glycerol blend was replaced with albedo (20% total albedo). Additional decreases in TS were seen as the percentage of albedo in the blend was increased further. The initial modulus behaved in a similar fashion. Elongation to break (EB) appeared to be relatively unaffected by the addition of albedo when water or citric acid, pH 4 was in the processing water (Fig. 1B). When the processing water contained HCl at pH 2.1, EB appeared to pass through a maximum when 20% of the pectin was replaced with albedo. A comparison of TS or IM at constant albedo composition revealed little if any differences due to the addition of acid to the processing water.

For purposes of comparison, a control, Sample 6-1, Table 3, made from an optimal blend of pectin, high amylose starch, and glycerol (P/A/S/G, 39/0/31/30) also was extruded and tested. This sample, was comparable to samples with 20% albedo but had higher values for mechanical properties than the values obtained with the samples containing 35% or more albedo (samples 3, 4, 5-2 and 5-3, Table 3).

Another series of samples (samples 7, Table 3) was extruded using pectin/high amylose starch/albedo/glycerol blends. The pectin and glycerol levels of these films were identical to those used in control sample, 6-1. The purpose of this series was to determine the effect on mechanical properties of replacing starch with albedo in sample 6-1. Blends were made replacing one third and two thirds of the starch with albedo. Each was processed using water and pH 2 HCl. As above, materials were compression molded and tested for tensile properties on the Instron. Sample 6-1 was shown to have mechanical properties which were slightly poorer than films in which about two thirds of the starch had been substituted with albedo. The tensile properties of the extruded/compressed films (samples 7, Table 3) were, overall, significantly better (higher in TS and IM) than any of the samples in this study containing only pectin/albedo/glycerol. For the sample with the 39/10/21/30 composition ratio, the presence of HCl in the processing water led to increased values for all three of the tensile parameters measured over the sample with the same composition but with no acid in the processing water. Comparison of samples with the 39/21/10/30 composition ratio revealed little differences between samples with and without added acid.

In a series of experiments, samples with P/A/S/G ratios of 39/10/21/30 and 39/21/10/30 were extruded, dispersed and redissolved in HPLC grade water and cast into films for mechanical testing. These were compared with the samples of identical composition which were extruded and compressed

Table 4
Mechanical properties of pectin/high amylose starch/albedo/glycerol films

| P/A/S/G ratio | pH | Prep. method | Tensile strength (MPa) | Elongation to break (%) | Initial modulus (MPa) |
|---|---|---|---|---|---|
| 39/10/21/30 | NA | Compression | 5.1 (1.4) | 20.3 (7.4) | 44.7 (5.6) |
|  | 2.1 | Compression | 7.9 (1.1) | 24.5 (5.4) | 78.3 (21.4) |
| 39/21/10/30 | 2.1 | Compression | 6.8 (1.1) | 25.3 (2.9) | 65.8 (8.0) |
|  | NA | Compression | 6.8 (1.2) | 22.0 (4.8) | 84.8 (8.0) |
| 39/10/21/30 | NA | Redissolution | 8.2 (0.6) | 46.0 (6.1) | 34.0 (8.0) |
|  | 2.1 | Redissolution | 8.3 (1.6) | 44.5 (4.1) | 39.1 (5.4) |
| 39/21/10/30 | 2.1 | Redissolution | 5.4 (0.8) | 37.9 (8.0) | 25.6 (3.9) |
|  | NA | Redissolution | 6.8 (1.0) | 41.7 (3.3) | 27.1 (5.9) |

values in parentheses are standard deviations.

(see Table 4). The films made by redissolving the extruded material gave mechanical properties which were somewhat different than the extruded, compression molded films of these compositions. Tensile strengths were about the same whereas elongation to break was somewhat higher and initial modulus was somewhat lower. Thus, it appears that compressing the blend into film tends to increase intermolecular interactions between pectin itself and between pectin and other polysaccharides. Processing in a manner to increase pectin interactions is likely to decrease EB and increase IM.

Finally, a series of pectin/albedo/glycerol films were made by casting from solutions heated in a microwave oven in closed vessels. These were the same raw materials that were used in the extrusion experiments not containing starch. Albedo dispersed in dilute acid was heated in a microwave oven to somewhat emulate conditions in an extruder in that both temperature and pressure were raised above ambient. Glycerol and pectin were then added to the solution and allowed to dissolve at room temperature. The films were cast from solution by a method similar to that which was used to make pectin/glycerol and pectin/starch/glycerol films in our previous work (Coffin & Fishman, 1993, 1994; Fishman et al., 1996). The control film had 70% pectin and 30% glycerol. The test films were made by substituting 20, 30 and 50% of the pectin with albedo. The goal was to assess the effect of temperature, pressure, pH and composition on pectin films in the absence of compression. The albedo was heated in the microwave oven with citric acid at pH 2 and pH 3, and hydrochloric acid at pH 2 and pH 3. Heating times were 3 and 4 min. At 3 min the temperature reached 120 °C and

Table 5
Mechanical properties of microwave prepared samples

| % Albedo | Acid | pH | Time (min) | Tensile strength (MPa) | Elongation to break (%) | Initial modulus (MPa) |
|---|---|---|---|---|---|---|
| 0 | HCl | 2 | – | 21.5 (6.1) | 19.2 (4.9) | 375.6 (28.5) |
| 20 | HCl | 2 | 3 | 5.6 (1.1) | 15.3 (3.3) | 68.4 (6.3) |
|  | HCl | 2 | 4 | 11.8 (1.8) | 25.4 (4.1) | 84.4 (15.4) |
| 35 | HCl | 2 | 3 | 4.1 (0.3) | 21.8 (1.7) | 32.7 (1.8) |
|  | HCl | 2 | 4 | 7.3 (1.5) | 22.6 (1.8) | 57.8 (13.0) |
| 50 | HCl | 2 | 3 | 3.3 (0.5) | 25.0 (1.7) | 17.8 (3.9) |
|  | HCl | 2 | 4 | 5.1 (1.9) | 32.9 (5.2) | 21.2 (7.4) |
| 0 | HCl | 3 | - | 25.6 (2.4) | 17.2 (2.6) | 574.4 (80.0) |
| 20 | HCl | 3 | 3 | 3.8 (0.7) | 13.9 (3.7) | 66.5 (12.2) |
|  | HCl | 3 | 4 | 5.7 (0.3) | 21.3 (1.7) | 74.3 (14.2) |
| 35 | HCl | 3 | 3 | 3.2 (0.4) | 21.6 (1.8) | 29.7 (3.9) |
|  | HCl | 3 | 4 | 4.6 (0.8) | 25.6 (1.8) | 35.9 (6.3) |
| 50 | HCl | 3 | 3 | 2.4 (0.7) | 21.7 (2.1) | 15.4 (4.2) |
|  | HCl | 3 | 4 | 2.9 (0.8) | 23.7 (4.4) | 17.3 (2.9) |
| 0 | Citric | 2 | – | 5.6 (1.0) | 21.8 (2.8) | 26.6 (1.6) |
| 20 | Citric | 2 | 3′ | 4.9 (0.8) | 28.2 (2.7) | 18.0 (1.5) |
|  | Citric | 2 | 4 | 5.5 (1.3) | 31.5 (3.2) | 18.0 (2.6) |
| 35 | Citric | 2 | 3 | 4.7 (1.1) | 32.6 (5.1) | 14.6 (1.6) |
|  | Citric | 2 | 4 | 2.7 (0.9) | 31.8 (4.1) | 8.7 (2.0) |
| 0 | Citric | 3 | – | 20.0 (6.5) | 17.8 (6.7) | 302.9 (26.2) |
| 20 | Citric | 3 | 3 | 4.1 (1.0) | 22.2 (2.0) | 32.4 (5.3) |
|  | Citric | 3 | 4 | 3.2 (1.0) | 19.5 (2.9) | 29.6 (10.7) |
| 35 | Citric | 3 | 3 | 3.1 (0.4) | 30.0 (3.6) | 14.1 (2.5) |
|  | Citric | 3 | 4 | 2.6 (0.4) | 28.9 (7.0) | 12.1 (2.3) |

values in parentheses are standard deviations.

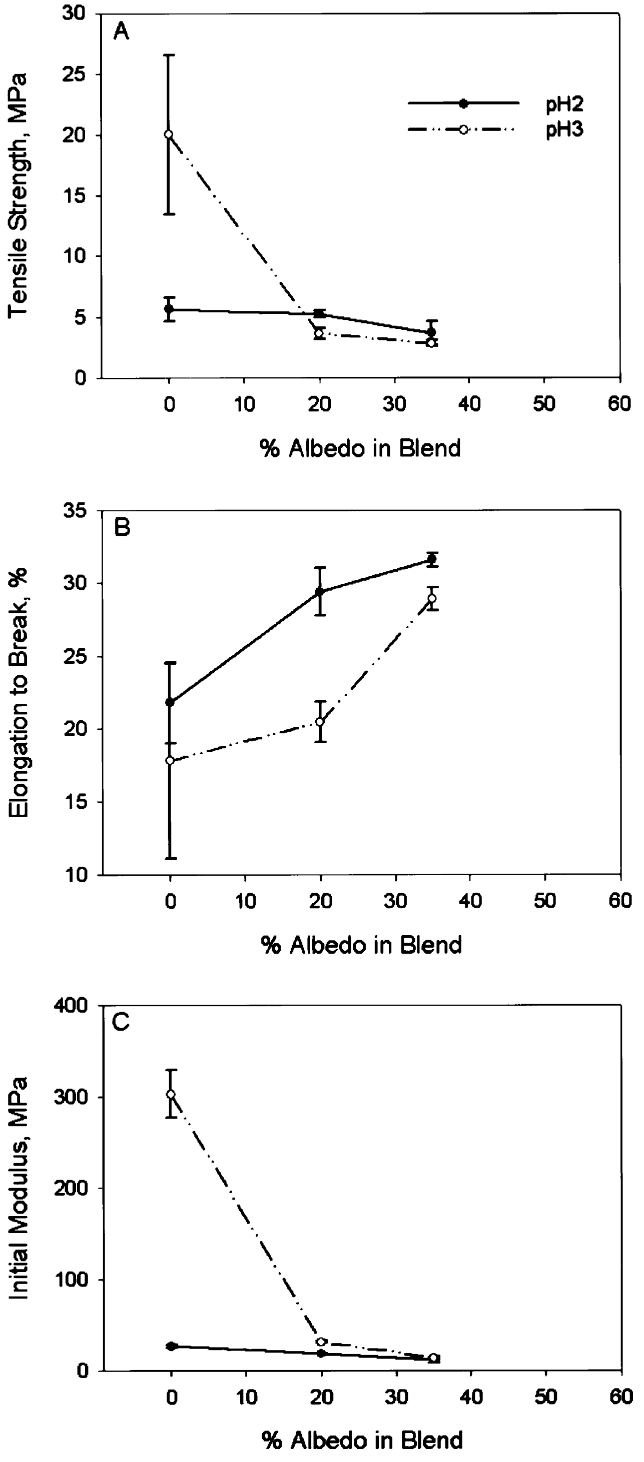

Fig. 2. Effect of albedo level and citric acid pH on the tensile properties of cast films prepared using microwave pretreatment of albedo for pectin/albedo/glycerol blends.

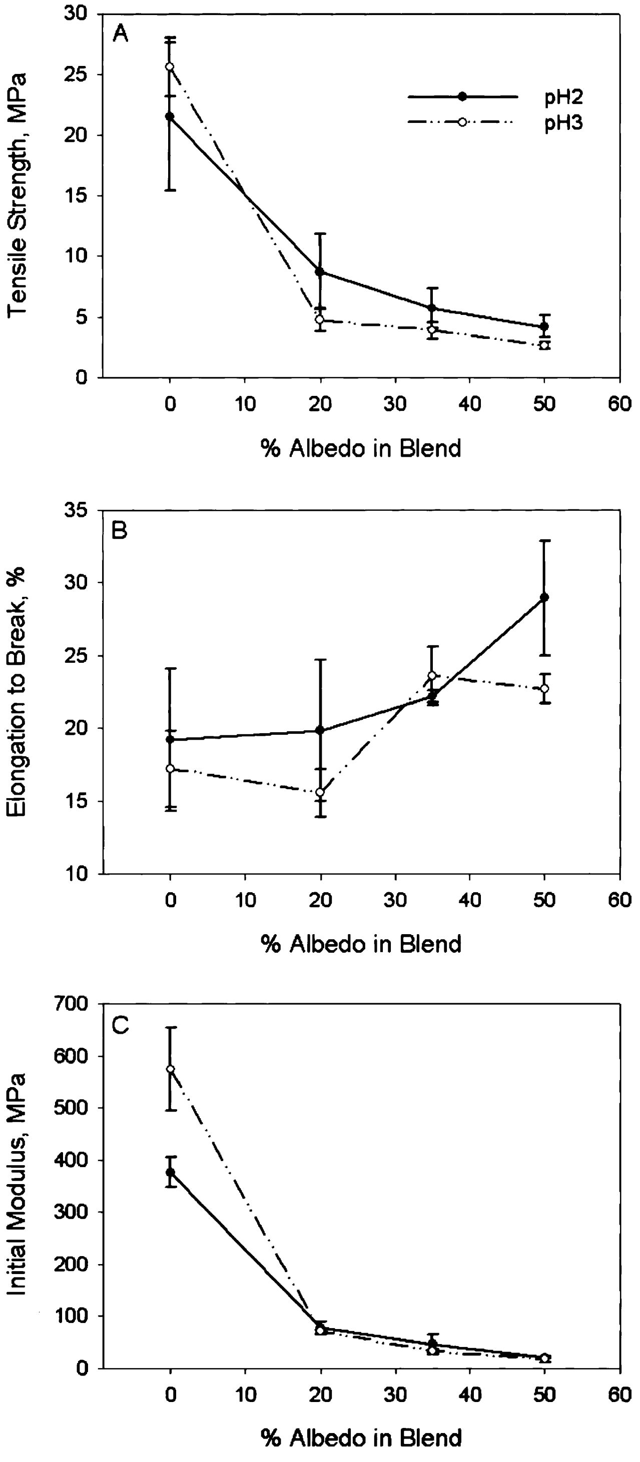

Fig. 3. Effect of albedo level and hydrochloric acid pH on the tensile properties of cast films prepared using microwave pretreatment of albedo for pectin/albedo/glycerol blends.

the pressure about 25 psi above ambient whereas at 4 min they reached 140 °C and about 40 psi above ambient, respectively. The results of these experiments are shown in Table 5, and are plotted in Fig. 2 (citric acid in the dispersion fluid) and 3 (HCl in the dispersion fluid). In most experiments time of heating and final temperature did not make a significant difference in tensile properties, so data for the two heating times were combined in Figs. 2 and 3.

As when films were extruded, there was a significant decrease in TS and IM with increasing albedo level of cast films (see Figs. 2 and 3). Unlike the extruded samples, EB clearly increased with increasing albedo in the blend. When pectin/albedo/glycerol films were cast from citric acid at pH 3 (Fig. 2), there was a very large drop off in TS and IM and an increase in EB over films containing no albedo. Nevertheless, at pH 2 the values found for TS and IM with no added albedo were nearly as low as those for the samples containing albedo. These differences between the two pH levels of citric acid may not have been due to an increase in acid strength but rather due to the large concentration of citric acid (about 16%) required to reach pH 2. That amount of citric acid may have plasticized the film.

For samples prepared by microwave heating and solution casting with aqueous HCl as the solvent (Fig. 3), TS and IM dropped off with increasing amounts of albedo in the sample, and EB was somewhat erratic but tended to increase with increasing albedo level. This tensile behavior was similar to that which occurred in the presence of citric acid at pH 3.

Overall, these results indicated that extrusion with albedo present lowers TS, EB and IM in pectin/glycerol films. Extrusion with replacement of about two thirds of the starch with albedo in optimal pectin/starch/glycerol films will not significantly deteriorate mechanical properties. Microwave/ solution casting experiments with albedo present did not significantly improve TS, EB or IM values over those obtained in extrusion experiments. Nevertheless, even in the absence of starch, free standing films were obtained by extrusion in the presence of albedo.

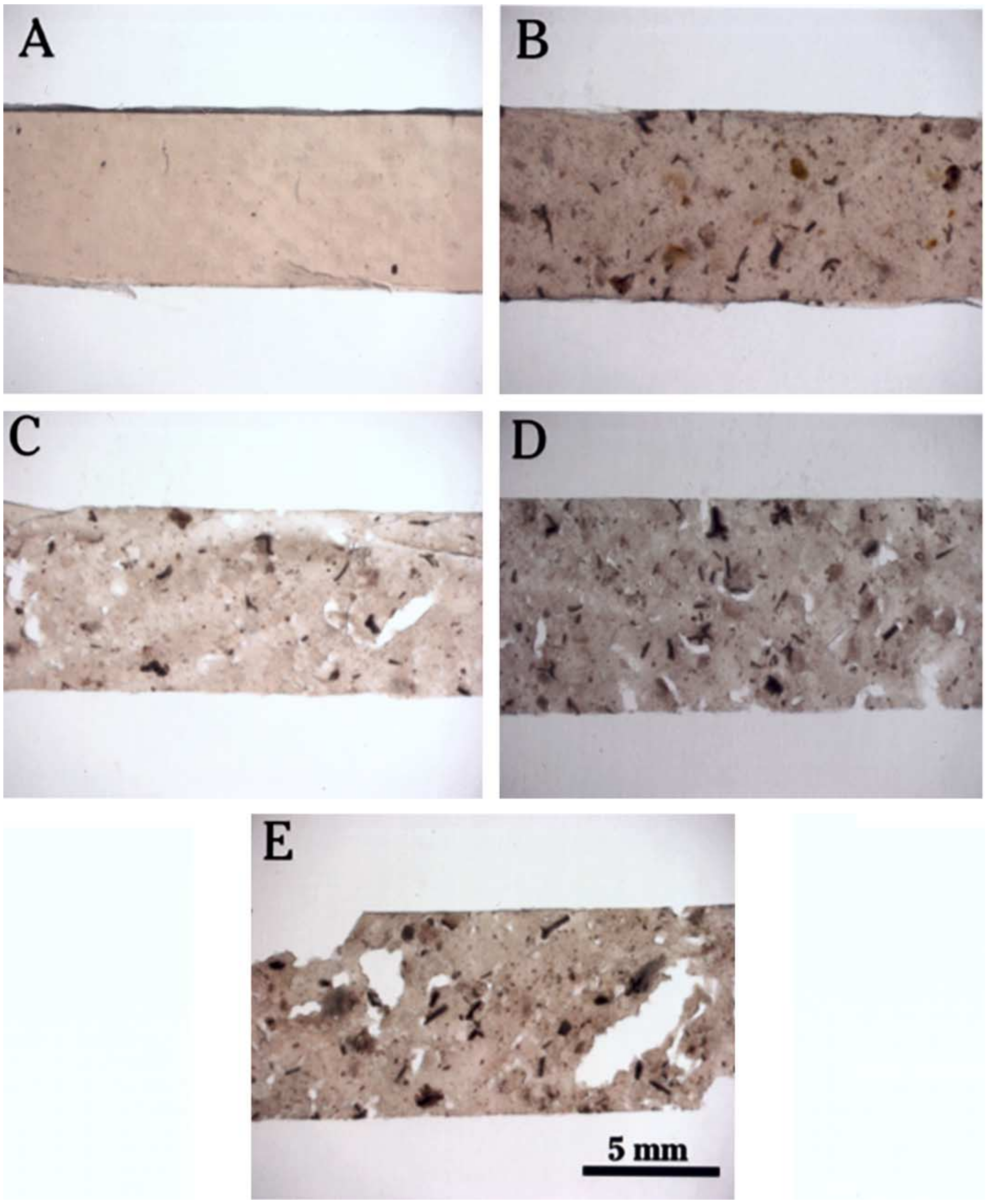

Fig. 4. Optical micrographs of pectin/albedo/glycerol films extruded with hydrochloric acid at pH 2 and compression molded. P/A/G ratios: (A) 70/00/30, (B) 50/20/30, (C) 35/35/30, (D) 20/50/30, (E) 20/50/30, no HCl.

Visual and optical microscopic examination of the extruded films indicated that the amount of particulate matter incorporated into the extruded product increased with the amount of albedo in the feed. Samples prepared using hydrochloric acid appeared to have somewhat smaller amounts of particulate matter incorporated into extruded films than did those fabricated with neat water or aqueous citric acid. Typical optical micrographs of the upper surface of films extruded with aqueous HCl are imaged in Fig. 4. The areas of homogeneous grey represent solubilized matter. Darker areas represent particulate matter. White areas indicate the presence of holes in the film. Few, if any, particulates were present in the material containing no albedo (Fig. 4A). Of films containing albedo, the sample with P/A/G composition, 50/20/30 (Fig. 4B) appears to contain the least amount of particulate matter. Fig. 4C–E have increasing amounts of albedo in the feed and proportionately more observable particulate matter. Unlike Fig. 4A and B, holes are visible in Fig. 4C and D. The sample imaged in Fig. 4E had the same composition as the sample imaged in Fig. 4D but the processing water contained no acid. Thus, less pectin was solubilized from the albedo and more particulates and holes were observed. These observations strongly suggest that hydrochloric acid acted more strongly to break up the albedo than either neat water or aqueous citric acid at pH 4. The appearance of holes at higher levels of particulate matter may indicate that unsolubilized albedo is somewhat incompatible with solubles in the composite of pectin and albedo. We note that the universal mechanical testing discussed above did not reflect the existence of holes in the film in that these were not included in the part of the films tested. This probably explains why added acid in the processing fluid had little or no effect on

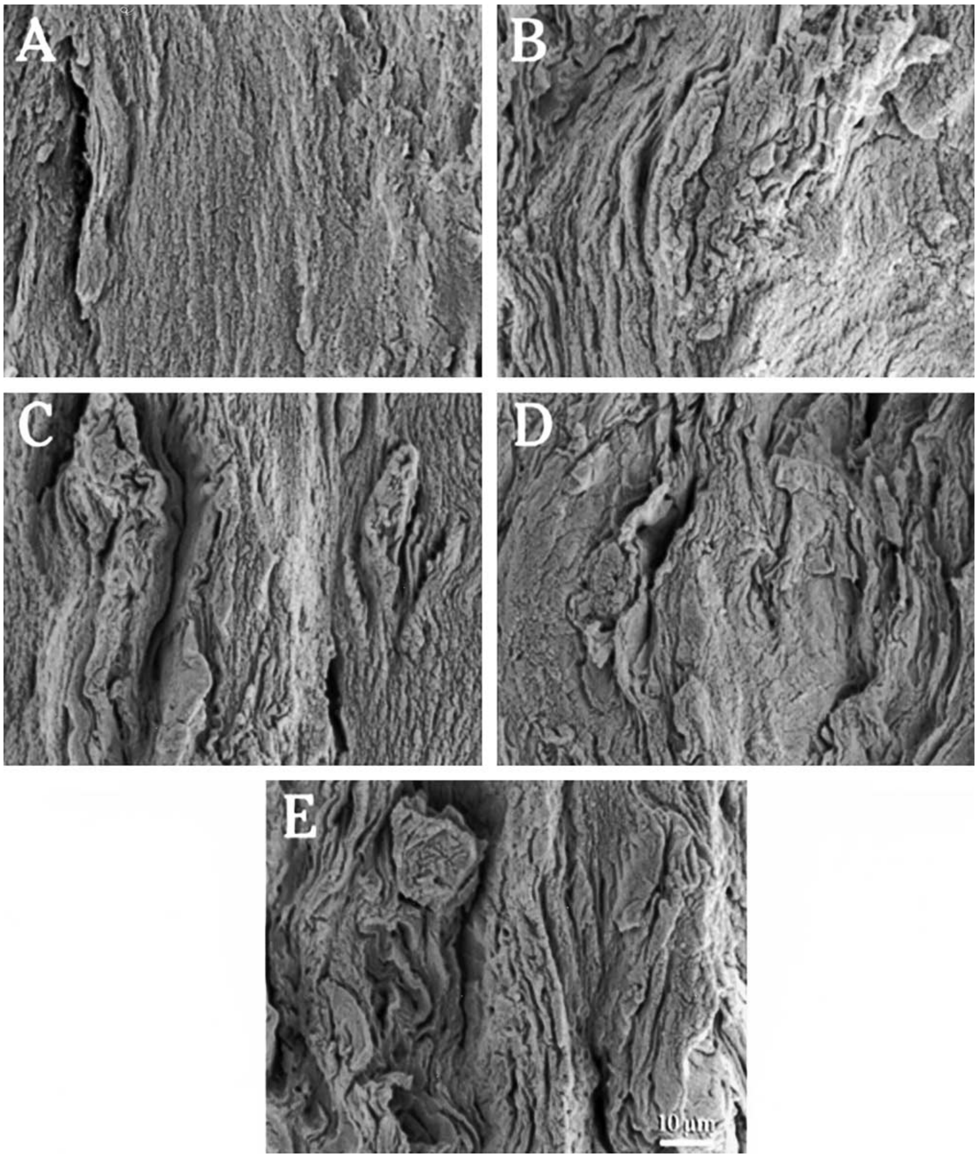

Fig. 5. SEM photomicrographs of pectin/albedo/glycerol films extruded with hydrochloric acid at pH 2 and compression molded. 2500X. P/A/G ratios: (A) 70/00/30, (B) 50/20/30, (C) 35/35/30, (D) 20/50/30, (E) 20/50/30, no HCl.

mechanical properties even though holes were imaged by optical microscopy.

Fig. 5 contains scanning electron micrographs (SEM) of freeze fractured extruded films with compositions which are equivalent to those which are shown in Fig. 4. The control sample containing no albedo (Fig. 5A) had a fairly smooth and uniform appearance with little or no evidence of particulates. Increasing the albedo level in samples in Fig. 5B–D produced samples in which striations and crevices became more pronounced with increased percentage of albedo in the film. In view of the optical micrographs, the appearance of striations could be interpreted as interfaces or micro-crevices between pectin and the insoluble remains of the albedo at the microstructure level. Sample 5E with a P/A/G composition 20/50/30 has the largest amount of unsolubilized albedo in that the extrusion was performed in water so that less pectin was solubilized than in sample 5D which was extruded in the presence of HCl. The general appearance appears to be that of layers pressed together. Thus interpretations of film images at the microstructure and visible levels appear to be consistent with one another.

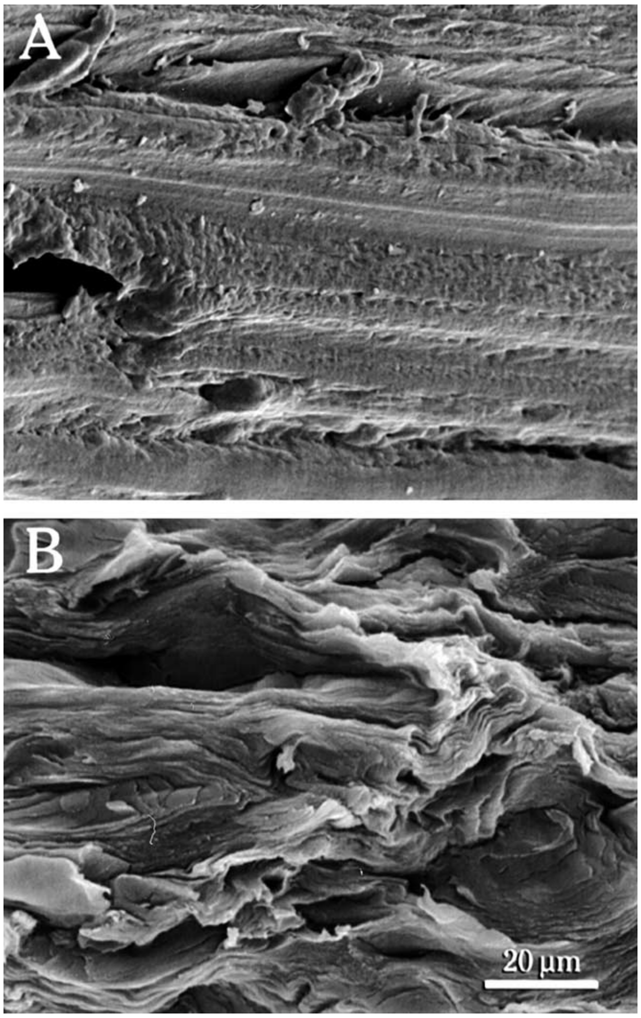

Fig. 6. SEM photomicrographs of pectin/albedo/glycerol films extruded with citric acid at pH 4 and compression molded. 1000X. P/A/G ratios: (A) 70/00/30, (B) 20/50/30.

Fig. 6B contains a freeze fractured SEM of a film with a P/A/G ratio of 20/50/30 which was extruded with pH 4 citric acid solution. Included for comparison is a film also extruded with pH 4 citric acid which has a P/A/G ratio of 70/00/30 (Fig. 6A). The film in Fig. 6B has more visible crevices than the film in Fig. 6A. Furthermore the film in 6B also has more visible and bigger crevices than the film in 5D which is of identical composition but was extruded with HCl, pH 2 rather than pH 4 citric acid. Moreover the image in Fig. 6B more closely resembles the image in 5E which was processed in water than it does 5D. Comparisons of 6A with 6B reveal that pectin forms a somewhat incompatible composite with albedo. Since processing in pH 2 HCl, rather than pH 4 citric acid or water produces fewer crevices, we conclude that pH2 HCl solubilizes pectin at the expense of albedo, thus producing fewer crevices than processing either in pH 4 citric acid or water.

In Fig. 7 are freeze fractured SEMs of pectin/starch/albedo/glycerol samples. Unlike SEM images of pectin/albedo/glycerol films shown in Figs. 5 and 6, only a few crevices are visible in Fig. 7A–D. The images in Fig. 7 are very similar in appearance to pectin/starch/glycerol cast films that we have made previously (Fishman et al., 1996). In that study, it was concluded that pectin forms a compatible composite with high amylose starch. In this as well as the earlier study, starch particles were visible within the polymer matrix. Nevertheless, these films are coherent in appearance. It appears that the starch acts to compatibilize the pectin and the albedo. The result is that P/A/S/G films have greater integrity and improved properties compared to P/A/G films. In the case of P/A/S/G films, SEM images are consistent with the tensile data obtained.

Selected films were analyzed by dynamic mechanical analysis. Fig. 8 comprised of DMA curves for samples extruded with HCl. These samples have 0, 20, 35, and 50% albedo, 30% glycerol and the remainder pectin. A cast film comprised of 70% pectin and 30% glycerol was analyzed for comparison. All samples gave somewhat lower values than the cast film control. This behavior has been noticed before (Fishman, et al., 2000). The extruded samples containing 0, 20, and 35% albedo (0, 28, and 50% pectin replacement) exhibited storage modulus ($E'$) and loss modulus ($E''$) curves (Fig. 8A and B) which decreased in value as the amount of albedo in the blend increased. The sample containing 50% albedo (72% pectin replacement) had $E'$ and $E''$ curves which were even significantly lower than those for the other samples. The data for all samples were well behaved from $-100$ to 0 °C. Above 0 °C, even at the small deformations being measured, the sample containing 50% albedo appeared to be breaking up.

The temperature dependence of tan $\delta$ is shown in Fig. 8C. Tan $\delta$ is the ratio of $E''/E'$. Overall tan $\delta$ increases with increasing temperature. The rise in tan $\delta$ indicates that $E''$ is decreasing with temperature more slowly than $E'$. Two peaks are observed in all curves. The peak in the range

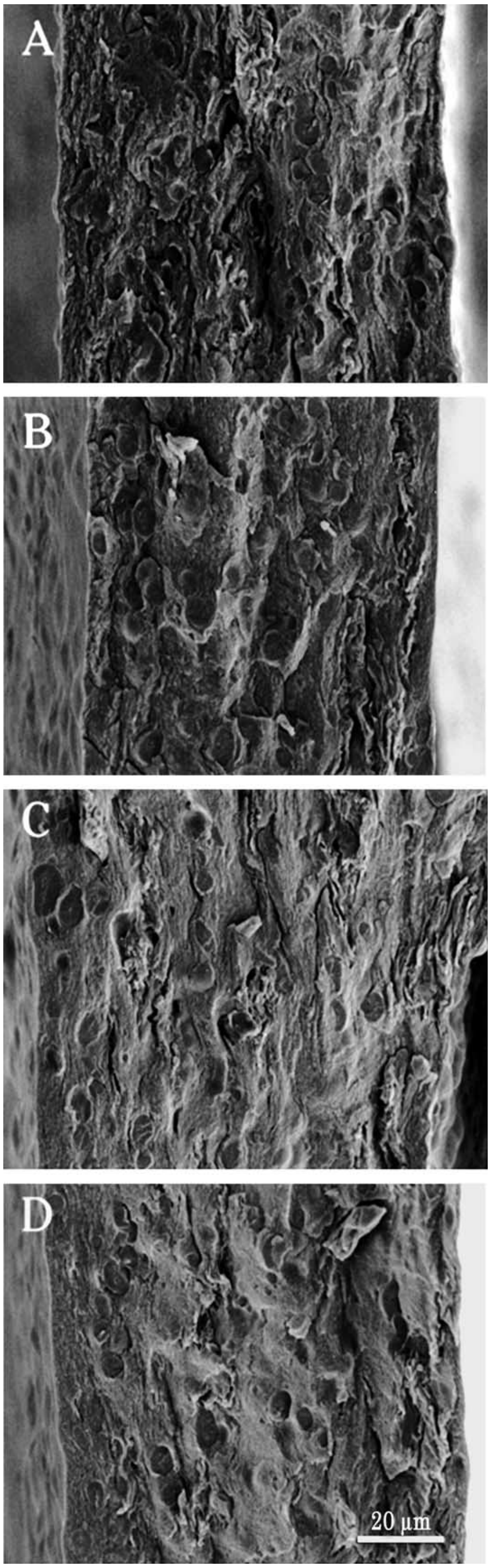

Fig. 7. SEM photomicrographs of pectin/starch/albedo/glycerol films extruded with water and hydrochloric acid at pH 2 and compression molded. 1000X. P/S/A/G ratios: (A) 39/21/10/30, water; (B) 39/21/10/30, HCl; (C) 39/10/21/30, HCl; (D) 39/10/21/30, water.

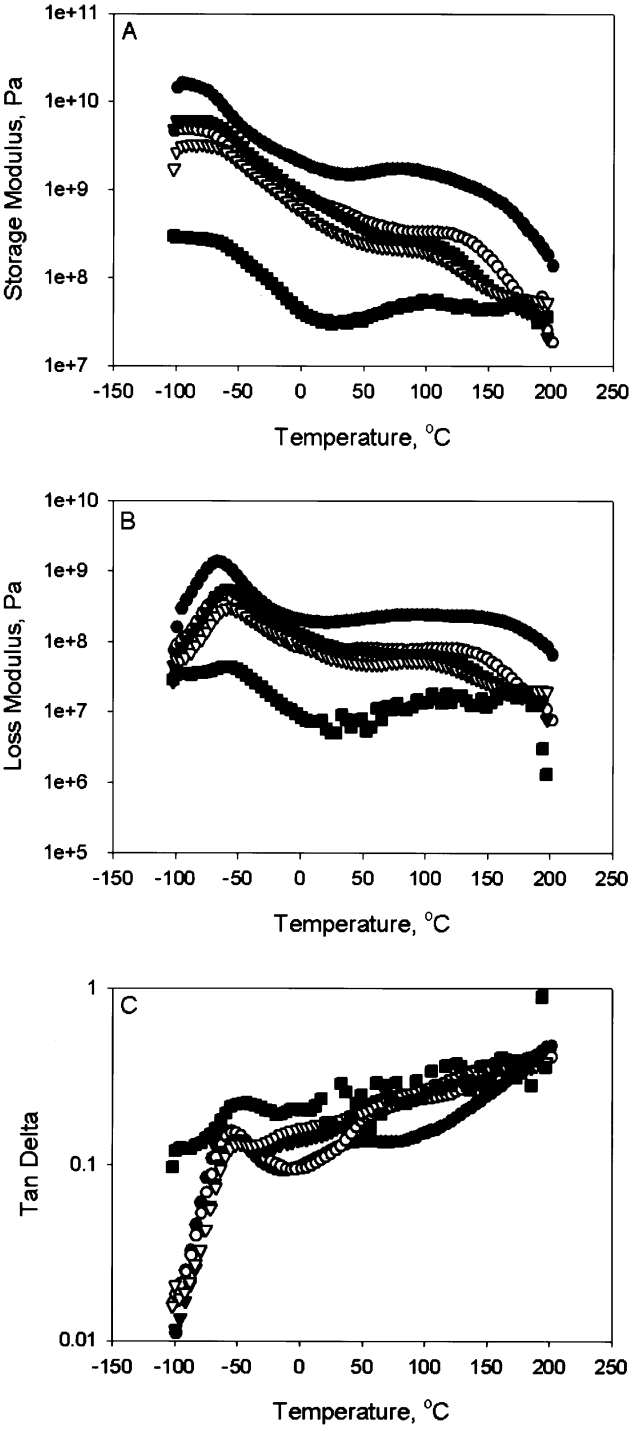

Fig. 8. Effect of blend composition on the dynamic mechanical properties of pectin/albedo/glycerol extruded and compression molded into films, and comparison to a cast pectin/glycerol films. ● PG 70/30, ○ PAG 70/0/30, ▼ PAG 50/20/30, ▽ PAG 35/35/30, ■ PAG 20/50/30.

centered about −50 °C is the onset of a glass to rubbery flow transition ($T_g$). A second peak appears at or above 0 °C. For the cast pectin film this occurs in the range of 45 °C whereas it occurs at a somewhat higher temperature for the extruded film. This second order transition may be related to the onset of translational motion of the entire molecule $T_{||}$

(Sperling, 1992). $T_{||}$ typically occurs at temperatures above $T_g$ and for the films under study may be facilitated by the relatively large amount of glycerol present. Compression molding of extruded films may increase pectin- pectin interactions causing a delay in the onset of $T_{||}$. The early onset of $T_{||}$ for samples containing albedo as compared to those not containing albedo may be indicative of the lower compatibility between pectin and albedo than between pectin and itself.

DMA analyses also were obtained for pectin/starch/albedo/glycerol samples. Two samples were processed in water and two in HCl. Typical curves for the four samples are shown in Fig. 9. While the data varied somewhat from sample to sample, all four materials showed rather similar behavior in

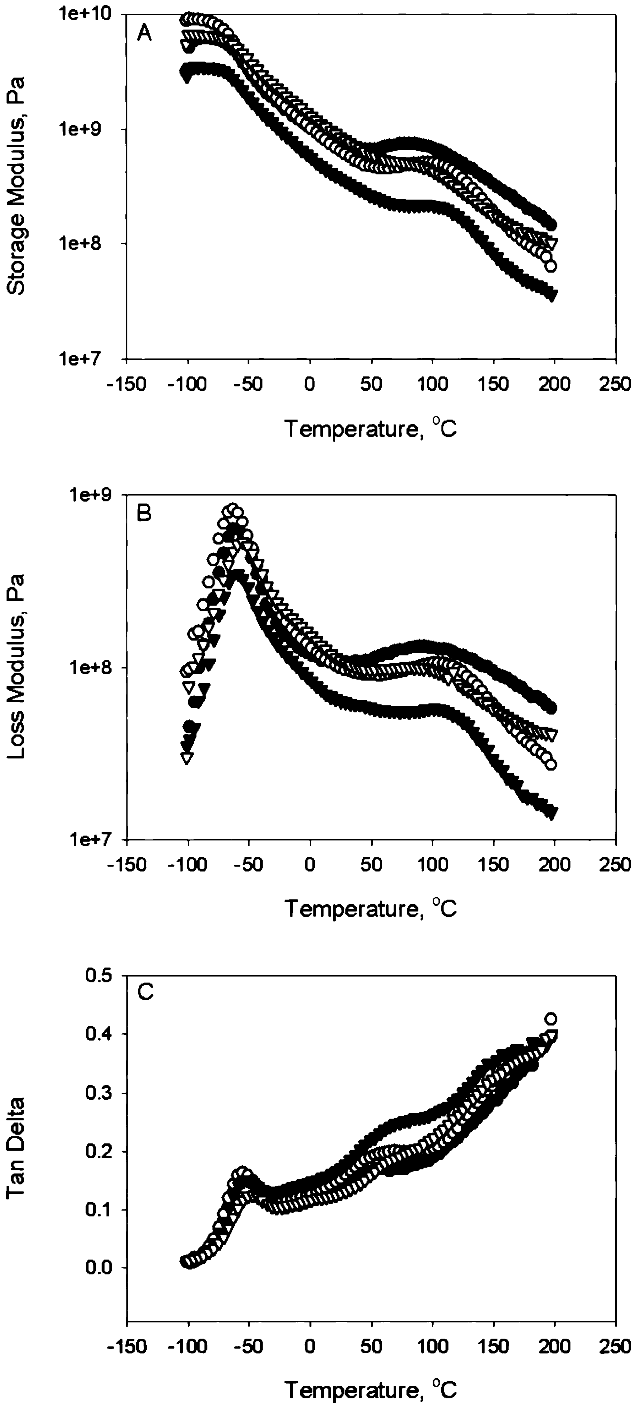

Fig. 9. Effect of blend composition and hydrochloric acid on the dynamic mechanical properties of pectin/starch/albedo/glycerol blends extruded and compression molded into films. ● PSAG 39/21/10/30, ○ PSAG 39/21/10/30 HCl, ▼ PSAG 39/10/21/30 HCl, ▽ PSAG 39/10/21/30.

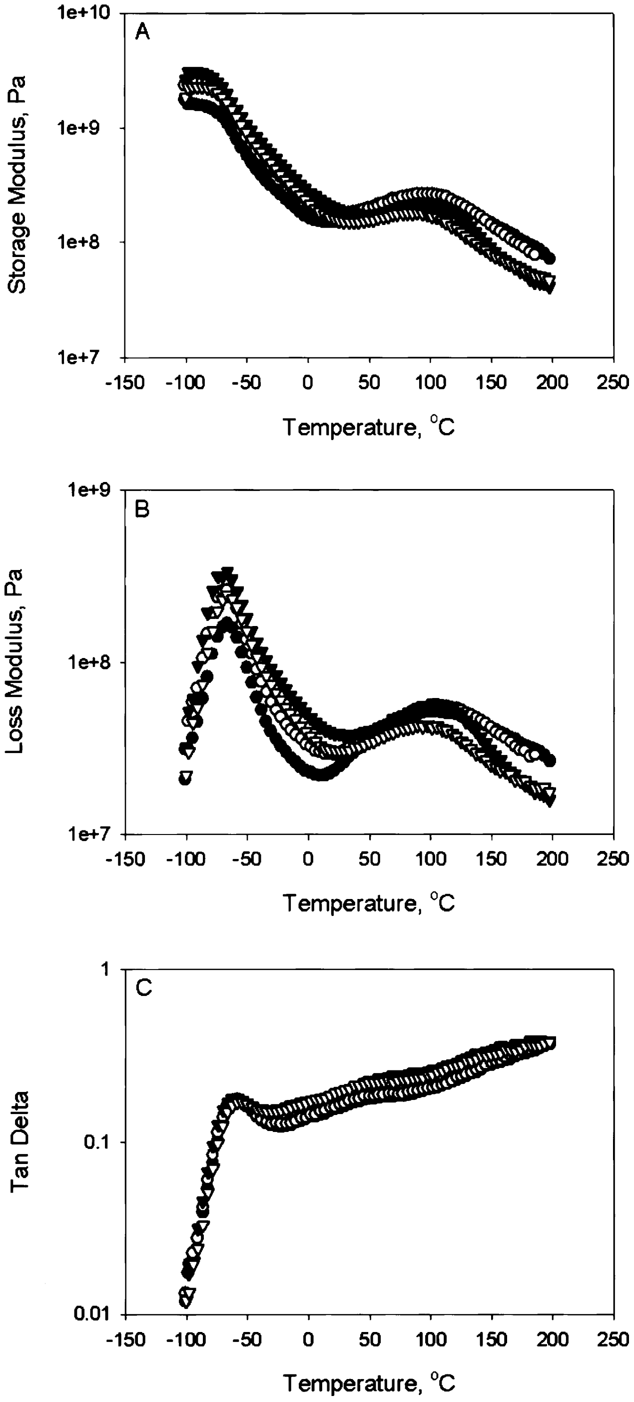

Fig. 10. Effect of blend composition and hydrochloric acid on the dynamic mechanical properties of redissolved and solution cast films made from extruded pectin/starch/albedo/glycerol blends. ● PSAG 39/21/10/30, ○ PSAG 39/21/10/30 HCl, ▼ PSAG 39/10/21/30 HCl, ▽ PSAG 39/10/21/30.

the temperature dependence of $E'$, $E''$ and tan $\delta$. There appeared to be an identifiable difference in $E'$ values (Fig. 9A) at all temperatures between samples made using the two different albedo levels when HCl was the processing fluid. When water was the processing fluid, $E'$ values differed only when the temperature exceeded 50 °C. The storage modulus for the samples with the lower albedo level (39/21/10/30) decreased from its plateau value at about −70 °C to a peak at about +85 °C for the water sample and at +100 °C for the HCl sample. The second peak was followed by a further decline in modulus. All the curves for the loss modulus (Fig. 9B) showed $T_g$ and $T_{||}$ transitions. The loss tangent curves for all samples showed the same general features, with a $T_g$ peak at about −50 to −55 °C and a broader $T_{||}$ peak at about 50 °C. The general shapes of the curves for the pectin/starch/albedo/glycerol samples (Fig. 9) were similar to those for the pectin/starch/albedo blends (Fig. 8) for samples containing 35% or more pectin (50% or less replacement of pectin).

Fig. 10 shows the DMA curves of extruded pectin/starch/albedo/glycerol samples which were re-dissolved and cast into films. Unlike the films whose mechanical properties were shown in Fig. 9, these materials were not compressed and molded into films. DMA revealed that the dynamic mechanical properties of these materials were comparable to extruded P/S/G and P/A/S/G compressed and molded films as well as cast films which were not extruded as long as compositions were comparable. It does appear that differences due to processing fluid have essentially disappeared. Overall, $E'$ and $E''$ of re-dissolved extruded films are some what lower than the extruded compression molded films.

## 4. Conclusion

Based on the tensile data, DMA studies, optical microscope and SEM analysis, we found that the extruded pectin/albedo/starch/glycerol blends provided the best mechanical properties of any of the albedo containing materials studied. Properties were at least as good as the extruded pectin/starch/glycerol blends which we researched. Research appears to indicate that these materials could be used in applications requiring moderate strength characteristics. Dynamic mechanical properties at moderate pectin replacement levels appear to be as good as found with cast films. Furthermore, optical microscopy revealed that extrusion in the presence of dilute HCl was more effective in disintegrating albedo than either water or dilute citric acid.

## Acknowledgements

We thank André White and Jamal Booker for their help in carrying out the extrusion runs. We also thank Dr Peter Cooke and Mr Douglas Soroka of the Microscopic Imaging Group for their work in obtaining the scanning electron micrographs.

## References

Coffin, D. R., & Fishman, M. L. (1993). Viscoelastic properties of pectin/starch blends. *Journal of Agricultural and Food Chemistry*, *41*, 1192–1197.

Coffin, D. R., & Fishman, M. L. (1994). Physical and mechanical properties of highly plasticized pectin/starch films. *Journal of Applied Polymer Science*, *54*, 1311–1320.

Coffin, D. R., Fishman, M. L., & Cooke, P. H. (1995). Mechanical and microstructural properties of pectin/starch films. *Journal of Applied Polymer Science*, *57*, 663–670.

Coffin, D. R., Fishman, M. L., & Ly, T. V. (1996). Thermomechanical properties of blends of pectin and poly(vinyl alcohol). *Journal of Applied Polymer Science*, *61*, 71–79.

Fishman, M. L., Chau, H. K., Hoagland, P. D., & Ayyad, K. A. (2000). Characterization of pectin flash-extracted from orange albedo by microwave heating, under pressure. *Carbohydrate Research*, *323*, 126–138.

Fishman, M. L., & Coffin, D. R (1995). Films fabricated from mixtures of pectin and starch. US Patent 5,451,673, September 19, 1995.

Fishman, M. L., & Coffin, D. R. (1998). Mechanical, microstructural and solubility properties of pectin/poly(vinyl alcohol) blends. *Carbohydrate Polymers*, *35*, 195–203.

Fishman, M. L., Coffin, D. R., Konstance, R. P., & Onwulata, C. I. (2000). Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydrate Polymers*, *41*, 317–325.

Fishman, M. L., Coffin, D. R., Unruh, J. J., & Ly, T. (1996). Pectin/starch/glycerol films: blends or composites. *Journal of Macromolecular Science: Pure and Applied Chemistry*, *A33*, 639–654.

Hwang, J.-K., Kim, C.-L., & Kim, C.-T. (1998). Extrusion of apple pomace facilitates pectin extraction. *Journal of Food Science*, *63*, 841–844.

May, C. D. (1995). Industrial pectins: sources, production and applications. *Carbohydrate Polymers*, *12*, 79–99.

Otey, F. H., Mark, A. M., Melhtretter, C. L., & Russell, C. R. (1974). Starch based film for degradable agricultural mulch. *Industrial Engineering Chemical Products Research and Development*, *13*, 90–92.

Otey, F. H., Westhoff, R. P., & Doane, W. M. (1980). Starch-based blown films. *Industrial Engineering Chemical Products Research and Development*, *19*, 592–595.

Ralet, M.-C., Axelos, M. A., & Thibault, J.-F. (1994). Gelation properties of extruded lemon cell walls and their water-soluble pectins. *Carbohydrate Research*, *260*, 271–282.

Ralet, M.-C., & Thibault, J.-F. (1994). Extraction and characterization of very highly methylated pectins from lemon cell walls. *Carbohydrate Research*, *260*, 283–296.

Ralet, M.-C., Thibault, J.-F., & Della Valle, G. (1991). Solubilization of sugar-beet pulp cell wall polysaccharides by extrusion-cooking. *Lebensmittel Wissenschaft und Technologie*, *24*, 107–112.

Sperling, L. H. (1992). *Introduction to physical polymer science*. New York: Wiley, 329p.

Willett, J. L., Millard, M. M., & Jasberg, B. K. (1997). Extrusion of waxy maize starch: melt rheology and molecular weight degradation of amylopectin. *Polymer*, *38*, 5983–5989.