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Extrusion of pectin/starch blends plasticized with glycerol☆

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Abstract

The microstructural and thermal dynamic mechanical properties of extruded pectin/starch/glycerol (PSG) edible and biodegradable films were measured by scanning electron microscopy (SEM) and thermal dynamic mechanical analysis (TDMA). SEM revealed that the temperature profile (TP) in the extruder and the amount of water present during extrusion could be used to control the degree to which the starch was gelatinized. TDMA revealed that moisture and TP during extrusion and by inference the amount of starch gelatinization had little effect on the mechanical properties of PSG films. Furthermore, TDMA revealed that PSG films underwent a glass transition commencing at about −50°C and two other thermal transitions above room temperature. Finally, it was concluded that the properties of extruded PSG films were comparable to those cast from solution. © 2000 Published by Elsevier Science Ltd.

Keywords: Pectin/starch blends; Glycerol; Plasticization

1. Introduction

The desire to add value to under-used agricultural commodities has led us to search for new uses for pectin, a co-product of fruit juice, sunflower oil and sugar from sugar beet. Pectin is a major structural component of cell walls consisting mainly of partially methyl esterified poly($\alpha(1 \rightarrow 4)$D-galacturonic acid) containing rhamnose inserts in the backbone and neutral sugar side chains. It is both water soluble and biodegradable.

When blended with starch and plasticized with glycerol, pectin forms edible and biodegradable films which have a wide range of good mechanical properties (Coffin & Fishman, 1993; Fishman & Coffin, 1995; Fishman, Coffin, Unruh & Ly, 1996) and excellent oxygen barrier properties (Coffin & Fishman, 1994). Pectin is also miscible with poly(vinyl alcohol) in all proportions, and together they form films which also have excellent mechanical properties (Coffin & Fishman, 1997; Coffin, Fishman & Ly, 1996; Fishman & Coffin, 1998). Potential industrial uses for the pectin/starch/glycerol (PSG) and pectin/poly(vinyl alcohol) films include water soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices. In addition edible bags for soup and noodle ingredients can be fabricated from PSG films.

All of these films in the studies cited above, however, were prepared by casting from relatively dilute water solutions (5–8 wt.%) onto inert substrates and allowing them to air dry at room temperature. While casting is a practical laboratory method and there are commercial processes employing solution casting of films, nevertheless, extrusion is an obvious alternative. Extrusion is often preferred to casting as the method of fabricating films because the throughput of the process is faster and less energy is required for the removal of water. Furthermore, the starch has to be pre-gelatinized when casting films whereas the starch granules can be gelatinized in situ during the extrusion process. All of these factors reduce the production costs of fabricating PSG films by extrusion rather than by casting (Westover, 1967).

Extrusion is the process of choice for common thermoplastic materials such as polyethylene, polypropylene, and poly(ethylene terephthalate) (Wolinski, 1967). Nevertheless an extensive amount of research also has been carried out on the extrusion of biopolymers. For example, blends of corn starch with synthetic thermoplastic materials and other biopolymers have been extruded (Otey, Mark, Mehltretter & Russell, 1974; Otey, Westhoff & Doane, 1980; Shogren, Swanson & Thompson, 1992; Willett, Jasberg & Swanson, 1995; Willett, Millard & Jasberg, 1997). Sodium alginate has been solution extruded into a chitosan/$CaCl_2$ coagulating bath to prepare microcapsules for drug delivery (Lee,

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Table 1
Extruder temperature profiles

Profile	Zone								
	1	2	3	4	5	6	7	8	9
1	35	35	55	70	100	110	100	90	90
2	35	35	55	70	100	110	110	100	90
3	35	35	55	70	110	120	120	100	90
4	35	35	55	60	75	85	90	85	80
5	35	55	80	110	120	100	85	60	35
6	35	60	90	120	140	110	80	60	35

Park & Ha, 1997), and alginate gels have been produced by an extrusion/cross-linking process (Li, Altreuter & Gentile, 1996). Previous work in our laboratories has involved the extrusion of corn–soy blends for the preparation of instantized emergency rations (Konstance et al., 1998).

In this paper, we describe the extrusion of PSG blends into films and some of their mechanical and microstructural properties. Furthermore, we compare the properties of these films with those of comparable solution cast films of PSG.

2. Experimental procedures

2.1. Materials

Pectin used in these studies was MexPec 1400, supplied by the Grindsted Division of Danisco Brands (Kansas City, KS). Starch in the form of granules was Amylomaize VII supplied by American Maize Products Co. (now Cerestar) of Hammond, IN. Reagent grade glycerol was purchased from Aldrich Chemical Co. (Milwaukee, WI). All of these materials were used as received with no further purification. Local tap water was used in all of the extrusion runs.

2.2. Extrusion

Blends of pectin, high amylose starch granules, and glycerol with a variety of compositions were extruded using a Werner Pfleiderer ZSK30 twin screw extruder (Krupp, Werner & Pfleiderer Co., Ramsey, NJ). Mass flow rates for the blends ranged from 27 to 102 g/min (1.62–6.12 kg/h). The water to solids feed rates were varied between 0.43 and 2.85 ml/g to produce samples with a range of moisture contents about 30–75%. Six different extruder temperature profiles were used as given in Table 1 and plotted in Fig. 1. In Trials 1–3, the screw speed was 350 rpm whereas in Trial 4 some extrusions were at 350 and others at 450 rpm.

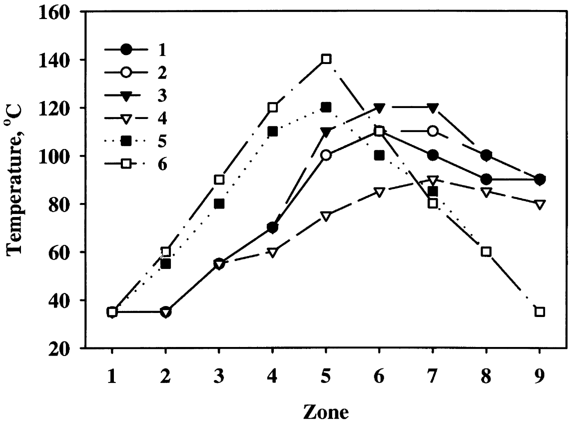

Fig. 1. Extruder temperature profile. Profiles are numbered in graph legend.

Method 1 employed in Trials 1 and 2, consisted of mixing 10% water with 90% pectin/starch blend (w/w) in the bowl of a Hobart (model C-100-T, Hobart Mfg. Co., Troy, OH) mixer, followed by blending with glycerol. This mixture was allowed to stand overnight, and was then ground to a powder in a commercial Waring food processor.

Method 2 employed in Trials 3 and 4, consisted of pre-mixing dry pectin and starch in a plastic bucket followed by slowly adding the pre-mix to glycerol in the bowl of a Hobart dough mixer. Mixing was continued until the blend appeared uniformly dry. Then this blend was covered and allowed to stand overnight. Finally, the blend was attrited to a free flowing powder by grinding in the food processor.

Unlike particles prepared by Method 1, those prepared by the Method 2 ground more easily and gave a softer powder with relatively few hard particles. Nevertheless, hard particles that remained, regardless of preparation method, eventually were ground up by the feed screw.

The PSG 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 hopper to barrel over a fixed time interval.

In Trial 1, the product was extruded through a 5 mm × 22 mm stainless steel slit die whereas in subsequent trials, a 1.5 mm × 5 mm stainless steel die was used. For a given set of processing conditions, runs within trials were allowed to reach steady state before collecting samples. Typically steady state was reached in 5–10 min. At steady state, a number of 6–8 in. strips were cut off at the die face and placed in Zip-Loc storage bags for future measurement. Some samples were calendered between the rolls of a double drum dryer to obtain samples sufficiently thin for mechanical property testing. Prior to testing, the samples were vacuum dried overnight at room temperature to remove all but bound water.

In Trials 1 and 2, water feed rate was varied at constant solids feed rate whereas in Trials 3 and 4, water feed rate was constant while solids feed rate was varied. Varying the ratio of solids feed rate to water feed rate allowed us vary the moisture level during extrusion of blends and thus observe the effect of this variable on the physical properties of the extrudate. Blends were replicated at constant temperature profile and feed composition before changing to the next material composition.

In Trials 3 and 4, prior to SEM examination of samples or

Table 2
Percentage water in extruded blends

Sample	Temperature profiles[a]	P/S/G ratio (w/w/w)	Water feed rate (WFR) (ml/min)	Solids feed rate (SFR) (g/min)	WFR/SFR	H_2O (%)
101[b]	1	78/0/22	27	30–35	0.83	60.3
102	1	78/0/22	36	30–35	1.11	53.5
103	1	78/0/22	17	30–35	0.52	47.7
104	2	78/0/22	53	30–35	1.63	64.3
105	2	78/0/22	53	30–35	1.63	70.1
106	3	67/11/22	53	30–35	1.63	65.1
107	3	67/11/22	36	30–35	1.11	54.5
108	3	56/22/22	53	30–35	1.63	62.3
109	3	56/22/22	36	30–35	1.11	52.6
110	4	56/22/22	53	30–35	1.63	64.1
111	4	56/22/22	36	30–35	1.11	55.1
112	4	67/11/22	36	30–35	1.11	55.5
113	4	67/11/22	53	30–35	1.63	63.6
114	4	78/0/22	53	30–35	1.63	63.3
115	4	78/0/22	36	30–35	1.11	58.0
116	4	78/0/22	17	30–35	0.52	42.3
201	4	67/11/22	53	27	1.96	71.6
202	4	67/11/22	77	27	2.85	75.4
203	4	67/11/22	44	27	1.63	66.5
204	3	67/11/22	44	27	1.63	65.2
205	3	67/11/22	52	27	1.93	68.2
206	3	67/11/22	77	27	2.85	73.0
301	4	39/31/30	44	30	1.47	59.0
302	4	39/31/30	44	42.5	1.04	49.0
303	4	39/31/30	44	59.5	0.74	43.2
304	4	49/21/30	44	30	1.47	60.0
305	4	49/21/30	44	42.5	1.04	53.6
306	4	49/21/30	44	59.5	0.74	43.7
307	3	39/31/30	44	30	1.47	57.5
308	3	39/31/30	44	42.5	1.04	47.6
309	3	39/31/30	44	59.5	0.74	40.1
310	3	49/21/30	44	30	1.47	58.3
311	3	49/21/30	44	42.5	1.04	48.9
312	3	49/21/30	44	59.5	0.74	41.5
401	5	39/31/30	44	30	1.47	67.7
402	5	39/31/30	44	30	1.47	64.3
403	5	39/31/30	44	68	0.65	44.7
404	5	39/31/30	44	68	0.65	43.8
405	5	39/31/30	44	102	0.43	35.0
406	5	39/31/30	44	102	0.43	34.6
407	6	39/31/30	44	30	1.47	61.9
408	6	39/31/30	44	30	1.47	59.3
409	6	39/31/30	44	68	0.65	40.6
410	6	39/31/30	44	68	0.65	40.6
411	6	39/31/30	44	102	0.43	31.0
412	6	39/31/30	44	102	0.43	29.7

[a] See Table 1 and Fig. 1 for profiles.
[b] First digit is trial number, following digit(s) is(are) run number(s).

in the case of mechanical testing for Trial 3 samples, extruded strips were calendered with a double drum dryer in which the nip was set at about 0.15 mm. It was observed that samples underwent expansion after calendering and were somewhat thicker than the gap between the dryer drums.

2.3. Moisture level determination

Moisture levels in the extruded samples were determined gravimetrically by accurately weighing out a 2–4 g sample for each material, air drying for 48 h followed by vacuum drying to constant weight, and then reweighing the dried samples. Moisture values in Trial 2 were determined using the rapid moisture analyzer.

2.4. Mechanical properties

Dynamic mechanical properties were determined using a Rheometrics RSA II Solids Analyzer (Rheometric Scientific,

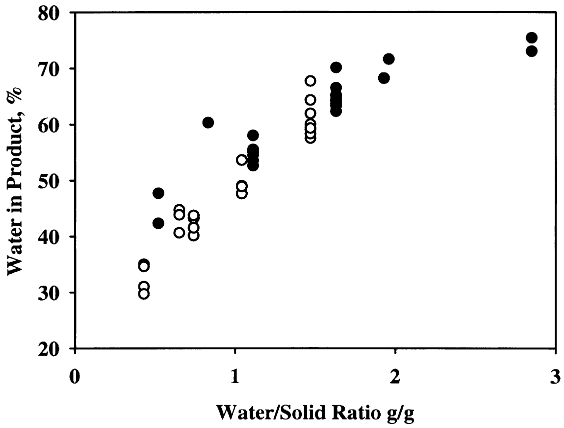

Fig. 2. Percentage of water in extruded blends against ratio of water to solids feed rate: Trials 1 and 2 (●); Trials 3 and 4 (○).

Piscataway, NJ). Samples were cut 1.5 in. long and 2–3 mm wide. Sample thicknesses ranged from 0.4 to 0.7 mm. Testing was done as described previously (Coffin & Fishman, 1994).

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 five minutes, 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 fractured 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

The temperature profiles used in the extruder for various runs are given in Table 1. A plot of temperature against zone for each profile is given in Fig. 1. Comparison reveals that profiles 5 and 6 rise and fall in temperature more rapidly than profiles 1–4.

Table 2 gives the percentage of water in extruded blends with various temperature profiles, compositions, water feed rates and solids feed rates. Fig. 2 is a plot of percentage water in extrudate against ratio of water to solids feed rate. The percentage of water in the extrudate increased with increasing water to solids feed rate ratio. The water content of extrudate from Trials 1 and 2 which had 10% water added to the feedstock prior to extrusion appeared to be slightly higher than extrudates from Trials 3 and 4 in which water was not added to the feedstock prior to extrusion. Over the range 0.43–2.85 water to solids feed rate ratio, the percentage of water in the extrudate ranged from 30 to 75%. For the most part, moisture levels in the extruded samples from all of the trials were very close to the values expected from the input material balance. Runs set at temperature profile 4, the only profile with no temperature zone set at 100°C or higher, gave a moisture level 1 or 2% higher than runs performed with the other temperature profiles. Nevertheless, in all cases, there was very little evaporation from the samples as indicated by material balances based on weight of initial feedstock. Pectin/starch/glycerol ratio (w/w/w) appeared to have no effect on moisture content of the extrudate.

Scanning electron micrographs of fracture surfaces of pectin films containing 22% glycerol by weight but no starch from Trial 1 are shown in Fig. 3. In these two samples, moisture content varied whereas temperature profile was a constant. Therefore differences on the appearance of fracture surfaces were attributed to differences in moisture content. Comparison of the surface of sample 116 in Fig. 3A, water content 42% with that of sample 114 in Fig. 3B, water content 63% shows that the rugosity of the image in Fig. 3A appears greater than the rugosity of that in Fig. 3B. The temperature profile during extrusion for these two surfaces was profile 4, the lowest temperature profile

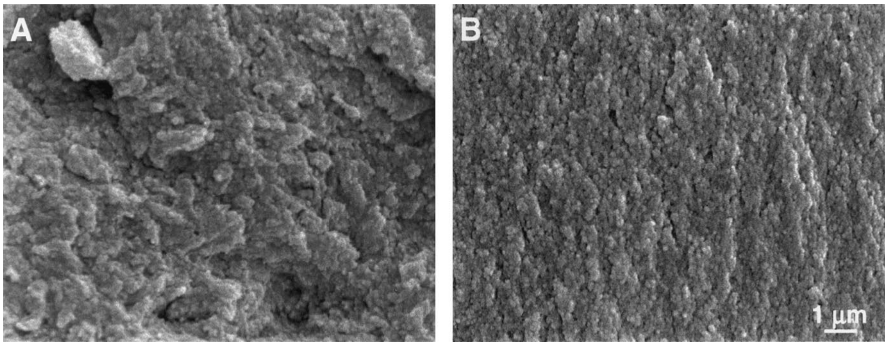

Fig. 3. Fracture surfaces of P/S/G films, 78/0/22 (w/w/w), TP 4: (A) sample 116, 42.3% water; (B) sample 114, 63.3% water.

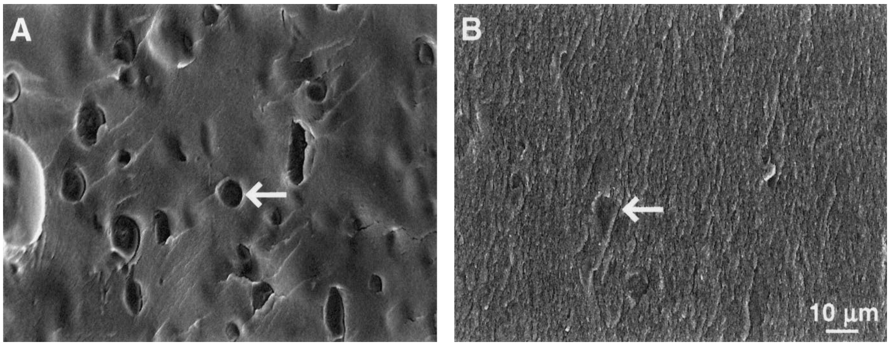

Fig. 4. Fracture surfaces of P/S/G films, 67/11/22 (w/w/w): (A) sample 201, TP 4, 71.6% water; (B) sample 206, TP 3, 73.0% water. Arrows indicate starch granules.

used. A comparable experiment using profile 1, the highest temperature profile, gave similar results (micrographs not shown). Interestingly, the surface features shown in Fig. 3B, namely a fine beaded microstructure, is similar to the surface appearance of a solution cast pectin/glycerol film (Fishman & Coffin, 1995). Because solution cast films are cast from relatively dilute solution, possibly these results indicate that adding more water during extrusion tends to produce films which most closely resemble comparable solution cast pectin/glycerol films.

In Fig. 4 are shown fracture surface SEM images of films from trial 2 in which the pectin/starch/glycerol (P/S/G) ratio by weight (w/w/w) was 67/11/22 and a pectin/starch ratio of about 86/14 (w/w). In Fig. 4A, sample 201 (see Table 2), with the lowest temperature profile 4 is used in the extruder whereas in Fig. 4B, sample 206 (see Table 2), with higher temperature profile 3 is used in the extruder. The water content of these two samples is fairly close, 71.6% for sample 201 and 73.0% for sample 206. Comparison of the fracture surfaces for both of these samples, reveals that sample 201 in Fig. 4A extruded with the low temperature profile 4, shows evidence of many more ungelatinized or partially gelatinized starch granules than sample 206 in Fig. 4B which was extruded with temperature profile 3. The greater abundance of circular structures appearing in Fig. 4A as compared to Fig. 4B most closely resembles fracture surfaces obtained from solution casting of films in which the starch was virtually ungelatinized (Fishman & Coffin, 1995). It should be noted that areas of pectin surrounding the starch granules appear smoother than comparable areas when pectin, ungelatinized starch and glycerol were cast into films. This might indicate some disordering of pectin that might not occur during solution casting.

In Trial 3, P/S/G ratios of 39/31/30 (w/w/w) and 49/21/30 (w/w/w) corresponding to pectin/starch ratios of 70/30 (w/w) and 55/45 (w/w) were obtained as extrudates. As in the case of Trial 2, the temperature profiles during extrusion were profiles 3 and 4. Furthermore, the water content of the extrudate was changed by changing the ratio of water feed rate to solids feed rate (see Fig. 2). Comparison of the SEMs for samples 301 and 307 (see Table 2) in Fig. 5A and B revealed that starch granules were more visible and larger when extrusion was with low temperature profile 4 rather than high temperature profile 3. At the high temperature profile 3, comparison of the SEMs for samples 310 and 312 (see Table 2) in Fig. 6A and B again revealed less visible and smaller starch granules for both samples. However, when the moisture content in the film was 41.5% (Fig. 6B), rather than 58.3% (Fig. 6A), large cavities also were present in the sample.

In Trial 4, the P/S/G ratio of the extrudates was 39/31/30 (w/w/w). Samples were extruded with temperature profiles

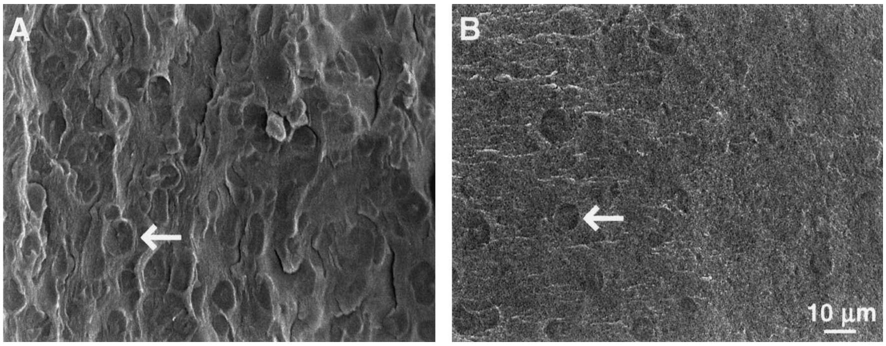

Fig. 5. Fracture surfaces of P/S/G films, 39/31/30 (w/w/w): (A) sample 301, TP 4, 59.0% water; (B) sample 307, TP 3, 57.5% water. Arrows indicate starch granules.

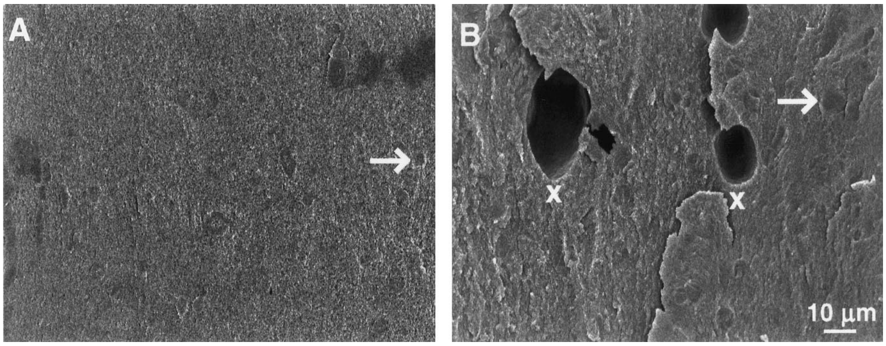

Fig. 6. Fracture surfaces of P/S/G films, 49/21/30 (w/w/w); TP 3: (A) sample 310, 58.3% water; (B) sample 312, 41.5% water. Arrows indicate starch granules; × indicates cavities.

5 and 6. None of the extrudates were calendered in this trial. As mentioned previously, the temperatures in profiles 5 and 6 rise and fall more rapidly than the temperatures in profiles 1–4. In Fig. 7A and B are scanning electron micrographs of samples 402 and 406 extruded with profile 5. The temperature maximum was 120°C for profile 5, the same maximum as used in profile 3. The sample shown in Fig. 5B, extruded with profile 3, had the same P/S/G composition and a comparable water content as the sample shown in Fig. 7A, 57.5% against 64.3%. In Fig. 5B starch granules are barely visible, thus it appears that they are highly gelatinized. In Fig. 7A, the surface appears rougher, the granules are somewhat more visible and appear to be slightly larger. In the case of the sample 406 shown in Fig. 7B, the water content was found to be 34.6% which was much lower than the water content found for the samples in either Fig. 5B or 7A. Starch granules are barely visible in the SEM of sample 406. As in the case of sample 312 in Fig. 6B there appears to be cavities as well in the images in Fig. 7B. Since samples 406 and 312 had low moisture contents, 34.6 and 41.5%, respectively and relatively high temperature profiles, perhaps these conditions were responsible for the presence of cavities. SEM images of samples 407–412 extruded under temperature profile 6, maximum temperature 140°C, were comparable to images of sample 406 in Fig. 7A which was extruded under temperature profile 5.

Previously thermal dynamic mechanical analysis (TDMA) studies were conducted on P/S/G films cast from solution (Fishman & Coffin, 1995). TDMA was used to measure the storage moduli, the loss moduli and tan δ as a function of temperature. The storage modulus is a measure of the energy stored and recovered in a cyclic deformation whereas the loss modulus is a measure of the energy dissipated or lost as heat in a cyclic deformation. Tan δ is simply the ratio of the energy lost to the energy stored in a cyclic deformation (Ferry, 1980). A decrease in the storage modulus indicates that the material is becoming less elastic or conversely more permanently deformable whereas an increase in tan δ indicates a material is becoming more permanently deformable and less elastic. A change of slope or a maximum in the storage or loss modulus against temperature curve is indicative of a molecular transition in a material as is a maximum in a tan δ against temperature curve. T_g, or the glass transition is an example of a molecular transition in which a rise in temperature initiates an increase in molecular motion which manifests itself as the material being transformed from a glass to a rubber.

TDMA studies revealed that neat pectin films (i.e. films containing only pectin) were stiff, brittle, and had a slowly decreasing storage modulus of about 9–7 × 10^3 MPa over the temperature range -100 to $+200$°C. Plasticization of films at a pectin/glycerol ratio of about 7/3 (w/w) produced

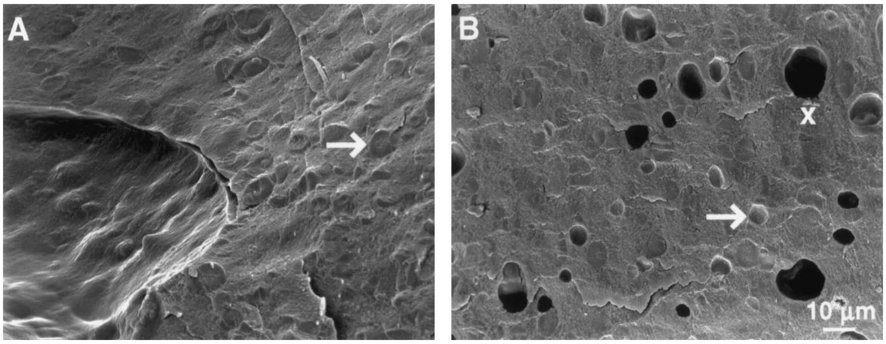

Fig. 7. Fracture surfaces of P/S/G films, 39/31/30 (w/w/w); TP 5: (A) sample 402, 64.3% water; (B) sample 406, TP 3, 34.6% water. Arrow indicates starch granule; × indicates cavities.

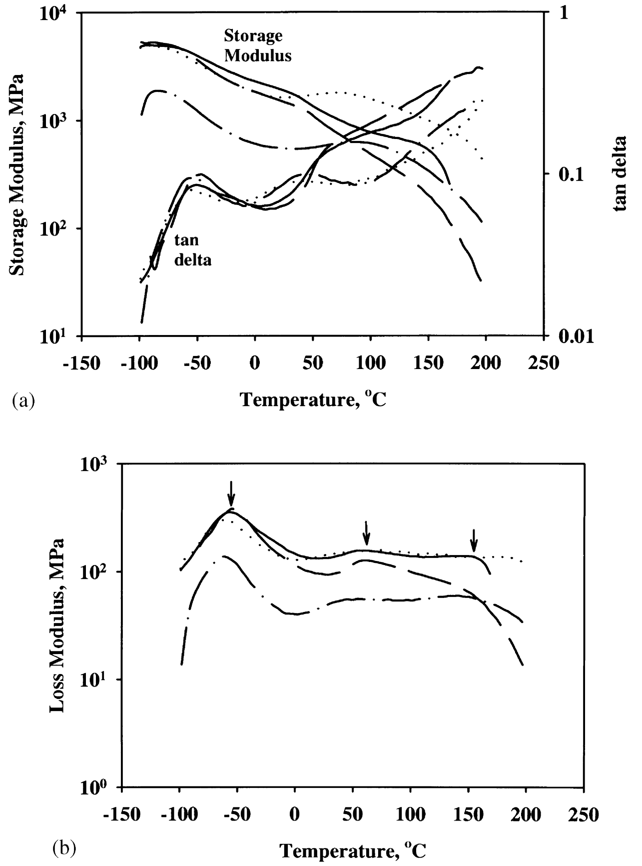

Fig. 8. Effect of blend composition on thermal dynamic mechanical properties of films. Samples 105 (–), 108 (- - -), 110 (-··-) and 114 (· · ·). (a) Storage modulus and tan δ. (b) Loss modulus. Arrows indicate transitions described in text.

films with a glass transition below −50°C and a second broad but shallow transition in the range of 50°C and beyond. Furthermore the addition of 30% of glycerol caused a drop in storage moduli of about one order of magnitude over the temperature range −100 to +180°C. In the glycerol range of 60–70%, raising the temperature from −100 to 0°C lowers the storage modulus by several orders of magnitude. At 60–70% glycerol the broad transition above 50°C is resolved into two transitions. Addition of 30–45% starch to P/G films tends to attenuate the effects of glycerol and induce more shallow transitions.

In Fig. 8a are temperature dependent storage moduli and tan δ curves for samples 105, 108, 110 and 114 which were produced in Trial 1. The loss moduli for these same samples are in Fig. 8b. As in the case of solution cast films, all extruded samples exhibited a T_g below −50°C as indicated by maxima in tan δ and loss moduli curves (see Fig. 8a and b). By examining the storage modulus or tan δ curves it is difficult to determine if there are one or possibly two broad, shallow thermal transitions above room temperature. The loss modulus curve (Fig. 8b) seems to indicate two thermal transitions above room temperature. Comparison of samples 105 and 114 which contain a P/S/G ratio of 78/0/22 (w/w/w), and about 70 and 63% water after extrusion revealed that the storage moduli of sample 114 was fairly close to that of sample 105. These samples only differed in that sample 105 was extruded under temperature profile 2 whereas sample 114 was extruded under the lower temperature profile 4. The temperature dependence of the loss and tan δ curves were almost identical for the two samples indicating that extrusion temperature had little or no effect on the flexibility or the relative change in flexibility of these two samples. Comparison of sample 110, P/S/G ratio 56/22/22 (w/w/w) and sample 114 revealed that replacing 22% of pectin in sample 114 with an equal amount of starch to obtain sample 110 appeared to lower the storage moduli somewhat. Comparison of the temperature dependent storage moduli (Fig. 8a) and loss moduli (Fig. 8b) of sample 108 with that of sample 110 which had the same P/S/G ratio revealed that below room temperature, sample 110 had the lower moduli but that at higher temperatures sample 110 had higher moduli. Moreover the tan δ curves were fairly close. These results may indicate that the absolute values of the moduli were not appreciably different within experimental error. These samples differed in that sample 108 was extruded under temperature profile 3 whereas sample 110 was extruded under the lower temperature profile 4. From these experiments it appears that solution cast and extruded P/G films behave in a similar fashion with respect to their thermal transitions when starch or glycerol is added. Temperature profile during extrusion did not appear to have a strong effect on mechanical properties, if at all.

In Fig. 9a are temperature dependent storage and tan δ curves for samples 203 and 204 from trial 2 whereas in Fig. 9b are the temperature dependent loss curves for the same samples. The P/S/G ratio in these sample was 67/11/22 (w/w/w) and the moisture content in these films after extrusion was 66.5 and 65.2%, respectively. Sample 203 was extruded under temperature profile 4 and sample 204 was extruded under higher temperature profile 3. Storage, loss and tan δ curves were similar for both samples. Furthermore, both samples gave a T_g below −50°C and two thermal transitions above 50°C as was obtained for samples 108 and 110 in Trial 1. SEMs showed many ungelatinized starch granules for temperature profile 4 whereas starch granules were barely visible for profile 3 (cf. images in Fig. 4a and b). These results would lead one to conclude that degree of starch gelatinization has little effect on the mechanical properties of the films. This was found to be true for solution cast PSG films (Fishman & Coffin, 1995). In that case the lack of effect of degree of starch gelatinization on the mechanical properties of films was attributed to strong interactions between starch and pectin which made the polymers highly compatible in films regardless of starch particle size.

In Fig. 10a are temperature dependent storage and tan δ curves for samples 301, 302 and 303 from Trial 3 whereas in Fig. 10b are the temperature dependent

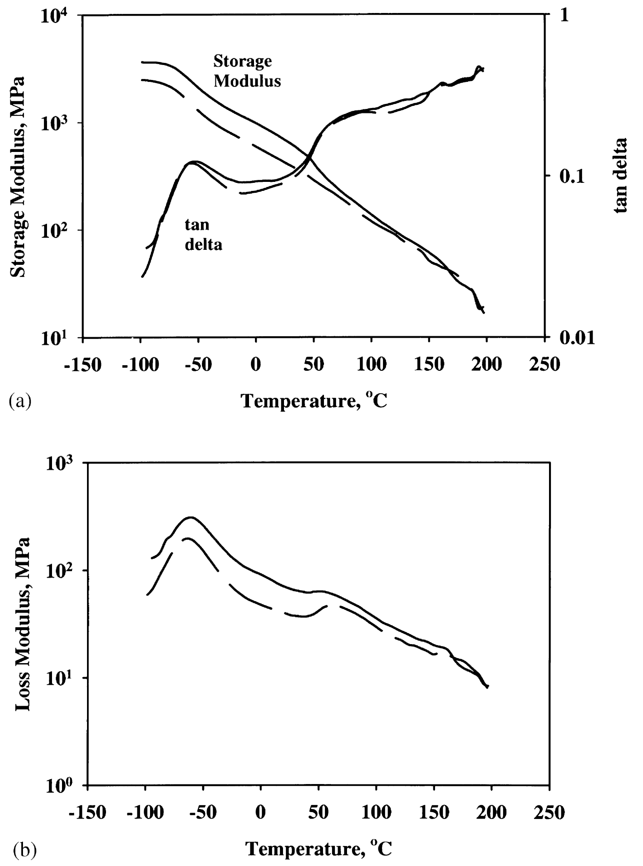

Fig. 9. Effect of temperature profile on thermal dynamic mechanical properties of films. Samples 203 (–) and 204 (- - -). (a) Storage modulus and tan δ. (b) Loss modulus.

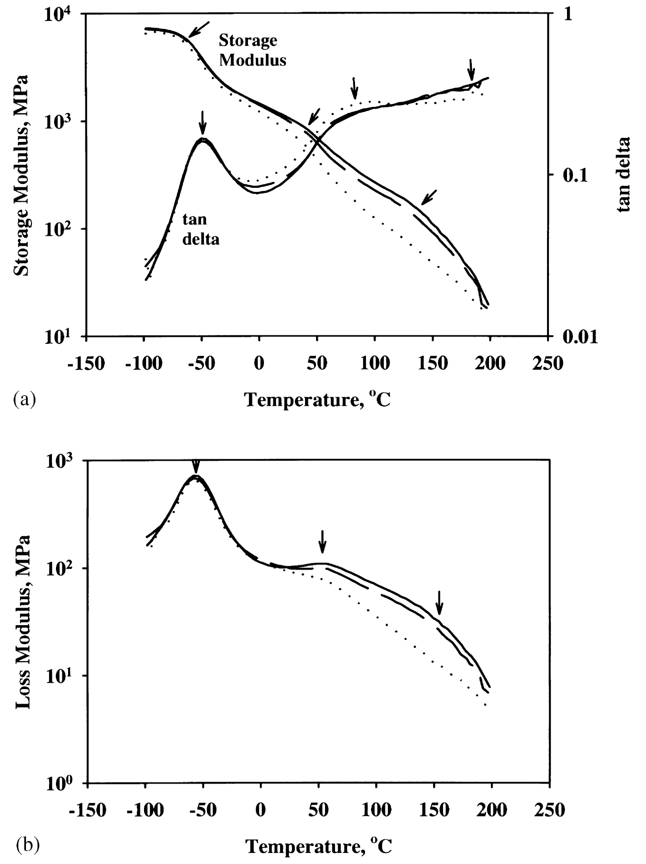

Fig. 10. Effect of water content on thermal dynamic mechanical properties of films. Samples 301 (–), 302 (- - -) and 303 (· · ·), TP 4. (a) Storage modulus and tan δ. (b) Loss modulus. Arrows indicate transitions described in text.

loss curves for the same samples. The P/S/G ratio in these samples was 39/31/30 (w/w/w), the P/S ratio 55/45 (w/w), they were processed under temperature profile 4 and the water content 59.0, 49.0 and 43.2%, respectively. All of these samples showed the same three thermal transitions as before and were almost superimposable in spite of differing moisture contents. In Fig. 11a are temperature dependent storage and tan δ curves for samples 307, 308 and 309 from trial 3 whereas in Fig. 11b are the temperature dependent loss curves for the same samples. The temperature profile for these samples was 3. The moisture contents of 307, 308 and 309 were the same, respectively, as those of 301, 302 and 303. All six samples gave similar storage, tan δ and loss curves. From this trial and previous results from cast films (Fishman et al., 1996), we conclude that moisture content and the temperature profile during extrusion have little or no effect on the thermodynamic mechanical properties of PSG films. Nevertheless, as indicated in the introduction, extrusion is faster, more economical, and eliminates a pre-gelatinization step when compared to film casting. Furthermore, whereas degree of starch gelatinization has little effect on the film mechanical properties, it affects the optical clarity of the films. Optical clarity may be important for some applications.

4. Conclusions

In conclusion, with analysis by SEM and TDMA, we have demonstrated that by extruding pectin/glycerol and PSG blends, one can fabricate films with microstructure and thermal dynamic mechanical properties comparable to those obtained by casting from solutions containing the same materials. As shown by TDMA, plasticized pectin and pectin starch films have a large glass transition at about −50°C indicating that these films are reasonably flexible at room temperature. The storage modulus of these films at room temperature is above 10^3 MPa. This is indicative of tensile properties that are useful for many thin film applications. Based on measurements of PSG films with comparable mechanical properties (Fishman et al., 1996), one may expect that these films will have an elongation to break of about 10–20%. Further, based on this study and on earlier work on solution cast films, we conclude that PSG

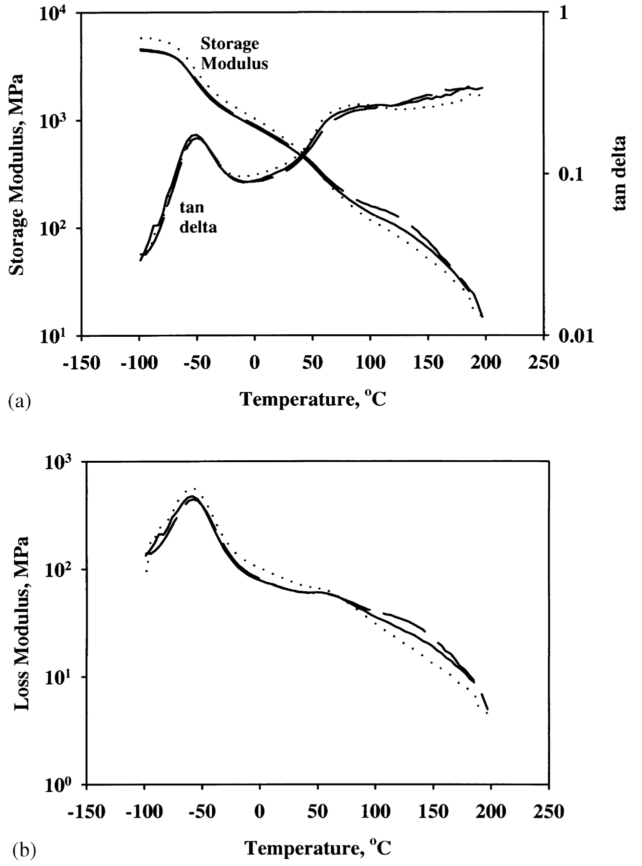

Fig. 11. Effect of water content on thermal dynamic mechanical properties of films. Samples 307 (–), 308 (- - -) and 309 (· · ·), TP 3. (a) Storage modulus and tan δ. (b) Loss modulus.

films will be useful for the applications mentioned in the Introduction.

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