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Two stage extrusion of plasticized pectin/poly(vinyl alcohol) blends ☆

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Abstract

Blends of pectin with starch (high amylose and normal), poly(vinyl alcohol) (PVOH), and glycerol were extruded in a twin screw extruder, pelletized, and then further processed into blown film and extruded sheet using a single screw extruder. The samples were analyzed using tensile measurements, dynamic mechanical analysis, and scanning electron microscopy. PVOH levels of 24% or greater were necessary to successfully make blown film, while extruded sheet could be made at a level of 16% PVOH. Tensile strength and initial modulus of the extruded sheets were slightly higher in the machine direction than in the cross direction, while the reverse was true for elongation to break. For the blown films tensile strength tended to be higher in the transverse direction than in the machine direction, while the reverse was seen for initial modulus. Increased levels of PVOH led to increases in tensile strength and elongation to break, while initial modulus was decreased. Morphology as determined by SEM visually indicated stretching in the transverse direction of the blown films. The second stage extrusion appeared to promote α-helix formation in the high amylose starch.

Keywords: Pectin; Poly(vinyl alcohol); Extrusion; Film blowing; Extruded sheets

1. Introduction

For some time we have been interested in the utilization of value added agricultural commodities, particularly pectin. Our interest extends to both the pectin itself, and to cost effective processes to utilize it. Pectin is most widely available as a co-product in the production of fruit juices, and is also available from the remains of sugar beets after the sugar is extracted. It is a structural component of plant cell walls, consisting primarily of partially methyl esterified poly(α(1 → 4)galacturonic acid) containing rhamnose inserts in the backbone with neutral sugar side chains.

Blends of starch and synthetic polymers have been extensively studied for many years (Otey, Mark, Mehltretter, & Russell, 1974; Otey, Westhoff, & Doane, 1980; Walia, Lawton, Shogren, & Felker, 2001; Zhou & Willett, 2001; Walia, Lawton, & Shogren, 2002). Other work has specifically involved blends with poly(vinyl alcohol) (Chiellini, Cinelli, Imam, & Mao, 2001; Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). In these latter studies it was shown that PVOH imparted significant strength to starch melts allowing for easier processing and improved product stability.

In our previous work we have shown that plasticized blends of pectin and pectin with high amylose starch can be successfully extruded using a twin screw extruder (Fishman, Coffin, Konstance, & Onwulata, 2000; Fishman, Coffin, Onwulata, & Konstance, 2004). These materials gave properties which were comparable to cast films made of the same compositions.

This work is an extension of our extensive studies on cast films of pectin, high amylose starch, and glycerol

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(Coffin & Fishman, 1993; Coffin & Fishman, 1994; Coffin & Fishman, 1995; Fishman, Coffin, Unruh, & Ly, 1996), as well as our studies on pectin blends containing poly(vinyl alcohol) (Coffin, Fishman, & Ly, 1996; Coffin & Fishman, 1997; Fishman & Coffin, 1998). These studies showed plasticized pectin/starch films to give excellent mechanical and oxygen barrier properties. The films containing poly (vinyl alcohol) (PVOH) also gave excellent mechanical properties over a very wide range of compositions.

2. Experimental

2.1. Materials

The pectin used was MexPec 1400, supplied by the Grindsted Division of Danisco-Cultor, Kansas City, KS. High amylose starch in granule form was Amylogel 03003 (formerly Amylomaize VII) supplied by Cerestar Corp. of Hammond, IN. The common starch was Pure Food Powder from Tate & Lyle NA, Decatur, IL. The poly(vinyl alcohol) was Airvol 523S, supplied by Air Products Corp., Allentown, PA. It has a molecular weight of 120,000 and a degree of hydrolysis of 88%. Reagent grade glycerol (99.5+%) was purchased from Aldrich Chemical Corp., Milwaukee, WI. Water used in the extrusion runs was domestic tap water. The cast films were made using HPLC grade de-ionized water.

2.2. Extrusion

The extrusions were run using blends with various ratios of pectin (P), high amylose starch (S), PVOH, and glycerol (G). Normal corn starch replaced high amylose starch in one of the blends. A flow diagram for the processes used is shown in Fig. 1. The blends were first extruded in a twin screw extruder to form ribbons. These were dried and ground into a powder, pelletized, and then extruded both as flat sheet and as blown film using a single screw extruder. The compositions of the blends used are shown in Table 1. Ribbon samples of each blend were retained, and some were compression molded and tested.

The first stage extrusions were done in a Werner-Pfleiderer ZSK30 twin screw extruder (Krupp, Werner-Pfleiderer Co., Ramsey, NJ). The method and conditions used were essentially the same as those we have used earlier (Fishman et al., 2000, 2004). The solids:water ratio was maintained at 40:60. The actual barrel temperatures and die temperatures used in these experiments are given in Table 2. With the samples made using 24% and 32% PVOH, it was necessary to lower the barrel and die temperatures in order to be able to successfully extrude and collect the materials.

Prior to running the second stage extrusions the ground powders were reprocessed into pellets on a Brabender PL2000 extruder at 30 rpm, using a 30/1 L/D barrel, 3/1 compression screw and a 4.7 mm (3/16 in.) die. There are three temperature zones on the extruder, along with a heated die. These temperature profiles are also given in Table 2.

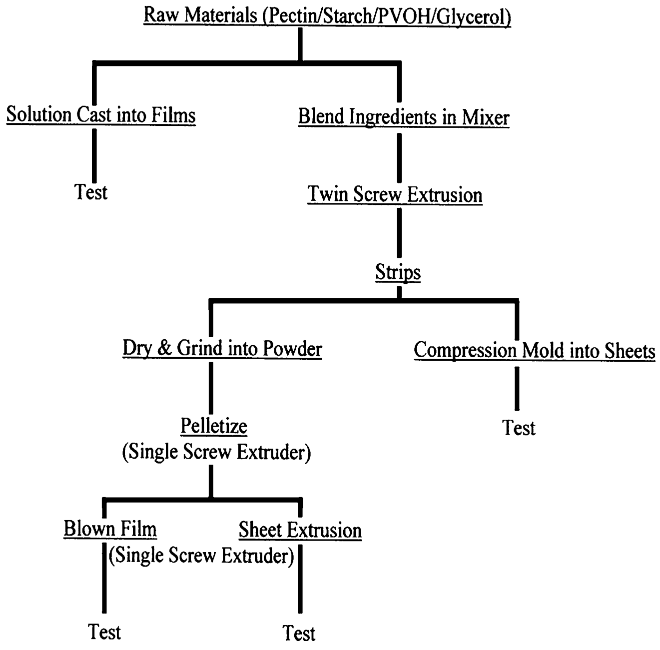

Fig. 1. Processing flow diagram.

The second stage extrusions were done using the same Brabender extruder, barrel, and die. The barrel and die temperatures for the film blowing and ribbon extrusions are also shown in Table 2. The film blowing die had a1 inch (25.4 mm) orifice. The ribbon die used was 4 in. (101.6 mm) wide with a 0.02 in. (0.51 mm) slit. Screw speed was 20 rpm for the film blowing, and 30 rpm for the sheet extrusion. Two slightly different die temperatures were used for the film blowing of the 24% and 32% PVOH samples.

Extrusion ribbons from some of the first stage extrusions were compression molded for testing. This was done at room temperature using a pressure of 5000 psi in a Carver press and the samples were dried using procedures described earlier (Fishman et al., 2004).

Cast films were made by casting onto polycarbonate plates using the methods we employed in our previous studies (Coffin & Fishman, 1994; Fishman & Coffin, 1998).

Table 1
Polymer blend compositions

Sample	Pectin	Starch	Poly(vinyl alcohol)	Glycerol
30/24/16/30	30	24	16	30
38/16/16/30	38	16	16	30
54/00/16/30	54	0	16	30
35/28/19/19	35	28	19	19
32/14/24/30	32	14	24	30
27/11/32/30	27	11	32	30
32/14/24/30[a]	32	14	24	30

[a] High amylose starch was replaced with normal corn starch.

Table 2
Material processing parameters

Extrusion conditions									
Condition 1									
Zone	1	2	3	4	5	6	7	8	9
Temperature (°C)	35	35	50	75	110	120	100	100	90
Condition 2									
Zone	1	2	3	4	5	6	7	8	9
Temperature (°C)	35	35	50	75	95	100	100	85	70

Material	Torque (N m)	Pressure (bar)	Temperature profile zones 1/2/3/die (°C)
Pelletizing conditions			
P/S/PA/G[a]			
30/24/16/30	30	90	140/140/135/135
38/16/16/30	34	90	140/140/135/130
54/00/16/30	40	110	140/140/135/130
35/28/19/19	20–70	110–300	145/145/145/145
32/24/16/30	35	83	140/140/135/130
27/11/32/30	24	56	140/140/135/130
32/14/24/30[b]	27	65	140/140/135/130
Film blowing conditions			
P/S/PA/G			
30/24/16/30	69	170	130/140/140/145
38/16/16/30	69	170	135/140/140/145
54/00/16/30	50–76	170	140/140/145/130
35/28/19/19	40–70	110–300	150/155/155/155
32/24/16/30	69	180	135/140/140/145
27/11/32/30	57	141	135/140/140/145
32/14/24/30[b]	59	143	135/140/140/145
Ribbon extrusion conditions			
P/S/PA/G			
30/24/16/30	62	90	145/145/140/140
38/16/16/30	64	150	145/145/140/140
54/00/16/30	50–60	140–170	150/150/145/145
35/28/19/19	60–90	160–200	160/160/155/150

[a] Pectin/starch/poly(vinyl alcohol)/glycerol.

[b] High amylose starch was replaced with normal corn starch.

2.3. Microscopy

Samples were prepared for scanning electron microscopy (SEM) by the freeze fracture method. This consisted of soaking rectangular strips 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, Hatfield, 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), or with a FEI Quanta 200 (FEI Co., Hillsboro, OR), both operated in the secondary electron imaging mode.

2.4. Mechanical properties

Dynamic mechanical properties were determined using a Rheometrics RSA II Solids Analyzer (TA Instruments, New Castle, DE). Samples were cut 1.5 in. long and 3–7 mm wide. Testing was done as described previously (Coffin & Fishman, 1994; Fishman et al., 2000). Testing was done in both the machine and cross direction for the flat extruded sheets, and in the machine and transverse directions for the blown films. Sample thickness ranged from 0.1 to 0.5 mm for the extruded and compression molded films, and from 0.06 to 0.1 mm for the solution cast films.

Tensile testing was done on a modified Instron model 1122 tensile tester using Testworks v.3.1 or v.4 software as described in our previous work (Fishman & Coffin, 1998; Fishman et al., 1996). Testing was done in both the machine direction (MD) and cross direction (XD) for the flat extruded sheets, and in the MD and transverse direction (TD) for the blown film.

2.5. X-ray diffraction analysis

X-ray diffraction analysis was run on four of the ground samples. Three preparations of each of these blends were analyzed. These were: compression molded strips made from the first stage extrusion, ground dried powder made from this extrusion, and extruded sheet made from the powder. The compression molded strips and extruded sheets were ground to a powder to run the test. Data were obtained using a Philips PW 1830 generator table with the PW 1820 goniometer attachment. Measurements were done by the step method with a step size of 0.05 (2Θ) at 4 s per step.

3. Results and discussion

The first three samples (30/24/16/30, 38/16/16/30, and 54/00/16/30) had identical levels of PVOH (16%) and glycerol (30%), but contained different proportions of pectin and starch: 55:45, 70:30, and 100:0, respectively. The fourth sample (35/28/19/19) maintained the same pectin/starch/PVOH ratio as the sample with the 55:45 pectin/starch ratio, but contained a lower proportion of glycerol. The next two samples both had a 70:30 pectin/starch ratio, and contained 24% and 32% PVOH, respectively. Both contained 30% glycerol. The final sample was identical to the sample containing 24% PVOH, except that the high amylose starch was replaced by normal starch (common food starch).

Solution cast films were prepared from all seven of the compositions used in this study, and the resulting films were analyzed by tensile testing and DMA analysis. The tensile results are shown in Tables 3 and 4.

Strips retained from the first stage extrusion for 30/24/16/30, 38/16/16/30, 54/00/16/30, and 35/28/19/19 were compression molded using a Carver press, and then air and vacuum dried. These were tested for tensile and DMA properties, with the tensile results being shown in Table 3.

The ability to successfully blow film from these pectin/PVOH blends depended primarily on the level of PVOH present in the extruded blends, and to a lesser extent depended on the level of glycerol. Samples 30/24/16/30, 38/16/16/30, 54/00/16/30, and 35/28/19/19 did not process well in the film blowing experiments, and testable samples could not be obtained, as there was little or no bubble expansion. The sample containing only 19% glycerol was, by far, the hardest to process. The three blends containing PVOH levels of 24% and 32% were much easier to process by film blowing than those containing lower PVOH levels.

The four samples which could not be made into blown film were readily extruded into sheets. Samples 30/24/16/30 (P/S ratio 55:45) and 38/16/16/30 (P/S ratio 70:30) were the easiest to run, while 35/28/19/19 (P/S ratio 55:45) was the most difficult. Presumably, lowering the amount of glycerol increased resistance to flow in the extruder.

Table 3
Tensile properties of sheet extruded, compression molded, and cast films

Sample	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (MPa)
Extruded sheets			
P/S/PA/G[a]			
30/24/16/30 MD[b]	4.69 (0.13)[d]	55.78 (5.72)	43.22 (4.65)
38/16/16/30 MD	4.69 (0.14)	36.30 (2.31)	60.83 (3.25)
54/00/16/30 MD	3.92 (0.18)	18.16 (2.47)	71.74 (8.91)
35/28/19/19 MD	9.69 (0.66)	46.06 (6.16)	98.08 (11.23)
30/24/16/30 XD[c]	4.21 (0.23)	65.04 (1.55)	36.76 (2.10)
38/16/16/30 XD	3.91 (0.15)	39.29 (5.34)	51.34 (2.17)
54/00/16/30 XD	3.53 (0.29)	19.02 (4.84)	64.88 (8.80)
35/28/19/19 XD	8.54 (0.24)	33.62 (3.26)	115.96 (7.00)
Compression molded sheets			
P/S/PA/G			
30/24/16/30	3.57 (0.54)	38.75 (7.58)	27.88 (3.07)
38/16/16/30	4.25 (0.63)	31.60 (5.45)	39.92 (5.86)
54/00/16/30	4.07 (0.84)	36.15 (8.59)	42.82 (3.42)
35/28/19/19	6.59 (0.40)	17.78 (4.48)	94.31 (23.14)
Cast films			
P/S/PA/G			
30/24/16/30	10.99 (1.26)	43.08 (5.40)	40.43 (4.84)
38/16/16/30	12.98 (1.04)	51.49 (5.45)	45.87 (8.09)
54/00/16/30	16.44 (2.59)	36.34 (9.89)	106.67 (18.24)
35/28/19/19	19.32 (1.87)	36.38 (4.06)	201.19 (29.69)

[a] Pectin/starch/poly(vinyl alcohol)/glycerol.
[b] MD = machine direction.
[c] XD = cross direction.
[d] Standard deviation of five measurements.

Table 4
Tensile strength of blown films

Sample	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (MPa)
P/S/PA/G[a]			
32/14/24/30 TD[b]	4.04 (0.56)[d]	196.9 (18.4)	30.94 (4.15)
32/14/24/30 MD[c]	3.70 (0.31)	88.2 (17.5)	48.22 (9.63)
27/11/32/30 TD	7.87 (1.33)	278.8 (26.5)	23.40 (2.61)
27/11/32/30 MD	7.31 (0.82)	346.6 (44.2)	25.19 (2.64)
32/14/24/30 TD[e]	3.59 (0.29)	86.0 (17.8)	33.28 (2.56)
32/14/24/30 MD[e]	3.48 (0.18)	151.8 (38.6)	39.55 (7.70)
Cast films			
P/S/PA/G			
32/14/24/30	9.83 (1.66)	42.7 (5.4)	70.34 (8.70)
27/11/32/30	5.40 (0.64)	38.5 (4.0)	50.08 (4.91)
32/14/24/30[e]	7.56 (1.80)	26.4 (8.1)	80.22 (9.86)

[a] Pectin/starch/poly(vinyl alcohol)/glycerol.
[b] Transverse direction.
[c] Machine direction.
[d] Standard deviation of five measurements.
[e] High amylose starch was replaced with normal corn starch.

Tensile properties of the extruded sheets (Table 3) were determined in both the MD (i.e., parallel to sample flow in the extruder) and the XD (i.e., perpendicular to sample flow in the extruder) of the samples. Tensile strength and elongation to break were both seen to decrease with increasing pectin/starch ratio. Conversely, initial modulus was seen to increase with increasing pectin/starch ratio. In every case, the tensile strengths determined in the MD of the extruded sheets were found to be slightly higher than those found in the XD. The same general trend was seen with initial modulus, although the value for the sample containing only 19% glycerol was lower in the MD. In the case of elongation to break (EB), the values were generally slightly higher in the XD than in the MD. These results suggest that some molecular orientation took place during the sheet extrusion, and that the higher melt viscosity of the 19% glycerol sample may have retarded orientation under the conditions used. They also indicate that strength and elongation are enhanced by the pectin, while stiffness is enhanced by increasing starch.

For samples having the same composition, single stage compression molded sheets generally appeared have somewhat lower tensile properties than the two stage extruded sheets (Table 3). To some extent this may have resulted because the one stage compression molded sheets were less dense than the two stage extruded sheets. This lower density was due to directly compressing wet extruded ribbons.

Cast films gave much higher tensile strengths than either the one stage compression molded films or the extruded sheets (Table 3). EB values were similar for the cast films and the two extruded materials. Comparison of cast films with extruded films revealed that when no starch was present or the glycerol level was 19%, the cast films had higher values of initial modulus. Initial modulus for the sheet extruded films were higher or comparable to cast films.

Tensile properties were determined for blown film and cast films at two PVOH levels. Data were obtained in both the transverse direction (TD) and the machine direction (MD) of the blown films. The results are presented in Table 4. In general, the tensile strengths in the transverse direction of the sample were somewhat higher or comparable than those in the machine direction, whereas the reverse was true for initial modulus. No trend was discernable for values of EB between machine direction and transverse direction testing. Nevertheless, there was a significant difference in EB values between samples based on PVOH content. The tensile properties of the blown film samples made using high amylose starch were slightly better than those made using common starch. At almost all compositions, tensile strength and initial modulus was higher for cast films than for blown films. On the other hand, EB was significantly higher when blown film EB values were compared with EB values for cast films.

Comparison of EB values for the blown film with the lower PVOH levels in extruded films (Table 3) revealed that elongation to break increased from about 40% at 16% PVOH to nearly 300% with 32% PVOH. The initial modulus showed a significant decrease with increasing PVOH level, falling roughly by half as the PVOH level increased from 16% to 32%. Tensile strength was roughly the same at both 16% and 24% PVOH, but then increased by more than 75% when the level of PVOH in the blend was raised to 32%.

Samples were analyzed by dynamic mechanical analysis (DMA) in the tensile mode using methods employed previously (Coffin & Fishman, 1994; Coffin et al., 1996). Representative DMA plots are shown for the extruded sheet samples in Figs. 2 and 3, and those for the blown film samples are shown in Figs. 4 and 5. All of the samples exhibited the expected glycerol induced glass transition for pectin in the loss modulus (not shown) and loss tangent curves at around −55 to −60 °C, as well as a peak near 0–10 °C attributed to the PVOH softening point (Fig. 2B, 3B, 4B, 5B). The appearance of two transitions indicates that the sample is a composite rather than a true blend. In all curves a third transition can be observed above room temperature which in pectin/starch/glycerol films has been attributed to the onset of entire molecular motion (Fishman et al., 2004). This transition may be associated with the large percentages of glycerol used in these films.

Over the compositional ranges measured, Figs. 2A and 3A (extruded films) reveal that below about 50 °C, increasing the percentage of starch at the expense of pectin has no effect on the storage modulus. Above 50 °C, eliminating starch increases the storage modulus. Lowering glycerol at constant pectin/starch ratio (55:45) also increases the storage modulus.

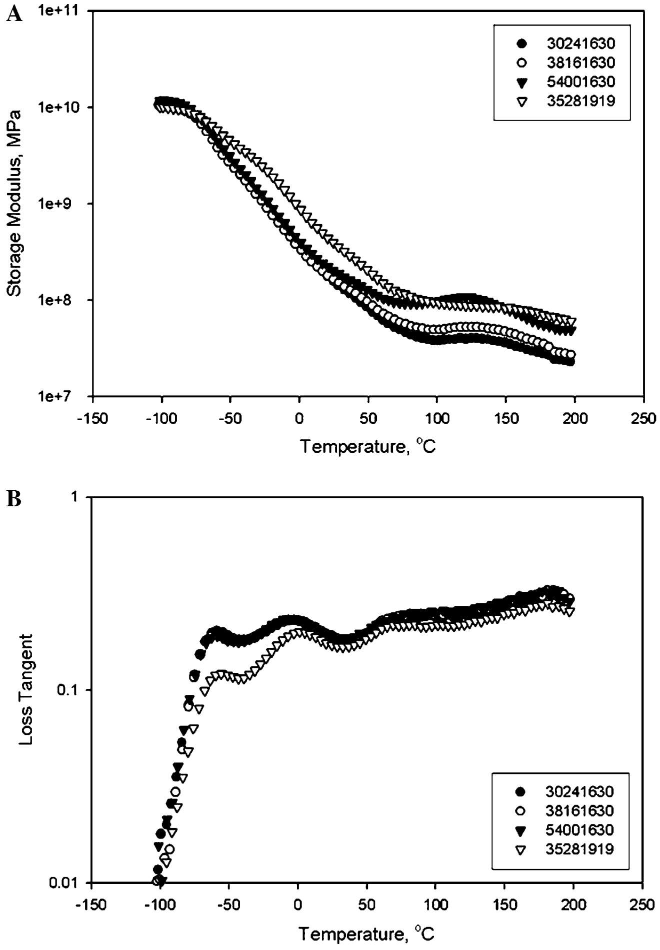

Fig. 2. DMA curves of extruded sheet in the machine direction. (A) Storage modulus. (B) Loss tangent.

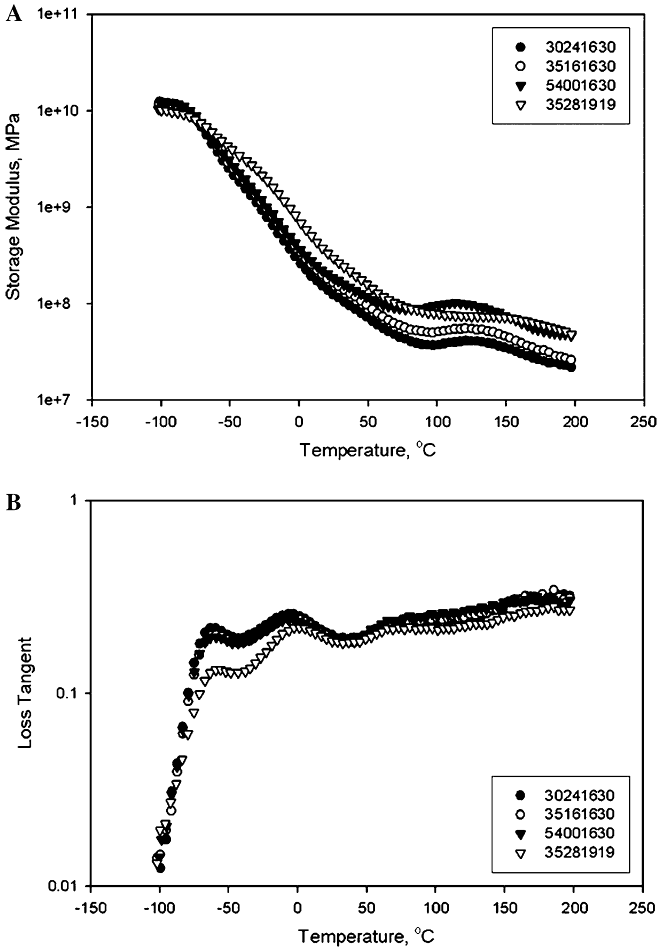

Fig. 3. DMA curves of extruded sheet in the cross direction. (A) Storage modulus. (B) Loss tangent.

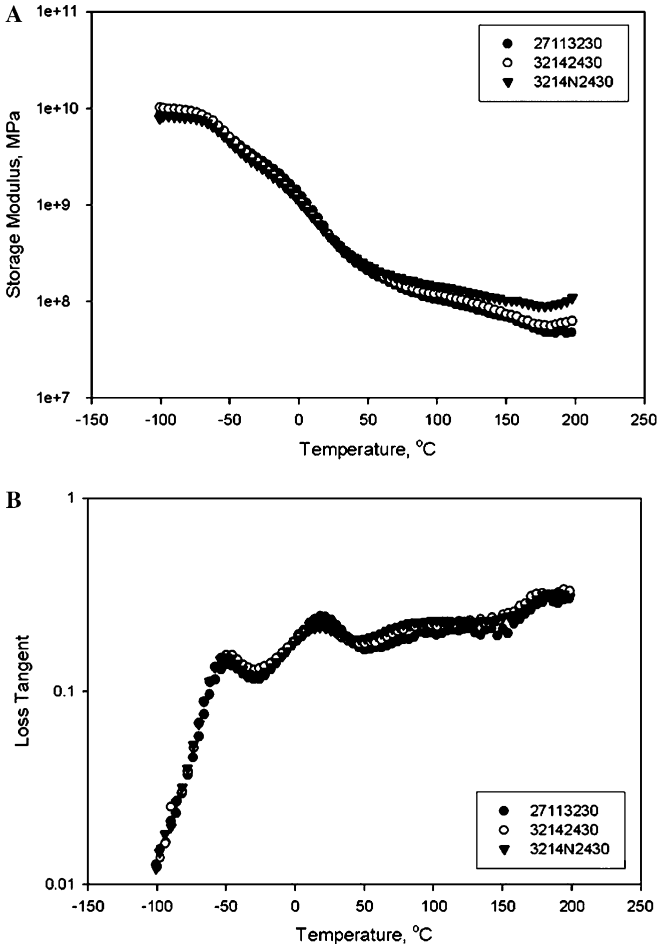

Fig. 4. DMA curves of blown film in the machine direction. (A) Storage modulus. (B) Loss tangent. 32142430 contains high amylose starch; 3214N2430 contains normal starch.

Over the compositional ranges measured, Fig. 4A and 5A (blown films) reveal that the storage modulus is independent of composition. Substituting normal starch for high amylose starch only affects the storage modulus by raising it above about 140 °C.

Relatively little difference was seen between the properties in the machine direction and the cross direction for the extruded sheets, and between the machine direction and transverse direction for the blown film samples. This is not particularly surprising. The level of tension in the sheet extrusion was not particularly high, so that the molecular orientation obtained was probably not great enough to induce a large difference in properties in different directions in the sheet. Since the orientation obtained in film blowing is biaxial (extension both along the flow direction and in the transverse direction), the net effect should be to increase properties in both the machine and transverse directions and not necessarily to give preferred orientation or enhanced properties in a particular orientation. The samples containing normal starch behaved in a fashion similar to samples containing high amylose starch except that they broke at about 150 °C when tested in the transverse direction. Sample containing high amylose starch did not fail even when the temperature was 200 °C.

There was a noticeable difference between the extruded sheet samples (Figs. 2 and 3) and the blown film samples (Figs. 4 and 5) over most of the temperature range studied. This was seen for both the storage modulus and the loss modulus. For both parameters, the values were higher for the blown film samples. This seems to indicate that a higher degree of molecular orientation was able to be achieved for blown film over extruded films. The additional added PVOH used made it possible to have a strong enough bubble to readily process the materials so that a sufficient stretch could be obtained with the enhanced properties.

Scanning electron micrographs were obtained of fracture surfaces for all of the extruded sheet samples. The magnification used was 1000×. This was done for samples cut in both the machine and the cross direction. There did not appear to be any significant differences between the samples on either the machine or cross direction surfaces. Typical micrographs for the machine direction fracture surfaces of the four compositions are shown in Fig. 6. All of the samples containing starch exhibited some ungelati-

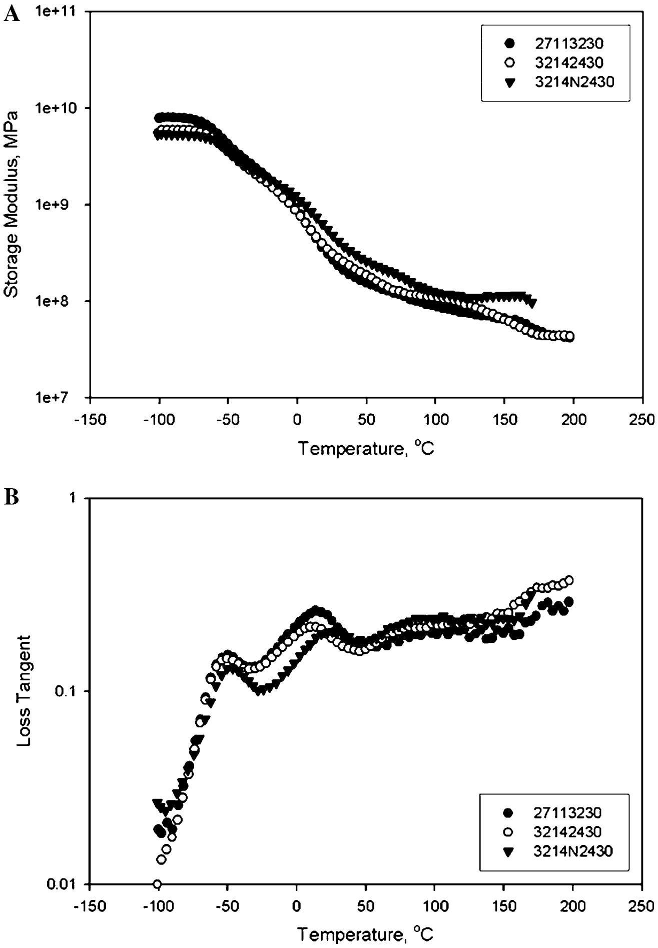

Fig. 5. DMA curves of blown film in the transverse direction. (A) Storage modulus. (B) Loss tangent. 32142430 contains high amylose starch; 3214N2430 contains normal starch.

nized starch granules. They show up as the featureless 3–5 μm sized areas in the images which are round to oval in shape. The pectin, PVOH, and glycerol in the rest of the matrix are indistinguishable from one another in the four images. Although these samples tended to resemble the plasticized pectin/starch films that we studied earlier (Fishman et al., 1996) they also exhibited structures comparable to the PVOH rich areas in our unplasticized pectin/PVOH films (Fishman & Coffin, 1998).

Scanning electron micrographs were also obtained for the compression molded and solution cast films (not shown). Images of the fracture surfaces for these samples were very similar to those obtained on the fracture faces of the extruded ribbon samples.

The scanning electron micrographs for the machine direction surfaces of the blown film samples, which contained PVOH at higher levels than the extruded sheet samples, were somewhat different in appearance, although there were many similarities. These are shown in Fig. 7. Ungelatinized starch granules were visible in the two samples containing high amylose starch (see images A and B). Much less evidence was seen of ungelatinized starch granules in the sample made with normal starch. The PVOH structures were quite visible in these samples as well, particularly at higher magnifications. While the extruded sheet samples looked to be relatively isotropic in the SEM images, the blown film samples appeared to have indications of "flow" parallel to the transverse or annular surface of the bubble. This is indicative of stretching in the transverse direction during processing, and is consistent with the enhanced mechanical properties of the blown film materials.

Four compositions were selected for X-ray diffraction analysis. For each composition chosen, three forms were evaluated. These were the dried and ground powder used to prepare the extruded sheet sample, the extruded sheet sample, and the compression molded sample. The latter two samples were ground to powder prior to running the X-ray diffractions. The curves for the composition, 35/28/19/19, which was representative of all the samples, are shown in Fig. 8. The baselines of the curves are offset for clarity. The primary feature of interest in the diffraction curves is the scattering peat at $2\Theta \approx 19.4°$ which is due to the amylose helix formation. This peak was absent in sample 54/00/16/30 which contains no starch, and increased as the starch content increased in the other three samples. In each of the blends containing starch, the peak for the amylose appears to be the largest in the extruded sheet. This may mean that amylose helix formation is promoted by the conditions used for the single screw extrusion.

4. Conclusions

The results of this study show that pectin/starch/PVOH/glycerol blends can be successfully extruded in a two stage process using both a twin screw extruder and a single screw extruder to form strong extruded sheets with a thickness of 0.4 mm or less, and blown into films with thicknesses of less than 0.15 mm. The ability to carry out these processing operations was very composition dependent.

The samples made using levels of 24% and 32% PVOH had sufficiently high melt strength and extensibility to form a good bubble in the film blowing operation, enabling the manufacture of useful samples which could be easily tested. These had enhanced elongation values and dynamic mechanical properties compared to the extruded sheets, and were thin enough to be true films. The tensile properties obtained using high amylose starch were slightly higher than those obtained with common food grade starch. Although the dynamic moduli were slightly better for the common starch above about 50 °C, samples with this starch tested in the transverse direction tended to break at about 150 °C.

The sample containing only 19% glycerol plasticizer was very difficult to process, exhibiting almost no expansion in the film blowing process. The three samples which contained 16% PVOH and 30% glycerol were somewhat easier to process, but gave difficulty getting a good bubble which

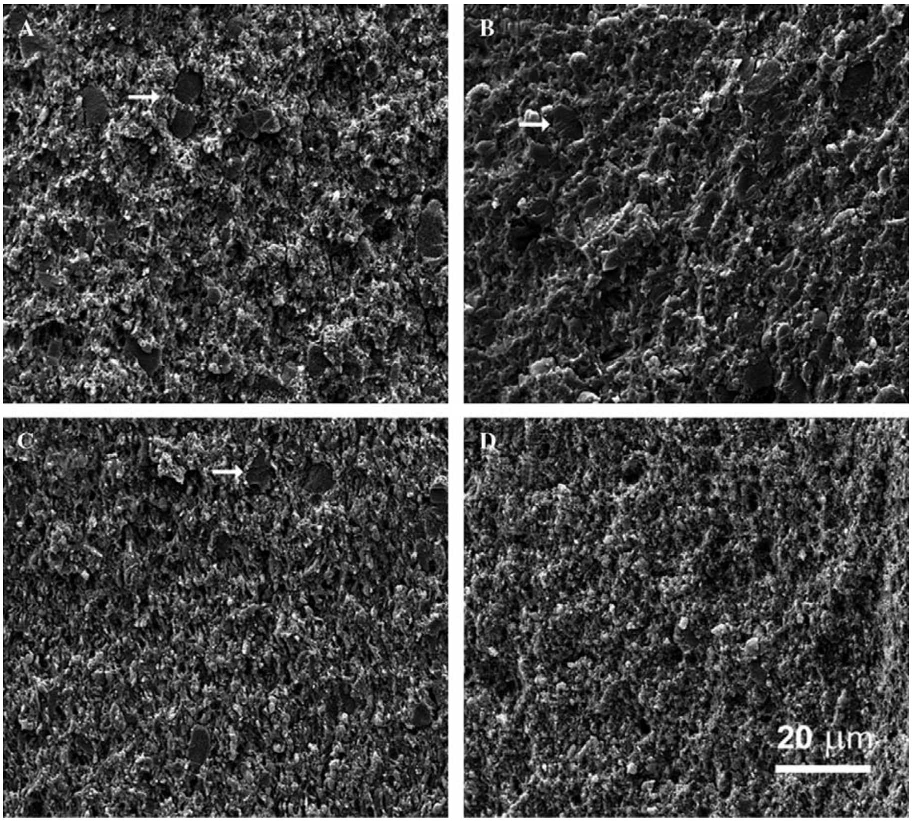

Fig. 6. Scanning electron micrographs of machine direction fracture faces of extruded sheets. (A) 30/24/16/30; (B) 35/28/19/19; (C) 35/16/16/30; (D) 54/00/16/30. Arrows show location of starch particles.

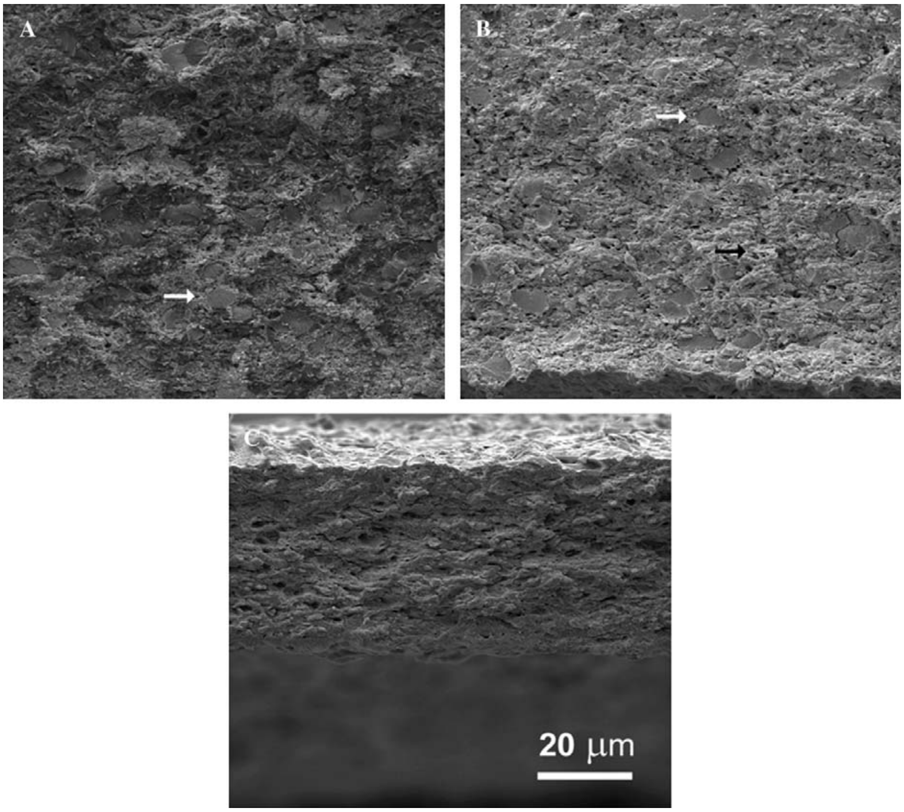

Fig. 7. Scanning electron micrographs of machine direction fracture faces of blown film. (A) 32/14/24/30; (B) 27/11/32/30; (C) 32/14N/24/30. Arrows show location of areas starch (white arrows) and PVOH (black arrow).

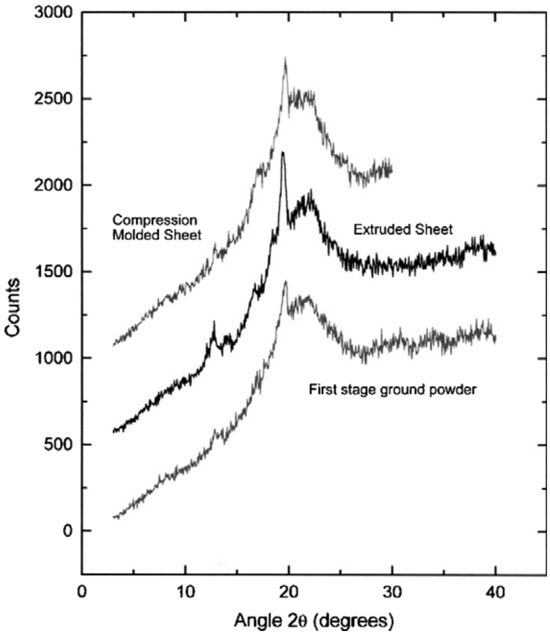

Fig. 8. X-ray diffraction scans of extruded pectin/starch/poly(vinyl alcohol)/glycerol blends. Peak at $2\Theta \approx 19.4°$ is due to presence of amylose helices.

would expand sufficiently to get a significant amount of orientation. Some orientation appears to have been obtained in the extruded sheets made with these samples based on the tensile strength data.

The morphology of the extruded sheet samples were seen to be similar to those of cast films studied earlier. In addition, the micrographs of the blown film materials also seemed to show transverse "flow" patterns caused by the expansion of the polymer bubble during the processing.

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