

# Mechanical, microstructural and solubility properties of pectin/poly(vinyl alcohol) blends<sup>1</sup>

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Citrus pectin was blended and cast into films with poly(vinyl alcohol) (PVOH). PVOH and pectin were miscible in all proportions. Dynamic mechanical analysis revealed that pectin controls exhibited no thermal transitions, whereas PVOH controls exhibited a glass transition temperature ( $T_g$ ) over a broad temperature range commencing at about 0°C and ending about 50°C. A mixture of 49% pectin, 21% PVOH and 30% glycerol exhibited lower storage moduli and more flexibility than comparable mixtures of either pectin/PVOH or pectin/glycerol. Scanning electron microscopy and phase contrast optical microscopy indicated that the mixture was biphasic and a compatible composite either of PVOH in pectin or pectin in PVOH depending on which macromolecule was in excess. Elongation to break measurements revealed that pectin/PVOH films underwent a brittle to ductile transition with increasing PVOH composition. The addition of glycerol to pectin/PVOH films increased ductility significantly when films were relatively brittle. Initial moduli (IM) as a function of composition gave complex curves which exhibited either one or two local maxima depending on such factors as degree of hydrolysis and molar mass of the PVOH in addition to the moisture content of the film. Solubility studies in water revealed that, at 30 and 50°C, only films with 30% PVOH or less were soluble. At 70°C, all compositions were soluble but films containing pectin dissolved more rapidly than those without. The solution kinetics of pectin/PVOH films with 30% or less PVOH were approximated with zero-order kinetics and activation energies were about 3–5 kcal mol<sup>-1</sup>. In general, addition of PVOH to pectin films resulted in films with more PVOH-like properties and addition of pectin to PVOH films resulted in films with more pectin-like properties. © 1998 Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

The desire to add value to underused agricultural commodities has prompted us to search for new uses for pectin, a co-product of fruit juice, sugar beet and sunflower seed case processing. Pectin, a complex polysaccharide, is mainly a copolymer of  $\alpha$ 1→4-linked D-galacturonic acid and its methyl ester (Fishman, 1992). It is water soluble, biodegradable, and forms edible films in pure form or when blended with other polysaccharides such as starch (Coffin and Fishman, 1993, Fishman et al., 1996).

Several new uses could be realized if pectin were able to replace industrial films fabricated from poly(vinyl alcohol) (PVOH). Some uses of these films include water-soluble pouches for packaging detergents and insecticides, flushable liners and laundry bags for contaminated linens (Marten, 1997). Other uses of PVOH are as a coating for paper and a temporary protective coating for metal finishes. Since the utility of a material as a coating is closely related to its film-forming properties, pectin might replace PVOH in these applications as well. It would be advantageous to replace PVOH with pectin in that PVOH is constructed from non-renewable resources and is less biodegradable than pectin.

Recently Coffin et al. (1996) have shown that pectin can form films when blended with PVOH and is miscible with it in all proportions. Thus pectin has the potential to partially replace PVOH in several of its uses. In addition to being a

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<sup>1</sup>Mention of brand or firm names does not constitute an endorsement by the US Department of Agriculture over others of a similar nature not mentioned.

good film former, other properties often required of a material intended to replace PVOH in the above mentioned uses include comparable mechanical strength, elasticity and water solubility. In the previous study, dynamic mechanical analysis (DMA) revealed that addition of PVOH to pectin depressed the glass transition ( $T_g$ ) of the blends. Moreover, at temperatures above  $T_g$ , dynamic moduli decreased with increasing composition of PVOH. It also was observed that the addition of glycerol to pectin/PVOH blends depressed the  $T_g$  values even further. These results suggested that the addition of PVOH and glycerol to pectin films would increase film elasticity at the expense of film strength.

Here, we measure dynamic moduli, tensile properties, aqueous solubility and use scanning electron microscopy (SEM) to better understand how pectin interacts with PVOH in films. Furthermore, we provide data which will enable one to assess which formulations are more likely to be useful for one of the particular applications mentioned above.

## MATERIALS AND METHODS

### Materials

Citrus pectin, MexPec 1400, with a degree of methyl esterification of 71% obtained from Grindsted Products, Inc. (Kansas City, KS) was used as received. Six grades of poly(vinyl alcohol) were purchased from Aldrich Chemical Co. (Milwaukee WI) and were used without further purification. The degree of ester hydrolysis, molar mass (i.e. molecular weight), and designations of these samples are given in Table 1. Reagent-grade glycerol (99 + %) was from Aldrich Chemical Co. and was used as received.

H.p.l.c.-grade water was prepared by passing house-deionized water through a Modulab Polisher I water system (Continental Water Systems Corp., San Antonio, TX).

### Film preparation

Films were prepared by dissolving pectin in a dilute solution of poly(vinyl alcohol) and spreading the solution on a Lexan<sup>TM</sup> plate using a 'Microm' film applicator (Paul N. Gardner Co., Pompano Beach, FL). The wet film thickness was about 2.5 mm. Films were allowed to air-dry overnight, followed by vacuum drying for 30 min at room temperature. Some films were equilibrated at 52% relative humidity by storing in a desiccator over a saturated solution of  $\text{NaHSO}_4$  or at 15% relative humidity by storing over a saturated solution of LiCl. Additional details of film preparation have been published elsewhere (Coffin et al., 1996).

### Mechanical testing

DMA was performed on a Rheometrics RSA II analyzer (Piscataway, NJ) using a film-testing fixture as described previously (Coffin et al., 1996). Initial modulus (IM), tensile

strength (TS), and elongation to break (EB) were measured on an Instron model 1122 universal testing machine. Gauge length was 25.0 mm, sample width was 5.0 mm, sample thickness was about 0.06–0.08 mm, crosshead speed was 5 mm  $\text{min}^{-1}$  and room temperature was 23°C.

### Microscopy

Sample preparation for scanning electron microscopy (SEM) consisted of soaking rectangular strips of films (ca. 0.5 × 2 cm) in absolute ethanol for 24–48 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 strips with fractures occurring normal to the long axis were thawed by immersion in absolute ethanol for 5 min, then critical point dried from liquid carbon dioxide. Dried strip fragments were mounted on specimen stubs with fractured 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 at an instrumental magnification of 10 000 ×.

Samples were prepared for optical phase contrast microscopy by immersing a small (2–3 mm square) pieces of dry film in Type B immersion oil (Cargille Laboratories, Cedar Grove, NJ) and sandwiching them between surfaces of a glass microscope slide and a number 1 glass cover slip. Samples were observed with a model BH optical microscope (Olympus Microscopes, Melville, NY), fitted with optics for phase contrast and a halogen light source. Projected images of the film at a magnification of 1700 × were digitized with a model 68 nuvicon tube television camera (DAGE-MTI, Michigan City, IA), controlled with a Data Translation (Marlboro, MA), Model DT2853 frame grabber, using Image Pro Plus software (Media Cybernetics, Silver Spring, MD).

### Dissolution of films

Test films were cut into 1 cm squares from a template and weighed. Squares were submerged in 40 ml of distilled, deionized water in a constant temperature vessel that was

**Table 1. Degree of hydrolysis (DH) and molar mass range (MMR) of poly(vinyl alcohol)**

Sample	DH (%)	MMR ( $\times 10^{-3}$ )
87/31	87–89	31–50
98/31	98–99	31–50
99 + /50	99 +	50
87/124	87–89	124–186
98/124	98–99	124–186
99 + /124	99 +	124–186

thermostated to  $\pm 0.1^\circ\text{C}$ . The water was stirred by a 9.5 mm magnetic stirring head. The time required for the square to completely disappear was measured with a stopwatch. Each experiment was run in triplicate.

## RESULTS AND DISCUSSION

Fig. 1 summarizes the effects of glycerol and PVOH(99 + /124) on the storage modulus of pectin films. The storage modulus is the in-phase stress divided by strain for a material undergoing a small sinusoidal deformation (Ferry, 1980). For the dynamic experiments described here, the storage modulus is a measure of the energy stored and recovered per cycle of extension for materials being strained a small distance, in this case 0.023 mm. The virtually temperature-independent storage modulus of pectin reveals that it forms a rather stiff but brittle film over a wide range of temperatures. A blend of 70% pectin, 30% PVOH has a slightly lower storage moduli than pectin alone, possibly indicating a slight plasticizing effect of PVOH on pectin. Such would be the case if pectin-PVOH interactions were weaker than pectin-pectin interactions. Addition of 30% glycerol (wt/wt) lowers the storage modulus of pectin somewhat more than PVOH and clearly introduces a glass transition ( $T_g$ ) as indicated by the change in the slope of the modulus with temperature in Fig. 1. Table 2 lists the  $T_g$  values of all samples measured in Fig. 1. At temperatures below their  $T_g$  materials are stiff, whereas above their  $T_g$  they are flexible. Thus the data in Fig. 1 demonstrates that glycerol plasticizes pectin. Previously, we have suggested a possible mechanism for this behavior based on FTIR data (Fishman et al., 1993) and on electron microscope evidence

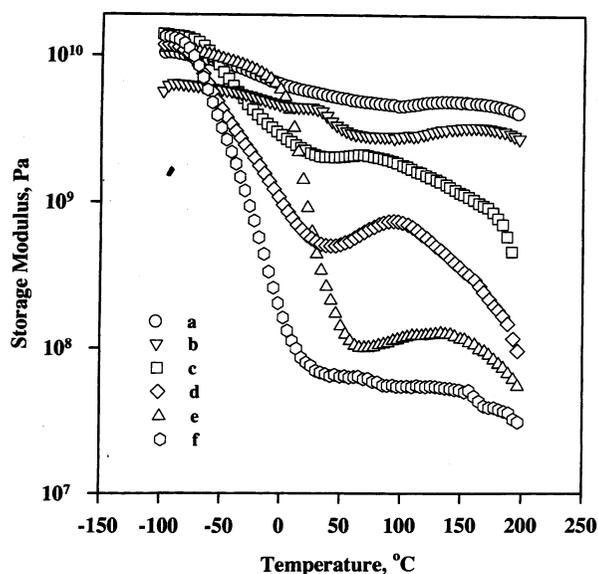


Fig. 1. Effect of glycerol and PVOH (99 + /124) on storage modulus of pectin films. (a) Pectin; (b) 70% pectin/30% PVOH; (c) 70% pectin/30% glycerol; (d) 49% pectin/21% PVOH/30% glycerol; (e) PVOH; (f) PVOH/30% glycerol

Table 2. Glass transition temperature ( $T_g$ )<sup>a</sup> and value of storage modulus ( $E'$ ) at  $T_g$  obtained by dynamic mechanical analysis for selected films

Sample	$T_g$ ( $^\circ\text{C}$ )
Pectin	None
Pectin/PVOH <sup>b</sup> (70:30) <sup>c</sup>	43
Pectin/glycerol (70:30)	-33
Pectin/PVOH/glycerol (49:21:30)	-27
PVOH	24
PVOH/glycerol (70:30)	-26

<sup>a</sup> $T_g$  values were determined by drawing tangents to the portions of the curves horizontal to the  $x$ -axis in Figure 1 above and below the glass transition, and then by drawing a tangent to the portion of the curve vertical to the  $x$ -axis which passes through the glass transition range. The temperature midway between the intersections of the horizontal tangent line and falling on the vertical tangent line was taken to be the glass transition temperature. This temperature coincides with the inflection point of the curve

<sup>b</sup>All PVOH samples measured in this table were 99 + /124

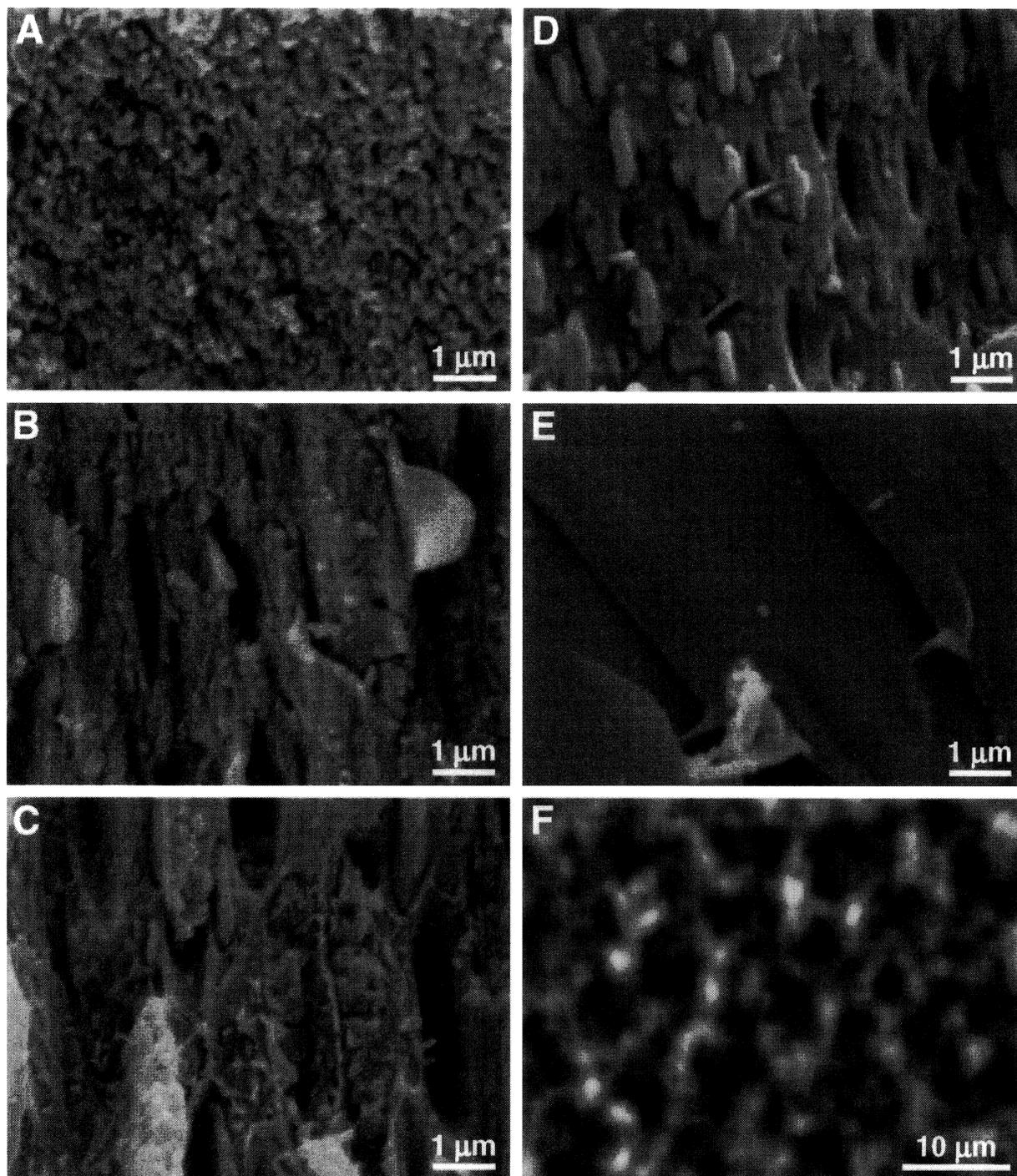
<sup>c</sup>Numbers in parentheses are composition in percentage (wt:wt)

(Fishman et al., 1993). Namely that glycerol breaks intermolecular pectin-pectin hydrogen bonds through preferential solvation (i.e. substitution of pectin-pectin hydrogen bonds with pectin-glycerol hydrogen bonds), and thereby facilitates chain slippage when pectin films are stressed. A blended film of 49% pectin, 21% PVOH and 30% glycerol gave a DMA thermogram which more closely resembled the pure PVOH curve than the pure pectin curve. Furthermore, the pectin/PVOH/glycerol blend had lower moduli than either pectin/PVOH or pectin/glycerol even if the effects of each were subtracted from the moduli of pure pectin. Possibly the reason for this synergistic effect on flexibility is that glycerol plasticizes pectin and PVOH. This appears to be true in that the storage moduli of PVOH containing 30% glycerol are lower and the  $T_g$  occurs at lower temperatures than for neat PVOH (see Fig. 1). The storage moduli of plasticized PVOH above  $T_g$  (horizontal portion of curve) is below  $10^8$  Pa, whereas the comparable portion of the neat PVOH curve is for the most part above  $10^8$  Pa. Furthermore, the  $T_g$  of plasticized PVOH is  $-26^\circ\text{C}$ , whereas the  $T_g$  of neat PVOH is  $24^\circ\text{C}$ .

To better understand the distribution of pectin and PVOH in film blends, SEMs ( $10\,000\times$ ) of fractured surfaces were imaged. Fig. 2A reveals that the fracture plane of the pure pectin film was uneven and consisted of small ridges and crevices which were oriented parallel to the film plane. By way of comparison, Fig. 2E, the fracture plane of the pure PVOH film (98/124) appears smooth except for a few small linear ridges which may represent irregularities in the fracture planes. Fig. 2B-D reveal that the matrix of the fracture plane becomes increasingly smoother with increasingly lower ratios (wt:wt) of pectin to PVOH (i.e. 7:3, 1:1, 3:7, respectively). In Fig. 2D asymmetric objects are visible, many of which are completely separated and appear to have left holes in the plastic matrix in which they were embedded prior to fracture. These objects have a broad distribution of sizes which appear to be up to 2-3  $\mu\text{m}$  in length

and widths which range up to  $0.3\ \mu\text{m}$ . Crevices or holes appear in all fracture plane images except for PVOH (Fig. 2E). Comparison of Fig. 2A with Fig. 2D reveals that these asymmetric structures have a smoother surface than the pectin structures in Fig. 2A. This may indicate that these structures are pectin coated with PVOH. A set of micrographs were obtained of fractured films containing comparable ratios of pectin and PVOH but with 30% by weight of

glycerol. These images were similar to those obtained in the absence of glycerol. A plausible interpretation of these fracture surface images is that pectin/PVOH mixtures form compatible composites at all ratios. Thus at high pectin:PVOH ratios, one might expect films to behave as if they were comprised of a pectin matrix into which islands of PVOH were incorporated (i.e. PVOH in pectin composites). Whereas at low pectin:PVOH ratios one might predict that



**Fig. 2.** Microscopy of pectin/PVOH (98/124) films. (A) SEM of freeze-fractured pectin film; (B) SEM of freeze-fractured film, ratio 70:30; (C) SEM of freeze-fractured film, ratio 50:50; (D) SEM of freeze-fractured film, ratio 30:70; (E) SEM of freeze-fractured PVOH film; (F) phase-contrast optical microscopy of film, 50:50 ratio

films will behave as if they were pectin in PVOH composites. It is of interest to note that pectin/PVOH films for the most part appear transparent to the naked eye which is a necessary but not sufficient condition for compatibility in polymer blends (MacKnight et al., 1978). The SEM images appear to dictate against the possibility of pectin/PVOH films being true blends. Fig. 2F is an image of the film containing a 50:50 pectin:PVOH ratio examined under a phase-contrast optical microscope. This image clearly confirms the existence of two distinct phases. Optically dense phases appeared to be interconnected through lucent phases. Images taken at pectin:PVOH ratios of 3:7 and 7:3 (not shown) also indicate two phases.

As shown by the thermomechanical data in Fig. 1, neat PVOH films are flexible at room temperature and above, unlike neat pectin films which are quite brittle over a wide temperature range. In Fig. 3A–D, we have measured the elongation to break (EB) at room temperature to determine the change in flexibility as a function of the percentage PVOH in the film. These measurements were performed for six samples of PVOH at 15 and 52% relative humidity (RH). All samples increased their EB slightly with increas-

ing % PVOH up to and above 50%. Above a certain composition, depending on RH or PVOH sample, there was a rapid change in EB with % PVOH. In general, the onset of this large transition from brittle to ductile with increasing % PVOH occurred at lower percentages of PVOH when RH was 52% (Fig. 3A,B) rather than 15% RH (Fig. 3C,D). This rapid change in flexibility above a certain percentage of PVOH may signal the composition range at which the film changed from a pectin-filled composite to a PVOH-filled composite. The decrease in % PVOH, about 20% PVOH or more, at the onset of the flexibility transition with increase in RH, is for the most part probably a measure of the plasticizing effect of water on pectin. Previously, we have shown that water acts as a plasticizer on pectin/starch films (Fishman et al., 1996). At 52% RH, the brittle to ductile transition (BDT) commenced at about 50% PVOH for all samples but those containing PVOH samples 87/31 and 98/31. The three films containing PVOH with molar masses at or above  $124 \times 10^3$  (Fig. 3A) showed a gradual increase in flexibility starting at a PVOH composition of about 30%. The films containing the lowest molar mass (i.e. molecular weight) samples of PVOH, 87/31 and 98/31 (Fig. 3B), did not undergo the flexibility transition until about 70%

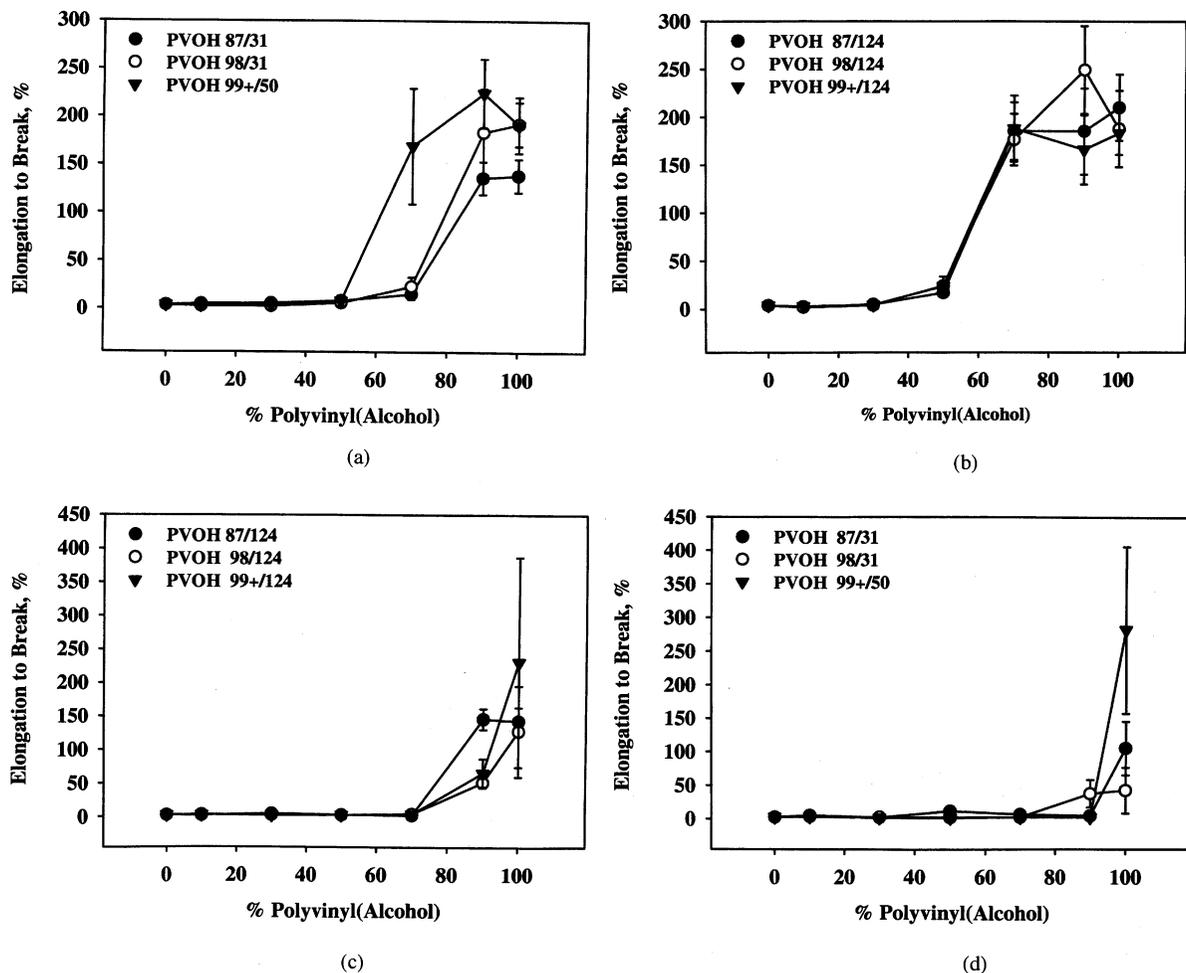


Fig. 3. Elongation to break for pectin/PVOH films. (A) RH 52%, high molar mass PVOH; (B) RH 52%, low molar mass PVOH; (C) RH 15% RH high molar mass PVOH; (D) RH 15% low molar mass PVOH

of the film was PVOH. Thus at 52% RH, molar mass was more important than degree of hydrolysis in determining percentage of PVOH at the start of BDT. Furthermore, at 52% RH, the % of PVOH at the start of BDT was higher for samples 87/31 and 98/31 than the other four samples containing higher molar mass PVOH. At 15% RH, for samples in the molar mass range  $124\text{--}186 \times 10^3$  (Fig. 3C), the onset of the BDT clearly occurred at about 70% PVOH, but the rise in % elongation with % PVOH was greater for the sample with DH 99 + than samples with DH 98 or 87. For two of the three samples with molar masses at  $50 \times 10^3$  or less (Fig. 3D) and measured at 15% RH, the onset of BDT did not occur until the samples contained more than 90% PVOH. One sample 98/31, appeared to have an onset of BDT at 70% PVOH but % elongation was about the same or lower than the other two low molar mass samples. Therefore, for 15% RH, also, it was concluded that molar mass was the key factor in determining percentage of PVOH at the onset of BDT. It is of interest to note that BDT has been observed even in fully compatible blends of polymer pairs in which one polymer was stiff and the other was flexible. An example of such a case is blends of

poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene (MacKnight et al., 1978).

In Fig. 4A–D, we have measured the effect of % PVOH in the blend on the initial modulus. The data in all four figures were fitted by linear least-squares to fourth-order polynomials. Lower-order polynomials generally gave poorer fits. The  $r^2$  values for the plots in Fig. 4 are given in Table 3. In general, the ‘goodness of fit’ for these plots depended on the precision with which the initial moduli (IM) were measured. At 52% RH, the precision of data was sufficiently good to observe local fluctuations as well as overall trends in IM with changing polymer composition. Overall, IM decreased with increasing percentage of PVOH. This result is consistent with previous DMA data (Coffin et al., 1996) which showed a decreasing storage and loss moduli with increasing % PVOH in pectin/PVOH blends. The curves in Fig. 4A of blends containing high molar mass PVOH are bimodal with relative maxima at the high composition ends of the plots. For composites, self interactions between pectin and PVOH, respectively, are expected to predominate over cross-interactions between pectin and PVOH. Thus, at

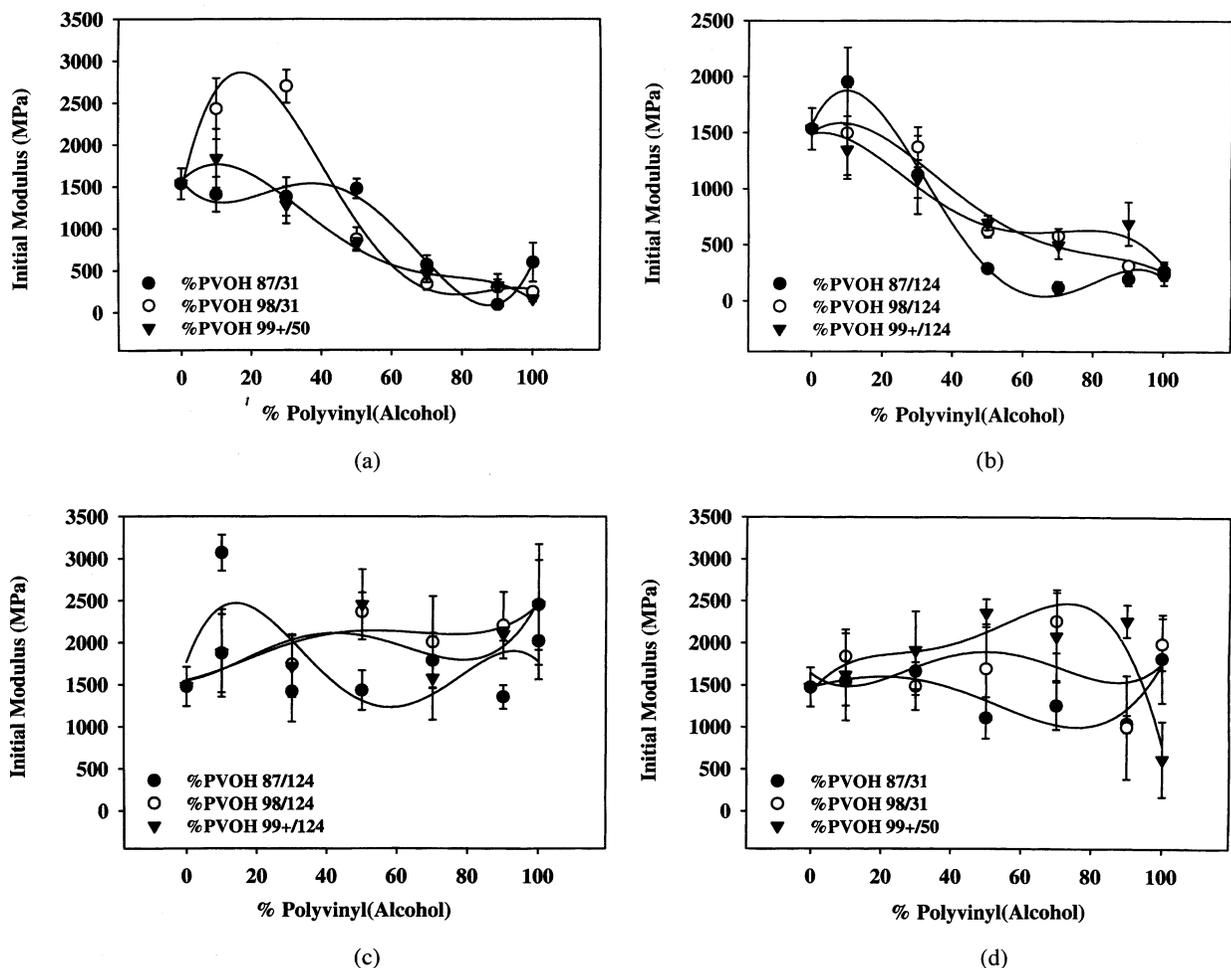


Fig. 4. Initial modulus for pectin/PVOH films. (A) RH 52%, high molar mass PVOH; (B) RH 52%, low molar mass PVOH; (C) RH 15% RH high molar mass PVOH; (D) RH 15% low molar mass PVOH

Table 4. Tensile strength (MPa) of various pectin/poly(vinyl alcohol) (PVOH) blends

%PVOH	RH	Sample					
		87/31	98/31	99 + /50	87/124	98/124	99 + /124
0	52	41(9) <sup>a</sup>	41(9)	41(9)	41(9)	41(9)	41(9)
	15	31(8)	31(8)	31(8)	31(8)	31(8)	31(8)
10	52	52(4)	55(9)	45(11)	35(14)	23(12)	35(9)
	15	50(4)	50(9)	48(11)	63(15)	51(11)	44(15)
30	52	48(6)	59(8)	37(7)	36(1)	40(2)	35(8)
	15	39(12)	41(5)	36(6)	47(12)	38(6)	39(9)
50	52	52(2)	22(4)	33(6)	17(3)	36(2)	45(3)
	15	42(7)	34(7)	40(3)	40(7)	60(4)	63(6)
70	52	17(2)	18(1)	37(1)	32(2)	46(3)	45(3)
	15	34(6)	46(8)	45(4)	36(9)	57(15)	49(3)
90	52	22(3)	28(6)	40(3)	37(4)	48(9)	43(5)
	15	28(3)	22(7)	38(8)	36(5)	60(7)	64(2)
100	52	37(1)	34(4)	33(5)	39(5)	42(7)	41(5)
	15	52(9)	50(10)	37(12)	52(10)	71(8)	64(9)

<sup>a</sup>Number in parenthesis is standard deviation of five replicates

## CONCLUSION

Pectin/PVOH films form compatible biphasic composites over a wide range of compositions. These films undergo brittle to ductile transitions with increasing concentrations of PVOH. Addition of glycerol to pectin/PVOH films can significantly increase the ductility of these films when relatively brittle. The solubility of pectin/PVOH films are temperature and composition dependent. At 30, 50 and 70°C, respectively, films containing 30% or less PVOH were more soluble than neat PVOH films measured at the same temperature. At 70°C, all compositions of films containing pectin/PVOH are more soluble than neat PVOH films.

In general, addition of PVOH to pectin films resulted in films with more PVOH-like properties, and addition of pectin to PVOH films gave more pectin-like properties to PVOH films.

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Table 5. Arrhenius plot constants for the dissolution of pectin/PVOH films

% PVOH	$E^a$ (kcal mol <sup>-1</sup> )	$A^b$ (g s <sup>-1</sup> )	$r^2$
0	4.76	0.105	0.99
10	4.74	0.11	0.96
30	3.03	0.0076	0.97

<sup>a</sup>Activation energy

<sup>b</sup>Pre-exponential constant

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high pectin levels, the small amount of PVOH present might tend to enhance pectin self-interactions resulting in a relative maximum. Likewise, at high PVOH, the small amount of pectin present might tend to enhance PVOH self-interactions again resulting in a local maximum. If the relative maxima in IM are greater at high pectin:PVOH ratios than at low ratios, one might conclude that pectin self-interactions are stronger than PVOH self-interactions. In the middle range of compositions, where the relative amounts of pectin and PVOH tend to be equal, more cross-interactions prevail. If pectin–PVOH cross-interactions are weaker than the respective self-interactions, one would expect (as occurs in Fig. 4A) relative minima in IM to occur in the middle range compositions where significant amounts of both pectin and PVOH are present. The exact composition of the minimum is probably related to the difference in IM values at the two maxima. For example, in Fig. 4A, the IM of the relative maximum at high pectin:PVOH ratios is much larger than the IM of the relative maximum at low pectin:PVOH ratios in the blend containing PVOH sample 87/124. In that case, the minimum is shifted toward compositions with lower pectin:PVOH ratios, i.e. about 62% PVOH. In the cases of the blends containing PVOH samples 98/124 and 99 + /124 the differences in IM values at the relative maxima are less and the minimums occur closer to 55% PVOH. In Fig. 4B, the 98/31 sample has the biggest IM difference between relative maxima, and the relative minimum occurs at about 75% PVOH, whereas the 99 + /50 sample has a much smaller IM difference between relative maxima and the relative minimum occurs at about 50% PVOH. The 87/31 sample exhibits a broad monomodal peak with the maximum centered at about 40%–50% PVOH. This may be a case in which cross-interactions between pectin and PVOH predominate over interactions of either polymer for itself. Because of the large number of factors governing polymer–polymer interactions in these systems, it is difficult to explain why in this particular case cross-interactions between polymers seem to predominate. It may be due to a unique combination of factors related to the PVOH in this system, such as the relatively high percentage of acetate groups present and relatively low molar mass in conjunction with the presence of a high moisture content.

Fig. 4C,D contains IM plotted against percentage PVOH at 15% RH. As indicated by the  $r^2$  values for these plots (see Table 3), the polynomial fits of the data are not as good as those obtained for comparable data collected at 52% RH, undoubtedly due to the poorer precision in measuring IM at this RH. This in turn did not allow local fluctuations in IM with polymer composition to be measured as accurately at 15% as at 52% RH. Nevertheless, some generalizations are still possible. At 15% RH, the stiffness of PVOH approaches, and in some samples exceeds, that of pectin. Therefore, by ignoring local fluctuations in IM with changes in polymer composition, one observes a flat or slightly positive overall trend in IM with increasing percentage PVOH. Comparison of Fig. 4A,B with Fig. 4C,D reveals that an

increase in moisture reduces the IM of film high in PVOH to a greater extent than the IM of films high in pectin. It also appears that plots of IM against composition are either monomodal or bimodal and that there are differences in local fluctuations of IM with polymer composition due to both the molar mass and degree of hydrolysis.

Tensile strengths (TS) were measured for the six types of blends at 15 and 52% RH. Changes in TS with composition were relatively small because differences in TS between pectin and PVOH are relatively small. At 52% RH, values ranged between 17 and 52 MPa whereas at 15% RH they ranged between 22 and 64 MPa. The results of these experiments are in Table 4.

The data in Fig. 5 were collected to determine the effect of glycerol on the mechanical properties of pectin/PVOH blends. PVOH sample 99 + /124 was blended with pectin, the RH was 52% and the sample was measured at ambient temperature. In Fig. 5A, EB was measured for films with pectin:PVOH ratios of 70:30 and 50:50 (wt/wt), respectively. As indicated by Fig. 3A, both samples were at compositions at which the EB had not yet begun its rapid rise with composition. In both cases, the addition of glycerol produced a significant increase in EB. The IM (see Fig. 5B) decreased with increasing glycerol concentration for both blends, whereas only the sample with the 50:50 pectin:PVOH ratio shows a steady decrease in TS (see Fig. 5C) with increasing glycerol concentration in the film. TS passed through a maximum at 10% glycerol for the blend containing a 70:30 pectin:PVOH ratio. The measured value of TS at 0% glycerol may be lower than the actual value due to brittleness of the sample. Possibly, these samples developed minute edge cracks during sample preparation. These could cause sample to have a lower TS.

In Fig. 6A, we have plotted the time required for water to dissolve a 1 cm<sup>2</sup> piece of film for various pectin:PVOH ratios and at three temperatures. At 30 and 50°C, only films containing 30% or less PVOH were found soluble. Samples containing 50% or more of PVOH at 30 and 50°C were found insoluble. At 70°C pectin/PVOH films are soluble over the entire composition range. Furthermore,

**Table 3. Correlation coefficients ( $r^2$ ) for fourth-order equations relating initial modulus to blend composition**

Sample	Relative humidity (RH)	$r^2$
87/31	52	0.983
	15	0.722
98/31	52	0.972
	15	0.111
99 + /50	52	0.993
	15	0.835
87/124	52	0.992
	15	0.394
98/124	52	0.970
	15	0.770
99 + /124	52	0.961
	15	0.599

at 70°C, all pectin/PVOH blends are more soluble than neat PVOH films. Above 70% PVOH, solubility decreases rapidly with increasing percentage of PVOH in the films. In Fig. 6B, we have plotted the log of the rate constant ( $k$ ) of dissolution in water against  $1/T$  according to Eq. (1), an Arrhenius plot, for pectin/PVOH films containing 0, 10

and 30% PVOH.

$$\log k = -E/2.303RT + \text{Log } A \quad (1)$$

Where  $E$  is activation energy,  $T$  is absolute temperature,  $R$  is the gas law constant and  $A$  is a pre-exponential constant. The rate constant was obtained from the time of complete dissolution by assuming the rate of dissolution was linear and followed zero-order kinetics. The dissolution of thin films of poly(methyl methacrylate) (PMMA) in mixtures of 2-butanone (MEK) and 2-propanol were found to follow zero-order kinetics and gave fairly linear rate plots (Price and Buley, 1994). Table 5 contains  $E$  and  $A$  values for the three film compositions measured. The 0 and 10% PVOH films have about the same values for  $E$  and  $A$ , whereas the 30% PVOH film has lower values of  $E$  and  $A$  than the other two. Because  $k$  is directly proportional to  $A$  but inversely related to  $E$ , the lowering of both values tends to offset the effect of each other on  $k$ . Thus, changes in  $k$  values with composition tend to be moderate to small over the range 0%–30% PVOH. By way of comparison, the  $E$  value found for PMMA in MEK was two to three times higher than the  $E$  values for pectin/PVOH films in water.

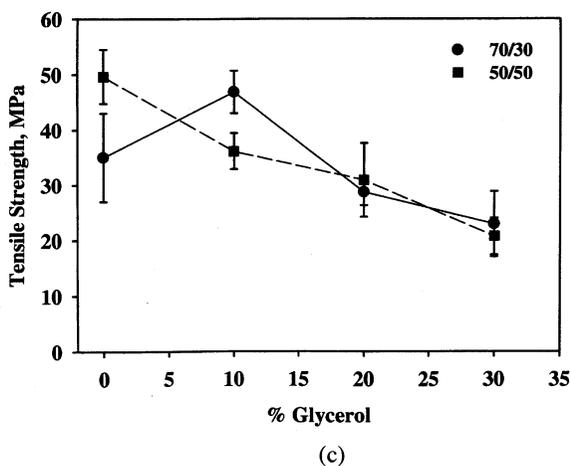
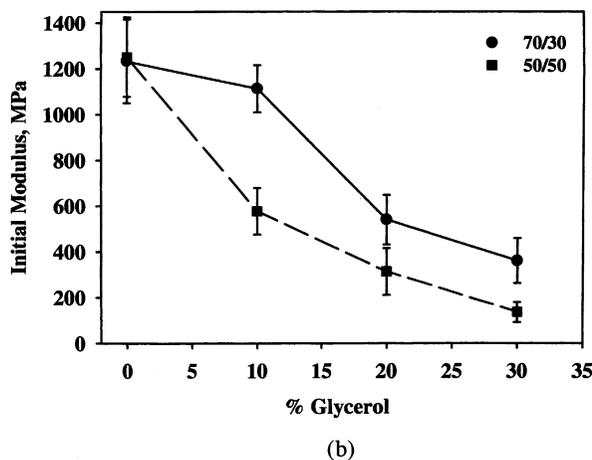
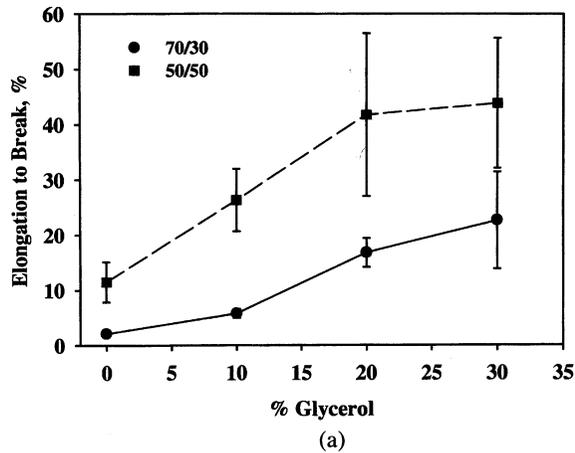


Fig. 5. Effect of glycerol on mechanical properties of pectin/PVOH (99 + /124) films. (A) Elongation to break; (B) initial modulus; (C) tensile Strength

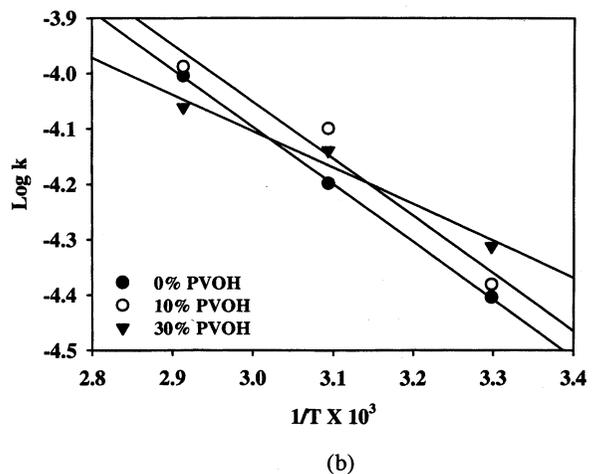
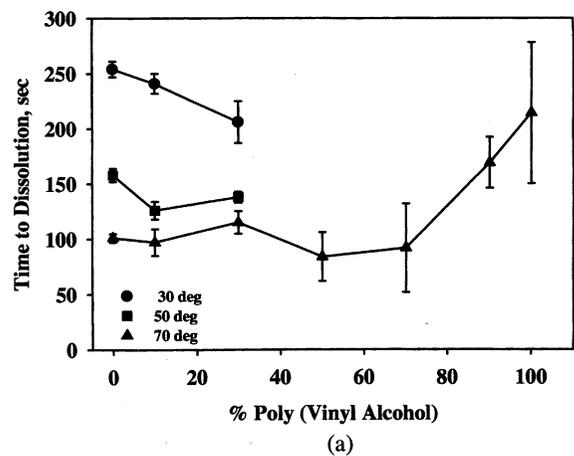


Fig. 6. Solubility properties of pectin/PVOH (98/124) films. (A) Time of dissolution; (B) Arrhenius plots for films containing 0, 10 and 30% PVOH