

# Thermomechanical Properties of Blends of Pectin and Poly(vinyl alcohol)

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## SYNOPSIS

Blends of citrus pectin and several types of poly(vinyl alcohol) were investigated to determine the effects of compositional variables and polymer type on film properties. Some films were also plasticized with glycerol. Films were cast from water onto Lexan<sup>®</sup> plates, dried, and removed. Thermomechanical properties were obtained using a dynamic mechanical analyzer, and thermodynamic transitions were also obtained using a differential scanning calorimeter. Increasing the amount of poly(vinyl alcohol) in the blends reduced the storage and loss modulus of the films above the glass transition temperature ( $T_g$ ). The  $T_g$  values observed decreased as the amount of PVOH in the blend increased. Addition of glycerol depressed the PVOH  $T_g$  and merged it into the  $T_g$  of the pectin/glycerol blend. Changes in the molecular weight and degree of ester hydrolysis of poly(vinyl alcohol) exerted a rather small effect on the blends. © 1996 John Wiley & Sons, Inc.†

## INTRODUCTION

A rapidly growing area of research and industrial activity is the study and use of biopolymers. This includes a wide range of biopolymers that have been used by themselves or in combination with other biopolymers.<sup>1-6</sup> In other cases some biopolymers, particularly starch, have been blended with synthetic polymers that are totally resistant to biodegradation.<sup>7-9</sup> As a result of the studies in this area, a broad spectrum of polymer compositions and properties have been obtained.

Of particular interest to us are films based on pectin, a component of fruit cell walls. Work in our laboratory has shown plasticized blends of pectin and starch to exhibit useful properties as free standing films.<sup>10-12</sup> These films exhibit good modulus and tensile properties; however, a fairly high level of

plasticizer (>50% by weight) is needed to obtain high elongations to break. Such high plasticizer loadings can result in blocking problems, and have significant potential for plasticizer leaching.

Some synthetic polymers exhibit susceptibility to biodegradation, and as such, are of interest to us for use in blends with natural biodegradable pectin polymers. One such material is poly(vinyl alcohol) (PVOH). Poly(vinyl alcohol) polymers are strong tough materials that can be easily obtained in a variety of molecular weights. They are made by hydrolysis of poly(vinyl acetate) and can be made with any convenient level of residual acetate side chains. The molecular weight of the PVOH is dependent on the molecular weight of the precursor poly(vinyl acetate). Differences in the amount of residual acetate groups present can result in significant property differences among these materials.<sup>13</sup>

The water resistance of PVOH is at its minimum, and its water solubility is at a maximum for materials where 87–89% of the ester groups in the precursor poly(vinyl acetate) have been hydrolyzed to the alcohol. At lower levels of hydrolysis (higher acetate content) the polymer is more hydrophobic and, thus, more resistant to water. Increased levels of

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hydrolysis allow higher levels of intramolecular hydrogen bonding, which makes the polymer less able to hydrogen bond with water, significantly increasing the water resistance of the polymer.<sup>13</sup>

Because poly(vinyl alcohol) has good tensile strength and a high elongation to break, it is a good candidate to blend with pectin to impart toughness to its films. The water solubility of the two polymers facilitates blending and processing of these polymers. Mixtures of a thermoplastic synthetic polymer and a nonthermoplastic biopolymer, both of which exhibit biodegradability, have the potential for use in a variety of applications.

## EXPERIMENTAL

### Materials

MexPec 1400, a citrus pectin with a degree of methyl esterification of 71%, was provided by Grindsted Products, Inc. (Kansas City, KS) and was used as received.

Six different grades of poly(vinyl alcohol) purchased from Aldrich Chemical Co. were used. Three were identified as having a molecular weight range of 124–186,000. These had degrees of ester hydrolysis of 99+%, 98–99%, and 87–89%. Two samples had a molecular weight range of 31–50,000, and had degrees of ester hydrolysis of 98–99% and 87–89%. One sample had a molecular weight of 50,000 and a degree of ester hydrolysis of 99+%. All samples were used as received. The molecular weights and degree of ester hydrolysis for the samples are summarized in Table I.

Glycerol (99+%), was reagent grade and was purchased from Aldrich Chemical Co. It was used as received.

Water was HPLC grade made from deionized water using a Modulab Polisher I water system (Continental Water Systems, Inc.).

### Film Preparation

Films were prepared by dissolving pectin in dilute solutions of poly(vinyl alcohol), and casting them on Lexan<sup>®</sup> plates using a "Microm" film applicator (Paul N. Gardner Co., Pompano Beach, FL). A wet film thickness of 98 mil (2.5 mm) was used. The films were then allowed to air dry overnight. After air drying, the samples were vacuum dried for 30 min at room temperature. The films were removed from the coating plates with a razor blade. Prior to

**Table I Poly(vinyl alcohol) Properties**

Sample	Molecular Weight $\times 10^{-3}$	% Ester Hydrolysis
1	31–50	87–89
2	31–50	98–99
3	50	99
4	124–186	87–89
5	124–186	98–99
6	124–186	99+

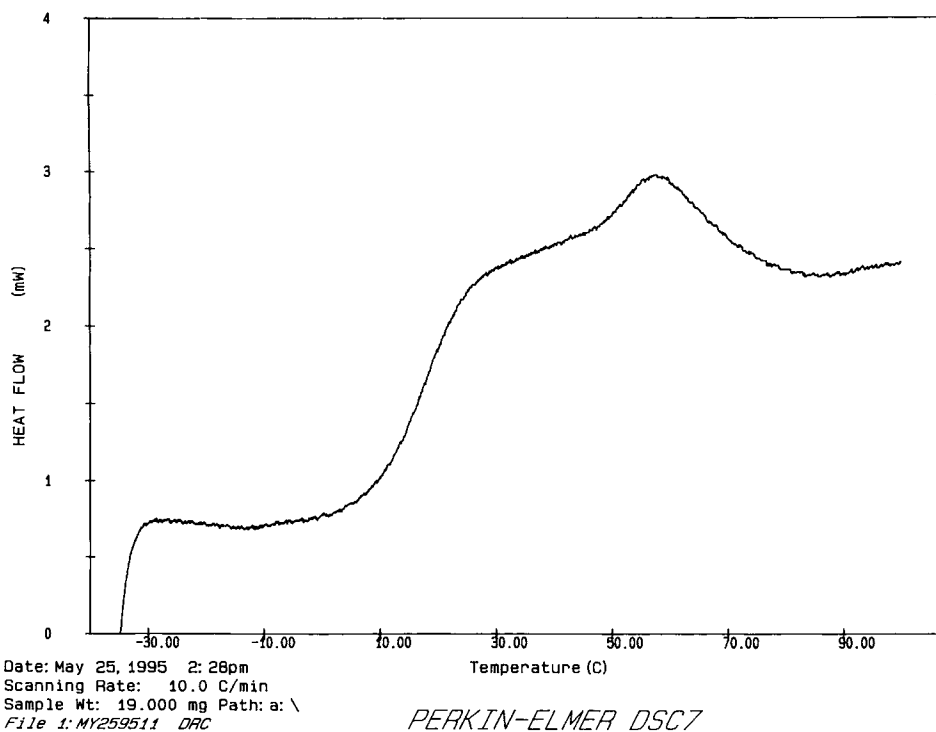
testing, the samples were stored in a desiccator with a relative humidity of 50% maintained by a saturated solution of sodium bisulfate.

Stock solutions of poly(vinyl alcohol) with a concentration of 10.0% by weight were made by dissolving the polymers in water using the method recommended by Air Products Co.<sup>14</sup> This involved dispersing the polymer in cold water and then heating the dispersion with vigorous agitation at 85, 93, or 96°C for 30 min, depending on the degree of ester hydrolysis. The temperature required increased with increasing degree of ester hydrolysis, and attaining the minimum temperature specified is essential for complete dissolution of the polymers. No changes in degree of hydrolysis occur during heating, and the samples maintain solubility after cooling.<sup>14</sup> The solutions were stored in a refrigerator prior to use to avoid bacterial attack.

The pectin/poly(vinyl alcohol) solutions were prepared by weighing the appropriate amount of the PVOH solution into a 50 mL beaker, adding sufficient water to give a total solution weight of 37.5 g, and then adding the desired amount of pectin with stirring. For those samples where glycerol was used, it was added to the water/poly(vinyl alcohol) mixture prior to the addition of pectin. In each sample the total weight of pectin plus poly(vinyl alcohol) plus glycerol was equal to 2.5 g. The samples were mixed until there was no evidence of undissolved solids, usually 2–3 h.

### Differential Scanning Calorimetry

Differential scanning calorimetry runs were made using a Perkin–Elmer DSC 7 instrument equipped with a chiller for operation at subambient temperatures. Approximately 20 mg samples were accurately weighed into Perkin–Elmer large volume stainless steel DSC pans capable of withstanding internal pressures of 350 psi. Circular film samples that fit into the pans were cut out using a cork borer.



**Figure 1** Differential scanning calorimetry thermogram of Poly(vinyl alcohol) of 124–186,000 mol wt and 98–99% degree of ester hydrolysis.

All runs were made with an empty pan in the reference sample holder, and the instrument was placed in a nitrogen glove box.

The samples were loaded into the instrument at 25°C, and the temperature was then lowered to –40°C. After stabilizing at this temperature, the samples were held for an additional 2 min, and were then heated from –40 to 100°C at 10°C/min.

### Mechanical Testing

Dynamic mechanical analysis (DMA) was done on a Rheometrics RSA II solids analyzer (Piscataway, NJ) using a film-testing fixture. Liquid nitrogen was used for cooling to subambient temperatures. Test samples were cut from the films with a razor blade. Nominal dimensions of the samples were  $6.9 \times 38.1 \times 0.08$  mm. Sample thickness was measured with a micrometer, and sample width was measured with a millimeter ruler. The gap between the jaws at the beginning of each test was 23.0 mm.

A nominal strain of 0.1% was used in all cases, with an applied frequency of 10 rad/sec (1.59 Hz). Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan$ ) were determined as a function of tem-

perature. Data were taken from –100 to 200°C using a heating rate of 10°C/min. One data point was taken every 24 s. Data analysis was carried out using the Rheometrics RHIOS software.

### RESULTS

Six samples of PVOH were blended with the pectin. The properties of these PVOH samples are given in Table I. Blends of the pectin were made with each polymer which contained 10, 30, and 50% by weight poly(vinyl alcohol). Films made from these blends, as well as films made from each individual PVOH and the pectin by themselves, were analyzed by dynamic mechanical analysis (DMA) to determine the size and temperature of the thermal transitions present. The pure poly(vinyl alcohol) films were also analyzed by DSC to further characterize the transitions.

Cast films of all six PVOH samples showed two broad overlapping thermal transitions by differential scanning calorimetry. A typical scan is shown in Figure 1. The first transitions occurred at 19–23°C for the 50,000 molecular weight samples, and at 20–

27°C for the 124–186,000 molecular weight samples. The higher temperature transition occurred at 63–66°C for the 50,000 molecular weight samples, and at 57–60°C for the 124–186,000 molecular weight samples. For the 50,000 molecular weight samples, the lower temperature transition was about 5–7°C lower than for the 124–186,000 samples, whereas they were 6–8°C higher at the upper temperature transition. The areas of the individual peaks could not be resolved. The total area of the two peaks averaged 16.5 J/g for the 124–186,000 molecular weight samples, and about 18.1 J/g for the 50,000 molecular weight samples. Unlike molecular weight, degree of residual esterification had little or no effect on the thermal behavior of PVOH.

DSC curves of the poly(vinyl alcohol) powders with a degree of ester hydrolysis of 98–99% showed a single peak at 56 and 54°C, respectively, for the 50,000 and 124,000 molecular weight materials. Thus, the higher temperature peak in the DSC curves of the films corresponds to the PVOH glass transition temperature. These relative values are consistent with those found in the films. The glass transition temperature of PVOH has been reported to be 85°C.<sup>15</sup> The lower temperature peak in the DSC curves apparently corresponds to some other second order transition caused during the preparation of the films.

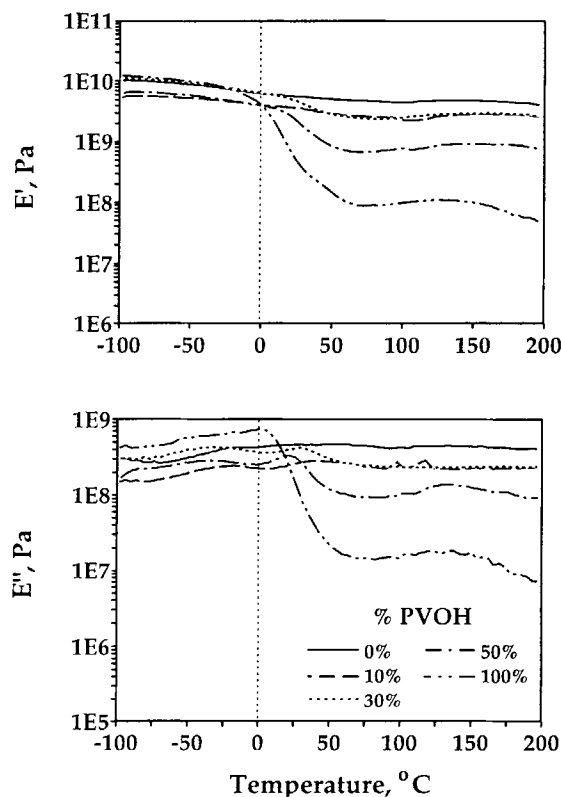
No thermal transitions were noted in the pure pectin film up to a temperature of 200°C. Apparently pectin does not have a glass transition temperature or melting point in the temperature range studied.

In the dynamic mechanical analysis experiments, the presence of glass transitions was noted by large and fairly sharp changes in the mechanical properties of the films with temperature. The thermo-mechanical properties measured were the storage modulus ( $E'$ ), the loss modulus ( $E''$ ) and the loss tangent ( $\tan \delta$ ). A glass transition shows up in the storage modulus curve as a rapid drop in the modulus. In the loss modulus and loss tangent curves the transitions show up as a peak. Shrinkage induced by rearrangement of the polymer molecules may show up as a gradual increase in the storage modulus with increasing temperature, or as a peak in both the storage modulus and loss modulus curves.

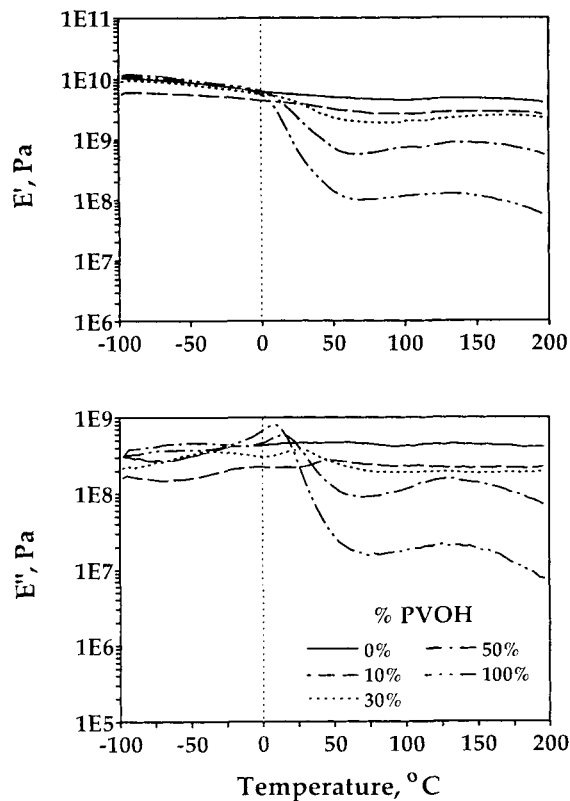
All of the blends showed a distinct glass transition temperature attributable to the PVOH. The size of the transition was proportional to the amount of PVOH in the blend. The general features of the thermograms were similar for both molecular weights and for all three degrees of ester hydrolysis. This is shown for the storage modulus and loss

modulus of a typical set of compositions for a 50,000 molecular weight sample in Figure 2, and for a 124–186,000 molecular weight sample in Figure 3.

If we consider the blended film to be a pectin film modified by PVOH, the temperature at which the glass transition of the blend occurred was found to decrease as the amount of PVOH in the blend increased. Alternatively, if we consider the blend to be a PVOH film modified by pectin, then the addition of pectin to the PVOH resulted in an increase in the glass transition temperature of PVOH. Figure 4 shows the effect of film composition on the glass transition temperature of the pectin/PVOH blends. In general, the glass transition temperature of PVOH in the blended films was found to be near 45°C when it was present at the 10% level by weight in the pectin. By way of contrast, the  $T_g$  was about 5°C in the pure PVOH films when the location of the  $T_g$  was marked by the location of the peak in the  $E''$  curve. The change was essentially linear with changes in composition. Correlation coefficients of greater than 0.95 were found in all cases. Using the



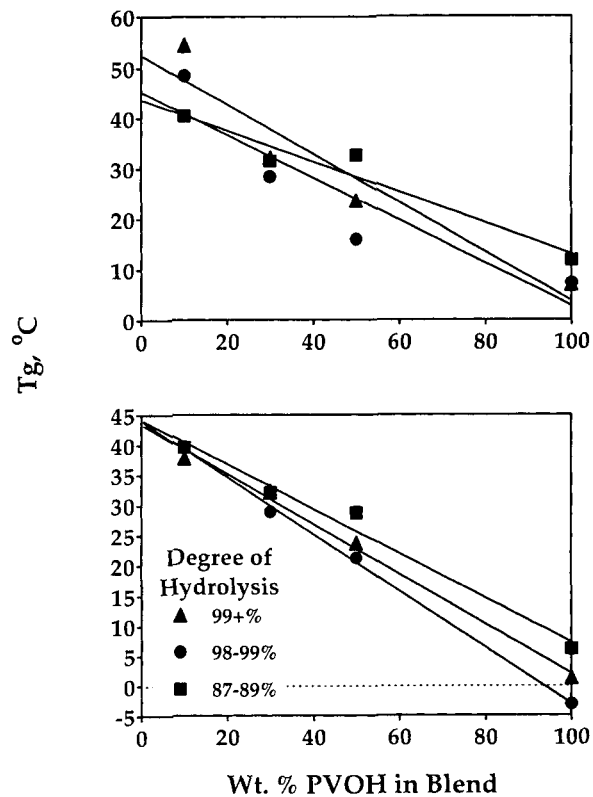
**Figure 2** Effect of PVOH content on the (a) storage modulus and (b) loss modulus of films containing pectin and PVOH with 50,000 mol wt and 99+% degree of hydrolysis.



**Figure 3** Effect of PVOH content on the (a) storage modulus and (b) loss modulus of films containing pectin and PVOH with 124–186,000 mol wt and 99+% degree of hydrolysis.

peak in the tan plot to determine the  $T_g$  consistently gave values 5–10°C higher. This increase in the  $T_g$  of the PVOH with increasing amounts of the pectin, which shows no glass transition over the wide temperature range investigated, is expected behavior for glassy polymer mixtures.

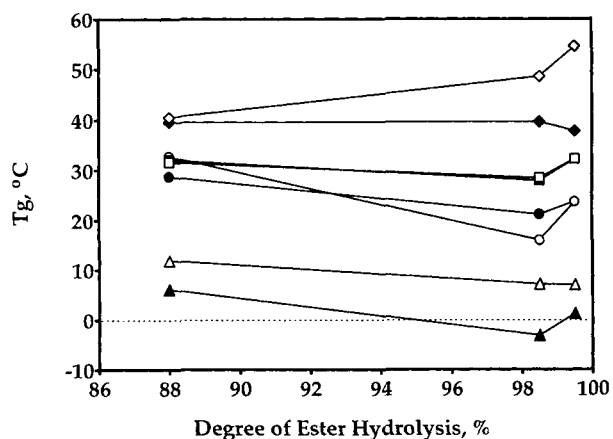
The effect of the degree of hydrolysis on the  $T_g$  of the blends for the different compositions is shown in Figure 5. There appears to be little change with degree of hydrolysis, although there does seem to be a very slight upward trend with increasing ester content. This small change with ester content is less marked in the samples containing only 10% PVOH, but this is to be expected because the low level of the PVOH makes the exact temperature of the transition somewhat more difficult to determine. No strong trend was noted with the effect of molecular weight. Although the glass transitions seen in the pure PVOH samples are definitely higher for the higher molecular weight samples, no real difference was seen between the glass transition temperatures observed for the different molecular weight polymers



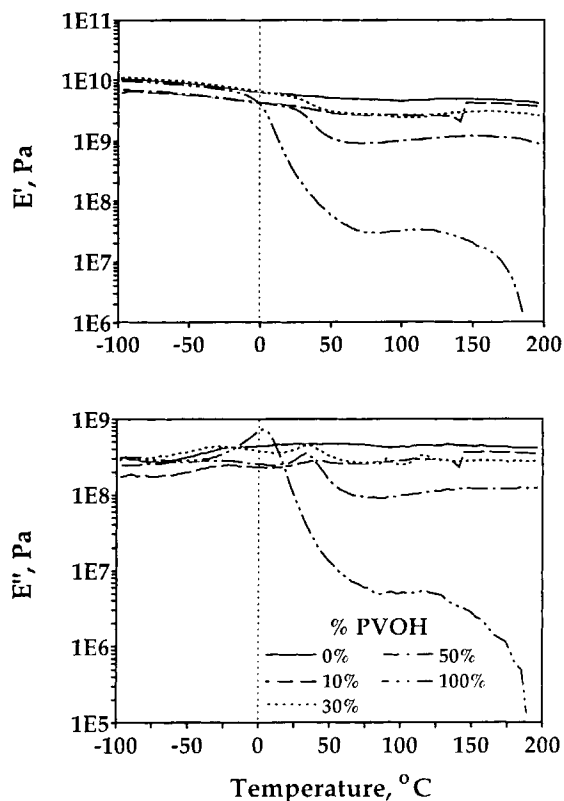
**Figure 4** Effect of PVOH content on glass transition temperature, (a) 124–186,000 mol wt, (b) 50,000 mol wt.

in the blends with pectin. The variability of the  $T_g$  values when measured by the DSC method was 2–6°C. A similar variability was found by DMA.

The storage modulus is a measure of the elastic properties of the films.<sup>16</sup> Below the glass transition



**Figure 5** Effect of degree of ester hydrolysis on glass transition temperature. Open symbols—124–186,000 mol wt; filled symbols—50,000 mol wt; %PVOH—◆ 10%, ■ 30%, ● 50%, ▲ 100%.



**Figure 6** Effect of PVOH content on the (a) storage modulus and (b) loss modulus of films containing pectin and PVOH with 50,000 mol wt and 87–89% degree of hydrolysis.

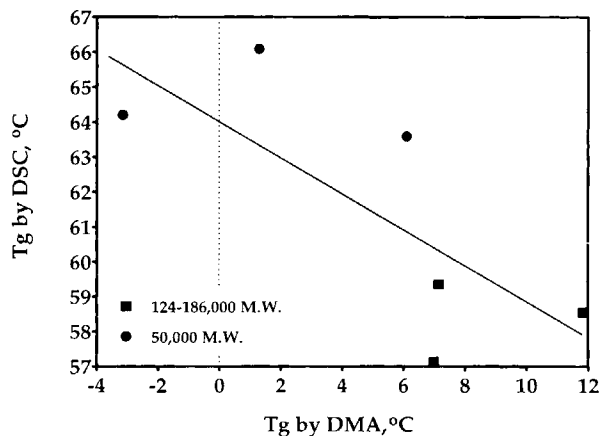
temperature, all of the films had a relatively constant value for the storage modulus in the range of 0.5 to  $1 \times 10^{10}$  Pa. Above the glass transition temperature the storage modulus decreased by about one to one and a half orders of magnitude over the next 50°C above  $T_g$  as the PVOH content was increased from 0 to 50% by weight. It then plateaued, as can be seen in Figures 2 and 3. The drop in storage modulus above  $T_g$  is relatively proportional to the amount of PVOH present in the blend. Similar behavior pattern was observed for the loss modulus, where the modulus exhibited a large drop following the  $T_g$  peak. Reproducibility of the modulus values was found to be  $\pm 15\%$ .

There was very little difference in the temperature behavior of the two moduli with molecular weight. Curves for the blends containing the different molecular weight PVOHs were essentially superimposable over the entire temperature range for all compositions, including the pure PVOH samples. However, there was a very noticeable change seen with differences in the degree of ester hydrolysis of the samples.

For both molecular weights, samples with 98% or higher degree of ester hydrolysis exhibited essentially identical behavior. Samples made using the PVOH with 87–89% hydrolysis, however, behaved quite differently from those more highly hydrolyzed. Nevertheless, in those samples there was no difference due to molecular weight. For both of these polymers, the plateau values of the two moduli above  $T_g$  were significantly lower than for the other PVOH samples. This difference was also very visible in the 50% blends, but was difficult to see in the blends containing lower levels of the PVOH. The loss and storage modulus data for the samples containing various amounts of the 50,000 molecular weight PVOH with 87–80% hydrolysis are shown in Figure 6.

There was a substantial difference between the glass transition temperatures determined by DSC and those found using dynamic mechanical analysis. This apparent discrepancy can be explained by the difference in the properties measured by the two methods. DSC measures the heat taken up as the polymer changes from the glassy to the rubbery state. Dynamic mechanical analysis, on the other hand, measures the dynamic stiffness of the sample. It is quite normal for the storage modulus of a material to begin a rapid decrease prior to the actual  $T_g$  as increased molecular motion begins to occur in the polymer chains. A linear correlation ( $r^2 = 0.55$ ) was found between the  $T_g$  values found by DSC and those found by dynamic mechanical analysis. This is shown in Figure 7.

Figure 8 shows the plasticizing effect of glycerol on a 70/30 pectin/PVOH blend containing the higher molecular weight PVOH with the highest de-



**Figure 7** Comparison of  $T_g$  determined by DMA with that determined by DSC.

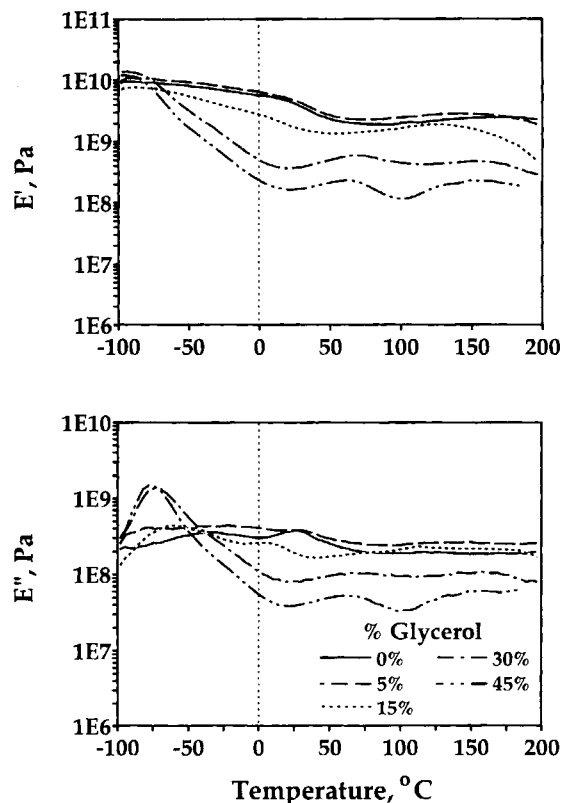
gree of ester hydrolysis. The addition of glycerol has a large effect on both the storage and loss modulus behavior of this polymer blend, particularly with 15% or more glycerol.

The addition of 5% glycerol had little effect on the storage modulus curve, but appeared to decrease the magnitude of the  $T_g$  peak in the loss modulus curve somewhat. With 15% glycerol, the  $T_g$  peak was found to decrease in temperature by about 20°C, and a new peak appeared that was due to the interaction of the glycerol with the pectin, and was identified in previous work.<sup>11</sup> At higher glycerol levels (30 and 45%), the glass transition of the PVOH seemed to disappear, and new peaks appeared above 60°C, indicating the presence of new thermal transitions. These are probably a result of film shrinkage. In addition, both the storage and loss modulus of blends containing 30 and 45% glycerol were much lower than those for the blends containing lower amounts of glycerol at temperatures above about -60°C. At temperatures below about -80°C, all of the blends had close to the same storage modulus values.

## DISCUSSION

The thermomechanical properties of citrus pectin films are profoundly changed by the addition of 10 to 50% PVOH by weight. Pectin does not have a glass transition below its decomposition temperature, which is in the range of 190–200°C, whereas PVOH has a glass transition temperature in the vicinity of room temperature. In blends with pectin, PVOH imparts its  $T_g$  to the blend. In the absence of glycerol there appears to be only one glass transition in the polymer blends.

Increasing the amount of PVOH in the blend always resulted in the  $T_g$  moving toward lower temperatures. The  $T_g$  of the unplasticized pectin is higher than its decomposition temperature and, therefore, cannot be actually measured. In any true blend of two glassy polymers, the glass transition temperature of the mixture is intermediate between those of the two separate components. Typically, the  $T_g$  of the blend is somewhat depressed compared to the arithmetic average of the two individual  $T_g$  values. The depression is due to a reciprocal dependence of  $T_g$  on concentration. While depressed relative to the arithmetic average of the two glass transition temperatures, the  $T_g$  of the blend is always higher than that of the component with the lower  $T_g$ . Here, PVOH has a lower  $T_g$  than pectin. In this



**Figure 8** Effect of glycerol content on the (a) storage modulus and (b) loss modulus of pectin/PVOH blend containing 30% PVOH with 124–186,000 mol wt and 99+% degree of ester hydrolysis.

case, pectin, the component whose  $T_g$  is above that of the blend, tends to immobilize the molecules of the PVOH, thereby effectively increasing the glass transition temperature of that component.

As shown by the data in Figure 5, the molecular weight of the PVOH had a small but noticeable effect on the temperature of its glass transition in the blends and in films by itself. The relative values observed between the two molecular weights in the films fabricated from the blends and in the pure resin powders show the same trends. In both cases, DSC and DMA, the lower molecular weight samples, had the higher  $T_g$  values, even if by only a few degrees. Degree of ester hydrolysis also had little effect on the  $T_g$  in the blends. There appeared to be a very slight increase in  $T_g$  with decreasing degree of ester hydrolysis (increased ester content). The increase in  $T_g$  became less evident as the proportion of PVOH in the blend decreased, and the differences were small enough that they are within the variability of the measurements.

Of more practical significance from an end use perspective are the values for the storage and loss modulus for the different blends at various temperatures. Essentially, there were no difference in blend moduli between the two different molecular weights for any of the three degrees of hydrolysis. Nor were the modulus values different between the two different molecular weight samples of the pure PVOH for any of the individual degrees of ester hydrolysis. However, the behavior of the storage and loss modulus for the samples with the 87–89% degree of hydrolysis were quite different than that of the polymers that were more fully hydrolyzed. Above  $T_g$ , both the storage modulus and loss modulus of these two PVOH samples were about one-third of the values observed with the more fully hydrolyzed materials. This larger decrease in modulus above  $T_g$  did not seem to have much of an effect on the modulus values observed in the blends with pectin.

Possibly these lower modulus materials had a small effect on the modulus values of the blends because the observed moduli in the films are a composition weighted arithmetic average of the moduli of the two individual components. Because the modulus for the pectin is so much higher than that of either of the PVOH samples above  $T_g$ , even relatively large changes in the modulus of the PVOH will have only a small effect on the arithmetic average modulus of the blend when one is replaced for the other, except for blends which contain very little pectin. Only at this extreme does the PVOH have a modulus comparable to that of the blend.

In the blends containing 50% PVOH, there was a small rise in the value of the storage modulus above about 70°C followed by a small decline past about 130°C. This appears to indicate some shrinkage and stiffening is occurring in the film, followed by some additional softening of the film at still higher temperatures. This phenomenon is attributable to the poly(vinyl alcohol), because this behavior is not observed in the pectin alone. Previously<sup>11</sup> we have shown this behavior to occur in plasticized blends of pectin and starch. The PVOH chains are more mobile than the unplasticized pectin chains, thereby allowing molecular rearrangement to occur more easily.

Plasticization of a 70/30 blend of pectin and PVOH with glycerol increases chain mobility as the glycerol content is increased. Thus, the  $T_g$  of the PVOH is depressed until it merges into the  $T_g$  of

the pectin that has been induced by the addition of the glycerol.

## CONCLUSIONS

The addition of PVOH of two different molecular weights and three different degrees of ester hydrolysis into blends with high methoxy citrus pectin imparts a glass transition into the blends. The temperature of this transition decreased as the amount of PVOH in the blend was increased, but was relatively insensitive to the type of PVOH used. The  $T_g$  ranged from about 5 to 45°C, depending on the composition. Below the glass transition temperature the storage modulus and loss modulus of the blends were insensitive to both the PVOH type and the amount of PVOH present in the blend. Above the  $T_g$  there was little or no effect of the PVOH type on the modulus values of the blends. The PVOH samples themselves showed no effect of molecular weight on either of the two moduli; however, the values for both polymers with the lowest degree of ester hydrolysis were about one-third of the values of the other four materials. This difference did not show up in the blended films because the moduli for the PVOH samples above  $T_g$  were all so much lower than the values from the pectin.

The addition of glycerol plasticizer to the blends depressed the  $T_g$  of the PVOH, increased the molecular mobility of both the pectin and the PVOH, and allowed for noticeable shrinkage through molecular rearrangement to occur with enhanced packing efficiency of the molecules.

Addition of the PVOH improves the toughness of the pectin films by the addition of a ductile material that is at or near its glass transition temperature, thereby decreasing the brittleness of the films.

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## REFERENCES

1. C. M. Buchanan, D. D. Dorschel, R. M. Gardner, R. J. Komarek, and A. W. White, *J. Macromol. Sci., Pure Appl. Chem.*, **A32**, 683–697 (1995).
2. A. M. Reed and D. K. Gilding, *Polymer*, **22**, 494–498 (1981).
3. P. R. Gruber, *Corn Utilization Conference V*, June 8–10, 1994, St. Louis, MO.
4. R. A. Gross, G. A. Birrer, A. M. Cromwick, S. A. Gianos, and S. P. McCarthy, in *Biotechnology Polymers*,



- C. G. Gebelein, Ed., Technomic Press, Lancaster, PA, 1993, pp. 200–213.
5. R. W. Lenz, Y. B. Kim, and R. C. Fuller, *Microbiol. Rev.*, **103**, 207–214 (1992).
  6. E. Shimamura, K. Kasuya, G. Kobayashi, T. Shiotani, Y. Shima, and Y. Doi, *Macromolecules*, **27**, 878–880 (1994).
  7. F. H. Otey, R. P. Westhoff, and C. R. Russell, *Ind. Eng. Chem., Prod. Res. Dev.*, **16**, 305–308 (1977).
  8. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem., Prod. Res. Dev.*, **19**, 592–595 (1980).
  9. W. M. Doane, *Starch/Starke*, **44**, 293–295 (1992).
  10. D. R. Coffin and M. L. Fishman, *J. Agric. Food Chem.*, **41**, 1192–1197 (1993).
  11. D. R. Coffin and M. L. Fishman, *J. Appl. Polym. Sci.*, **54**, 1311–1320 (1994).
  12. D. R. Coffin and M. L. Fishman, *J. Appl. Polym. Sci.*, **57**, 663–670 (1995).
  13. C. P. Argana and E. P. Czerwin, in *Water-Soluble Resins*, 2nd ed., R. L. Davidson and M. Sittig, Eds., Reinhold Book Corp., New York, 1968, pp. 109–130.
  14. Air Products, *AIRVOL<sup>®</sup> Polyvinyl Alcohol product brochure*, Allentown, PA, 1993.
  15. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley Interscience, New York, 1975, pp. III-150.
  16. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 30.

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