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PECTIN/STARCH/GLYCEROL FILMS: BLENDS OR COMPOSITES?†

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ABSTRACT

The miscibility of pectin (P), starch (S), and glycerol (G) in films was investigated by dynamic mechanical analysis (DMA), tensile measurements, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and film dissolution studies. DMA revealed that P/S/G films exhibit up to three thermodynamic transitions prior to film degradation when heated. Transitions appear to be induced or enhanced by the addition of glycerol. The lowest transition occurred below −50°C, the second above room temperature and below 100°C, and the third above 100°C. DMA and SEM on P/S/G films containing starch solubilized for various lengths of time revealed that a tenfold difference in the particle size of starch produced no more than a 20% difference in the dynamic moduli. Tensile measurements revealed that changes in glycerol content or relative humidity induced greater changes in mechanical properties than time of starch solubilization (gelatinization). FT-IR spectra of P/S/G films revealed that the microstructure around ester and carboxylic acid side chains of pectin was changed significantly by the level of glycerol and relatively little by varying the starch level. Results from dissolution studies were consistent with the idea that P/S/G films are highly compatible composites of starch in pectin.

†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.

INTRODUCTION

The societal desire to introduce more rapidly degrading materials into the ecological environment and to fabricate items from renewable and sustainable resources has prompted us to search for materials with film-forming properties which were constructed entirely from agricultural coproducts. One such system we investigated consisted of the plant polysaccharides pectin (P) and starch (S), with glycerol (G) added as a plasticizer [1-3].

In studying P/S/G films we found that we could fabricate films over a wide range of component compositions. Pectin retained its film-forming ability even if 45% of it was replaced with starch and the mixture contained 25% polymer and 75% glycerol. Mechanical properties of these polymer mixtures ranged from strong and stiff to highly flexible. At the pectin/starch ratio of 9:1, adding glycerol induced up to three thermal transitions. The lowest one was a glass transition which occurred below −50°C. With increasing amounts of glycerol, film flexibility increased at the expense of film strength. At the highest glycerol content, the film behaved like a plasticsol. Partially replacing pectin with starch reversed trends induced by the addition of glycerol. Substituting starch for pectin increased film strength and decreased its flexibility. For example, at pectin/starch ratios of 11:9 and 30% or more glycerol, the T_g still remained but the two transitions occurring above room temperature merged into one extremely broad transition. Based on earlier studies conducted in this laboratory [4, 5] on pectin, we hypothesized that glycerol increased the flexibility of pectin by two modes of action. By one mode of action, glycerol dissociated stiff networks of pectin held together by polymer-polymer interactions, and by the second it aided the motion of dissociated pectin chains by lubricating the passage between chains under stress.

SEM studies and dynamic mechanical analysis as a function of starch solubilization times [3] revealed that a large reduction in starch particle size had a relatively small effect on the loss and storage moduli of P/S/G films over a broad temperature range. These results were rather surprising in that reports of other blends containing starch have emphasized the importance of "destructurizing" starch in order to form compatible blends with suitable mechanical properties [6].

Here, we tested further the validity of our previous conclusions concerning the effect of starch particle size by additional measurements on P/S/G films. Toward this end we examined the miscibility of P, S, and G in films by changes in FT-IR spectra and by changes in scanning electron micrographs (SEM) of freeze-fractured surfaces as a function of starch solubilization at higher magnification than previously [3]. In addition, we measured the effect of starch solubilization, addition of glycerol, and moisture on Young's modulus, tensile strength, and elongation to break. We also measured the effect of pectin/starch ratio on the rate of film disintegration in water to elucidate further the miscibility of pectin and starch in films.

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 without further purification. Amylomaize VII starch granules (ca. 70% amylose, 30% amylopectin) were provided by American Maize Products Co. (Chicago, IL) and were solubilized (gelatinized) as received. Glycerol was ACS reagent grade purchased from Aldrich Chemical Co. (Milwaukee, WI) and was used as received.

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

Film Fabrication

A typical film was prepared by mixing a solubilized starch solution into a pectin solution containing glycerol and spreading it on a glass plate with a "Microm" film applicator (Paul N. Gardner Co., Pompano Beach, FL). Films were dried in air overnight and then under vacuum at room temperature for 30 minutes. The wet film thickness was 2-2.5 mm whereas that of the dried films was 0.06-0.08 mm.

Typically, pectin was dissolved by slowly adding 1.05 g to 20 mL of stirred water containing 0.75 g of glycerol. The solutions which resulted were stirred for another 1-2 hours until all of the pectin appeared to be dissolved. Solubilized starch was prepared by mixing 0.70 g of starch with 10.0 mL of water in a Parr microwave bomb (Parr Instrument Co., Moline, IL) and heating in an Amana model RSW348P Radarange microwave oven. Solubilization times varied from 10 to 105 seconds. Hot starch solutions were mixed with pectin as quickly as possible to minimize starch retrogradation prior to mixing.

Mechanical Testing

Thermal dynamic mechanical analysis (TDMA) was performed on a Rheometrics RSA II Solids Analyzer (Piscataway, NJ) using a film-testing fixture as described previously [1, 2]. Young's modulus, tensile strength, and elongation to break were measured on an Instron model 1122. Gauge length was 50.0 mm, sample width was 6.0 mm, sample thickness was about 0.06-0.08 mm, crosshead speed was 10 mm/min, and room temperature was 23°C.

Microscopy

Rectangular strips of films (ca. 0.5 × 2 cm) were soaked in absolute ethanol for 24-48 hours and then immersed in liquid nitrogen and cooled for 5 minutes. 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 minutes and 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. Photographic images of fractured faces were recorded on positive film using a JSM840A scanning electron microscope (JEOL, USA, Peabody, MA) in the secondary electron imaging mode at an instrumental magnification of 4500×.

FT-IR Spectroscopy

Films were cast on CaF_2 windows by placing 12 drops of a 2.5% (w/v) solution containing pectin, starch, and glycerol, drying overnight at room temperature in a dry box purged with nitrogen, followed by vacuum drying for 30 minutes at room temperature.

Spectra were obtained using a Nicolet 740 FT-IR spectrometer equipped with a MCT-B detector and the Nicolet 660 data system. After purging the sample chamber for 30 minutes, data were collected. For each sample, 512 interferograms were collected, co-added, phase-corrected, apodized (Happ-Genzel function), and fast-Fourier transformed. Nominal instrument resolution was 2 cm^{-1} with one data point every 1 cm^{-1}.

Dissolution of Films

Test films were cut into 1 centimeter squares from a template. Squares were submerged in 40 mL of deionized water in a constant temperature vessel that was thermostatted to ±0.1°C. The water was stirred by a magnetic stirring bar. The time required for the square to completely disappear was measured with a stopwatch. Each experiment was run in triplicate.

RESULTS AND DISCUSSION

In P/S/G films that we have fabricated, pectin is the most abundant polymeric component and the one that is largely responsible for imparting film-forming properties to the mixture. The relationship between component composition and film properties can be explained satisfactorily by considering the properties of a pure pectin film and observing how its properties are changed with the addition of glycerol and then starch. TDMA revealed that pure pectin films exhibit no thermal transitions over the temperature range -100 to $+180$°C (Fig. 1). Addition of glycerol to pectin films induces up to three thermodynamic transitions prior to film degradation when heated. The lowest transition occurs below -50°C, the second above room temperature and below 100°C, and the third above 100°C. Increasing the percentage of glycerol in the film decreases the moduli and increases the drop in moduli with temperature. In the 60 to 70% glycerol range, raising the temperature from -100 to 0°C lowers the storage moduli by several orders of magnitude. From the large drop in the storage moduli, it was concluded that the lowest transition was a T_g. At 45% glycerol and below, there is a broad shallow transition covering the temperature range 25 to 175°C. In the glycerol range of 60 to 70%, the broad transition is resolved into two transitions. The second transition is in the range 25 to 75°C and the third transition is in the range 125 to 160°C. Both of these transitions exhibit relative maxima in storage and loss moduli (loss curves not shown).

Adding starch to pectin/glycerol films appears to attenuate the effects of glycerol, particularly at glycerol levels above 45% and P/S ratios below 9:1 [2]. At P:S ratios of 9:1, the effect of starch is minimal. Lowering P/S ratios at amounts of glycerol above 45% raises the moduli and induces more shallow transitions. At a P/S ratio of 55:45 and a glycerol level of 60%, the TDMA curve becomes almost

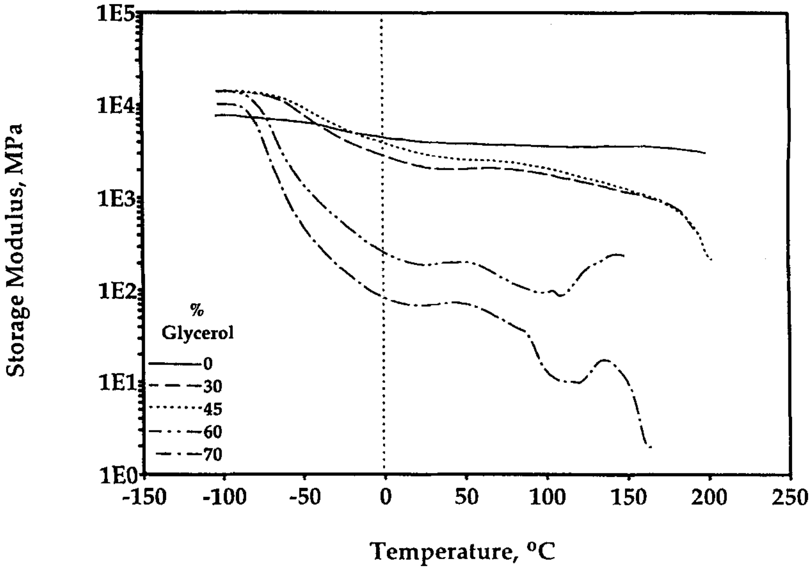

FIG. 1. Effect of glycerol level and temperature on the storage modulus of pectin films.

superimposable with curves obtained at 30 and 45% glycerol. The T_g is still visible, and the second and third transitions have merged.

The effect of starch microwave heating time (MHT) on moduli at constant P/S ratio is shown by the data from TDMA in Fig. 2. Here the P/S ratio is 60:40, the percentage of glycerol is 30%, and the overall P/S/G ratios are 42:28:30. The data in Fig. 2 reveal that changes in moduli with MHT are rather small. SEMs (10,000×) of the fractured surfaces of films composed of 70% pectin, 30% glycerol (Fig. 3A) and 42:28:30 P/S/G ratios after MHT of 10 seconds (Fig. 3B), 45 seconds (Fig. 3C), and 105 seconds (Fig. 3D) revealed differences in film fracture surfaces. Figure 3(A) is the fracture surface of a P/G film. The figure reveals that the fracture plane was uneven and consisted of small ridges and crevices which were oriented parallel to the film plane. The plane surfaces were composed of close packed beads which were about 0.1–0.2 μm in diameter. Figure 3(B) is representative of P/S/G film fracture surfaces containing starch heated for 0 to 20 seconds. Here we see the typical beadlike microstructures found in pectin films but with ridges and crevices oriented around separate smooth circular areas of 5–10 μm in diameter. These circular areas correspond to fractures through whole starch granules. No fracture planes identifiable with top or bottom surfaces of starch granules were found, indicating that the preferred planes of fracture were through the granule itself. Since none of the cleaved granules appeared dislodged and no surfaces with holes 5–10 μm in diameter were found, we concluded that there was strong adhesion between the pectin-starch interface. Figure 3(C) shows an SEM image of the film fracture surface after an MHT of 45 seconds for starch. This figure is representative of fracture surfaces containing starch heated in the range of 30 to 60 seconds. In this time domain, fracture planes were often splintered but flat over large areas, and it

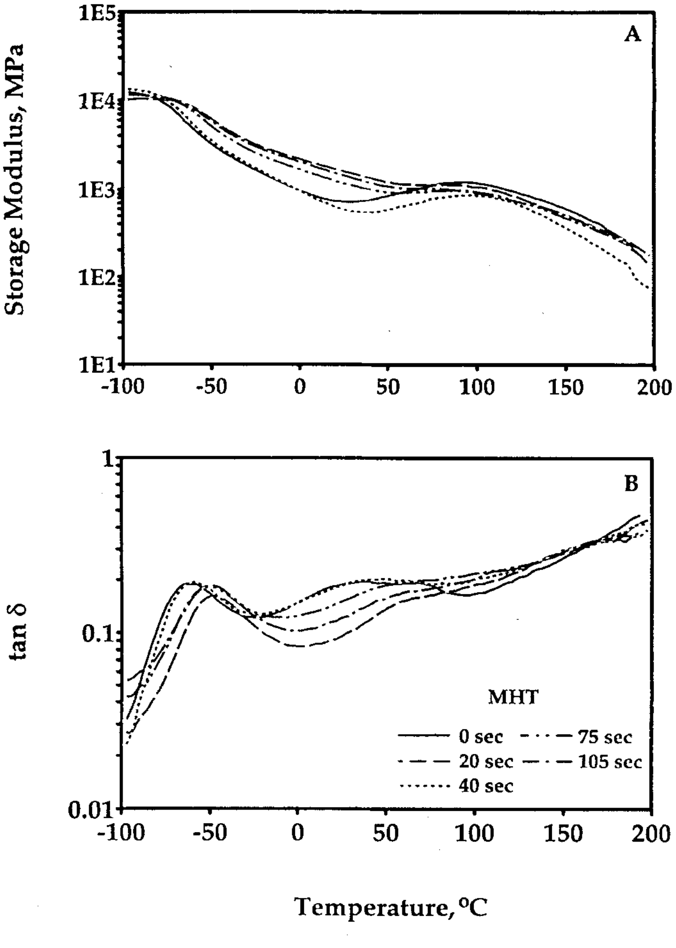

FIG. 2. Effect of microwave heating time and temperature on (A) storage modulus and (B) tan δ of P/S/G films with the ratio 42:28:30.

was difficult to distinguish areas of pectin from areas of starch. Circular areas corresponding to outlines of fractured granules were rare, and the fine beaded microstructure of pectin films was absent. Figure 3(D) shows the fracture surface after an MHT of 105 seconds for starch. This time domain is representative of fracture surfaces containing starch which was heated from 75 to 105 seconds. Between 75 and 105 seconds MHT, fractured faces were composed of the typical beaded microstructure of pectin surrounding separate small circular areas of about 1 μm in diameter. These circular areas exhibit the smoothness of the large circular areas which we have previously identified as starch granules in Fig. 3(B). These granules, which were always present in fractured form, might represent a retrograded or recrystallized form of starch which was embedded in pectin.

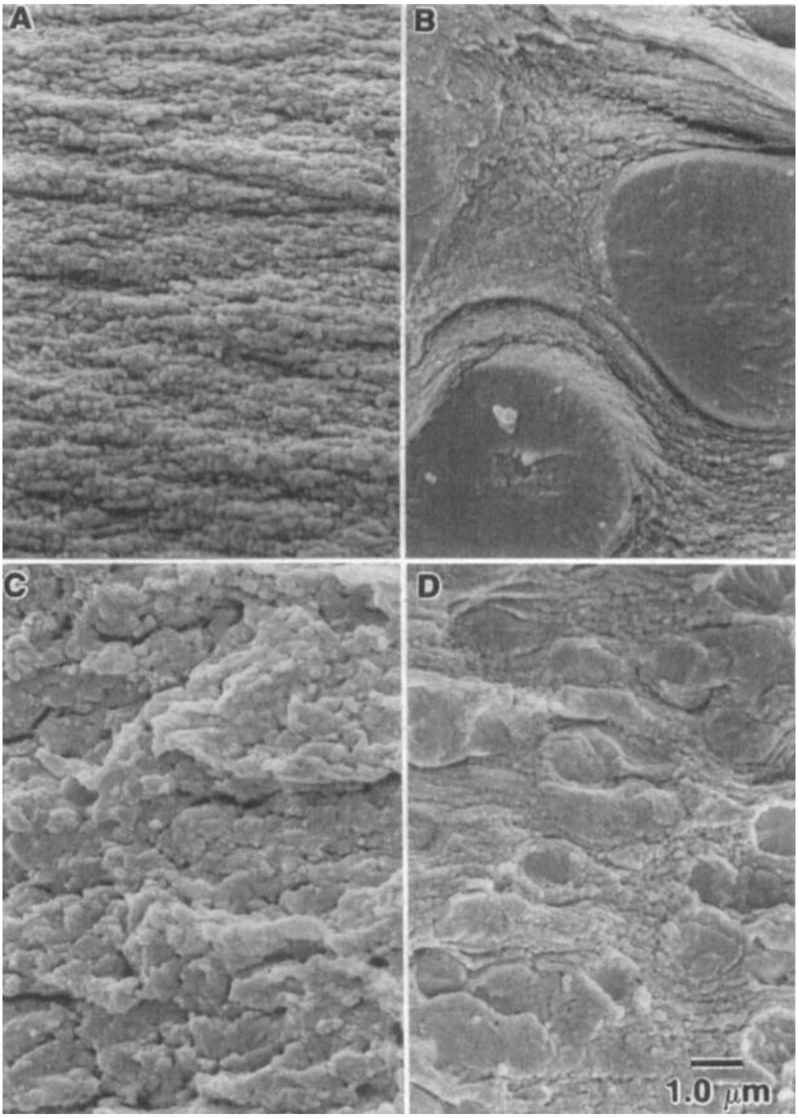

FIG. 3. Fracture surfaces of (A) pectin film; (B) P/S/G film (42:28:30); MHT, 10 seconds; (C) MHT 45 seconds; (D) MHT 105 seconds.

In an effort to verify certain aspects of the TDMA data, the tensile properties of P/S/G films were measured on an Instron testing machine. In these experiments the relative humidity was 40%. The data in Fig. 4 show the effect of added glycerol and P/S ratio on Young's modulus. These tests were performed at 23°C. All films were dried under vacuum for ½ hour prior to Instron testing. At virtually all P/S ratios, moduli decreased with increasing glycerol content. A similar trend was ob-

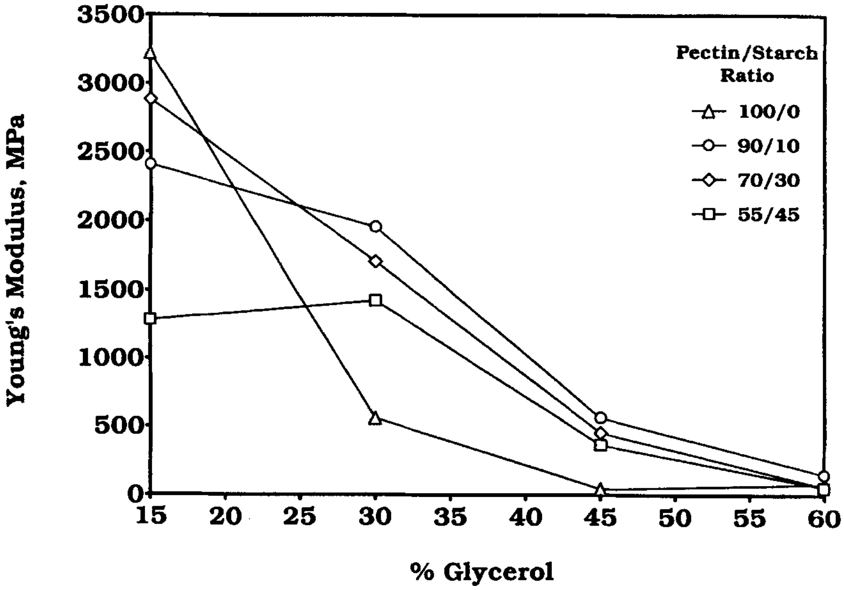

FIG. 4. Effect of glycerol and pectin/starch ratio on Young's modulus.

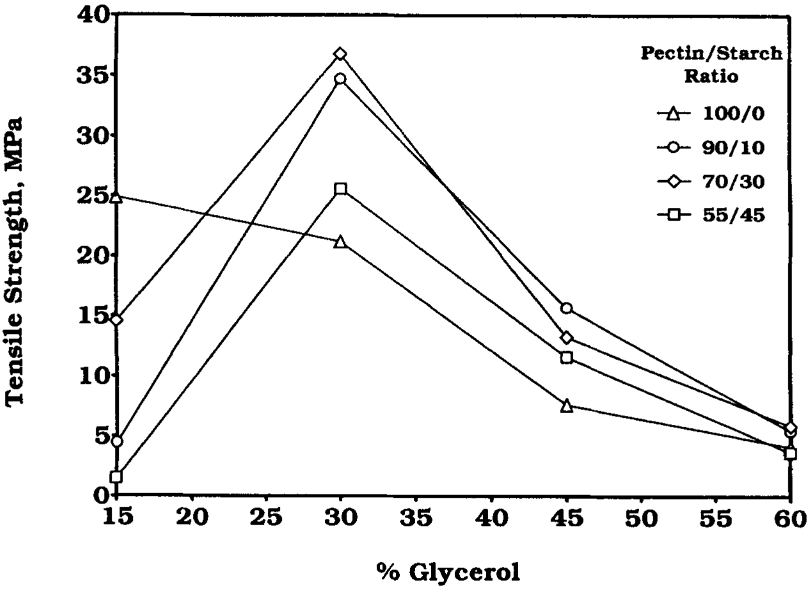

FIG. 5. Effect of glycerol and pectin/starch ratio on tensile strength.

served for the storage modulus of pectin when glycerol was added. (see Fig. 1). The effect of P/S ratio on Young's modulus decreased with increasing glycerol content (see Fig. 4). At constant P/S ratio, tensile strength as a function of added glycerol passes through a maximum at 30% glycerol (Fig. 5). At constant glycerol content, tensile strength decreases with decreasing P/S ratio, but as in the case of Young's modulus, the effect of P/S ratio decreases with increasing glycerol content. Elongation to break (Fig. 6) increases slowly with the addition of glycerol up to about 30% glycerol. Above 30% glycerol, a more rapid increase of elongation to break occurs with the addition of glycerol. Below 30% added glycerol, P/S ratio has little or no effect on elongation to break. Above 30% added glycerol, decreasing P/S ratio appears to increase elongation to break. Comparison of the data in Fig. 4 with that in Fig. 6 revealed that a reciprocal relationship exists between elongation to break and Young's modulus when measuring the effect of added glycerol.

Figure 7 contains data on the effects of relative humidity and added glycerol on Young's modulus for starches microwave heated for 10, 60, and 90 seconds. At a 60:40 P/S ratio, increasing the relative humidity from 0 to 57% or the glycerol content from 30 to 45% appears to have a much greater lowering effect on Young's modulus than an approximate tenfold decrease in starch particle size. In agreement with the data shown in Fig. 2, the data of Fig. 7 show that MHT or particle size has a small effect on Young's modulus. The data in Fig. 8 demonstrate that increasing relative humidity and glycerol content also decreases tensile strength whereas once again starch particle size has a small effect on tensile strength. The data in Fig. 9 reveal that increasing relative humidity and glycerol content also increases the elon-

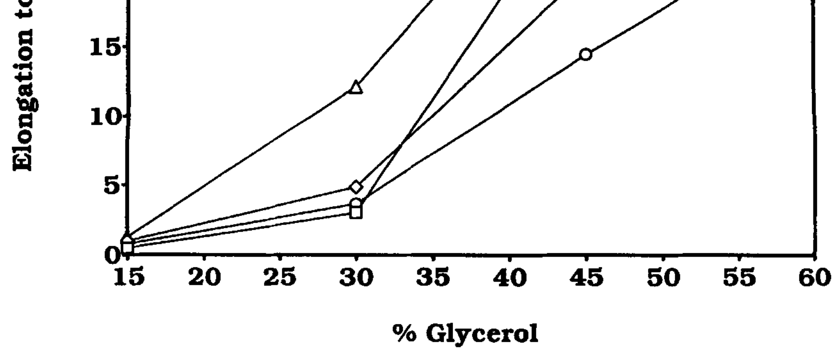

FIG. 6. Effect of glycerol and pectin/starch ratio on elongation to break.

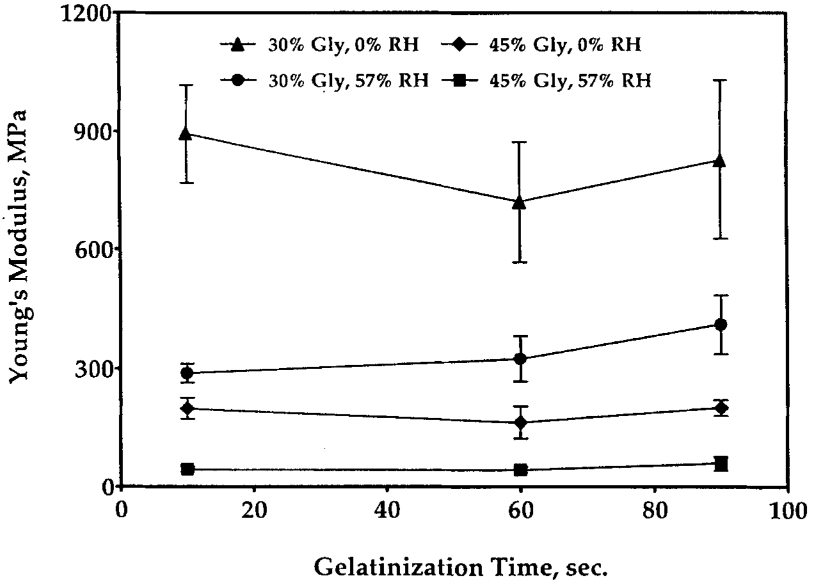

FIG. 7. Effect of MHT, relative humidity (RH), and percentage glycerol on Young's modulus of a P/S/G film (42:28:30).

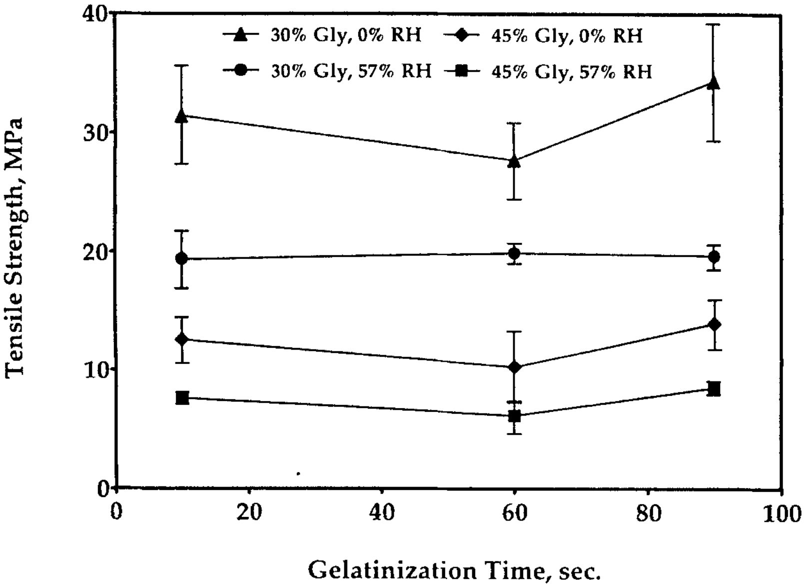

FIG. 8. Effect of MHT, relative humidity (RH), and percentage glycerol on tensile strength of a P/S/G film (42:28:30).

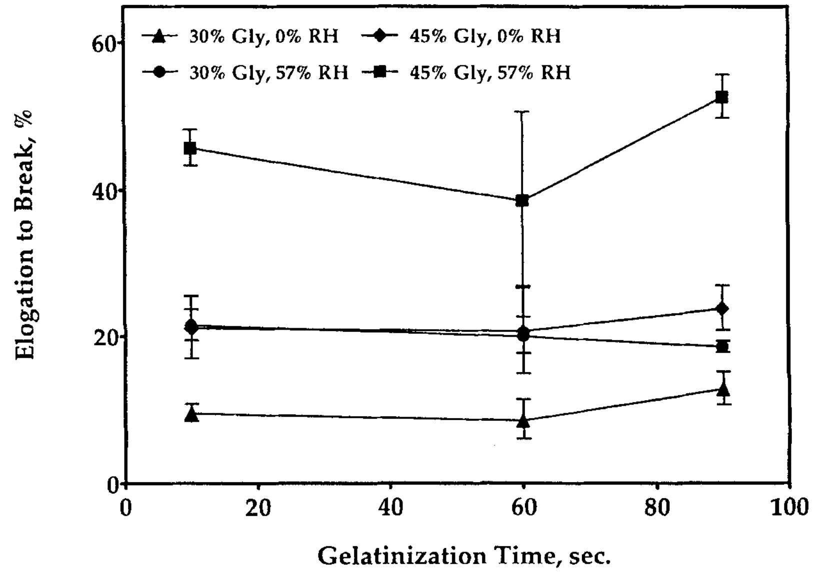

FIG. 9. Effect of MHT, relative humidity (RH), and percentage glycerol on elongation to break of a P/S/G film (42:28:30).

gation to break whereas once again an approximate tenfold decrease in particle size has a somewhat smaller effect on elongation to break.

FT-IR spectra of P/S/G films were taken to provide information concerning the microstructure around ester and carboxylic acid side chains in the backbone of pectin. Pectin, unlike starch or glycerol, exhibits infrared absorption bands in the regions near 1610 and 1740 cm^{-1}. For pectin dissolved in D_2O, absorption bands occur at about 1730, 1740, and 1607 cm^{-1}. These arise from the carboxylic acid C=O stretching band, the methyl ester C=O stretching band, and the antisymmetric COO^- stretching band, respectively. The carboxylic acid band overlaps the ester band sufficiently that these appear as one broad band [7]. In Fig. 10 are shown FT-IR spectra in the spectral region 1500–1800 cm^{-1} of P/S/G films with components in the ratio 55:45:0 and 22:18:60. Two broad bands were observed, one with a peak in the 1609–1616 cm^{-1} range and one in the 1746–1750 cm^{-1} range. Because the broad peak in the 1609–1616 cm^{-1} range is attributable to carboxylate ions, the films were analyzed for various metal ions by x-ray microanalysis. No metal ions were found, indicating their absence above the 1000 ppm level. Possibly, a significant portion of the carboxyl protons are hydrated, thereby forming ion pairs with carboxylate ions.

In Fig. 11 we have plotted the carboxylate wavenumber against temperature for P/S/G films that contained starch with MHTs of 10, 60, and 90 seconds. The P/S/G ratio in these films is 42:28:30. In all cases the wavenumber increased with temperature. In the case of metal salts of glucuronic acid, a configurational isomer of galacturonic acid, it has been demonstrated that the carboxylate ion forms stronger hydrogen bonds than the neutral acid [8]. Since it is well established that increasing temperature breaks hydrogen bonds, the breaking of carboxylate hydro-

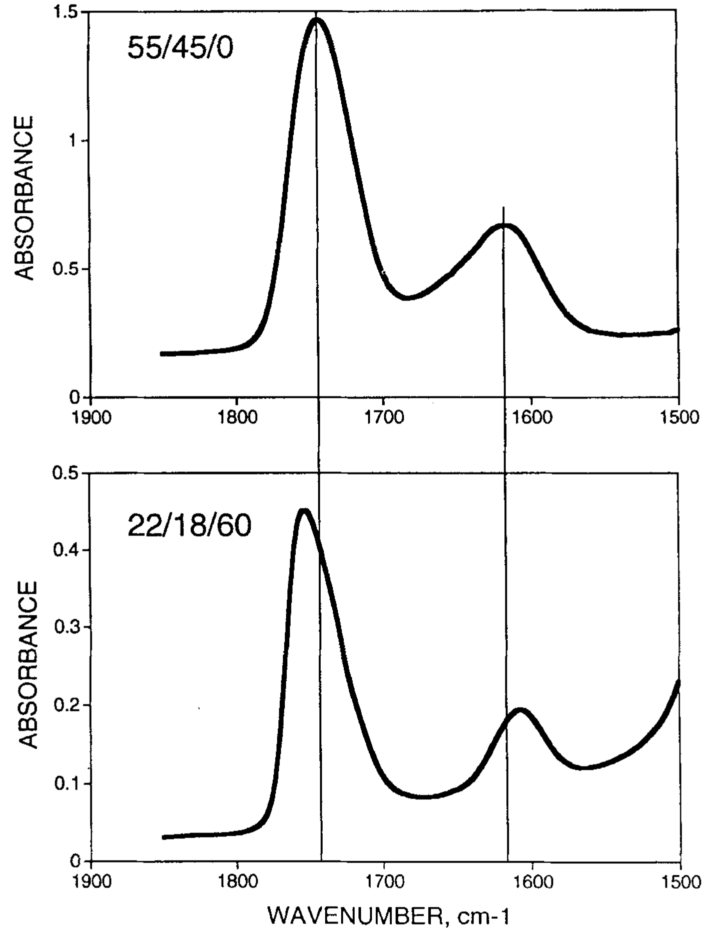

FIG. 10. Typical FT-IR spectra for P/S/G films with two different compositions. Spectra taken in the region 1500–1850 cm^{-1}.

gen bonds must be related to an increase in wavenumber. The data in Fig. 11 also reveal that increasing MHT from 10 to 60 seconds produces a small drop in carboxylate wavenumber and a further increase to 90 seconds produces no additional change in the wavenumber. The difference due to MHT decreases with increasing temperature. This drop in wavenumber may be due to a small increase in hydrogen bonding between pectin and starch. In Fig. 12 we have plotted the ester wavenumber against temperature for P/S/G films that contained starch with MHTs of 10, 60 and 90 seconds. This data appears to indicate little or no effect on the ester bond with MHT or temperature.

In Fig. 13 we show that increasing glycerol content decreases the carboxylate carbonyl wavenumber at several pectin/starch ratios. Possibly, increasing the amount of glycerol increases the number of pectin–glycerol hydrogen bonds, some

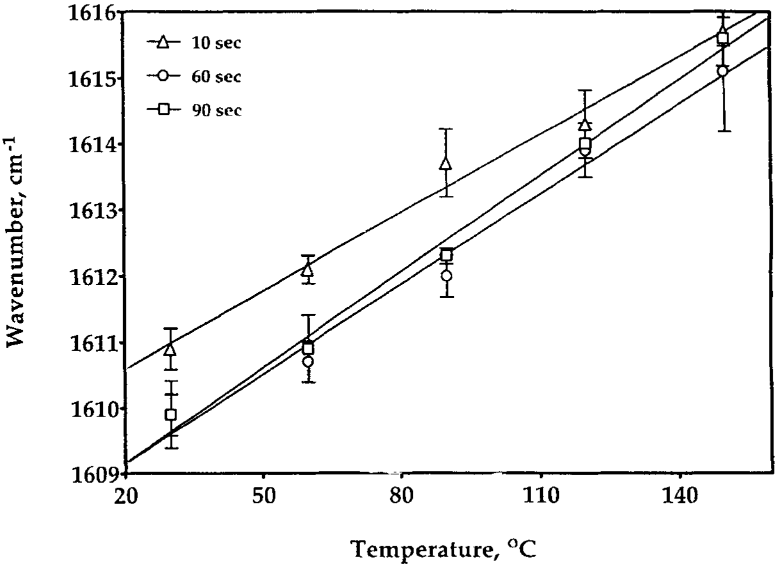

FIG. 11. Effect of temperature and MHT on wavenumber of carboxylate in P/S/G films (42:28:30).

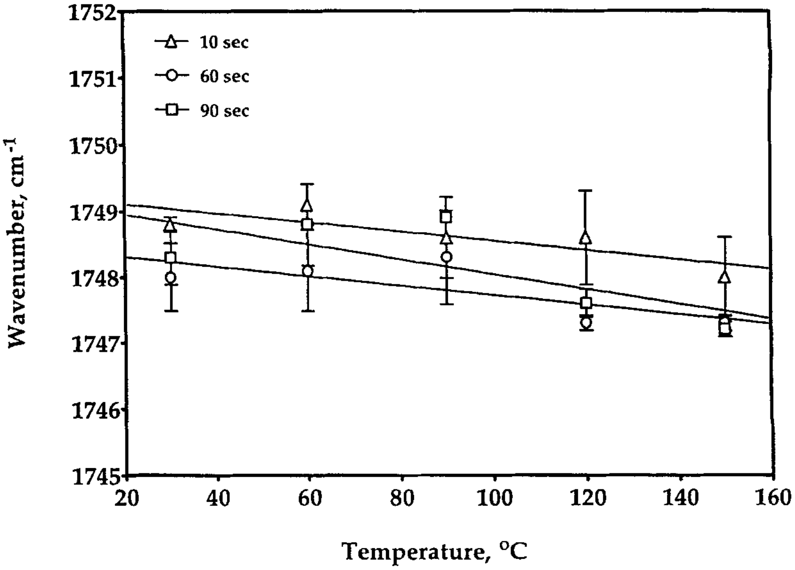

FIG. 12. Effect of temperature and MHT on wavenumber of methylester in P/S/G films (42:28:30).

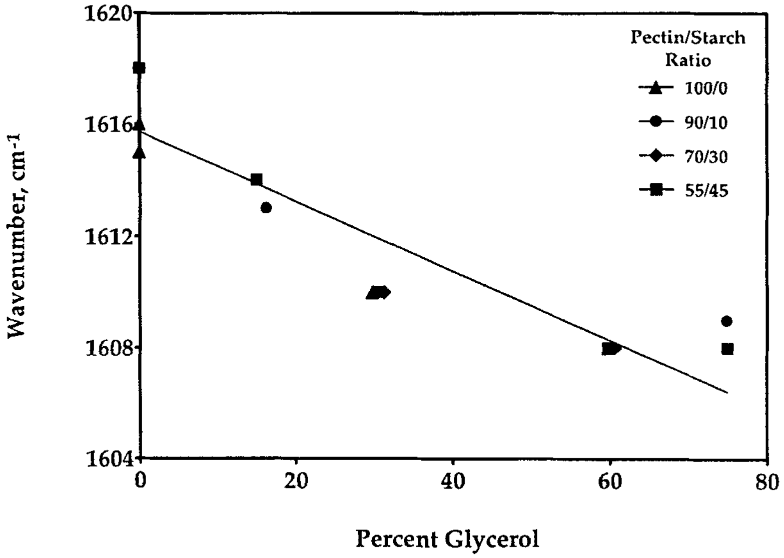

FIG. 13. Effect of glycerol and pectin/starch ratio on wavenumber of carboxylate in P/S/G films.

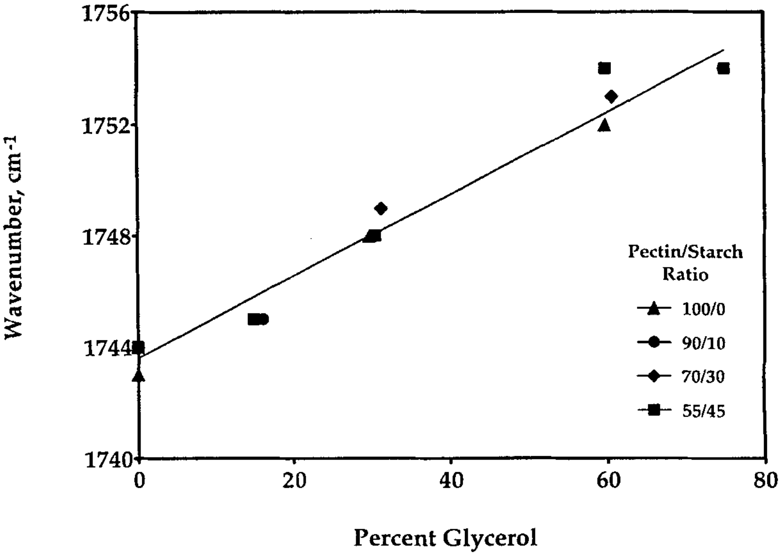

FIG. 14. Effect of glycerol and pectin/starch ratio on wavenumber of methylester in P/S/G films.

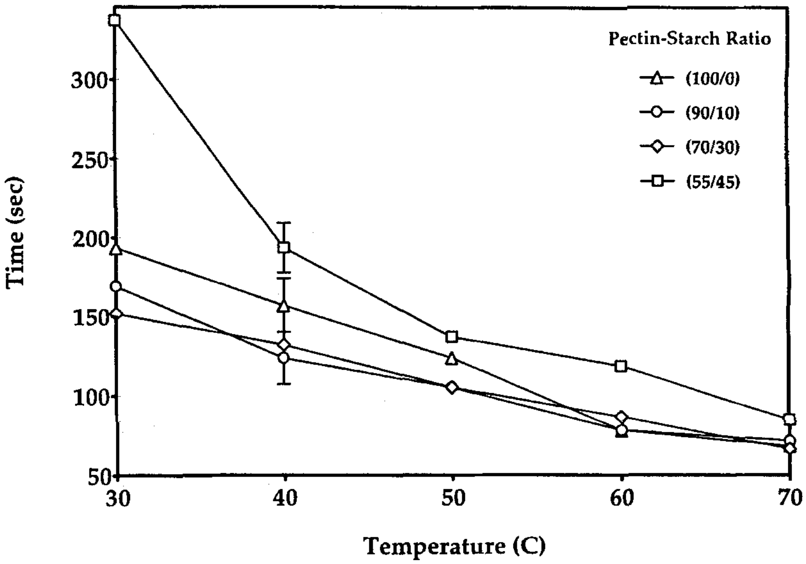

FIG. 15. Effect of temperature and pectin/starch ratio on dissolution time of P/S/G films.

of these at the expense of pectin-pectin hydrogen bonds. This interpretation is consistent with disassociation of pectin by glycerol that was observed previously [4, 5]. In Fig. 14 we show that increasing glycerol content increases the ester carbonyl wavenumber at several pectin/starch ratios. A rise in the wavenumber of the ester carbonyl with glycerol content also indicates an increase in hydrogen bonding [9]. The P/S ratio appears to have little or no effect on either the ester or carboxylate carbonyl wavenumber in this last experiment.

In Fig. 15 the times required for the dissolution in water of several P/S/G films containing 70% polymer and 30% glycerol were measured as a function of temperature. In these films the P/S ratios were 100:0, 90:10, 70:30, and 55:45. The MHT for the starch was 60 seconds. Generally, dissolution times decreased with increasing temperatures. At 70°C, all films dissolved in less than 100 seconds. At temperatures of 50°C or less, films with P:S ratios of 90:10 or 70:30 dissolved more rapidly than the pectin-glycerol controls whereas the film with a P/S ratio of 55:45 dissolved more slowly. All starch-containing films induced a cloudiness in the solution upon dissolution of the film. Cloudiness tended to decrease as the temperature increased. These results tend to indicate that the starch retrograded in the films and is consistent with the concept that islands of starch are embedded in a continuous matrix of pectin. Retrograded clumps of starch should become more soluble as the temperature increases. Furthermore, with decreasing P/S ratio, one might expect that films would dissolve more slowly due to the greater insolubility of starch as compared to pectin. The lower solubility would be most noticeable at lower temperatures.

CONCLUSIONS

Adding glycerol to pectin films induces up to three thermal transitions. The lowest transition is probably a T_g which is enabled by the ability of glycerol to dissociate crosslinked hydrogen-bonded pectin networks into its component chain-like structures [4, 5]. Shifts in the wavenumber of the carboxylic acid carbonyls with the addition of glycerol may indicate that glycerol is breaking intermolecular hydrogen bonds between pectin chains through preferential solvation. Interactions between pectin and glycerol would also account for the ability of large amounts of glycerol to be incorporated into PS films and the small effect of glycerol on elongation to break when the glycerol content is below 30%. Microscopy indicates that inclusion bodies of starch can be incorporated into a layered matrix of pectin. Freeze-fractured surfaces of the films indicate that the areas of starch are not dislodged from the surface upon fracture except possibly for a few particles when the starch is reduced to particle sizes of about 1 μm after being subjected to long gelatinization times. These results would indicate that there is strong adhesion between starch inclusion bodies and the pectin matrix which in turn would account for the compatibility of starch and pectin in films. The high compatibility of pectin and starch might explain why starch particle size had such a small effect on mechanical properties of films in the range of 1 to 10 μm. In fact, plasticization with glycerol or with glycerol and water combined had a greater effect on film mechanical properties than changing the particle size from 1 to 10 μm. Results from dissolution studies were consistent with the concept that under the conditions studied, P/S/G films were highly compatible starch in pectin composites. Moreover, these films have potential applications in those situations in which rapidly dissolving water-soluble films are desirable.

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