

Mechanical and Microstructural Properties of Pectin/Starch Films

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SYNOPSIS

Films were made from blends of high methoxy pectin and high amylose starch gelatinized in a microwave oven in the presence and absence of glycerol at times ranging from 10 to 105 s. Three thermodynamic transitions were observed when storage modulus, loss modulus, and loss tangent were plotted against temperature. All three transitions gave minima when the transition temperature was plotted against time of gelatinization. Overall, there were only modest changes in these moduli over the range of gelatinization times studied, with little difference between films made with the starch gelatinized in either the presence or absence of glycerol. Starch granules were found to disappear at gelatinization times between 20 and 30 s, although much smaller starch particles seemed to recur at gelatinization times of 75 s and above. The minima found in the transition temperature and modulus plots were believed to result from a minimum in the amount of intermolecular interactions between the starch molecules. © 1995 John Wiley & Sons, Inc.*

INTRODUCTION

There is currently a wide revival of interest in the use of biopolymers for applications in which synthetic polymers have traditionally been the materials of choice. Materials of interest include poly(lactic acid)¹ and poly(hydroxyalkanoates),^{2,3} as well as plant-based materials such as starch⁴⁻⁶ and pectin.^{7,8} Such materials may be biodegradable and recyclable, and, therefore, may help satisfy increasing consumer and regulatory demands for materials with these properties.

The mechanical properties of polymeric films are strongly influenced by their material composition, their processing history, and the effect that processing has on the microstructure of the sample. For melt processed films, this history includes melting and extrusion temperature, as well as cooling rate. In the case of solution cast films, solubilizing conditions can play a significant role in determining

mechanical properties, particularly in the case of crystalline or semicrystalline polymers such as starch. Factors affecting mechanical properties include time and temperature of solubilization, and the solubility of the polymer in the solvent system used.

To take advantage of its polymeric properties, it has been suggested that starch must be gelatinized, i.e., melted and solubilized.⁹ Starch is gelatinized to disintegrate granules and overcome the strong crystalline intramolecular forces prior to mixing with a second polymer such as pectin. The resulting mixture is then cast into a film. Often, gelatinization is achieved by heating a dispersion of starch granules in water under pressure at elevated temperatures. The disruption of the starch granules and the resulting degree of solubilization are highly dependent on the time and temperature conditions to which the starch is exposed. Thus, we expected that gelatinization conditions would have a strong influence on the structure and mechanical properties of the cast films.

Because glycerol might be expected to solvate starch differently than water, and because we are using it as a plasticizer, we decided to investigate the effect of glycerol on the solubilization of the starch. This was done by adding it to the starch

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dispersion prior to gelatinization, or by adding it into the mix by dissolving pectin in aqueous glycerol.

In this work we intended to determine the effect of starch gelatinization time on the morphology present in plasticized pectin/starch films and the result of gelatinization time on the mechanical properties of the films. Also, we intended to determine if the presence of glycerol in the solvent during gelatinization had any effect on the microstructure or mechanical properties of the cast films.

MATERIALS AND METHODS

Materials

MexPec 1400, a citrus pectin with a degree of methyl esterification of 71% and an ash content of less than 1%, was provided by Grindsted Products, Inc. (Kansas City, KS) and was used as received. It is identified as DM71.

Amylomaize VII (ca. 70% amylose, 30% amylopectin) was provided by American Maize Products Co. (Chicago, IL). It was used as received.

Glycerol was ACS reagent grade purchased from Aldrich Chemical Co., and was used as received.

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

Film Preparation

Films were prepared by mixing gelatinized starch solutions into pectin solutions, casting the resulting mixture onto a glass plate using a "Microm" film applicator (Paul N. Gardner Co., Pompano Beach, FL) and allowing the films to air dry over night. After air drying, the samples were vacuum dried at room temperature. Films were removed from the coating plates with a razor blade.

Pectin was dissolved by slowly adding 1.05 g to 20.0 mL of HPLC grade water with stirring. The solutions were stirred for 1–2 h until all of the pectin appeared to be dissolved. Gelatinized starch solutions were prepared by mixing 0.70 g of starch with 10.0 mL of HPLC grade water in a Parr microwave bomb (Parr Instrument Co., Moline, IL) and heating in an Amana Model RSW348P Radarange microwave oven at full power. Gelatinization times of 10, 20, 30, 40, 45, 60, 75, 90, and 105 s were used. Hot starch solutions were mixed with the pectin as quickly as possible to minimize starch retrogradation by cooling. Two samples were made for each gelatinization time. In one procedure, glycerol was added

to the water used to dissolve the pectin, and in the other procedure, glycerol was added to the starch gelatinization dispersion prior to microwave heating. In both cases, 0.75 g of glycerol was used.

Mechanical Properties

Mechanical testing was done on a Rheometrics RSA II Solids Analyzer (Rheometrics, Inc, Piscataway, NJ) using a film-testing fixture. Liquid nitrogen was used for cooling. A nominal strain of 0.1% was used, with an applied frequency of 10 rad/s (1.59 Hz). Testing was done from -100 to 200°C at a heating rate of $10^{\circ}\text{C}/\text{min}$. The storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were determined for each sample over this temperature range.

Test samples were cut from the films with a razor blade. Nominal dimensions of the samples were $6.4 \times 38.1 \times 0.05$ 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. Data analysis was carried out using the Rheometrics RHIOS software.

Microscopy

Small rectangular segments (3×20 mm) of films, prepared using nine different microwave gelatinization times, were excised and dehydrated by immersion in 20 mL of ethanol for 2 h. Film segments were blotted dry, plunged into liquid nitrogen, and cooled for 5 min. Frozen film segments were fractured into fragments by bending against the surface of a brass block in liquid nitrogen. Fragments were removed from liquid nitrogen, thawed by immersion in ethanol, and critical point dried from liquid CO_2 . Dried fragments were trimmed and mounted on aluminum stubs using colloidal silver adhesive and coated with a thin layer of gold by DC sputtering. Images of oriented fracture faces were collected on photographic film using a JEOL 840A scanning electron microscope (JEOL USA, Peabody, MA) in the secondary electron image mode.

RESULTS

Dynamic Mechanical Analysis

Nineteen films were made using DM71 pectin, Amylomaize VII, and glycerol. The pectin/starch/glycerol weight ratio for all of the films was 42:28:30, as this composition offered a good compromise

between mechanical strength and flexibility.⁸ Starch gelatinization times ranged from 10 to 105 s. In nine films, the glycerol was added to the pectin solution, and the starch was gelatinized in water. In another nine samples, the starch was gelatinized in aqueous glycerol. In one sample, glycerol was mixed with pectin and then a slurry of ungelatinized starch was mixed in to give a control sample with zero gelatinization time.

The storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were determined for each of the 19 samples over the temperature range of -100 to 200°C . Three points on each curve were selected for comparison. The first was the peak occurring at low temperatures in the loss modulus and loss tangent curves and the equivalent point on the storage modulus curve where the modulus begins to drop rapidly with increasing temperature. The second was the subsequent minimum that occurs at a higher temperature in each curve, and the third was the maximum in the curve that follows the minimum. These points are indicated on the typical curve shown in Figure 1, and are referred to as T_1 , T_2 , and T_3 , respectively.

The temperature at each of these points was determined, as were the corresponding storage modulus, loss modulus, and loss tangent. These were then each plotted as a function of starch gelatinization time to determine what effect the gelatinization time had on the temperature of the transition and the physical properties measured at that point.

In the samples where glycerol was added with the pectin and the starch was gelatinized with water only, the temperatures at which T_1 , T_2 , and T_3 oc-

curred each went through a minimum at gelatinization times of 40 to 45 s. The values at the other gelatinization times were relatively constant, except for the sample with ungelatinized starch the values were comparable to those found at 40–45 s. For T_1 , the minimum was approximately 10°C lower than the temperature observed at the other gelatinization times for the two modulus values and for $\tan \delta$. For T_2 , the corresponding difference was about 25° for E' and $\tan \delta$, and 10° for E'' . For T_3 , the difference was 5 – 10° for the two moduli, and 20° for $\tan \delta$. These trends are shown in Figure 2.

The storage modulus and loss modulus for T_1 underwent a moderate (15–25%) decrease as the gelatinization time was increased from 10 to 105 s, whereas the loss tangent showed an increase. There appeared to be a maximum at 40–45 s when the loss tangent was plotted against gelatinization time. No distinct minimum or maximum was seen with either of the two moduli when plotted against gelatinization time. These data, as well as the equivalent data for T_2 and T_3 , are plotted in Figure 3.

At T_2 , the storage modulus showed a moderate decline with increasing gelatinization time, while the loss modulus did not show a definable trend. Both did show a minimum at gelatinization times of 40–45 s. The loss tangent curve showed a moderate increase with gelatinization time, and had a maximum at 40–45 s.

For T_3 , the storage modulus showed a moderate decrease with increasing gelatinization time with no relative minimum or maximum, while the loss modulus seemed to have a minimum at 30–40 s of gelatinization time. Again, the loss tangent showed a

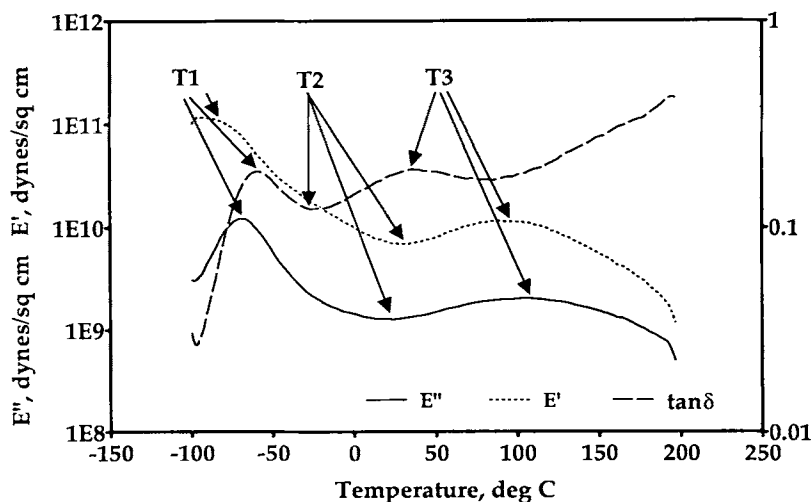


Figure 1 Typical plot of storage modulus, loss modulus, and loss tangent as a function of temperature.

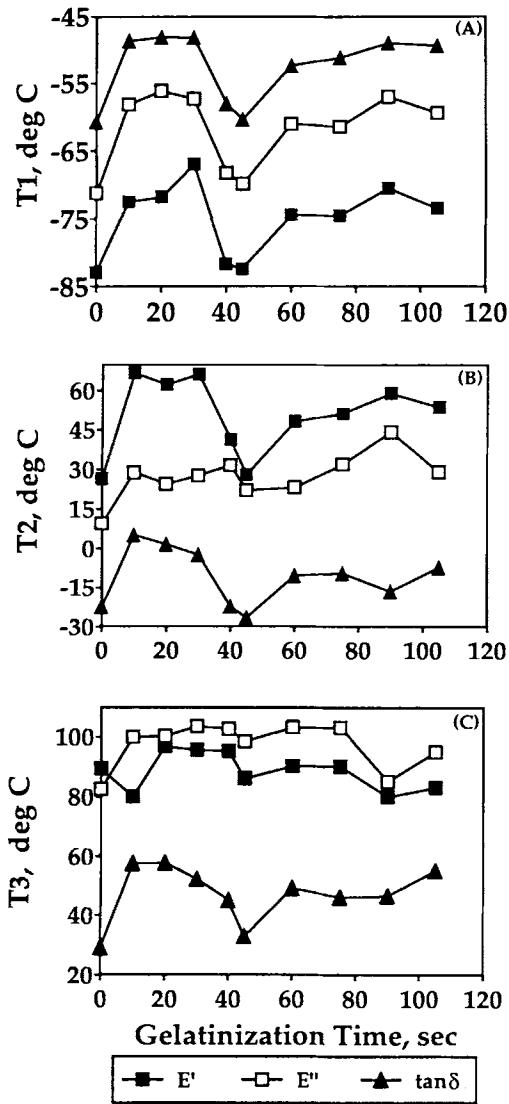


Figure 2 Effect of gelatinization time in water on temperature of thermal transitions in E', E'', and tan δ plots. (A) T₁, (B) T₂, (C) T₃.

small increase with gelatinization time, and had a maximum at gelatinization times of 40–45 s.

In all cases, there was a significant amount of scatter in these plots when plotted with a linear y-axis. When the data were plotted on a logarithmic scale as is usually the case for these variables, the degree of apparent variation was relatively small.

When the glycerol was added to the aqueous starch dispersion prior to gelatinization, somewhat different behavior was observed, both for the temperature dependence of the transitions and for the modulus and loss tangent values associated with them. Consistent differences were noted between the sets of values obtained with and without glycerol in the gelatinization.

For T₁, a slight upward trend with gelatinization time was seen for the transition temperature on the curves of both moduli and the loss tangent. No real evidence of a specific minimum or maximum was seen. Similar behavior was seen for T₂, although in this case no upward or downward trend was seen for the transition on the tan δ curve. The trends for T₃ were all slightly upward with increasing gelatinization time. These trends are shown in Figure 4.

Both E' and E'' at T₁ showed a slight decrease with increasing starch gelatinization time. In both cases there was a definite minimum at a gelatinization time of 40 s. The loss tangent showed a slight downward trend, with no evidence of a maximum

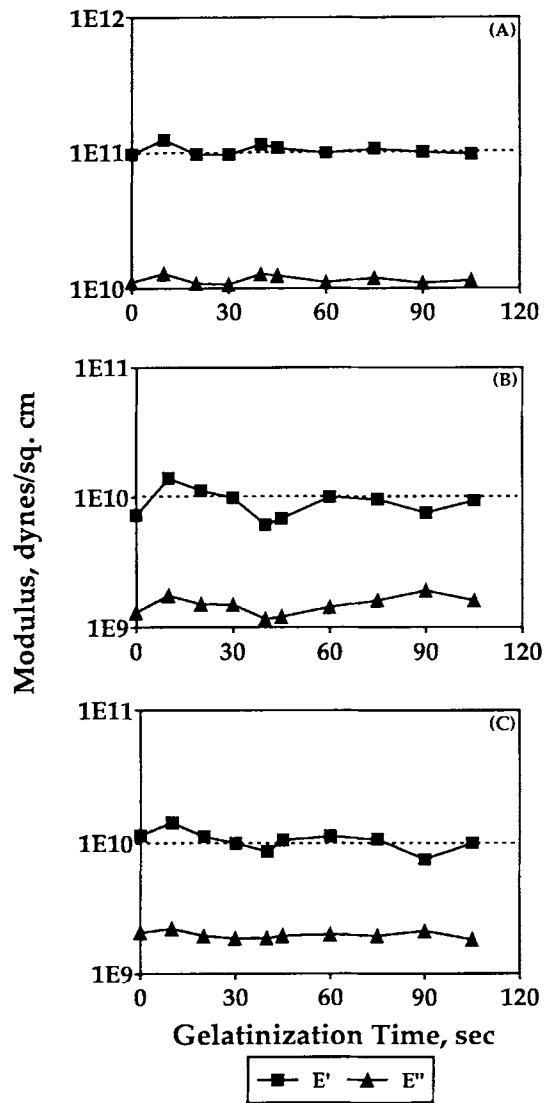


Figure 3 Effect of gelatinization time in water on storage modulus (E') and loss modulus (E''). (A) T₁, (B) T₂, (C) T₃.

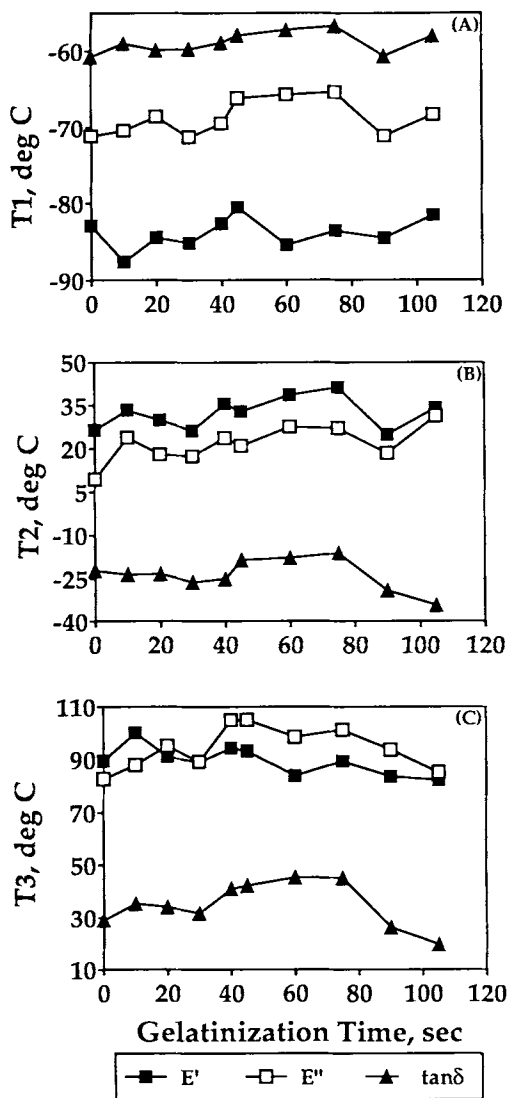


Figure 4 Effect of gelatinization time in glycerol/water on temperature of thermal transitions in E', E'', and tan δ plots. (A) T₁, (B) T₂, (C) T₃.

or minimum. For T₂, E' showed a moderate increase with increasing gelatinization time, although the value dropped sharply for 105 s. E'' showed no strong trend with gelatinization time, but did exhibit a minimum at 40 s. There was no trend for the loss tangent value. At T₃, no trend was seen for E', whereas a moderate downward trend with increasing gelatinization time was seen for E''. There also appeared to be a minimum for E'' at 40 s. A slight downward trend was seen with the loss tangent. The modulus trends are shown in Figure 5.

A comparison of the values for T₁, T₂, and T₃ between the samples where the starch was gelatinized in the presence of glycerol and those where it

was gelatinized in its absence showed that the temperatures at which the transitions occurred were typically 10°C lower for the films made from starch gelatinized in the presence of glycerol. At the same time, the values for the storage modulus and loss modulus at these transitions did not differ significantly between the two methods of gelatinization.

Scanning Electron Microscopy

Fractured faces of both types of films displayed three general types of structural organization that were linked to gelatinization times. The first type included films made from mixtures gelatinized for 0 to 20 s.

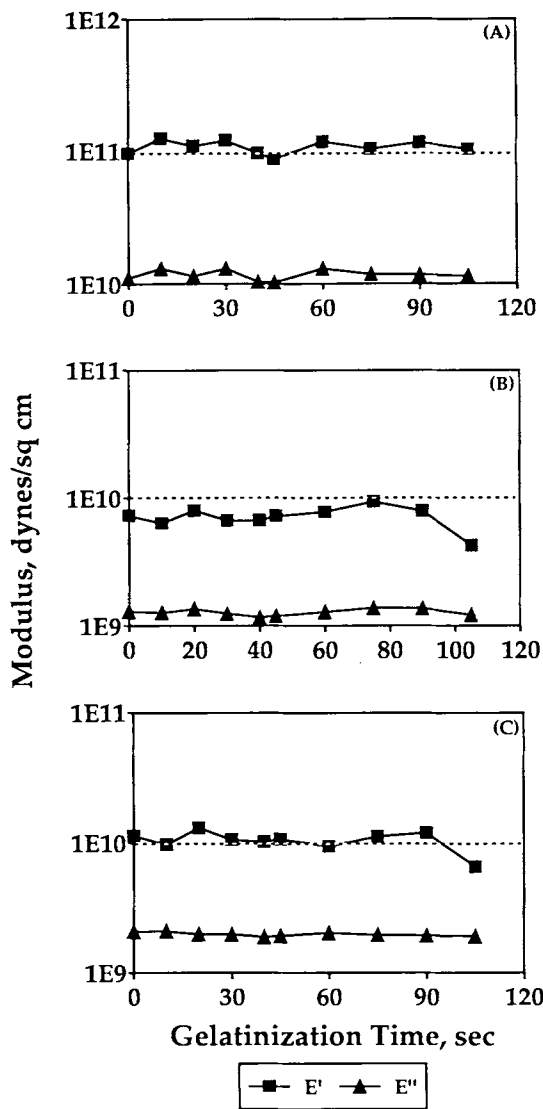


Figure 5 Effect of gelatinization time in glycerol/water on storage modulus (E') and loss modulus (E''). (A) T₁, (B) T₂, (C) T₃.

These contained fractured and nonfractured starch granules ranging from 5–10 μm in diameter, which were uniformly distributed and embedded within a smooth, continuous pectin matrix [Fig. 6(a) and (d)]. The second type included films made from mixtures gelatinized for 30 to 60 s. In these, starch granules or recognizable remnants were rarely found. Instead, the films were composed of a homogeneous granular matrix that often split unevenly along the planes of fracture [Fig. 6(b) and 6(e)]. The third type of organization, present in films made from mixtures gelatinized for 75 to 105 s, was characterized by a uniform and close-packed distribution of 1 μm diameter particles embedded in a homogeneous smooth matrix [Fig. 6(c) and (f)].

DISCUSSION

The disappearance of the starch granules with increasing gelatinization time was an expected occurrence as the increasing gelatinization times result in higher temperatures being obtained (10). The nature of the microwave gelatinization process is such that the sample sees a continually increasing temperature as the exposure to the microwave radiation continues. Thus, longer gelatinization times lead to both higher exposure temperatures, and longer exposure to the elevated temperatures. As a consequence, the gelatinization time at which the starch granules disappear is a result of both kinetic and thermodynamic factors. Thirty sec was the shortest gelatinization time in which there was any indication that the starch slurry had been heated above room temperature.

Both sets of samples showed almost exactly the same trend for the disappearance of the starch granules with time. Thus, it would appear that the presence of the glycerol had little or no effect on the solubilization of the granules at the micrometer level of magnification.

For the samples using starch gelatinized in pure water, the minimum observed in the transition temperature/gelatinization time plots for T_1 , T_2 , and T_3 occurred just beyond this point at gelatinization times of 40–45 s. This would seem to indicate that the starch granules were essentially completely disrupted after 30 s of gelatinization, but that slightly more time was necessary to more completely disrupt the intermolecular structure on a smaller scale and allow the starch molecules to mix more intimately in with the pectin. The samples made using starch gelatinized in the presence of glycerol did not show the distinct minimum in the transition temperatures

found with the other films, however. The decrease seen in the transition temperatures of the films made with the starch gelatinized in the presence of glycerol relative to those observed where the starch had been gelatinized in pure water may indicate an enhanced degree of mixing between the two biopolymers.

The presence or absence of glycerol had only a small effect on film moduli values or starch granule size. In general, the storage and loss modulus both declined moderately with increasing gelatinization time both with and without glycerol in the gelatinization bomb. However, these declines were on the order of 20% or less.

Apparently, changes in the starch microstructure had a relatively small effect on the overall modulus behavior of the films, except perhaps in compositions made using gelatinization times of 40–45 s. Possibly the starch is acting more as a filler than as a secondary polymeric component. The somewhat higher modulus values observed at the lower gelatinization times could be a result of the starch granules acting as particulate reinforcers of the pectin matrix. The volume fraction of the 1 μm particles seen at the higher gelatinization times may not be large enough to cause the same matrix reinforcement that occurred at larger granule size (i.e., at gelatinization times of less than 30 s).

Some degree of gelatinization seems to be necessary to obtain a visually acceptable film. Films made using the ungelatinized starch showed a layered surface pattern that suggested there was separation of the starch granules from the casting solution during the drying step. The layered pattern was not visible in micrographs of films with starch gelatinized for 10 s, the shortest gelatinization time employed.

CONCLUSIONS

The microstructure of films made from blends of high methoxy pectin and gelatinized high amylose starch was significantly affected by the heating time used to gelatinize the starch. Starch granules disappeared at heating times between 20 and 30 s, and much smaller starch particles seemed to reappear at gelatinization times of 75 s or more. These changes in structure resulted in only modest changes in the mechanical properties of the films as measured by storage modulus and loss modulus.

The temperatures of three selected transitions on the modulus curves were relatively unaffected by gelatinization time, except at times of 40–45 s in the absence of glycerol in the gelatinization solutions

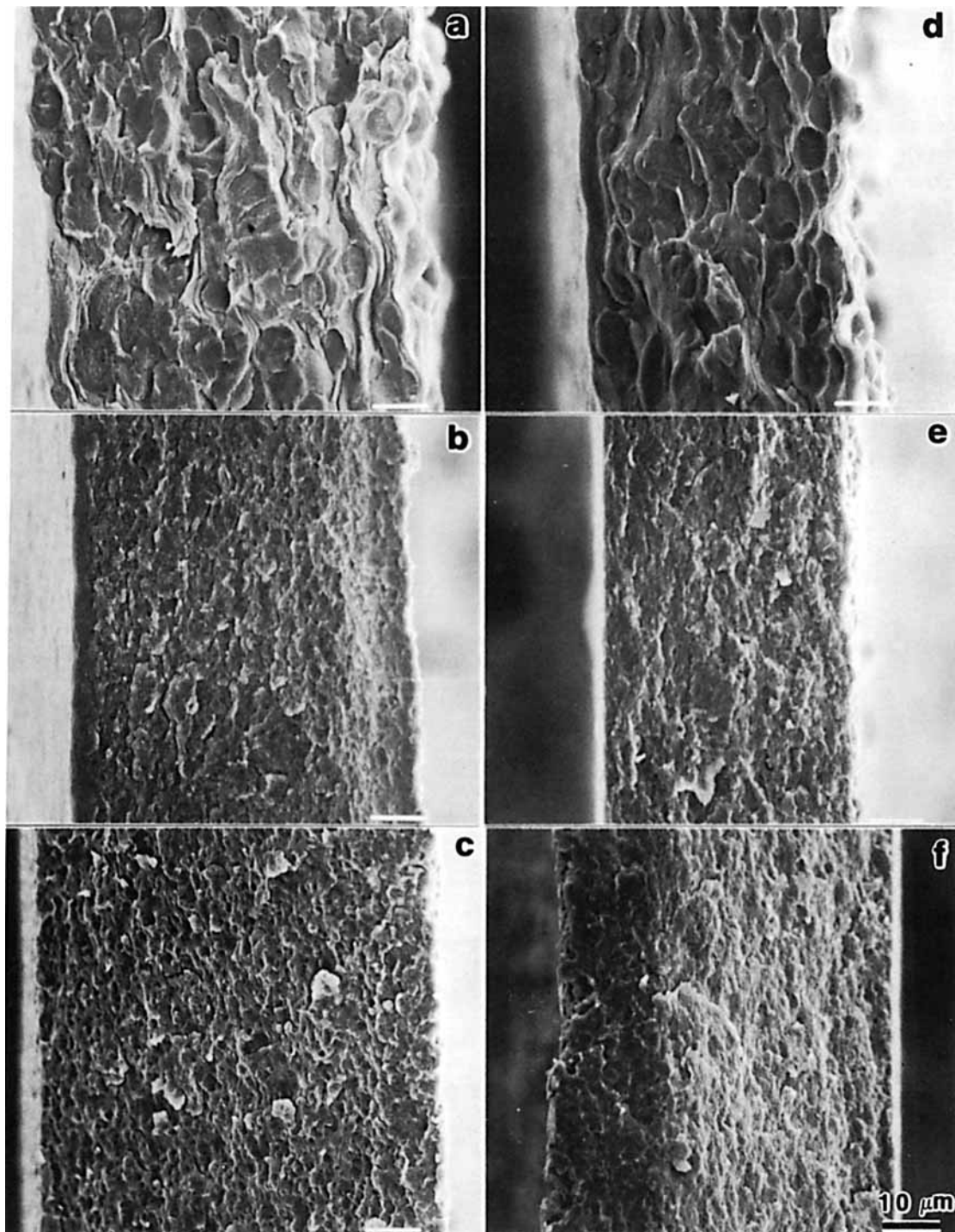


Figure 6 Electron micrographs of film cross-sections. Starch gelatinized in water; (A) 20 s gelatinization time, (B) 45 s gelatinization time, (C) 90 s gelatinization time. Starch gelatinized in glycerol/water; (D) 20 s gelatinization time, (E) 45 s gelatinization time, (F) 90 s gelatinization time.

where the transitions were lowered by 10–25°C. This minimum also tended to show up for the two moduli as well under both types of gelatinization conditions, although it was not usually as pronounced. The transitions were all lowered by about 10°C when the gelatinization solutions contained the glycerol to be used for the plasticizer, possibly indicating an enhanced degree of mixing of the starch and pectin.

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Received October 24, 1994

Accepted December 18, 1994