

Viscoelastic Properties of Pectin/Starch Blends

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Blends of lime and citrus pectin and starch were investigated to characterize their ability to form strong self-supporting films. Films were made both without plasticizer and with glycerine, urea, and poly(ethylene glycol) as plasticizers. The films were cast from water onto polycarbonate plates, allowed to dry, and removed. Mechanical analysis was done using a Rheometrics RSA II solids analyzer. These blends were found to form strong high-modulus films. The use of glycerine as a plasticizer resulted in the best films. Variations in composition allowed excellent control of the film properties.

INTRODUCTION

Pectins are a class of complex water-soluble polysaccharides found in the cell walls of higher plants (Steven, 1983). The backbone consists predominantly of blocks of poly(galacturonic acid) residues interrupted by short rhamnose inserts. The galacturonate residues are methyl esterified to various extents depending on the plant source. Neutral sugars are present in side chains attached to the backbone. These materials have found extensive use in processed foods as a result of their gelling properties.

The results of a considerable amount of work in this laboratory to determine the solution properties and shape of various pectins using high-performance size exclusion chromatography (HPSEC), viscometry, electron microscopy, and infrared spectroscopy (Fishman et al., 1984a,b, 1986, 1989a,b, 1992; Purcell et al., 1987) have shown pectin to be a collection of aggregated rigid rods or segmented rods which themselves may aggregate into a gel network. In solution pectin may contain on average up to four chains per rod or segmented rod.

Films made from natural products are of increasing scientific and commercial interest. These types of materials are not only inherently biodegradable but also potentially recyclable and may even be used in some *in vivo* pharmaceutical applications. The variety of uses, the possibility of multiple methods of reuse and disposal, and the replacement of fossil-based raw materials with renewable ones suggest that these materials are excellent candidates for commercial development.

Pectin is one of several water-soluble film forming polysaccharides. These include alginates, carrageenans, and cellulose ethers. There has been considerable work on films of the first two materials in recent years (Kester et al., 1986), although this has been mostly as coating films. (Carboxymethyl)cellulose and other of the cellulose ethers have been used as paper coatings, as food coatings, and as components of bilayer films (Glicksman, 1984). Several studies of chitin and chitosan films, including self-supporting films, have also been carried out (Averback, 1979; Hosokawa et al., 1990; Wong et al., 1990).

A number of studies have been done on pectin films, dating mostly from the 1930s into the 1950s (Henglein et al., 1936, 1939; Maclay et al., 1947; Schultz et al., 1948, 1949; Miers et al., 1953; Swenson et al., 1953). Generally these studies involved derivatized pectins and the use of

polyvalent cations such as calcium. Much of the work was on coatings for foods. Schultz et al. (1948, 1949) prepared films from low methoxyl (<11%) pectin and found tensile strength for these films to decrease with increasing methoxyl level. The films all had similar tensile strengths on the order of 9×10^8 dyn/cm² with and without added calcium. The most recent work appears to be that of Hind et al. (1978), who studied blends of pectin and (carboxymethyl)cellulose for use as cigarette papers.

There are many agricultural sources of pectin that are currently underutilized. Thus, pectin is potentially a large-volume raw material since it is a major component of fruits and vegetables and therefore is plentiful in agricultural wastes. The extended conformation of the molecule and the presence of aggregation in solution are properties similar to those found in some synthetic high polymers (Arpin et al., 1976, 1977; Wong et al., 1978). These molecular properties suggest that pectin films will have desirable physical and mechanical properties.

Starch too is inherently biodegradable and has been investigated as a component in biodegradable films for applications such as agricultural mulch and pharmaceutical caplets (Otey et al., 1977, 1980, 1987; Silbiger et al., 1991). Amylose films modified with amylopectin were originally made and characterized over 40 years ago (Wolff et al., 1951; Rankin et al., 1958; Mark et al., 1966). Water saturated with 1-butanol was used to dissolve the starch. These films had physical properties comparable to those of commercial plastic films (tensile strength approximately 6×10^8 dyn/cm²), although they were water sensitive and embrittled easily. These values are very similar to those found for the pectin/starch films in this work. The more recent work by Otey and others uses the addition of thermoplastics at fairly high levels to obtain materials that are highly flexible and do not embrittle. It is expected that since amylose is linear and amylopectin is highly branched, the varieties of corn starch high in amylose would result in better films (Young et al., 1984).

In addition to its biodegradability, starch also significantly lowers the cost of films into which it is incorporated. Although amylo maize VII starch costs about 2.5 times as much as common food grade starch, it is 90–95% less expensive than food grade pectin.

MATERIALS AND METHODS

Materials. Two samples of lime pectin (Type 1500 and Type 1200) were provided by Grindsted Products, Inc. (Kansas City, KS). These are identified as DM74 and DM65. A sample of citrus pectin was provided by H. P. Bulmers, Ltd. (Hereford, England). This is identified as DM59. The intrinsic viscosities

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Table I. Sample Compositions

	% pectin		% starch		% pectin		% starch	
pectin	pectin	starch	pectin	starch	pectin	starch	pectin	starch
DM59	89.9	10.1	DM65	94.9	5.1	DM74	90.1	9.9
	77.5	22.5		77.4	22.6		77.5	22.5
	65.0	35.0		59.9	40.1		65.2	34.8

of the samples in 0.05 M NaCl were previously found to be 5.27, 3.82, and 1.70 dL/g, respectively, and the degrees of methyl esterification were 74%, 65%, and 59% (Fishman et al., 1989a). The materials were used as received.

Amylo maize VII (ca. 70% amylose, 30% amylopectin) and waxy maize (ca. 100% amylopectin) were provided by American Maize Co. (Hammond, IN). They were used as received.

All other reagents and chemicals used were of ACS reagent grade. Water was of HPLC grade prepared with a Modulab Polisher I water system.

Intrinsic Viscosities. Intrinsic viscosities of the three pectins were determined at 35 °C in both HPLC grade water and 0.05 M NaCl using a Ubbelohde viscometer. The solvent flow time was 96 s. Linear extrapolations to zero concentration were made to obtain intrinsic viscosities in the 0.05 M NaCl solutions. To obtain the zero intercept in water, the reciprocal of the reduced specific viscosity was plotted vs the square root of concentration (Tanford, 1963).

Film Preparation. Films were prepared by mixing solutions of pectin (and glycerine or other plasticizer) with gelatinized starch solutions, casting them on a LEXAN plate using a Microm film applicator (Paul N. Gardner Co., Pompano Beach, FL), and allowing the films to air-dry overnight. After air-drying, the samples were vacuum-dried for 30 min at room temperature. Films were removed from the coating plates with a razor blade.

Pectin was dissolved by slowly adding 1.00 ± 0.01 g of pectin to 20 mL of HPLC grade water with stirring. When glycerine, urea, or poly(ethylene glycol) was added as a plasticizer, they were mixed with the water prior to pectin addition. The solutions were stirred for 1–2 h until all of the pectin appeared to be dissolved.

Gelatinized starch solutions were prepared by mixing the appropriate amount of starch (0.05–0.67 g) with 10 mL of HPLC grade water in a Parr microwave bomb (Parr Instrument Co., Moline, IL) and heating in a 700-W Amana Model R321T Radarange microwave oven for 3 min at 50% of full power.

The gelatinized starch solutions were cooled in a water bath at room temperature for 25 min and then added to the pectin solutions with stirring. The mixtures were allowed to stir for an additional hour prior to film casting.

Mechanical Testing. Mechanical testing was done on a Rheometrics RSA II solids analyzer (Piscataway, NJ) using a film-testing fixture. Air was used for sample chamber temperature control on runs starting from ambient temperature. Liquid nitrogen was used for runs starting below room temperature. A nominal strain 0.1% was used in all cases, with an applied frequency of 10 rad/s (1.59 Hz).

Test samples were cut from the films with a razor blade. Nominal dimensions of the samples were 6.4 mm \times 38.1 mm \times 0.04 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.

RESULTS

Initially nine experiments were run to determine the optimum type of pectin to use and the optimum pectin/starch ratio. All samples contained high-amylose starch (amylo maize VII). Pure pectin samples were run as controls. The compositions of the formulations are shown in Table I.

Pectin/starch films made with the two lime pectins (DM65 and DM74) were somewhat brittle but could be tested. The films made with citrus pectin (DM59), however, were too brittle and fragile to be tested. Attempts to prepare comparable films containing starch that was

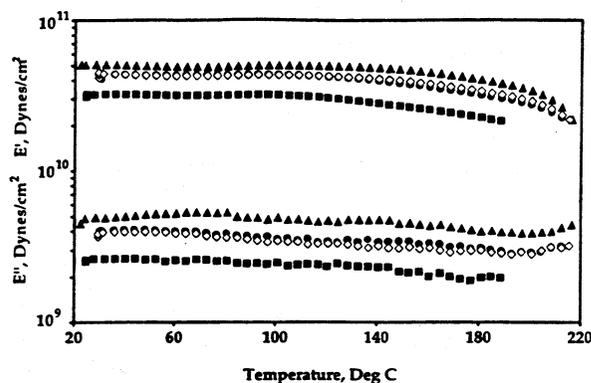


Figure 1. Effect of pectin/starch ratio on loss modulus and storage modulus for pectin DM74/amylo maize VII blends. \blacktriangle , 100/0; \circ , 90/10; \diamond , 77/23; \blacksquare , 65/35.

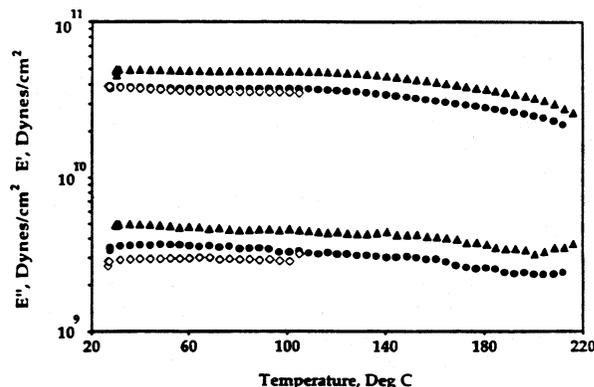


Figure 2. Effect of pectin/starch ratio on loss modulus and storage modulus for pectin DM65/amylo maize VII blends. \blacktriangle , 95/5; \circ , 77/23; \diamond , 60/40.

essentially all amylopectin (waxy maize) in place of amylo maize VII failed. These films were generally so brittle that it was not possible to adequately remove them from the casting substrate.

For samples made with lime pectin DM74 there was a gradual decrease in both the storage modulus (E') and loss modulus (E'') as the amount of starch present increased from 0% to 35% by weight. At 35% starch both moduli were one-third lower than for the sample containing no starch. These differences were consistent over the temperature range 25–210 °C (Figure 1). The film containing 35% starch was noticeably more brittle than films containing less starch.

The samples containing lime pectin DM65 also showed similar variations in E' and E'' at starch levels in the films up to 40%. Again, the differences were consistent over the entire temperature range (Figure 2), and increased brittleness was noticed at the highest starch level.

All samples tested had values of E' and E'' at room temperature that were approximately an order of magnitude higher than those for polyethylene. Unlike polyethylene, the pectin/starch films do not show a large decrease in modulus with increasing temperature.

While the high film moduli were encouraging because they open up many potential uses, the films were too brittle for use in many applications. Therefore, plasticizers were added to the system to obtain films which were more flexible and less susceptible to brittle failure. Four plasticizers were used—urea, glycerine, poly(ethylene glycol) 300, and poly(ethylene glycol) 1000. All of these plasticizers have been used in other polymer systems. The effect of these plasticizers at the 20 wt % level on the

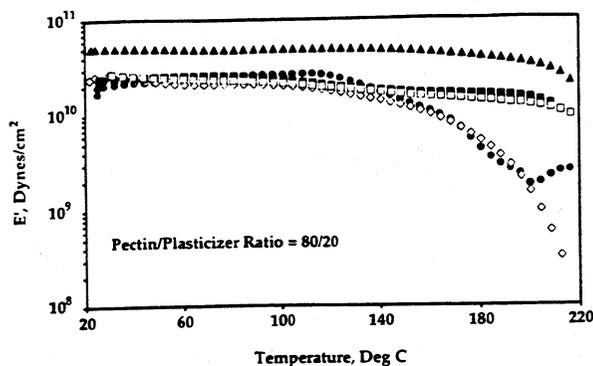


Figure 3. Effect of plasticizer type on storage modulus for pectin DM74. \blacktriangle , None; \diamond , glycerine; \square , PEG1000; \bullet , urea; \blacksquare , PEG300.

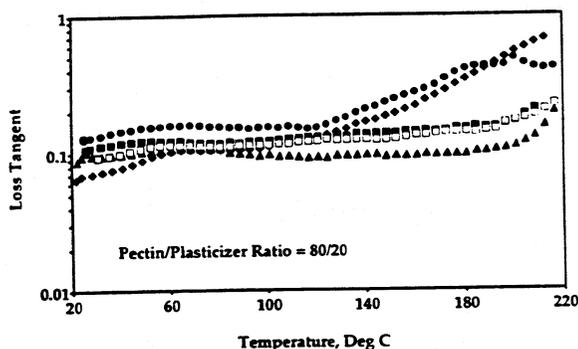


Figure 4. Effect of plasticizer type on loss tangent for pectin DM74. \blacktriangle , None; \diamond , glycerine; \square , PEG1000; \bullet , urea; \blacksquare , PEG300.

Table II. Sample Compositions

sample	pectin/starch ratio	% glycerine	sample	pectin/starch ratio	% glycerine
1	95/5	9.0	6	85/15	26.6
2	95/5	18.5	7	75/25	9.4
3	95/5	25.6	8	75/25	19.2
4	85/15	9.0	9	75/25	27.7
5	85/15	19.0			

storage modulus of DM74 pectin is shown in Figure 3, while the effect on $\tan \delta$ is shown in Figure 4.

All four of the plasticizers caused a decrease in both storage modulus and loss modulus over the entire temperature range compared to unplasticized pectin. At room temperature this decrease was about 50% in all cases. Up to 130 °C there was little difference among the four materials. However, above this temperature the E' plots of the two PEG-modified samples continued to parallel that of the pure pectin, whereas the values for both the urea- and glycerine-plasticized samples showed a very large drop relative to the pure pectin. This drop exceeded an order of magnitude. Even with the plasticizers, the modulus values of the pectins were still higher than for unplasticized polyethylenes.

The loss modulus (data not shown) behaved similarly except that E'' for the glycerine- and urea-plasticized samples diverged from the behavior of the poly(ethylene glycol)-modified samples at about 170 °C rather than at 130 °C. There was an unexplained hump in the curve for the urea-plasticized material which did not occur in the other samples.

To test the effects of plasticizer level on the mechanical properties of pectin/starch films, nine samples of DM74 type pectin were evaluated at three different starch levels. Each of these polyblends was plasticized with three levels of glycerine. While both glycerine and urea showed a much greater plasticizing effect than the polyglycols, glycerine

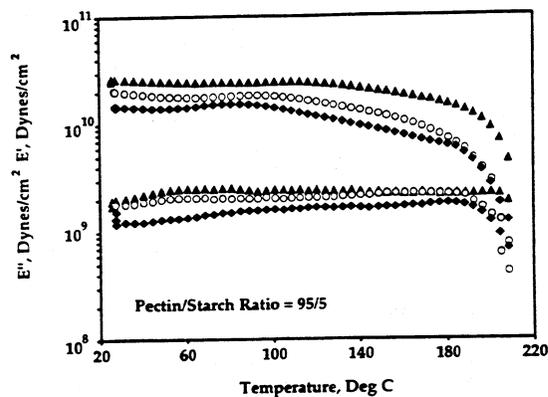


Figure 5. Effect of glycerine level on loss modulus and storage modulus for 95/5 blends of pectin DM74 and amylo maize VII. \blacktriangle , 9% glycerine; \circ , 19% glycerine; \blacklozenge , 26% glycerine.

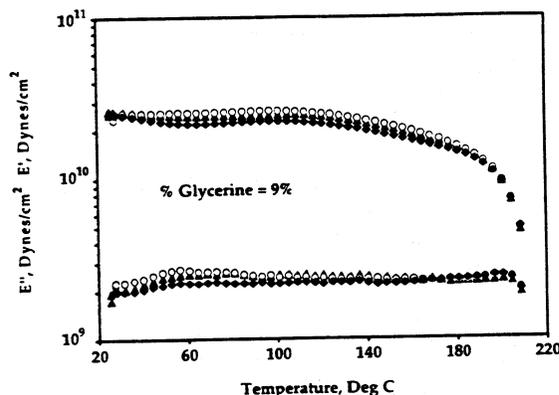


Figure 6. Effect of starch level on storage modulus and loss modulus of pectin DM74 blends at constant glycerine level (9%). \blacktriangle , 95/5; \circ , 85/15; \blacklozenge , 75/25.

was selected because it is acceptable as a food additive. The compositions used are shown in Table II. The results were compared to determine the effects of both starch and glycerine levels on the mechanical properties of the films.

No trend was seen in the effect of starch level on the breaking strength and elongation to break of the films. The films containing 9% glycerine had elongations to break of about 1% and breaking strengths of about 1.7×10^8 dyn/cm². Those with glycerine contents of 19% and 26% had breaking strengths of about 3.5×10^8 dyn/cm² and elongations of 2-3%.

Figure 5 shows typical behavior for the effect of glycerine level on storage modulus and loss modulus at constant pectin/starch ratio, whereas Figure 6 shows typical behavior for the effect of varying pectin/starch ratio at constant glycerine level.

All of the samples showed a typical decrease in modulus with increasing temperature, with the rate of decrease becoming more rapid at higher temperatures, particularly above 185 °C. Pure pectin, and the pectin/starch blends with no glycerine, did not show this decline until about 200 °C. In general, both the storage and loss modulus curves were shifted to lower values with increasing glycerine level at constant pectin/starch ratio. It was noted, however, that glycerine affected the loss modulus to a smaller extent at the higher starch levels and seemed to have no effect below 180 °C with the 75/25 pectin starch ratio.

Over the range of starch used, there was essentially no effect of the pectin/starch ratio seen on the film properties at constant glycerine level. This held true for both the

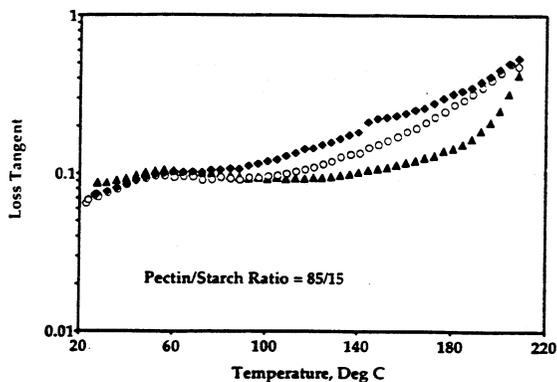


Figure 7. Effect of glycerine level on loss tangent of pectin DM74 blends at constant pectin/starch ration (85/15). \blacktriangle , 9% glycerine; \circ , 19% glycerine; \blacklozenge , 27% glycerine.

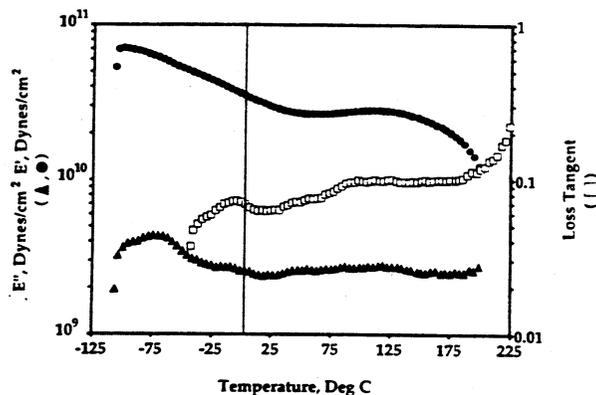


Figure 8. DM74/amylo maize VII-glycerine, 9.4% glycerine, 75/25 pectin/starch ratio.

storage modulus and the loss modulus. This seems surprising but may be due to the relatively limited range of starch concentrations used.

The loss tangent ($\tan \delta$) represents the relative contribution of the viscous and elastic components of the complex modulus in the material properties. The effect of increasing the glycerine level at constant pectin/starch ratio was to increase $\tan \delta$, particularly at temperatures above 100 °C. This represents an increasing relative contribution by the viscous component of the material. A typical example of this behavior is shown in Figure 7. Changing the pectin/starch ratio at constant glycerine content (not shown) had little or no effect.

From room temperature to 200 °C, no thermal transitions were apparent in any of the materials analyzed. With some samples a small broad hump was seen in the vicinity of 60 °C, possibly attributable to water. To determine if subambient melting or glass transitions might be present, samples plasticized with three glycerine levels and a pectin/starch ratio of 75/25 were tested from -100 to +200 °C. The results of these experiments are shown in Figures 8-10.

For all three samples a very distinct transition was observed at about 60 °C. The area under the peak increased linearly with increasing glycerine content, indicating that the transition involved the glycerine. The temperature at which the transition occurred increased by 6-8 °C when the glycerine content increased from 9% to 19%. No further change occurred in the sample plasticized with 27% glycerine.

The intrinsic viscosities of the three pectins were run and compared with the values obtained previously (Fishman et al., 1984b). The values found are shown in Table

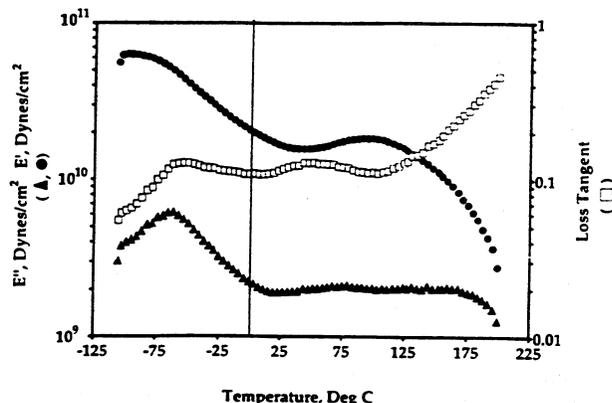


Figure 9. DM74/amylo maize VII-glycerine, 19.2% glycerine, 72/25 pectin/starch ratio.

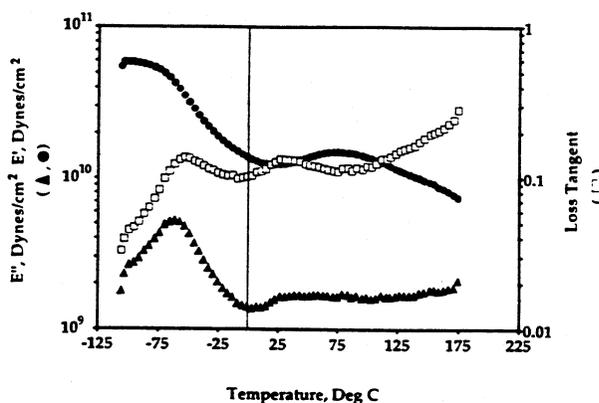


Figure 10. DM74/amylo maize VII-glycerine, 27.7% glycerine, 75/25 pectin/starch ratio.

Table III. Sample Intrinsic Viscosities

pectin	intrinsic viscosity, dL/g	
	0.05 M NaCl	H ₂ O
DM59	2.1	8.4
DM65	3.7	9.1
DM74	5.3	12.8

III and are essentially the same as those found before, indicating that the pectin samples had not degraded with time. The higher values found in water compared to 0.05 M NaCl indicate the presence of increased aggregation in water compared to an ionic solution (Fishman et al., 1989a).

It was noted that films containing only pectin were slightly tacky. This tackiness seemed to be reduced or eliminated in the samples that contained starch. Increasing the glycerine content increased the tack of the films; however, this was overcome at higher starch levels. It appears that the starch is a useful additive to control or eliminate tack in these films.

DISCUSSION

Plasticized films made from blends of high molecular weight lime pectin and high-amylose starch appear to have properties in the range to make them potentially useful in some film applications. The properties appear to be somewhat plasticizer specific and are very dependent on the level of plasticizer present. The particular pectin used seems to be the most important factor in obtaining the best properties.

The level of glycerine present in the films had a noticeable effect on the tenacity and elongation to break of the films. Both elongation and tenacity roughly doubled as the glycerine content was raised from 9% to 19%. No

further increase was seen at 27% glycerine. While a definite plasticizing effect is indicated by these results, the effect is relatively small as the highest elongation found was 3%. Significantly higher plasticizer levels may be necessary to obtain large increases in elongation to break.

The pectin and pectin/starch films all exhibited high initial modulus values in the range $3\text{--}5 \times 10^{10}$ dyn/cm² but had low elongations to break (1–3%) and were fairly brittle. This brittleness increased as the starch content of the films increased and appeared to be greatest in the samples containing pectin with the lower degrees of methylation (and thus also lower molecular weight). This can be explained, at least partially, in terms of the conformational properties of the molecule.

Unlike random coil polymers, pectin molecules are nearly fully extended both in solution and in the solid state. Therefore, extension of the material does not occur by uncoiling but rather by slippage of the chains past each other and possibly by covalent bond stretching. This leads to early fracture of the materials, particularly as there was very little orientation present in these samples as a result of the casting method used.

All of the samples containing amylo maize VII starch were hazy and were found to be biphasic by microscopic examination. The films containing waxy maize tended to be much more transparent but were still biphasic. Thus, the linear nature of this high-amylose starch contributed more to the strength and modulus of the blend than did the high-amylopectin material. The amylo maize VII seemed to act as a second polymeric component, whereas the waxy maize acted more as a non-load-bearing filler.

The DM59 pectin had the lowest intrinsic viscosity of the pectins used. The fact that the films prepared with it split as they dried may indicate that the molecular weight of the material is below the critical molecular weight of pectin necessary for adequate film properties.

The difference in effect on film properties between glycerine and urea on the one hand and the poly(ethylene glycol)s on the other seems to be due to different plasticizing mechanisms, attributable to differences in molecular properties. All of these materials exert a plasticizing effect by decreasing the pectin–pectin, pectin–starch, and possibly starch–starch interactions. However, the glycerine and urea also appear to act as good “solvents” for the polymers, thus behaving as more efficient plasticizers and causing a melting-type transition at lower temperatures.

The relatively small effect of amylo maize VII on the film properties indicates that this starch is not disruptive of the pectin structure and that it contributes to the load-bearing properties of the films. Since the backbone structure of the amylose is physically similar to that of the pectin, it seems reasonable that the modulus is only slightly affected.

Waxy maize is unable to contribute substantially to the film properties because of the high degree of chain branching in the amylopectin. This decreases its ability to act as a load-bearing structure and is typical of highly branched polymers.

The effect of increasing the glycerine level on the thermomechanical properties of the films was that expected from the behavior of most other polymer/plasticizer systems (Immergut et al., 1968). Thus, films could be made that span the range from very brittle to highly flexible. Qualitatively, it appeared that tack was controllable by varying the starch level. This is a highly useful and desirable function, as the tackiness, or lack thereof, can be important in many applications. The peak seen in

the E'' curves at -60°C is probably due to a glass transition or other phase behavior involving glycerine, as its size is directly proportional to the amount of glycerine present.

CONCLUSIONS

Plasticized pectin/starch blends can be made into strong, fairly flexible films with tensile strengths on the order of 3×10^8 dyn/cm², approximating those of commercial plastic films, and elongations of 1–3%. The room temperature storage and loss moduli of the films were $1.5\text{--}6 \times 10^{10}$ and $1.3\text{--}5 \times 10^9$ dyn/cm², respectively, depending on composition. This is equal to or higher than what is found in many commercial films.

Addition of glycerine as a plasticizer resulted in a very definite loss of brittleness of the films, making them much more flexible. Higher levels of plasticizer may be necessary for optimum performance. The effect of temperature on the moduli was relatively small in unplasticized samples and did not appear to be important in the plasticized ones until a temperature of 130–180 °C was reached.

The addition of starch had a moderately negative impact on the mechanical properties of the unplasticized films. In the plasticized films, however, it seemed to have less impact on these properties. Starch also greatly reduced the tackiness of the films, which may be useful for some applications. Because of its very low cost compared to pectin and its tack reduction properties, starch is an important component in these films.

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Received for review November 10, 1992. Revised manuscript received April 19, 1993. Accepted May 12, 1993. Mention of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.