

Physical and Mechanical Properties of Highly Plasticized Pectin/Starch Films

DAVID R. COFFIN* and MARSHALL L. FISHMAN

U. S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 E. Mermaid Lane, Philadelphia, Pennsylvania 19118

SYNOPSIS

Blends of citrus pectin and high amylose starch plasticized with glycerine were investigated to determine the effect of compositional variables on film properties. Several films with representative compositions were made from sugar beet and almond pectin, and tested for comparison. The films were cast from water onto glass plates, dried, and removed. Mechanical analysis was done using a Rheometrics RSA II solids analyzer. Increasing the glycerine concentration led to decreases in static modulus, dynamic modulus, and tensile strength, but to increases in elongation. Increasing levels of starch in the blend lowered the effect of glycerine on mechanical properties. Oxygen permeability of the films was extremely low. Sugar-beet pectin and almond pectin gave films with mechanical properties comparable to those made with citrus pectin. © 1994 John Wiley & Sons, Inc.†

INTRODUCTION

Biopolymers are increasingly being studied and used for applications in which synthetic polymers have traditionally been the materials of choice. The impetus for the heightened interest in this new technology is the need to increase the use of biodegradable and recyclable materials to limit the volume of material sent to landfills, and the desire to use renewable raw material sources instead of nonrenewable petroleum sources. One promising system of this type consists of plasticized blends of high methoxyl pectin and high amylose starch.

Pectin films were first made and characterized in the 1940s.¹⁻³ These were made with low methoxyl pectin, however, and required the use of calcium or other multivalent cations as crosslinking agents. These materials exhibited fair mechanical properties, but had poor folding endurance, and little subsequent work was done to advance their use.

Previous work in our laboratory has shown that plasticized films made from high methoxy lime pectin and high amylose starch have very good mechanical properties, and appear to be suitable for use in commercial applications where strong biodegradable films are advantageous.⁴ In that study, we showed that the best pectin for use in films has the highest molecular weight and degree of methyl esterification. The use of glycerine or other suitable plasticizer is necessary to make a sufficiently flexible and nonbrittle film. Addition of a large proportion of high amylose starch resulted in only modest decreases in the dynamic mechanical properties (storage modulus and loss modulus) of the films, had a beneficial effect on their surface properties, and reduced material costs.

The current work expands on our previous studies, and more fully characterizes the effect of composition on pectin/starch film properties. Citrus pectin of sufficiently high methoxyl content and molecular weight is shown to have mechanical properties essentially equivalent to those of the high methoxyl lime pectin films studied earlier. The lime pectin is no longer available commercially, and therefore we decided to use the most similar commercial citrus pectin. Furthermore, a wider range of film properties was obtained by the use of an in-

* To whom correspondence should be addressed.

Reference to a brand or firm name does *not* constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature.

Journal of Applied Polymer Science, Vol. 54, 1311-1320 (1994)
© 1994 John Wiley & Sons, Inc. † This article is a US Government work and, as such, is in the public domain in the United States of America.

CCC 0021-8995/94/091311-10

creased range of plasticizer levels. In addition, pectin from two other sources, sugar beets and almonds, was shown to have comparable mechanical properties to the citrus pectin. The pectin-containing byproducts from these foods are currently under-used wastes, and the pectin from sugar beets has been considered inferior to citrus pectin because of its inability to gel.⁵ We also show in this work that plasticized citrus pectin/starch films have very low oxygen permeability compared to petroleum-based polymers. In addition, increased emphasis was placed on determination of low-temperature material properties and thermal transitions.

EXPERIMENTAL

Materials

MexPec 1400, a citrus pectin with a degree of methylesterification 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 (about 70% amylose, 30% amylopectin) was provided by American Maize Co. (Hammond, IN). It was used as received.

Sugar-beet pectin was kindly supplied by Dr. Ferdinand le Grand of the University of Florida, and was used as received.

Almond pectin was extracted from dried almond hulls, which were a gift from Mr. David Swisshelm of the Almond Hullers and Processors Association of California. The hulls were extracted initially with ethanol to remove color bodies. After drying, the hulls were extracted again at 85°C with aqueous HCl (pH 1) for 1 h. The solution was filtered hot, cooled to room temperature, and neutralized to pH 4. Ethanol was added to the filtrate to precipitate the neutralized pectin. The precipitate was washed with 80% ethanol, followed by washing with 95% ethanol. The isolated pectin was vacuum-filtered and dried. The yield of pectin was approximately 6% of the weight of the hulls.

All other reagents and chemicals used were ACS reagent grade. Water was HPLC grade prepared using a Modulab Polisher I water system (Continental Water Systems, Inc.).

Intrinsic Viscosity

Intrinsic viscosities were determined at 35°C in 0.05 M NaCl using a Ubbelohde viscometer (Cannon Instruments, State College, PA). The solvent flow time was 96 s.

Molecular Weight Determination

Molecular weights were determined by high-performance size-exclusion chromatography (HPSEC) using SynChropak (SynChron, Inc.) columns (100; 1,000; and 4,000 Å) for separation and a DAWN F multi-angle laser light-scattering detector (Wyatt Technology Corp., Santa Barbara, CA). The solvent used was 0.05 M NaNO₃. Details of the sample preparation procedures were reported previously.⁶

Film Preparation

Films were prepared by mixing solutions of pectin and glycerine with gelatinized starch solutions, casting them on a glass 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. Wet film thicknesses of 2–2.5 mm were used, giving dry film thicknesses of 0.04–0.05 mm.

The pectin was dissolved by slowly adding a measured amount to 20 or 25 mL of HPLC grade water with stirring. The glycerine plasticizer was added to the water prior to the addition of the pectin. The solutions were stirred for 1–2 h until all the pectin appeared to be dissolved. The total concentration of pectin and glycerine in the solutions was about 5% to 7% by weight.

Gelatinized starch solutions were prepared by mixing the appropriate amount of starch (0.05 g to 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-watt Amana Model R321T Radarange microwave oven for 3 min at 50% of full power.

The gelatinized starch solutions were cooled in a waterbath 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. Testing was done within one day of sample preparation. Both tensile tests and dynamic mechanical analysis were carried out. Test samples were cut from the films with a razor blade. Nominal dimensions of the samples were 6.4 mm × 38.1 mm × 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.

Tensile data were obtained at room temperature using a strain rate of 0.005 sec^{-1} (30%/min). Tensile strength, initial modulus, and elongation to break were measured. A maximum elongation of 13% could be obtained due to instrument constraints.

For dynamic tensile measurements, 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 ($\tan \delta$) were determined as a function of temperature. Data were taken from -100°C to 200°C , using a heating rate of $10^\circ\text{C}/\text{min}$. Ambient humidity during testing was from 30% to 50%. Each sample was equilibrated in the sample chamber under dry nitrogen at the starting temperature prior to running the test.

Oxygen Permeability Testing

Oxygen permeability testing was carried out by Mr. Paul Dell of the U. S. Army Natick Research, Development, and Engineering Center, Natick, MA, using a MOCON OX-TRAN 2/20 oxygen permeability tester (Modern Controls, Inc., Minneapolis, MN). The samples were tested at 22°C using dry air and dry nitrogen, and the relative humidity seen by the samples was less than 2% in all cases.

RESULTS

Intrinsic viscosities in 0.05 M NaCl for DM71, sugar-beet pectin, and almond pectin were determined to be 5.70, 2.58, and 2.24 dL/g respectively. Their respective weight average molecular weights were found to be 1.9×10^5 , 5.8×10^5 , and 1.2×10^5 daltons. Centrifuged solutions of the sugar-beet pectin were extremely difficult to filter, indicating the presence of a microgel. This was confirmed by the presence of extremely large scattering at elution volumes where refractive index indicated only extremely low concentrations of material were present. Therefore, this calculated value is probably anomalously high.

Twenty-two films were made with DM71, which encompassed a wide range of compositions. Pectin/starch ratios of 100 : 0, 90 : 10, 80 : 20, 70 : 30, 65 : 35, and 55 : 45 were used. The glycerine plasticizer contents used were nominally 15%, 30%, 45%, 60%, and 75% by weight.

The effect of glycerine content on the tensile properties of the DM71 films with a pectin/starch ratio of 90 : 10 is shown in Table I. There was little change in tensile strength and a small increase in elongation to break, along with a decrease in initial modulus at glycerine levels up to 45 wt %. Beyond 45%, modulus and tensile strength fell off rapidly, while elongation to break increased rapidly. For the films containing 60% and 75% glycerine, sample rupture had not occurred by the instrument limit of 13% elongation.

In dynamic mechanical analysis, the storage modulus (E') is defined as the stress in phase with the strain in a sinusoidal deformation divided by the strain, and is a measure of the energy stored and recovered per cycle. The loss modulus (E'') is defined as the stress 90° out of phase with the strain divided by the strain, and is a measure of the energy dissipated per cycle of the deformation. The ratio E''/E' is referred to as the loss tangent, $\tan \delta$.⁷

Figures 1–3 show the effect of glycerine content on the storage modulus of films with pectin starch ratios of 90 : 10, 70 : 30, and 55 : 45, respectively. These are representative of the range of behavior seen across the entire composition range. A comparison of these figures revealed two trends. The first is that the addition of the glycerine generally decreased the modulus over most of the temperature range studied except at the highest starch level studied. This is particularly true at pectin/starch ratios of 100 : 0 and 90 : 10, but is also apparent at higher pectin/starch ratios as well. The other trend noted was that the effect of glycerine on the storage modulus dramatically decreases at percentages of starch above 10% in the biopolyblend. There seems to be relatively little change from -100°C to 25°C ; but above this temperature range, increasing the amount of starch in the blend results in materials in which the modulus is less and less affected by the addition of plasticizer. In fact, with the 55 : 45 pec-

Table I Effect of Glycerine on Tensile Properties of DM71 at Pectin/Starch Ratio = 90 : 10

% Glycerine	Tensile Strength (Pa)	Modulus (Pa)	Elongation to Break (%)
16	2.7×10^7	3.4×10^9	1.8
30	2.0×10^7	2.6×10^9	1.2
45	2.7×10^7	1.7×10^9	3.1
60	$> 1.7 \times 10^7$	7.6×10^8	> 13.0
75	$> 3.4 \times 10^6$	7.5×10^7	> 13.0

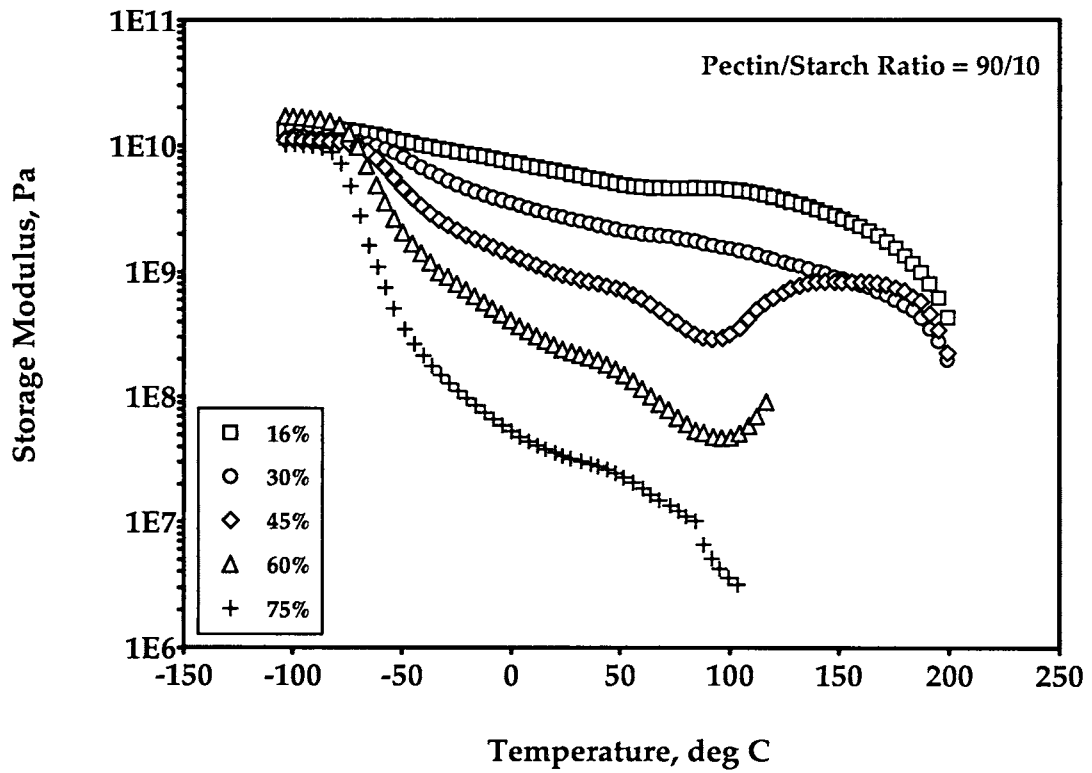


Figure 1 Effect of glycerine level on storage modulus for 90 : 10 blends of pectin DM71 and Amylomaize VII.

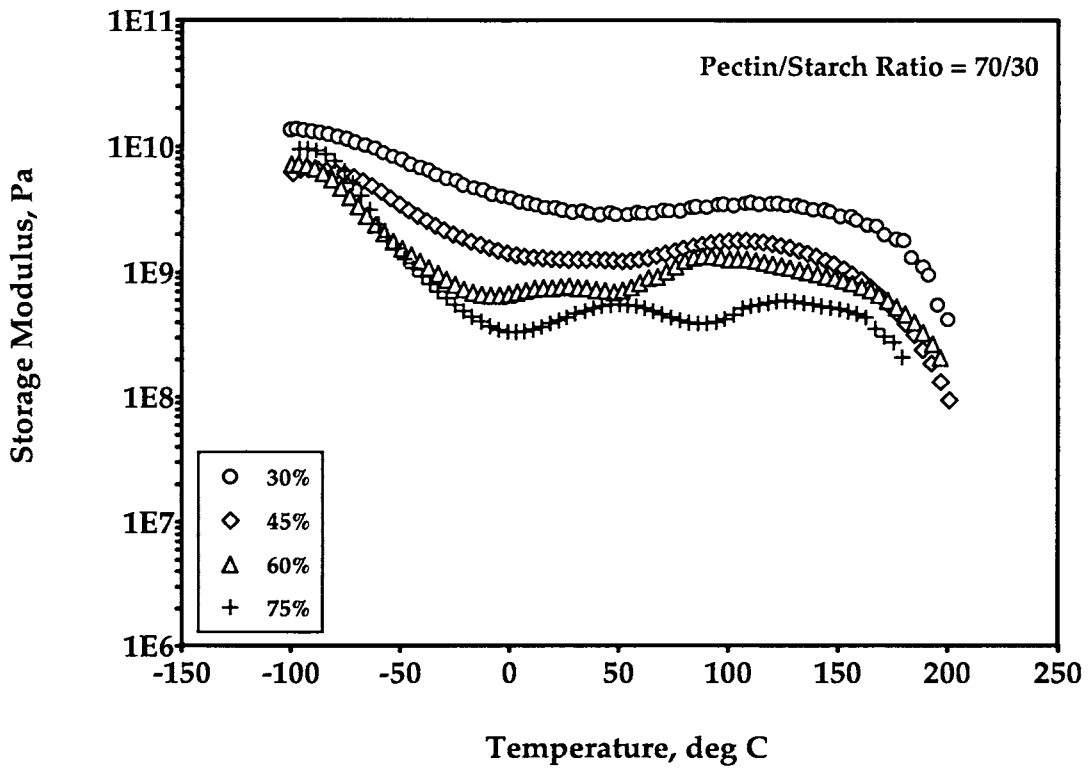


Figure 2 Effect of glycerine level on storage modulus for 70 : 30 blends of pectin DM71 and Amylomaize VII.

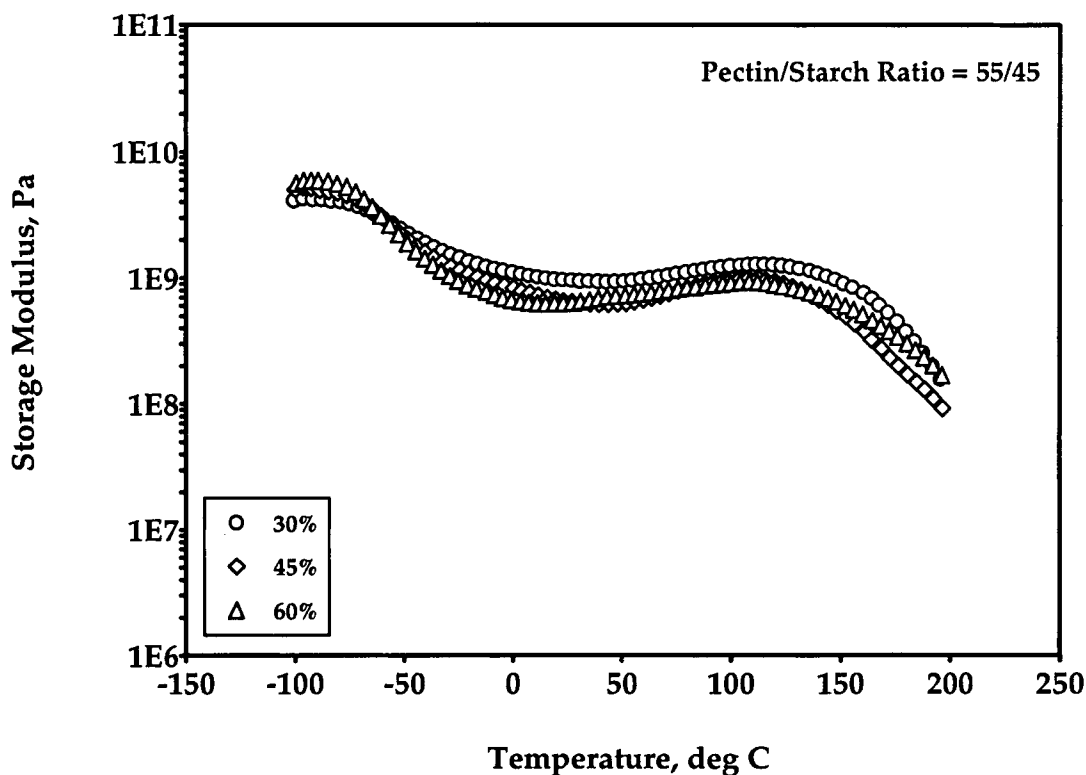


Figure 3 Effect of glycerine level on storage modulus for 55 : 45 blends of pectin DM71 and Amylomaize VII.

tin/starch ratio there was very little effect of the plasticizer on the modulus, and materials with both low and high glycerine levels have essentially the same dynamic properties.

Very similar trends were also seen in the loss modulus. This is shown in Figures 4-6. Again, there was a very large decrease in the modulus over the temperature range for the samples with pectin/starch ratios of 100 : 0 and 90 : 10; while at the lower pectin/starch ratios (higher starch content), the effect of glycerine became progressively less. As with the storage modulus, there was almost no effect of the glycerine at the 55 : 45 pectin/starch ratio.

A notable feature of the loss modulus curves was the presence of a large peak which occurred at -55° to -75°C . This peak, which is not present in the absence of glycerine, indicates a transition involving or caused by the glycerine. We previously showed the peak area to be directly proportional to the concentration of glycerine in lime pectin films, with a pectin/starch ratio of 75 : 25.¹ This same proportionality was found here with all the starch levels investigated, and also in the absence of starch.

Another interesting feature of the peak was the dependence of the temperature at which it occurred on the amount of glycerine in the film. At pectin/

starch ratios of 100 : 0 and 90 : 10, the peak maximum occurred at about -55° with glycerine concentrations of 15% to 30%, and at about -75° with glycerine concentrations of 60% to 75%. At the lower pectin/starch ratios, the location of the peak shifted from about -65° at 30% glycerine to about -75° at 60% glycerine. The convergence of the peak temperature dependence seems to parallel the decreasing effect of glycerine as a plasticizer with increasing levels of starch in the films.

In all the samples tested, $\tan \delta$ was found to generally increase with increasing temperature. An increase in $\tan \delta$ with temperature indicates that materials are becoming relatively more viscous in nature with rising temperature.

All the citrus pectin films were thermally stable up to about 180°C , as was evidenced by samples which exhibited little or no color change or embrittlement if not heated beyond 180° , whereas those samples heated to 190 – 200°C turned a dark brown and tended to embrittle.

The effect of differences in moisture content on the properties was minimized as the samples were vacuum-dried, tested within one day of preparation, and equilibrated in the sample chamber under dry nitrogen at the start temperature prior to beginning

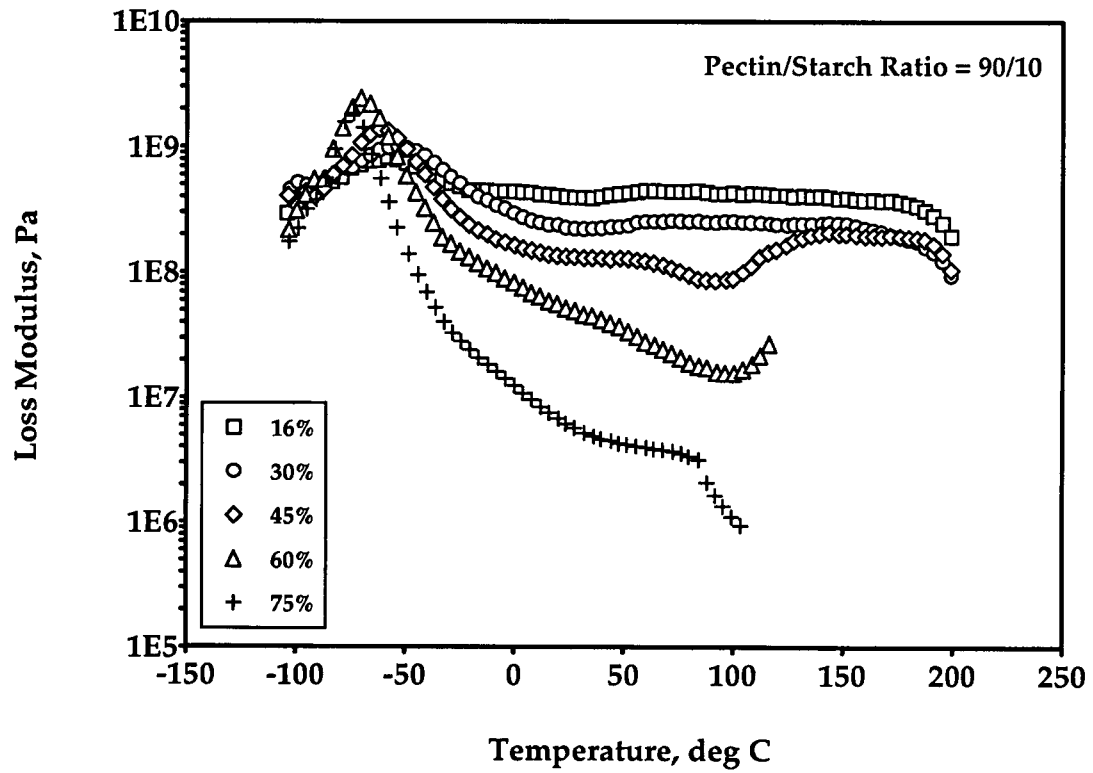


Figure 4 Effect of glycerine level on loss modulus for 90 : 10 blends of pectin DM71 and Amylomaize VII.

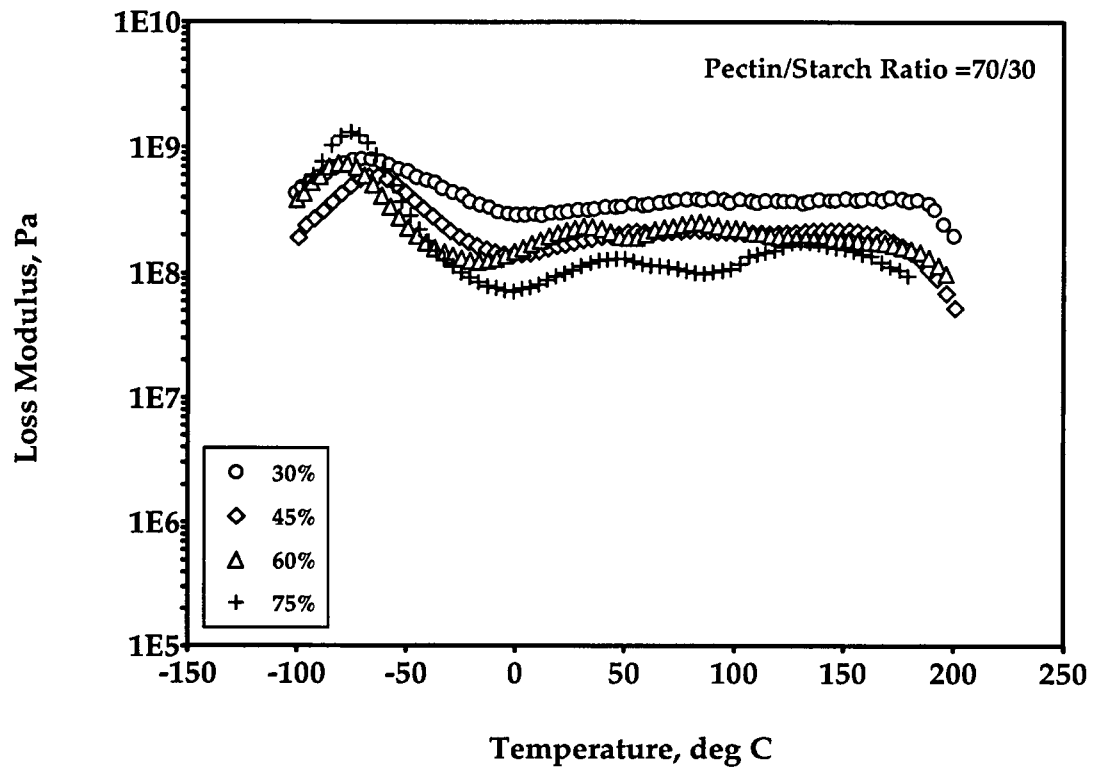


Figure 5 Effect of glycerine level on loss modulus for 70 : 30 blends of pectin DM71 and Amylomaize VII.

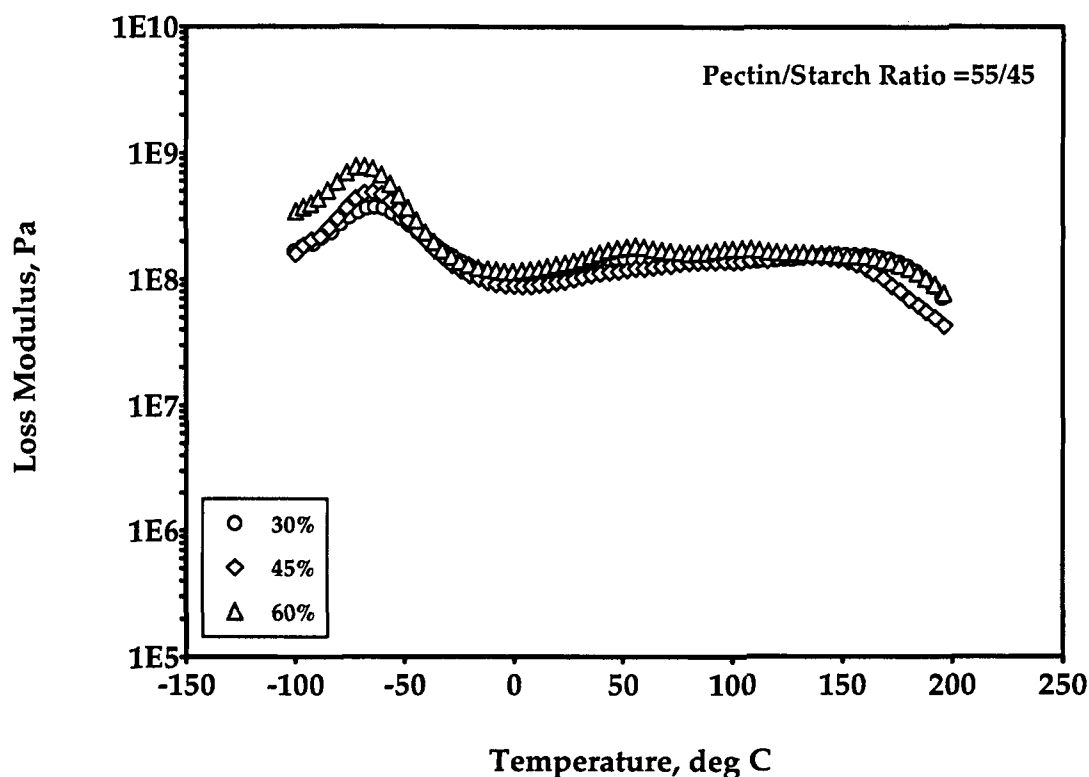


Figure 6 Effect of glycerine level on loss modulus for 55 : 45 blends of pectin DM71 and Amylomaize VII.

the tests. This was expected to minimize the amount of moisture present in the films during testing.

Because these films are being considered as possible packaging films for foods, their oxygen permeability is of considerable importance. For this reason, oxygen permeability was measured on several films. The results are given in Table II, and the differences between them are considered to be significant.⁸ The values of 1.2 to 3.7 mL/m²/day are considerably better than the values of 40–50 mL/m²/day obtained for poly(ethylene terephthalate) and 1,500–10,000 mL/m²/day found for polyethylene.⁹ It appears that increasing the amount of starch present lowers the oxygen permeability, while

Table II Oxygen Permeability Pectin DM71–Amylomaize VII Blends

Pectin/Starch Ratio	% Glycerine	O ₂ Permeability (mL/m ² /day)
100 : 0	30	1.7
80 : 20	30	1.2
100 : 0	50	3.7
80 : 20	50	2.2

increasing the glycerine level increases the permeability.

Representative plasticized pectin/starch films made with sugar-beet pectin and almond pectin were prepared in the same way as the DM71-based films, and were also evaluated by dynamic mechanical analysis. The sugar-beet pectin gave films which were slightly off-color and looked similar to the DM71 films, whereas almond pectin films were brown. Citrus pectin films were almost colorless. The experimental data are shown in Figures 7 and 8. The comparison of these plots with those of DM71 films of similar compositions shows that sugar-beet pectin makes films with mechanical properties essentially equivalent to those of citrus pectin-based films. Almond pectin showed higher modulus values than DM71 below 25°C; but at higher temperatures, it exhibited a greater temperature-dependence for the modulus, resulting in lower moduli at these temperatures compared to the citrus pectin.

DISCUSSION

The values found for the storage and loss modulus of the DM71-based films were very close to those

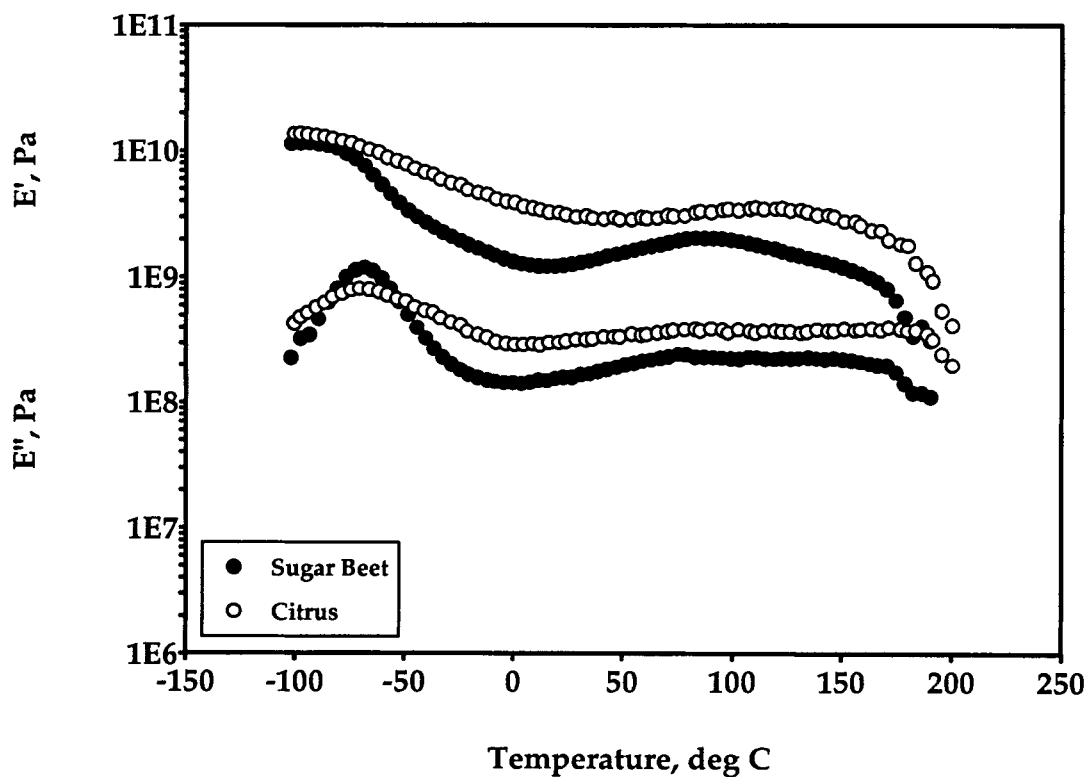


Figure 7 Comparison of sugar-beet pectin and DM71 with 70 : 30 pectin/starch ratio and 30% glycerine.

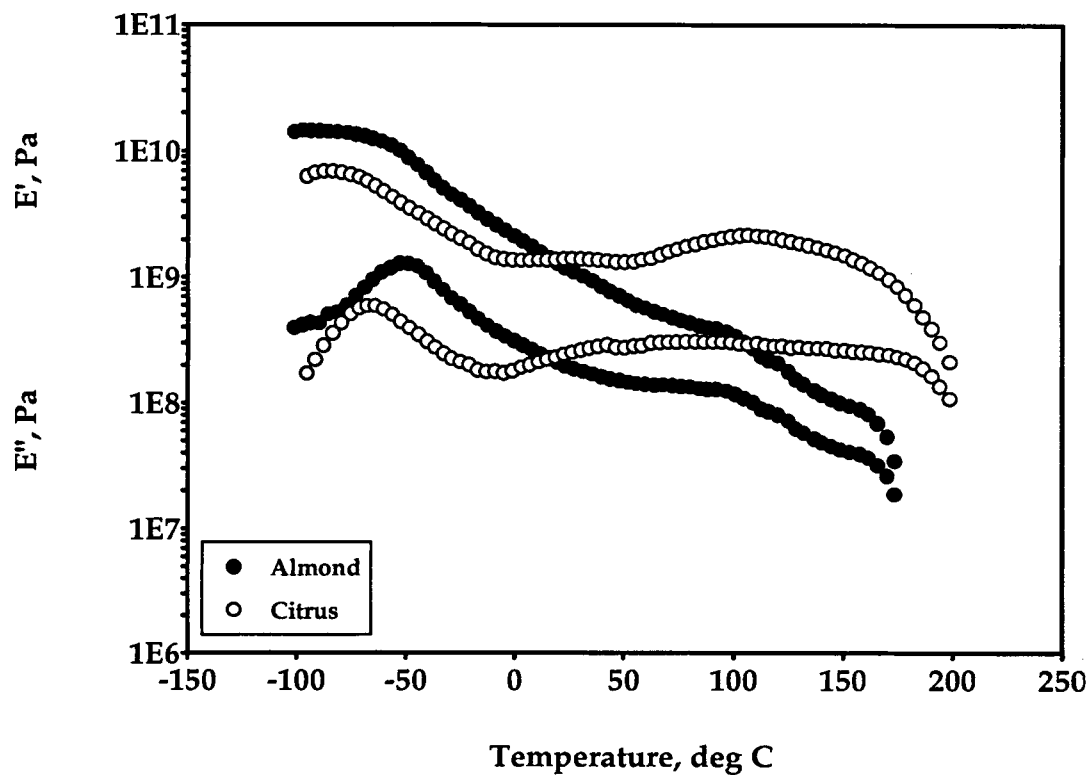


Figure 8 Comparison of almond pectin and DM71 with 80 : 20 pectin/starch ratio and 45% glycerine.

found previously⁴ for lime pectin, with a degree of methyl esterification of 74% in comparable formulations. Comparison of viscometric data for the lime and citrus pectins indicated that they are similar in molecular weight. Thus, it does not appear that there is any substantial difference between them in chemical structure or branching as a result of the difference in their source.

The composition of the DM71 films had a profound effect on their tensile and dynamic mechanical properties. Both the glycerine and the high amylose starch were important in this regard.

For films with a pectin/starch ratio of 90 : 10, tensile strength changed little, while elongation to break increased and initial modulus decreased when the level of glycerine was increased from 16% to 45%. Increasing the glycerine from 45% to 60% resulted in a dramatic drop in tensile strength and modulus, while the elongation to break increased from 2-3% to greater than 13% (the instrument limit). These increases probably resulted because of the increase in interstitial volume between polymer chains as glycerine content increased.

Amylomaize VII and glycerine combined to affect the dynamic mechanical properties of pectin films significantly. At low levels of starch (10% or less of the polyblend component of the film), glycerine had a very strong influence on both the storage and loss moduli of the polyblend films. The ability of glycerine to lower the modulus of the film increased with increasing temperature; and below -75° , the storage modulus for all the films, regardless of composition, converged to about 10^{10} Pa. As the amount of starch was increased, the portion of the moduli curves above about 25° became much less sensitive to the effect of glycerine addition; and with the 55 : 45 pectin/starch blend, the effect of glycerine was practically nonexistent.

Possibly, differences in the effect of plasticizer on moduli are related to differences in solid-state crystallinity between pectin and the high amylose starch. The pectin is readily water-soluble and is amorphous in the solid state. Amylose on the other hand, is soluble only with difficulty, and is crystalline in the solid state. Glycerine tends to interact readily with the amorphous pectin; but reaches into the starch domains much less easily, thus more easily plasticizing the pectin. As the proportion of starch in the polyblend increases, the fraction of amorphous domains decreases, thereby limiting the ability of the matrix to be plasticized.

The peak in the loss modulus curves at -55° to -75° is also sensitive to both glycerine and starch levels in the films. At starch contents up to 30%,

the peak occurs near -55° for glycerine levels of 45% and below, and near -75° at glycerine levels of 60% and above. At higher starch contents, glycerine content has little effect on the position of the peak, which becomes centered at -65° .

This behavior indicates that glycerine exists as both a bound and an unbound species in the films. Below about 50%, glycerine exists predominantly in the bound form; but above this level, the unbound form takes on greater importance. Since glycerine tends to be excluded from the starch, higher starch levels may tend to average out the effects of the bound and unbound glycerine in the transition peak.

Sugar-beet pectin film mechanical properties compared quite favorably with those of the DM71 films of similar composition. Almond pectin had better properties (up to about 25°C), with the moduli continuing to decrease at higher temperatures rather than leveling off as occurred with the citrus and sugar-beet pectins. That the sugar-beet pectin, and to a lesser extent, the almond pectin, had properties comparable to DM71 was somewhat surprising at first, as both of them had intrinsic viscosities which were well below that of the citrus pectin. Since all three pectins had high molecular weights ($> 120,000$), it is probable that they were all well above the molecular weight cutoff required for good mechanical strength. It is also possible that differences in the degree of aggregation in solution may have had a greater effect on properties in the liquid state than in the solid state.

The low oxygen permeability of the films may be due either to the polarity of the polymers, their morphology, or both. Interestingly, chitosan, another polysaccharide, is also known to have low permeability to oxygen.⁹

CONCLUSIONS

Plasticized blends of DM71 citrus pectin and high amylose starch can be made into strong, tough, flexible films with modulus values which can vary by as much as two orders of magnitude. Tensile strengths can also be varied over a very wide range. Increasing the amount of starch significantly decreases the effectiveness of glycerine in reducing the modulus. This may result from the higher crystallinity level of starch compared to pectin.

The mechanism of plasticization involves both bound and unbound glycerine. Bound glycerine leads to gradual changes in physical properties; however, the unbound glycerine acts more as a solvent, and leads to much greater changes in properties. Plas-

ticization is inhibited by the crystallinity of the amylose in the starch component.

Sugar-beet pectin provides films with mechanical properties very similar to those made with citrus and lime pectins; and almond pectin does so at temperatures up to 25°C and shows a greater decrease in the moduli with temperature at higher temperatures.

The authors thank Ms. Stacey Crummedy for running many of the dynamic mechanical analysis tests; and Dr. David Kaplan and Mr. Paul Dell of the U. S. Army Natick Research, Development, and Engineering Center for carrying out the oxygen permeability studies and for their helpful discussions.

REFERENCES

1. W. D. Maclay and H. S. Owens, *Modern Packaging*, **22**, 157-158 (1948).
2. T. H. Schultz, H. S. Owens, and W. D. Maclay, *J. Colloid Sci.*, **3**, 53-62 (1948).
3. T. H. Schultz, J. C. Miers, and H. S. Owens, et al., *J. Phys. Colloid Chem.*, **53**, 1320-1330 (1949).
4. D. R. Coffin and M. L. Fishman, *J. Agric. Food Chem.*, **41**, 1192-1197 (1993).
5. J. M. BeMiller, in *Chemistry and Function of Pectins*, ACS Symp. Ser. 310, M. L. Fishman and J. J. Jen, Eds., American Chemical Society, Washington, DC, 1986.
6. M. L. Fishman, D. T. Gillespie, and S. M. Sondey, et al., *J. Agric. Food Chem.*, **37**, 584-591 (1989).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 30-31.
8. P. Dell, U. S. Army Natick Research, Engineering, and Development Center, private communication, 1993.
9. J. M. Mayer, et al., in *Fundamentals of Biodegradable Materials and Packaging*, D. Kaplan, E. Thomas, and C. Ching, Eds., Technomic Publishing Co., Lancaster, PA, 1993.

Received October 22, 1993

Accepted May 30, 1994