

Structure and Properties of Starch/Poly(ethylene-co-vinyl alcohol) Blown Films

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ABSTRACT: Blends of native corn starch and poly(ethylene-co-vinyl alcohol) (EVOH), with starch : EVOH ratios of 1 : 1 (SE-50) and 2 : 1 (SE-67A, SE-67B), were processed into blown films. SE-67A had a higher glycerol and water content and was processed at 5°C higher than was SE-67B. The films were conditioned to various moisture contents by equilibrating at a constant relative humidity and by oven drying at 41°C. Equilibrium moisture content, which ranged from 2 to 11%, increased with increasing starch content at a given relative humidity. Mechanical properties depended strongly on starch and moisture content as well as on processing history. The extension to break of SE-50 was only about one-third that of EVOH, while that of the 2 : 1 blends was even lower. SE-67A exhibited a higher extension to break, lower tensile strength and modulus, and greater moisture sensitivity than those of SE-67B. Differential scanning calorimetry and dynamic mechanical analysis revealed evidence of interactions between starch and EVOH, probably indicative of extensive intermixing but not necessarily miscibility. Scanning electron micrographs of fracture surfaces revealed extensive differences in texture with microcracking in SE-50 and SE-67A. The combination of the analytical results provide a basis for explaining many aspects of the mechanical behavior including the marked difference in properties between SE-67A and SE-67B. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2613–2622, 1997

Key words: starch; poly(ethylene co-vinyl alcohol); blown film extrusion; blends

INTRODUCTION

In recent years, there has been a great deal of interest in developing biodegradable materials to replace conventional plastics. Potential applications include trash bags, utensils, beverage cups and lids, packaging foams, and agricultural mulch film. Materials containing starch are especially desirable because starch is inexpensive (approximately 10¢/lb for native corn starch), readily biodegradable, and derived from an annually renew-

able resource. Starch is primarily composed of amylose, a linear polymer of α -1,4-linked glucose units, and amylopectin, a highly branched polymer of α -1,4-linked glucose units connected by 1,6-linkages. Depending on the source, starch can have an amylose content as high as 85% or as low as 0%. Native corn starch contains approximately 25% amylose.

At sufficient levels of pressure, temperature, and moisture content, gelatinization, a breaking up of the granular structure of the starch accompanied by a decrease in crystallinity, is induced.¹ Starch can be processed into films and other materials by conventional thermoplastic methods such

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as twin-screw extrusion.¹ However, films formed from thermoplastic starch tend to be rigid and brittle. The properties of the films vary with moisture content and therefore with relative humidity. At high moisture content, strength is reduced, while at low moisture content, flexibility is reduced.^{2,3} In addition, gelatinized corn starch has been shown to become increasingly brittle with time even at constant moisture.⁴ These problems need to be overcome in order for starch-based plastics to be useful for biodegradable materials applications. Three approaches have been used to improve the mechanical properties and moisture resistance of starch-based materials: graft copolymerization,^{5,6} derivatization,^{2,3,7} and blending with other polymers.

Graft polymerization and derivatization of starch have two disadvantages: First, the process of carrying out the reactions and purifying the products adds to the cost of the finished materials. Second, the chemical modifications may interfere with the biodegradation of the starch. Consequently, the most frequently utilized method for incorporating starch into plastic materials has been to blend starch with other polymers, such as polyethylene,⁸ poly(ethylene-*co*-acrylic acid),⁸⁻¹⁰ polyhydroxyalkanoates,¹¹ polycaprolactone,¹² cellulose acetate,¹³ and poly(vinyl alcohol) (PVOH).^{7,14-16}

There are several advantages to PVOH: It is readily biodegradable and is an excellent oxygen barrier.¹⁷ However, PVOH is also highly sensitive to moisture, which renders starch/PVOH blends unsuitable for many applications. For this reason, poly(ethylene-*co*-vinyl alcohol) (EVOH) has been explored as an alternative to PVOH.¹⁸⁻²¹ EVOH is a random copolymer of PVOH and polyethylene and is, therefore, less hydrophilic than is PVOH. Its properties depend on the ethylene/vinyl alcohol composition ratio. EVOH with an ethylene content of 38 mol % exhibits good mechanical properties (tensile strength = 65 MPa; elongation = 280%)²² and good oxygen barrier properties (oxygen transmission rate = 0.4 cm³ 25m/m² day).²³

It has been predicted that EVOH would be biodegradable because it is made up of short blocks of PVOH, which is biodegradable, and polyethylene, which is biodegradable at molecular weights lower than 500.²⁴ However, the biodegradability of EVOH is still under investigation.²⁵ Because starch is much less expensive and more readily biodegradable than is EVOH, it is desirable to maximize the starch content in starch/EVOH blends as long as an acceptable level of perfor-

Table I Compositions of Starch/EVOH Blends^a

Component	SE-50	SE-67A	SE-67B
Corn starch	0.50	0.67	0.67
EVOH	0.50	0.33	0.33
Glycerol	0.20	0.27	0.24
Water	0.13	0.18	0.16

^a Values are expressed as the weight of the component divided by the total weight of starch and EVOH.

mance is maintained. In this study, starch/EVOH blends plasticized with water and glycerol are processed into blown films. The films are conditioned to different moisture contents and examined by tensile testing, thermal analysis, dynamic mechanical analysis, and scanning electron microscopy to relate the mechanical properties of the films as a function of moisture content to their structure.

EXPERIMENTAL

Materials

EVOH (H101A, 38 mol % ethylene, EVAL Company of America) was obtained in pellet form and ground into powder using a Brinkmann Retsch cryogenic mill. Powdered EVOH, corn (maize) starch (25% amylose, Argo), glycerol (Fisher Scientific), and water were combined in a Purnell International Type FM 10/4-4 Henschel mixer at 200–500 rpm for several minutes. Before mixing, the starch and water were combined and kneaded by hand; the glycerol and EVOH were then added sequentially. Blends were prepared with two starch/EVOH ratios as shown in Table I.

Processing

The blends were processed into blown films using a Brabender twin-screw extruder with four heated zones and a blown film die. The screws are counterrotating with a diameter of 42 mm. The blown film die has an interior diameter of 2.54 cm and a gap size of 0.05 cm. The barrel temperatures are shown in Table II. The screw speed was 40 rpm and the feed rate was constant for all formulations. During each run, the radius of the blown film tube varied from approximately 60 to 150 mm. Consequently, the film thickness varied from 0.02 to 0.14 mm.

Table II Processing Temperatures (in °C) of starch/EVOH blends

Blend	Zone 1	Zone 2	Zone 3	Zone 4
SE-50	90	120	135	134
SE-67A	90	118	131	131
SE-67B	90	117	126	126

Analytical Methods

Films were conditioned to equilibrium moisture content at 25°C in three constant-humidity chambers (32 ± 5 , 56 ± 5 , and $75 \pm 5\%$ RH). To ensure that the equilibrium moisture content was reached, the films were maintained in the chambers for a minimum of 14 days. Additionally, films were dried for 3 days at 41°C.

Moisture contents of the films were determined on a Mettler Model DL18 Karl Fischer Autotitrator equipped with a drying oven. The oven temperature was 220°C and the stir time was 5 min. The results were confirmed by thermogravimetric analysis on a TA Instruments Model 2950 using a scan rate of 10°C/min.

Tensile properties were measured on an Instron Model 4204 tensile tester with a 90.7 kg load cell and a crosshead speed of 12.7 mm/min. Rectangular samples (25.4 mm wide) were used, with a gauge length of 25.4 mm. Each tensile test was performed immediately after removing the film from the humidity chamber or the oven. Each result was based on the average of 10 replicates. Measurements were made in both the machine and radial directions. The overall trends were the same in both directions and, therefore, only the machine-direction results are discussed in detail.

Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer DSC-7 with a liquid nitrogen cooling accessory. The scan rate was 10°C/min and the temperature range was -20 to 180°C. High-volume stainless-steel pans were used to minimize water loss during the experiments.

Dynamic mechanical analysis (DMA) was carried out on a Seiko DMS 210 in the tension mode. The frequency was 1 Hz, the scan rate was 4°C/min, and the temperature range was -150 to 280°C.

For scanning electron microscopy, samples were cut and freeze-fractured in liquid N₂. The samples were sputter-coated with AuPd in a Balzers MED010 sputter coater to impart conductivity. The microstructure of each sample was exam-

ined with a Zeiss CSM 950 SEM operated at 5 kV and recorded with Polaroid Type 52 film.

RESULTS

Film Formation

Three starch/EVOH blends were prepared, one (SE-50) with a starch : EVOH ratio of 1 : 1 and two (SE-67A and SE-67B) with a starch : EVOH ratio of 2 : 1 (Table I). Water and glycerol were included as plasticizers. Water facilitates processing by significantly lowering the melting temperature and melt viscosity of starch¹ as well as the melting temperature of EVOH.²⁰ Glycerol is added primarily to reduce the vapor pressure of the water, thereby allowing processing of the blends above 100°C without boiling of water on exit from the die with the consequent formation of voids in the films.

In all the blends, the weight ratio of glycerol to water is 3 : 2. However, the plasticizer content differs throughout the series (Table I). The ratio of plasticizer to solid is highest in SE-67A, somewhat lower in SE-67B, and lowest in SE-50. The ratio of plasticizer to starch is the same in SE-50 and SE-67A and lower in SE-67B.

During each run, the barrel temperatures were adjusted so as to produce films of uniform thickness and texture, with no voids or visible heterogeneities. In all cases, the film obtained was translucent and appeared visually to be uniform, suggesting that the components were well mixed. The final processing temperatures are shown in Table II. It should be noted that the processing temperatures for SE-67B are lower than those for SE-67A despite the lower plasticizer content of SE-67B.

Equilibrium Moisture Content

The moisture contents of the starch/EVOH blends were measured after equilibration at constant relative humidity and after drying for 3 days at 41°C.

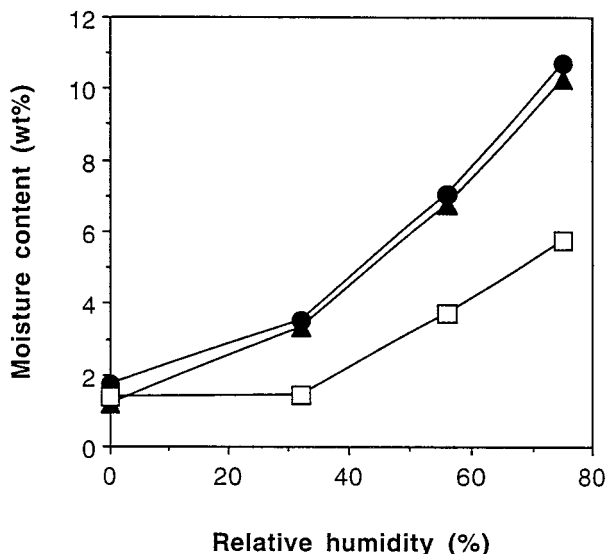


Figure 1 Equilibrium moisture contents of starch/EVOH films: (□) EVOH; (○) SE-50; (●) SE-67.

The results are shown in Figure 1, along with values for a commercial EVOH film with the same ethylene content as the EVOH used in the blends. Values for the films that were dried for 3 days at 41°C are plotted at 0% RH. The overall moisture content of the starch/EVOH films ranges from 2 to 11% and is nearly independent of the starch content. The values are similar to those reported by George et al. for starch/EVOH blends containing 15% glycerol.¹⁹ The upward curvature of the data is consistent with other studies which have shown a sharp rise in moisture content above 70% RH.^{19,26} At relative humidities greater than 40%, the moisture content of the blends is twice as high as that of EVOH. This indicates that the moisture content of the starch phase is much greater than that of the EVOH phase.

To estimate how much water is associated with the starch phase, a calculation was made based on the assumption that the moisture content of the films is a weighted total of the expected moisture contents of the individual components:

$$M(f) = M(s)W_s + M(e)W_e$$

where $M(f)$, $M(s)$, and $M(e)$ are the moisture contents of the entire film, the starch phase, and the EVOH phase, respectively, and W_s and W_e are the weight fractions of starch and EVOH, respectively. Known values of $M(f)$ and $M(e)$ are used

to derive $M(s)$, which is plotted in Figure 2. Published values for the equilibrium moisture content of pure, unprocessed starch are also plotted in Figure 2.²⁶ The estimated moisture content of the starch phase in the blends are nearly twice as high as the values for EVOH (Fig. 1), but slightly lower than the values reported for unprocessed starch. The latter difference may be due to changes induced in the starch by processing, as well as to the constraint imposed by the lower moisture content of the continuous EVOH matrix.

Mechanical Properties

Mechanical properties were measured after conditioning the films at constant relative humidity or after oven drying for 3 days at 41°C. The results are plotted as a function of moisture content in Figures 3–5.

The elongation to break (Fig. 3) increases with moisture content for all the films, as expected, but there are marked differences between the individual films that are most evident at low moisture content. The elongation to break of EVOH remains high, greater than 150%, even at a moisture content of only 2%. For SE-50, however, the elongation to break at the lowest moisture is only 50%, and for SE-67A and SE-67B, it is less than 10%. The precipitous drop in elongation to break with increasing starch content indicates that

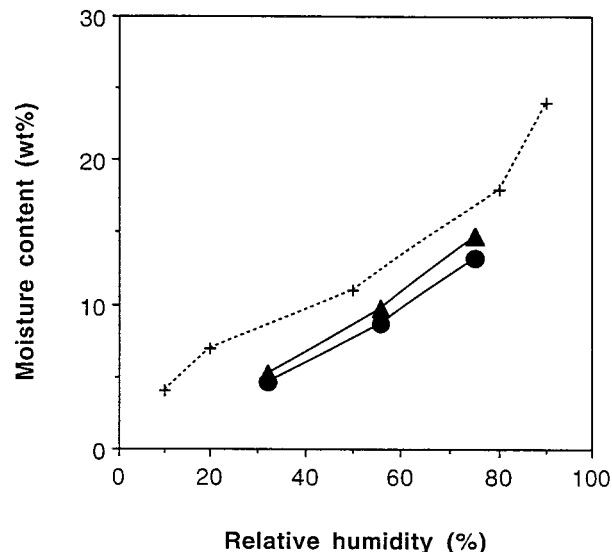


Figure 2 Estimated equilibrium moisture contents of the starch phase in starch/EVOH films: (+) starch; (▲) SE-50; (●) SE-67.

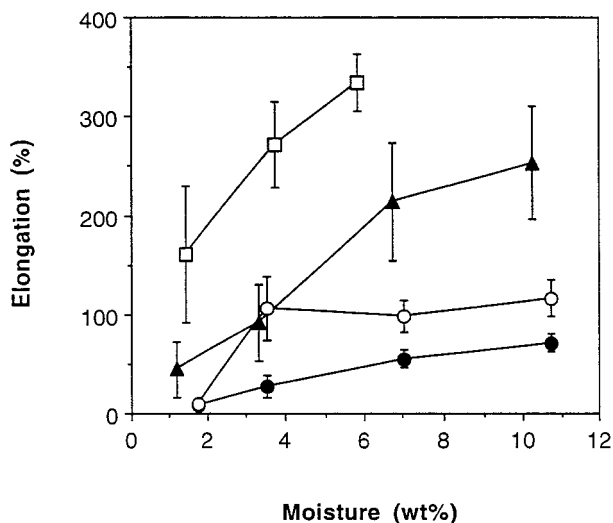


Figure 3 Ultimate elongation of starch/EVOH films as a function of moisture content: (□) EVOH; (▲) SE-50; (○) SE-67A; (●) SE-67B.

starch is the brittle phase at low moisture content. Based on a simple series model, consisting of rigid starch and ductile EVOH elements, the elongation to break would be expected to decrease in proportion to the volume fraction of starch. The much larger measured reduction indicates that the series model is not an adequate representation of the structure of the films. In SE-50, the elongation to break rises steeply and continuously

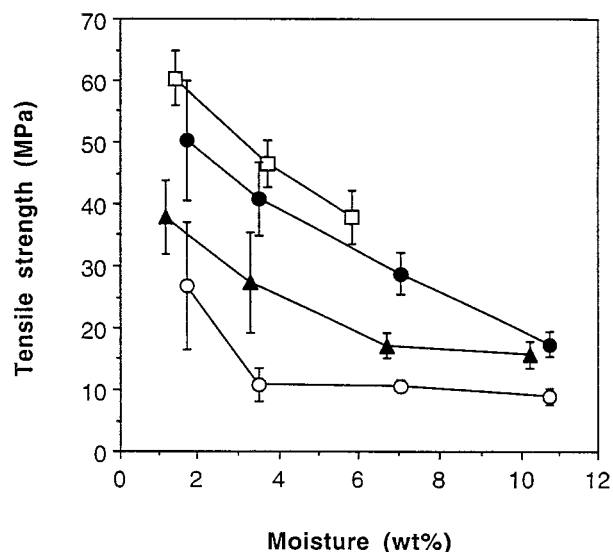


Figure 4 Tensile strength of starch/EVOH films as a function of moisture content: (□) EVOH; (▲) SE-50; (○) SE-67A; (●) SE-67B.

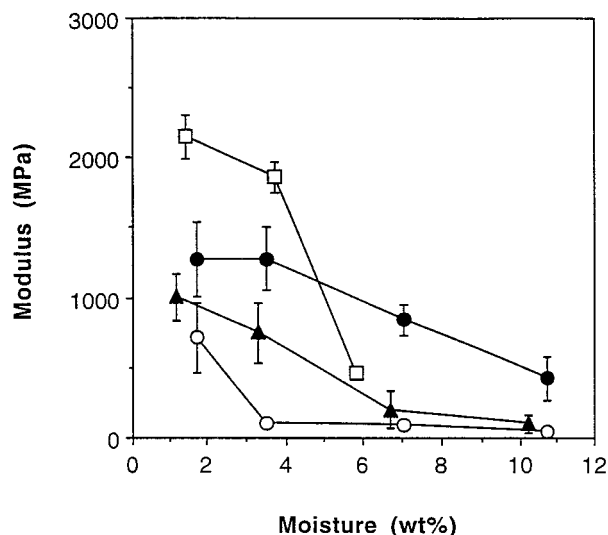


Figure 5 Young's modulus of starch/EVOH films as a function of moisture content: (□) EVOH; (▲) SE-50; (○) SE-67A; (●) SE-67B.

with increasing moisture content above 3%. The dramatic increase in elongation to break in SE-67A at 3% moisture content, given the above discussion, must be due to the effect of moisture on the starch phase, but the elongation to break fails to increase further with increasing moisture. The behavior contrasts with the slow, progressive increase in elongation to break in SE-67B.

The tensile strength (Fig. 4) decreases rapidly with increasing moisture content for all compositions, but, as with elongation to break, there are significant differences in the individual samples. The tensile strength of SE-50 is approximately half that of EVOH. However, the tensile strength of SE-67B is almost as high as that of EVOH and much higher than that of SE-67A. The trend in the tensile strength of SE-67A with moisture is the inverse of the elongation to break and indicates that the failure of the elongation to break to increase with moisture content is due to the low tensile strength of this film.

Initial modulus data as a function of moisture content are shown in Figure 5. The rapid decrease in modulus with increasing moisture content is similar to the tensile strength behavior. The strong dependence of the modulus on starch content also follows the same trends as those of the tensile strength data. The modulus of SE-67A drops precipitously at 3.5% moisture, in parallel with the tensile strength behavior. The dependence of the modulus on starch content is in con-

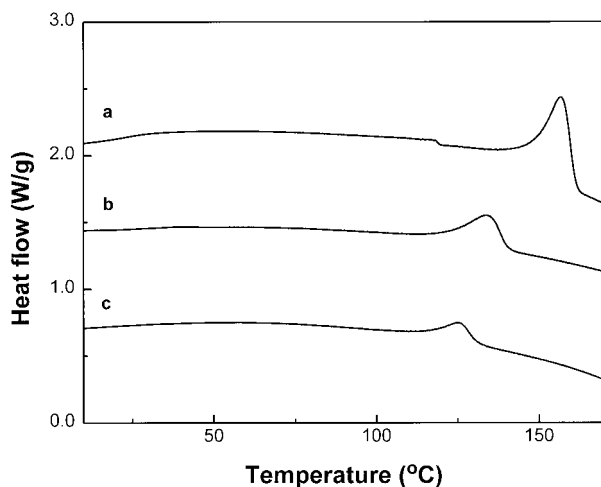


Figure 6 DSC second heating scans of films conditioned at $56 \pm 5\%$ RH: (a) EVOH; (b) SE-50; (c) (SE67A).

trast to the study by George et al., in which the modulus of starch/EVOH blends was virtually independent of composition for starch contents between 0 and 70%.¹⁹ It is also of interest that at the lowest moisture level, about 2%, the modulus values for the three blends are all approximately half the value for EVOH.

Differential Scanning Calorimetry

All the transitions that can be observed by DSC (glass transition, melting) are assigned to EVOH. No transitions arising from starch can be seen. DSC second-heating results of EVOH, SE-50, and SE-67A conditioned at 56% are shown in Figure 6. Results for other humidities are all quantitatively similar. Shogren reported glass transitions in second-heat DSC scans of methanol-extracted corn starch containing 11–25% moisture.⁴ The T_g ranged from 10°C at 25% moisture to 120°C at 11% moisture. In the current study, the moisture contents are lower than 11%, and, therefore, the T_g of starch is expected to be above 120°C. As a result, the starch glass transition temperature may be obscured by the EVOH melting endotherm that occurs in this region.

A clear EVOH glass transition (Fig. 6) can be seen in the EVOH films but not in the blends. This could be due both to the lower concentration of EVOH in the blends and to interactions between starch and EVOH, which appear to broaden the transition observed by dynamic mechanical analysis, as discussed below. The glass transition temperature of EVOH as a function of moisture

content is shown in Figure 7. As expected, the T_g decreases with moisture content because of the plasticizing effect of water.

The EVOH melting temperature as a function of moisture content for the pure EVOH and two starch/EVOH blends is also shown in Figure 7. There appear to be two effects of blending. The melting temperature decreases with increasing moisture content for all films, as expected.²⁰ However, the EVOH melting temperature is significantly lower in the blends than in the pure EVOH film even at very low moisture content. For example, at a moisture content of 3.5%, the T_m of EVOH is 158°C, 141°C (SE-50), and 134°C (SE-67A) for starch contents of 0%, 50%, and 67%, respectively. The enthalpy (ΔH) of the EVOH melting peak, normalized to the EVOH content, decreases with starch content. There is also a more modest decrease with increasing moisture content. At moisture contents of 1 and 6%, SE-50 has enthalpy values of 32 and 28 J/g, respectively, while SE-67A has enthalpy values of 25 and 20 J/g, respectively. The reduction in both T_m and ΔH with increasing starch content indicates that there are interactions between starch and EVOH that interfere with the crystallization of EVOH.

Dynamic Mechanical Analysis

DMA measurements (Fig. 8) were made on EVOH and starch/EVOH films that were dried at

Transition temperatures of starch/EVOH films

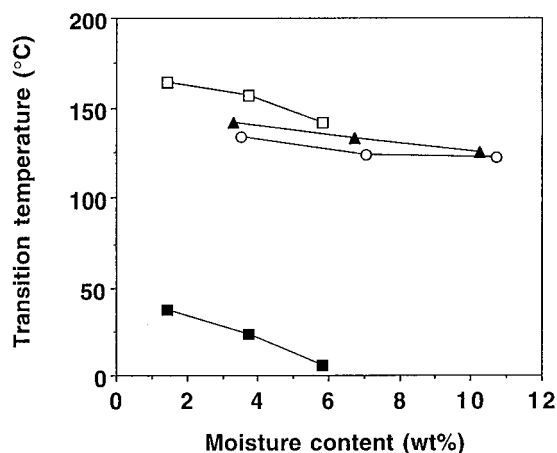


Figure 7 Glass transition temperature of EVOH (■) as a function of moisture content, as determined by DSC. Crystalline melting temperature of EVOH as a function of moisture content and composition, as determined by DSC: (□) EVOH; (▲) SE-50; (○) SE-67A.

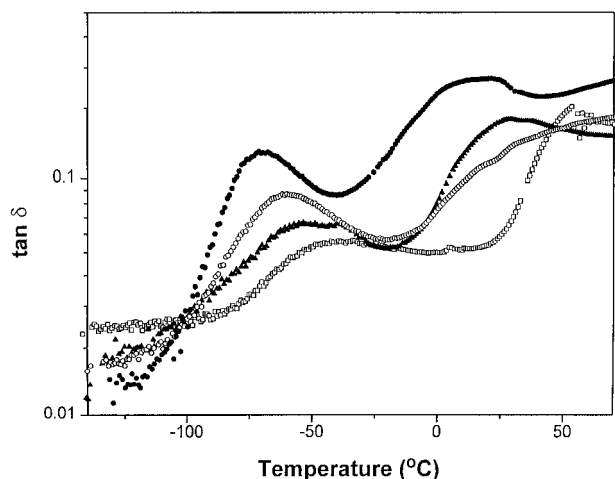


Figure 8 DMA $\tan \delta$ curves at 1 Hz for starch/EVOH films: (\square) EVOH; (\blacktriangle) SE-50; (\circ) SE-67A; (\bullet) SE-67B.

41°C and, therefore, contained less than 2% water. In the EVOH curve, there is a rise in $\tan \delta$, culminating in a peak at 52°C, which is about 10°C higher than the T_g measured by DSC at a comparable moisture content (Fig. 7). In SE-50 and SE-67B, this peak is considerably broader and has shifted downward in temperature to 28 and 18°C, respectively. In SE-67A, no peak can be seen in this region, possibly because the T_g of EVOH merges with another process. The broadness of these transitions in the blends may account for the difficulty in observing a glass transition by DSC. The decrease in the T_g of EVOH with increasing starch content may be due in part to plasticization by glycerol, as well as to interactions between starch and EVOH.

A broad low temperature peak occurs in all of the samples in the region of -80 to -30°C . In EVOH, the peak maximum occurs at about -38°C , which is well above the peak maximum in SE-67B at -70°C and in SE-67A at -60°C . The peak in the latter two samples is attributed to the starch component based on results reported by Shogren at -100 to -90°C in starch ribbon with 14% water content.⁴ While glycerol is present in the blends, the DSC fails to show a T_g for glycerol at the expected temperature of -80°C and therefore the glycerol is not expected to contribute to the DMA transition at -60°C . The broad peak in SE-50 with a midpoint at about -48°C appears to be a composite of the starch and the EVOH contributions, indicating that the starch transition has moved to higher temperature in this blend. It is interesting to note that both the low-

and high-temperature $\tan \delta$ maxima occur at higher temperatures in SE-67A than in SE-67B, despite the somewhat higher glycerol content in the former sample.

Electron Microscopy

The scanning electron micrographs of the fracture surfaces of the various samples appear in Figure 9. The films containing starch show no evidence of undisturbed granules, indicating that the granular structure of the starch has been substantially destroyed during processing. The fracture surface of the pure EVOH film shows a steplike layered structure with some indication of ductility in the presence of surface roughness and the irregularity of the edges of the layers. The fracture surface of SE-50 exhibits an overall granular or nodular appearance. On closer examination, the surface is found to be made up of irregular strands with indications of a spherical substructure on the scale of about 0.3 microns, as well as separate spherical particles. There are open valleys running along the length of some strands as well as frequently occurring voids, which give the impression that there is weak cohesion between the underlying structural elements. The fracture surface of SE-67A has a more uniform, overall granular appearance than that of SE-50. However, it is possible to make out a faint pattern of convoluted strands with separations between the strands which again appear to suggest weak cohesion. The fracture surface of SE-67B appears to be similar to that of SE-67A, but it is distinguished by a high density of distinct microcracks, with a clearly indicated directional preference. Closer examination reveals a faint striated texture, consisting of filaments which are generally oriented parallel to the direction of the microcracks.

DISCUSSION

A key issue with the starch blends is to account for the differences in the mechanical behavior in terms of the morphology of the blends. The differences in the low- and high-temperature $\tan \delta$ peaks of the three blends provide some clues about the differences in the degree of blend homogeneity and the interactions between the starch and EVOH components. In SE-50, the presence of a well-defined high-temperature EVOH peak at 52°C indicates that this blend is inhomogeneous

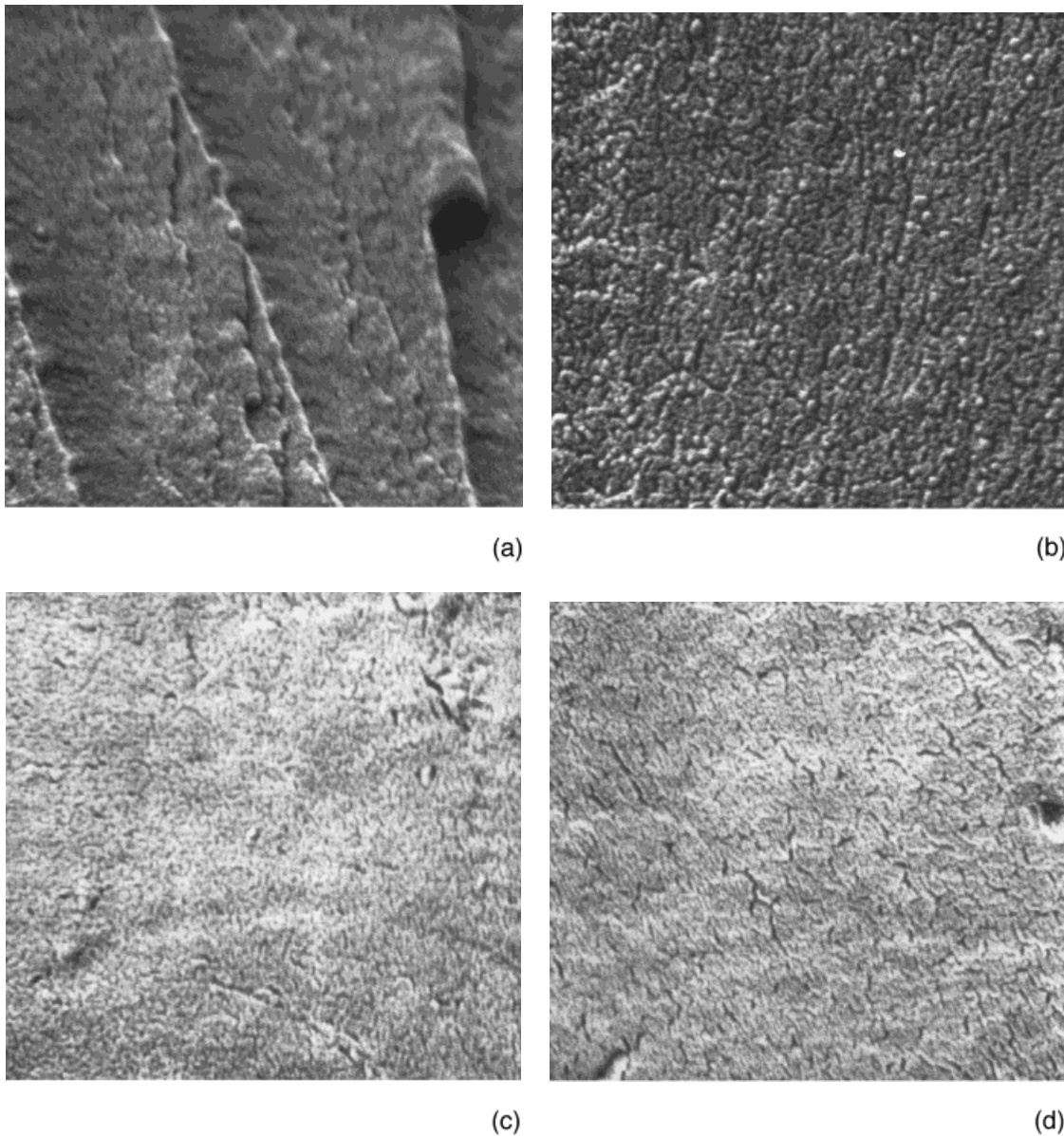


Figure 9 Scanning electron microphotographs (5000 \times) of starch/EVOH films: (a) EVOH; (b) SE-50; (c) SE-67A; (d) SE-67B.

and contains distinct starch and EVOH regions, presumably with EVOH as the continuous phase. However, the broad low-temperature peak at -48°C , which appears to be a composite of the low-temperature starch and EVOH peaks, indicates that there are also significant interactions between the two components. The occurrence of these interactions imply intimate mixing which would occur at phase boundaries.²⁷

In SE-67B, there is both a distinct, but broadened high-temperature EVOH peak and a well-

defined low-temperature starch peak. In comparison, in SE-67A, the high-temperature $\tan \delta$ region is shifted upward and is diffuse. There is also an upward shift of the low-temperature starch $\tan \delta$ peak which overlaps the low-temperature EVOH process. These features indicate that the scale of inhomogeneity in SE-67A is smaller than in SE-67B, giving rise to more extensive interactions between the starch and EVOH components. This interpretation is consistent with the expectation that the lower processing temperature and the

lower plasticizer content with SE-67B would result in larger-scale inhomogeneities in this blend. Furthermore, if the blend is on the edge of phase inversion, the structure and properties of the blend can be sensitive to slight changes in plasticizer content and processing conditions. The contrast in the tensile strength and modulus of SE-67B compared to SE-67A is consistent with a difference in phase continuity. The low values and high moisture sensitivity of SE-67A suggest that starch is the continuous phase in this material. The similarities in the moisture response of these properties in SE-67B and SE-50 suggest that EVOH is the continuous phase in both of these blends.

The electron micrographs provide additional support for the foregoing conclusions. It has been noted that the micrographs of SE-67A show the most uniform fracture surface of the three blends. The fracture surface is free of any readily distinguishable substructure and exhibits the lowest occurrence of microcracks. This is consistent with the evidence from the DMA data indicating that the scale of inhomogeneity in SE-67A is smaller than in SE-67B. By comparison, in SE-50, the increase in the starch and EVOH interactions, indicated by the overlap in the corresponding low-temperature peaks, can be attributed to the increase in EVOH which equals the starch content. The frequent occurrence of microcracks in SE-50 and SE-67B is an indication of stress at the boundary between the starch and EVOH regions and poor cohesion between the compositionally different regions. Stresses capable of causing microcracking are expected to arise from the rapid evaporation of water that occurs with release of pressure when the extrudate is forced through the die to form the blown film. The stresses would be greater in SE-50 and SE-67B due to the larger-scale inhomogeneity in these blends.

CONCLUSIONS

This study has shown that starch/EVOH, suitably plasticized with water and glycerol, can be processed into blown films of consistent quality, with 2 : 1 (SE-67A and SE-67B) as well as 1 : 1 (SE-67B) starch/EVOH ratios. The blends SE-67A and SE-67B differ in that the latter blend was processed at a lower temperature in combination with a somewhat lower glycerol and water content. The main problem is to determine how the

composition and processing conditions translate into the observed set of mechanical properties. The study has revealed three factors which could affect the mechanical properties: the occurrence of extensive interaction between the starch and EVOH with implications about the scale of phase inhomogeneities; the possibility of an inversion in phase continuity in the two 2 : 1 blends; and discontinuities such as voids and microcracking.

The electron micrographs show that SE-50 is microscopically inhomogeneous with a fibrillar texture, presumably formed by the EVOH. The presence of voids and microcracks at the interface of the structural elements indicates that this material is not fully consolidated, probably due to stresses developed during processing and poor cohesion between the compositionally different elements. These flaws could be responsible for the large reduction in the elongation to break in the blend compared to EVOH, which exceeds the reduction expected from the amount of added starch. The properties of SE-67A are affected by moisture to the greatest extent of the three blends, especially the tensile strength and modulus. In comparison, SE-67B retains a much higher tensile strength and modulus with increasing moisture, although the elongation to break is low, as expected from the large density of small microcracks. The contrast in the mechanical properties between SE-67A and SE-67B is best explained by differences in phase continuity and the scale of inhomogeneity: a continuous EVOH phase and larger regions of inhomogeneity in SE-67B compared to a continuous starch matrix and smaller regions of inhomogeneity in SE-67A.

The practical goal of this work was to develop biodegradable starch-containing films with a useful range of mechanical properties. From an economic perspective, it is necessary to incorporate the highest starch content consistent with the required mechanical properties. The high starch content would confer the additional benefit of an improvement in the biodegradability. The blend, SE-67B, appears to offer the most favorable combination of mechanical properties at the desired 2 : 1 starch to EVOH ratio. The low elongation at low moisture content is offset, to a degree, by the high tensile strength and modulus. At high moisture content, the modulus has increased to a limited extent and the tensile strength and modulus remain even higher than in SE-50. The remarkable difference in the properties of SE-67B and SE-67A, at the same high starch/EVOH ratio,

suggests that it might be possible to produce blown films with a 2 : 1 starch/EVOH ratio that achieve a useful combination of properties by careful control of plasticizer content and processing conditions. However, a remaining deficiency is the increasingly brittle nature of the films as a function of storage time. It is not known whether this is due to a continuing loss of moisture or to ongoing changes in the structure of the film. If due to the loss of moisture, the increased brittleness might be overcome by the introduction of another, more permanent plasticizer to replace the lost water.

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