Effects of Water Content on the Properties of Starch/Poly(ethylene–vinyl alcohol) Blends

PAUL A. DELL[1,*] and WILLIAM G. KOHLMAN[2]

[1]Geo-Centers Inc., 7 Wells Avenue, Newton Centre, Massachusetts 02159; [2]U.S. Army Natick Research, Development and Engineering Center, Kansas St., Natick, Massachusetts 01760

SYNOPSIS

The physical properties of unmodified starch, poly(ethylene vinyl alcohol), glycerol, and water mixtures are reported. Thermal and melt-flow properties of the preprocessed, physically mixed materials were determined along with the tensile properties and morphology of injection-molded microtensile samples. Melt-flow properties were measured by a capillary rheometer, and the water content was varied from 4 to 18%. The morphology, rheology, and tensile properties are all highly related to the percentage of water present. A transition in the tensile properties and morphology of the blends was observed at approximately 11% moisture content. © 1994 John Wiley & Sons, Inc.[†]

INTRODUCTION

The effects of water and other plasticizers on starch have been studied previously,[1–3] and a comprehensive review of various starches and their structures was given by Zobel.[4] There has been little reported work on starch poly(ethylene–vinyl alcohol) (EVAL) blends, specifically in the area of plasticizer content and its effect on physical properties. In this study, the effects of water content on changes in the thermal, melt flow, and tensile properties of the polymer blends, along with morphology, are examined. A number of thermal and rheological measurement methods such as TGA, cone-and-plate viscometers, and rotating cylinder viscometers could not be used at temperatures above 100°C since the water would volatilize off and change the composition of the mixtures.

Starch/EVAL and other polymer blends are important for possible use in biodegradable materials.[5–9] Starch is of interest because of its low cost, availability as a renewable resource, and its established biodegradability. Studies have been conducted with various starches on the effects of water, glycols, and other plasticizers, but these have been mostly on unmodified starches in doughs for the food industry[10–12] or on pretreated starches[13–16] for the plastics industry. The use of starch as a component for plastics has often focused on modified or pretreated starch and poly(vinyl alcohol) blends or starch as a filler in polyethylene (PE).[17–21] Some research has also been conducted on starch-poly(ethylene-co-acrylic acid) (EAA) blends.[22] The disadvantages of the EAA films are that they require premixing with large amounts of water, which adds to processing costs; they require urea, which decomposes into ammonia, and that they are not 100% biodegradable (100% mineralization). Starch/EVAL blends do not need to be premixed with a large amount of water, there is no need for urea, and data suggest that EVAL is biodegradable.[5] EVAL is also of interest due to its excellent oxygen barrier properties. In addition to injection molding, starch/EVAL blends can be processed into blown film.[8] The properties of both the preprocessed mix and the injection-molded microtensile samples of starch, EVAL, glycerol, and water are reported here.

EXPERIMENTAL

Materials

EVAL was provided by Eval Co. of America (Lisle, IL) with a melt index of 1.6 at 190°C and 38 mol %

---

ethylene. The starch used was food-grade Argo corn (maize) starch produced by CPC International (Englewood Cliffs, NJ), with approximately 30% amylose and 70% amylopectin. The glycerol was purchased from Sigma Chemical Co. (St. Louis, MO). The water was deionized by a Millipore Milli-Ro system (Bedford, MA).

Mixing

A typical starch/EVAL blend consisted of 40 g of starch, 40 g of EVAL, 30 g of glycerol, and an appropriate amount of water to achieve the desired moisture content. Blends were prepared by combining the dry materials (starch and EVAL) in a sealable PE bag, adding the glycerol and the water, and mixing by hand until a uniform consistency was established. The blend was left in the sealed bag for 24 h before testing began, to allow for the starch to absorb the glycerol and/or water.

Moisture Analysis

Water content was determined with a Model 903H Moisture Evolution Analyzer (TA Instruments, Inc., New Castle, DE) that uses an electrolytic cell to conduct a Coulombic measurement of water content. The instrument was calibrated with 2 mg of water at 150°C for 40 min. Each sample was run twice to ensure accuracy. The moisture levels reported are the average values.

Mechanical Properties

A bench-top injection molder (Model CS-183, Custom Scientific Instruments, Inc., Cedar Knolls, NJ) was used to mold the microtensile specimens. The dimensions of the microtensile specimens were in accordance with the ASTM method D1708 (38.1 mm length, 15.88 mm width, 3.2 mm thickness). The specimens were processed at 185°C and injected into a room-temperature mold. The microtensile bars
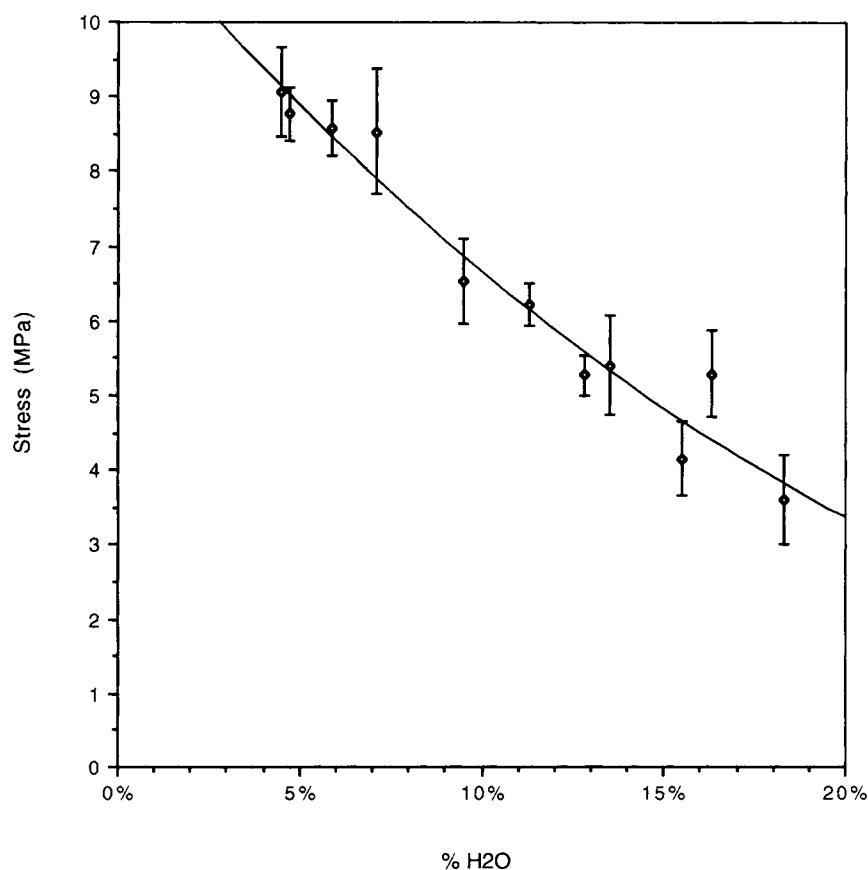

Figure 1 Influence of water content on stress at maximum load (N = 8–10, standard deviation is shown): ($\Diamond$) starch/EVAL.
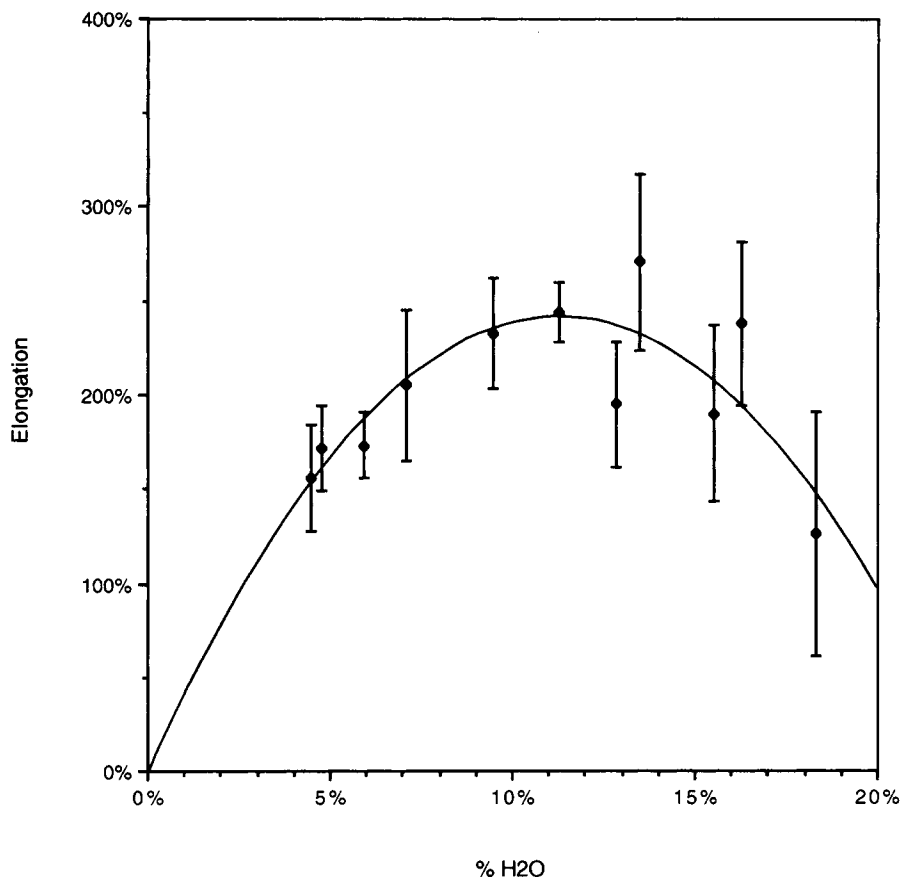
Figure 2   Influence of water content on elongation at maximum load (N 8–10, standard deviation is shown): (♦) starch/EVAL.

were stored in PE bags and tested within 48 h to minimize possible aging effects. Tensile properties were measured using the Instron universal testing machine (Canton, MA) Model 4204 with a 200 lb (90.7 kg) load cell and a 0.05 in./min (0.127 cm/min) crosshead speed.

The tensile values given are calculated at the maximum load sustained during the testing profile. The maximum load sustained was generally near the breaking point of the material. The stress is calculated from the load at maximum load divided by the initial cross-sectional area of the specimen. The elongation is calculated from the crosshead distance traveled to the point of maximum load sustained.

Thermal Properties

Differential scanning calorimetry (DSC) measurements were conducted on TA Instruments (Models

910 and 912). Large-volume stainless-steel pans were filled with material and then sealed along with a Viton rubber O-ring (Perkin-Elmer, Norwalk, CT) in the top portion of the pan to suppress vaporization and water loss. The thermal cycle was from ambient to 200°C, back to ambient, again to 200°C, and back to ambient, all at 10°C/min. The results given are from the second heating and cooling cycle. The first cycle was used to melt the blend to improve homogeneity and to impart a known thermal history to the sample. The melting and crystallization values were taken at the peak of the exotherms or endotherms.

Melt-flow Properties

Melt-rheological measurements were conducted on a constant shear rate type capillary rheometer (Instron Model 3213 Capillary Rheometer running
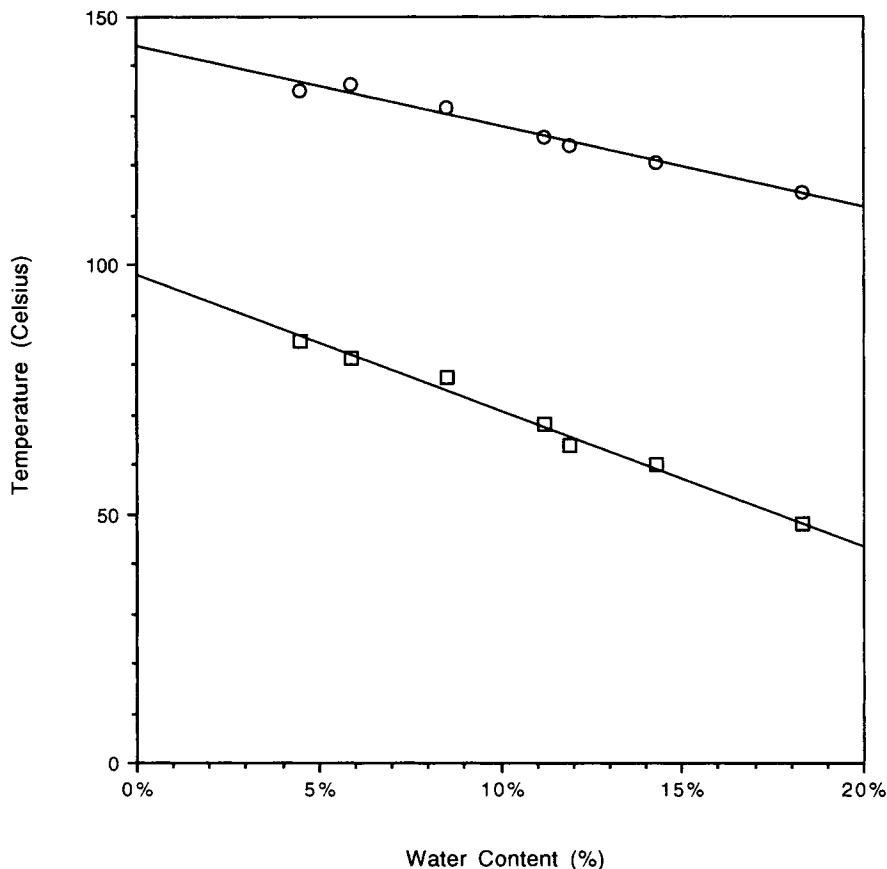
Figure 3   Influence of water content on melting and crystallization temperatures on starch/EVAL blends: (O) melting temperature; (□) crystallization temperature.

RheoSoft software). The capillary was circular, with a length/diameter ratio of 40 (5.0897 cm. length, 0.127 cm. inner diameter). The materials were tested at 135°C over identical velocity profiles, but some blends could not be tested at the highest shear rates due to high load values. The Rabinowitsch correction method as calculated by the RheoSoft software was used to correct the shear rate, shear stress, and viscosity values.

To minimize water loss, a preform was made of the material (a cylinder of approximately 0.953 cm diameter and 20.3 cm length) of each blend to expedite the loading of the blends into the capillary rheometer. The blends were packed into glass tubes, which were sealed at one end. The tubes were then sealed at the other end and heated at 120°C for 2 h, followed by cooling at room temperature for 2 h. Then, the glass was fractured to remove the starch/ EVAL preform, and the preform was sealed into a PE bag until loading into the capillary rheometer. Once loaded, the material was compressed slightly with the plunger and then allowed to equilibrate for 5 min.

Microscopy

Samples for optical microscopy were viewed and photographed using a Zeiss (Thornwood, NY) Model 61455 optical microscope at 400× magnification. The samples were cut from an end of the microtensile samples, placed on a glass slide, and stained with Melzer's reagent, which is a solution containing iodine and ethanol. The iodine permits visualization of the starch granule size and dispersity by causing the starch to appear dark.

Scanning electron microscopy (SEM) was conducted on a Zeiss Model CSM 950 computerized scanning microscope. The samples were mounted and sputter-coated with a gold palladium alloy using a Balzers Union (Liechtenstein) Model MED 010 sputter coater. The samples were not dried or treated in any other way before coating and viewing.
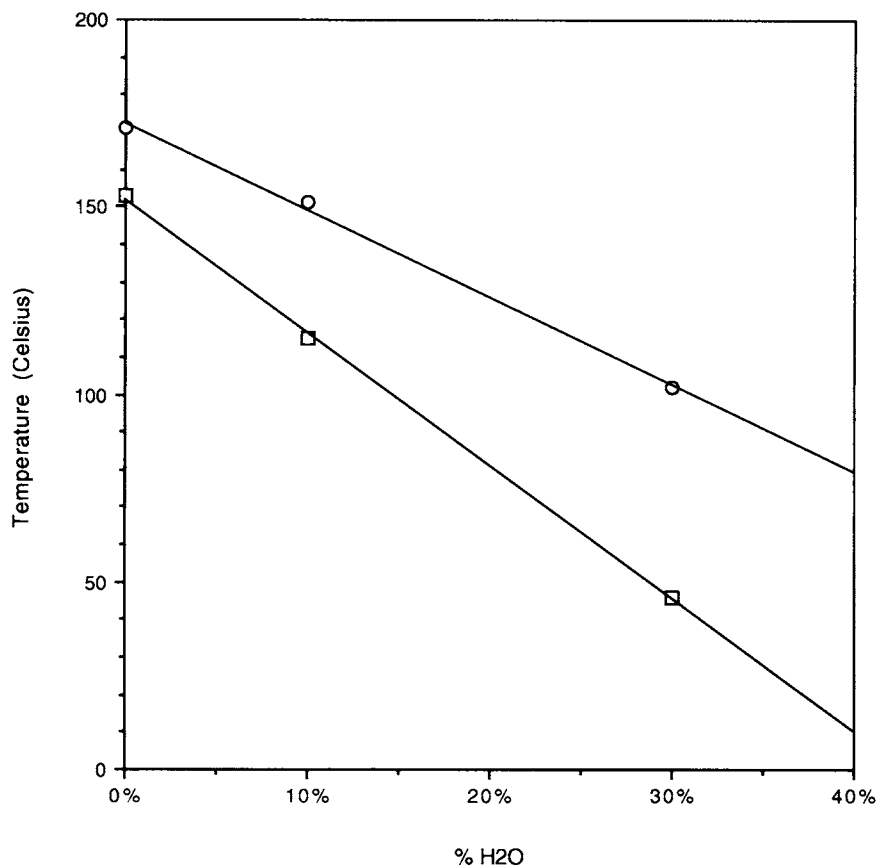
Figure 4 Influence of water content on melting and crystallization temperatures on EVAL: (O) melting temperature; (□) crystallization temperature.

RESULTS AND DISCUSSION

Mechanical Properties

Water content affects the tensile properties of microtensile starch/EVAL specimens. In Figure 1, the stress at maximum load is plotted vs. water content for the microtensile samples. There is an inverse relationship between the maximum stress and the water content. The relationship may be described by a second-order equation. The deviation from linearity may result from processing in which the higher moisture content blends have a greater moisture loss.

The elongation at maximum load of the starch/EVAL blend specimens (Fig. 2) increases steadily with the water content until approximately 11% moisture. Above 11% moisture, the data become erratic. An elongation maximum is expected at some point due to the decreasing strength of the material exhibited in the stress curve (Fig. 1). This elonga-

tional maximum at approximately 11% water region also appears to correlate with a transition in the surface structure of the microtensile specimens, which will be discussed later.

The transition at 11% water in the starch/EVAL blends may be the result of two competing forces. The transition may be due to the water playing a dual role as both a plasticizer and a blowing agent.[23] The plasticization role of the water will lower the melting temperature of the blend (Fig. 3), lower the viscosity (refer to Melt-flow Properties section), and permit a more thorough mixing of the blend under the processing conditions. The water's plasticization of the blend will increase the elongation. Water's effect as a blowing agent would create defects that would likely lower the maximum tensile strength and the maximum elongation of the specimens. The competing roles of water as a plasticizer and blowing agent may be the explanation for the apparent transition in the elongational values around the 11% water region.
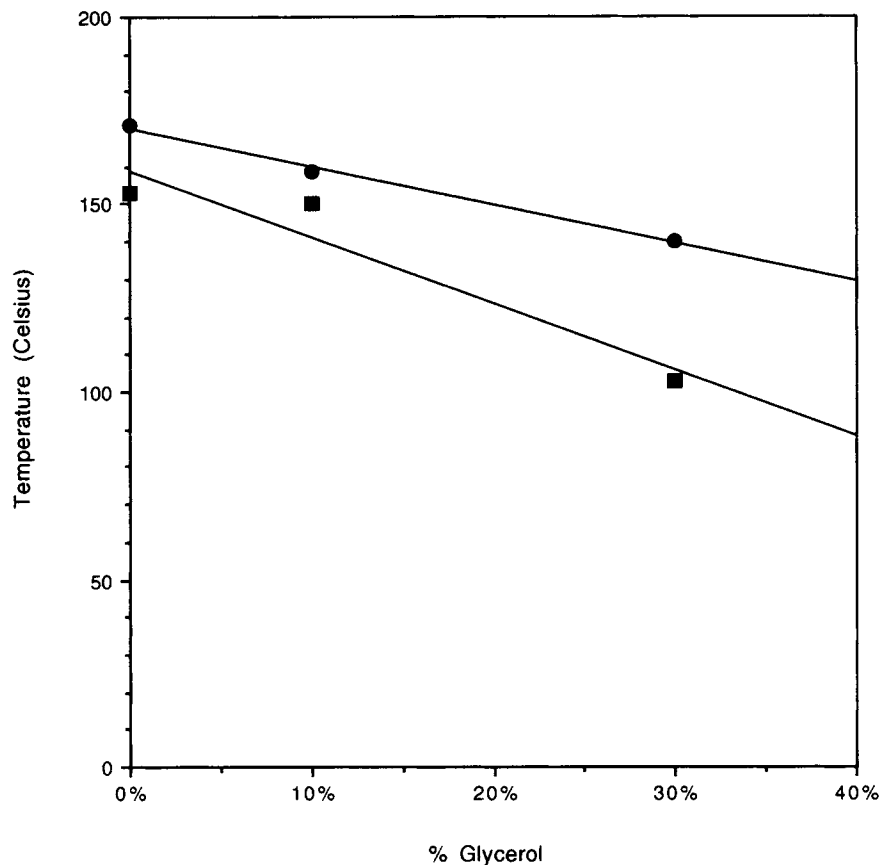
Figure 5   Influence of glycerol content on melting and crystallization temperatures on EVAL: (●) melting temperature; (■) crystallization temperature.

Thermal Properties

The melting and crystallization temperatures vs. water content are given in Figure 3. Increasing the water content lowers both the melting and crystallization temperatures of the starch/EVAL blends. The relationship between the thermal behavior and water content is linear between 4 and 18%. The equation of the fitted curve for the melting temperature as a function of the water content is

$$T_m = 144.20 - 162.61x$$

with a correlation value (R^2) of 0.976. The equation for the crystallization temperature as a function of the water content is

$$T_c = 97.93 - 270.68x$$

with an R^2 value of 0.988. It should be noted that the y-intercepts give theoretical values for the T_m and T_c for 0% moisture.

Glycerol also contributes to lowering the melting and crystallization temperatures of EVAL. The effects of both water (Fig. 4) and glycerol (Fig. 5) over the range of 0–30% on EVAL alone are shown. The percent values given in the graphs in Figures 4 and 5 are calculated from the composition of the ingredients, not from the moisture evolution analyzer measurements on the blends. Water has a greater effect than does glycerol on reducing the melting and crystallization temperatures of the EVAL.

Melt-flow Properties

In Figure 6, the viscosity of the blends decreases as the water content increases. This is due to the water's plasticization effect on the EVAL. The melting
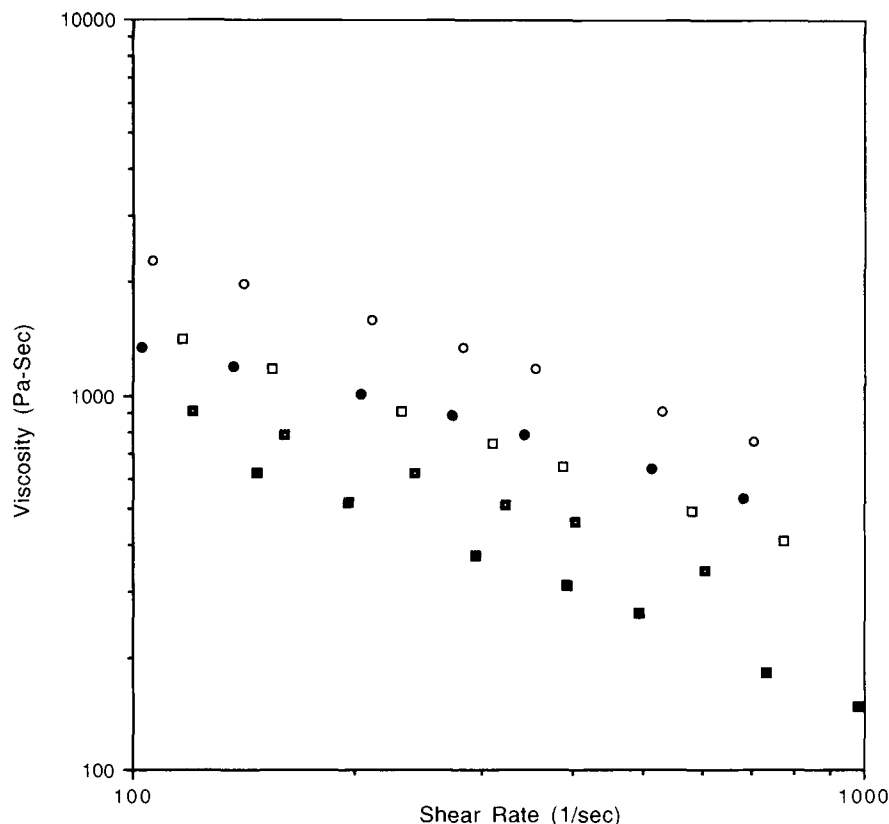
Figure 6 Viscosity vs. shear rate of EVAL at two temperatures and starch/EVAL blends with three different moisture contents: (O) EVAL at 180°C (< 1% H_2O); (●) EVAL at 200°C (< 1% H_2O); (□) 9.5% H_2O starch/EVAL at 135°C; (◙) 13.7% H_2O starch/EVAL at 135°C; (■) 15.5% H_2O starch/EVAL at 135°C.

point of dry EVAL is 175°C[24] and the melting point of the starch/EVAL blends with glycerol and water is 30–50°C lower. The starch/EVAL blends with glycerol and water are melt processable at 145°C or lower, as opposed to the 175°C and above needed to process the EVAL resin alone. This can be shown in the viscosity curves; the curve of the starch/EVAL blend at 135°C with 9.5% H_2O is comparable to the viscosity curve of EVAL at 200°C (Fig. 6). This lowering of the processing temperature is beneficial because the lower temperatures would avoid degradation of the starch and save energy.

The flow behavior is of a highly non-Newtonian pseudoplastic nature and can be approximated using the power law model. The power law factor varies greatly (0.25–0.5) with water content. If the power law factor is plotted vs. percent H_2O (Fig. 7), the result shows a scattered data set with a possible region of interest around 11–13% water. The data set may be approximated by a simple line that yields

on R^2 value of 0.519, but a fit may also be made with a third-order polynomial that yields an R^2 value of 0.625. There is no a priori justification for fitting a third-order polynomial to the power law factor vs. water curve, but complex behavior would be expected from a blend of two polymers and two plasticizers.

In starch-based materials, the shear history of the material is important. In the capillary rheometer studies reported here, no shear has been applied to the blends before testing. Further studies may be conducted using a preshearing capillary rheometer, such as the Rheoplast rheometer (Courbon Co., France). The Rheoplast device is capable of delivering a specific amount of shear to a material in a closed system.[25] Another option would be to measure the effects of the specific mechanical energy on the flow behavior by use of an in-line rheometer. The Rheopac is a slit die rheometer that has been used to measure the viscosity of maize and potato starches with moisture contents between 5 and 20%.[26,27]
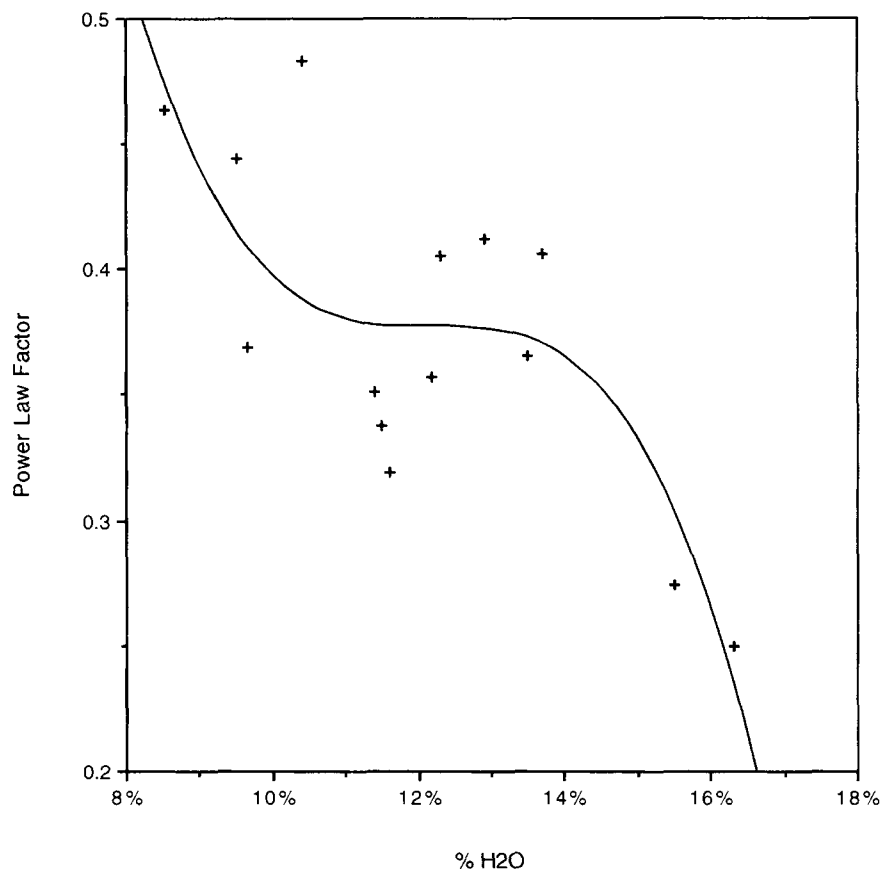
Figure 7 Influence of water content on the power law factor from capillary rheometry experiments: (+) power law factor.

Morphology

The optical photographs of starch/EVAL samples stained with Melzer's reagent show the morphology of the starch granules in the injection-molded samples. In the microtensile sample containing 6.62% H_2O [Fig. 8(A)], the starch granules are intact and apparently acting only as a filler in the EVAL. With 11.6% water [Fig. 8(B)], the starch granules are fragmented and dispersed. As the water level increases to 16.3% [Fig. 8(C)], almost all the starch granules are fragmented and more evenly dispersed. The water content greatly effects the morphology of the starch granules in the specimens.

The starch morphology changes may explain, in part, the decrease in the stress at maximum load (Fig. 1). When the granules are intact [Fig. 8(A)], the EVAL can form a continuous phase around the starch granules, which are acting only as a filler. As the moisture level is increased and the starch granules fragment, the starch may continue to act as a

filler; but since the starch is finer and more dispersed, it produces more heterogeneity in the EVAL phase. Another possibility is that the starch may be forming its own continuous phase, which is a weaker network than the EVAL phase. If an interpenetrating polymer network of starch and EVAL is being formed, the starch phase of the system is reducing the maximum stress that the sample can sustain and it is also creating a more elastic polymeric material (Fig. 2).

SEM photomicrographs also provide insight into the materials. The photographs in Figure 9 are representative of the surface of the samples, although there was variability in the surface of all the samples. At 4–9% moisture contents [Fig. 9(A)], the surface is rough with many holes and bumps on the order of 5–10 μm. In the 9–13% moisture region [Fig. 9(B) and (C)], the surface appears smoother and the spherical surface features are on the order of 1 μm in Figure 9(B) and are even smaller in Figure 9(C). As the moisture level increases, the surface features
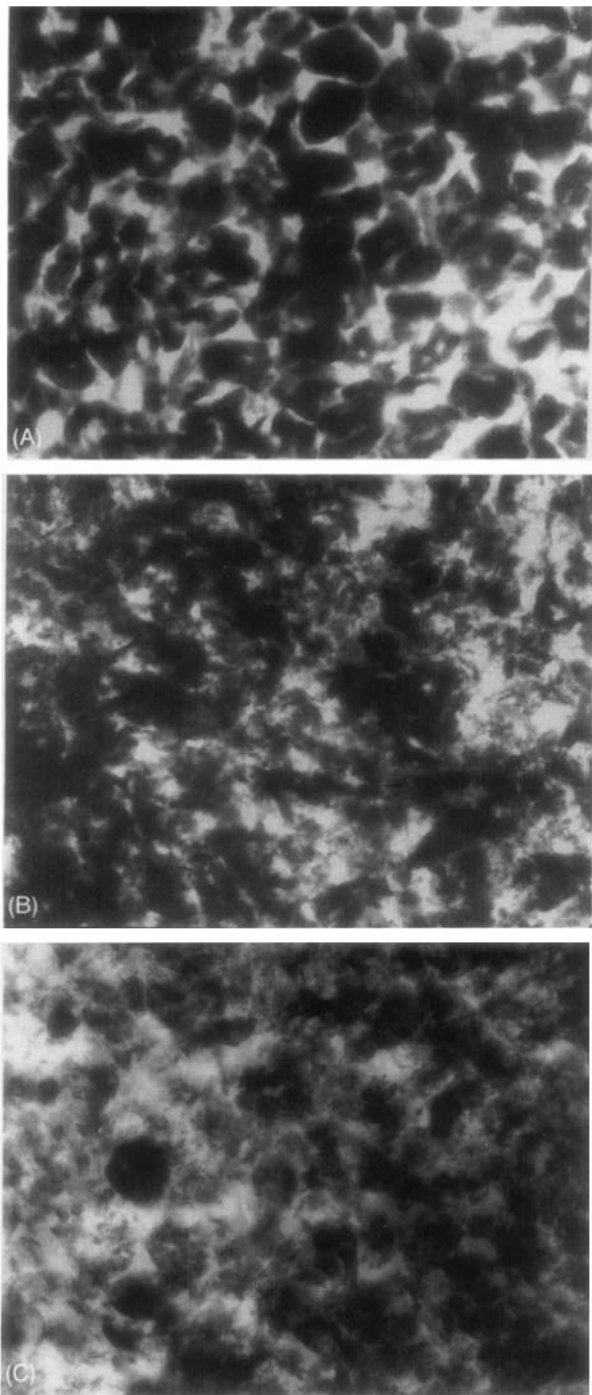
Figure 8 Optical photographs of starch/EVAL micro-tensile at 400× magnification: (A) 6.62% H_2O; (B) 11.6% H_2O; (C) 16.5% H_2O.

change only slightly. Above 13% water [Fig. 9(D)], the surface appears slightly rougher, but without holes or bumps. The larger surface features on the lower moisture content samples may be due, in part,

to the higher viscosity, which would make it more difficult for the material to fully fill and form into the mold. Over the entire range of moisture contents, occasionally small holes (1 μ) appear that seem to be the result of water volatilizing off during processing. The irregularity of these holes may be the result of temperature fluctuations or entrapped air.

SEM photomicrographs were also taken of the capillary rheometer extrudate. The morphology varied with the moisture content and the shear rate. At low shear rates (10–100 1/s), small cracks were visible at 2000× magnification (Fig. 10). The cracks were connected at slight indentations and gave the surface the appearance of an orange peel. At high shear rates (500–1000 1/s), the cracks were not evident and the surface was smoother. A smooth surface also appeared on some low shear rate extrudate samples around the 11% moisture region.

CONCLUSIONS

Water content affects the physical and thermal properties of starch/EVAL blends. Based on the iodine-stained photos and the thermal studies, the starch and EVAL are not miscible in the presence of glycerol and water. The effects of water on the tensile properties are likely due to the fragmentation of the starch and the plasticization of both the starch and EVAL as the water content is increased. The fragmentation of the starch is disruptive to the EVAL phase, which lowers its strength.[28] The water's plasticization effect is imparting greater elasticity to the materials and aiding the processing of the blends by lowering the melting temperature. The lowering of the melting and crystallization temperatures of the EVAL is likely the result of the interaction of the hydroxyl groups of EVAL with the water. SEM photomicrographs confirm that the surface of the polymer blends also varies with water content. The larger surface features on the 4–9% moisture levels is likely the result of incomplete melting and appearance of intact starch granules. As the water level increases, the surface is more uniform due to the lower melting temperature, which allows for a more thorough mixing; also, the fragmentation of the starch granules lends itself to a smoother and more uniform surface. The transition in the tensile properties and changes in morphology around the 11% moisture region suggest that this is an optimal value for the elongation properties and surface morphology of these starch/EVAL blends.
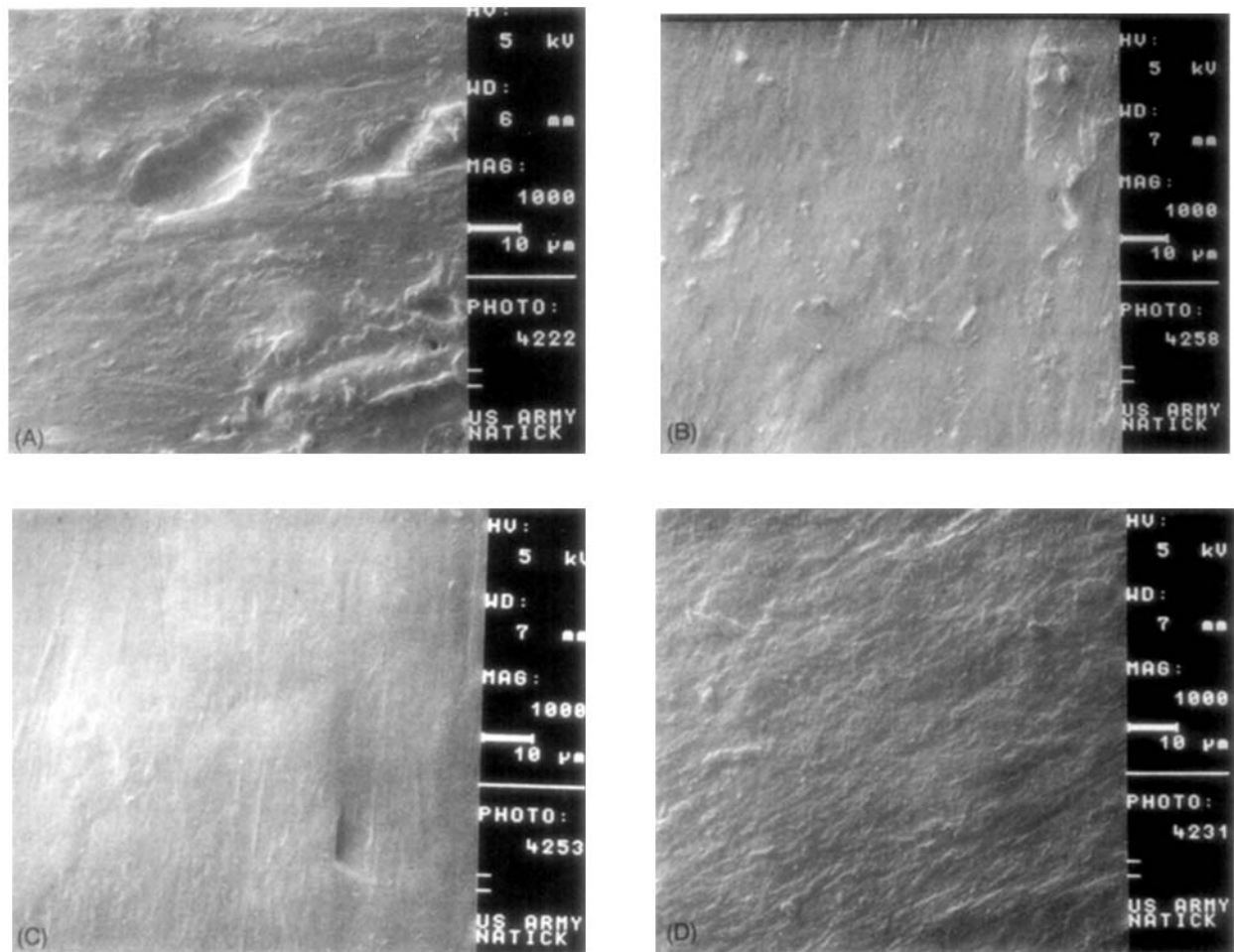
Figure 9 SEM photographs of starch/EVAL microtensile samples at 1000X magnification: (A) 6.62% H_2O; (B) 9.22% H_2O; (C) 11.2% H_2O; (D) 16.5% H_2O.
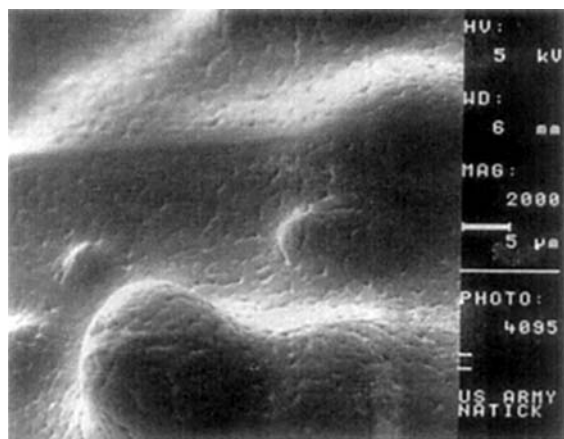

Figure 10 SEM photograph of starch/EVAL capillary rheometry extrudate.

REFERENCES

1. R. Shogren, in *Fundamentals of Biodegradable Materials and Packaging*, D. Kaplan, E. Thomas, and C. Ching, Eds., Technomic, Lancaster, PA, to appear.
2. J. W. Donovan, *Biopolymers*, **18**, 263 (1979).
3. J. Levievre, *J. Appl. Polym. Sci.*, **18**, 293 (1974).

4. H. F. Zobel, *Starch/Stärke,* **40,** 44 (1988).

5. J. M. Mayer, A. L. Allen, P. A. Dell, J. E. McCassie, A. E. Shupe, P. J. Stenhouse, E. A. Welch, and D. L. Kaplan, *Polymer Chemistry Pre-Prints: Spring-Denver,* American Chemical Society, Washington, DC, to appear.

6. J. M. Mayer, J. E. McCassie, D. H. Ball, R. E. Stote, J. R. Wright, A. E. Shupe, P. J. Stenhouse, P. A. Dell, M. J. Hepfinger, E. A. Costa, E. T. Reese, and D. L. Kaplan, in *Fundamentals of Biodegradable Materials and Packaging,* D. Kaplan, E. Thomas, and C. Ching, Eds., Technomic, Lancaster, PA, to appear.

7. P. J. Stenhouse, J. Ratto, and P. A. Dell, in *Polysaccharide/Synthetic Polymer for Biopolymer Blends,* Symposium by Paper and Textile Division of ACS, Chicago, August 22–27, (1993), to appear.

8. P. J. Stenhouse, J. Mayer, M. Hepfinger, E. Costa, P. Dell, and D. Kaplan, in *Fundamentals of Biodegradable Materials and Packaging,* D. Kaplan, E. Thomas, and C. Ching, Eds., Technomic, Lancaster, PA, to appear.

9. S. Simmons, C. Weigand, R. Albalak, R. Armstrong, and E. Thomas, in *Fundamentals of Biodegradable Materials and Packaging,* D. Kaplan, E. Thomas, and C. Ching, Eds., Technomic, Lancaster, PA, to appear.

10. K. L. Mackey and R. Y. Ofoli, *J. Food Sci.,* **55,** 417 (1990).

11. R. Chinnaswamy and M. A. Hanna, *Cereal Chem.,* **65**(2), 138 (1988).

12. V. J. Davidson, in *Food Extrusion Science and Technology,* J. L. Kokini, Chi-Tang Ho, and M. V. Karwe, Eds., Marcel Dekker, New York, 1992, Chap. 17.

13. R. L. Shogren, C. L. Swanson, and A. R. Thompson, *Starch/Stärke,* **44,** 335 (1992).

14. C. Basioli, V. Bellotti, L. Del Giudice, and R. Lombi, Eur. Pat. Appl. EP 400,532 (1990).

15. F. H. Otey and R. P. Westhoff, U.S. Pat. 4,454,268 (1984).

16. R. J. Dennenberg, R. J. Bothast, and T. P. Abbott, *J. App. Polym. Sci.,* **22,** 459 (1978).

17. R. P. Westhoff, W. F. Kwolek, and F. H. Otey, *Starch/Stärke,* **31,** 163 (1979).

18. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Prod. Res. Dev.,* **19,** 592 (1980).

19. R. Chinnaswamy and M. A. Hanna, *Starch/Stärke,* **43,** 396 (1991).

20. W. Wiedmann and E. Strobel, *Starch/Stärke,* **43,** 138 (1991).

21. S. M. Goheen and R. P. Wool, *J. Appl. Polym. Sci.,* **42,** 2691 (1991).

22. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res.,* **26,** 1659 (1987).

23. A. C. Smith, in *Food Extrusion Science and Technology,* J. L. Kokini, Chi-Tang Ho, and M. V. Karwe, Eds., Marcel Dekker, New York, 1992, Chap. 36, p. 601.

24. EVAL Company of America product information sheets, 1992.

25. B. Vergnes and J. P. Villemaire, *Rheol. Acta,* **26,** 570 (1987).

26. G. Della Valle, B. Vergnes, and J. Tayeb, *ENTROPIE,* **169,** 59 (1992).

27. G. Della Valle, B. Vergnes, J. Tayeb, and Y. Boché, in *Theoretical and Applied Rheology,* P. Moldenaers and R. Keunings, Eds., *Proceedings of the XIth International Congress on Rheology,* Brussels, Belgium, August 17–21, 1992, Elsevier, Brussels, 1992.

28. C. L. Swanson, R. L. Shorgren, G. F. Fanta, and S. H. Imam, *J. Environ. Polym. Degrad.,* **1,** 155 (1993).