

Mechanical Properties of Thermoplastic Starch/Poly(hydroxy ester ether) Blends: Effect of Moisture During and After Processing

PARVINDER S. WALIA,¹ JOHN W. LAWTON,² RANDAL L. SHOGREN²

¹ Chemistry Department, Olin Hall, Bradley University, 1501 W. Bradley Avenue, Peoria, Illinois 61625

² Plant Polymer Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 N. University St., Peoria, Illinois 61604

Received 2 October 2000; accepted 29 July 2001

ABSTRACT: The mechanical properties of thermoplastic starch (TPS) and poly(hydroxy ester ether) (PHEE) blends were studied as a function of the starch concentration. The moisture level present during processing significantly affects the morphology. A dispersed droplet morphology was observed even at very high starch levels at low moisture levels. On the other hand, the dispersed phase was significantly deformed under high moisture conditions, leading to fibrillar and laminar types of morphologies at high starch levels. The change in morphology has a significant effect on the mechanical properties. The presence of elongated starch domains improved the tensile strength and modulus of the blends with no loss in ductility. The blend modulus could be effectively represented by the particular morphology present at any given starch concentration range, using a generalized form of Kerner's equation. The properties of the blends changed with the conditioning time and relative humidity (RH), due to the change in the moisture content of each phase. An attempt was made to express the blend modulus as a function of the relative modulus of the two phases, calculated at any given RH or conditioning time. The data could be shifted fairly well from one RH to another under equilibrium conditions. However, a shift from one conditioning time to another was difficult, owing to the slower kinetics of moisture exchange at higher amounts of PHEE, which has to be taken into account. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 121–131, 2002; DOI 10.1002/app.10271

Key words: biodegradable; blends; morphology; mechanical properties

INTRODUCTION

Starch is an abundantly available, low-cost, annually renewable natural resource. Due to these

beneficial properties, there has been considerable research for the development of starch-based biodegradable plastic materials.¹ Earlier work focused on the use of native granular starch as a filler in rubber and plastics. Only low levels of starch could be used in filled systems due to the inherent loss in mechanical properties at high loadings. Hence, more recently, thermoplastic starch (TPS) has been blended with other biodegradable polymers. TPS is formed when the granular structure of starch is totally disrupted under high-shear, high-temperature extrusion conditions and in the presence of plasticizers, such as water. The properties of TPS blends will depend on the morphology produced during processing.

Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

Correspondence to: P. S. Walia, Engineering Sciences Polymer Processing, The Dow Chemical Co., 433 Building, Midland, MI 48640.

Contract grant sponsor: Agricultural Research Service (ARS) and Biotechnology Research and Development Corp. (BRDC); contract grant number: 58-3K95-8-0634.

Journal of Applied Polymer Science, Vol. 84, 121–131 (2002)
© 2002 John Wiley & Sons, Inc.

Unfortunately, there has been little research in understanding the processing–morphology–property relationships in TPS blends.²

Moisture plays a crucial and fairly complex role during and after extrusion. In an earlier publication,³ it was shown that the moisture level present during extrusion influenced the rheological conditions during the blending process. In particular, the viscosity ratio could vary over two orders of magnitude in the often used 15–30% moisture range. Consequently, the morphology developed during processing is strongly dependent on the plasticizer level and temperature used during processing. There is also moisture exchange between TPS and poly(hydroxy ester ether) (PHEE) during extrusion, which affects the rheology as well as the postextrusion moisture content of each phase. Furthermore, on conditioning the extruded blends, there is exchange of moisture between each of the component phases and the environment. In this article, the tensile properties of blends processed at different moisture levels were studied to characterize the relationship between the morphology and the properties.

Starch is a hygroscopic material and will absorb varying amounts of moisture under different relative humidity (RH) conditions, for example, 7% at 20% RH to 24% at 90% RH.⁴ The glass transition temperature (T_g) of starch varies substantially with the moisture content, changing from 140°C at 20% RH to 18°C at 90% RH.⁴ A wide range of mechanical properties are possible due to broad changes in the T_g . A limiting factor in the successful use of TPS products is the embrittlement at low RHs and the low modulus and strength at high RHs. Hence, a major objective of blending TPS with other polymers is to improve the water resistance as well as the mechanical properties. Blending of TPS with PHEE partially mitigates this problem due to the very low water permeability of PHEE. The mechanical properties of PHEE are, however, also sensitive to the water content. The mechanical properties–moisture relationship of PHEE was studied in detail by St. Lawrence et al.⁵ The modulus and tensile strength decreases with an increasing moisture content, for example, the modulus decreases from a value of 1000 MPa at 0% RH to about 40 MPa at 50%RH.⁵ This is due to the change in the T_g of PHEE from 45°C in the dry state to 10°C at 5% moisture³ (Fig. 1). The changing moisture content of each phase adds complexity in understanding the mechanical properties of the blends exposed

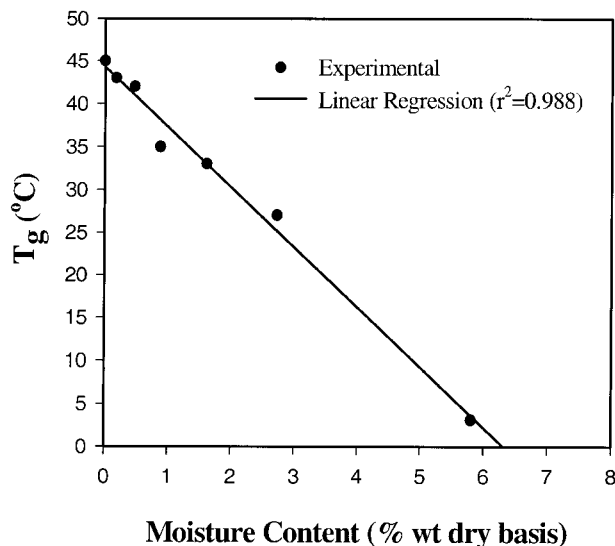


Figure 1 Plot of glass transition temperature versus moisture content for PHEE.

to varying humidity conditions. Such an understanding is necessary for the successful utilization of starch-based plastics. This article attempts to address this problem by relating the blend properties to the moisture content of each phase and the particular morphology present.

Modeling of Blend Mechanical Properties

Nielson and Landel⁶ gave a generalized form of the Kerner equation to predict the Young's modulus (E) of blends containing dispersed particles (2) in the matrix (1):

$$\frac{E}{E_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \quad (1)$$

$A = k_E - 1$; k_E is the generalized Einstein coefficient;

$$B = \frac{E_2/E_1 - 1}{E_2/E_1 + A}; \quad \psi = 1 + \frac{1 - \phi_m}{\phi_m^2}$$

and ϕ_m is the maximum packing fraction.

To predict the blend properties, the modulus for each phase and an estimate of the maximum packing fraction is needed. This general form is preferred to Kerner's equation since it is valid over the entire range of stiffness values of the dispersed and matrix phases. In addition, the same equation can be used to predict the blend

modulus when the dispersed phase is in the shape of fibers and ribbons.⁶ The shape factor A changes with the aspect ratio (L/D) of the dispersed phase and plays a crucial role in determining the degree of reinforcement. For the case of spherical particles, $k_E = 2.5$ and $A = 1.5$. For modulus measured in the direction of the aligned fibers, A is simply equal to $2L/D$. Hence, the modulus is much greater for the case of long rods. Aspect ratios greater than 100 are required to obtain a maximum modulus and, therefore, ribbons are especially effective. For very high aspect ratios, the longitudinal modulus can be expressed by the parallel model:

$$E = E_1\varphi_1 + E_2\varphi_2 \quad (2)$$

The parallel model can also be successfully used for the case of thin ribbons. The strength of fiber-filled composites is harder to predict due to the complex fracture phenomena. Only in the case of infinitely long aligned fibers is the strength given by the mixture rule, when testing is done in the direction of the fiber alignment. The composite strength does depend on the length of the fibers/ribbons. For continuous blends, modulus can be represented by⁶

$$E^n = E_1^n\varphi_1 + E_2^n\varphi_2 \quad (3)$$

where n is a constant from +1 to -1.

EXPERIMENTAL

Materials

Native normal cornstarch (Buffalo 3401, Corn Products International, Englewood Cliffs, NJ) was used. The cornstarch is composed roughly of 30% by weight amylose and 70% amylopectin and possesses about 10% moisture at ambient conditions.

PHEE was supplied by The Dow Chemical Company (Midland, MI). PHEE is a hydroxy-functional polyester⁷ prepared by the reaction of the diglycidyl ether of bisphenol A and adipic acid using quaternary ammonium halide salts as initiators.⁸ These polyesters have excellent barrier and good tensile properties^{9,10} and show strong adhesion to starch.¹¹ PHEE has been shown to be readily biodegradable in a laboratory-scale compost environment.¹⁰

Processing

Blends were extruded on a Leistritz 18-mm corotating twin-screw extruder. Cornstarch was gelatinized with water (30% wt/wt) in the first extrusion run. The extrusion was carried out with a temperature profile of 70, 90, 90, 90, 90, and 50°C and a screw speed of 100–150 min⁻¹. The last zone was cooled to prevent excessive water vaporization. There was negligible water loss during processing, as determined by moisture analysis of the extruded filaments. The gelatinized starch was pelletized and conditioned to the appropriate moisture level before blending with PHEE in a second extrusion run at 120°C and a screw speed of 100–150 min⁻¹. The concentration of TPS was varied from 10 to 80% by weight and the moisture content of TPS was varied from 15 to 30%. It should be noted that any processing moisture content mentioned is based on preextruded TPS on a wet basis.

Testing

Tensile testing was carried out on the extruded filaments (4–6 mm diameter) on an Instron Model 4201 universal testing machine. The samples were held 40 mm apart in pneumatic grips and pulled at a rate of 10 mm/min. Rubber-coated grips were used since the samples slipped with the smooth grips and failed within the serrated grips. Under these testing conditions, the effective gauge length can be higher than the actual separation between the grips, due to the deformation within the grips. This can affect the absolute values of the modulus and the percent elongation. This error was ignored since the intention was to compare values for the different blends and it was assumed that the effective gauge length does not vary from sample to sample. Testing was performed on at least five samples conditioned at 50% RH and a 23°C room temperature for 2 weeks and after they had attained an equilibrium weight (roughly 6 weeks). Testing was also done on samples conditioned in desiccators containing saturated salts of LiCl, CaCl₂ · 6H₂O, and NH₄Cl/KNO₃, which gave 15, 33, and 73% RH, respectively.

X-ray analysis was performed on a Phillips Model PW 1820 automated powder diffractometer operating at 40 kV and 30 mA. The scan was over a scattering angle (2θ) of 4–40°C and a step size of 0.05 2θ units. Glass transition measurements were made on a Perkin–Elmer DSC-7 differential

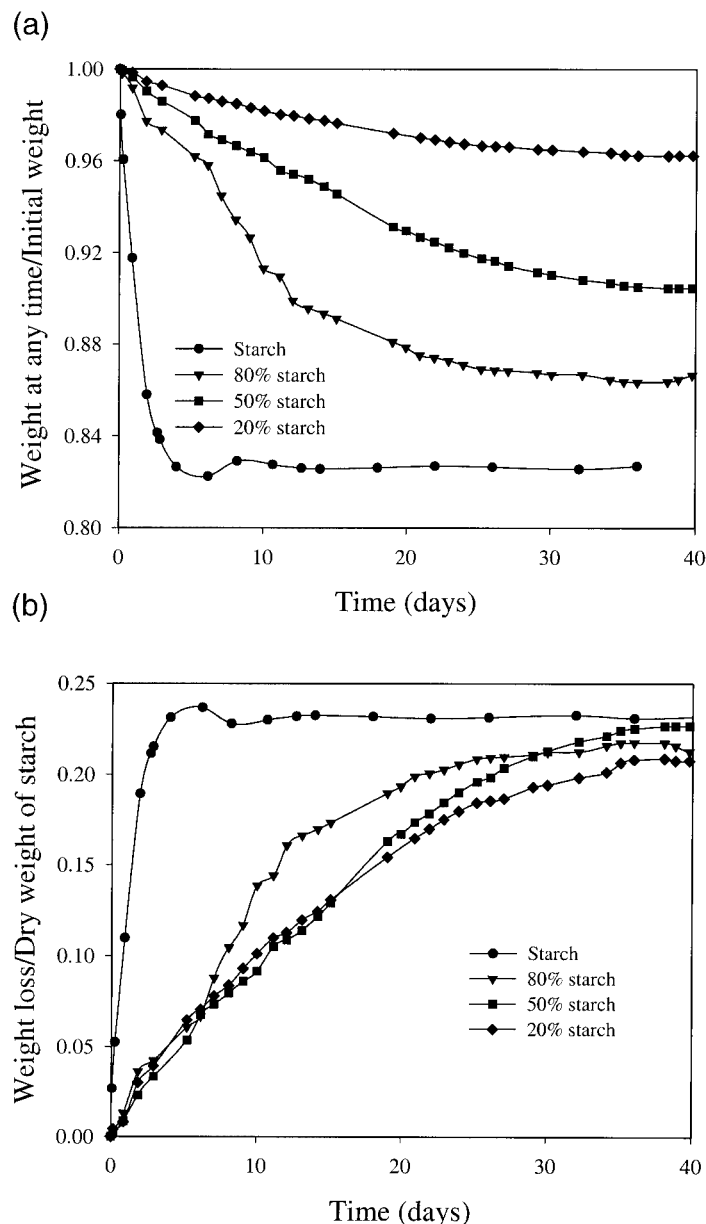


Figure 2 Equilibration plots of 20, 50, 80, and 100% starch blends processed at a 25% moisture level and conditioned at 50% RH: (a) weight at any time/initial weight and (b) weight loss/dry weight of starch as a function of time.

scanning calorimeter (DSC) with a liquid nitrogen cooling accessory. The heating scan was normally from -30 to 70°C at the rate of $10^{\circ}\text{C}/\text{min}$. Hermetically sealed stainless-steel pans were used to minimize water loss during the scans. Moisture content was determined using an infrared detector (Ohaus Model MB200, Ohaus Corp., Florham Park, NJ) by heating at 170°C for 5 min, followed by 105°C for 15 min.

RESULTS AND DISCUSSION

Starch was gelatinized in a first extrusion run to eliminate any intact or partially melted starch granules which can affect the mechanical properties.¹² Scanning electron microscopy and X-ray diffraction tests showed a complete destruction of the granular structure and crystallinity. TPS was then conditioned to 16, 19, and 25% moisture (wet

basis) and blended with PHEE in a second extrusion run. Tensile tests were made on the extruded filaments after aging at different RHs for 2 weeks and after an equilibrium weight had been reached. Starch, being hygroscopic, reaches an equilibrium moisture fairly rapidly (within hours). However, the blends, even at a 80% starch level, do not reach an equilibrium weight in 2 weeks. This is essentially due to the slower desorption of moisture from starch in the presence of PHEE. Figure 2 illustrates the kinetics of the desorption process for the blends processed at 25% moisture starch and conditioned at 50% RH. It is clear that, irrespective of the blend concentration, it takes almost 1 month until equilibration is reached.

Figure 3 shows the modulus, ultimate tensile strength, and percent elongation for the 25% moisture blends conditioned at different RHs for 2 weeks. The shapes of the modulus and tensile strength plots are very similar. The blends conditioned at low humidities (15 and 33% RH) could not be tested at high starch concentrations since the extremely brittle filaments tended to crack while being loaded into the pneumatic grips. The modulus and tensile strength increase while the percent elongation decreases with decreasing RH due to the lower moisture levels present. To understand the shape of the graphs, the morphology of the blends has to be considered. A comprehensive discussion of the morphology can be found in ref. 3 and only a summary is provided in Table I. At a processing moisture content of 25%, dispersed starch droplets are present until a 40% starch level and fibers/ribbons oriented along the length of the filaments are present in the 40–70% starch range. Up to 40% starch, there is only a slight loss in strength and a slight increase in the modulus. There is substantial reinforcement in the 40–70% starch range due to the presence of fibers/ribbons, accompanied with a loss in ductility. This can be more clearly seen in the stress–strain plots (Fig. 4) of the blends where a clear change from ductile to brittle behavior can be seen in the 40–80% starch range.

As mentioned earlier, the blends have not reached an equilibrium moisture content at the end of 2 weeks. It should be pointed out that PHEE also loses moisture during the conditioning process, although very slowly. The starting PHEE moisture content is high since PHEE picks up moisture from the wet starch during extrusion. Even though the ambient moisture content of PHEE is only about 1%, it is 4.4 and 3.2% in the

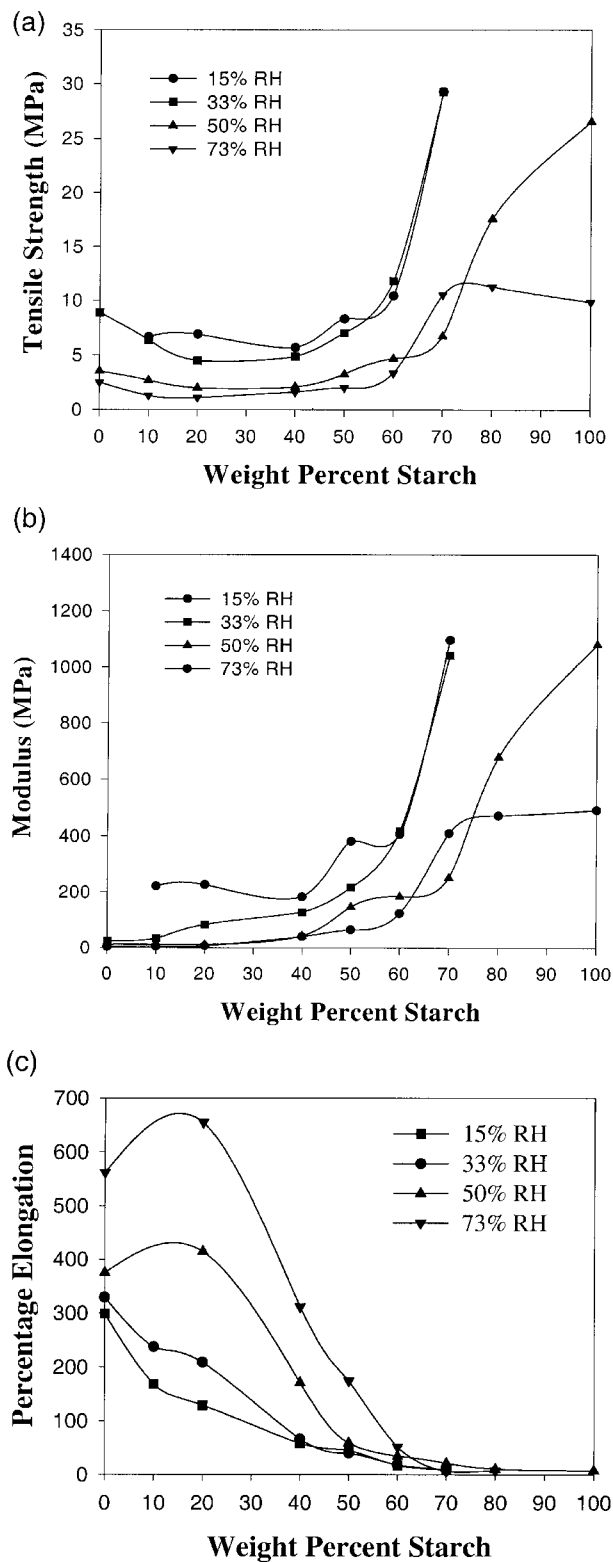
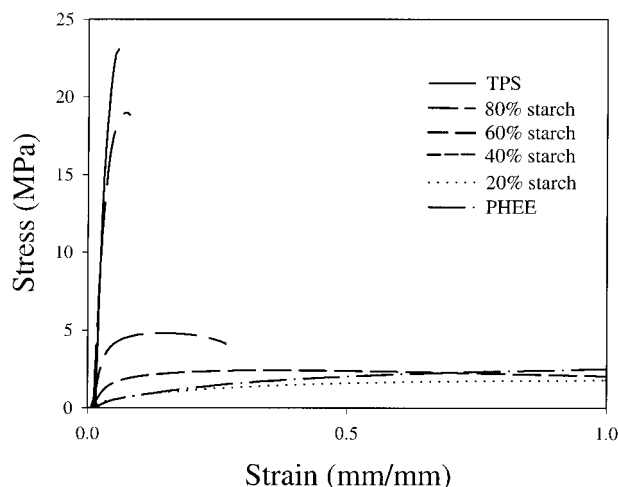
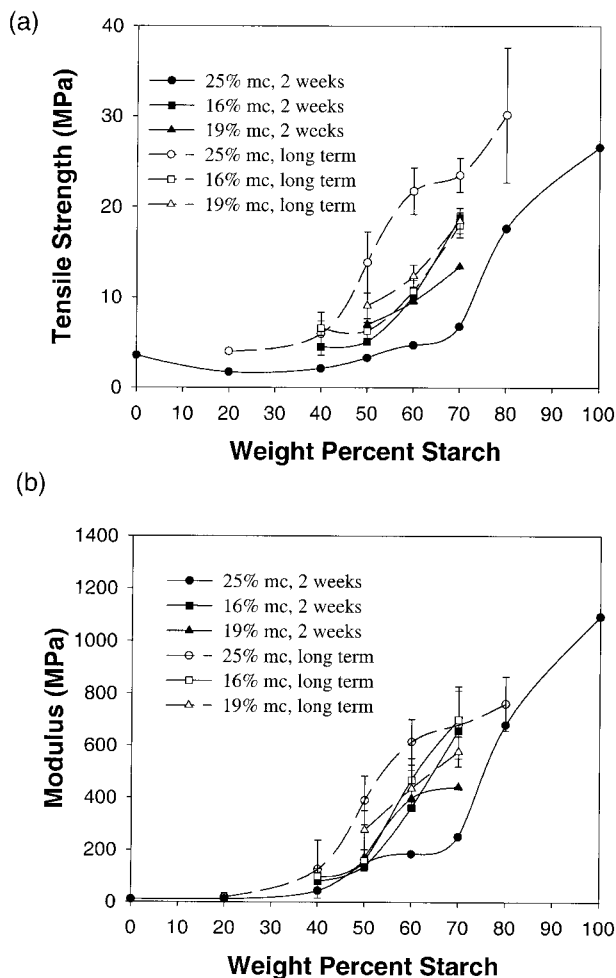


Figure 3 Tensile properties of TPS/PHEE blends processed at 25% moisture starch and conditioned at various RHs for 2 weeks: (a) tensile strength; (b) modulus, and (c) percent elongation versus starch concentration.

Table I Types of Morphologies Present in Blends Processed at Different Moisture-Level Starch

25% Moisture	16% Moisture
Dispersed Droplets 0–40% starch Fibrillar (fiberlike) 50–70% starch	Dispersed Droplets 0–60% starch
Stratified Lamellar (sheetlike) 60–70% starch	Cocontinuous 60–80% starch
Cocontinuous 60–80% starch	

blends extruded at 25 and 16% starch moisture, respectively.³ The moisture content of PHEE was estimated by measuring its T_g in the blend and using Figure 1. The difference arises due to the higher amount of water transfer for blends processed at higher moisture levels. It was shown that there is an apparent linear relationship between the postextrusion moisture content of PHEE and the preextrusion moisture content of TPS.³ On conditioning, there is a change in the moisture content of PHEE to the equilibrium value of 1.8% at 50% RH (corresponding to a T_g of 30°C). More importantly, during the conditioning process, the T_g of PHEE changes from below room temperature to 30°C and there is a substantial increase in the modulus and tensile strength. The

**Figure 4** Stress-strain plots of different concentration blends processed at 25% moisture starch and conditioned at 50% RH for 2 weeks.**Figure 5** Effect of conditioning time at 50% RH on the tensile properties of TPS/PHEE blends processed at different moisture levels: (a) tensile strength; (b) modulus.

desorption of moisture in starch also increases its T_g and the modulus. The moisture content of each phase and, consequently, the relative modulus play a crucial role in the level of reinforcement. The properties of pure PHEE reported in Figure 2 are estimated at the moisture content of PHEE in the blend at the end of 2 weeks, using the data of St. Lawrence et al.⁵

Figure 5 shows the change in tensile properties with the conditioning time at 50% RH for the blends processed at different moisture levels. There is a significant increase in the strength and the modulus for the case of the 25% moisture blend but a much smaller increase for the 16 and 19% moisture blends. For the 16 and 19% moisture blends, the starting moisture level of starch is closer to the equilib-

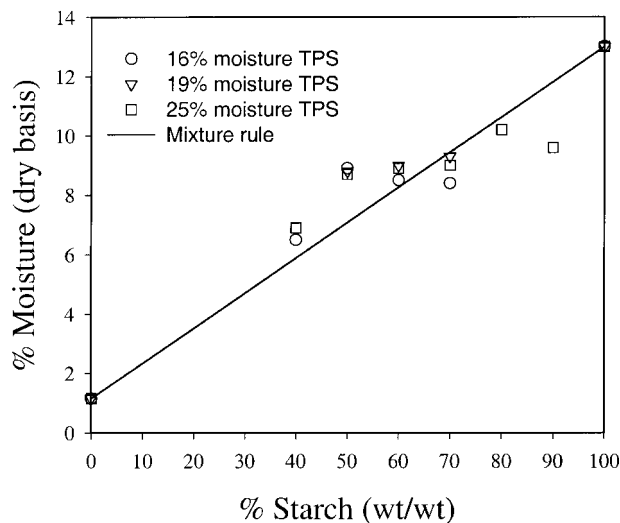


Figure 6 Equilibrium moisture content of TPS/PHEE blends conditioned at 50% RH.

rium value of 11% and there is little change in the properties from 2 weeks to equilibrium. Also, the starting moisture level of PHEE is closer to the equilibrium value of 1.8% for the case of the 16 and 19% moisture blends. There is an obvious assumption that both phases in the blend equilibrate to the same moisture level as in the pure form, which is not strictly correct.

Figure 6 shows that the moisture content of the blends deviates somewhat from the sum of the moisture contents of the pure components.

Since the starting moisture level in the three types of blends is different, it is important to ensure that they reach similar moisture levels in order to compare their properties on an equal basis. This was ensured by conditioning the blends until they attained an equilibrium moisture level. Figure 6 confirms that the three types of blends equilibrate to the same moisture content at all starch concentrations. The different blends also showed an identical PHEE T_g value of approximately 30°C on long-term conditioning, confirming that the moisture level was the same in the PHEE phase. Since the total moisture level is the same in the different blends, it implies that the starch phase also has the same moisture level.

Retrogradation or recrystallization can occur in TPS if the T_g is below the conditioning temperature. Physical aging can occur even if the T_g is above the conditioning temperature. This process involves a decrease in the free volume but no crystallization. Both these processes can have a significant impact on the final mechanical properties.^{2,12} Shogren and Jasberg¹³ showed that pure TPS at 20 or 30% moisture underwent little change in the tensile strength on conditioning at

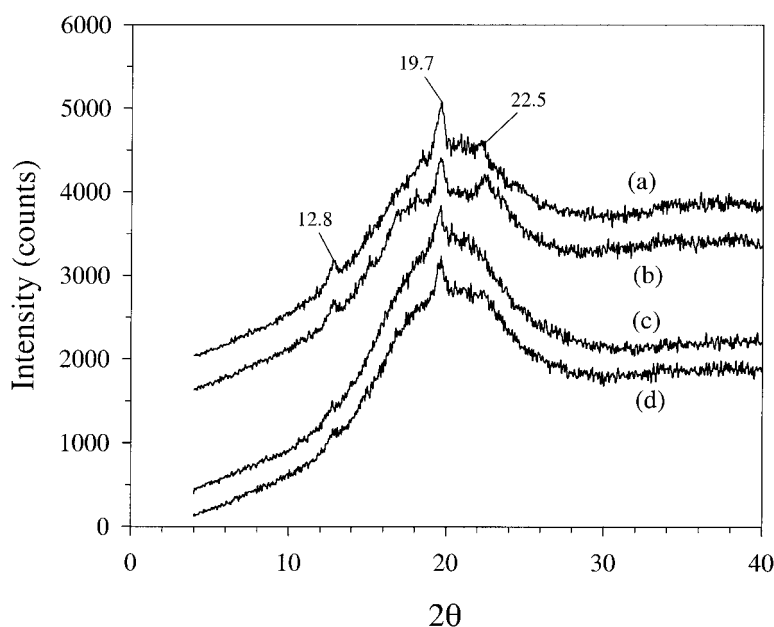


Figure 7 X-ray diffraction plots of TPS/PHEE blends conditioned to equilibrium at 50% RH: (a) 70% starch, 25% moisture; (b) 70% starch, 16% moisture; (c) 40% starch, 25% moisture; (d) 40% starch, 16% moisture.

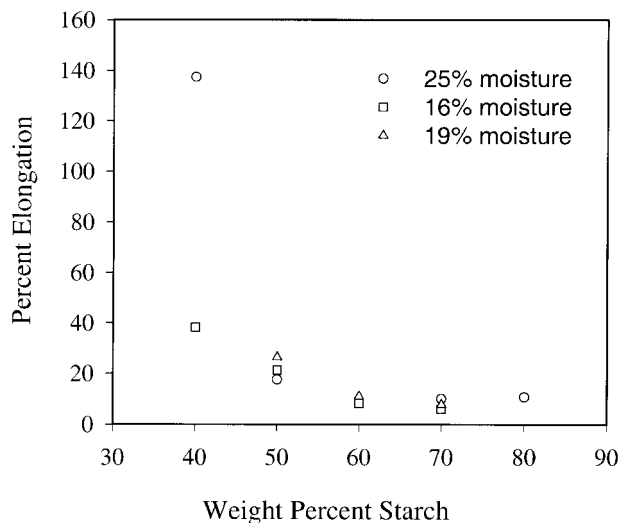


Figure 8 Percent elongation versus starch concentration for TPS/PHEE blends conditioned to equilibrium at 50% RH as a function of starch moisture content during processing.

50% RH for as long as 150 days. They used the same type of cornstarch as used in this work. There was a more noticeable change in the percent elongation. However, more importantly, the final properties were the same, irrespective of the starting moisture level of TPS before conditioning. Figure 7 shows the X-ray diffraction patterns of 40 and 70% starch blends processed at 16 and 25% moisture starch and conditioned to equilibrium at 50% RH. The peaks at $2\theta = 12.8, 19.7,$ and 22.5°C have been attributed to amylose, which has formed helical inclusion complexes with lipid or been recrystallized in the *B* and *A* forms.¹³ It is clear that the scans are identical for the two blends at both starch concentrations. This confirms that the nature and degree of recrystallization is the same even though the moisture histories of the two blends are different. Hence, any differences in the final properties of the blends cannot be attributed to differences in the aging behavior of starch.

The tensile strength of the different blends conditioned to equilibrium at 50% RH can be seen in Figure 5(a). At starch concentrations greater than 40%, the blends processed at a 25% moisture level show significantly higher tensile strengths than those of the 16 or 19% moisture blends. The differences among the 16 and 25% moisture level blends are in excess of the standard error (only shown for the case of equilibrium properties). The tensile strength of the different blends is practi-

cally the same at the 40% starch level. Figure 5(b) shows that there is a similar trend with the modulus, although the differences are less and confined to the 40–70% starch levels. The percent elongation is plotted in Figure 8 (error bars are omitted for the sake of clarity) and the different blends have similar values, except at a 40% starch level, where the 25% moisture blend displays a much higher elongation.

As shown in Table I, to a 40% starch level, both the 16 and 25% moisture level blends show a dispersed droplet morphology. However, the average particle size is much higher at the 16% moisture level (roughly 100 compared to 10 μm).³ Since the tensile strength and modulus are the same at this starch level, it appears that these properties are insensitive to the particle size in the 10–100 μm range. Similar results were seen for the case of granular cornstarch-filled PHEE.¹⁴ At the 50 and 60% starch level, elongated morphologies exist with the 25% moisture blends. Hence, the improvements in the tensile properties for the 25% moisture blends are related to the presence of fibrillar and laminar morphologies at these starch concentrations. It should be noted that the testing was performed in the same direction in which the elongated domains are oriented.

Figure 9 shows a comparison of the experimen-

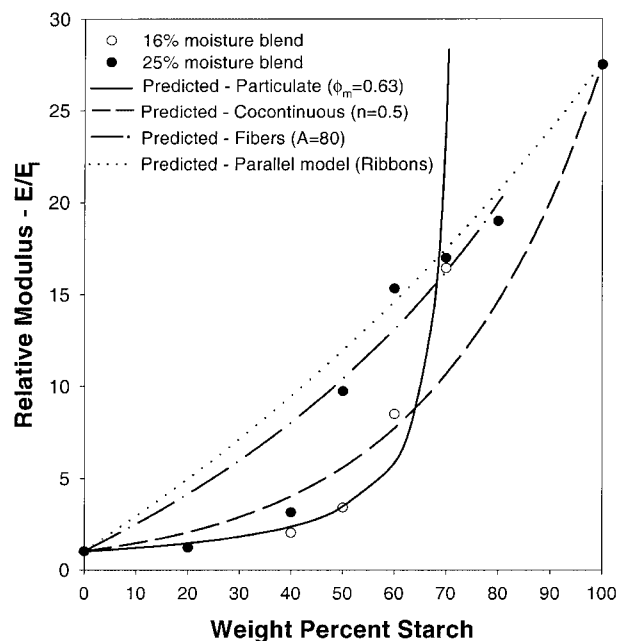


Figure 9 Comparison of morphological predictions and experimental data for blends processed at 16 and 25% moisture and conditioned to equilibrium at 50% RH.

tal modulus to the predictions based on the different morphologies [eqs. (1)–(3)] for 16 and 25% moisture blends conditioned to equilibrium at 50% RH. For the case of the spherical particles, ϕ_m was taken as 0.63, which is the theoretical random packing value and is also close to the value estimated for the case of cornstarch/PHEE composites.^{15,16} For the case of fibers/ribbons, ϕ_m was simply taken as 0.82, the value for random close packing of the aligned fibers. For the cocontinuity equation, n was arbitrarily chosen as 0.5. Figure 9 clearly shows that the experimental data for the 16% moisture blend closely follows the predictions of the dispersed droplet system. In contrast, the 25% blend follows the prediction for the particle model to a 40% starch level but falls closer to the predictions of fibers and ribbons in the 40–80% starch range.

The morphology of the blends is determined by the extrusion conditions, particularly, the moisture level. During conditioning, there is change in the water content of the two phases but the morphology remains fixed. This implies that, on conditioning, the shape factor A and the maximum packing fraction ϕ_{\max} are constant but the factor B would change since the modulus of both phases and, hence, the E_2/E_1 ratio is changing. It has been shown that the composite modulus is very sensitive to E_2/E_1 .^{6,17} It is possible that the effect of a changing moisture content can be examined indirectly using the E_2/E_1 ratio.

A complex combination of different morphologies is present in the 50–80% starch range for the 25% moisture blend. Instead of trying to calculate the possible contribution from each type of morphology, eq. (1) was used to describe the data in the entire concentration range. There are obvious simplifying assumptions and errors in this approach: It is not known how well this model describes the data for TPS blends, although it was shown by Willett¹⁷ that the above model does describe the modulus data for the case of cornstarch/PE composites containing the ethylene-coacrylic acid copolymer. Also, values for the maximum packing fraction for starch fibers are not known. With this approach, the change in morphology is simply represented through factor A . Hence, in principle, at one RH, eq. (1) can be used to determine A at different starch concentrations, and then using these values of $A = f(\phi)$, the modulus can be predicted at different RHs. Table II shows the fitted A values determined from the data for the case of the 25% moisture blends conditioned to equilibrium at 50% RH. It was as-

Table II Shape Factor A Estimated from the 25% Moisture Blends Conditioned to Equilibrium at 50% RH

Starch Concentration (% wt)	A
10–40	1.5
50	55
60	4
	(parallel model)
70	180
80	30

sumed that the spherical particle condition was valid for a starch concentration less than 40% by weight ($A = 1.5$). For concentrations in the 40–80% starch range, A was estimated from eq. (1). Although this is simply a fitting procedure, the trend shown is experimentally observed, with A (or elongation) increasing from 40 to 60% starch and then decreasing at 70 and 80% starch as cocontinuity sets in.

The results obtained from the above-mentioned procedure are illustrated in Figure 10(a), where the relative modulus (E/E_1) is plotted versus the starch concentration for the case of a 25% moisture blend conditioned to equilibrium at 50 and 73% RH. The prediction curve for the 73% RH case is estimated using the A values listed in Table II and the equilibrium modulus values for the pure components. There is reasonable agreement between the experimental data and the model predictions. In Figure 10(b), a similar shifting of the data is attempted for the case of the blends conditioned at 50% RH for 2 weeks. It is evident that the model overpredicts the experimental data in the 40–70% starch range. The 80% starch point is, however, fairly close to the prediction. The trouble in such an analysis is in the use of the component modulus values, since the composite modulus is very sensitive to E_2/E_1 . The T_g (-23°C) value of pure PHEE is similar to its value in the blends. Hence, the modulus based on the pure PHEE conditioned for 2 weeks describes well the condition of PHEE in the blend. However, for the case of TPS, a different situation exists: Pure TPS is essentially conditioned in 2 weeks but the starch in the blends is losing moisture at varying rates, depending on the blend concentration. This is evident from Figure 2, where, clearly, at 14 days, the starch phase in the 80% blend sample has lost much more moisture

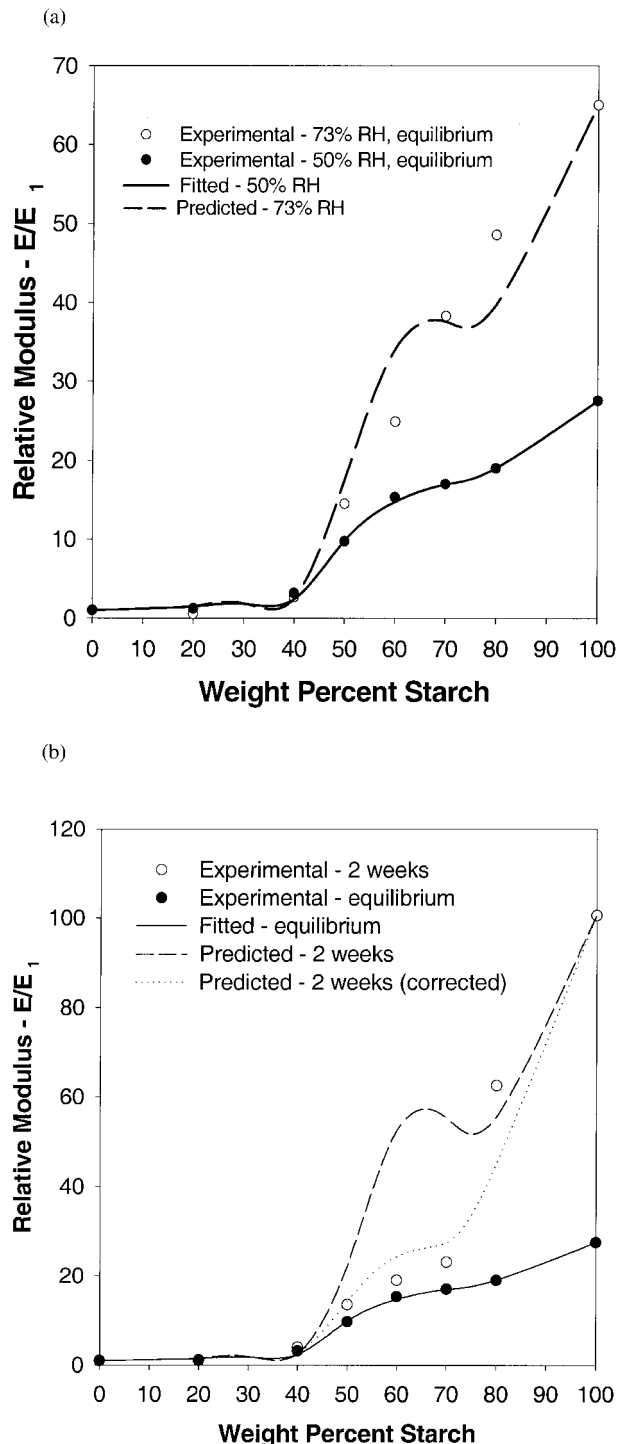


Figure 10 Comparison of predicted and experimental data for blends processed at 25% moisture (a) as a function of RH and (b) as a function of conditioning time.

than has the 20 or 50% blend sample. Hence, the modulus of the TPS phase in these blends is going to vary with the starch concentration. From Fig-

ure 2, the actual moisture content of TPS in the 50% blend is estimated to be 18% on a wet basis. This corresponds to a TPS modulus value of roughly 500 MPa. The corresponding value for the 80% starch blend is 13.5% moisture and the modulus can be interpolated to 700 MPa, assuming a linear relationship between the modulus and the moisture content.¹⁸ It is assumed that the moisture content of TPS is roughly 18% in the entire 40–70% blends. The corrected prediction line is shown in Figure 10(b) and is much closer to the actual experimental data. Hence, the properties can at least be roughly estimated at any given conditioning time if the kinetics of moisture exchange are known for each phase.

CONCLUSIONS

The morphology generated during processing is a strong function of the initial level of the plasticizer present. The blends processed at the higher moisture level showed a better tensile strength and modulus due to the presence of fibrillar and laminar morphologies which were oriented in the flow direction. The properties of the blends could be effectively represented by the particular morphology present in a given starch concentration range. If knowledge about the effect of the processing conditions on the morphology is available, the final mechanical properties can be effectively controlled.

The blend properties change with the RH and aging time due to the change in the moisture content of the component phases. It is theoretically possible to model the blend properties by the changing properties of the individual phases. The data could be shifted fairly well from one RH to another, under equilibrium conditions, but not from one aging time to another, owing to the different kinetics of moisture exchange at different blend concentrations. This situation can be improved by correcting to the actual moisture (and, hence, the modulus) condition.

This research was conducted under a Co-operative Research and Development Agreement (CRADA), No. 58-3K95-8-0634, between the Agricultural Research Service (ARS) and the Biotechnology Research and Development Corp. (BRDC). The authors wish to thank Andrew J. Thomas and Tim Bond for assistance in the extrusion work, Gary Grose for the X-ray diffraction analysis, and Dr. St. Lawrence for very useful discussions about the mechanical modeling.

REFERENCES

1. Shogren, R. L.; Fanta, G. F.; Doane, W. M. *Starch/Starke* 1993, 45, 276.
2. Van Soest, J. J. G. *Agro-Food-Ind Hi-Tec* 1997, 8, 17.
3. Walia, P. S.; Lawton, J. W.; Shogren, R. L.; Felker, F. C. *Polymer* 1999, 41, 8083.
4. Shogren, R. L. In *Biodegradable Polymers and Packaging*; Ching, C.; Kaplan, D. L.; Thomas, E. L., Eds.; Technomic: Lancaster, PA, 1993; pp 141–150.
5. St. Lawrence, S.; Willett, J. L.; Carriere, C., submitted for publication in *Polymer*.
6. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994.
7. Mang, M. N.; White, J. E. U.S. Patent 5 171 820, 1992.
8. Mang, M. N.; White, J. E.; Haag, A. P.; Kram, S. L.; Brown, C. N. Papers presented at the Chicago, IL, Meeting of ACS, 1995; Vol. 36, p 180.
9. Mang, M. N.; White, J. E.; Kram, S. L.; Bailey, R. E.; Swanson, P. E. *Proc ACS Div Polym Mater Sci Eng* 1997, 76, 412.
10. Rick, D. L.; Davis, J. W.; Lickly, T. D.; Mang, M. N. In *6th Annual Meeting of the BEDPS*, San Diego, 1997.
11. Willett, J. L. *Polym Prepr Div Polym Chem Proc, ACS Boston Meeting*, 1998, 39, 112.
12. Van Soest, J. J. G.; Vilegantart, J. F. G. *Trends Biotechnol* 1997, 15, 208.
13. Shogren, R. L.; Jasberg, B. K. *J Environ Polym Degrad* 1994, 2, 99.
14. Willett, J. L.; St. Lawrence, S.; Doane, W. M.; Mang, M. N.; White, J. E., submitted for publication in *J Appl Polym Sci*.
15. Willett, J. L., submitted for publication in *J Appl Polym Sci*.
16. Zhou, G.; Willett, J. L.; Carriere, C., submitted for publication in *Polym Eng Sci*.
17. Willett, J. L. *J Appl Polym Sci* 1994, 54, 1685.
18. Kirby, A. R.; Clark, S. A.; Parker, R.; Smith, A. C. *J Mater Sci* 1993, 28, 5937.