Mechanical Properties of LDPE/Granular Starch Composites*

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SYNOPSIS

The mechanical properties of composites of granular starch and low density polyethylene (PE) have been studied as functions of starch volume fraction ϕ, granule size, and presence of compatibilizer. Property–volume fraction relationships were interpreted using various theories of composite properties. The dependence of elongation ($\epsilon \sim \phi^{1/3}$) and tensile strength ($\sigma \sim \phi^{2/3}$) agree with theoretical predictions, although the proportionality constants are less negative than theoretical values. The addition of compatibilizer (ethylene-co-acrylic acid copolymer, EAA) did not significantly affect the elongation or tensile strength, but significantly increased the composite tensile modulus. The cornstarch/PE moduli could be described by the Kerner or Halpin-Tsai equations. Analysis of the composite moduli data using the Halpin-Tsai equation allowed the estimation of the modulus of granular starch. The value obtained, 15 GPa, is considerably greater than most unfilled synthetic polymers of commercial importance, but significantly lower than the modulus of cellulose. It is also greater than a previously reported value of 2.7 GPa. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Starch is a polysaccharide produced by many plants as a storage polymer. It is comprised of glucose monomers joined by α-(1-4) linkages. In its native form, starch is usually stored in granules. The average granule size varies from source to source; rice starch granules are roughly 3 μ in diameter, while potato starch granules are about 35 μ in diameter. Corn starch, the major form of starch produced in the U.S., has an average granule size of approximately 10 μ.[1]

The use of granular starch as a filler for rubber and plastics was investigated by the U.S. Department of Agriculture's Northern Regional Research Center during the 1970s.[2] Independent work by Griffin on starch/polyethylene blends stimulated interest in the use of starch as a biodegradable additive to PE resins.[3] Various starch/resin formulations have also been reported,[4-8] and some of these are commercially available. Much of this work focused on the use of compatibilizers to improve the composite properties by improving the adhesion between the resin and the starch granules.

The addition of granular starch to PE follows the general trend of filler effects on polymer properties. Elongation and tensile strength decrease as the starch content increases, and the modulus increases due to the stiffening effect of the granules. It has been reported that the reduction in elongation and tensile strength in starch/PE composites increases with increasing granule size.[5] Jane et al.[4] reported that the addition of high molecular weight oxidized PE (OPE) improved the tensile strength and elongation of starch/PE composites with 15% starch content. The ratios of OPE/starch ranged from 0.30 to 0.50. It was suggested that ester formation and hydrogen bonding between carboxyl groups in the OPE and hydroxyl groups on the starch granule surface were responsible for the improvement in properties.

Despite the interest in starch as a biodegradable filler, little has been done to analyze the properties

of starch/synthetic polymer composites in terms of theories of composite properties. The properties of linear low density PE blown films with starch contents up to 25% have been reported,[5,8] but the results were not interpreted using any composite models. In fact, the models discussed below are not directly applicable to blown films due to the high degree of biaxial orientation resulting from the film blowing process. Schroeter and Hobelsberger[6] studied composites of granular starch and polycaprolactone (PCL). They evaluated the composite modulus using a linear additivity model; their results will be examined in the Discussion section. Fritz and Widmann[7] reported tensile strength data for composites of starch with PE or polypropylene (PP); surface treatment of the starch with silane coupling agents improved the tensile strength. Only the results of Schroeter and Hobelsberger were discussed in terms of theories of composite properties.

The objective of this work is to measure the elongation, tensile strength, and tensile modulus of starch/LDPE composites. The effects of starch volume fraction, granule size, and compatibilizer are presented. Data are interpreted using theories developed to describe the mechanical properties of composites.

Mechanical Properties of Composites

Several theories of the dependence of composite properties on filler volume fraction ϕ and geometry have been developed. In a simple model based on the Mullins effect in filled rubber, Nielsen[9-11] derived the following relationship between elongation and ϕ:

$$\epsilon_c = \epsilon_0 (1 - \Phi^{1/3}) \tag{1}$$

where ϵ_c is the elongation to break (or yield) of the composite and ϵ_0 is the corresponding elongation of the unfilled polymer. Perfect adhesion between polymer matrix and filler is assumed in this model. The fundamental mechanism of this model is the requirement that the polymer matrix confined between two particles must undergo a larger strain than the macroscopic strain because the rigid filler particles do not elongate. This material will then fail (or yield) at a lower macroscopic strain than the same polymer without particles. Equation (1) has been shown to describe the behavior of some glass bead-filled composites.[12,13]

Nicolais and Narkis[14] developed a geometric model for the tensile (yield) strength σ of a composite with "uniformly" distributed spherical filler particles of equal radius:

$$\sigma_c = \sigma_0 (1 - 1.21\phi^{2/3}) \tag{2}$$

The subscripts c and 0 represent the composite and the matrix polymer, respectively. This model is based on the assumption that the tensile strength decrease is due to the reduction in effective cross-section area caused by the spherical filler particles. No adhesion between the matrix and the filler particles is assumed. Because the applied stress is not transferred to the rigid filler particles, the actual stress in the polymer matrix is higher due to the reduction in load-bearing surface area. Several composite systems have been found to follow Eq. (2).[15,16] More complex models that incorporate varying degrees of adhesion and stress concentration effects have been developed.[9,10] Equation (2) has been generalized by Nielsen to the following form:

$$\sigma_c = \sigma_0 \left(1 - \left(\frac{\phi}{\phi_m} \right)^{2/3} \right) \tag{3}$$

where ϕ_m is the maximum volume fraction the filler can obtain due to packing considerations.[11] This generalization was suggested because Eq. (2) does not account for particle size distribution effects. Because smaller spheres are able to fill the interstices between larger spheres, ϕ_m can be greater than that calculated for uniform size spheres, but will always be less than 1. The factor 1.21 in Eq. (2) corresponds to a ϕ_m of 0.75, close to the value of 0.74 for either hexagonal close packing or face centered cubic packing of uniform spheres. Slopes of Eq. (2), which are different than 1.21, may reflect not only adhesion effects but also particle size distribution effects. For spherical particles, ϕ_m is in the range 0.5 to 0.75, corresponding to slopes in the range 1.6 to 1.21.

Various models have been proposed to describe the effect of filler particles on modulus.[10,11,16] The Kerner equation has seen widespread use in describing the modulus of particle-filled composites. Kerner's derivation is based on the calculation of the shear modulus and bulk modulus of a macroscopically isotropic and homogeneous composite, and can be used to describe the bulk, shear, or elastic (Young's) moduli of filled composites.[11] For systems in which the filler is much more rigid than the matrix, the Kerner equation can be simplified to the form

$$E = E_0 \left[1 + \left(\frac{\phi}{1 - \phi} \right) \left\{ \frac{15(1 - \nu)}{(8 - 10\nu)} \right\} \right] \tag{4}$$

E is the modulus of the composite, E_0 is the matrix modulus, ϕ is the volume fraction of filler, and ν is Poisson's ratio of the matrix.

The Halpin-Tsai equation provides another description of the effect of filler particles on modulus.[11,16,17] The equation has the general form

$$E = E_0\left\{\frac{1 + \zeta\eta\phi}{1 - \eta\phi}\right\} \tag{5}$$

where

$$\eta = \frac{R - 1}{R + \zeta} \tag{6}$$

ζ is a measure of the reinforcement geometry and is a function of the loading conditions.[17] R is the ratio of the filler modulus to the matrix modulus. For the case of spherical filler particles one has

$$\zeta = \frac{7 - 5\nu}{8 - 10\nu} \tag{7}$$

Halpin and Kardos have pointed out that the Halpin-Tsai equation, which also holds for different moduli, is an approximate form of Kerner's equation.[17]

EXPERIMENTAL DETAILS

The starches used in this study were unmodified cornstarch (CS) (Buffalo 3401, CPC International) and unmodified potato starch (PS) (A. E. Staley). Both starches were vacuum dried to a moisture content of less than 1% before blending and processing. PE was Petrothene 345-196 (Quantum Chemical), a low-density PE with a Melt Index of 1.8 g/10 min. Primacor 5981 (Dow), a copolymer of ethylene and acrylic acid (EAA) with approximately 20% (w/w) acrylic acid, and a Melt Index of 300 g/10 min, was used as a compatibilizer. Both resins were obtained in the form of pellets.

To improve dry blending, the resin pellets were cryogenically ground into powders using a Retsch mill. Appropriate amounts of resin and starch were blended to give composites with 10%, 20%, 30%, and 40% starch by weight. When EAA was incorporated, it was added at a level of 5% based on the starch. In this manner, the starch/EAA ratio was constant for each formula; the maximum EAA content was 2% of the total solids. Assuming all of the EAA migrated to the starch/PE interface, this level

of EAA would provide a coating approximately 0.15 μ thick on the granule surface.

Weight fractions were converted to volume fractions using the relation

$$\phi_i = \frac{\omega_i / \rho_i}{\Sigma\omega_i / \rho_i} \tag{8}$$

where ω_i and ρ_i are the weight fraction and density of component i in the composite. Densities of 1.4 g/cm^3 for starch and 0.92 g/cm^3 for PE were use for the calculation of volume fractions.

The formulations were compounded into pellets with a Brabender PL 2000 torque rheometer equipped with a single screw extruder barrel (19 mm diameter, 30/1 L/D). A two-stage screw with a fluted mixing section oriented at 45° to the screw axis (13 to 18 L/D) and slotted flights in the second metering section was used. The temperature profile was 130/135/140/140°C from the conveying section to the die. Screw speed was 40 rpm. The melt was extruded through a single strand die, air cooled, and pelletized. Pellets were kept in sealed plastics bags until molding to minimize moisture regain from the atmosphere.

Tensile specimens (ASTM D638, Type V) were molded on a Rabit HY-4 ram-type injection molding machine (Mining and Chemical Products Corp.) with a single cavity mold. The barrel temperature was 150°C and the probe temperature was 150–155°C. Cycle times were approximately 20 s. The mold temperature was maintained by a Grant LTD 20 circulating fluid thermal control unit set at 70°C. Plunger piston pressures ranged from about 500 psi to 900 psi, depending on the starch content. No mold release agent was used.

Tensile tests were performed on an Instron model 4201 testing system with a computer control and data acquisition/analysis package. Samples were strained at a rate of 200%/min at 22°C and 50% relative humidity, with a gage length of 10 mm. A minimum of five samples were tested for each formulation, and average values of the elongation to break, tensile strength, and elastic modulus were calculated. The elastic modulus (hereinafter referred to as the modulus) was determined from the slope of the linear portion of the stress–strain curves; the tensile strength is the maximum load divided by the original cross-section area. Coefficients of variation (the ratio of the standard deviation to the mean) were typically between 0.05 and 0.10. Before testing, samples were conditioned at 20%, 50%, or 80% relative humidity for 28 days.

RESULTS

Cornstarch Composites

Because of its hygroscopic nature, starch absorbs moisture from the atmosphere until equilibrium is reached. The moisture content of starch at 50% RH and 22°C is approximately 12%.[18] Because water is an effective plasticizer for starch, the equilibrium moisture content would be expected to affect the mechanical properties. However, it has been shown that the equilibration times of molded starch/polyolefin composites is on the order of months, even when immersed in water.[19] Therefore, only the results after 28 days of conditioning will be presented. No significant changes in elongation and tensile strength were observed between the 7 days and 28 days conditioning time; the modulus values were slightly higher after 28 days conditioning.

Figure 1 shows the reduction in elongation to break of the CS/PE composites. The elongation is normalized to the elongation of the PE, and plotted against $\phi^{1/3}$ according to Eq. (1). The results for blends without and with EAA agree well with the $\phi^{1/3}$ prediction of Eq. (1). The relative humidity during conditioning has little effect on the elongation. The presence of EAA has no significant effect on the elongation.

The solid line in Figure 1 is the prediction of Eq. (1). It is seen that the experimental values fall on a line with a slope that is less negative than the
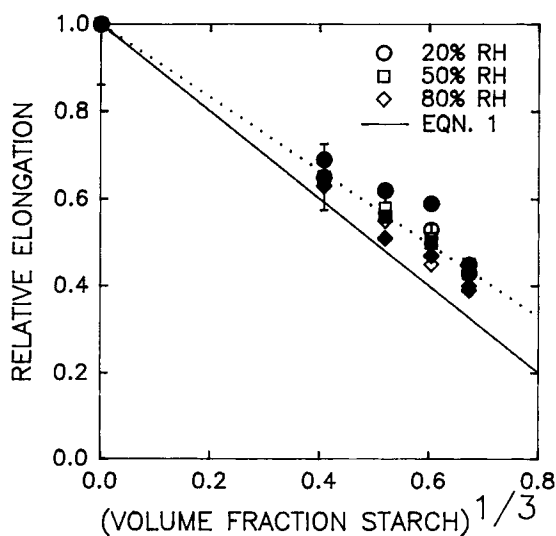

Figure 2 Relative tensile strength of cornstarch/PE composites at 20% RH, 50% RH, and 80% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.

predicted value of -1. The dotted line is the least squares fit obtained by averaging all six sets of data at each value of ϕ. Error bars are shown for the data obtained at 50% RH for CS/PE composites with EAA, and are representative of all the data sets. The derivation of Eq. (1) assumes perfect adhesion between the matrix and filler. The reduced slope seen in Figure 1 may reflect weak or imperfect adhesion between the PE and the starch granule surface. Given the expected high surface energy between the hydrophobic PE and the hydrophilic starch, one would expect a low degree of adhesion.

Tensile strength results for the cornstarch composites are shown in Figure 2. The results are normalized to the PE values and plotted in accordance with Eqs. (2) and (3); error bars and the least squares fit were determined as in Figure 1. As with the elongation data, neither relative humidity nor EAA significantly affect the results. The data are linear with respect to $\phi^{2/3}$, but have slopes that are less negative than the value of -1.21 predicted by Eq. (2).

The derivation of Eqs. (2) and (3) assumes little or no adhesion between the matrix and filler. If perfect adhesion were present, then the loading stresses would be transferred to the filler phase, and no reduction in effective surface area would result. The slope seen in Figure 2 suggests that some degree of adhesion exists between the LDPE and the cornstarch, although it is not sufficient to prevent the area reduction mechanism from reducing the tensile

Figure 1 Relative elongation of cornstarch/PE composites at 20% RH, 50% RH, and 80% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.
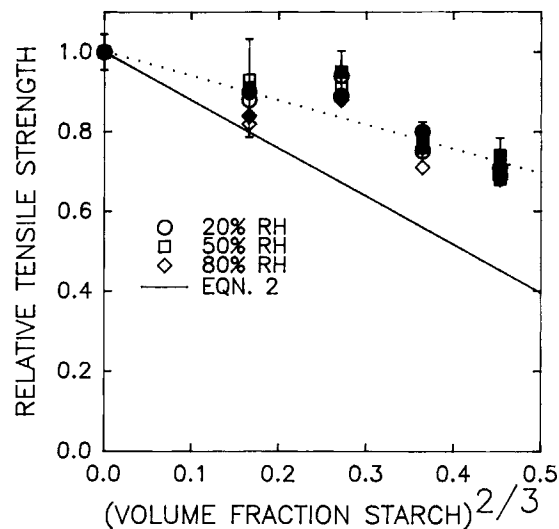
strength. Particle size distribution effects on the slope from Figure 2 will be presented in the Discussion section.

Modulus data are shown in Figure 3; a plot of the Kerner equation [Eq. (4)] is also included. Because the cornstarch is stiffer than the PE, a large increase in modulus is observed as the starch content increases. No significant changes due to RH are observed, but the presence of EAA profoundly influences the modulus, especially at higher starch loadings. Product literature for the EAA lists representative modulus values of approximately 20 MPa, and extruded blends of the PE and EAA show a decrease in modulus as the EAA content increases (unpublished results). Therefore, it is apparent that the modulus increase observed upon addition of EAA is due to improved adhesion between the starch and the matrix, and not a stiffening of the matrix by the EAA. This result indicates that the EAA migrates to the CS/PE interface during melt processing. Note that the EAA:CS ratio of 0.05 is much lower than the OPE:starch ratio reported by Jane et al.[4]

The agreement between the modulus data of composites with EAA and the Kerner equation suggest that the starch modulus is considerably greater than the PE modulus. Because EAA does not improve the elongation and tensile strength, the improvement in adhesion must be effective only during the initial (elastic) stage of loading, where the modulus is measured. Above a critical stress, debonding probably occurs at the starch/resin interface and
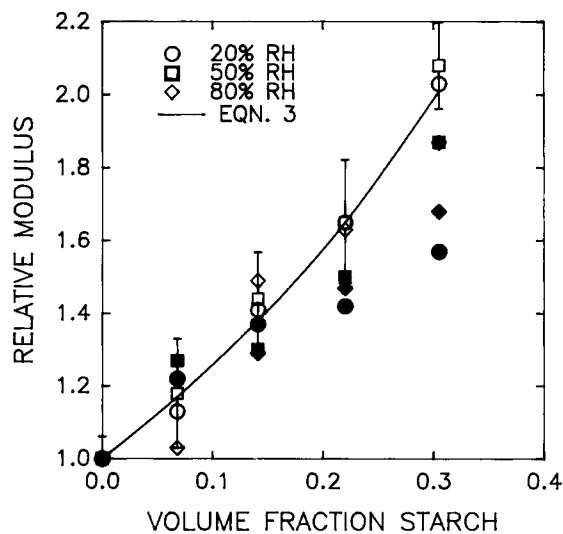

Figure 3 Relative modulus of cornstarch/PE composites at 20% RH, 50% RH, and 80% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.
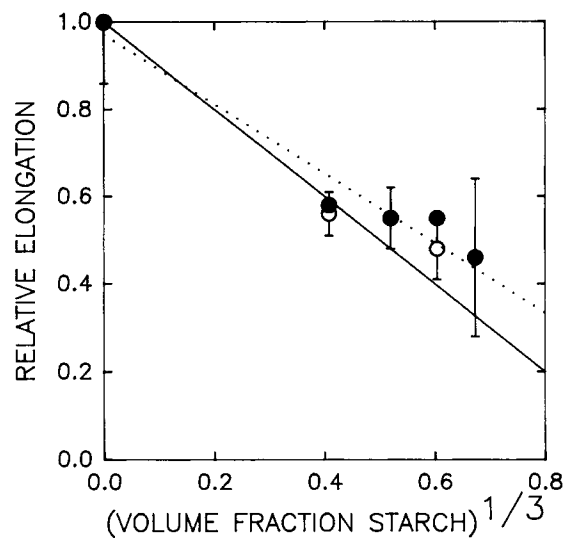

Figure 4 Relative elongation of potato starch/PE composites at 50% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.

the EAA has no influence on properties after this point.

Potato Starch Composites

Elongation data after 28 days at 50% RH for composites with potato starch are shown in Figure 4. The dotted line through the data is the least squares fit to the average of samples with and without EAA; the intercept is 0.97. As with the cornstarch composites, the relative elongation decreases with $\phi^{1/3}$ according to Eq. (1) with a slope that is less negative than the theoretical prediction of -1. The addition of EAA has no significant effect on elongation of the composites, also in agreement with the cornstarch materials.

The relative tensile strengths after 28 days at 50% RH are shown in Figure 5. As before, the dotted line through the data is the least squares fit to the average values. The loss in tensile strength with starch content follows the $\phi^{2/3}$ prediction of Eq. (2), but with a slope that is less negative than the theoretical value of -1.21. EAA has no significant effect on the tensile strength of the potato starch composites.

In contrast to the elongation and tensile strength data, the presence of EAA significantly increases the modulus of the potato starch/PE composites, as shown in Figure 6. This effect is more pronounced at higher starch loadings. Note, however, that the modulus values fall below the prediction of the Kerner equation.

In general, the potato starch/PE composites and the cornstarch/PE composites were similar in behavior.

DISCUSSION

Elongation and Tensile Strength

The elongation and tensile strength data follow the predicted behavior with respect to filler volume fraction ϕ [Eqs. (1), (2), and (3)]. In each case, however, the slopes of the lines are less negative than the predicted values. For the elongation, the observed slopes were -0.84 (CS/PE) and -0.78 (PS/PE), compared to the predicted value of -1.00 from Eq. (1). The observed slopes for the relative tensile strength were -0.64 (CS/PE) and -0.78 (PS/PE), compared to the predicted value of -1.21 [see Eq. (2)].

Similar tensile strength results were observed by Fritz and Widmann in starch/PE and starch/PP composites without compatibilizer.[7] When the relative tensile strength was plotted against $\phi^{2/3}$, the slopes were -0.49 for the PE composites and -1.04 for the PP composites. They also report that the addition of a silane coupling agent to ethylene-co-vinyl acetate with 40% cornstarch increases the load at 50% elongation and decreases the elongation to break. These results are in agreement with the predictions of Eqs. (1) and (2), and illustrate the effect of particle/matrix adhesion on mechanical properties.
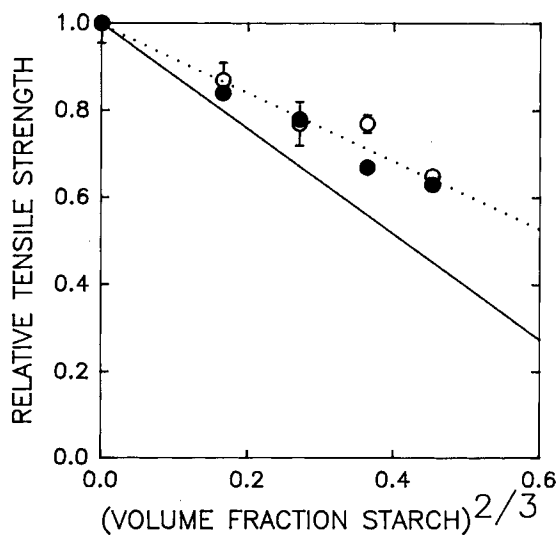

Figure 5   Relative tensile strength of potato starch/PE composites at 50% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.
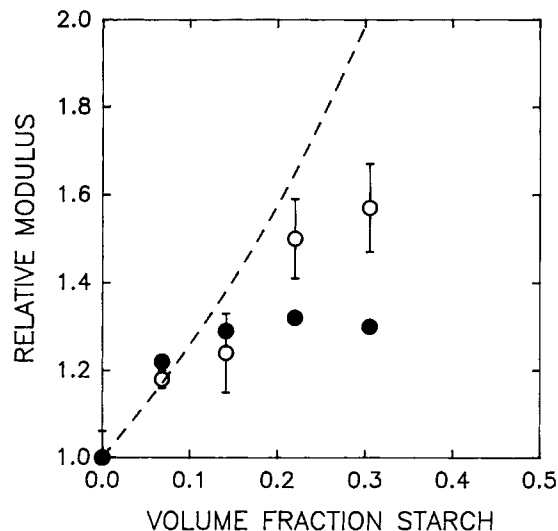

Figure 6   Relative modulus of potato starch/PE composites at 50% RH. Filled symbols: no EAA; open symbols: with EAA. Conditioning time: 28 days.

Interface adhesion effects have been observed in ABS composites filled with glass beads.[12] Poor adhesion was promoted by solvent cleaning the bead surfaces before use; good adhesion was promoted by use of a coupling agent. When the relative elongation was plotted against $\phi^{1/3}$, the composites with poor adhesion had a lower slope (higher elongation) than those with good adhesion, in agreement with the assumption of perfect adhesion inherent in Eq. (1). The reduced tensile strength/$\phi^{2/3}$ slope was lower (i.e., greater tensile strength) in the case of good adhesion. This result agrees with the mechanism of no adhesion assumed in the derivation of Eq. (2). Similar adhesion effects were observed in epoxy/glass bead composites studied by Kenyon and Duffy.[13] These results indicate that improved particle–matrix adhesion increases the tensile strength but decreases the elongation.

Using Eq. (3), the lower tensile strength slopes can be interpreted in terms of particle size distribution effects. Slopes lower in magnitude than 1.21 would suggest a maximum packing fraction greater than 0.75. The use of ϕ_m to interpret the slope has at least two limitations. First, as mentioned above, reasonable values of ϕ_m constrain the slope to the range of 1.2 to 1.6. Slopes less than 1 imply maximum packing fractions greater than 1, which are physically impossible. Second, the packing fraction of starch can be estimated from bulk density and specific gravity data. Starch has a bulk density of approximately 0.65 g/cm^3, while the particle density is 1.4 g/cm^3. These values suggest the packing frac-

tion of starch is approximately 0.45; this would give a slope of 1.7, much greater than the observed slopes. Therefore, it appears that adhesion has a greater impact on the tensile strength than particle size distribution in these composites.

Comparison of the starch/PE results to those discussed above suggests that the adhesion between the PE and the granule surface is intermediate between no adhesion and good adhesion. This result is somewhat surprising, given the hydrophobic nature of the PE matrix and the hydrophilic surface of the starch granule.

Modulus

Although EAA has no significant effect on elongation and tensile strength, it significantly enhances the stiffness of the starch/PE blends. Because EAA has a lower modulus than the PE, this effect must be due to enhanced adhesion at the starch/PE interface. Nielsen[11] has pointed out that "good adhesion is not important as long as the frictional forces between the phases are not exceeded by the applied external stresses." It, therefore, appears that the EAA improves adhesion, or reduces slippage at the PE/granule interface, during the initial stages of loading. Once a critical stress is exceeded, the differences between blends with and without EAA are diminished as slippage or debonding occur at the PE/starch interface.

In Figure 3, it is seen that the Kerner equation [Eq. (4)] does not fit the CS/PE modulus data well when no EAA is present. The addition of EAA increases the modulus values to the extent that the Kerner equation is an adequate fit to the data. This result indicates that the modulus of the starch is considerably higher than the PE modulus of 64 MPa, because the approximate form of Kerner [Eq. (4)] is derived on the assumption that $E_f >> E_m$.

The Halpin-Tsai equation [Eq. (5)] provides a method of estimating the modulus of the starch granules, because the term η contains R, the ratio of the filler modulus to the matrix modulus. Therefore, fitting the data of Figures 3 and 6 to Eq. (5) allows one to extract a value of the starch modulus.

Two factors must be considered in the use of Eq. (5) to determine the starch modulus. The first is the sensitivity of the Halpin-Tsai equation to the value of R. This effect is illustrated in Figure 7. As R increases from 2 to 32, the composite modulus at a given value of ϕ increases rapidly. For $R > 32$, the rate of increase diminishes; there is less than 1% difference between the values of Eq. (5) when R increases from 128 to infinity. Therefore, if R ex-
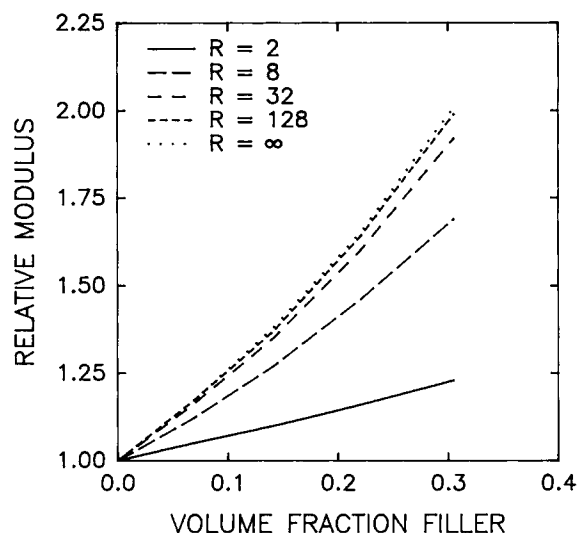

Figure 7 Effect of changing the modulus ratio R in the Halpin-Tsai equation. Poisson's ratio = 0.50.

ceeds approximately 30, the Halpin-Tsai equation can only be used to establish an effective lower limit on the filler modulus.

The second factor is due to the presence of Poisson's ratio ν in Eq. (5). This effect is illustrated in Figure 8 for spherical filler particles. When ν is increased from the experimentally determined value of 0.43 for LDPE[20] to 0.5 with R constant, the calculated modulus increases. The relative change is small at low values of R, and increases to approximately 5% at large R. The effect of increasing ν at large values of R is the same as increasing R at constant ν.

The following procedure was used to calculate the modulus of starch granules. A value of Poisson's ratio ν of 0.43 was used, taken from data for LDPE from ref. 20; this fixed the parameter ζ of Eq. (5) at 1.31 when cornstarch, with essentially spherical particles, was the filler. Equation (5) was fitted to the experimental values of the composite relative modulus using the curve fit routine in SigmaPlot scientific graphing software, and a value of η was given by the curve fit.

Using the calculated values of η and Eq. (6), the cornstarch granule modulus was calculated to be 710 MPa without EAA and 15 GPa with EAA. The negligible effect of relative humidity on the composite moduli (see Fig. 3) suggests moisture sorption by the starch granules is not the source of this large discrepancy. In addition, the presence of EAA on the starch particle surface should not affect the granule modulus. Therefore, the 15 GPa value for the granule modulus seems to be a more realistic

estimate. This result demonstrates the role of EAA in improving adhesion at the starch/PE interface during the initial stages of deformation, and the effect of adhesion on mechanical properties.

The calculated granule modulus of 15 GPa is greater than the moduli of most unfilled commercial polymers ($E \approx 1$ GPa to 4 GPa). It is less than reported values of modulus of cellulose fibers, which range from 128 to 173 GPa for cellulose I and 48 to 88 GPa for cellulose II.[21,22] The difference between the two forms of cellulose has been attributed to number of intramolecular hydrogen bonds between monomers.

Schroeter and Hobelsberger[6] calculated the modulus of starch by analyzing the properties of blends of potato starch and epoxy resin or polycaprolactone (PCL) at a strain rate of 1%/min. Although the initial moisture content of the starch was reported, the starch was not dried before use, and the moisture content after the composite preparation was not reported. They assumed a linear additivity of properties with respect to ϕ. The starch/PCL composites showed a steady increase in modulus with starch content, although the starch/epoxy composites exhibited no change in modulus with starch content. They calculated modulus values of 2.73 GPa and 2.66 GPa, respectively, and concluded that the modulus of starch under these conditions was 2.7 GPa.

Compared with the results obtained in this work, the value of 2.7 GPa appears to be too low. Although the modulus determined by Schroeter and Hobelsberger would be expected to be lower due to moisture content and strain rate differences, there are other reasons for this assertion. Despite the definite upward curvature of the reduced modulus plot, predicted by both the Kerner and Halpin-Tsai equations, they used a linear fit. In fact, the Kerner equation provides a good fit to the starch/PCL data, indicating the starch modulus is much larger than that of the PCL (i.e., $R > 30$). In addition, their assumption of linear additivity of properties is inappropriate for the starch/PCL composites. Linear additivity is applicable under the condition $\zeta \rightarrow \infty$ [see Eq. (5)]; this assumption is valid only for the case of longitudinal modulus in composites with extremely long fibers.[11,16] For the case of $\zeta = \infty$, Eq. (5) yields the linear mixing equation. For spherical filler particles, the appropriate form of ζ is given by Eq. (7).

The assumption of linear mixing behavior also ignores nonlinear phase inversion effects that occur at high filler contents. Phase inversion requires the use of coupled equations (Kerner or Halpin-Tsai) to describe the full composition range.[11] Hsu and
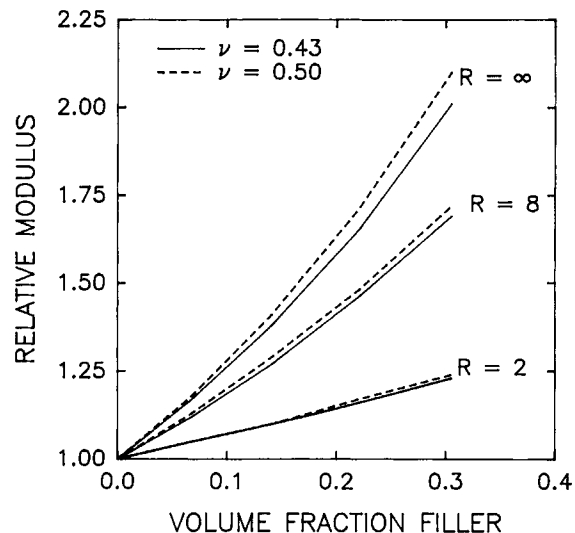

Figure 8 Effect of changing Poisson's ratio ν in the Halpin-Tsai equation at different values of the modulus ratio R.

Wu[23] have shown that percolation effects introduce nonlinearity into the modulus behavior of polymer blends, and Peanasky et al.[24] have shown that percolation effects are important in determining the properties of starch/PE blends. Percolation theory has been used to describe the modulus of polyepichlorohydrin filled with either glass beads or wollastonite.[25] Because of percolation effects, extrapolating the reduced modulus line to pure starch yields a starch modulus value lower than the actual value. The curvature in the reduced modulus plot indicates the importance of accounting for the nonlinear percolation effects.

The modulus of potato starch granules can be calculated with the Halpin-Tsai equation using the data of Schroeter and Hoebelsberger.[6] Because potato starch granules are oval in shape, a value of ζ other than Eq. (7) must be used. Nielsen has discussed the dependence of ζ on filler aspect ratio.[11] When Eq. (5) was fitted to the starch/PCL composite data, best fits were obtained when ζ was in the range of 1.8 to 2.0. The corresponding modulus values were 11.9 GPa to 16.8 GPa, which agree well with the value for cornstarch determined from the PE composites. ζ values of 1.8 to 2.0 correspond to aspect ratios of approximately 2 to 3, which are not unreasonable for potato starch granules.[26]

Figure 9 shows the starch/PCL modulus data of ref. 20 plotted according to Eq. (5) with a $\zeta = 1.9$ and $E_{st} = 14.0$ GPa. If the Schroeter and Hoebelsberger value of 2.7 GPa is used for the starch modulus, with $\zeta = 1.9$, the calculated curve falls well
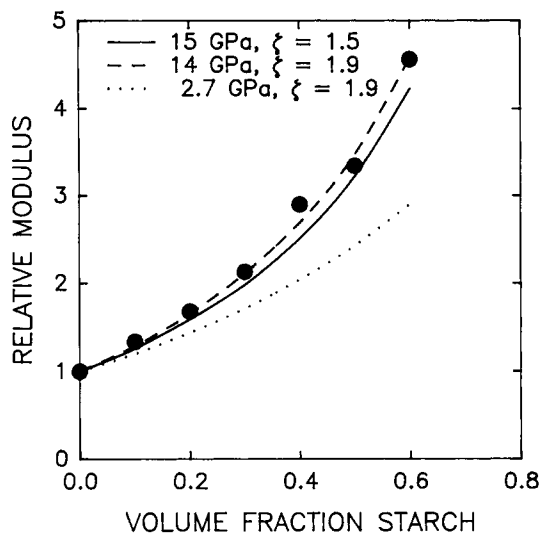
Figure 9   Relative modulus data of potato starch/polycaprolactone composites.[30] Curves are calculated using the Halpin-Tsai equation.

below the data points (dotted line). When the value of 15 GPa determined for cornstarch is used, with ζ = 1.5 (Poisson's ratio = 0.5), the calculated curve describes the data much better (solid line). These results support the assertion that a modulus value of 2.7 GPa is too low for granular starch, and illustrate the importance of the form factor when using the Halpin-Tsai equation to calculate filler modulus values.

Because the starch granule contains both amorphous and crystalline regions,[18] the calculated granule moduli are averages reflecting the contributions of each phase. Inasmuch as cellulose has relatively little branching, and is more crystalline than starch, it is not surprising that the modulus of starch determined in this work is less than that of cellulose. Chain packing differences may also play a role in the modulus difference. In cellulose I and II, the chains are arranged in sheets.[27] There is considerable evidence that in native starch, the chains are arranged in double helices in the crystallites regions of the granules.[18] Regardless of the differences between cellulose and starch crystalline structure, the hydrogen bonding in the starch granule gives it a much higher modulus than semicrystalline polymers such as polyethylene terphthalate (2–4 GPa) and polyamide 6,6 (1–3 GPa) which have less (if any) hydrogen bonding.

Particle Size Effects

Although the particle size does not appear in the Eqs. (1–4), it is well known that particle size influ-

ences composite properties.[10,11,28] As the particle size decreases, the yield strength, ultimate tensile strength, and modulus reinforcement increase at constant filler content. Alter[28] has reported decreases in the elongation at yield or break as the particle size decreases, while Nielsen presents data that show the opposite trend.[11] The particle sizes in Alter's work ranged from 0.02 to 0.20 microns, while the particle sizes reported by Nielsen range from 33 to 480 microns. Potato starch granules typically have an average diameter of 35 microns, about three times the diameter of cornstarch granules. Lim et al.[5] have shown that the elongation and tensile strength of LLDPE blown films with granular starch decrease as the average granule diameter increases. Because the starch particle diameters are the same order of magnitude as the film thicknesses studied by Lim et al., particle size effects may be more significant in thin films than in the thicker cross section moldings used in this work.

The effects of granule size on elongation, tensile strength, and modulus are shown in Figures 10, 11, and 12, respectively. The larger diameter of the potato starch has no effect on relative elongation when compared to cornstarch (Fig. 10). On the other hand, Figure 11 shows that the potato starch composites have tensile strengths significantly lower than those of the cornstarch composites. This effect of particle size on tensile strength is similar to that reported by Nielsen,[11] Alter,[28] and Lim et al.[5] The tensile strength of granular starch/PE composites is more sensitive to granule size effects than the elongation.
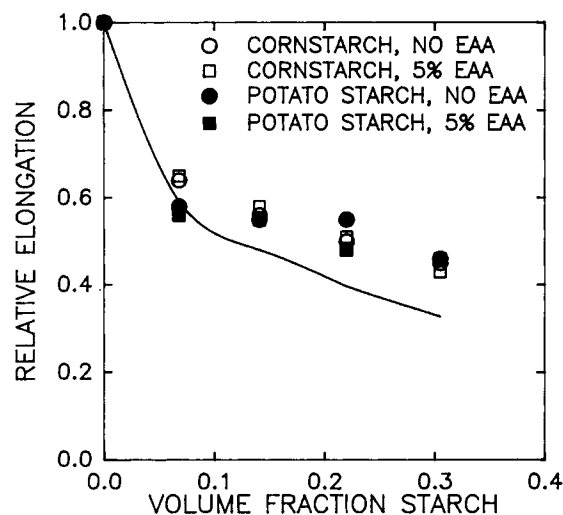

Figure 10   Particle size effect on the relative elongation of starch/PE composites. Conditioning time: 28 days at 50% RH. See Figures 1 and 4 for error bars.

This discrepancy can be rationalized as follows. The Griffith model predicts that crack growth will occur in a sample with an internal flaw of length 2 h when the stress σ exceeds a critical value given by

$$\sigma = \left(\frac{2E\gamma}{\pi h}\right)^{1/2} \tag{9}$$

where E is the modulus and γ is the surface energy. When the applied stress exceeds this value, the stored elastic energy is released as crack growth proceeds. If the matrix debonds from the starch granules, the result is a void approximately the size of the granule. Because the potato starch granules are larger than the cornstarch granules, larger voids will result after debonding. Therefore, crack growth will occur at a lower stress in the potato starch composites. On the other hand, the elongation will not be affected as much because debonding relieves the mechanism assumed in Eq. (1).

The relative modulus of the composites are shown in Figure 12. The modulus behavior is similar to the tensile strength; at a given starch content, the cornstarch composite has a greater modulus than the potato starch modulus. Similar behavior was observed by Alter[28] for PE, styrene-butadiene rubber, and natural rubber composites with mineral fillers.

Granule modulus values calculated from the potato starch/PE composites were 450 MPa and 220 MPa with and without EAA, respectively. The potato starch granule modulus with EAA is considerably less than the values calculated above for corn-
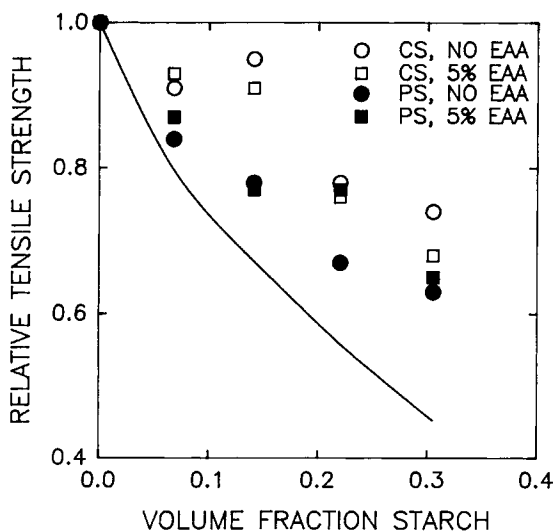

Figure 12 Particle size effect on the relative modulus of starch/PE composites. Conditioning time: 28 days at 50% RH. See Figures 3 and 6 for error bars.

starch and that calculated from potato starch/PCL composite data of ref. 20. This lower value may reflect a lower degree of adhesion relative to the cornstarch in PE. Potato starch contains anionic phosphate groups, which may alter the adhesion of the EAA to the granule surface. The substantial difference between PE and PCL data suggests the degree of adhesion between matrix and filler is crucial in the reinforcing effect of the filler. Another possible explanation of the lower value may be the increased surface area of the ellipsoidal potato starch particles. Because these particles have greater surface area than the more spherical cornstarch particles, the layer of EAA will be thinner. It may be that a critical compatibilizer thickness layer is necessary for adequate adhesion, and the EAA layer on the potato starch granules falls below this value.

CONCLUSION

The mechanical properties of starch/PE composites were measured as a function of starch volume fraction ϕ, starch particle type and size, and presence or absence of compatibilizer. Results were interpreted in terms of theories developed to describe the elongation, tensile strength, and modulus of filled composites. The elongation and tensile strength decreased with increasing ϕ in agreement with theoretical predictions, although the proportionality constants were lower than predicted. The composite modulus increased with increasing ϕ. The addition

Figure 11 Particle size effect on the relative tensile strength of starch/PE composites. Conditioning time: 28 days at 50% RH. See Figures 2 and 5 for error bars.
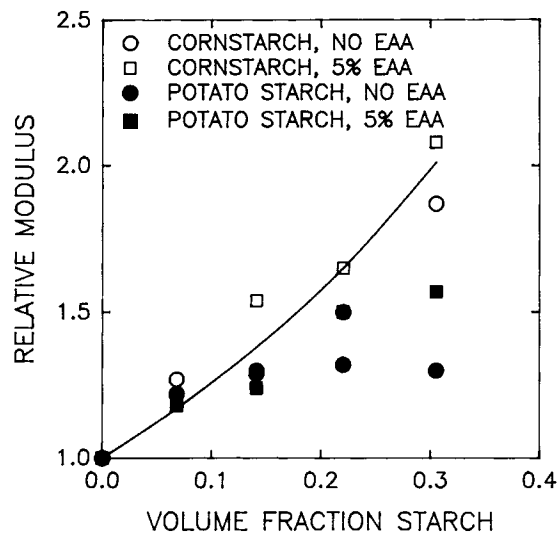
of EAA compatibilizer had no effect on elongation and tensile strength, but significantly increased the composite modulus. Composites with potato starch, with larger particles than cornstarch, had lower tensile strengths and moduli than corresponding cornstarch/PE composites; particle size had no effect on elongation. A cornstarch granule modulus value of 15 GPa was calculated from composites with EAA. Analysis of literature data for the modulus of potato starch/polycaprolactone composites yielded a modulus range of 12 GPa to 16 GPa, in good agreement with the cornstarch value. The calculated starch moduli are approximately one-fourth the value for cellulose II, and are 5–10 times greater than values for semicrystalline polymers such as PET and polyamide 6,6.

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