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Effect of moisture content on tensile properties of starch/poly(hydroxyester ether) composite materials[☆]

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Abstract

The effect of moisture content on the mechanical properties of starch/poly(hydroxyester ether) (PHEE) composite materials has been characterized. Cornstarch with either 1 or 10% moisture content was extruded with PHEE. Total moisture content (TMC) during subsequent injection molding ranged from 1.0 to 10% (total solids basis). Starch granule structure, determined by X-ray diffraction and scanning electron microscopy, was progressively disrupted but not completely destroyed (as in thermoplastic starch) as TMC during molding increased. Tensile strength and modulus values were not significantly impacted when the TMC was 6% or less. As TMC increased above 6%, both properties decreased rapidly, while strain to break increased. Tensile strength increased when samples prepared at high TMC were equilibrated to a lower value. Changes in weight average molecular weight of the PHEE during processing were not significant as measured by gel permeation chromatography, even at the highest moisture contents. The effects of TMC on mechanical properties of starch/PHEE materials are shown to be due to changes in the viscoelastic response of the PHEE matrix, by comparison of starch/PHEE results to those of neat PHEE [Polymer 42 (2001) 5643]. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Moisture content; Mechanical properties

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1. Introduction

There is global interest in developing biodegradable materials as replacements for non-biodegradable thermoplastics used in disposable applications. While a variety of biodegradable polymers have been developed, their cost is often considerably greater than that of conventional commodity thermoplastic polymers. Starch is an annually renewable, low cost material which offers an opportunity to reduce cost and maintain, if not enhance, biodegradability. Under appropriate extrusion conditions with sufficient moisture (or other plasticizer) present, native starch can be converted into a thermoplastic melt in which the granule structure and inherent crystallinity are destroyed. Starch may also be dried and used as a filler, in which case the granule structure and crystallinity are preserved.

Bhattacharya et al. have characterized blends of starch with anhydride-containing copolymers [1–3]. Blends containing up to 70 wt% starch were processed using either batch mixers or twin-screw extruders, followed by injection molding. When starch was processed with ambient moisture content (≈ 10%), partial melting of the starch granules was observed. The extent of starch melting was attributed to the shear stresses generated during processing, and increased with starch content or processing intensity as measured by specific mechanical energy. No systematic study over a range of moisture contents during processing or testing was reported. Their results do, however, indicate the importance of moisture content during processing (extrusion, injection molding, etc.) of starch-based materials.

Recently, we have reported on a new class of materials based on granular starch and poly(hydroxyester ether)s, or PHEEs [4–9]. PHEEs are thermoplastic polyesters produced by the reaction between diacids and diepoxides [10–12]. Water is an effective plasticizer for both starch and PHEE, and has been shown to significantly impact the rheology, morphology, and tensile properties of thermoplastic starch, TPS/PHEE blends [13,14] and the

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[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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stress–strain behavior of PHEE [8]. In this report, the effect of total moisture content (TMC) on the mechanical properties of starch/PHEE materials is reported, in which the native granule structure of the starch is not completely disrupted.

2. Materials and methods

Cornstarch was Buffalo 3401 (CPC International, Englewood Cliffs, NJ) with an ambient moisture content of 10%. PHEE, provided by Dow Chemical Company (Midland, MI), was based on adipic acid and DGEBPA (diglycidyl ether of Bisphenol A). It is an amorphous polymer with a T_g of 45 °C when dry [8,13]. Starch was either dried to approximately 1% moisture content, or used as received with ambient moisture content. All formulations were prepared at a 60/39/1 dry weight ratio of starch/PHEE/Wax OP. Wax OP (Hoechst, Charlotte, NC) is a processing aid to improve injection molding. TMC is based on water content of the starch/PHEE blends; therefore, TMC was 6.0% during extrusion when ambient moisture starch was used and 1.0% or less when dry starch was used. The 60/40 starch/PHEE weight ratio corresponds to volume fractions of 0.55 (starch) and 0.44 (PHEE).

Starch/PHEE blends were prepared by extrusion compounding with a Werner–Pfleiderer ZSK-30 twin-screw extruder. Extruder temperature control zones were set to 52/120/165/165/165/165/130/125 °C (feed to die). A typical melting/mixing screw configuration was used, with a total feed rate of 9 kg/h and a screw speed of 150 rpm. PHEE was fed to the extruder and melted; starch was premixed with Wax OP and added downstream. Both component feeds were metered using gravimetric feeders (AccuRate, Whitewater, WI). Strands were extruded through two dies (2 mm diameter), cooled with air and dry ice, and subsequently pelletized. After extrusion, TMC was 2.2% for the material prepared with ambient moisture starch, indicating that most of the water flashed off during extrusion. TMC of the extrudate prepared with dried starch was 1.1%. Water was subsequently added to starch/PHEE pellets to reach the desired TMC levels, and pellets stored overnight in sealed bags before injection molding. Tensile bars (ASTM D 638, type IV) were injection molded on a Cincinnati Milacron injection molding machine (model ACT-75B8) with a four cavity mold. Processing temperatures during molding were between 115 °C (first heating zone) and 180 °C (nozzle); mold temperature was maintained between 35 and 45 °C.

Tensile properties were evaluated using an Instron model 4201 universal testing machine. At least five specimens of each formulation were used. Crosshead speed was 50 mm/min, giving a nominal strain rate of $0.017\ \mathrm{s}^{-1}$. Modulus values were calculated by the instrument software using the slope of the initial portion of the stress–strain curves. Injection molded specimens were conditioned at 22 °C and 50% relative humidity for 24 h or 7 days before measuring properties.

PHEE molecular weights were determined by gel permeation chromatography (GPC) with THF as a solvent and a PHEE concentration of 0.1 wt%. Two PLGel Mixed-C columns were used in series, with a flow rate of 1 ml/min and a UV detector. Polystyrene standards (M_w range 580–156,000) were used to construct calibration curves.

Samples for X-ray diffraction (XRD) analysis were prepared by dissolving the PHEE with THF; starch was collected on a filter and air-dried. XRD spectra were taken with a Philips APD PW1830 generator operating at 40 kV and 30 mA (Cu Kα) with a PW1820 goniometer. Data were collected in 0.05° 2θ, 4-second steps. Fracture surfaces of tensile specimens were sputter coated with Au/Pd and observed using a JEOL 6400V scanning electron microscope.

Samples for DSC analysis were cryogenically ground using a Fritsch mill. Samples of 10–20 mg were placed in stainless steel DSC pans and hermetically sealed. Glass transitions were measured using a Perkin–Elmer DSC7 thermal analysis system with a CCA7 liquid nitrogen cooling accessory. An indium standard was used for calibration. The scan range was −30 to 70 °C at a heating rate of 10 °C/min. Instrument software was used to determine T_g using the midpoint value. Onset points were 3–4 °C lower than the midpoints.

Moisture contents were measured using an Ohaus MB-200 moisture analyzer by heating at 170 °C for 5 min followed by 15 min at 105 °C [13].

3. Results and discussion

3.1. Molecular weight analysis

Polyesters are susceptible to hydrolysis during processing at elevated temperatures in the presence of water. PHEE molecular weights before and after processing were measured using GPC to characterize changes during processing. As shown in Table 1, the weight average molecular weight M_w was not significantly changed by processing in the presence of moisture. The M_w value in Table 1 for the unprocessed PHEE agrees well with the

Table 1
Molecular weight averages of PHEE before and after processing with starch and water

	M_n	M_w
Not processed	9800	67,600
Processed (6.0/1.7)	6600	72,200
Processed (6.0/8.9)	6400	64,900

Numbers in parentheses refer to TMC during extrusion/injection molding.

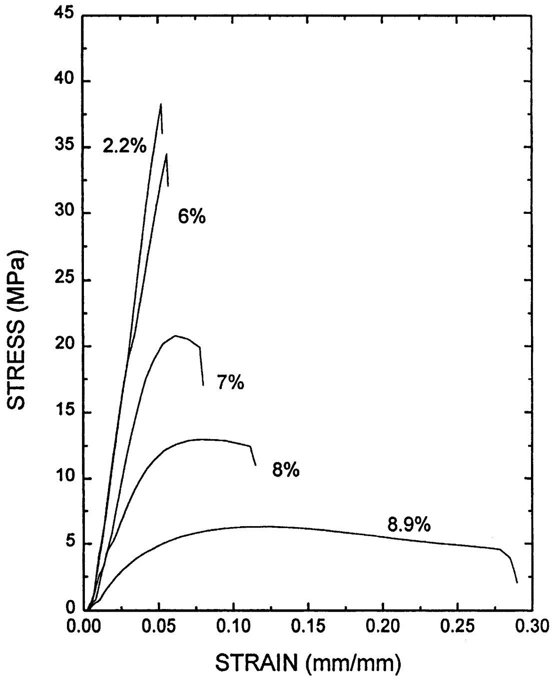

Fig. 1. Stress–strain curves for starch/PHEE; TMC is indicated for each curve. Samples were conditioned for 1 day at 50% relative humidity and 22 °C.

value (64,400) determined by static light scattering in *N*,*N*-dimethylacetamide [15]. TMC during extrusion was 6.0% for both processed samples, while TMC during injection molding was either 1.7 or 8.9%. The number average molecular weight M_n decreased from 9800 to 6500 after processing. Although the change in M_n appears to be substantial, visual inspection of the elution curves (not shown) indicates minor changes only in the lowest molecular weight portion of the distribution. Since M_n is sensitive to the low molecular fraction of the molecular weight distribution, it is not surprising that a reduction was observed. Melt processing of PHEE in the presence of starch and water does not significantly alter the high molecular weight components of the distribution.

3.2. Tensile properties

Representative stress–strain curves after 24 h conditioning for starch/PHEE at various moisture contents are shown in Fig. 1. Tensile properties were dependent on TMC during and after injection molding; TMC during extrusion had no effect. When TMC is approximately 6% or less, the materials are brittle and no yield point is seen. As TMC exceeds 6%, the materials become more ductile; the maximum stress drops and a yield point is seen. Strain to break steadily increases from approximately 0.06 to approximately 0.30 as TMC increases above 6%.

Tensile properties derived from Fig. 1 are shown in Fig. 2. In Fig. 2(a), it is seen that tensile strength decreases gradually from 40 MPa at 1% TMC to 33 MPa at 6% TMC.

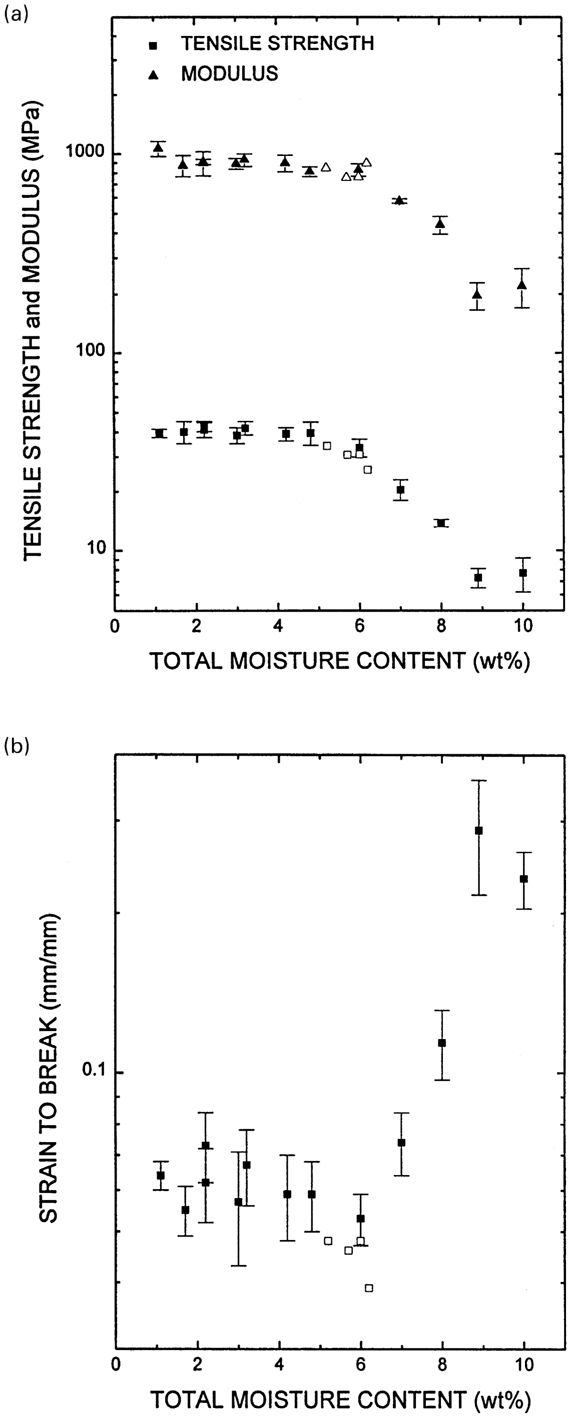

Fig. 2. Tensile properties of starch/PHEE at different TMCs. Samples were conditioned for 1 day at 50% relative humidity and 22 °C. (a) Tensile strength and modulus; (b) strain to break. Open symbols denote samples after drying from higher initial moisture content to lower values before measurement of tensile properties (see text).

As TMC is increased from 6 to 8.9%, tensile strength rapidly decreases to 11 MPa. The modulus data display similar behavior. There is a gradual decrease in modulus as TMC increases from 1 to 6%, followed by a large drop as TMC increases to 8.9%.

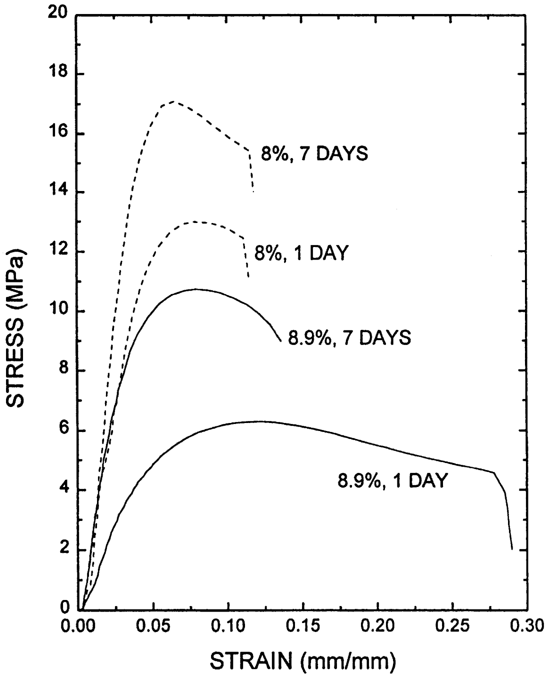

Fig. 3. Stress–strain curves for starch/PHEE moisture content after 1 day and 7 days conditioning at 50% relative humidity and 22 °C. Moisture content during injection molding was 8% (- - -) or 8.9% (—).

Strain to break (ϵ_b) values also change with TMC, although in the opposite direction as tensile strength and modulus. As shown in Fig. 2(b), $\epsilon \approx 0.06$ until the TMC reaches 6%, at which point it increases rapidly to a value of approximately 0.30 at TMC of 8.9%. Toughness (area under the stress–strain curve) was essentially constant regardless of TMC (data not shown).

No significant changes in tensile properties were observed when the conditioning time was increased to 7 days, except when TMC was 8% or greater. At these initial moisture levels, tensile strength and modulus increased after 7 days of conditioning at 50% RH. Representative stress–strain curves are shown in Fig. 3. These changes can be attributed to decreases in TMC during conditioning. When TMC is approximately 8% or greater, the materials desorb water to approach their equilibrium moisture content at 50% RH (TMC ≈ 7%). As a result, the materials become more brittle as the moisture content is reduced. It should be noted that while the data of Fig. 3 indicate increased brittleness of the starch/PHEE as TMC decreases, the samples were not at equilibrium after conditioning for 1 week. Therefore, a gradient in moisture content exists in these samples across the specimen half-thickness. The stress–strain curves of Fig. 3 illustrate deformation of samples with non-equilibrium moisture distribution. However, it is clear that reducing the TMC increases the brittleness of starch/PHEE materials. Samples with TMC values lower than the 50% RH equilibrium will absorb water, and become more ductile. The insignificant change in samples with TMC less than approximately 6% after 7 days indicates that water desorption is more rapid than sorption under these conditions, implying that the diffusion coefficient of water in these materials increases with TMC. Walia et al. have noted that equilibration of TPS/PHEE blends can take up to 1 month [14].

To further examine the effect of reduced TMC on tensile properties, samples with moisture contents of 7% and greater were conditioned in a vacuum oven at 30 °C for 1 week. As shown by the open symbols in Fig. 2, tensile properties of the samples after drying were comparable to those of samples with equivalent initial moisture contents. The data of Figs. 2 and 3 suggest that the effect of TMC on the tensile properties of starch/PHEE materials is reversible.

St Lawrence et al. have reported the effects of moisture content on the tensile properties of the PHEE used in this work [8]. Changes in tensile properties were interpreted using the degree of undercooling, defined as $\Delta T = T_i - T_g$, where T_i is the test temperature (22 °C). As the moisture content of PHEE increases, T_g decreases and ΔT becomes less negative; when T_g falls below the test temperature, ΔT becomes positive. For the starch/PHEE materials in this work, ΔT is -12 °C at 6% TMC and -7 °C at 8.9% TMC (see below for T_g discussion). For TMC values less than 6%, ΔT is more negative (i.e. greater undercooling). St Lawrence et al. observed decreases in tensile strength and modulus of PHEE by factors of 2–3 as ΔT increased from -12.5 to -6 °C at comparable strain rates. As seen in Figs. 1 and 2, similar decreases are observed in the starch/PHEE materials. In addition, St Lawrence et al. show that over this range of ΔT and strain rate, the failure of PHEE changes from brittle to ductile. The same trend is observed when starch is present, as shown in the stress–strain curves in Fig. 1. Note that these changes occurred at negative degrees of undercooling, i.e. below T_g. The response of PHEE [8] and these starch/PHEE materials to increasing TMC is equivalent to that observed in many amorphous polymers as the test temperature approaches T_g [16].

The results of Figs. 1 and 2, and the analysis of St Lawrence et al. [8], suggest that the changes in tensile properties of starch/PHEE materials with TMC are primarily due to changes in the viscoelastic response of the PHEE matrix. Although the crystallinity of the starch decreases significantly (Fig. 5) when TMC is 7% or greater during processing, the starch acts primarily as a rigid filler over the entire TMC range, since for starch $\Delta T \approx -50$ °C at the highest TMC (estimated using T_g data from Shogren [17]). The relative tensile strength values for starch/PHEE materials, normalized to the pure PHEE value at comparable ΔT values and strain rates from St Lawrence et al. [8], are 0.75 at $\Delta T = -12$ °C and 0.35 at $\Delta T = -7$ °C.

3.3. Fracture surfaces

Scanning electron micrographs of fracture surfaces from several tensile specimens are shown in Fig. 4. When the starch/PHEE materials fracture in a brittle manner at TMCs

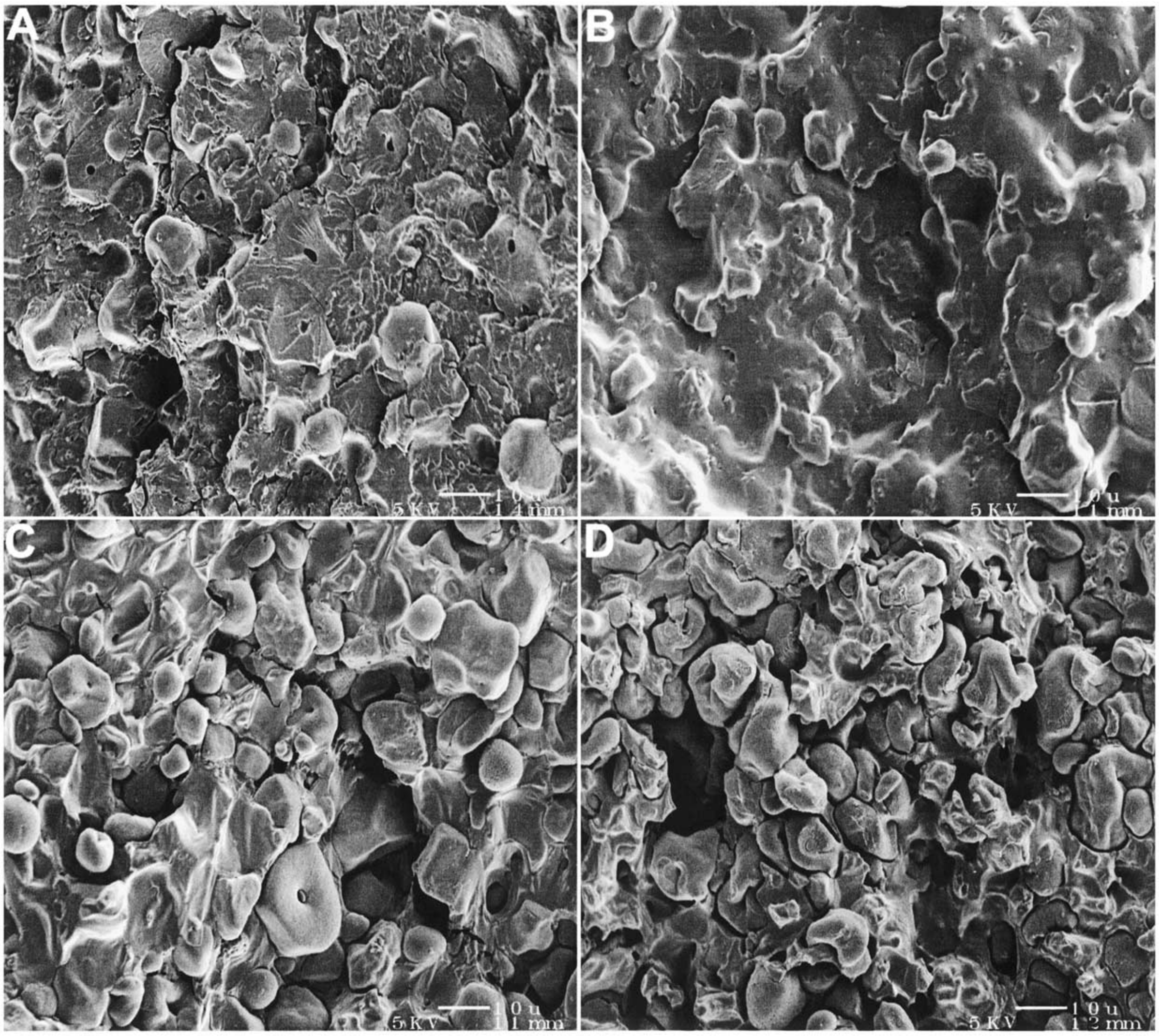

Fig. 4. Scanning electron micrographs of starch/PHEE fracture surfaces for samples with different TMCs (MC). (A) MC = 2.2% (brittle), (B) MC = 6% (brittle), (C) MC = 8% (ductile), and (D) MC = 8.9% (ductile). Magnification is 1000 × ; scale marker is 10 μm.

of 6% or less, the fracture surfaces contain numerous broken granules and unbroken granules coated with PHEE (Fig. 4(A) and (B)). These features indicate that the interfacial adhesion between the PHEE matrix and the starch granules is sufficient (on the time scale of the experiment) to withstand interfacial stresses generated during tensile deformation. Few if any debonded, intact starch granules are seen in the brittle starch/PHEE fracture surfaces, in contrast to other starch-filled materials [18–20].

When the TMC is increased beyond 6%, debonded granules as well as broken granules are seen (Fig. 4(C) and (D)). In addition, the starch granules are increasingly deformed from their native shape at the higher TMCs. Increasing TMC to 8.9% leads to extensive granule deformation, and debonding at the PHEE/granule interface during tensile deformation (Fig. 4(D)). It is not clear whether the debonding is due to changes in the viscoelasticity of the PHEE (time scale effects), the effects of increased water content on the interfacial adhesion, or both. The reduction in relative tensile strength with increasing TMC noted earlier is consistent with the increased debonding observed in Fig. 4(C) and (D).

3.4. X-ray diffraction analysis of starch structure

The granule deformation observed in Fig. 4(C) and (D) implies disruption of the starch granule structure when the TMC exceeds a value of approximately 6% during processing. One would expect to observe loss of crystallinity in XRD spectra of the starch in these formulations. Starch was extracted from tensile specimens shown in Fig. 4 by dissolving the PHEE matrix in THF. The samples were prepared using starch/PHEE originally extruded with ambient moisture starch (TMC = 6%), and injection molded at various TMC levels.

Diffraction patterns of the extracted starches are shown in Fig. 5. At low TMC, the diffraction pattern is that of native starch, indicating little if any disruption during

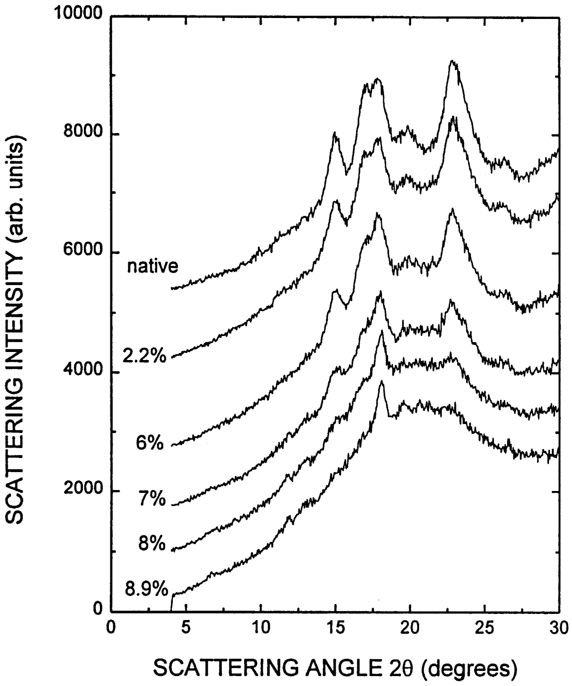

Fig. 5. XRD patterns for starch extracted from injection molded tensile specimens. TMCs are listed beside each curve.

processing. When TMC is 6%, the native diffraction pattern is still dominant, but there is evidence of an increase in scattering at $2\theta \approx 18°$. When TMC is increased further, to 8% and above, the diffraction peaks from the native starch disappear, and a strong peak at $2\theta \approx 18°$ appears. This peak, known as the 'E'-type amylose helix structure, has been observed in starches processed by twin-screw extrusion at moisture contents of 12–15% [21]. When starch is extruded at moisture content above approximately 18%, the E-helix peak disappears and is replaced by the V-helix peak at $2\theta \approx 20°$ [14,21]. Evidence that this peak is due to amylose complex formation is given by its absence in extruded waxy maize starch (containing no amylose), despite the identical X-ray scattering patterns of unprocessed WMS and normal starch (with approximately 25% amylose) such as the one used in this work [21]. The diffraction spectra in Fig. 5 clearly show that when the TMC exceeds approximately 6% significant disruption of the granule structure occurs under the injection molding conditions used here. The ambient moisture in the starch (10%) is not sufficient to disrupt granule structure during extrusion conditions used here. It appears that the observed disruption of granule structure has little if any impact on the tensile properties of the starch/PHEE materials.

Walia et al. observed continuity in the starch phase when TPS and PHEE were melt blended by extrusion at the same starch/PHEE weight ratio used in this work [13]. At the TMC levels used by Walia et al. (12–15%), TPS is a melt phase and the blend morphology is dependent on processing conditions. Fig. 4(d) suggests that the starch behaves as a filler at the highest TMC level used here, and the PHEE remains in the continuous phase. When samples shown in Fig. 4(a) and (d) were immersed in THF, both disintegrated, leaving suspended starch particles which quickly settled as a powder upon cessation of stirring. This result indicates that the PHEE forms the continuous phase when TMC is less than approximately 10% during extrusion and subsequent injection molding. The results of Walia et al. [13] indicate that TMC levels greater than 10% are required for the starch phase to develop continuity at a starch/PHEE weight ratio of 60/40.

3.5. Water partitioning between starch and PHEE

In the preceding discussion, moisture contents are based on total solids (starch and PHEE). It has been shown that water is an effective plasticizer for PHEE by thermal [13] and mechanical [8] measurements. At equilibrium for any value of TMC, water will partition itself between the starch and the PHEE phases. Water content in the PHEE in starch/PHEE materials can be estimated using data of Walia et al. [13] by measuring the PHEE T_g as a function of TMC.

Fig. 6(a) shows the PHEE glass transition measured by DSC for the materials after injection molding. Also shown is the PHEE T_g-moisture content data from Walia et al. [13]. PHEE moisture contents for the starch/PHEE materials were calculated using the PHEE data of Fig. 6. MC values for the starch phase were then calculated by assuming the TMC is the weighted sum of the contributions of the individual components

$$\mathrm{TMC} = \omega_{\mathrm{Starch}}\mathrm{MC}_{\mathrm{Starch}} + \omega_{\mathrm{PHEE}}\mathrm{MC}_{\mathrm{PHEE}} \tag{1}$$

where ωs are weight fractions. The calculated component moisture contents are plotted in Fig. 6(b).

A water partition coefficient K_P can be defined as

$$K_P = \frac{\mathrm{MC}_{\mathrm{PHEE}}}{\mathrm{MC}_{\mathrm{Starch}}} \tag{2}$$

and estimated from the slopes of the lines in Fig. 6(b) since $\mathrm{MC}_{\mathrm{PHEE}} \approx \mathrm{MC}_{\mathrm{Starch}} \approx 0$ as $\mathrm{TMC} \to 0$. The data of Fig. 6(b) yield a K_P value of 0.2 (±0.1). Therefore, it is observed that K_P is approximately constant over the TMC range of this work, and that the PHEE moisture content is approximately one-fifth that of the starch on a weight basis.

The calculated moisture contents shown in Fig. 6(b) are estimates based on changes in PHEE T_g with no starch present. It is assumed in the calculation of the moisture content values given in Fig. 6(b) that the presence of starch does not affect the T_g–MC relationship for PHEE, only the distribution of the moisture in the system. The temperature dependence of K_P is not known. Neither it is known how the time scale of interphase moisture migration in the starch/PHEE system compares to the time scale of temperature change in the DSC run. Both of these factors could affect the actual T_g values. Despite these uncertainties, it is clear that the changes in mechanical properties of starch/PHEE materials with moisture content can be attributed to the

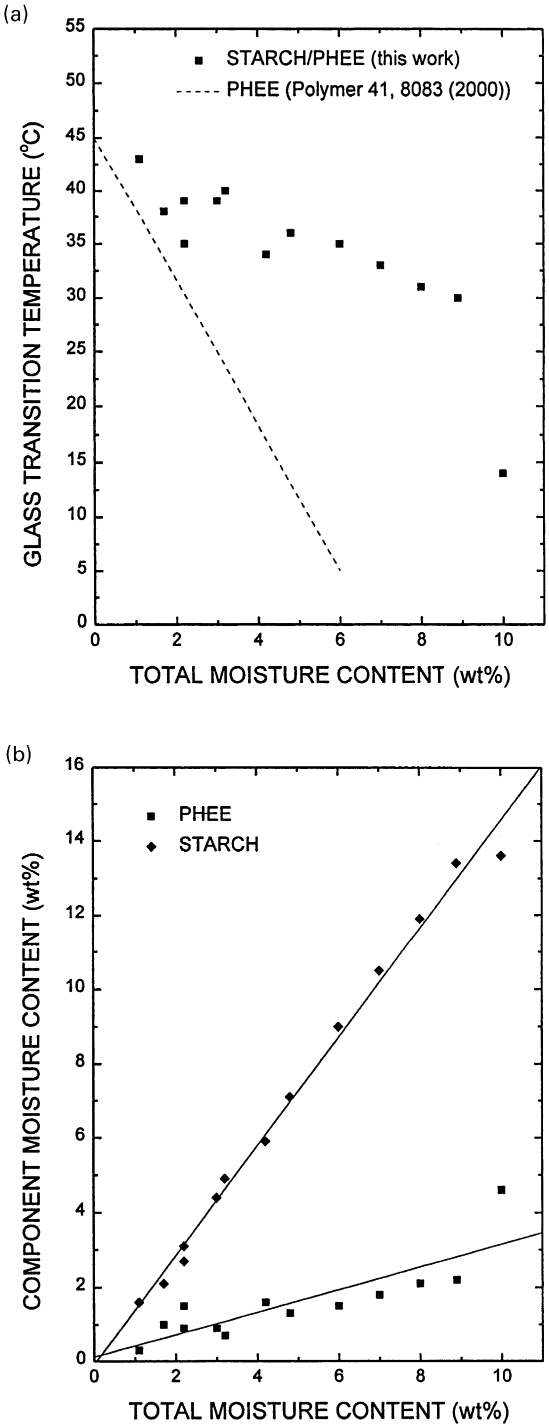

Fig. 6. Glass transition temperatures for PHEE and calculated component moisture contents in starch/PHEE materials. (a) T_g of PHEE; points represent this work, line represents Ref. [13]. (b) Moisture contents calculated using (a) and Eq. (1).

plasticizing effect of water on the PHEE matrix, regardless of the exact values of the component moisture contents at room temperature. Although the moisture content of the starch is approximately 5 times greater than that of the PHEE, the starch is sufficiently below its T_g to act as a dispersed brittle phase at room temperature ($\Delta T \approx -50$ °C).

4. Conclusions

The tensile properties of starch/PHEE materials are dependent on the TMC. When TMC is less than approximately 6%, the starch/PHEE materials display brittle behavior. As TMC increases, the starch/PHEE materials become more ductile and display a yield point. Reducing TMC by drying or conditioning increases brittleness to a level comparable to materials of equivalent initial TMC, even though the moisture distribution is non-equilibrium. Fracture surfaces of tensile specimens show broken starch granules and the absence of starch/PHEE debonding when TMC is less than approximately 7%. Above this TMC, debonding is observed. XRD and scanning electron microscopy results show that starch granule structure is progressively disrupted as TMC increases above approximately 7% during injection molding. The molecular weight of the PHEE is not significantly reduced by thermal and shear processing in the presence of moisture. Using published T_g data for the PHEE/water system, it is estimated that water partitions between the starch and PHEE phases at a weight ratio of approximately 5:1. Comparison of the starch/PHEE results with PHEE/water indicates that the tensile properties are primarily dependent on the changes in the viscoelastic response of the PHEE matrix with moisture content, and the starch acts as a rigid filler.

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