Aging and Moisture Effects on the Tensile Properties of Starch/Poly(hydroxyester ether) Composites

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ABSTRACT: The effects of starch and aging on the mechanical properties of starch/poly(hydroxyester ether) (PHEE) composite materials were characterized. Native or modified cornstarches were extruded with PHEE. Composites were aged for up to 20 months at either 23°C and 50% relative humidity (RH) or over calcium sulfate to keep the composites dry. The tensile strength (TS) of the composites was affected by the type of starch filler that they contained. Composites containing native or crosslinked starch had significantly greater TS than composites containing octenylsuccinated starch. It was thought that the octenylsuccinate modification of the starch granule affected the adhesion between the starch and PHEE. Aging the composites at 50% RH had a significant effect on the mechanical properties of the composites, with TS and Young's modulus (YM) significantly decreasing and the elongation to break significantly increasing after 20 months of storage. Composites stored at 50% RH absorbed water, which caused changes in the mechanical properties by plasticizing PHEE. Composites containing poly(lactic acid) and PHEE did not experience large reduction in TS and YM when aged at 50% RH, even though they also absorbed water. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3332–3339, 2006

Key words: aging; mechanical properties; biopolymers

INTRODUCTION

Starch used as a filler in polymer composites has receive considerable interest as a way of adding or aiding in the biodegradation of polymers and lowering their cost. Starch has been added to polymers as an inert filler for over 30 years. Griffin[1] reported that granular starch could be incorporated into low-density polyethylene films and impart some biodegradation. This work later led to the commercial production of polyethylene bags containing 7–10% starch. During the 1970s, research was also done on blending starches with other synthetic polymers. Westoff et al.[2] blended granular starch with poly(vinyl chloride) (PVC) up to 40 wt %. Griffin also investigated incorporating granular starch into polystyrene and PVC. Granular starch has also been added to poly(ethylene-*co*-acrylic acid),[3,4] poly(ethylene-*co*-vinyl alcohol),[5] and polypropylene.[6] Although it was known that these synthetic polymers would not biodegrade, it was hoped that the biodegradation of the starch would lead to a natural breakdown of the plastics. Because these composites do not truly biodegrade, considerable research has been conducted on blends of starch with biodegradable polymers. Granular starch has been blended with poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV),[7,8] polycaprolactone,[9] and poly(lactic acid). (PLA)[10,11] Granular starch composites of biodegradable polymers have suffered from the same issue as starch blends with traditional synthetic polymers. When they are used as fillers, the mechanical properties of starch-filled composites with respect to the neat polymer decrease as the starch content increases.[12,13] Diverse research has shown that the decline of starch-filled composites can be mitigated by the treatment of the surface of the starch granule to make it more hydrophobic or by the addition of a compatibilizing agent to the composite. Evangelista et al.[14] used *n*-octenylsuccinate to modify starch, and the properties of polyethylene starch-filled films were improved. Polyethylene-starch-filled films containing ethylene–acrylate copolymers showed enhanced properties over films not containing the copolymers.[15] Composites containing maleated polypropylene and starch showed signifi-

cantly improved tensile properties over composites made with unmodified polypropylene.[6] The mechanical properties of starch–PHBV composites were improved by the coating of the starch granules with poly(ethylene oxide).[16] Although these treatments do improve the mechanical properties of starch-containing composites, they also increase the overall cost of the composites. When biodegradability is desired, the treatments can have detrimental effects.

A new biodegradable polymer, poly(hydroxyester ether) (PHEE),[17–19] has been shown to adhere well to starch granules without the surface treatment of the granules or the addition of a compatibilizing agent.[20–24] The good adhesion between PHEE and starch granules allows a high starch content in composites. The starch granules generally do not debond from the PHEE matrix during tensile testing and often fracture rather than debond from the PHEE matrix.[23,24] Water is a plasticizer for PHEE, and the physical properties of neat PHEE depend on the moisture content.[25] The glass-transition temperature of PHEE decreases from 45°C in the dry state to 5°C at a 6% moisture content.[26,27] The total moisture content of starch/PHEE (40/60) composites has been shown to affect the tensile properties.[24] The tensile properties of the composites were not significantly affected when the total moisture content was 6% or less. Above a 6% moisture content, the tensile strength (TS) and modulus decreased rapidly. Composites with moisture contents greater than 7% showed extensive debonding of the PHEE from the starch granules. In this report, the effect of modified starch granules and the effect of aging the composites on the mechanical properties is reported.

EXPERIMENTAL

The normal cornstarch Buffalo 3401 (CPC International, Englewood Cliffs, NJ) was used. The following starches were obtained from National Starch and Chemical Corp. (Bridgewater, NJ): National 6912 (oxidized), Colflo 67 (acetylated), Flojel 75 (acid-modified), WNA (lightly crosslinked), DryFlo (octenylsuccinate-modified), Frigex W (propylated), Instant Corn (pregelatinized), and Absorbo (highly crosslinked). All the starches except for Buffalo 3401 and Absorbo were food-grade. PHEE, provided by Dow Chemical Co. (Midland, MI), was based on adipic acid and diglycidyl ether of bisphenol A. The starches were either dried to approximately 1% moisture content or used with the ambient moisture content. All formulations were prepared with equal weight fractions of starch and PHEE and contained 1% Wax OP (Hoechst, Charlotte, NC) as a processing aid to improve injection molding.

Starch–PHEE composites were processed on a Werner–Phleiderer ZSK-30 twin-screw extruder (Ramsey, NJ). Temperature control zones were set to 52/110/150/157/150/143/130°C (feed to die) for starch/PHEE blends and to 52/165/182/182/182/176/143°C for starch/PHEE/PLA blends. A typical melting/mixing screw configuration was used, with a total feed rate of 9 kg/h and a screw speed of 180 rpm. PHEE or PHEE/PLA was fed to the extruder and melted; starch was premixed with Wax OP and added downstream. Both component feeds were metered with gravimetric feeders (AccuRate, Whitewater, WI). Strands were extruded through two dies (2 mm in diameter) cooled with air and dry ice and were subsequently pelletized. After extrusion, the pellets were refrigerated until injection-molded.

Tensile bars (ASTM D 638, type IV) were injection-molded on a Cincinnati Milacron ACT-75B8 injection-molding machine (Batavia, OH) with a four-cavity mold. Processing temperatures were between 80 (first barrel heating zone) and 165°C (nozzle); the mold temperature was set between 38 and 50°C. For tensile bars containing PLA, the processing temperatures had to be raised to 121°C for the first zone and to 182°C for the nozzle. The mold temperature was 70°C.

The tensile properties were evaluated with an Instron model 4201 universal testing machine (Canton, MA). At least four specimens of each formulation and aging time were tested. The crosshead speed was 50 mm/min. Injection-molded tensile bars were conditioned at 23°C and 50% relative humidity (RH) for various lengths of time. Some bars were conditioned over anhydrous calcium sulfate (DriRite) at either 23 or −20°C for various lengths of time. Bars that were stored at −20°C were warmed to room temperature in zip-lock bags before testing. The fracture surfaces of the tensile bars were sputter-coated with Au/Pd and observed with a JEOL 6400V scanning electron microscope (Peabody, MA).

RESULTS

The fracture surface of a tensile bar (Fig. 1) containing native starch and PHEE showed numerous broken starch granules and granules coated with PHEE but no granules that debonded from the matrix. These features indicated the same good adhesion between starch and PHEE as shown before.[23,24] There was exceptional interfacial adhesion between the PHEE matrix and starch granules, compared to the interfacial adhesion found between other synthetic polymers and starch granules.

Previous work with starch and PHEE composites has shown that the adhesion between PHEE and starch granules is strong enough that the fractures pass through the starch granules rather than debonding the PHEE from the granules.[23,24,27] To better understand the effect of filler attributes on the composite properties, modified starches replaced native corn-
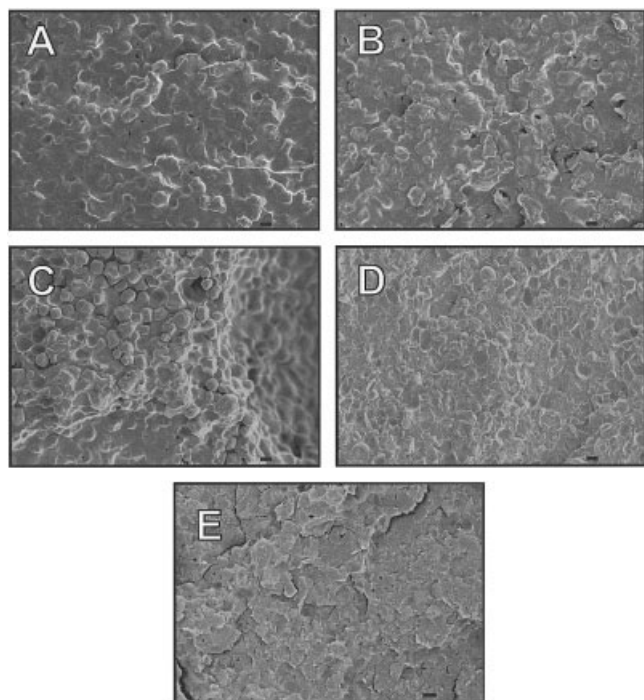
Figure 1 SEM images of fracture surfaces of composites aged 7 days at 23°C and 50% RH. The composites contained PHEE and (A) native starch, (B) crosslinked starch, (C) octenylsuccinated starch, (D) oxidized starch, and (E) native starch and PLA (original magnification = 500×, scale = 10 μm).

starch in the composite formulations. The modifications were expected to affect the tensile properties of the composites in two ways. First, some modifications were conjectured to weaken (i.e., oxidize) or strengthen (crosslinked) the granule, thereby weakening or strengthening the composites. Second, starch derivatives containing a monofunctional group (i.e., octenylsuccinated) were expected to affect the interface between the granules and PHEE, thereby weakening the composites. The tensile properties of these composites are given in Tables I–III. All the modifications significantly reduced TS and Young's modulus (YM), except for crosslinking. The composites made with crosslinked starch had significantly greater TS values after 7 days than composites made with native starch when stored at 50% RH. Whether this is an indication that crosslinked starch granules improved the TS of composites is difficult to confirm. Scanning electron microscopy (SEM) micrographs (Fig. 1) of the fracture surfaces from composites with crosslinked starch looked similar to fracture surfaces of composites with native starch. Both composites showed good adhesion, no debonding of the PHEE continuous phase and the granules, and a large number of broken granules. However, when the weak component of the composites was the filler and crosslinking increased the filler strength, then TS of the composite with increased filler strength was expected to increase. Starch granules modified through oxidation had significantly lower TS values than composites containing native starch granules. It is difficult to verify whether TS was reduced because the starch granule was weakened or because the modification affected the adhesion between the starch granules. SEM micrographs (Fig. 1) of

TABLE I
TS of the Starch-Filled Composites

Sample	TS (MPa)[a]					
	7 days	28 days	87 days	168 days	365 days	650 days
Stored at 23°C and 50% RH						
Native	a45.0B	a48.4B	a44.6A	bc18.4C	b20.5B	c14.2B
Oxidize	b34.5C	a39.6C	c30.6B	d19.3C	d17.1C	e13.9B
Succinated[b]	a27.8D	a29.2D	b22.4C	c14.5D	c15.9C	c14.5B
Crosslinked	b51.6A	a65.6A	b50.8A	c24.2B	c21.8B	d16.2B
PLA–PHEE[c]	b36.5C	a42.6C	a46.9A	b36.5A	b33.5A	b37.2A
Stored at 23°C over calcium sulfate						
Native	b49.8A	a60.1A	a62.5A	c42.6A	d28.7B	
Oxidize	bc25.5B	a41.7C	a40.8C	bc30.0B	c20.8C	
Succinated	b27.0B	a33.8D	a32.8D	c22.1C	c21.7C	
Crosslinked	b49.8A	a62.4A	a65.5A	c44.6A	d29.8B	
PLA–PHEE	c44.0A	b50.6B	a57.4B	c42.1A	d35.0A	
Stored at −20°C over calcium sulfate						
Native	bc48.5A	a60.4A	b52.4B	c40.5B	c42.0B	
Oxidize	b34.5C	a44.1C	a42.8C	bc31.5C	c29.0D	
Succinated	bc25.7D	a32.0D	ba29.4D	c24.5D	c23.8E	
Crosslinked	b49.5A	a63.7A	a66.6A	c45.2A	bc47.0A	
PLA–PHEE	b42.9B	a54.9B	a52.5B	b40.5B	c36.9C	

[a]Means with the same lowercase letter within a row are not significantly different, and means with the same uppercase letter within a column are not significantly different.
[b]Ocenylcuccinated starch.
[c]Composites containing native starch, PLA, and PHEE.

TABLE II
YM of the Starch-Filled Composites

Sample	YM (MPa)[a]					
	7 days	28 days	87 days	168 days	365 days	650 days
Stored at 23°C and 50% RH						
Native	c958C	a1462A	b1335BC	c921CD	d647B	e462BC
Oxidize	b1377A	a1542A	b1384BC	c1064B	d686B	e452BC
Succinated[b]	a1321A	a1415A	a1203C	b859D	c628B	d389C
Crosslinked	b1244AB	a1399A	a1487AB	c1040BC	d684B	d491B
PLA–PHEE[c]	c1068BC	ba1506A	a1652A	b1354A	c1096A	c929A
Stored at 23°C over calcium sulfate						
Native	c1266B	b1489A	a1729AB	b1392A	d678B	
Oxidize	c1267B	a1544A	a1571B	b1390A	d773B	
Succinated	c1285B	b1587A	a1879A	c1389A	d760B	
Crosslinked	c1179C	ba1488A	a1574B	b1409A	d725B	
PLA–PHEE	c1398A	b1562	a1872A	cb1461A	d1011A	
Stored at −20°C over calcium sulfate						
Native	b1209A	b1319C	a1798AB	b1249B	c974A	
Oxidize	c1307A	b1516BC	a1861AB	b1496A	d1085A	
Succinated	b1299A	a1723A	a1751B	b1350AB	c1006A	
Crosslinked	c1241A	cb1333C	a1865AB	b1428AB	d977A	
PLA–PHEE	c1288A	b1588AB	a1954A	b1494A	c1150A	

[a] Means with the same lowercase letter within a row are not significantly different, and means with the same uppercase letter within a column are not significantly different.
[b] Ocenylcuccinated starch.
[c] Composites containing native starch, PLA, and PHEE.

the composites containing oxidized starch showed a large number of broken granules but also showed granules that debonded from the matrix (voids), and the exposed whole granules did not appear to be coated with PHEE. The composites containing 1-octe-nylsuccinic anhydride modified starch were significantly the weakest composites tested, with TS of only 27 MPa in comparison with 45 MPa for composites containing native starch granules. The micrographs (Fig. 1) of composites containing octenylsuccinated

TABLE III
%E of the Starch-Filled Composites

Sample	%E					
	7 days	28 days	87 days	168 days	365 days	650 days
Stored at 23°C and 50% RH						
Native	b8.5A	b5.8B	b4.9AB	b11.9A	b15.0AB	a37.9A
Oxidize	cb4.6D	cb4.9CD	c3.2C	c3.0B	b12.7AB	a25.2A
Succinated[b]	c4.0D	c4.1D	c3.0C	c3.6B	b18.1AB	a33.8A
Crosslinked	c7.2B	c7.9A	c5.4A	c5.6B	b20.1A	a35.0A
PLA–PHEE[c]	cb5.9C	dc5.0BC	dc4.4B	d3.9B	a8.3B	ba6.7B
Stored at 23°C over calcium sulfate						
Native	b6.5A	b6.0A	b5.2B	b5.0A	a14.9A	
Oxidize	ba4.8BC	ba4.3BC	ba3.7CD	b3.3B	a5.0C	
Succinated	ba4.3C	b3.5C	b3.2D	b2.7B	a5.2C	
Crosslinked	b7.0A	cb6.3A	cb6.1A	c4.7A	a10.6B	
PLA–PHEE	ba5.3B	b4.8B	b4.2C	b4.4A	a7.8BC	
Stored at −20°C over calcium sulfate						
Native	a6.3A	a7.5A	b4.2B	b4.7AB	a6.6B	
Oxidize	b4.1B	a4.8B	c3.4BC	c3.3C	ba4.5C	
Succinated	ba3.4BC	ba3.1C	c1.9D	b2.8C	a3.9C	
Crosslinked	ba7.1A	ba7.2A	cb6.1A	c5.0A	a8.4A	
PLA–PHEE	b2.8C	a5.3B	b2.9CD	b3.7BC	a4.7C	

[a] Means with the same lowercase letter within a row are not significantly different, and means with the same uppercase letter within a column are not significantly different.
[b] Ocenylcuccinated starch.
[c] Composites containing native starch, PLA, and PHEE.

TABLE IV
Moisture Content of the Starch-Filled Composites

Sample	Moisture content (%)					
	7 days	28 days	87 days	168 days	365 days	650 days
Stored at 23°C and 50% RH						
Native	1.4	2.2	3.3	5.2	4.5	5.0
Oxidize	2.0	2.3	3.0	4.7	4.4	4.6
Succinated[a]	2.2	2.9	2.5	5.7	4.9	5.4
Crosslinked	1.6	2.2	2.5	5.4	4.7	4.8
PLA–PHEE[b]	2.7	2.8	2.7	5.7	5.4	5.6
Stored at 23°C over calcium sulfate						
Native	1.3	1.9	2.1	3.2	4.3	
Oxidize	1.4	1.9	1.9	3.1	4.6	
Succinated	2.0	2.3	2.2	3.7	4.3	
Crosslinked	1.4	2.4	2.2	3.4	4.4	
PLA–PHEE	2.3	2.2	2.5	4.4	4.2	
Stored at −20°C over calcium sulfate						
Native	1.3	1.5	1.1	1.6	1.2	
Oxidize	1.3	1.1	2.1	2.1	1.9	
Succinated	1.6	1.6	1.5	1.5	1.3	
Crosslinked	1.3	1.7	1.9	1.3	1.3	
PLA–PHEE	2.0	1.5	1.4	2.0	2.4	

[a] Ocenylcuccinated starch.
[b] Composites containing native starch, PLA, and PHEE.

starch granules showed almost no adhesion of the starch granules to the PHEE matrix and no broken granules. This hydrophobic substitution apparently interfered with the adhesion at the granule and PHEE interface.

TS and YM significantly decreased after aging at 23°C and 50% RH for over 20 months. These decreases are correlated with the absorption of water during storage at 50% RH. As shown in Table IV, the water absorption increased with the aging time from an average of approximately 1.5% after 7 days of storage to about 5% after 20 months. No differences in the amount of water absorbed or the rate of absorption were seen between the different composites.

TS and YM of starch–PHEE (40/60 w/w) composites decreased by 50% or more as the total moisture content exceeded 6%.[24] Under these conditions, the moisture content of the PHEE was sufficient for the transition from brittle fracture to ductile fracture.[25] The reduction in TS and YM was, therefore, due to the plasticizing effect of water on the PHEE matrix. With the data of ref. 24, the moisture content of PHEE in the aged samples of Table III was estimated to be approximately 1.7% when the total moisture content was 5%. At this moisture content, PHEE is ductile at the strain rate used in this work. Increased starch–PHEE debonding was also observed in ref. 24 at moisture contents greater than 6%. SEM micrographs (Fig. 2) of our aged composites also show large numbers of debonded starch granules. This debonding contributed to the reduction in TS by decreasing the load-bearing area of the continuous phase.

As the composites were aged, water was absorbed at the surface and diffused into the composites. The absorbed water increased the ductility in PHEE near the surface of the composites first, whereas PHEE in the interior of the composites remained brittle. This led to a gradient in the mechanical properties from the
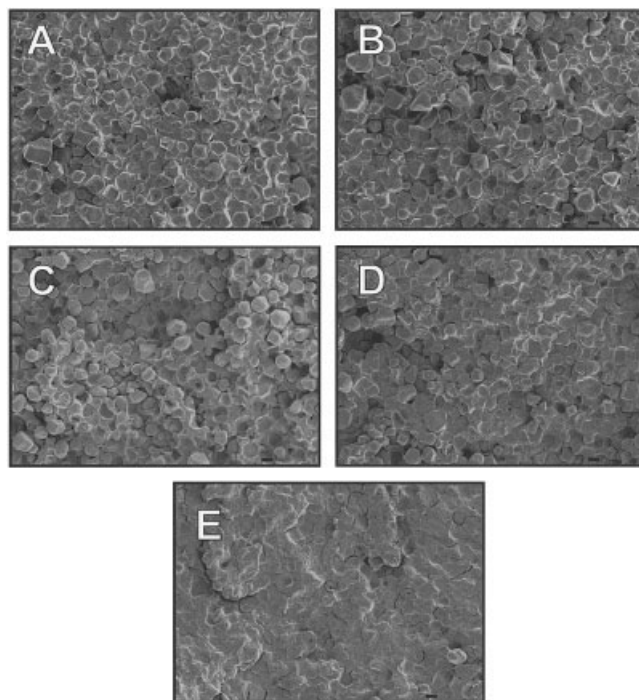

Figure 2 SEM images of fracture surfaces of composites aged 675 days at 23°C and 50% RH. The composites contained PHEE and (A) native starch, (B) crosslinked starch, (C) octenylsuccinated starch, (D) oxidized starch, and (E) native starch and PLA (original magnification = 500×, scale = 10 μm).
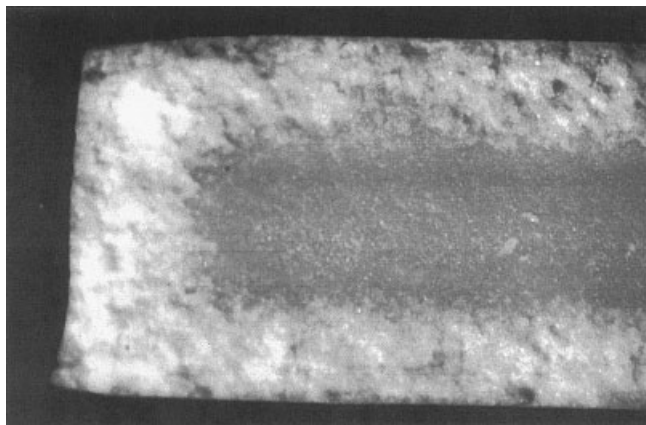
Figure 3 Fracture surface of a composite containing native starch and PHEE aged for 168 days at 23°C and 50% RH.

outer surface to the interior. Figure 3 shows the fracture surface of a composite of native starch and PHEE aged for 168 days at 50% RH. Clearly visible are an interior area with a smooth fracture surface and an outer region with a rougher texture. The SEM micrographs of fractured surfaces from brittle samples showed smooth surfaces. Even though the starch/ PHEE materials had not reached an equilibrium distribution of moisture after 168 days, it is clear that the increased ductility of PHEE in the outer region of the sample in Figure 3 led to a reduction in TS and YM, which is consistent with the results of ref. 24.

An examination of Table III shows that effects of starch–PHEE adhesion on TS are most pronounced at low moisture contents, at which PHEE is brittle. As the samples aged at 50% RH and absorbed water, differences in TS between the different starches diminished, and this reflected the increased ductility of PHEE. After 365 days, the TS values were all between 15.9 and 21.8 MPa, compared to a range of 27.8–51.6 MPa after 7 days. After 20 months of aging at 50% RH, there were no significant differences in TS for any of the starch PHEE composites. TS at this point was determined solely by PHEE; any differences in starch–PHEE adhesions were removed because debonding occurred in all samples during the timescale of tensile testing, as shown in Figure 2.

The absorbed water also had a significant effect on YM and the elongation to break (%E) of the composites, in agreement with previous results.[24,25] YM for the composites was reduced from an average for all of the composites of 1307 to 449 MPa after 20 months of storage, and %E increased from an average of 6–33% after aging. YM and %E of composites are known to be affected by added fillers; however, the type of filler was not expected to influence YM or %E. The added fillers, though modified, were still rigid fillers similar to unmodified native starch. There were small but significant differences in YM between the composites

at each of the time intervals tested (Table II). It is not clear why this variation took place because these fillers were not expected to affect YM differently. There was no trend seen for the composites with respect to the time interval. The difference may be due to the small sample size. There were significant differences in %E for composites aged at 50% RH for short times of less than 168 days (Table III). Composites filled with native starch or crosslinked starch had small but significantly greater %E values than composites filled with oxidized or octenylsuccinated starch. The reason for this difference may be the small sample size used to make comparisons because all the composites were brittle and did not have much elongation. The difference in %E between the composites disappeared after storage for longer periods of time because of the large effect that water had on the composites.

As discussed previously, absorbed water changed the nature of the failure of the composites during testing, as shown in Figure 4. Composites aged up to 87 days at 23°C and 50% RH were brittle, and no yield point was seen. The composites were ductile after aging for over 168 days. Similar failure mechanisms were observed for neat PHEE aged at different RHs.[25] All tested composites containing starch fillers and PHEE and aged under room conditions showed a similar trend. Brittle failure was observed with aging up to 87 days. After aging more than 87 days, the composites had ductile failure. Because the type of filler (i.e., native starch with good adhesion and octenylsuccinated starch with poor adhesion) had no effect on the type of failure observed, the continuous-phase PHEE must have controlled the type of failure in the composites.
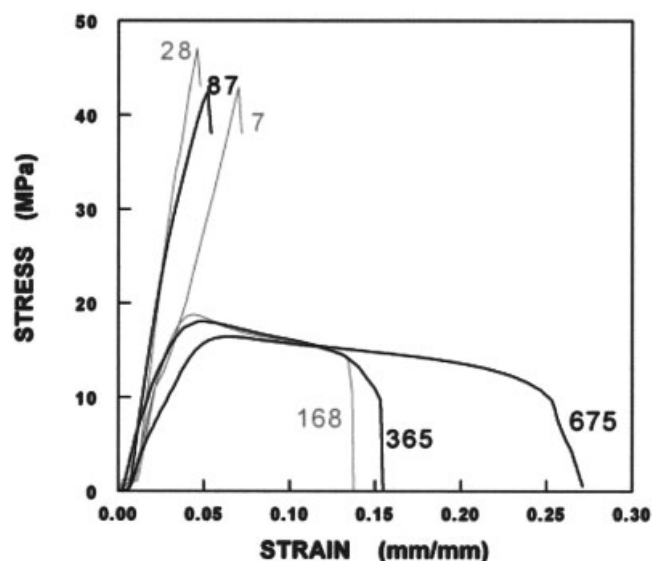

Figure 4 Stress–strain curves for aged composites containing native starch and PHEE. The aging time in days is indicated for each curve.

Starch-filled PHEE/PLA composites did not show significant changes in TS, YM, or %*E* after aging for 20 months at 50% RH (Tables I–III). The composites absorbed water to the same extent as composites containing only PHEE and starch (Table IV). No reduction in TS was observed, and this was consistent with the role of PLA as a continuous matrix in these materials. The SEM micrographs of the fracture surfaces from composites containing PLA and PHEE did not change with aging (Figs. 1 and 2). Because no change in debonding was apparent, water did not appear to impact the adhesion between the starch and PLA matrix. Aging composites containing native starch, PHEE, and PLA for 675 days did not affect the type of fracture that the composites had during tensile testing. Composites aged for 675 days had the same brittle failure as composites aged for just 7 days. All other tested composites containing PHEE and PLA also had brittle failure during tensile testing.

Aging the composites at 50% RH for a short time (from 7 to 28 days) significantly increased TS of composites containing crosslinked or oxidized starches or PLA. TS for samples containing native or octenylsuccinated starches also increased, but the increase was not significant at the 0.05 level. Similar trends were seen in YM of the composites, with a significant increase in YM seen for composites containing native or crosslinked starches or PLA. The reason for this increase may be that 7 days of aging was not enough time for internal stresses produced by injection molding to relax. Aging composites containing native starch, PHEE, and PLA also showed an increase in TS after aging 28 days at 50% RH.

To examine the effect of aging on starch–PHEE composites without the influence of water, specimens were aged under dry conditions at either 23 or $-20°C$ for 365 days. TS and YM of all the composites initially increased after aging (Tables I and II), similarly to those of specimens aged under room conditions. Because of the absorption of water by starch–PHEE composites aged under room conditions, a decrease in TS and YM was seen after aging beyond 28 days. Composites aged under dry conditions continued to increase significantly in YM up to 87 days. TS of the composites, though not showing a significant increase after aging for 87 days, remained unchanged and did not decrease as seen with composites aged under room conditions. Composites aged for longer than 87 days began to see a small decrease in TS and YM after aging longer than 87 days. YM was always statistically lowest after 365 days of aging, regardless of the type of filler or how the composites were aged. This indicates that YM of PHEE was influenced by time even without the plasticizing effect of water. TS of the composites was always lowest after 365 days of aging, even though composites stored at $-20°C$ were not significantly lower than composites stored for 7 days. Sam-

ples stored under dry conditions and 23°C showed significantly lower TS and YM after aging for 365 days than samples stored at $-20°C$ and dry. The reason for this is that water was absorbed by the samples stored at 23°C over calcium sulfate (Table IV). The storage chamber for these specimens was located in a 50% RH room, and the calcium sulfate must not have been changed often enough to maintain dry conditions. The effect of absorbed water was similar to that seen for composites aged under room conditions. TS and YM results for the composites aged at 23°C and dry for 365 days were similar to those of composites aged for 365 days under room conditions. %*E* of composites aged under dry conditions was low and was similar to %*E* of composites aged at room conditions for a short time (7–87 days), before water affected the composites. Unlike the composites aged at room temperature, %*E* of composites aged under dry conditions remained low during longer aging because no water was available to plasticize PHEE. Composites aged at 23°C over calcium sulfate did show increases in %*E* because of the inadvertent absorption of water. Composites aged under dry conditions showed the same unusual pattern seen in composites aged at room conditions. Composites containing native and crosslinked starch had significantly greater %*E* values than composites containing oxidized or octenylsuccinated starch. The %*E* values for these composites were always low, and the materials were all brittle, but %*E* was always greater for composites containing native and crosslinked starch at each of the times tested. Composites containing native starch, PHEE, and PLA had tensile properties after aging under dry conditions similar to those of composites aged under room conditions. All composites aged under dry conditions were brittle, even after aging for 365 days, except for a few composites that were aged at 23°C with calcium sulfate because of water absorption. The fracture surfaces of these composites aged at $-20°C$ showed good adhesion between PHEE and the filler for composites containing native and crosslinked starch and showed poor adhesion for composites containing octenylsuccinated starch. All the composite fracture surfaces that were aged for 365 days under dry conditions looked similar to the fracture surfaces of composites aged for only 7 days (Fig. 5). The adhesion between PHEE and unmodified starch remained unchanged after a year of aging when water was not present.

CONCLUSIONS

The tensile properties of starch–PHEE composites were affected by aging. TS and YM decreased with the aging time. Water had the greatest effect on the tensile properties of the composites. Composites aged at 50% RH saw the largest decrease in TS and YM because of the effect of absorbed water. Water reduced TS and
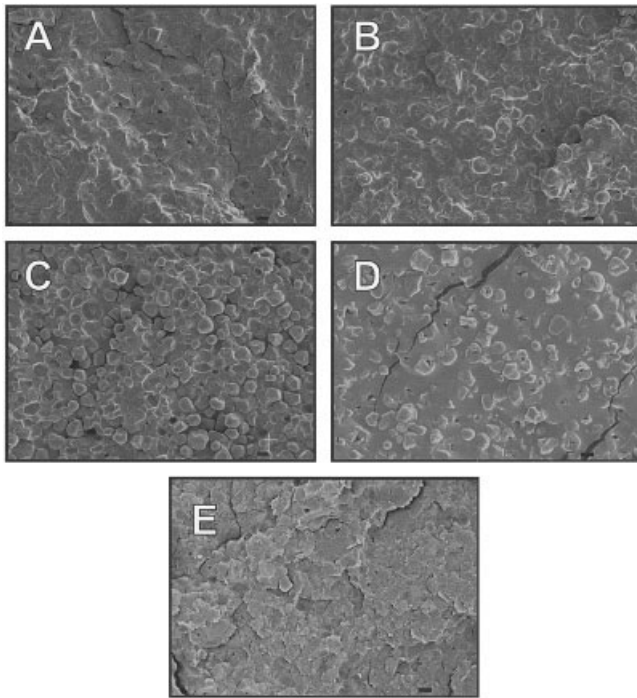
Figure 5 SEM images of fracture surfaces of composites aged 365 days at −20°C over calcium sulfate. The composites contained PHEE and (A) native starch, (B) crosslinked starch, (C) octenylsuccinated starch, (D) oxidized starch, and (E) native starch and PLA (original magnification = 500×, scale = 10 μm).

YM in two ways. First, water interfered with the adhesion of the starch and the PHEE matrix to reduce TS. Second, water plasticized the PHEE matrix, thus reducing YM and increasing %E. The increase in the water absorption caused the composites to change from being brittle to being more ductile. Aging for a short period of time caused TS and YM to increase. This was most likely due to the relaxation of internal stresses produced during injection molding. Composites containing native starch and equal amounts of PHEE and PLA were not affected by absorbed water and did not have the same reduction in TS and YM as composites containing starch filler and only PHEE. Samples containing PHEE and PLA did have a slight reduction in TS and YM after aging for 365 days. The type of starch filler also affected TS of the composites. Composites containing native or crosslinked starch had significantly greater TS than composites containing oxidized or octenylsuccinated starch. Native and crosslinked starch also had slightly greater elonga-

tions. The starch types did not affect YM of the composites, and this indicated that only the matrix controlled YM for these composites.

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