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Polyethylene/starch blends with enhanced oxygen barrier and mechanical properties: Effect of granule morphology damage by solid-state shear pulverization

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Abstract

A mechanical process called solid-state shear pulverization (SSSP) was used to create blends or composites of polyethylene (PE) and starch that resulted in damaged granular structures. Because starch granules are unchanged when polymer/starch blends are made by melt mixing, this is the first time that damage (surface roughening, cracking, and clustering) to starch granule morphology has been reported in polymer/starch blends or composites. These morphological changes result in a 29% reduction in oxygen permeability for a 70/30 wt% PE/starch blend made by SSSP relative to neat PE; this compares with a 21% reduction in oxygen permeability when a similar blend is made by melt processing. In addition, relative to neat PE, the tensile modulus of a 70/30 wt% PE/starch blend is increased by 20% in the damaged starch case (vs. 10% in the blend made by melt mixing) while the reduction in tensile strength is significantly smaller than that found in melt-mixed blends.

Keywords: Starch; Polyethylene; Solid-state shear pulverization

1. Introduction

Concerns over environmental impact such as global warming, use of renewable versus non-renewable resources, and the cost of synthetic polymers have recently motivated significant research in support of sustainable polymer systems in which one or more component is biodegradable and bio-based [1–3]. Starch is one of the most abundant and inexpensive sustainable polymers. There are many types of starch, each with a different combination of the linear polymer amylose and the branched polymer amylopectin [4]. As a result, there are many potential opportunities for preparing starch-based blends or composites which have tunable properties based on starch content and origin.

Polyethylene (PE) is the synthetic polymer that has been most commonly studied as a polymer matrix in blends with granular starch as filler [5–15]. Other polymers that have been investigated in polymer matrix/starch filler blends or composites include polypropylene (PP) [16–19], polycaprolactone [20–24], poly(lactic acid) (PLA) [25–31], and poly(hydroxyester ether) (PHEE) [30–37]. Some early research was premised on the hope that starch filler would increase the biodegradability of the synthetic polymer matrix, but it was demonstrated quantitatively that only the starch biodegrades when it is included in a matrix of non-biodegradable synthetic polymer [5]. More recently, many characteristics of PE melt mixed with starch granules have been studied including dispersion, thermal and mechanical properties, and water absorption. Studies examining mechanical properties have reported an increase in modulus but decreases in elongation at break and tensile strength with increasing starch content in immiscible PE/starch blends [6,7]. Other studies have focused on the effect of granule size on the PE/starch blend characteristics

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[7–10], with Lim et al. [9] noting that elongation and tensile strength are affected less when smaller granules are used. Research has also focused on chemically modifying either the PE or the starch to improve the compatibility of the resulting PE/starch blend [11–14]. However, regardless of how starch granules and PE (or PP, polycaprolactone, PLA, or PHEE) are melt mixed or how the polymers have been chemically modified, the size and shape of the starch granules are unchanged by melt processing in these blends [6,10,13,14].

In contrast to the null effect of melt mixing on the size and shape of starch granules in these synthetic polymer/starch blends, ball milling of neat starch granules has yielded significant changes in the size and shape of the granules, often referred to as ''damage'' [38–44]. (The fact that starch granule shape and size are affected by ball milling is not surprising; mechanical attrition accompanying ball milling is commonly used to modify the size and shape or to cause the amorphization of many materials that are much harder than starch [45–48].) Because of the intense level of mechanical work on the material accompanying ball milling, the starch granules undergo a range of physical damage including indentations on the granule surface, scratches through the outer shell, surface roughening, and sectional flattening [38]. Long milling times or higher amounts of work have yielded clumps or clusters of starch granules [39,40]. The changes in granule morphology accompanying ball milling have also been shown to affect the properties of starch. With increasing damage, neat starch exhibits an ability to absorb increasing levels of water at equilibrium [41–43]. Additionally, as compared with neat, undamaged granules, starch that has been extensively damaged by ball milling possesses modified crystallinity and gelatinization characteristics [44]. While the application of intense mechanical work to neat starch granules has yielded damage resulting in significant changes in starch morphology and properties, such damage has not yet been demonstrated in blends of starch with synthetic polymers.

(We note that several reports [49,50] in the literature have discussed the production of polymer/starch blends by intensive melt processing in which the starch is described as having undergone melting. In these cases, which involve polymers with polar groups that provide attractive interactions with hydroxyl groups within starch, there is a change in the starch morphology from the roughly spherical granules. However, the other characteristic features associated with ''damaged'' starch, including indentations on the granule surface, scratches through the outer shell, surface roughening, and sectional flattening, are not evident in these systems.)

Recent work has shown that ball milling can be used to create conventional polymer blends with well-dispersed nanoscale morphologies [51–53]. In addition, ball milling has been used to make biodegradable polymer nanocomposites [54,55]. Here we employ another mechanical process called solid-state shear pulverization (SSSP) [56–65] to create polymer/starch blends in which the size and shape of the starch granules are significantly damaged during the SSSP process. The SSSP process has a variety of advantages over other mechanical methods, such as ball milling, in that it is a continuous process with a range of tunable parameters. Additionally, SSSP is much milder compared with ball milling, resulting in controllable levels of chain scission, thereby allowing processing in the solid state under certain conditions with little or no reduction in molecular weight [59]. Solid-state shear pulverization has been studied as a process to recycle commingled plastics [56,57] as well as a method for producing immiscible blends with improved dispersion compared to melt-mixed blends [57,58,62], sometimes resulting in dispersed-phase domain sizes at or near the nanoscale [65]. In some cases, SSSP yields compatibilized immiscible blends through in situ block copolymer formation or by the addition of block or gradient copolymers to the blends during SSSP [60,61,64,65].

In this study, we use SSSP to create polymer/starch blends or composites with damaged starch granules. These materials are then compared with blends containing pristine (undamaged) starch. During pulverization, the starch granules in the blends become rougher and increase in size due to granule clustering. In 70/30 wt% high-density polyethylene (HDPE)/starch blends containing damaged starch, there is a decrease of 29% in oxygen permeability and a 20% increase in tensile modulus relative to neat HDPE. Both of these outcomes are better than those found in the blends made by melt processing.

2. Experimental

2.1. Materials

A commercially available cornstarch, Argo Starch, distributed by ACH Food Companies, was used in blend preparation. The matrix material was HDPE from Equistar Chemicals (Petrothene LM6007, with melt flow index = 0.8 g/10 min).

2.2. Blend production

Blends were produced by SSSP and began as mixtures of polymer pellets and starch powder ranging from 10 to 30 wt% (7–23 vol%) starch. The SSSP apparatus is a modified twin-screw extruder from Berstorff with a 25 mm diameter barrel. Major differences between the SSSP apparatus employed in this study and a conventional twin-screw melt extruder involve the ability to cool the barrel below room temperature (a −7 °C cooling medium is used to cool the barrels) and the use of tri-lobe rather than bi-lobe screw elements along a portion of the pulverizer screw. The high levels of shear stress achieved in SSSP result in repeated fragmentation and fusion of the blend materials. A detailed description of the apparatus is given elsewhere [57]. For these experiments, blends were processed utilizing a moderately harsh screw design involving two forward bi-lobe elements in the ''mixing zone'' and seven tri-lobe elements in the pulverization zone, of which four were forward, two neutral, and one reverse. Additionally, the pulverization zone had a 23 mm diameter barrel. A feed rate of 70–80 g/h and a screw speed of 300 rpm were employed.

Blends were also created using Minimax melt mixing or a batch CV Helicone mixer from DIT. In order to improve the level of mixing in the Minimax, three steel balls were

added during processing following a protocol described by Maric and Macosko [66].

2.3. Scanning electron microscopy (SEM)

A Hitachi S3500N scanning electron microscope was used to observe the morphology. Samples were examined using 5 kV accelerating voltage for powders and 10 kV accelerating voltage for solids. Solid samples were prepared by cutting with a razor blend in liquid nitrogen and then coating with a 3 nm gold layer using a Denton Desk III sputter coater. Number-average particle diameters of the starch were calculated using Scion Image Beta 4.0.2 image analysis software employing approximately 150 particles per sample. Scion calculated the area of each granule, and an approximate diameter was determined using a spherical particle assumption.

2.4. Thermogravimetric analysis (TGA)

Mass loss was monitored using a Mettler Toledo TGA/SDTA851. The system was calibrated using indium and aluminum in a 70 μL alumina pan. Samples weighing between 3 mg and 5 mg were run from 25 °C to 600 °C using a heating rate of 10 °C/min. The PE/starch blend samples were compression molded and allowed to equilibrate at ambient conditions for one month before analysis.

2.5. Oxygen permeation

Polymer films of approximately 0.5 mm were created using a hot press with 5 tons of ram force. (The film thickness was selected to prevent the starch from bridging the films. Samples with this thickness would not be used in conventional film applications but could find use in other packing materials.) Films were placed in an aluminum mask resulting in 5 cm^2 of permeable area. The masked films were analyzed for oxygen permeation using a MOCON OX-TRAN model 221. Films measured at 0% relative humidity were conditioned for several days to several weeks at ambient conditions (~23 °C and ~35% relative humidity) and then conditioned in the MOCON apparatus for 1 h at 23 °C and 0% relative humidity prior to measurement, which typically lasted from 3 h to 12 h. Films measured at 35% relative humidity were conditioned for several months at ambient conditions (~23 °C and ~35% relative humidity) and then conditioned in the MOCON apparatus for 24 h at 23 °C and 35% relative humidity prior to measurement, which typically lasted from 3 h to 4 h. Multiple films were run for each blend, and the results were averaged.

2.6. Mechanical properties

The Young's modulus and tensile strength were measured using a Minimat Tensile Tester. Samples (0.5 mm × 5.0 mm × 50 mm) were created using a hot press with 5 tons of ram force. The pressed samples remained at ambient conditions for several days before testing under the same conditions. Samples were anchored using a small piece of double-sided tape and clamped in rectangular brackets. They were then drawn at a rate of 2 mm/min. Multiple samples were run for each blend, and the results were averaged. The Young's modulus was determined from the slope of the initial stress–strain curve (<0.8% strain).

3. Results and discussion

Below we describe how the HDPE/starch blend or composite morphologies differ when processing is by melt mixing vs. SSSP, the latter leading to damaged starch. We then compare a series of properties in the HDPE/starch composites made by melt mixing and by SSSP, including oxygen barrier properties, tensile modulus, tensile strength, and thermogravimetric behavior related to water desorption.

3.1. HDPE/starch blend morphology

The granule size and shape of the as-received starch material are displayed in Fig. 1a. The starch has a variety of granule shapes including spherical, polyhedral, and oval. The individual granules have an average diameter of roughly 10 μm. Starch granules recovered after SSSP of neat starch are shown in Fig. 1b. Unlike results obtained by ball milling [38–44], starch granules that are processed by SSSP in the neat state do not undergo any damage. This may be understood to arise from the fact that the very small, hard starch granules pass

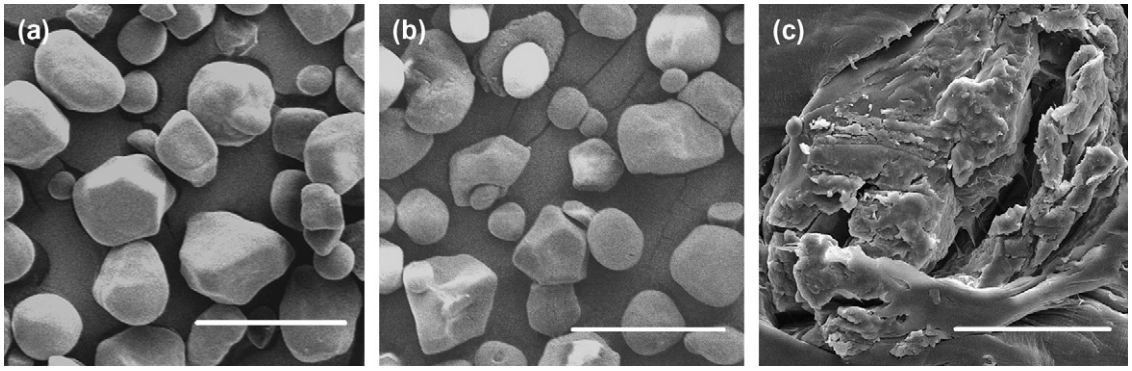

Fig. 1. Scanning electron micrographs of starch granules. (a) As received, (b) after pulverization in the neat state, and (c) after pulverization at 20 wt% with 80 wt% high-density polyethylene. Size bar = 25 μm in all micrographs.

easily through the clearance between the screw and barrel wall, thus minimizing the impact of the mechanical work that is apparent when larger polymer pellets or flakes are subjected to SSSP.

In stark, contrast to the null effects of pulverizing neat starch, significant granule damage is evident when starch is co-pulverized with HDPE. As shown in Fig. 1c, SSSP of a mix of starch granules (20 wt%) with HDPE pellets (80 wt%) can lead to substantial granule damage, including surface roughening, cracking, and diameter enlargement or clustering. The most likely reason that damage occurs in the blends but not with neat starch processed by SSSP is associated with the size scales of the materials being pulverized. From past experience, we have found that polymer blends in a pellet form are more successfully pulverized and mixed than a fine powder-like material. This is associated with the bulkier material (such as a pellet) beginning to ''mix'' in the lower shear zone of bi-lobe elements. The remaining incorporation and damage then occurs in the pulverization zone, which contains the tri-lobe elements. Thus, the addition of HDPE in pellet form improves the stresses imparted to the materials, resulting in damaged starch.

The effect of starch content on the granule morphology obtained in pulverized blends and melt-mixed blends is shown in Fig. 2. When 10 wt% starch is pulverized with HDPE (Fig. 2a), the granules exhibit moderate damage. When 20 wt% starch is in the pulverized blend (Fig. 2c), there is greater damage, especially increased surface roughening and clustering. When 30 wt% starch is pulverized with HDPE (Fig. 2e), even greater damage is evident, with highly irregular starch clusters being apparent. In contrast, in melt-mixed blends (Fig. 2b, d, and f), the granules have size, shape, and surface characteristics that are unchanged from the as-received starch. The null effect on the starch obtained in melt-mixed blends with HDPE is in agreement with previous research by Willett on LDPE/starch blends made by melt processing [6].

An approximate method for characterizing the level of clustering of starch granules accompanying the pulverization-induced damage is to determine the number-average particle or cluster diameter. The particle sizes for the pulverized HDPE/starch blends are listed in Table 1. As compared with the as-received starch particles, pulverization of a 90/10 wt% HDPE/starch blend results in about a 30% increase in number-average particle or cluster size. With SSSP of an 80/20 wt% HDPE/starch blend, the number-average starch particle or cluster size is almost twice that of the as-received starch, with nearly 40% of the particles or clusters having diameters exceeding 20 μm. In the 70/30 wt% HDPE/starch blends, a larger fraction of smaller particles or clusters are present, resulting in a reduction in number-average particle or cluster size as compared with the blend containing 20 wt% starch. While these numbers are a fair indication of cluster size, they do not account for the particle irregularity created by SSSP.

3.2. Oxygen permeation of HDPE/starch blends

The addition of an impermeable filler material to a polymer matrix has long been known to lead to improved barrier properties [67]. This change depends upon several factors including size and shape of the filler particle, extent of filler dispersion, and the level of filler in the sample. In the case of impermeable, spherical filler particles, the Maxwell model predicts the dependence of permeability coefficient, P, on filler volume fraction [68,69]:

$$P = P_{\text{matrix}}\left(\frac{2(1-\phi)}{2+\phi}\right) \tag{1}$$

where P_{matrix} is the permeability of the neat matrix material and ϕ is the volume fraction of the spherical, impermeable filler in the blend or composite.

Permeation studies on starch films have shown that these materials make excellent barriers to oxygen [70–72]. Starch films (with none of the glycerol that is commonly present in plasticized starch) have a permeation coefficient of ~0.1 cc mm/(m^2 day atm) at 57% relative humidity and room temperature [70]. As the humidity decreases, starch becomes an even better oxygen barrier [71]. Given that there is a factor of ~500 difference in the oxygen permeability of starch and HDPE (which, as measured in the current study, has an oxygen permeability coefficient of ~48 cc mm/(m^2 day atm)) to an excellent approximation it is only the HDPE matrix present in a HDPE/starch blend that is permeable to oxygen. Thus, if the as-received starch granules are approximated to be spheres, then, relative to the oxygen permeability in neat HDPE, a 30% decrease in oxygen permeability would be expected in the 70/30 wt % (77/23 vol%) HDPE/starch blends that are made by melt mixing. (This assumes that the densities of the starch and HDPE are 1.4 g/cm^3 [6] and 0.96 g/cm^3, respectively.)

Fig. 3 shows the first determination of oxygen permeability coefficients for polymer blends containing granular starch prepared either by SSSP or by melt mixing at 0% relative humidity. The incorporation of granular starch in the HDPE/starch blends made by melt mixing decreases the oxygen permeability coefficient substantially, although not to the extent expected based on the simple Maxwell model. For example, in the 70/30 wt% HDPE/starch blend made by melt mixing, the oxygen permeability coefficient is reduced by 21% relative to that of neat HDPE. This difference may result because the granules are not exactly spherical and because there may not be perfect wetting between the HDPE matrix and all of the dispersed starch granules. Relative to blends made by melt mixing, the HDPE/starch samples made by SSSP exhibit improved oxygen barrier properties. For example, in the 70/30 wt% HDPE/starch blend made by SSSP, the oxygen permeability coefficient is reduced by 29% relative to neat HDPE. This greater improvement in barrier properties with blends containing damaged starch may be the result of greater aspect ratios and irregular shapes of the filler contributing to greater tortuosity in the diffusive path of oxygen through the HDPE matrix. Further study of this effect is warranted.

Experiments performed at a higher relative humidity (35%) produced results that were nearly identical to the average values recorded when the films were run at 0% relative humidity. For example, for a 70/30 wt% HDPE/starch blend made by SSSP,

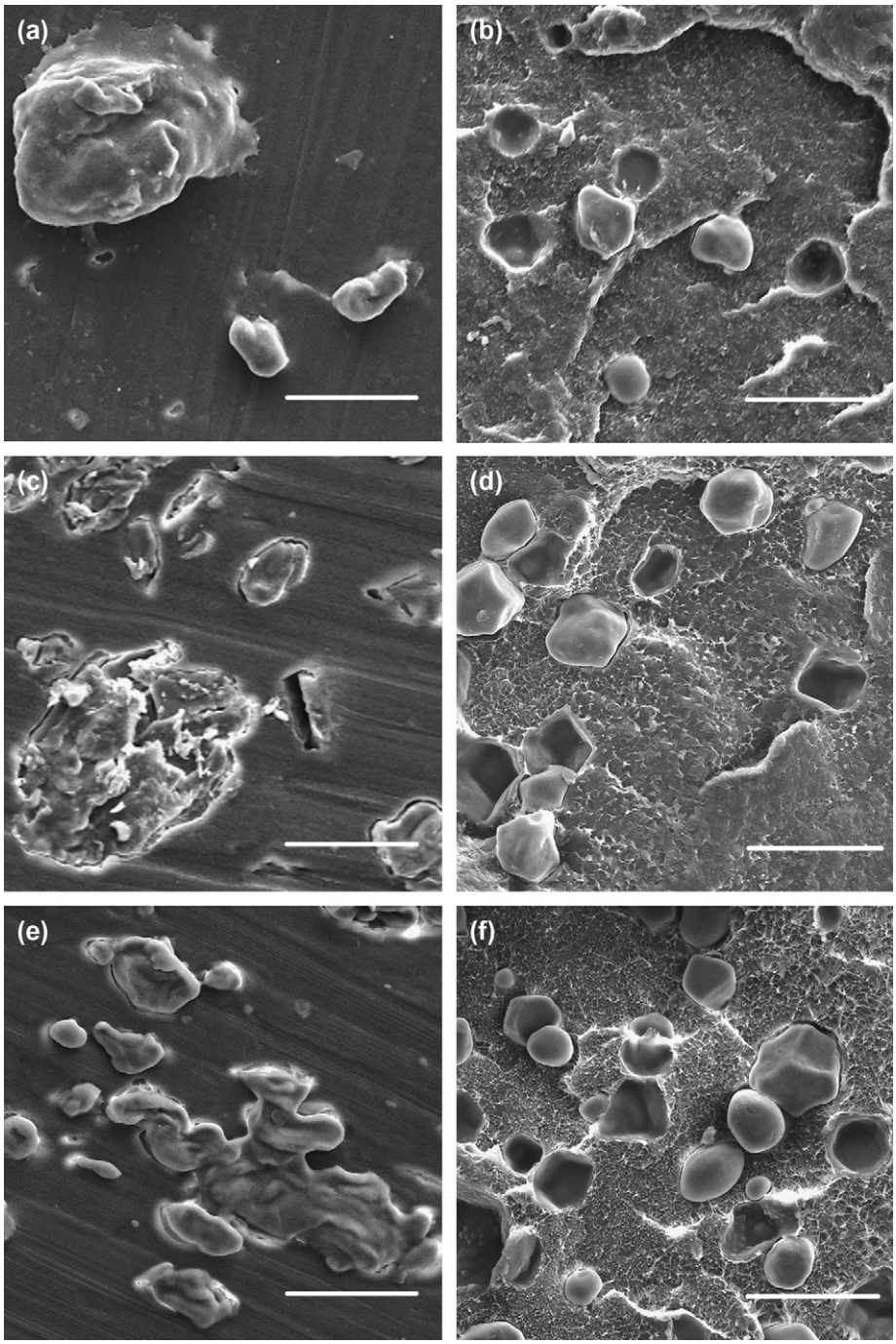

Fig. 2. Scanning electron micrographs of a 90/10 wt% HDPE/starch blend made by (a) pulverization and (b) melt mixing, an 80/20 wt% HDPE/starch blend made by (c) pulverization and (d) melt mixing, and a 70/30 wt% HDPE/starch blend made by (e) pulverization and (f) melt mixing. Size bar = 25 μm in all micrographs.

the average oxygen permeability coefficient is 34 cc mm/(m^2 day atm) at 0% relative humidity and 33 cc mm/(m^2 day atm) at 35% relative humidity. When made by melt mixing, the blend exhibited an average oxygen permeability coefficient of 38 cc mm/(m^2 day atm) at 0% relative humidity and 39 cc mm/(m^2 day atm) at 35% relative humidity. Since starch is highly sensitive to moisture content, additional tests will be performed at much higher relative humidities to verify whether the current trends remain for the pulverized and melt-processed samples.

We note that significant research has been focused on producing polymer–clay nanocomposites in order to achieve improved barrier properties [73–76]. With a 2.8 vol% clay/HDPE nanocomposite, Suter and co-workers [73] reported a 31% reduction in oxygen permeability coefficient relative to that of neat HDPE. This improvement in oxygen barrier properties is nearly identical to that obtained in our 70/30 wt % HDPE/starch blend made by SSSP. This indicates that incorporating starch in polymers by SSSP may lead to enhancements in barrier properties that are competitive with those

Table 1
Average particle size diameter and percent of large agglomerations in HDPE/starch blends made by SSSP

Material	Average particle diameter (μm)	Particles over 20 μm (%)
Neat starch	10.2	0
90/10 wt% HDPE/starch	13.2	15
80/20 wt% HDPE/starch	19.1	38
70/30 wt% HDPE/starch	13.1	12

obtained in nanocomposites and suggests a new avenue of research and development for starch-filled polymers.

3.3. Mechanical properties

Several studies have previously examined the mechanical properties of low density polyethylene (LDPE)/granular starch blends or composites [6,10,12]. These blends exhibited an increase in Young's modulus and a decrease in tensile strength with increasing starch filler content. Willett [6] demonstrated that the modulus, E, of the LDPE/starch composite could be successfully modeled using the Kerner equation [77] with modified proportionality constants:

$$E = E_0\left[1 + \left(\frac{\phi}{1-\phi}\right)\left\{\frac{15(1-\nu)}{(8-10\nu)}\right\}\right] \quad (2)$$

where E_0 is the matrix modulus, ϕ is the volume fraction of filler, and ν is the Poisson's ratio of the matrix (assumed to be 0.38, which is the average of reported literature values of the Poisson ratio for HDPE ranging from 0.35 to 0.40).

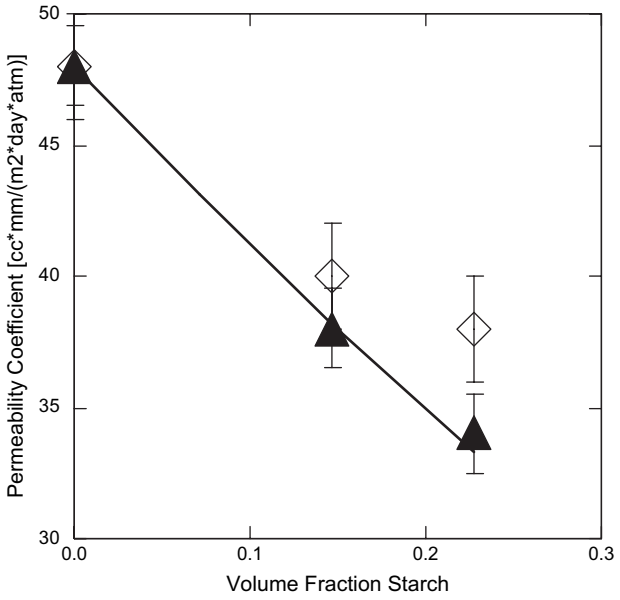

Fig. 3. Oxygen permeability of the HDPE/starch blends where the filled triangles are the blends produced using SSSP and open diamonds are the blends from melt mixing. The solid line indicates the theoretical values predicted by the Maxwell model. Error bars represent the standard error associated with the several measurements at each volume fraction of starch.

The HDPE/starch blends created in the present study show the same qualitative trends in mechanical properties as the previously characterized LDPE/starch blends: there is an increase in Young's modulus and a decrease in tensile strength with increasing starch filler content regardless of preparation method. Fig. 4 shows the modulus for the HDPE/starch blends created by SSSP or by melt mixing as well as the theoretical prediction using the Kerner equation. Both melt mixing and SSSP result in an increase in modulus since the starch is stiffer than the HDPE. However, in general the blends created using SSSP exhibit a larger increase in modulus than the blends produced by melt mixing. In all cases, the HDPE/starch blends resulted in a lower modulus than predicted by the Kerner equation. Willett [6] also found the LDPE/starch blends had a lower modulus than predicted by the Kerner equation although his experimental data were closer to the theoretical prediction than is observed in the HDPE/starch blends. The difference in modulus between LDPE and HDPE may contribute to this effect. (The form of the Kerner equation in Eq. (2) is for systems in which the rigidity of the filler is much greater than that of the matrix. The difference in rigidity is greater for LDPE than for HDPE.)

In contrast to the results on tensile modulus, the tensile strength in the HDPE/starch blends decreases with increasing starch filler regardless of preparation method, as shown in Fig. 5. This behavior is in qualitative agreement with the prediction from the geometric model by Nicolais and Narkis [78] for the tensile strength of a composite with identical, uniformly distributed spherical filler particles which experience no adhesion with the matrix:

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

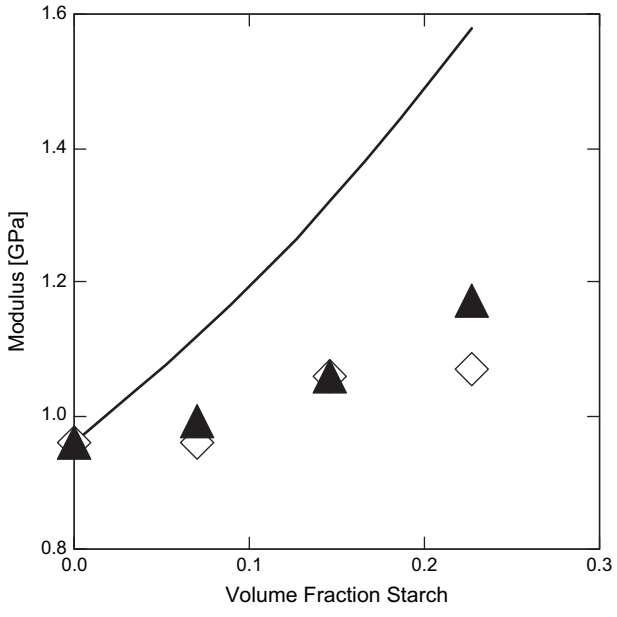

Fig. 4. Tensile modulus of the HDPE/starch blends: filled triangles represent blends produced using SSSP, and open diamonds represent blends produced by melt mixing. The solid curve indicates the dependence of modulus on volume fraction of filler predicted by the Kerner equation (Eq. (2)). Symbol sizes are equal to or larger than the standard deviations associated with the measurements.

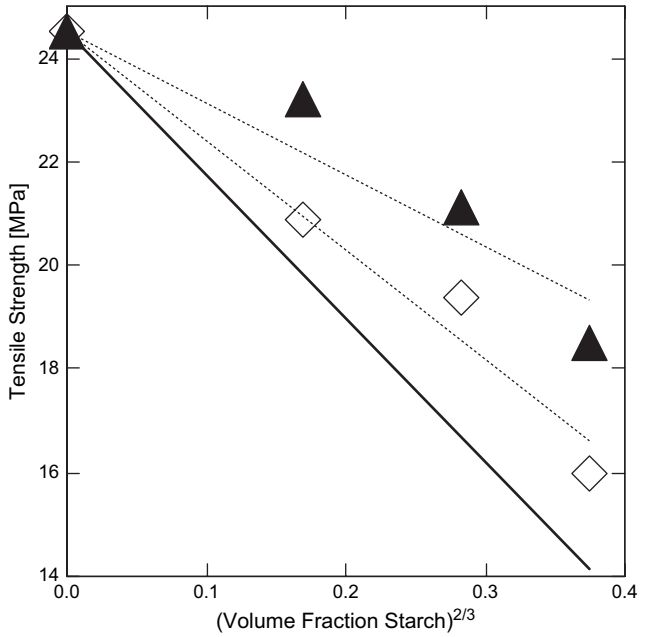

Fig. 5. Tensile strength of HDPE/starch blends: filled triangles represent blends produced using SSSP, and open diamonds represent blends produced by melt mixing. The solid line indicates the dependence of tensile strength on the 2/3 power of the volume fraction filler predicted by Eq. (3), and the dashed lines indicate best fit lines for the two blend systems. Symbol sizes are equal to or larger than the standard deviations associated with the measurements.

where σ_c is the composite tensile strength, σ_0 is the matrix tensile strength, and ϕ is the volume fraction of filler. Similar to the results by Willett [6] in LDPE/starch blends, the decrease in the tensile strength is smaller than predicted by Eq. (3). Instead of the slope of -1.21 indicated in Eq. (3), the melt-mixed samples are best fit by a slope of -0.87 while the samples made by SSSP are best fit by a slope of -0.57. The increased deviation in the SSSP-prepared samples is at least partially due to the assumption in Eq. (3) of spherical filler particles. As compared with Eq. (3), the reduced magnitude of the slopes obtained in the samples prepared by melt mixing or by SSSP indicates that there is some level of interaction or adhesion between the starch and HDPE. Additional deviation from the predicted slope may be associated with changes in the maximum packing fraction for the non-bonding starch filler upon damage.

These results indicate that the addition of starch to HDPE creates a stiffer material with less tensile strength, in agreement with previous research on LDPE/starch composites. However, because of the damage of the starch granules, the HDPE/starch blends made by SSSP have enhanced properties relative to the blends made by melt mixing, i.e., the blends made by SSSP have a greater modulus and exhibit a smaller reduction in tensile strength.

A comparison can also be made to mechanical properties recently obtained in PE nanocomposites containing 2.8 vol% clay. Besides characterizing the oxygen permeability of such nanocomposites, Suter and co-workers [73] also characterized the mechanical properties relative to neat HDPE. The improvements of the mechanical properties obtained in 70/30 wt% HDPE/starch blends made by SSSP relative to the mechanical properties in neat HDPE are close to but not as good as those obtained by Suter and co-workers in their HDPE–clay nanocomposite relative to neat HDPE. We obtained a 20% increase in tensile modulus and a 25% reduction in tensile strength in our 70/30 wt% HDPE/starch blend made by SSSP; in contrast, Suter and co-workers obtained a 25% increase in tensile modulus and a constant tensile strength.

Given that we have only tested one set of pulverization conditions, including screw design, in the production of our HDPE/starch blends made by SSSP, further investigation of the effect of screw design and other SSSP parameters on the damage to the granular starch and resulting effects on mechanical properties is needed. It may be possible to enhance further the mechanical properties and oxygen barrier characteristics obtained in the HDPE/starch system.

3.4. Thermogravimetric characterization

Monitoring the weight during a thermal ramp of the starch blends led to three distinct transitions. The first transition occurs between room temperature and 170 °C due to the loss of water from the sample. A second transition around 300 °C marks the degradation of the starch component in the blend. The final transition at 480 °C is due to the final degradation of the HDPE matrix. The last two transitions exhibited identical characteristics regardless of how the blends were prepared. On the other hand, the water transition had a different characteristic shape depending upon blend production method. Fig. 6 shows a close up of the water loss curves for the 70/30 wt% HDPE/starch blends. The initial slope of the pulverized sample is larger than the melt-mixed blend indicating that the

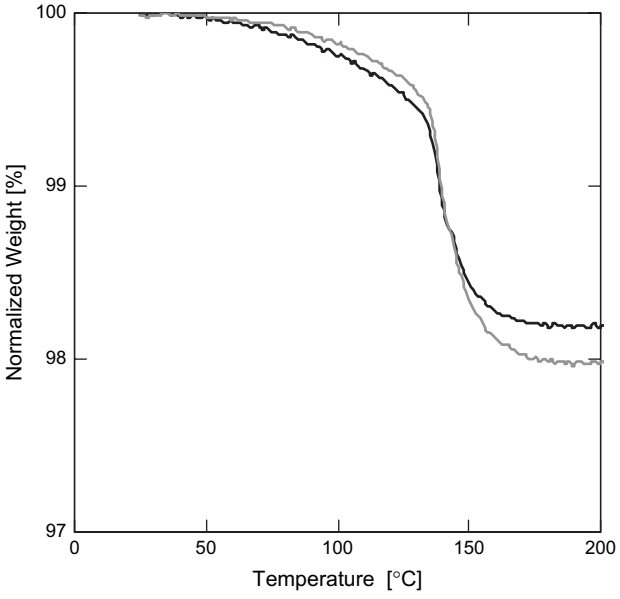

Fig. 6. Thermogravimetric analysis of mass loss associated with desorption of water upon heating 70/30 wt% HDPE/starch blends produced by SSSP (black curve) or melt mixing (grey curve).

SSSP samples lose water more easily at the lower temperatures. This is likely due to the fact that damaged starch has been shown to have a lower capacity for binding water particles at low moisture contents [41]. Once samples prepared by either method reach ~135 °C, the remaining water (bound to the outer starch shell) quickly desorbs. Similar trends were seen for all blend compositions.

In addition to affecting how the water bonds to the starch granule, damage of starch in the neat state has also been previously shown to affect the level of water absorbed by the material [43]. Thermogravimetric analysis of our various HDPE/starch blends indicates that, for a given composition of starch in the blend, there is no significant difference in the water content of the blends prepared by SSSP or melt mixing. However, regardless of how the blends were produced, there was much less water in the starch (5–6 wt% relative to starch in the 90/10 wt% blends and 7–8 wt% relative to starch in the 70/30 wt% blends) compared to the unprocessed starch granules which typically have ~12 wt% sorbed water. This decrease is due to the HDPE encasing the starch in the blends, which hinders water absorption.

4. Summary

Polymer/starch blends or composites containing damaged starch granules were produced for the first time using a novel process called solid-state shear pulverization. The damage to the starch included surface roughening, cracking, and/or clustering leading to highly irregular shapes, and is similar to that exhibited by neat starch that has been subjected to ball milling.

Various properties of the HDPE/starch blends were compared as functions of starch content and process method (melt mixing vs. SSSP). In the first measurement of the effect of starch filler on oxygen barrier properties in polymer/starch blends or composites, it was shown that producing HDPE/starch blends by melt mixing leads to a substantial reduction in oxygen permeability coefficient, which is expected based on the nearly impermeable nature of starch to oxygen. However, HDPE/starch blends made by SSSP exhibit enhanced oxygen barrier properties relative to blends made by melt mixing, which can be explained by the irregular shapes associated with the damaged starch dispersed in the HDPE matrix. All HDPE/starch blends exhibit an increase in tensile modulus and a reduction in tensile strength with increasing starch content. However, the mechanical properties are better in the blends made by SSSP than in those made by melt mixing, which, as with the barrier properties, can be explained by the damage to the starch caused by SSSP. Thermogravimetric analysis revealed that granular damage affects how water desorbs from the blends, although the overall water sorption in the blends is unchanged within error by the process method.

The oxygen barrier properties and tensile modulus of the 70/30 wt% HDPE/starch blend made by SSSP compare reasonably well with the properties reported for a HDPE–clay nanocomposite [73]. This suggests that polymer/starch blends made by SSSP may have technological promise even without considering their potential contribution to sustainability. Given that the current study employed only one set of SSSP process conditions to prepare the HDPE/starch blends, further study is warranted, especially to address the effects of SSSP screw design and the polymer matrix on the damage to starch and the resulting property enhancements that may be achieved in polymer/starch blends. Related investigations are underway.

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