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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