

Effect of Blend Composition and Structure on Biodegradation of Starch/Ecoflex-Filled Polyethylene Films

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ABSTRACT: A method to blend starches and polyethylene, and thus improve the environmental footprint, was investigated. Unlike traditional methods that utilize compatibilizers or rely on reactive extrusion to achieve the desired material compatibility, a high amylose starch, such as Gelose 80, was mixed with native starch, converted to thermoplastic starch, and compounded with Ecoflex and polyethylene. Films showed good integrity and were evaluated for mechanical properties, anaerobic biodegradability, and structure changes both before and after anaerobic sludge digestion. Mechanical properties were sufficient that these films might be utilized in a number of applications but were not recommended as a sustainable solution. Biodegradation was below the theoretical maximum, was

not a linear function of the amount of biodegradable materials incorporated in the films, and was depressed further as the proportion of polyethylene increased due to an encapsulation effect. Structural evaluation showed the components of the blends remained as separate phases and the structure of the Gelose 80 was reminiscent of interphase material. Biodegradation yield appeared to be principally driven by connectivity of the starches within the films to the anaerobic sludge digestion environment. Recommendations for additional studies were given. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1808–1816, 2011

Key words: biodegradable; biopolymers; blends; compatibilization; morphology

INTRODUCTION

Polyethylene is one of the cost-advantaged commodity polymers. It is widely used in all facets of industrial applications. A few examples of its ubiquitous products are liquid containers, automotive compartments, electrical appliances, furniture, and thermoplastic films or fibers. However, polyethylene is derived from limited petroleum resources and not biodegradable. In recent years, many attempts focus on incorporating sustainable and renewable materials such as starch into polyethylene-based blends to improve its environmental footprint. However, polyethylene and starch are highly incompatible. Simple blending of polyethylene and starch without compatibilizers results in poor mechanical properties at even very low incorporation of either material. The industry-wide approach is to use compatibilizers such as Epolene[®] C-16 (maleated polyethylene) from Eastman Chemical Company, or Polybond[®] series from Chemtura Corp., to create useful blends comprising starch up to 50%.^{1,2} Fantuzzo et al.³ addressed polyethylene-based blends for packaging films using Fusabond[®] resins from DuPont, as a compatibilizer.

Starch consists of two major molecules: amylose which has a linear molecular configuration and amylopectin which is branched every 25–30 glucose units. The typical molecular weight (MW) of amylose is about 10^5 to 10^6 g/mol. and the MW of amylopectin ranges from 10^7 to 10^9 g/mol. Percentages of these two molecules vary from starch to starch. In native corn starch, for example, the amylose composition is about 25%, and the remaining 75% is amylopectin.

Starch biopolymer limitation is frequently observed during processing to make thermoplastic starch. The extrusion of native corn starch inevitably involves forcing the corn starch through a small die orifice. The large and highly branched amylopectin molecules naturally resist this melt treatment.⁴ On the other hand; linear molecules such as amylose are believed to be processed easily. Therefore, artificial increase in amylose content of the starch mixture by adding high amylose starch is a proposed approach in this study.

It is well known that the neat polyethylene is highly refractory to any environmental degradation. Methods proposed to make polyethylene more degradable and abate adverse environmental effects include oxodegradable additives, starch, and grafted starch.^{5–8} A common processing method to make polyethylene-based blends relies on an extrusion technology or reactive extrusion to create compatible blends for specific applications. The blend becomes

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degradable when it and the additive are exposed to the microorganisms. However, the results derived from composting or wastewater treatment are not conclusive and in some cases, they are controversial.^{9–12} Greene¹³ did not observe any additive filled polyethylene biodegradation in composting or anaerobic sludge digestion, while Tena-Salcido et al.¹⁴ reported significant biodegradation (up to 90%) of polyethylene and starch blends in activated sludge and enzyme hydrolysis. Jakubowicz¹⁵ tested polyethylene films filled with Mn-stearate and showed 60% film biodegradation in the soil environment. These wide ranges of results call for additional study using industrially accepted standard testing method such as ASTM D6400 or ASTM D5210.

It is important to understand biodegradability of polymeric blends containing polyethylene material because such blends have a very attractive cost basis. It is also imperative to clarify environmental performance of biodegradable blends comprising polyethylene for guidance to material development efforts. The objective of this work is to:

- Create biodegradable polymer and polyethylene blends without using any compatibilizers
- Evaluate film mechanical properties
- Assess film anaerobic biodegradability
- Assess structural changes that occur with anaerobic digestion to determine what structures might limit degradation

EXPERIMENTAL

Materials

Native corn starch Cargill GumTM 03460 was purchased from Cargill, Inc. (Minneapolis, MN). High amylose starch, Gelose 80, was purchased from Penford Products (Centennial, CO). Glycerin was purchased from Cognis Corp. (Cincinnati, OH). Ecoflex[®] F BX 7011 was purchased from BASF (Florham Park, NJ). Linear low-density polyethylene, Dowlex 2045, was purchased from Dow Chemical Company (Midland, MI). Digested sludge was collected from Neenah-Menasha Regional Wastewater Treatment Facility in Neenah, WI. Solids content in the digested sludge was 2.5% with a pH in the range of 7.4–7.8. The sludge color was black because of the presence of organic matter.

Methods

Equipment

Thermoplastic blends of native and high amylose starches were made using ZSK-30 extruder (Werner and Pfleiderer Corp., Ramsey, NJ). The ZSK-30 extruder was a corotating, twin-screw extruder. The ex-

truder diameter was 30 mm with the length of the screws up to 1328 mm. The extruder had 14 barrels, numbered consecutively 1–14 from the feed hopper to the die. Starch and Ecoflex filled polyethylene films were cast using HAAKE Rheomex 252 Single Screw Extruder (Thermo Scientific, Waltham, MA). The Rheomex 252 extruder was a multi-barrel extruder with diameter of 19 mm and length of 476 mm.

Film production

The high amylose starch, Gelose 80 that contains 81% amylose, was first mixed with the native corn starch, Cargill GumTM 03460 that contains 19% amylose, at an equal weight ratio. The mixture was converted into thermoplastic starch through the extrusion with glycerin. The thermoplastic starch mix was then blended with the polyester Ecoflex F BX 7011 and the low linear density polyethylene Dowlex 2045 to make blends for film casting without using any compatibilizers.

Mixed thermoplastic starch. The native corn and high amylose starches were mixed and extruded to form the Mixed ThermoPlastic Starch (MTPS). Native corn and high amylose starch (50/50) were mixed using a Hobart mixer for 5 min. Final amylose content in the mixed starches is 49.5% estimated according to data from starch suppliers. The starch mixture was added to the K-Tron feeder (K-Tron America, Pitman, NJ) that vertically fed the mixture into the ZSK-30 extruder. The extruder was heated with the following sequential zone profile: 100, 120, 130, 140, 150, 145, and 140°C at the die. Pressure ranged from 2.41 to 2.76 MPa, and torque was at 45 to 50%. Glycerin was pumped into barrel number 2 at 20 wt %. The screw rotational speed was set to rotate at 2.5 Hz. The vent was closed at the end of the extruder without a need of releasing moisture. A three-hole die of 3 mm diameter that was separated by 10 mm space was used to shape the melt into strands that were cooled on a conveyer belt and then pelletized.

Film casting. The MTPS was then dry-mixed with Ecoflex and linear low-density polyethylene (PE) at four ratios for film casting. They were (A) 40% Ecoflex and 60% MTPS, (B) 50% PE and 50% A, (C) 40% PE and 60% A, and (D) 30% PE and 70% A. The operating conditions to convert the blends into the film were recorded (Table I). The changes in temperature, torque, and melt pressure were minor from one code to another. The converting process by film casting was successful and all films had a thickness range of 50–80 μm .

Mechanical properties

Films cast from the compounds considered were subjected to tensile testing to determine mechanical

TABLE I
Processing Conditions for Film Casting on HAAKE Extruder

Rheomex 252 single screw extruder	Film sample code			
	A	B	C	D
Film casting setting				
Zone 1 temp (°C)	120	140	140	130
Zone 2 temp (°C)	140	165	165	155
Zone 3 temp (°C)	160	175	175	165
Zone 4 (pump) temp (°C)	155	170	170	160
Zone 5 (die) temp (°C)	150	165	165	160
Screw speed (Hz)	1	1	1	1
Torque (N·m)	69–74	52–54	44–47	57–59
Melt pressure (MPa)	50–52	33–36	32–34	33–36
Melt temperature (°C)	165	170	171	177
Film thickness (µm)	50–80			

properties. Tensile testing was performed using the Sintech 1/D. Samples were tested in both the cross direction (CD) and machine direction (MD). Before testing, films were cut into dog-bone shaped samples with a center width of 3.0 mm. The samples were held in place by grips on the Sintech set to a gauge length of 18.0 mm. For the duration of the test, samples were stretched at a crosshead speed of 127 mm/min until breakage occurred. The computer program TestWorks 4 collected data points throughout the test and generated a stress (MPa) versus strain (%) curve from which peak stress, elongation, modulus, and toughness were determined. Data were reported as the mean of five measurements. Error bars reported in figures were one standard deviation calculated using a method outlined by Young.¹⁶

Biodegradation

Biodegradation measurement. ASTM D5210 was used to assess the film biodegradation in anaerobic conditions. The stepwise procedures were the same as those specified in ASTM D5210 and are not repeated here for the sake of brevity. The amount of each polymeric sample weighed about 0.2 g. Triplicates for each sample code were prepared for anaerobic digestion. The prepared liquid sludge volume was 100 mL and the incubation temperature was fixed at 35°C throughout the experiments. The gas evolution data, which were a combination of carbon dioxide and methane generated during sample anaerobic digestion, were averaged from each measurement. At the termination of the biodegradation study, the film samples were removed from the 125-mL serum bottles, rinsed with tap water, disinfected in isopropanol, again rinsed with tap water, and then air-dried.

Biodegradation calculations. Biodegradability of the carbohydrate polymers such as starch, wheat gluten, and algae can be estimated according to eq. (1) shown below:

$$\text{Biodegradability} = \frac{\sum V_{\text{Sample}} - \sum V_{\text{Blank}}}{V_{\text{Theoretical}}} \times 100\% \quad (1)$$

$\sum V_{\text{Sample}}$ is the total CO₂ and CH₄ volume measured from the sample vessel under standard conditions in milliliters. $\sum V_{\text{Blank}}$ is the CO₂ and CH₄ volume measured from the blank vessel under standard conditions in milliliters. $V_{\text{Theoretical}}$ is the maximum theoretical volume of the biogas (CO₂ and CH₄) evolved after complete biodegradation of the test material under standard conditions in milliliters. In addition to gaseous products that are accounted for according to ASTM D5210, other residual by-products and biomass formed by microorganisms during the anaerobic sludge digestion are not accounted for according to ASTM D5210 and were not accounted for here. Cellulose was used as the reference material so that biodegradation of carbohydrate samples can be compared. $V_{\text{Theoretical}}$ of the 0.2 g cellulose [(C₆H₁₀O₅)_n] was calculated to be 166 mL. The evolved (CO₂ + CH₄) volume is dependent on only the carbon amount regardless of the CO₂ and CH₄ ratio.^{17,18} For samples, actual carbon content (%) was analytically determined and used for $V_{\text{Theoretical}}$ estimates.

Film structure

Scanning electron microscopy (SEM) was used to characterize the surface and internal structure of films before and after biodegradation. Samples that did not receive anaerobic digestion were immersed in isopropanol for 1 h and air dried. For surface study, several representative samples were mounted with conductive tape, sputter coated with gold, and examined for surface structure. For study of the internal structure, several representative samples were immersed in ethanol, frozen by immersion in liquid nitrogen, and impact-sectioned with a single edge razor blade while in the liquid nitrogen. Sections were removed from the liquid nitrogen and placed on a metal surface to reach room temperature. Sections were either directly examined or phases were decorated by an oxygen plasma.¹⁹ For decoration, an Emitech K1050X barrel reactor operated at 40-W with an oxygen flow of 50 mL/min was sufficient to produce the blue-white plasma indicative of an oxygen-rich plasma. Both undecorated and decorated sections were vertically mounted, sputter-coated with gold, and examined. Micrographs illustrative of surface and internal structure were digitally captured.

RESULTS AND DISCUSSION

Film mechanical properties

Figure 1 represents the elongation of the starch, Ecoflex, and polyethylene composite films. The film MD

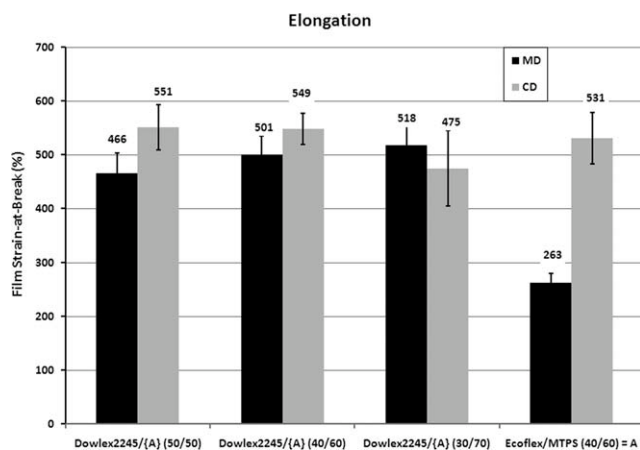


Figure 1 Starch, Ecoflex, and polyethylene film elongation ($n = 5$, 1 std. dev. error bars).

elongation of Ecoflex/MTPS (40/60) shows about 50% lower than CD elongation. That disparity significantly improved as polyethylene content increased from 30 to 50%. For the film blends containing polyethylene, the elongation ranged from 466 to 551%.

Figure 2 is the film peak stress for the composites. The film peak stress for Ecoflex/MTPS (40/60) was fairly low. It gradually improved as polyethylene content increased in the blends. However, their MD film peak stress values were about 100% greater than CD film peak stress.

Figure 3 shows the film modulus for the composites. The film modulus increased as the amount of polyethylene in the blends was increased; indicating the presence of polyethylene reduced the flexibility of the films. However, such increases in the film modulus were only limited to the cross-direction of the films. The MD modulus values were stable.

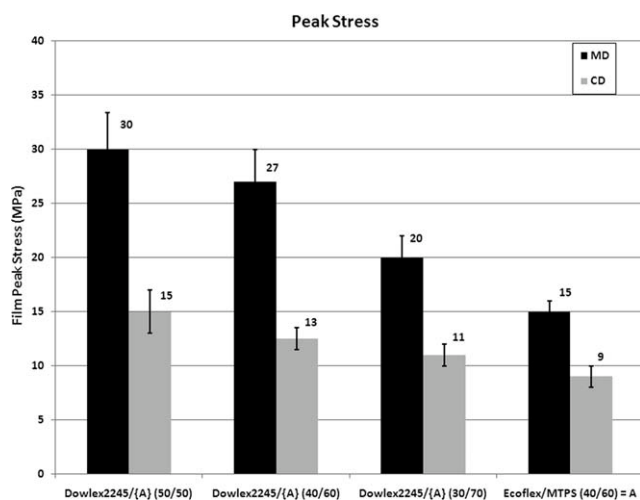


Figure 2 Starch, Ecoflex, and polyethylene film peak stress ($n = 5$, 1 std. dev. error bars).

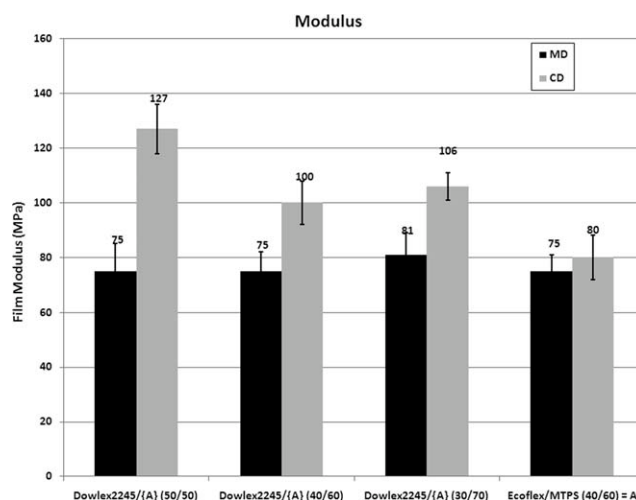


Figure 3 Starch, Ecoflex, and polyethylene film modulus ($n = 5$, 1 std. dev. error bars).

Figure 4 indicates the film toughness. Of the films made, Ecoflex/MTPS (40/60) had the lowest toughness whereas PE Dowlex 2245/[A] (50/50) had the highest toughness values. The improvement of the MD film toughness due to the presence of polyethylene was greater in the cross-direction of the films.

Biodegradation

Figure 5 displays the combination of CO_2 and CH_4 evolution over the course of the anaerobic sludge digestion (90 days) of the films. It seems that any meaningful biodegradation of the films occurred within the first 20 days. Films degraded little thereafter up to 90 days. On the other hand, cellulose powder as a control degraded mostly within the first 35 to 40 days and achieved about 85% biodegradation as estimated using eq. (1). For all film samples, carbon dioxide and methane generation as an indication of

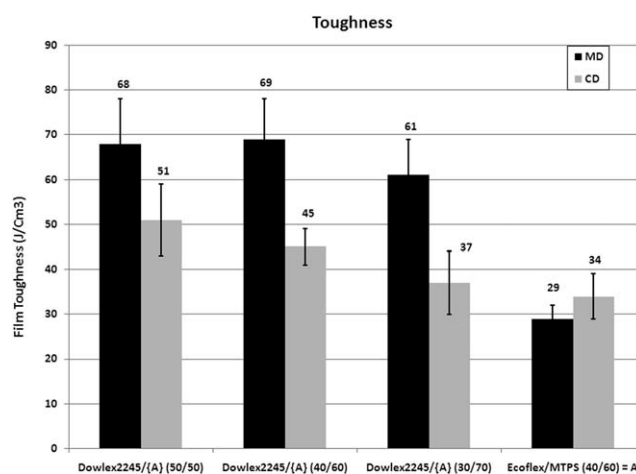


Figure 4 Starch, Ecoflex, and polyethylene film toughness ($n = 5$, 1 std. dev. error bars).

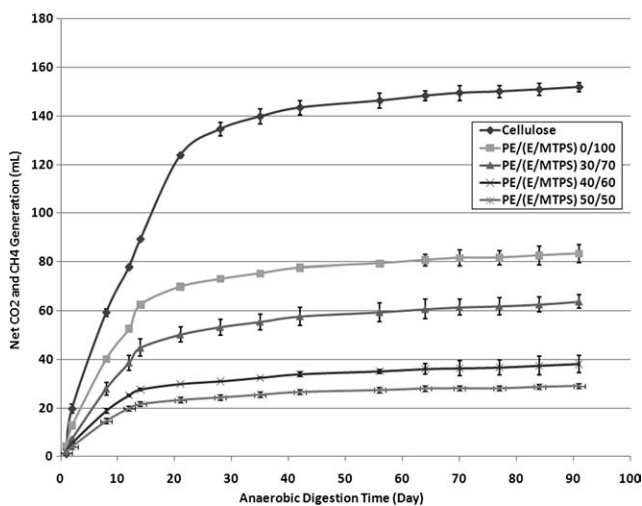


Figure 5 Film and reference cellulose anaerobic gas production ($n = 3$, 1 std. dev. error bars).

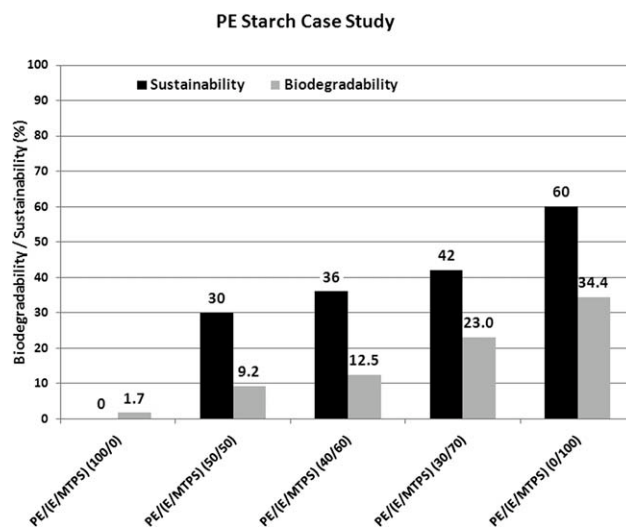


Figure 6 A percentage of film biodegradability in relation to available sustainable and renewable content in the blends ($n = 3$).

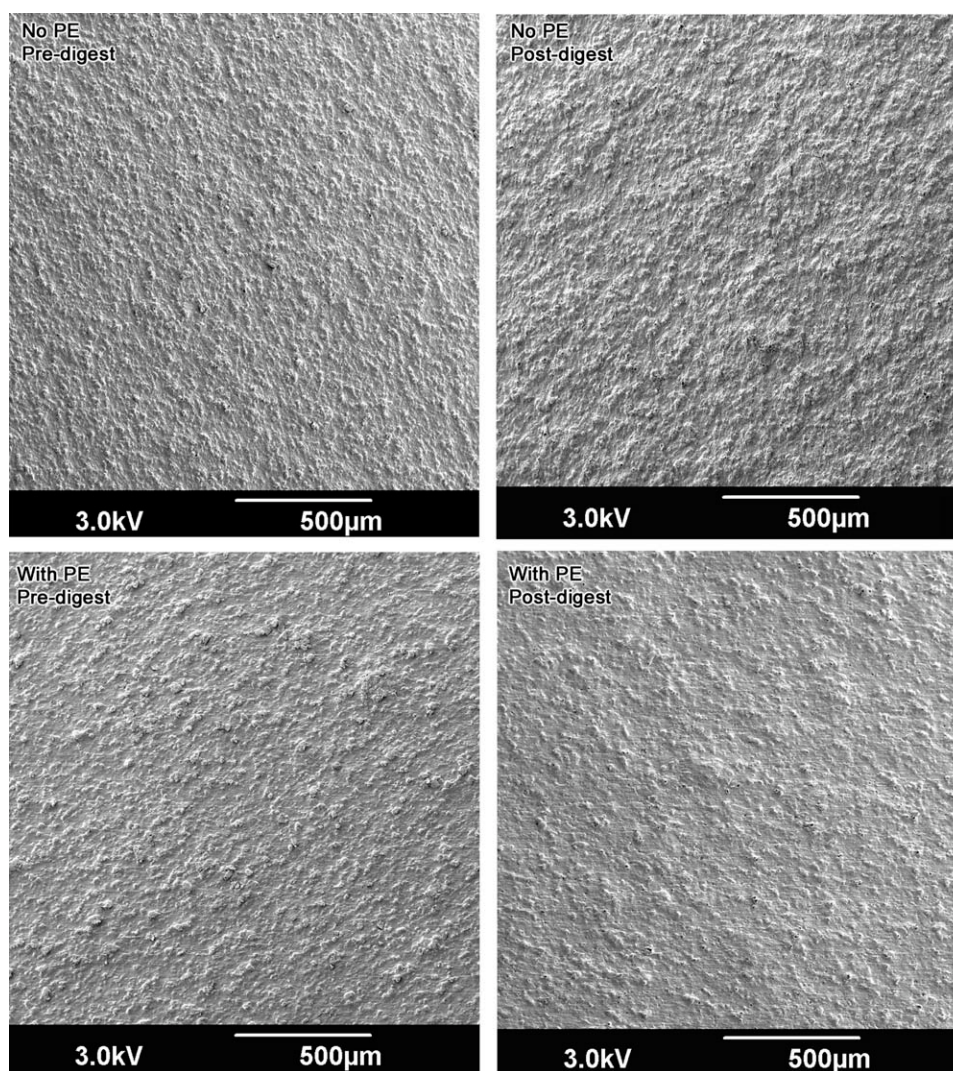


Figure 7 SEM micrographs of typical surfaces of the films without (upper) and with (lower) polyethylene both before (left) and after (right) anaerobic digestion.

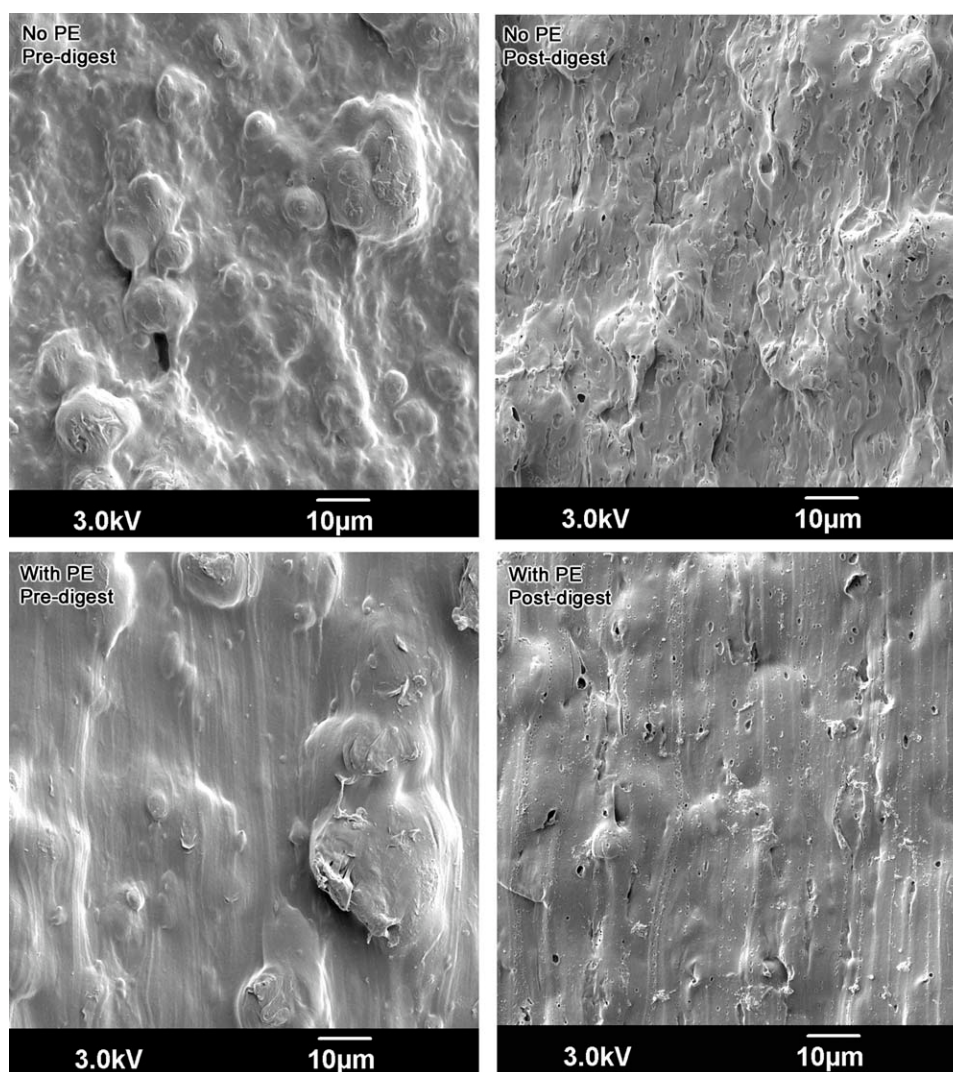


Figure 8 SEM micrographs showing details of the surfaces of the films without (upper) and with (lower) polyethylene both before (left) and after (right) anaerobic digestion.

the film biodegradation was below the biodegradability of the reference material even for the Ecoflex/MTPS (40/60), which contained no polyethylene. Supposedly, it should be fully biodegraded because it contained nothing but biodegradable materials. There are two possible explanations: one is plastic processing hindered material biodegradation and other is that Ecoflex biodegradation occurs in composting media or environment.²⁰ The three film samples containing polyethylene showed little gas generation. In this case, biodegradable materials (starch and Ecoflex) are blended and might be encapsulated more tightly due to the presence of polyethylene, thus reducing accessibility by microorganisms.

Ecoflex is a biodegradable polymer that is derived from petroleum resources. Although its biodegradation in compost was verified by Witt et al.²⁰ Ecoflex experienced a very slow degradation in other media.

The MTPS was made from native corn and high amylose starches, which are known to be biodegradable.²¹ However, the processed blend of two biodegradable materials did not achieve the needed level of biodegradation (Fig. 6) to achieve sustainability as sustainability refers to amount of renewable and biodegradable materials in the film blend. In theory, the film sample of PE/(E/MTPS) (0/100) should reach 60% biodegradation. However, it reached only 34.41% biodegradation during the 90 days of anaerobic sludge digestion.

For other samples in Figure 6, biodegradability was depressed further as the amount of polyethylene increased. This further supports the hypothesis that polyethylene encapsulated the biodegradable materials and rendered them inaccessible to biodegradation. In agreement with Greene,¹³ 1.7% mineralization of polyethylene was found.

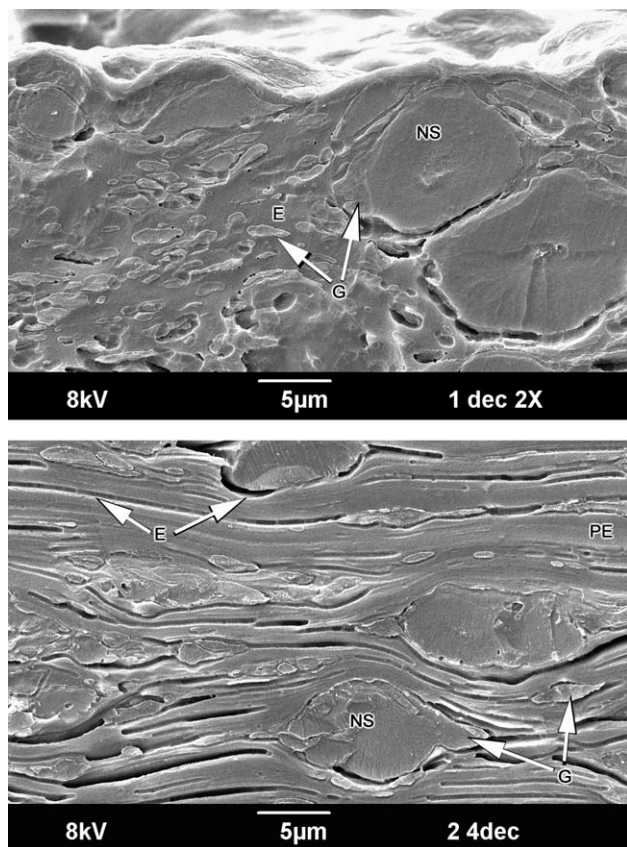


Figure 9 Sections of the film blended without (upper) and with (lower) PE were examined for phase mixing and structure. E, Ecoflex; G, Gelose; NS, Native Starch; PE, PolyEthylene.

Film structure

Before anaerobic digestion, the films without and with PE had similar surface structure with subtle distinction. Both had a high frequency of micrometer-scale nodules (Fig. 7). These nodules likely relate to the starch nodules as their density was lower on the film with PE (i.e., starch content was reduced by the addition of PE). Distinction of blend phases was lacking but surface striations oriented in the MD were present in the PE film (Fig. 8). Both films had occasional micrometer sized holes (Fig. 8).

Even after more than 13 weeks of anaerobic digestion, the surface structure of the films was only modestly affected by digestion. On the whole, digested films lacked fissures, buckles, or large pores and, in these features, were similar to the predigested structure (Fig. 7). Mounds with diameter in the 100- μm range but of low height were an additional feature of the digested films. It was not determined if these mounds were the result of swelling at that site or collapse of the surround material. The chief distinction between predigested and postdigested surfaces was the high abundance of micrometer-sized holes and pits in the surface of

the digested films (Fig. 8). The density of these features appeared greater in the film without PE.

With the exception of the glycerin, sections showed the components of the blended films remained distinct (Fig. 9). In the majority-Ecoflex film, relatively large native starch granules were easily observed. Domains of Gelose were present as micrometer-length lamellae dispersed in the continuous Ecoflex-phase or emanating from the Gelose that often surrounded starch granules. This latter observation suggests the Gelose was sheared from the starch to form the dispersed lamellae. When blended with PE, Ecoflex was dispersed to thin lamellae that were tens-of- μm in length. While often associated with Ecoflex, starch and Gelose were found as isolated domains fully surrounded by PE. For both blends, the dispersed phases were often separated by submicrometer thicknesses of the matrix. This latter observation extended to the surface of the film. Thus, submicrometer films of Ecoflex or PE isolated large nodules of starch from the external environment.

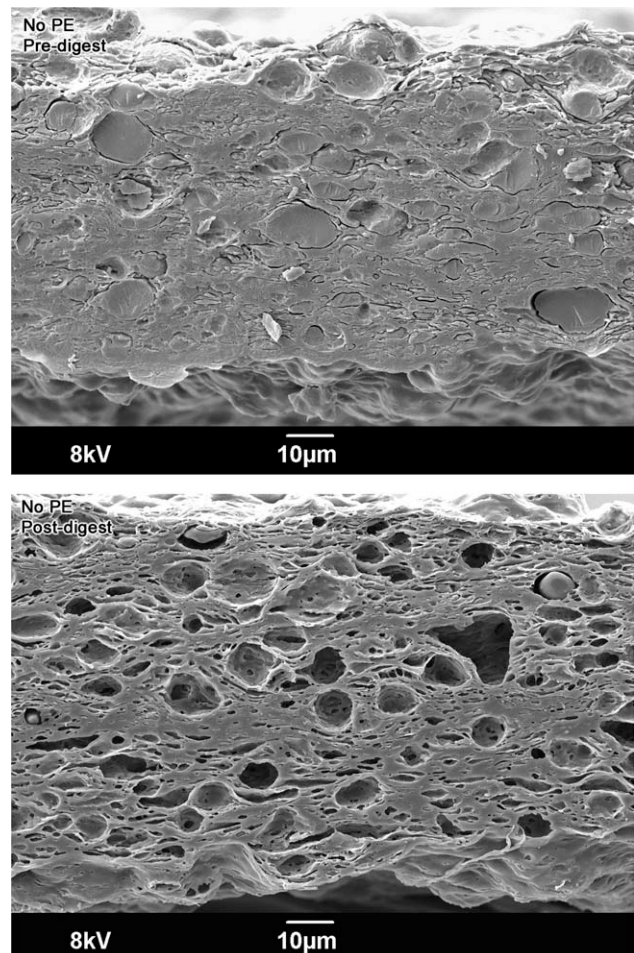


Figure 10 Sections were cut through a film without PE to illustrate the internal structure before (upper) and after (lower) anaerobic digestion.

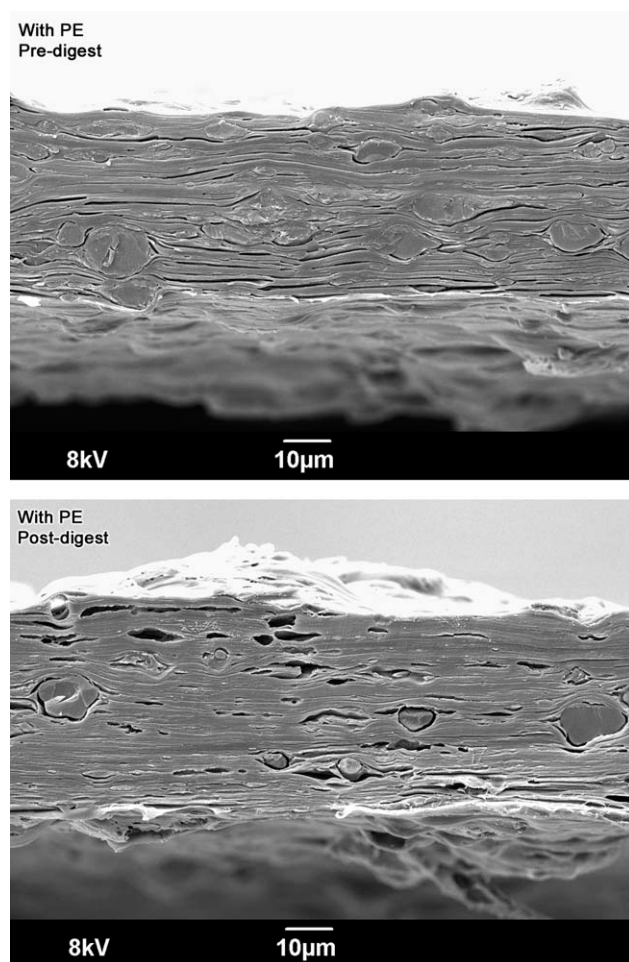


Figure 11 Sections were cut through the film with PE to illustrate the internal structure before (upper) and after (lower) anaerobic digestion.

Comparison of sections before and after digestion showed the majority of degradation in both films occurred internally (Figs. 10 and 11). For the film without PE, voids indicative of digested material were of sufficient density that only a highly porous skeleton of Ecoflex with occasional isolated domains of starch or Gelose remained after digestion. For the film with PE, voids were occasional and often lens-shaped. In the PE film, starch granules remained common, were sometimes at the center of the void-lens, and often the granules themselves were internally voided. Based on the void structure, both native and Gelose starches appear to be disproportionally absent in both films.

CONCLUSIONS

Film properties and structure

The blend compatibility is good, which is demonstrated from the film mechanical data. The blend containing starches, Ecoflex, and polyethylene was

successfully processed for film casting without relying on any compatibilizer. Such a result is not obtained without the addition of high amylose starch like Gelose 80. The film mechanical properties such as elongation, peak stress, etc. were improved as the amount of polyethylene was increased. These blends seem to be useful intermediates toward the goal of fully sustainable plastics. With some additional process refinement, these films can be utilized in a number of applications such as packaging or components for personal care products.

For the process conditions used here, all blend components remained distinct within the matrices. The majority of the native starch particles remained intact and were large enough to account for the nodular surface texture of the films. Shear transfer from both the Ecoflex and polyethylene was sufficient to strip Gelose 80 from the starch particles of the MTPS and disperse it into short lamellae within the matrices. Dispersion of Ecoflex into the polyethylene produced long, thin lamellae of Ecoflex within the polyethylene. Distribution of these phases was not uniform as a matrix-rich submicrometer layer was present on the surfaces of both the majority Ecoflex and polyethylene films.

Although there was no interphase material *per se* noted, Gelose 80 had a structure around the starch particles similar to what might be expected for an interphase. Compatibilizers often form interphase materials and are desirable as they can improve dispersion and interfacial adhesion of a second phase.²² While Gelose 80 did not appear to improve dispersion of the starch particles, improved interfacial adhesion might account for the improved mechanical properties found in this study. Study of failure samples, additional blend proportions, and structure seems warranted.

Biodegradation

Biodegradation was not a linear function of the amount of biodegradable materials incorporated in the films. For the film without polyethylene, the measured biodegradation was about 50% of the theoretical maximum. For films with polyethylene, biodegradability was depressed further as the proportion of polyethylene increased and reached only about thirty percent of the theoretical maximum at the highest polyethylene levels. This depression in biodegradability is consistent with reports in the literature.^{14,23}

For blends examined by microscopy, the majority of degradation occurred within the film and starches appear preferentially degraded. For the film without PE, a film of high internal but low surface porosity resulted. A similar surface structure was found on the PE film but internal porosity was much reduced.

For the matrix polymers and extrusion conditions examined here, starch domains at the surface of the film were covered by submicrometer films of the matrix polymers, which had lower degradation rates. Clearly, these surface-films were not completely biodegraded as starch-size pits were not found on the film surfaces but sections showed starch-sized voids at the near-surface depth of the films. Just as clearly, breaches at the micrometer-scale were sufficient to allow access to the internally contained starches, which were degraded nearly in-full for the film without PE but only partially in the film with PE.

Tena-Salcido et al.¹⁴ suggest connectivity of starches blended with PE plays a major role in biodegradability of these blends. Shujun et al.²³ suggest chemical modification of starches plays a role. Connectivity appears to be the more important factor here. Chemical modification by compatibilizers was not a factor as none were used and no chemically unique interphase material was apparent. Microscopy data showed submicrometer films of refractory plastics were of sufficient thickness not to be degraded and, thus, preclude access of microorganisms in the anaerobic digest sludge to the starch. If degradation occurred, large and usually complete starch domains were missing. In total, breaches of the refractory encapsulate to allow connection to the external environment appears to be the switch needed to allow biodegradation.

Some refractory material appears to be a consequence of any biodegradation process. Encapsulation of highly biodegradable phases by resistant phases accounted for the majority of the observations recorded here but is not likely the entire story. For example, Ecoflex was shown to have good biodegradation in composting studies²⁰ but degradation in the anaerobic sludge digestion used here was poor. Anaerobic sludge digestion is not preferred mode of the environment for Ecoflex material. By extension, we speculate on additional effects of connectivity adding the microenvironment within the plastic. Such a semiclosed system might fill with catabolic end products that are not favorable for continued digestion of the starches. Experiments that measure and manipulate connectivity in these blends could provide insight to improvement of sustainability.

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