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Starch-based extruded plastic films and evaluation of their biodegradable properties *

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Abstract

Plastic formulations containing up to 40% starch were prepared and blown into thin films using extrusion methods. Extruded films were evaluated for their biodegradability by exposing them to a consortium of starch degrading bacteria in the laboratory for 45 days and in the 'La Silla' river located in Monterrey, N.L. Mexico for up to 60 days. Biodegradability was assessed by measuring changes in weight loss and chemical composition of the films using Fourier transform infrared (FTIR) spectroscopy. While little or no degradation was apparent in control films made up of 100% low density polyethylene (LDPE) or 100% poly-(ethylene-co-acrylic acid) (EAA), most of the starch was depleted in starch-containing films exposed in the river. Starch degradation in films exposed to amylolytic bacteria in the laboratory was relatively slower. Also, increasing the amount of EAA from 25% to 50% substantially reduced starch depletion in these films.

Abbreviations: FTIR – Fourier transform infrared; LDPE – low density poly-(ethylene); EAA – poly-(ethylene-co-acrylic acid); SEM – Scanning electron microscopy

Introduction

Cornstarch is an inexpensive raw material derived from a renewable agricultural commodity. Because cornstarch is naturally biodegradable and has potentially useful thermoplastic properties, efforts are underway to utilize it as a replacement for petroleum-derived synthetic materials (Otey et al. 1977; Swanson et al. 1993), particularly in plastic articles for non-food consumer applications (Koch & Ropper 1989; Ropper & Koch 1988). Extrusion and injection molding methods have been used to blend starch with a variety of synthetic (Otey & Westhoff 1982; Jasberg et al. 1992) and other renewable polymers (Ramsey et al. 1993; Shogren 1994). Factors such as the amount of starch, plasticizers, binders and processing methods used for incorporating starch into plastics can influence both their mechanical properties as well as their accessibility to microbial attack (Fanta et al. 1992; Imam et al. 1993; Shogren et al. 1991, 1992; Snug & Nikolov 1992). Besides developing methods to detect starch degradation, efforts are also underway to achieve more efficient starch degradation in plastics (Burgess-Cassler et al. 1994; Imam et al. 1991, 1992, 1993, 1994; Imam and Harry-O'Kuru 1991). In keeping pace with its socio-economic developments, Mexico has inadvertently inherited a plastic litter problem of considerable magnitude. One approach to resolve this problem is to incorporate potentially biodegradable materials into plastics. Conceivably, once biodegradable materials have been depleted, the remnants of the plastic will

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be reduced into smaller pieces or fragments, hopefully easing the litter problem or making it more manageable for disposal. In this report we describe our efforts to incorporate cornstarch into plastics and to test their biodegradability in the laboratory by amylolytic bacteria as well as in the natural aquatic environment.

Materials and methods

Plastics.

Plastic films used in this study were prepared by the semi-dry method described by Otey and Westhoff (1982). Briefly, gelatinized cornstarch containing urea was mixed with a hot melted mixture of EAA and/or PE and extruded through a Brabender Plasticorder (model PC 200) equipped with a blow die.

Experimental location, sample preparation and sampling procedure

For biodegradation studies experiments were carried out between May 12 and July 26 of 1993 in the *La Silla* river located in La Pastora Zoo in Monterrey, Nuevo Leon, Mexico. The location was chosen because it offered a stable ecosystem with limited access to the general public and was in reasonable proximity to the laboratory. Approximately 5 x 5 cm pieces of each plastic were cut and weighed. Pieces were individually sandwiched between 7.5 cm ^{2} sections of polypropylene grid and laced around the edges with color coded nylon twine. Following the protocol described earlier (Imam et al. 1992) grids were suspended in a polypropylene basket and submerged in the river. A total of four plastic specimens per basket were suspended in triplicate for each time point. Three baskets were retrieved at each sampling day. Samples were collected on days 10, 24, 38, 48, and 60 and placed in a large plastic bag containing water from the site to avoid dehydration, and transported to the lab for further processing. Samples of each film in duplicate were carefully rinsed with distilled water to remove material accumulated on the surface. Specimens were air-dried at room temperature (24°C) for 5 days and weighed to determine the weight loss. For laboratory testing, a consortium consisting of several amylolytic bacteria designated as LD76 was used according to the method described by Gould et al. (1990) and samples were collected on days 5, 15, 30 and 45.

Table 1. Plastic formulations and physical properties.

Formulation	LDPE (%)	EAA (%)	Starch (%)	Urea (%)	TS* (MPa)	%E*
Starch-LDPE-EAA	25	25	40	10	8.43	84.57
Starch-EAA	0	50	40	10	6.64	90.15
LDPE	100	0	0	0	15.29	201.40
EAA	0	100	0	0	17.73	234.80

*TS – tensile strength; %E – percent elongation at break.

Mechanical testing

Tensile specimens were equilibrated at 23°C and 50% relative humidity for 28 days prior to testing. Tests were conducted on an Instron Universal testing Machine (Model 4201, Instron Corp., Canton, MA) using a gage length of 10 mm and a crosshead speed of 20 mm/ min, for tensile measurements.

Fourier transform infrared (FTIR) analyses

KBr pellets of plastic specimens were prepared for FTIR analysis as described earlier (Gould et al. 1990). Starch depletion in samples were estimated from FTIR spectra obtained on a KVB/Analect RFX-75 FTIR spectrometer.

Scanning electron microscopy (SEM)

Specimens were fixed in 1% glutaraldehyde and dehydrated for 10 minutes each in 50, 60, 70, 90 and 100% ethanol, and mounted on aluminum stubs. Specimens were sputter coated with gold-palladium and visualized under a JOEL model 1200 EX scanning electron microscope.

Results and discussion

A total of four films; starch-LDPE-EAA, starch-EAA, LDPE and EAA were extruded. The composition and mechanical properties of these films are described in Table 1. The first two formulations contained 40% starch (dry weight basis) and 10% urea, whereas the later two formulations were control LDPE and EAA films without starch.

While addition of starch to the plastic reduced both TS and% E of the extruded films (Table 1), physical properties of these films were, however, still sufficiently suitable for single use applications such as plastic mulches or grocery bags, etc.

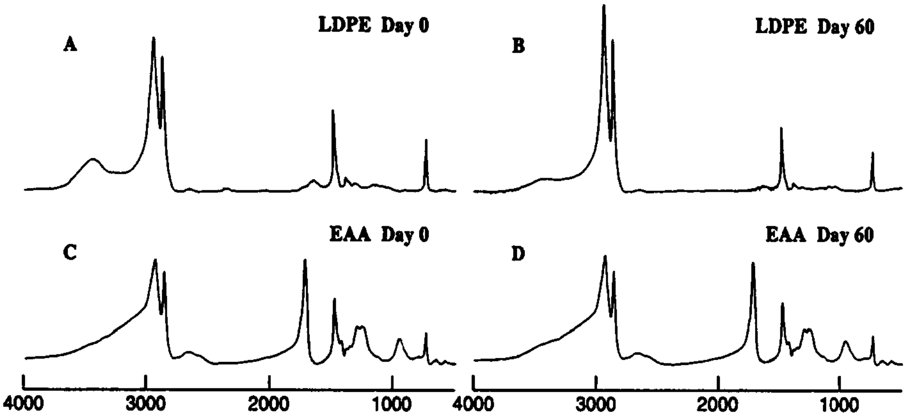

Figure 2. FTIR spectra of control LDPE and EAA films exposed in river for 0 days and 60 days.

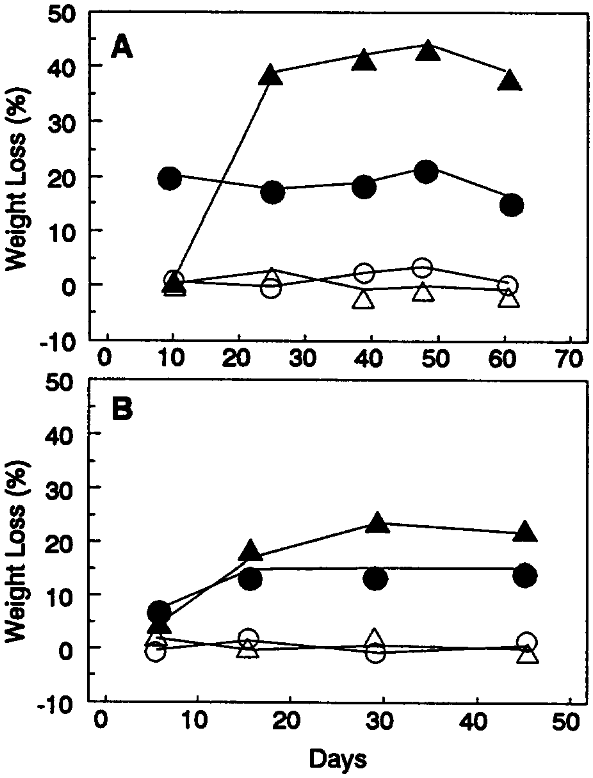

Figure 1. Weight loss in films exposed in river (a) and laboratory cultures (b). Starch-LDPE-EAA (▲), Starch-EAA (●), LDPE (△), EAA (○).

The starch-LDPE-EAA films suffered weight losses of about 40% after exposure in the river for 20 days (Figure 1a). Compared to the river environment, weight losses were considerably less in similar films exposed to a consortium of amylolytic bacteria (LD76) in the laboratory, approaching weight losses of only 23% by 30 days (Figure 1B). Little or no weight loss was apparent in control films (100% LDPE or 100% EAA) exposed for 60 days in the river or when incubated with amylolytic bacteria in culture flasks for 45 days (Figures 1a and 1b). Increasing the amount of EAA from 25% to 50% (by replacing 25% LDPE) in formulations substantially reduced the weight losses in these films to only 21% and 12% in river and laboratory cultures respectively (Figure 1a and 1b).

FTIR spectra of plastic films composed of pure LDPE and EAA are shown in Figure 2. The spectrum of PE (Figure 2a) exhibited characteristic C-H stretching bands at 2851 and 2921 cm^{-1}, and a weaker C-H bending absorbance at 1468 cm^{-1}. In addition a small band at 721 cm^{-1} was present. The spectrum of EAA (Figure 2c) was quite similar to PE with the exception of a C=O stretching band at 1705 cm^{-1} and some very minor bands in the fingerprint region. FTIR spectroscopic analyses of these samples indicated essentially no change in the spectra of the control LDPE and EAA films exposed in the river for 60 days (Figure 2b and 2d respectively). The FTIR spectrum of pure starch, on the other hand, exhibited a broad O-H stretching absorbance centered around 3400 cm^{-1}, a minor C-H stretching band at 2921 cm^{-1}, and a characteristic set of strong C-O stretching bands between 960–1190 cm^{-1} (Figure 3a). The starch-PE-EAA film exposed to the river, however, showed drastic reduction in absorption of peaks corresponding to both the hydroxyl and fingerprint regions of the spectra contributed mostly from starch (Figure 3a), indicating that more than 80%

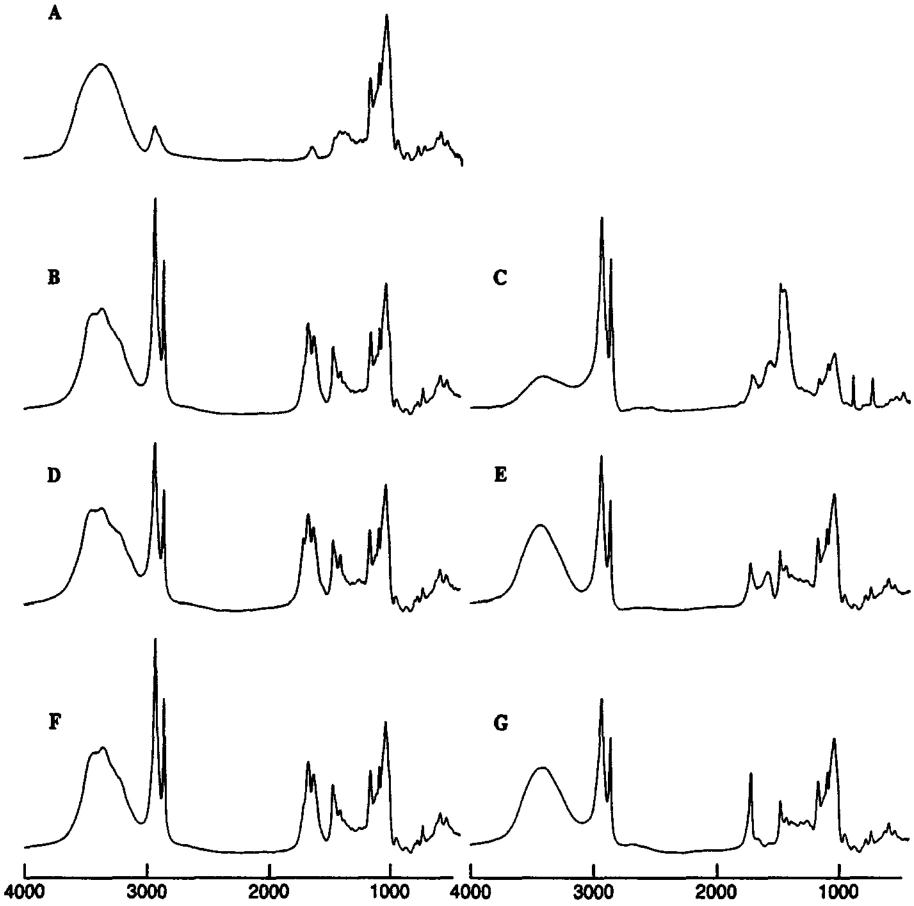

Figure 3. FTIR spectra of pure cornstarch (a); starch-LDPE-EAA film exposed for 0 days (b) and 60 days (c) in river; starch-EAA film exposed for 0 days (d) and 60 days (e) in river; and starch-LDPE-EAA film exposed for 0 days (f) and 45 days (g) to consortium of amylolytic bacteria in laboratory cultures.

of the starch present in these plastics had been degraded (Figures 3b and 3c). Again, starch degradation was comparatively much less in the starch-EAA film with higher (50%) EAA levels (Figures 3d and 3e). Figures 3f and 3g are spectra of starch-PE-EAA and starch-EAA films respectively that were incubated for 45 days with amylolytic bacteria and which indicate little starch depletion relative to the river environment and comparatively less starch depletion than in films with 50% EAA.

FTIR spectrometric analyses can be used to quantify biodegradation of polymers in composite blends. Methods have been developed for analyzing solid samples in KBr by FTIR spectrometry using the Beer-Lambert law. This KBr method has been shown to be accurate to < 5% standard error of prediction for starch, as well as for lipids and proteins (Gordon et al. 1993). Quantitative FTIR spectrometry measures only the relative amounts of individual components in a sample. The relative concentration of starch in starch-PE-EAA blend is computed from FTIR spectra of samples taken before and after degradation. In starch-PE-EAA blends, starch is the only component in the plastic that has significant absorbance in the 900–1190 cm^{-1} region, thus allowing one to roughly quantitate the loss of starch relative to plastic by simply integrating total absorbance over this spectral range. Previously FTIR has been used to quantify degradation of starch and polyhydroxybutyrate-co-valerate (Imam et al. 1995). Also in this report, the weight loss of starch in specimens when obtained gravimetrically and by estimation from FTIR spectra appears to be quite similar (Table 2). The calculated standard error for the four formulations given in Table 2 was 24%. This error was within acceptable limits considering the fact that PE and EAA losses were not known or included in the calculation.

Scanning electron microscopy provided further evidence that after exposure in the river for 60 days,

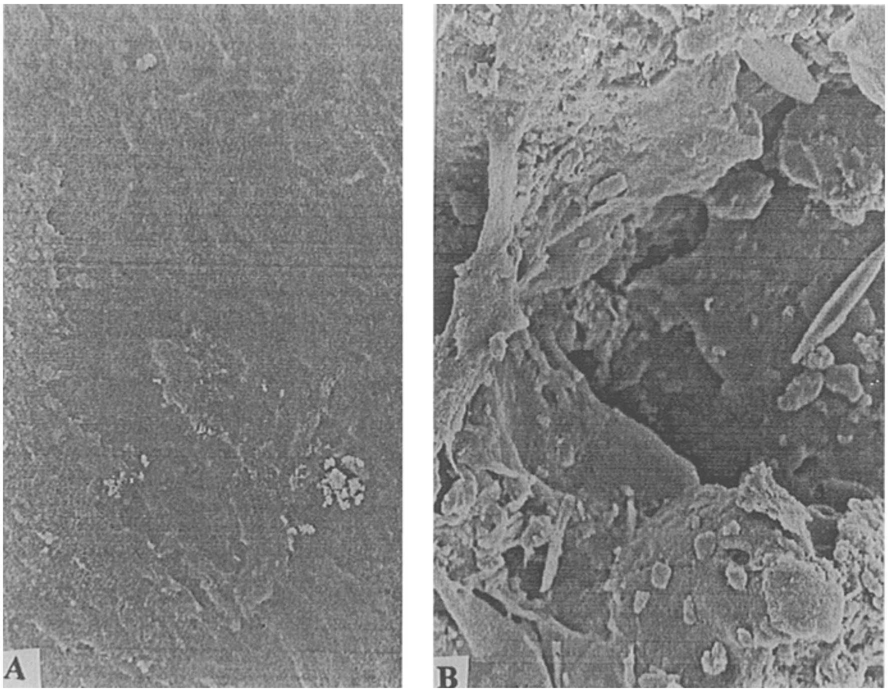

Figure 4. Scanning electron micrograph showing a control LDPE (*A*) and starch-LDPE-EAA (*B*) films after 60 day exposure in river.

Table 2. Quantification of starch from weight-loss data and from FTIR spectra.

Formulation	Weight loss (%)*	%FTIR**	%△***
RIVER			
Starch-LDPE-EAA (25%)	41	56	37
Starch-EAA (50%)	17	8	53
LABORATORY			
Starch-LDPE-EAA (25%)	22	23	5
Starch-EAA (50%)	12	9	25

*Weight loss data from figure 1.

**Calculated % loss from the FTIR absorbances in specimens exposed in river and in laboratory for 60 days and 45 days, respectively.

***%△=|(%Weight loss − %FTIR) / % Weight loss | × 100

only starch-PE-EAA films and not LDPE control films (other films not shown) exhibited considerable surface deterioration (Figure 4). Furthermore, microbiological examination of the surfaces exposed in the river indicated no difference in the microbial populations associated with control or starch-containing surfaces (data not shown). The bacteria were among the most predominant microorganisms associated with these surfaces together with occasionally present algae, protozoans and diatoms.

In environmental studies, weight loss due to biotic and abiotic factors other than biodegradation alone can not be ruled out with absolute certainty. The blown films used in this study were prepared by mixing gelatinized starch and hot melted PE and EAA together and extruding at high temperature and compression. From a processed matrix it is impossible to remove starch mechanically without removing the PE and EAA as well. Therefore, the presence of PE and EAA in starch blends provides an effective built-in control for verification that the removal of starch was due to the biodegradation process alone. Earlier studies (Gould et al. 1990) also showed that starch-containing plastic films incubated in sterile media (shaken at 125 rpm) for 60 days exhibited little or no change in either weight or FTIR absorption spectrum, suggesting that leaching of materials was not possible due to mechanical action alone. The FTIR data in this study provides support for the contention that loss of starch material was due to biodegradation alone. The FTIR spectra of starch blends exhibited reduction only in the IR absorption of bands contributed by starch and not of characteristic bands of PE and EAA, suggesting that the removal of starch from the blended matrix was quite selective and could have been achieved by amylolytic microbes and their secretory enzymes. Nevertheless, more effective starch degradation in the natural environment could be achieved when microbiological processes are accompanied by other interacting biological, chemical and physical processes (Burgess-Cassler et al. 1991, 1994; Gould et al. 1990; Imam et al. 1992). The absence of these processes may explain slow starch degradation under the controlled laboratory environment.

Both weight loss and FTIR data indicated that in the river more than 80% of the starch in films with 25% EAA had been depleted but starch depletion was dramatically reduced with increased EAA content of the plastic. This suggests that EAA somehow interferes with starch accessibility to microorganisms and their hydrolytic enzymes. In this regard, it has been suggested by Shogren et al. (1991) and verified by other investigators (Imam et al. 1993) that amylose in starch forms V-type exclusion complexes with EAA, thus making it highly resistant to starch-hydrolyzing enzymes. This might also explain why some of the starch in plastic films always remains conserved even after prolonged exposure to highly biodegrading conditions. Also in this regard, PE has been implicated in encapsulating starch under certain processing conditions, forming an impermeable barrier to hydrolytic enzymes (Imam et al. 1994).

Though results clearly indicate that petroleum-derived polymers do not degrade in the plastic films studied here, it is encouraging that rapid and appreciable starch depletion leads to considerable deterioration of the mechanical properties of these films, leaving behind a rather week plastic matrix prone to further physical disruption by a variety of biotic and abiotic factors. In this regard, Pometto and Lee (1990) have reported that incorporation of a pro-oxidant in formulations may help initiate chemical oxidation of PE, thus further accelerating the plastic deterioration process.

While quick and effective environmental degradation of single use consumer articles made from biodegradable plastics is highly desirable, in many cases, it will be equally advantageous to develop formulations where the onset of biodegradation is delayed or slowed down to extend the functional life of the material. This manuscript provides at least two new significant pieces of informations: Firstly, the increased EAA content in the formulation greatly reduced (or slowed) starch degradation. Secondly, upon exposure in the river, natural microbial flora was capable of degrading starch plastic, thus confirming the environmental usefulness of these blends if discarded in natural environments. Furthermore, most of the environmental degradation studies on biodegradable plastics have been limited to cold or temperate climates and to our knowledge this is the first attempt to evaluate biogdegradability of such plastics in a natural tropical environment.

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References

Burgess-Cassler A, Imam SH & Gould JM (1991) Novel high molecular weight amylase activities from bacteria degrading starch-plastic films. Appl. Environ. Microbiol. 57: 612–614

Burgess-Cassler A, Imam SH & Kinney MP (1994) Isolation and characterization of microbial amylolytic activities from pond larva attached to starch-plastic films. Biotechnol. Lett. 16: 565–568

Fanta GF, Swanson CL & Shogren RL (1992) Starch-poly (ethylene-co-acrylic acid) composite films. Effect of processing conditions on morphology and properties. J. Appl. Polym. Sci. 44: 2037–2042

Gordon, SH, Greene RV, Wheeler BC & James C (1993) Multivariate FTIR analysis of substrates for protein, polysaccharide, lipid and microbe content: potential for solid-state fermentations. Biotech. Adv. 11: 665–675

Gould JM, Gordon SH, Dexter LB & Swanson CL (1990) Biodegradation of starch-containing plastic. In: Glass JE & Swift G (Eds) Agriculture and Synthetic Polymers: Biodegradability and Utilization. ACS Symposium Series No. 433 (pp 65–75). American Chemical Society, Washington D.C.

Imam SH, Burgess-Cassler A, Cote GL, Gordon SH & Baker FL (1991) A study of cornstarch granule digestion by an high molecular weight α-amylase secreted by *Lactobacillus amylovorus*. Curr. Microbiol. 22: 365–370

Imam SH, Gordon SH, Burgess-Cassler A & Greene RV (1994) Accessibility of starch to enzymatic degradation in injection molded starch-plastic composites. J. Environ. Polym. Degrad. 3: 107–113

Imam SH, Gordon SH, Shogren, RL & Greene RV (1995) Biodegradation of starch-poly-(β-hydroxybutyrate-co-valerate) composites in municipal sludge. J. Environ. Polym. Degrad. (in press)

Imam SH, Gordon SH, Thompson AR, Harry-O'kuru, RE & Greene RV (1993) The use of CP/MAS ^{13}C-NMR for evaluation starch degradation in injection molded starch-plastic composites. Biotechnol. Techniq. 7: 791–794

Imam SH, Gould JM, Gordon SH, Kinney MP, Ramsey AM & Tosteson TR (1992) Fate of starch-containing plastic films exposed in aqueous habitats. Curr. Microbiol 25: 1–8

Imam SH & Gould JM (1990) Adhesion of an amylolytic *Arthrobacter sp.* to starch-containing plastic films. Appl. Environ. Microbiol. 56: 872–876

Imam SH & Harry-Ókuru RE (1991) Adhesive interactions between amylolytic bacterium *Lactobacillus amylovorus* and insoluble and derivatized cornstarch granules. Appl. Environ. Microbiol 57: 1128–1133

Jasberg BK, Swanson CL, Shogren RL & Doane WM (1992) Effect of moisture on injection molded starch-EAA-HDPE composites. J. Polym. Mater. 9: 163–170

Koch VH.& Ropper H (1989) New industrial products from starch. Starch/Stärke, 40: 121–131

Otey FH & Westhoff RP (1982) Biodegradable starch-based blown films. U. S. Patent 4,337,181

Otey FH, Westhoff RP & Russell CR (1977) Ind. Eng. Chem. Prod. Res. Dev. 16: 305–308

Pometto AL & Lee B (1990) Biodegradability of starch-based degradable plastics with a pro-oxidant by litter degrading microorganisms in pure culture shake flask studies. In: Polymers and Biodegradables. Corn Utilization Conference III Proceedings pp (183–186). National Corn Growers Association, St. Louis, MO

Ramsay BA, Langlade V, Carreau PJ & Ramsey JA (1993) Biodegradability and mechanical properties of poly-(β-hydroxybutyrate-co-β-hydroxyvalerate)-starch blends. Appl. Environ. Microbiol 59: 1242–1246

Ropper H & Koch VH (1988) New carbohydrate derivatives from biotechnical and chemical processes. Starch/Stärke. 40: 453–464

Shogren RL, Thompson AR, Felker FC, Harry-Ókuru RE, Gordon SH, Greene RV & Gould JM (1992) Polymer compatibility and biodegradation of starch-poly (ethylene-co-acrylic acid)-polyethylene blends. J. Appl. Polymer Sci. 44: 1971–1978

Shogren RL, Thompson AR, Greene RV, Gordon SH & Cote GL (1991) Complexes of starch-polysaccharides and poly (ethylene-co-acrylic acid): Structural characterization in the solid state. J. Appl. Polym Sci. 47: 2279–2286

Sung W, & Nikolov ZL (1992) Accelerated degradation studies of starch-filled polyethylene films. Ind. Eng. Chem Res. 31: 2332–2339

Swanson CL, Shogren RL, Fanta GF & Imam SH (1993) Starch-plastic materials - preparation, physical properties, and biodegradability. J. Environ. Polym. Degrad. 1: 155–165