

Degradation of Polyethylene–Starch Blends in Soil

S. M. GOHEEN and R. P. WOOL*

Department of Materials Science and Engineering, University of Illinois, 1304 W. Green Street, Urbana Illinois 61801

SYNOPSIS

Binary polymer films containing different percentages of corn starch and low-density polyethylene (LDPE) were exposed to soils over a period of 8 months and monitored for starch removal and chemical changes of the matrix using FTIR spectroscopy. A standard curve using the area of the C–O stretch band and an empirical second-degree polynomial to fit the data made it possible to calculate starch concentration over a wide range (0–46% by mass). Starch removal was found to proceed rapidly during the first 40 days and to near-completion in very high starch blends (52% and 67% by weight). Starch removal was slower, consisting of mostly surface removal in 29% starch blends. Weight loss data supported spectroscopic data showing similar gross features. Weight loss and spectroscopic data were consistent with percolation theory and suggested that starch removal continues past 240 days. Degradation rates in different soils containing different amounts of organic matter were approximately the same after a period of a few weeks. IR analysis did not show significant chemical changes in the polyethylene matrix after 240 days. However, the matrix did show evidence of swelling, an increase in surface area, and removal of low molecular weight components.

INTRODUCTION

The degradation of polymers may proceed by one or more mechanisms, including microbial degradation in which microorganisms such as fungi and bacteria consume the material,¹ macroorganism degradation in which insects and other macroorganisms masticate and digest the plastic,² photodegradation in which exposure to ultraviolet radiation produces radical reactions and chain scission,^{3–5} and chemical degradation in which chemical reactions cleave bonds and reduce the molecular weight of the polymer.^{6,7} The degradation mechanisms will vary depending on the polymer's environment and desired application.⁸

In this paper, we focus on the aerobic microbial degradation of corn starch and low-density polyethylene (LDPE) binary blends in soil. Polyethylene is believed to be catabolized by microbes at the chain ends. Because of its high molecular weight, this process is slow and may take hundreds of years.^{3,9–12}

Starch has been used as a filler in polymer blends to speed the degradation.^{6,13,14} Providing enough starch is added to the polyethylene, microbes consume the starch, creating pores in the plastic that increase the surface area of the polyethylene matrix and provide opportunities for its degradation.^{13,15,16} Fourier transform infrared spectroscopy (FTIR) is used to determine the depletion of starch during the degradation and to monitor if any chemical changes occur in the matrix.^{3,16} Analysis of the weight loss is also employed to supplement the IR results.^{1,6,17}

EXPERIMENTAL

Material Preparation

The corn starch was supplied by Cargill Inc. and was melt blended with LDPE supplied by Quantum Chemical Co. in a Brabender Data Processing Plasticorder model PL2000 with a 350 cc capacity mixing head attachment, as described in Ref. 15. The LDPE had a peak melting point of 110°C determined by differential scanning calorimetry. The material was mixed at 140°C and 60 rpm for 30 min. The blends were then compression molded into plates of thick-

* To whom correspondence should be addressed.

Table I Characteristics of Types of Soil Used in Indoor Burial Experiment

Soil Name	Parent Material	Surface Texture/Color
Drummer	Loess	Silty clay loam/dark
Cisne	Loess	Silt loam/mod. dark
Bloomfield	Sandy	Fine sand/light

ness 0.95 and 1.95 mm using 13×13 cm window frame molds. Experimental and standard samples were cut from these plates and compression molded in a Carver Press at 140°C and 8500 lb for 12 min using the Specac IR Constant Thickness Film Maker to a thickness of 0.082 ± 0.007 mm. LDPE samples were compression molded from pellets under the same conditions.

Soil Burial and Removal

Samples were buried in three types of Illinois soil shown in Table I.¹⁸ The soils were obtained from farmland top soil biannually in March before planting and in October after harvesting. Soils were sifted to remove large clumps, plant debris, and macroorganisms with a $\frac{1}{8}$ in. screen into plastic boxes ($15 \times 10 \times 6.5$ in.) with holes cut in the lid.¹⁹ Twenty-mesh stainless-steel wire cloth lined the bottom and sides of the box to lift the 5 in. of soil slightly and increase air circulation (refer to Fig. 1). Soils were kept moist with deionized water and stored in a room at ambient humidity (37–92%) and temperature (63 – 79°F). Drummer and Cisne soils were maintained at approximately 20% moisture by weight. Bloomfield soil was maintained at a lower moisture level (5–10%) because of its high sand content.¹⁹

The thin film circular samples, less than 3 cm in diameter, were buried in a 4×5 array at a depth of 4 in. A control box contained only samples and no soil.

Faster degrading samples (52 and 67% starch blends) were removed once per month after the first month. Slower-degrading (29% starch blend and LDPE) and control samples were removed every other month after the first month. After removal, samples were washed in deionized water and dried at 50°C in a vacuum oven for 24 h. Samples were then allowed to equilibrate to ambient temperature and humidity for at least 24 h before testing.^{3,16,19} The mass of each sample was measured before and after degradation using a Perkin-Elmer AD-4 Autobalance.

An outdoor soil burial experiment was used to compare field tests with the controlled indoor experiment. Outside burial provides a realistic environment with seasonal changes, less control of soil wetness and temperature, and the presence of macroorganisms. Samples and soil were placed in perforated plastic cups cut to permit access of macroorganisms and moisture [see Fig. 2(a) and (b)]. The cups that were buried at a depth of 6–8 in. allowed a plug of soil to be pulled for easy retrieval of the degrading samples. Each set was staked off for further ease in relocating samples. The plot was subject to ambient conditions of moisture and temperature.

Determination of Starch Concentration

The IR vibrations of polyethylene and starch are shown in Table II.^{16,20–23} Spectra of LDPE and a 15% by weight starch/polyethylene blend are shown in Figures 3(a) and (b). Starch was monitored by the broad C–O stretching band at 958 – 1190 cm^{-1} .¹⁶

INDOOR SOIL BOX

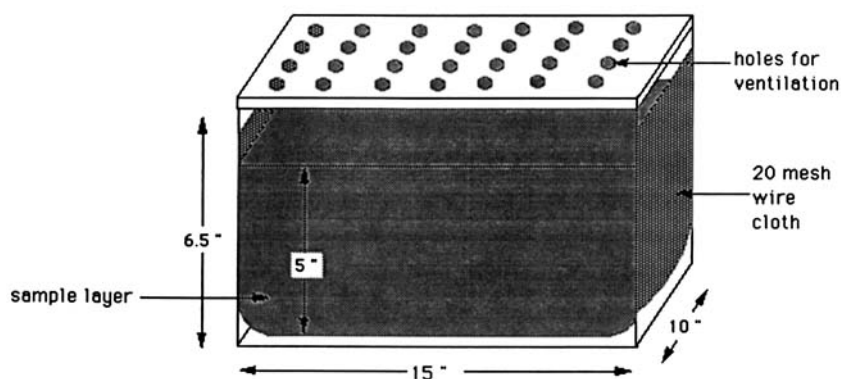


Figure 1 Sketch of soil box used in indoor experiment.

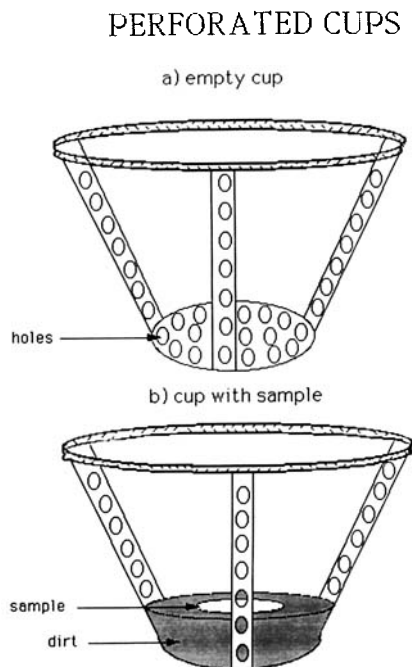


Figure 2 Sketches of perforated cups used in outdoor burial experiment: (a) empty and (b) showing placement of sample.

The only other bands independent of polyethylene are the OH bands; however, these bands are unreliable for quantitative analysis due to their dependence on water content and atmospheric conditions.²⁴

FTIR spectroscopy was performed on a Nicolet 7199 with a resolution of 4 cm^{-1} using a Happ-Genzel apodization function. Beer's law ($A = abc$) states that if the absorptivity (a) of the material is constant, which is true for a given material at a given wavelength, and the path length or thickness (b) is constant, the absorbance (A) will be a linear function of concentration (c). Therefore, standard calibration or working curves may be generated by plotting the absorbance over a range of known concentrations.²⁵ Calibration curves were generated by integrating the absorbance of the starch band using Simpson's rule at different known starch concentrations between 0 and 60% starch by volume (0 and 71% by mass). Below 30% starch by weight, a Lorentzian curve-fitting interpolation²⁶ was employed between data points. Above 30% by weight of starch, Simpson's integration was applied to the absorbance data points without interpolation.

Different base-line calculations give very different absorbance measurements, especially in films with a high starch concentration. For FTIR measurements in which the C—O stretch band strongly

overlaps other bands at the higher wavenumbers, the base-line was taken at the midpoint of this band (1074 cm^{-1}) from the sloping line between 958 and 1850 (a point where lines are absent). Experimentation with different base-line calculations showed that fairly reliable results could be obtained with several different base-line calculations as long as the same base-line method was applied to both the experimental samples and the standard curve.^{24,27} The result of a nonzero intercept for the standard curve is partially due to the choice of a baseline.²⁵

Both the 52 and 67% starch blends became too opaque at approximately 25 days to measure starch concentration using transmission FTIR. Attenuated total reflectance (ATR) may be used to give information on surface changes; however, in an effort to compare overall changes in the starch concentration of these blends with that of the 29% starch sample and to determine soil effects on the degradation rate, the 67% starch samples that were degraded in Drummer soil and all the 52% binary samples were pressed again under the same conditions as the initial pressing and measured using transmission FTIR.

The Specac IR Constant Thickness Film Maker

Table II Infrared Vibrations and Assignments for Starch/LDPE Blends

Major IR Bands of Components	
Frequency (cm^{-1})	Assignment and Remarks
LDPE	
2850, 2920 (s)	C—H stretching
1460, 1471 (m-s)	CH ₂ scissor and <i>asym</i> bend
1377, 1369, 1352 (w)	C—H bend due to CH ₂ and CH ₃
720, 730 (m-w)	CH ₂ rocking
Starch	
3000–3650 (s, br)	O—H stretching with absorbed water
2850, 2920 (s)	C—H stretching
1640 (w-m)	δ (O—H) bend (absorbed water)
1462 (m, sh)	CH ₂ bending
1445–1325 (m-s)	C—H bending and wagging
1243, 1205 (m-s)	O—H bending
960–1190 (s, br)	C—O stretching (C—O—C and C—O—H)
400–930 (w-m, br)	O—H deformation (broadened by water), C—O—C bend, ring vibrations

* w = weak, m = medium, s = strong, sh = shoulder, br = broad.

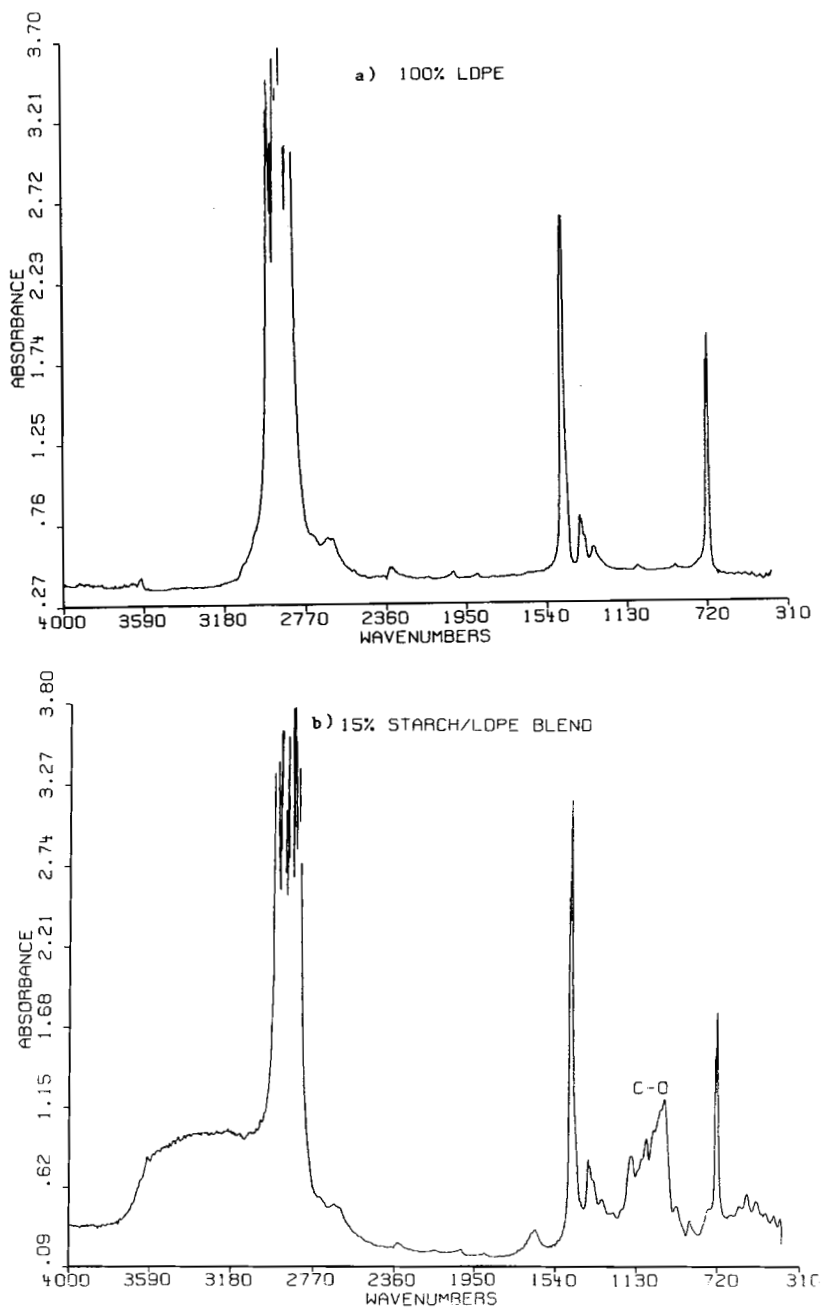


Figure 3 Infrared spectrum of (a) 100% LDPE and (b) 15% starch/LDPE blend indicating C—O stretch used for quantitative analysis.

has a thickness tolerance better than $\pm 10 \mu\text{m}$; however, to correct for path-length variations, the integrated absorbance was multiplied by the ratio of the average thickness of samples used to generate the standard curve ($82 \mu\text{m}$) and the sample thickness. Thickness measurements were made with a digital micrometer screw.²⁸

RESULTS AND DISCUSSION

Starch Concentration Calibration Curve

The calibration curve for IR absorbance vs. starch concentration in the range 0–46% by weight is shown in Figure 4. The calibration curve samples had an

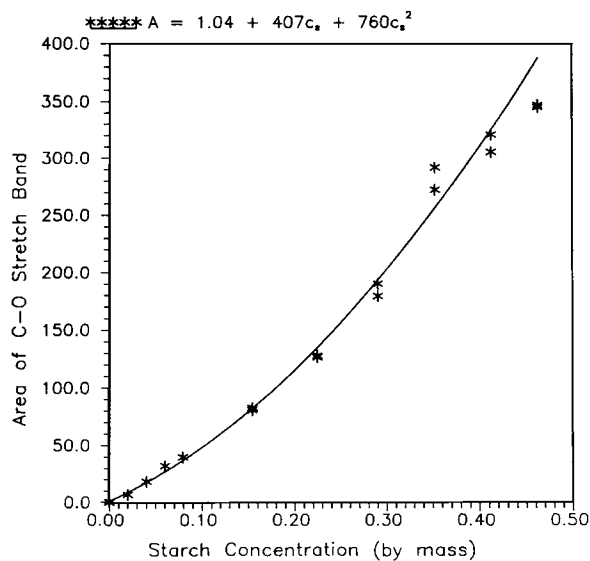


Figure 4 Standard curve used in calculating starch concentration from IR absorbance.

average thickness of $82 (\pm 3) \mu\text{m}$. An empirical second-degree polynomial equation provided the best fit to the data²⁵:

$$A = 1.04 + 407c + 760c^2 \quad (1)$$

Application of eq. (1) to films of varying thickness can be done to an excellent approximation by multiplying the coefficients by the ratio of the film thickness. It may also be used for nonbinary samples. For example, a starch/EAA (ethylene acrylic acid copolymer)/LDPE blend has a thickness of $0.145 \pm .005 \text{ mm}$ and an integrated absorbance $A = 373.48 \text{ cm}^{-1}$ after spectral subtraction of EAA using the C=O band. Correcting for thickness, $(.082/.145) A = 211.21 \text{ cm}^{-1}$ and employing eq. (1) gives $c = 32.2\%$ starch by weight. The manufacturer's reported nominal value was 30% by weight of starch. The calibration curve shown in Figure 4 was used to analyze the undegraded 29% samples and all degraded materials.

Optical Changes vs. Time

Figure 5 shows the effects of soil burial on several samples. The dark spot at the top of each disc is the label. The 52 and 67% (by weight) blends exhibited color changes indicating microbial growth, and in some cases small holes appeared, indicating complete removal of starch in isolated regions. Fungal hyphae could be observed by optical microscopy before washing. All the blends exhibited increases in opacity due to starch removal, as judged by the dis-

appearance of the graph lines beneath the films. The decrease in transmittance was most noticeable for the 52 and 67% blends that became nonuniformly opaque between 20 and 25 days, with complete opacity occurring between 25 and 40 days. It will be shown later that most of the starch is removed in that time interval. The sample with 29% by weight starch retained considerable clarity after 6 months. This behavior is consistent with the observation and computer simulation analysis that little or no degradation of PE/starch blends occurs below the percolation threshold of 31% by volume, or 40% by weight starch, as reported in Refs. 8 and 15. No change was observed in the LDPE control sample.

The diameter of the samples in Figure 5 showed little change with time. However, the thickness was found to change slightly during the degradation. Initially, the binary blends showed a slight decrease in thickness (2–5%) until the second month and then increased by the sixth or seventh month (5–10%). This may be due to the loose PE network that forms when the starch is preferentially removed by microbial invasion. The microbes may also play a role in swelling the network. Relating thickness changes to changes in the absorbed water band at 1640 cm^{-1} provides evidence that absorbed water retained in the capillaries of the network may contribute to the swelling.¹⁵ The thickness changes occurred despite the fact that the samples lost as much as 50% of their weight, as shown in the next section.

Weight Loss

The weight loss of samples during degradation in Drummer soil is shown in Figure 6 where the mass of the sample, normalized with respect to its initial mass, is plotted vs. time. Most of the weight is lost in the first 40 days, and then the rate proceeds more slowly. At long times (240 days), the weight ratio, M , for the 67% sample is 0.44, which means that 56% of the sample has been removed. If the weight loss were due only to starch removal, then we would expect to have $67\% - 56\% = 11\%$ of starch remaining. For the 52% sample, we have $M = 0.59$ at 240 days such that we have the equivalent of $52\% - 41\% = 11\%$ starch remaining. For the 29% sample, $M = 0.87$ at 240 days such that $29\% - 13\% = 16\%$ of the starch remains. This analysis is checked by IR spectroscopy in the next section.

The percolation theory of microbial invasion of polymer/starch blends of infinite size gives the accessed fraction, f/p , of the initial volume fraction p , of starch as^{15,29}

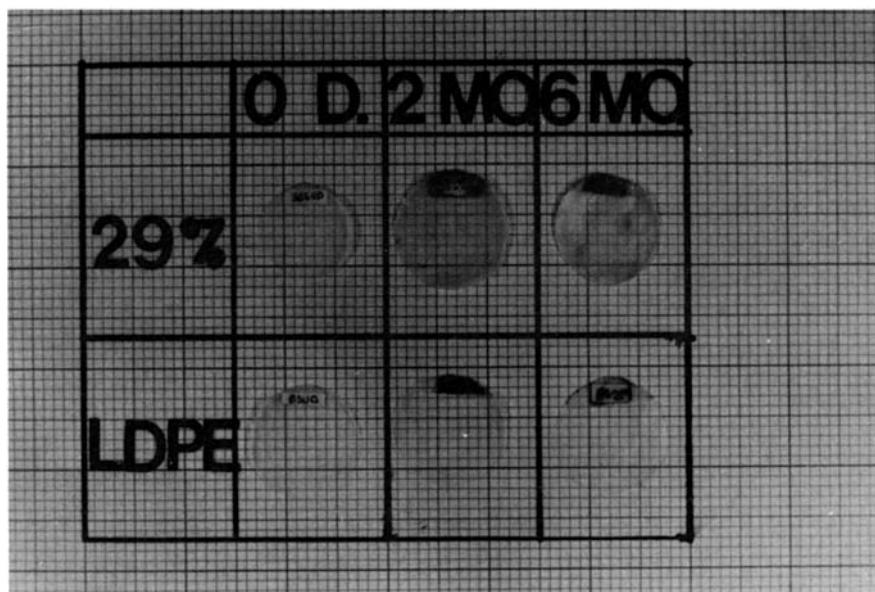
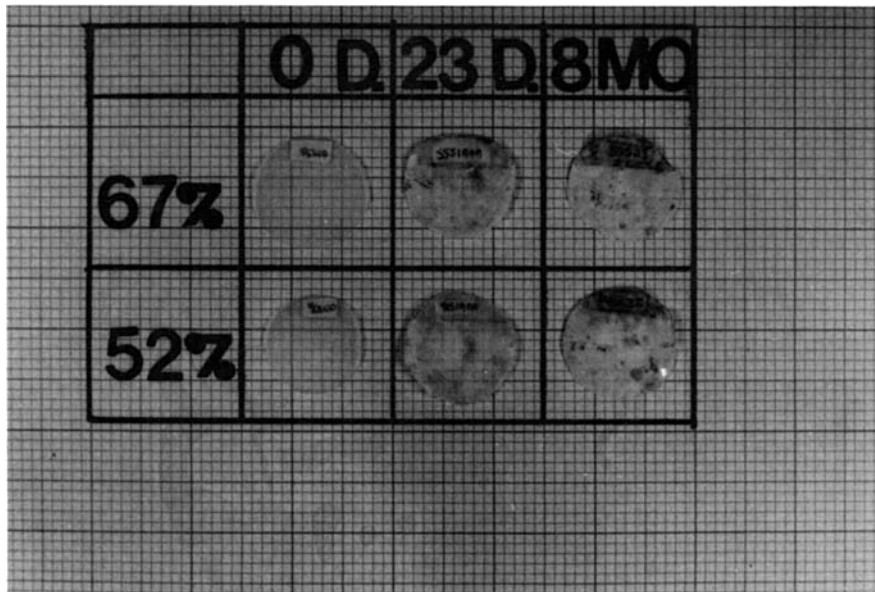


Figure 5 Picture of samples degraded in soil. Increase in opacity is noticeable especially for 52 and 67% starch samples. No changes apparent for LDPE.

$$f/p = (p - p_c)^v \quad (2)$$

where $p_c = 0.3117$ is the percolation threshold by volume and the critical exponent $v = 0.4$. Equation (2) is valid in the range $0.3117 < p < 0.340$.

The volume fraction of starch, p , is determined from the weight fraction of starch, W , starch density, γ , and polymer density, g , as

$$p = W/\gamma/[W/\gamma + (1 - W)/g] \quad (3)$$

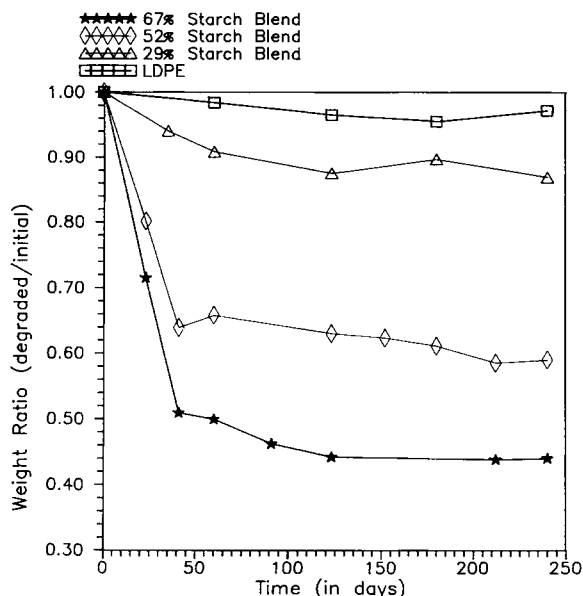


Figure 6 Changes in the weight ratio (degraded/initial sample weight) in samples exposed to Drummer soil.

For the binary blends, the starch density is $\gamma = 1.44$ g/cc and the polyethylene density is $g = 0.928$ g/cc.

Peanasky et al. modeled microbial invasion from top and bottom surfaces of polymer films by computer simulation. The starch accessibility as a function of starch concentration by volume for varying thicknesses is shown in Figure 7.¹⁵ For a film thickness of $80 \mu\text{m}$, which is about eight times the starch diameter of $10 \mu\text{m}$, curve B may be used to determine the limit of starch accessed. From eq. (3), the sample with the mass fraction of starch $W = 0.667$ has a corresponding volume fraction $p = 0.563$. From Figure 7, microbial degradation should remove about 99% of the starch. The experimental value obtained from Figure 6 is 84%. For a sample with $W = 0.521$ and $p = 0.412$, percolation modeling gives a value of 94%, which compares to the experimental value of 79%. The sample with $W = 29\%$ is below the percolation threshold, and the weight loss is largely due to removal of starch from the surface layer. The accessed fraction determined from computer simulation is about 44%, whereas Figure 6 gives an experimental value of 45%. Therefore, computer simulation indicates that starch which is still accessible to microbes remains in the 52 and 67% samples. Some of the difference is inevitably due to errors in determining a degradation rate from weight loss data; however, it also suggests that starch removal continues past 240 days.

The LDPE samples buried in soil also lost mass

when compared to the control LDPE samples, about 4% in 8 months. This may be due to degradation of some low molecular weight species in the material,¹⁰ a speculation supported by the relative low melting point (110°C) of the LDPE, which suggests the presence of a relatively high number of low molecular weight species in the polyethylene. A more detailed analysis of the component changes in the mass loss experiment should also consider the change in PE and its effect on the fraction of starch accessed. For example, with the 29% sample, the accessed starch drops from 45% to about 31% when the 4% change in PE is considered.

Changes in PE mass may be greater at $p > p_c$ because of the internal surface area increase. When $W = 67\%$ and $p = 56.3\%$, the increase in internal surface area A , per cc, due to starch removal is given by $A = 6p/d$, where $d = 10 \mu\text{m}$ is the starch particle diameter, such that $A = 3378 \text{ cm}^2/\text{cc}$. Thus, the relative increase in surface area compared to a 1 cc cube of PE is greater than 3000 times. This increase could result in further degradation of PE in the blend compared to the pure material.

Many potential errors exist in measuring a degradation rate by weight loss. The mass of fungi, bacteria, and dirt not removed during washing as well as partial removal of the sample labels during degradation and the cleaning process may account for

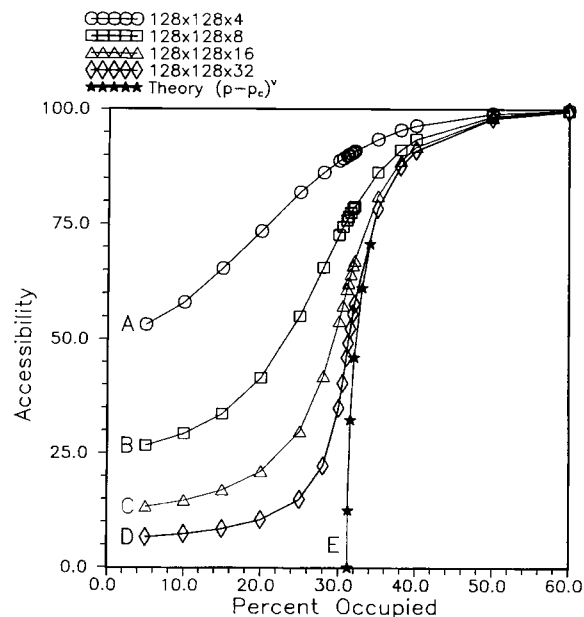


Figure 7 The accessibility of starch, computer modeled by bilateral microbial invasion of the film, as functions of starch concentration by volume and lattice size.

errors in measuring the mass. The 1640 cm^{-1} band, which is a measure of the water content,²⁰⁻²³ may vary significantly between degraded and undegraded samples, probably due both to vacuum drying and the increase in pores as the starch is removed. Therefore, an absolute degradation rate should not be inferred from the weight loss data on its own.

More accurate information comes from changes in starch concentration as measured by IR analysis.

Changes in Starch Concentration

FTIR spectra comparing the undegraded and degraded samples as shown in Figures 8(a) and (b)

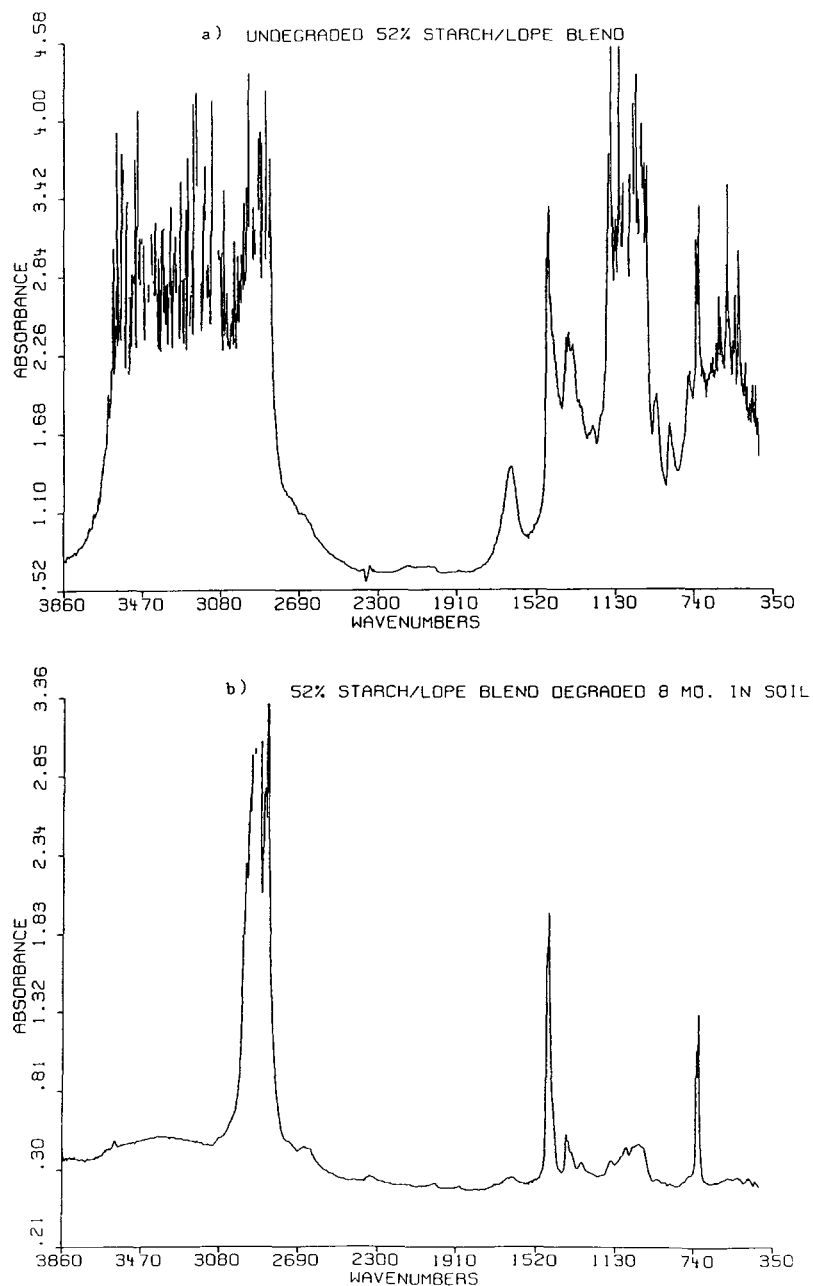


Figure 8 IR spectra of (a) an undegraded 52% starch blend and (b) a 52% starch blend degraded in soil for 8 months and thinned by pressing showing change in C—O stretch band after degradation.

indicate that the starch is preferentially removed leaving the PE network. Figure 9 shows a plot of starch concentration as a function of time for samples buried in Drummer soil. The degradation of the 52 and 67% blends is marked by rapid starch removal in the first 40 days during which the majority of starch is accessed and then by a gradual decrease to about 7–10% starch after 8 months for both blends. This result is similar to 11% obtained by the mass change analysis when it was assumed that only the starch was removed.

The 29% blend shows a gradual decrease to a starch concentration of 21% after 8 months, which is consistent with the surface removal of starch. The mass change analysis gives a starch concentration of 16% after 240 days, indicating a greater rate than that obtained by IR analysis. The 67 and 52% samples lost a little more starch (about 1–4%) than predicted by the mass change and were in closer agreement with the percolation analysis. However, the samples continue to degrade after 240 days, and the theoretical amounts of starch (99 and 94%, respectively) may eventually be removed.

It should be noted that samples were not put back in the soil once they were removed, washed, and dried. This accounts for the apparent gain of starch concentration in some cases due to errors of a few

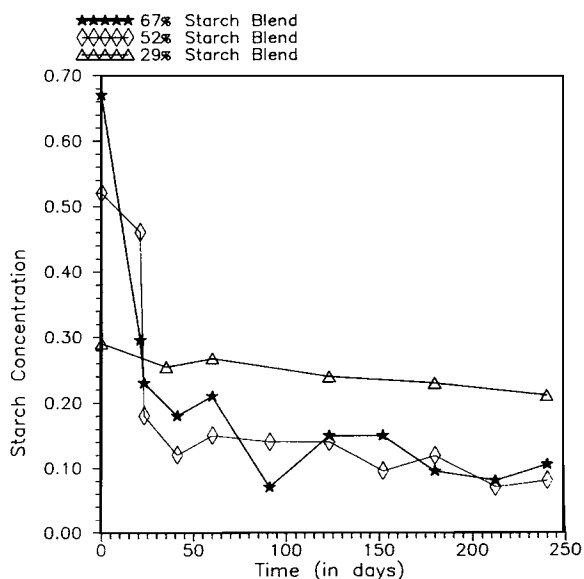


Figure 9 Changes in starch concentration during degradation in Drummer soil. Fifty-two and 67% starch samples after 23 days were thinned by hot pressing to allow transmission by IR beam. The initial starch concentrations for the 52 and 67% samples were not calculated as they were out of the linear range of the standard curve.

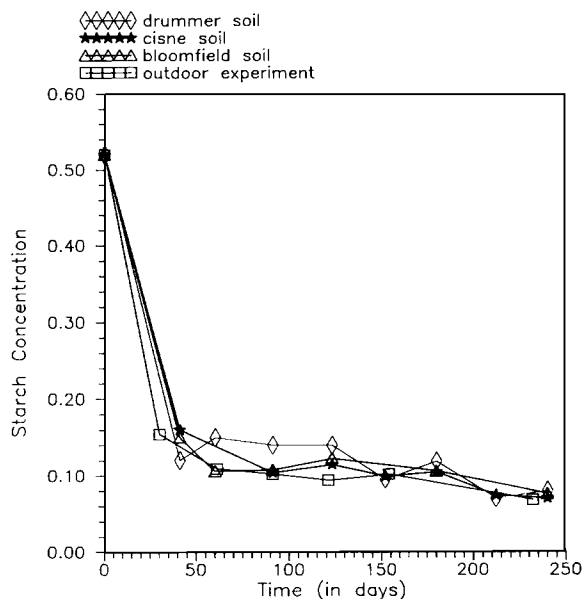


Figure 10 Changes in starch concentration during degradation for the 52% samples comparing the different soils. All samples after 23 days were thinned by hot pressing to allow transmission by the IR beam. The initial concentrations were not calculated as they were out of the linear range of the standard curve.

percent in measuring starch concentration and variations between individual samples. Errors involved in determining starch concentration of polymer blends using FTIR spectroscopy include deviations from the calibration curve (Fig. 4) mainly due to changing absorption coefficients during degradation and variations in path length, uneven starch distribution, and choice of a base line. For degraded samples, an additional error may be to overestimate the starch concentration because of the presence of enzymes that are not completely removed by washing and that could contribute to the C–O stretch band.

Effect of Soil Variety on Degradation

Figure 10 shows the change in starch concentration for the 52% starch blend buried in three different indoor soils and one outdoor environment. Within experimental error, we cannot assign any change in rate to soil variety. Wool and Cole¹ using CO₂ as a measure of starch removal from Otey films (40% starch, 25% PE, 25% EAA, and 10% urea) found the removal of starch to be fastest in sandy soil compared to clay loam soil. Complete removal of starch required between 20 and 90 days depending on the type of soil. Figure 10 indicates that the deg-

radiation rate was not affected by the type of soil at least for exposure over several months. All the 52% blend samples that were reheated in the Carver press to obtain transmission data exhibited a reduction in starch content to approximately 7–8% after 8 months. However, differences in degradation rates during exposure times of less than 1 month may occur, particularly in the early stage of degradation.

Effect of Degradation on Polyethylene

Changes in the polyethylene matrix were analyzed by two indices used by Albertsson et al.³ to monitor degradation rates in polyethylene: the 1715/1465 ketone carbonyl index ($-\text{C}=\text{O}-$) and the 1640/1465 double bond ($-\text{C}=\text{C}-$) index. Also examined were bands at 1740 (the ester carbonyl $-\text{COO}-$), 905–915 (the double bond $-\text{CH}_2=\text{C}-$), and the doublet band at 720, 730 in which the relative intensity gives information about crystallinity. Both the carbonyl and the double-bond indices are expected to increase at least initially if the matrix is being degraded.³ The only significant trend that was observed was a slight decrease in the 1640/1465 double-bond index of the binary blends over time. However, this could also be attributed to a decrease in the absorbed water starch band at 1640 as starch is removed rather than to any changes in the matrix. This study is continuing with PE matrices of varying molecular weights.

SUMMARY AND CONCLUSIONS

The following conclusions can be drawn from our work:

1. Since there is no significant difference between degradation rates of the plastics in the indoor and outdoor experiments, the method of soil burial outlined in this paper may be used for aerobic microbial degradation experiments on polymer blends.
2. The starch concentration may be accurately measured over a wide range using the C—O stretching band and a standard calibration curve with a second-degree polynomial fit. This method works even for nonbinary blends as long as an independent band exists for spectroscopic subtraction of the other component(s).
3. Both weight loss and FTIR data show that high-percentage starch binary blends (52 and 67%) exhibit an extensive removal of the starch during the first 40 days, whereas lower-percentage starch blends (< 30% by mass) exhibit a slower and probably incomplete removal of the starch.
4. The quantity of starch removed from different blends is consistent with percolation theory, although final values are lower than expected in the 67 and 52% blends, indicating starch removal continues past 240 days.
5. FTIR analysis shows that the starch is removed while leaving the polyethylene matrix intact. No evidence is seen during the first 8 months for degradation of the polyethylene.
6. The content of organic matter in the soil appears to make little difference in the degradation rates of the blends after 1 month.

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