

Thermogravimetric Determination of Starch Content in Starch–Polyethylene Blend Films

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SYNOPSIS

Thermogravimetric analysis as a technique for rapid determination of starch content in LDPE/starch blend films was investigated. The percent weight loss in a specified temperature range, under a constant heating rate, correlated well with the starch content of films in the range of 0–12 wt % starch, as determined by chemical analysis. The method was used to estimate the residual starch content of LDPE/starch films, containing approximately 6.0% starch, exposed under several biotic exposure conditions. Generally 87–88% of the initial starch content was present in the films after different types of environmental exposures.

INTRODUCTION

Incorporation of starch into a polyolefin matrix was proposed by Griffin as an effective means of accelerating the deterioration of plastics under biotic environmental exposure conditions.^{1,2} The inclusion of starch, a readily biodegradable biopolymer, into the synthetic polymer is believed to result in rapid enzymatic hydrolysis of the starch under biotic exposure conditions, leading to a void-containing matrix. The reduced mechanical integrity of the ensuing void-containing matrix leads to its facile deterioration, and perhaps even promotes subsequent biodegradation of the synthetic polymer, due to the increased surface area available for interaction with microorganisms. With several modifications, aimed at improving the rate of breakdown of the plastic material, the basic concept is currently used in commercial polyethylene films for packaging, diaper lining, and compost bag applications.

In studies on biodeterioration, as well as compounding/processing, of polyethylene/starch blends, it is important to determine accurately the level of starch in the blend. Several methods have been proposed for this purpose.

A chemical analytical procedure, based on spectroscopic determination of the hydrolyzed starch, has been described.³ The polyethylene (LDPE) component of the blend is dissolved in decalin, and the resulting starch is hydrolyzed with 1 M HCl at 100°C. The hydrolyzate in aqueous solution is used to estimate the starch content using the phenol-sulfuric acid method, due to Dubois et al.⁴ This two-step procedure was shown to yield estimates of starch content, which varied by –9 to +22% from the expected 6% level of starch in LDPE. The difficulty in completely separating the decalin and water phases prior to spectrophotometry, and the non-specificity of the phenol-sulfuric acid reagent, are drawbacks of this technique, which also takes several hours to carry out.

Fourier Transform Infrared spectroscopic (FTIR) Analysis might also be used to determine the starch levels.^{5,6} While the use of this technique has been reported for films containing relatively high levels of about 40% starch, its usefulness as a quantitative technique with films containing 0–12% levels of starch has not been fully demonstrated. Reported procedures involve either grinding the film, and incorporating it in a KBr pellet,⁵ or direct FTIR analysis of film samples.⁶ FTIR analysis is, however, difficult to carry out with thick films, particularly with those that have been exposed to a soil environment.

Starch undergoes thermal degradation at much lower temperatures as compared to polyethylenes.

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Morita⁷ studied the thermal degradation of corn starch under nonoxidative conditions by differential thermal analysis (DTA). The DTA curves were characterized by two endothermic peaks in the region 135–310°C, followed by two exothermic peaks in the 375–520°C region. With a suitable heating rate, it should be possible to observe the degradation of starch component and that of polyethylene as separate events in a thermogravimetric run. Thermogravimetry, therefore, might potentially be used to quantify the starch levels in starch/LDPE blends. The present work investigates the usefulness of thermogravimetry in determining the starch levels in as-prepared and partially deteriorated starch/polyethylene blend films.

EXPERIMENTAL

Plastic Films

Three sets of low density polyethylene films containing (1) no additives, (2) starch, and (3) starch and metal compound pro-oxidants were prepared by extrusion blowing. Different samples with starch contents varying from 0–12 wt % were prepared. The processing was carried out by Archer Daniels Midland Company, the manufacturer of the masterbatch.

All films were based on Rexene 503 (LDPE) resin and were blown using a Bolco International Machine equipped with a 2 inch die. The die body temperature was maintained at 180°C during extrusion at a rate of 40 lbs/h. A blow up ratio of 3.5 was used.

A series of films (about 50 μm in thickness), containing different levels of starch (in the 0–12% by weight range) was prepared by using appropriate mixes of the starch-containing masterbatch and the virgin resin. Films were wrapped in opaque paper, placed in plastic bags, and stored in a refrigerator until use. This series of films is referred to as ADM(1) films in the Discussion Section.

Thermogravimetry

A Perkin-Elmer Model TGS-2 Thermogravimetric System, with a microprocessor-driven temperature control unit and a TADS data station, was used. The plastic film samples were cut into discs 5 mm in diameter. Several discs cut from different parts of the sample film were combined to obtain a stack of discs, which served as a single sample. The weight of this sample was recorded accurately and was generally in the range of 6–10 mg.

The sample pan was placed in the balance system in equipment and the temperature was raised from 50° to 450°C at a heating rate of 10°C/min. The weight of the sample pan was continuously recorded as a function of the temperature.

Data generally showed a distinct and consistent, nonreversible loss in weight, attributed to the pyrolysis of starch, in the temperature interval of 280°C–340°C. The loss in weight of the sample was used to estimate the percent starch in the sample.

Sample Exposure

Four types of exposure environments were used in this study: (1) outdoor soil burial exposure, (2) laboratory-accelerated soil burial, (3) exposure to an enzyme medium, and (4) laboratory-accelerated exposure in water.

1. Outdoor soil burial exposure was carried out at Research Triangle Institute during March–September, 1990. Samples were buried at a test site about 6 in. below the surface, horizontally, in a topsoil. Only the sample films with ~ 6% by weight starch were used in this exposure, which was carried out for a period of up to 20 weeks. Sampling was at 6, 10, 12, 16, and 20 weeks.
2. Accelerated soil burial was carried out in the lab using “Black Kow” brand topsoil, with 1% garden soil inoculum mixed in. Urea (0.01% of the weight of sample) and K_2HPO_4 (0.05% of the weight of sample) were added to the soil and its water content was adjusted to 20% (about 60% of the water-holding capacity of the soil). Exposures were carried out in closed plastic boxes containing soil and were maintained at 37°C. Boxes were opened for aeration periodically.
3. The enzymatic degradation experiment used an alpha-amylase, derived from *Bacillus* sp. type XI-B Lot 39F 0442 (Sigma Chemical Co.). The film sample (approximately 3 g) was immersed in a solution of the enzyme (45 K units of enzyme in 500 mL) in pH 6.9 buffer and was maintained at a constant temperature of 37°C. The enzyme solution was replaced with fresh enzyme twice during the exposure. The samples were removed at the end of 40 days, and were washed and dried before testing.
4. Accelerated exposure in water was carried out using a basal mineral salt (BMS) medium [MgSO_4 (23 mg), CaCl_2 (28 mg), KH_2PO_4

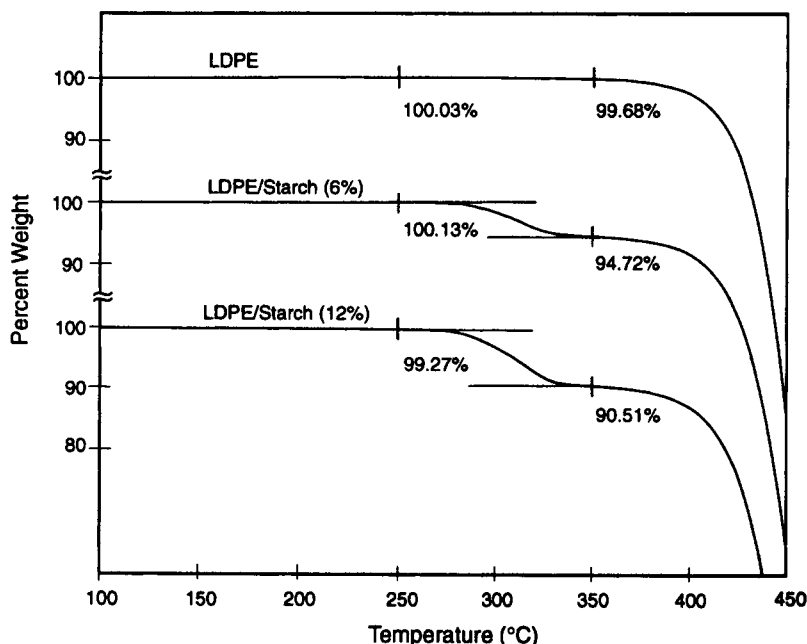


Figure 1 Typical tracings from the thermogravimetric analysis of LDPE films and LDPE/starch blend films.

(44 mg), $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (67 mg), NH_4Cl (3.4 mg), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mg) and $(\text{NH}_4)_2\text{SO}_4$ (40 mg), per L of deionized water]. The medium was seeded with soil extract from 15 g of garden soil. The film samples were placed in the solution, which was aerated continuously and was maintained at 37°C . After exposure for 40 days, the sample was removed, washed, and dried at room temperature.

RESULTS AND DISCUSSION

Films Prior to Environmental Exposure

The thermogravimetric technique essentially involves continuous monitoring of the weight of a sample as a function of temperature, using a sensitive microbalance. Typical TGA traces obtained for the polyethylene/starch blend film samples, containing 6 and 12% by weight of starch, are shown in Figures 1(b) and (c), respectively. A very distinct weight loss is seen with both samples in the temperature interval of 250°C to 350°C , at a heating rate of $10^\circ\text{C}/\text{min}$. Polyethylene film that does not contain starch shows only a negligible weight loss in the same temperature interval (Fig. 1a), suggesting the loss in weight to be due to partial or complete pyrolytic volatilization of the starch. This loss in weight might therefore be used to quantify

the starch content in the sample. Polyethylene itself undergoes weight loss due to thermal degradation at significantly higher temperatures, but does not contribute to the weight loss at the temperature range under discussion.

A series of LDPE/starch blends with different starch contents [designated ADM(1)] was prepared and blown into films, approximately $50\ \mu\text{m}$ in thickness, for the study. The weight loss observed in TGA runs on these samples is given in Table I, along with the anticipated percentage of starch in each film sample. The latter was obtained using a published spectrophotometric technique by Fratzke et al.,³ sometimes referred to as the "Iowa method," described in the Introduction. As shown in Figure 2, the data from the two methods correlate well linearly (correlation coefficient, $r = 1.00$) and the plot yielded a gradient of 0.85. The gradient is not unity, indicating that either one or both techniques do not quantify the absolute amount of starch in the sample. The weight loss associated with the film, compounded with approximately 6% starch, yielded an average weight loss of 5.62% with a standard deviation of 0.14 ($n = 6$).

A second series of samples [designated ADM(2)] was prepared using a mix of film sample sections from the control LDPE film that did not contain added starch, and a freshly-compounded and blown LDPE/starch blend film of the same thickness that contained about 6% starch. Appropriate weight

Table I TGA and FTIR Spectroscopic Data for As-Prepared LDPE/Starch Blend Films

Sample Type	Estimated ^a Starch Content (%)	Measured ^b Starch Content (%)	Weight Fraction	Weight Decrease Obtained by TGA (%)	Relative Intensity Obtained by FTIR
ADM (1)	0	0.0	—	0.35	0.08
	2	1.8	—	1.92	0.16
	4	1.9	—	2.17	0.15
	6	5.9	—	5.40	0.36
	8	7.1	—	6.46	0.40
	10	8.1	—	7.66	0.56
	12	10.2	—	8.75	0.63
ADM (2)	6	—	0.00	0.44	—
		—	0.20	1.73	—
		—	0.33	2.72	—
		—	0.50	3.79	—
		—	0.68	4.73	—
		—	0.80	5.59	—
		—	1.00	6.84	—

^a Nominal starch content provided by film processor.

^b Starch content determined by chemical/spectroscopic analysis. Data provided by Archer Daniels Midland Company.

fractions were selected to obtain several test samples (each consisting of a mixed stack of discs cut from two films) containing 0 to about 6% of starch. Figure 3 shows the dependence of the percent weight loss, in the temperature range 194°C–350°C, on the weight fraction of starch containing LDPE in the mix. The plot again shows good linearity and a gradient of 6.35 ($r = 1.00$). The data are listed in Table I.

The ADM(1) series of samples containing different levels of starch in the range of 0–12 weight percent, as determined by the spectrophotometric method, was thin enough to allow direct FTIR analysis. Good transmission spectra were obtained without resorting to the KBr pellet technique pre-

viously used in the literature.⁵ The freeze-grinding process, involved in the published technique, probably frees the starch granules from plastic matrix to some extent and may yield better spectra. Direct FTIR spectroscopic studies on LDPE films containing starch were also reported.⁶ Usually, the area under a selected waveband in the absorption spectrum of the film is used to estimate starch content. However, the dependence of the peak area on starch content is not linear over large ranges of starch levels.⁶ The starch generally exhibits a sharp absorption band at 960–1190 cm, generally assigned to C—O stretching. With the present films, this band appeared as a shoulder on a polymer-related peak adjacent to it, precluding the use of peak area to quantify the absorption band. The peak intensity of this

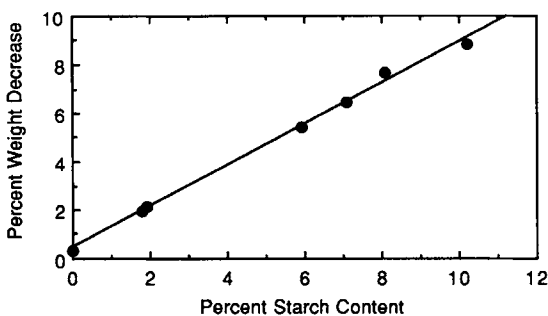


Figure 2 The dependence of the percent decrease in weight in TGA on the starch content of starch/LDPE blend films [ADM(1)] series as determined by the Iowa method.

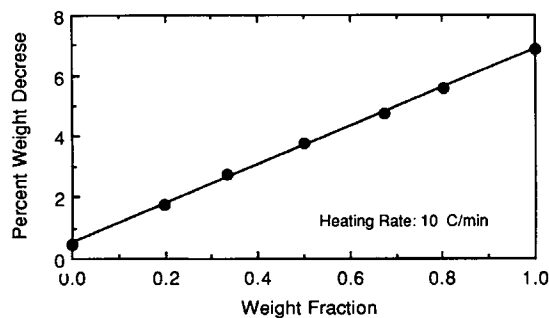


Figure 3 The dependence of the percent decrease in weight in TGA on the starch content of mixtures of LDPE films with LDPE/starch (6%) films [ADM(2) series].

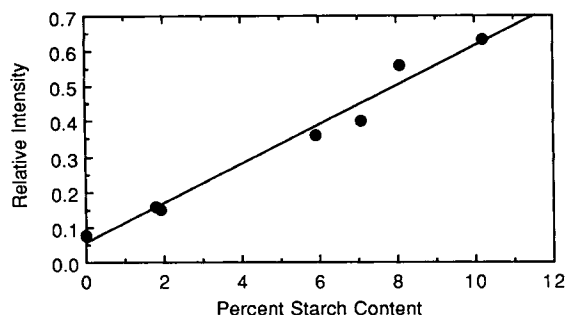


Figure 4 Intensity of the 980 cm^{-1} shoulder relative to 1460 cm^{-1} band in FTIR spectra of starch/LDPE films [ADM(1) series] containing different levels of starch as determined by the Iowa method.

shoulder, at 980 cm^{-1} , relative to that of the band at 1460 cm^{-1} which is assigned to CH_2 bending in polyethylene, was used to quantify the starch content. Figure 4 illustrates the data which is also included in Table I. The data shows a linear dependence ($r = 0.98$) and a gradient of 5.56, in agreement with the TGA result. Repeat determinations carried out using the film sample, with approximately 6% starch, yielded an average relative peak intensity of 0.37 with a standard deviation of only 0.01.

Assuming that the chemical analytical method yields an accurate estimate of the starch content of the blend films, the above data suggests that both

the TGA determination and the direct FTIR analysis of the LDPE/starch films are suitable for determining the starch content of "as prepared" LDPE/starch blend films. The FTIR method is faster than thermogravimetric analysis, but both these methods would be much faster to use than the chemical method.

Films after Environmental Exposure

To be of practical use, an analytical method for determination of starch in a polyolefin film must be applicable to samples that have been exposed under different environmental conditions in order to induce at least a partial biodegradation of the starch fraction. Exposure to biotic environments causes enzymatic hydrolysis of some of the starch and also innervation of the polymer matrix by microbial biomass. This tended to affect the transparency of the plastic film making it difficult to obtain good FTIR spectra without the use of a KBr or a mull technique. The presence of microbial biomass within the plastic matrix may introduce additional polysaccharide material into the polymer, which undergoes thermal degradation in the same temperature range as starch and interferes with the TGA technique.

TGA measurements were carried out on the ADM(1) series of films exposed outdoors in a biotic soil environment. Table II shows the percent de-

Table II Effect of Environmental Exposure on Starch Content

Exposure ^a	Duration (week)	Initial Starch Content (%)	% Weight Change at $250^{\circ}\text{--}350^{\circ}\text{C}^{\text{b}}$	Percentage of Residual Starch after Exposure
1. Outdoor Soil Burial	0	~6	5.20	100
	6		4.59	87
	10		4.98	95
	12		4.58	87
	16		5.85	>100
	20		6.19	>100
2. Laboratory Soil Burial at 37°C	0	~2	1.92	100
	16		1.73	88
	0	~6	5.40	100
	16		5.03	93
	0	~12	8.75	100
	16		7.69	87
3. α -Amylase at 37°C	0	~6	5.61	100
	6		5.20	92
4. Soil Inoculum at 37°C in Mineral Salt Medium	0	~6	5.61	100
	6		4.96	88

^a All exposures used film samples. No shredding, cutting, or grinding were used to increase the surface area exposed to microbes.

^b Total weight change was assumed to be due to complete pyrolysis of starch.

crease in weight in the temperature range 250°C–350°C, obtained by the TGA technique for these samples. The percent weight loss obtained for samples exposed for 6 and 12 weeks were smaller than those for the unexposed samples, indicating some degradation of starch obtained at short durations of exposure. Assuming this decrease, W_d , is solely due to pyrolysis of the starch fraction, the percent change in the starch fraction due to biotic exposure could be calculated using the following expression.

Percent residual starch

$$= \frac{W_d \text{ of exposed blend} - W_d \text{ of unexposed LDPE}}{W_d \text{ of unexposed blend} - W_d \text{ of unexposed LDPE}} \times 100$$

Note that the W_d value for the unexposed LDPE film is used in both the numerator and denominator of the expression. LDPE is not expected to undergo any biodegradation in the time scale of exposure used in this study, and the TGA behavior of exposed and unexposed LDPE films is assumed to be the same. LDPE film does show a 0.35% weight loss within the specified temperature interval, possibly due to loss of moisture or low molecular weight additives, and this value was used as W_d (LDPE unexposed) in the above equation. As shown in Table II, the residual starch content was about 90% for samples exposed for short durations outdoors.

At longer periods of 16 to 20 weeks exposure, however, the W_d values were larger than the initial weight fractions of starch. A possible source of variation might be due to the presence of metal compound pro-oxidant in the films. A TGA tracing, which is essentially flat in the temperature range of 250°C to 350°C, is a necessary prerequisite for accurate determination of weight loss by this technique. Unlike unexposed films and those exposed for relatively short durations, the films exposed for 16 and 20 weeks in soil showed some weight losses at temperatures as low as 180°C. This might be due, at least in part, to volatilization of low-molecular weight species formed because of the metal-catalyzed thermal oxidation of the polyethylene itself during exposure. ADM(1) material contained iron and magnesium compounds to make it enhanced photodegradable and thermally oxidizable. The pro-oxidant nature of these metal compounds in thermooxidation of polyolefins is well known.⁸ Interestingly, samples of ADM(1) material exposed outdoors in sunlight under essentially abiotic conditions also yielded a TGA tracing showing significant

weight losses at < 180°C, presumably due to volatilization. Perhaps a second source of error is introduced by the possible presence of biomass in the matrix. These pyrolyzable organic materials in the polymer tend to overestimate the residual starch content in exposed films, as measured by thermogravimetry.

ADM(1) series of samples with approximately 2, 6, and 12% starch (nominal starch contents as provided by film processor) was used in the laboratory-accelerated soil burial exposures carried out at 37°C. Table II shows the W_d values obtained from TGA increases with the level of starch for both exposed and unexposed materials. However, with 16 weeks of exposure, the residual starch levels in the films were 83–93% of their initial starch content.

Two sets of exposed samples (exposed in soil for 16 weeks, and exposed to soil under laboratory accelerated conditions for 16 weeks) were also investigated using the direct FTIR technique. However, no significant difference between the relative intensity in absorbance at 980 cm⁻¹, compared to the band at 1460 cm⁻¹, was obtained. The film samples after exposure to soil environments under the present exposure conditions were hazy and discolored.

A sample of film containing approximately 6% of starch was subjected to 6 weeks of α -amylase enzyme exposure, and also to a soil innoculum maintained at 37°C in a mineral salt medium. Both samples yielded TGA data, showing approximately a 10% reduction in the starch content.

Thus, regardless of the initial starch content of the film and the duration of exposure in the time-scale of 0–20 weeks, all exposure conditions resulted in less than about a 10% decrease in the starch content. Furthermore, this decrease in the level of starch occurs in the early stages of exposure. Austin⁹ carried out carbon dioxide evolution studies on LDPE/starch (6%) and found that the gas evolution levelled off after an initial phase lasting about 30 days under the conditions employed. The total CO₂ given off at that point accounted for degradation of less than 10% of the starch in the film. Electron microscopic observations showed the starch granules on the surface of the film to be attacked by the microorganisms within a 50 day period of exposure.⁹ Iannotti et al.,¹⁰ however, found 25–30% removal of starch from films containing 3, 6, and 9% starch within 24 weeks of soil burial. Values pertaining to the samples containing 6% starch were not separately reported. While this is a slightly higher value than that obtained in the present work, this is expected, as FTIR spectroscopy was used to quantify the level of residual starch.

Present data, as well as the reported data cited above, suggest that only a small fraction of about 10–15% of the total starch content is removed, at least during early exposure; this might be explained in terms of limited accessibility of the starch to microbes. Wool et al.,¹¹ described the invasion of a polymer/starch matrix by microorganisms and/or extracellular enzymes in terms of a scalar percolation theory. The minimum level of starch needed to achieve connectivity between starch domains, and therefore accessibility of the starch to biodegradation, is the percolation threshold. From simulation experiments, this level was found to be about 31% starch by volume. Below this level of starch content, the theoretical analysis, as well as acid hydrolysis studies carried out by them, showed less than 10% of the starch was accessible to hydrolysis. The assumption of random invasion of the matrix by the microbes/enzymes is perhaps an oversimplification, because of the concentration of organisms near the hydrolyzing starch granules due to chemotaxy and the rapid multiplication of organisms close to the sources of available nutrition (available starch granules). Nevertheless, the qualitative finding that, at levels close to 6% starch in polymer, little biodegradation of starch might be expected is a valid conclusion from their analysis. It is reasonable to expect that at higher levels of starch in the matrix, faster, readily observable biodegradation of starch will occur. Gould et al.,⁵ working with plastic films containing 40% starch, found the starch to be biodegraded almost totally, as evidenced by changes in FTIR spectra.

CONCLUSIONS

Thermogravimetry is a fast, convenient means of determining the level of starch dispersed within a polyethylene film. At least in the range of 0–12% by weight starch, the thermogravimetric weight loss in a selected temperature range correlates well with the starch content determined by a conventional extraction/spectrophotometric technique. The method might be also applicable to moderately deteriorated starch/polyethylene films as well. Generally, about a 10% decrease in starch content, regardless of the initial level of starch, was obtained over a 12 week period of soil exposure.

The main limitation of the method is that it did

not yield good data for samples exposed for longer periods of time. This might be due to interference by low-molecular weight oxidation products of polyethylene (formed rapidly due to the presence of metal compound catalysts), which volatilize in the temperature range where starch degrades. Biomass infiltrating the polymer matrix may also complicate the analysis in the case of heavily biodegraded samples.

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