

Weathering of Starch–Polyethylene Composite Films in the Marine Environment

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SYNOPSIS

Polyethylene and starch–polyethylene composite films were exposed outdoors in the strawline of a marsh and in sea water on flow-through seatables in the laboratory. The deterioration of these films following exposure was measured by determining changes in tensile properties, weight loss, starch loss, and carbonyl content of the sheet plastic films. Low rates of deterioration were observed for control and starch–polyethylene composite films submerged in sea water. In contrast, both starch–polyethylene composite and control polyethylene films rapidly deteriorated during exposure in the strawline of a marsh. Differences in the observed rate of deterioration of the films placed in the exposure sites is attributed primarily to photodegradation of the films placed in the strawline of a marsh. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Plastics were estimated to compose some 8% by weight of the municipal solid waste stream in 1988.¹ Many of the physical and chemical properties of plastics make them ideal materials for a variety of products and applications. Plastics can be manufactured to be durable, lightweight, flexible, impermeable, transparent, or opaque. Moreover, plastics are typically very resistant to degradation in the natural environment. As such, they are often considered to be environmental contaminants due to their widespread distribution and longevity. Recent studies have shown that plastic debris is widespread in the world's oceans.²

Plastic waste, along with other floatable debris, enters the marine environment via several pathways including litter, combined sewer overflows, solid-waste handling, and recreational and fishing boats.^{2,3} The plastic component of floatable debris may be in the form of large and small plastic pieces including plastic beads, packaging, diaper liners, tampon applicators, discarded fishing gear, and medically related waste. Aside from being an aesthetic problem,

floatable plastic debris has been identified as a hazard to a variety of marine organisms. At sea and on beaches, plastic debris is a threat to a variety of marine organisms including mammals, turtles, and birds.^{4–6} The washup of floatable wastes along beaches has also closed beaches, resulting in economic losses to coastal communities.⁷

Recently, starch–polyethylene composites have been developed in an effort to make the materials more susceptible to biological degradation.^{8,9} These starch–polyethylene composites are designed to increase the rate of degradation of the product and lessen impacts associated with discarded plastic wastes. These composites are a mixture of a readily degradable starch component within a polyethylene matrix and they may possess starch contents of up to 50% by weight.⁹ In addition to starch, these composites may also contain catalysts to oxidize the polymer to lower molecular weight byproducts, which may then be metabolized by microorganisms. If the incorporation of additives such as starch in plastic increases the susceptibility of the product to deterioration, impacts commonly associated with persistent plastics in the environment may be alleviated.

The degradation processes for starch–polyethylene composite films when they enter the marine environment are not well known. The objective of this

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study is to measure the rate and extent of deterioration of starch-polyethylene composite and control polyethylene films in sea water and the strawline of a marsh. Physical and chemical tests were conducted to determine the extent of deterioration of starch-polyethylene composite films during 13 months exposure in the marine environment.

EXPERIMENTAL

Film Descriptions

All starch-polyethylene composite and control polyethylene films were supplied by the Archer Daniels Midland Co., Decatur, IL (Table I). Low-density (LDPE) and linear low-density (LLDPE) polyethylene films were used as controls. Starch containing LDPE and LLDPE films were manufactured using the Griffin process.⁸ The starch-polyethylene composite films contain approximately 5.5% "masterbatch," which contains both starch and proident additives.

Film Preparation for Exposure Site Placement

Plexiglass frames (91.4 × 35.6 cm) were constructed to form a 10 square open grid using 2.5 × 0.64 cm strips of plexiglass. Methylene chloride was used to fuse the pieces of plexiglass to form the frames. Starch-polyethylene composite and control polyethylene films were cut into 15.9 × 16.5 cm sections and mounted into the plexiglass frames for placement in the exposure areas. An untreated cellophane film was also mounted into each rack. Each film was weighed prior to placement in the rack. The films were secured to the frame by a plexiglass washer and a nylon bolt assembly at each of the four corners. A soldering pen was used to melt the identification number for each film into the plexiglass frame.

Sea Water Exposure Site

Films were placed on flow-through seatables at the Flax Pond Marine Laboratory, Old Field, New York. Sea water was pumped from the marsh into the lab-

oratory through PVC pipes. The sea water PVC intake pipe lies within the entrance channel of the marsh 91.4 cm above the bottom. The intake pipe was equipped with a 0.32 cm screen to prevent large particles from entering the pumping system. Although large particles were removed at the intake pipe, the screen allowed the passage of biologically active sea water.

The fiberglass seatable (224 × 91.4 × 15.2 cm) was equipped with an adjustable overflow drain set to allow a sea water depth of 10.2 cm on the table. Sea water flows from the laboratory plumbing into a multichambered sediment settling tank prior to discharge onto the table. Sea water flowed onto the table at a rate of 2 L per minute, replacing the water on the seatable every 1.5 h.

On May 5, 1989, starch-polyethylene composite and control polyethylene films were submerged to a depth of 5.1 cm in the sea water on the seatable. A plexiglass railing was constructed and held in place with C-clamps to keep the plexiglass exposure frames and films submerged in sea water. Temperature and salinity of the sea water were recorded weekly. Films were removed from the seatable on a predetermined basis and returned to the laboratory for physical and chemical testing (Table II).

Strawline Exposure Site

Starch-polyethylene composite and control polyethylene films were placed in the strawline of a marsh on June 9, 1989. The exposure area was located in the marsh at the Flax Pond Marine Laboratory (Fig. 1). Flax Pond is a 0.5 km² estuarine marsh on the north shore of Long Island with a single channel connection to Long Island Sound. During high tide, the surface area of water is 574,000 m² with a volume of approximately 880,000 m³.¹⁰

The containment area was located in an area of the marsh that is not flooded by sea water during a normal tidal cycle. The exposure site may, however, be submerged by sea water during storm events or unusually high tides. A wooden, fenced-in containment area (183 × 488 × 61 cm) was built on the edge of the marsh to house the films. The containment area was designed to allow the films to be placed on the ground in a clearing within the marsh vegetation and was completely enclosed with wire fencing to allow the natural weathering of the films while preventing vandalism or disturbance by small animals. The containment area possessed two lids that could be opened independently for placement or retrieval of films.

Daily temperature and solar radiation readings were obtained from the weather station at the

Table I Starch-Polyethylene Composite and Control Polyethylene Films

Film	Film Description
1A	Low-density polyethylene (LDPE)
1B	LDPE + 5.5% cornstarch masterbatch
1C	Linear low-density polyethylene (LLDPE)
1D	LLDPE + 5.5% cornstarch masterbatch

Table II Exposure Site Sampling Activities

Month	Seatable	Days following Placement	Strawline	Days following Placement
$T = 0$	May 5, 1989	0	June 9, 1989	0
$T = 2$	July 7, 1989	63	August 9, 1989	61
$T = 4$	September 1, 1989	119	September 29, 1989	112
$T = 6$	November 2, 1989	181	December 5, 1989	179
$T = 9$	February 5, 1989	276	March 21, 1990	285
$T = 13$	June 8, 1990	399	July 20, 1990	406

Brookhaven National Laboratory, Upton, NY. Films were removed from the strawline on a predetermined basis and returned to the laboratory for physical and chemical testing (Table II).

The films were then towel-dried, placed in labeled zip lock bags, evacuated with argon, and stored in the dark at 20°C.

TESTING METHODS

Cleaning and Storage of Films

In the laboratory, the films were rinsed in tap water and sonicated in distilled-deionized water for 15 min.

Tensile Testing

An Instron Model 1011 Universal Testing Machine was used to determine the tensile properties of the starch-polyethylene composite and control polyethylene films following ASTM method D882.¹¹ A gauge length of 5.08 cm and a crosshead speed of

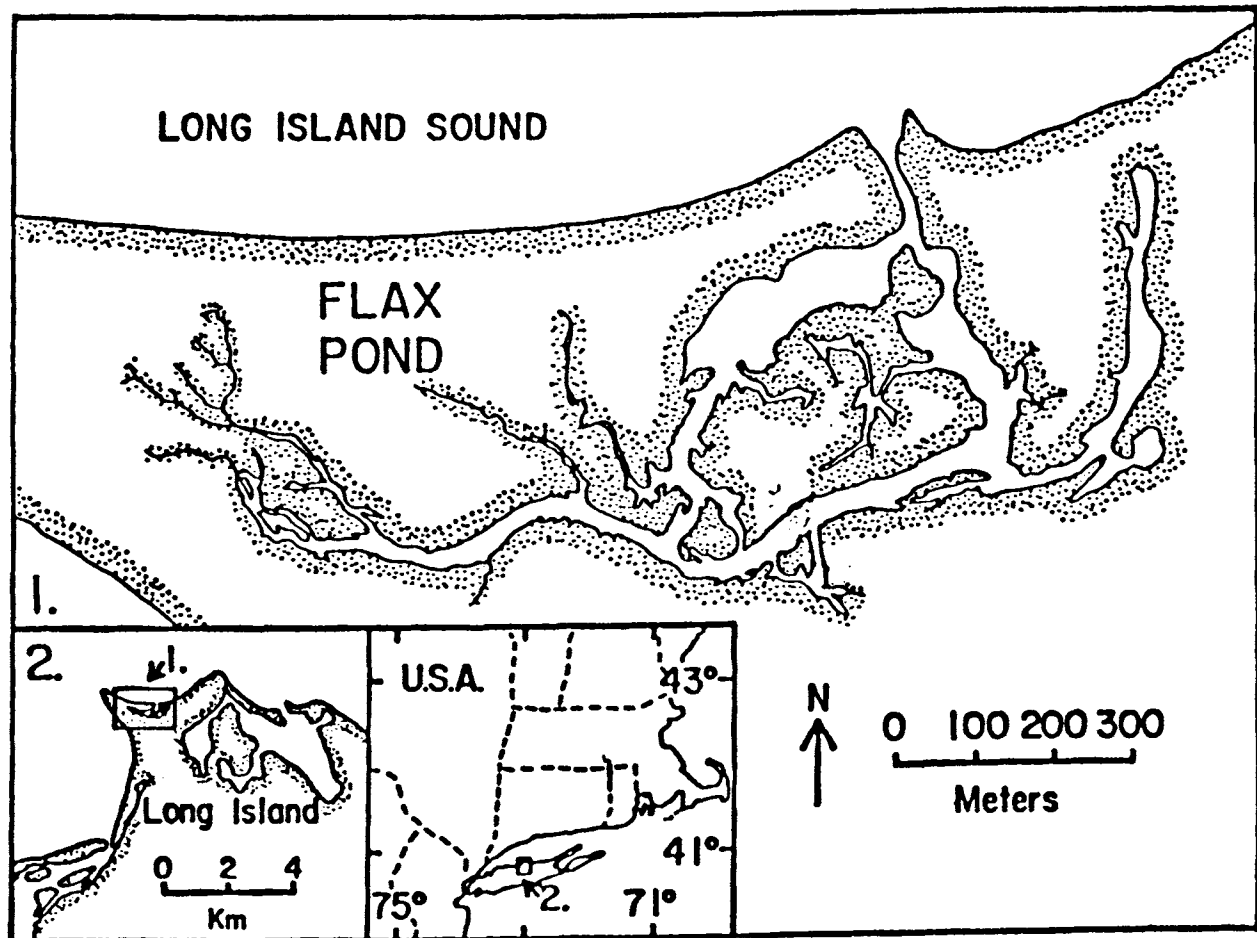


Figure 1 Strawline exposure site location, Old Field, NY.

50.8 cm/min was used. Six specimens were prepared for testing from each film retrieved from the exposure sites. Tensile strength at break and percent elongation at break were determined for each film.

Film Weight

Film weights (± 0.001 g) were obtained using a Sartorius Model 2462 HW analytical balance. Films were conditioned at 50% humidity and 23°C for 48 h prior to weighing.

FTIR Testing

Difference Fourier transform infrared (FTIR) spectroscopy was carried out on control polyethylene and starch-polyethylene composite films using a Perkin-Elmer Model 1600 spectrophotometer collecting 16 scans with a resolution of 4.0 cm^{-1} between 4400 and 450 cm^{-1} . Four replicates of each film were analyzed. Each spectrum was recorded and stored on a floppy disc and printed out with transmittance wavenumbers for analysis.

Chemical Method for Starch Determination

Quantitative starch determinations of preplacement and weathered starch-polyethylene composite films were conducted using a previously developed

method.¹² The method consists of dissolving the polyethylene component followed by the solubilization and partial hydrolysis of the starch component. The solubilized starch component was then isolated for carbohydrate analysis using the phenol-sulfuric acid method.

RESULTS

Air Temperature and Solar Radiation

Weekly average solar radiation for the 13-month exposure period is shown in Figure 2. The highest recorded solar radiation of 761 langleys/day was observed on June 11, 1989, whereas the lowest recorded solar radiation of 17 langleys/day occurred January 20, 1990.

Weekly average maximum and minimum temperatures are shown in Figure 3 for the 13-month exposure period. The highest recorded temperature was observed to be 34°C on July 23, 1989, whereas the lowest recorded temperature was observed to be -15°C on December 19, 1989.

Seatable Temperature and Salinity

Sea water salinity remained relatively constant throughout the 13-month exposure period (Fig. 4).

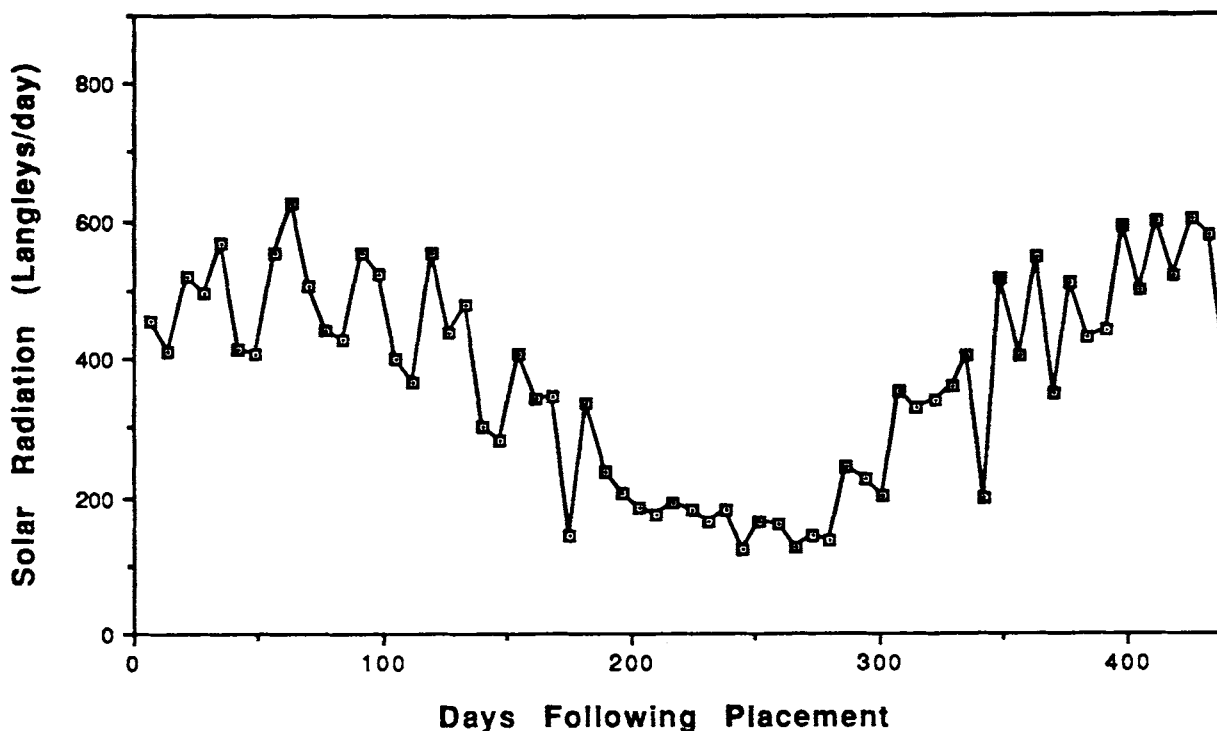


Figure 2 Average weekly solar radiation during the 13-month exposure period.

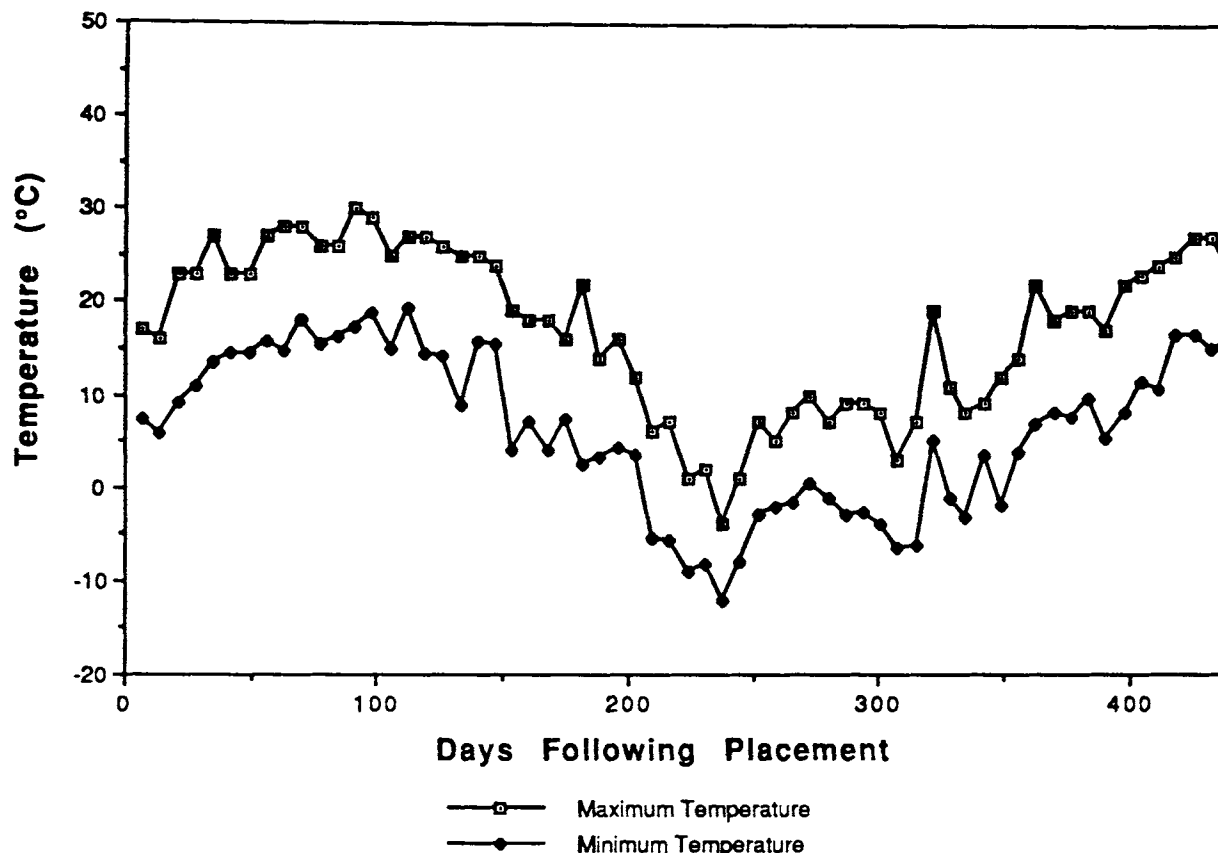


Figure 3 Average weekly maximum and minimum daily temperature during the 13-month exposure period.

Salinity varied from 24.5 ppt to 30.7 ppt with a mean of 27.4 ppt.

Temperature of the sea water varied seasonally (Fig. 4). Water temperature was warmest during the summer months, reaching a high of 24.0°C during August 1989. The lowest temperature of 3.0°C was measured during February 1990.

Tensile Properties

Seatable Exposure

Tensile strengths of both the control and starch-polyethylene composite films remained similar to their preplacement values over the entire 13-month exposure period, retaining greater than 86% of their initial tensile strength (Fig. 5).

LLDPE control film 1C and LLDPE starch-polyethylene composite film 1D retained greater than 87% of their initial % elongation during the 13-month exposure period (Fig. 6). In contrast, the % elongation for LDPE starch-polyethylene composite film 1B decreased by 70% of the preplacement

value, whereas the % elongation of the corresponding control LDPE film 1A only decreased 13% from the preplacement value.

Strawline Exposure

Decreases in the tensile strengths of starch-polyethylene composite and control films LDPE 1A, LLDPE 1C, and LLDPE 1D are observed over the 6-month sampling period, whereas the tensile strength of starch-polyethylene composite LDPE film 1B remained similar to preplacement values (Fig. 7).

The % elongation of both starch-polyethylene composite and control films rapidly decreased following exposure (Fig. 8). Following 2 months exposure, the % elongation for starch-polyethylene composite films LDPE 1B and LLDPE 1D decreased by 98 and 29%, respectively, of their preplacement values, whereas the % elongation of their corresponding control films decreased by 92 and 12% of their preplacement values. After 6 months, the % elongation for both control and starch-polyethylene

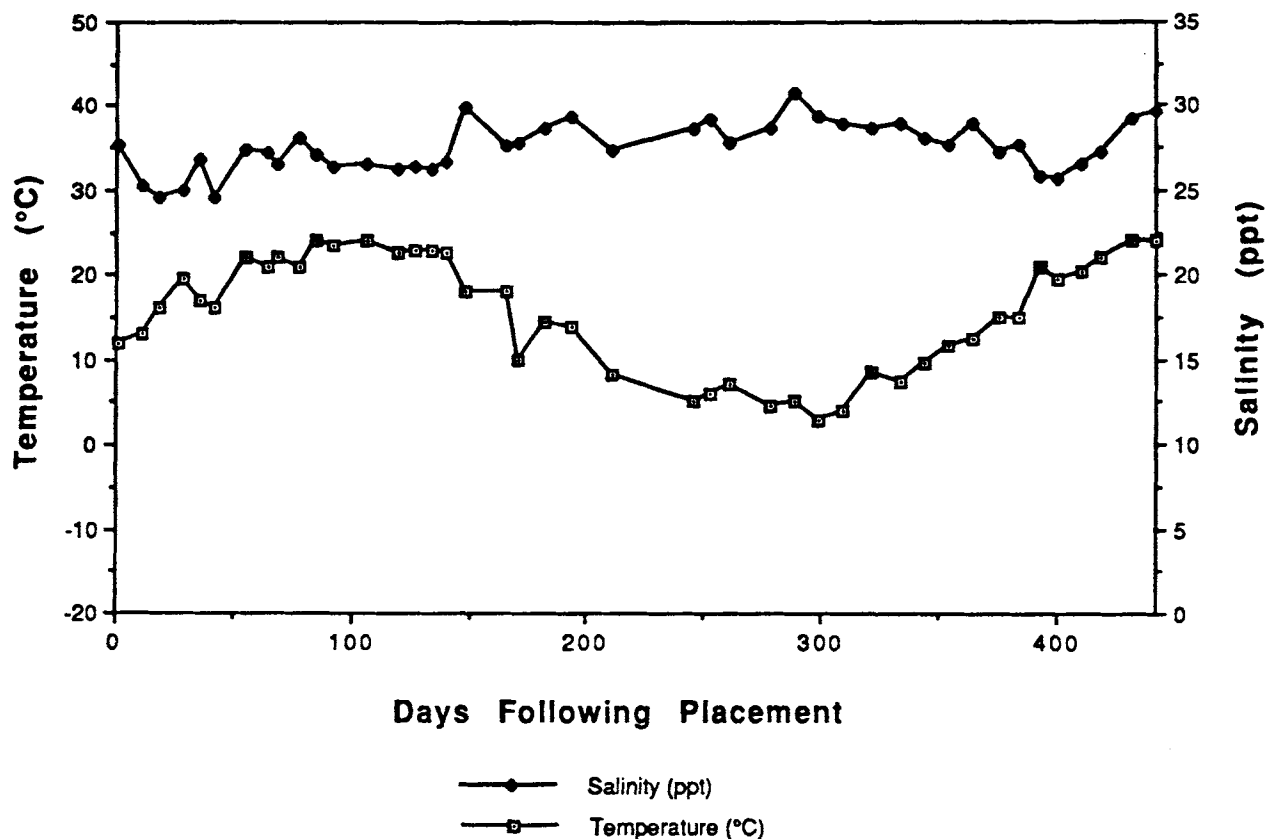


Figure 4 Seatable sea water temperature and salinity during the 13-month exposure period.

composite films decreased to less than 5% of their preplacement values and further testing was discontinued.

Weight Loss

Seatable Exposure

The weight of both starch-polyethylene composite and control LDPE and LLDPE films increased slightly when compared to preplacement values during the 13-month exposure period (Fig. 9). Weight increases may be due to water absorption by the starch and/or polyethylene in addition to biological material remaining on the films following cleaning. Both the LDPE and LLDPE control and starch-polyethylene composite films removed from the seatable retained dark green and brown pigments following cleaning.

Strawline Exposure

The weight of both starch-polyethylene composite and control LDPE and LLDPE films decreased as

time progressed (Fig. 10). Weight loss was most pronounced for the LDPE and LLDPE starch-polyethylene composite films. Following 13 months exposure, weight losses of 38 and 17% were observed for starch-polyethylene composite films LDPE 1B and LLDPE 1D, respectively. Both starch-polyethylene composite and control polyethylene films began tearing and fragmenting into smaller pieces following 4 months exposure.

FTIR Analysis of Starch-Polyethylene Composite and Control Polyethylene Films

The FTIR spectra of LDPE and LLDPE films show characteristic C—H stretching bands within the 3000–2840 cm^{-1} region, weaker C—H bending bands within the 1465–1450 cm^{-1} and 1375–1365 cm^{-1} regions, and C—H out-of-plane bending within the 740–719 cm^{-1} region (Fig. 11 and Table III). In addition to the functional groups common to LDPE and LLDPE, the starch-polyethylene composite films showed a broad O—H stretching absorbance in the 3600–3200 cm^{-1} region and a

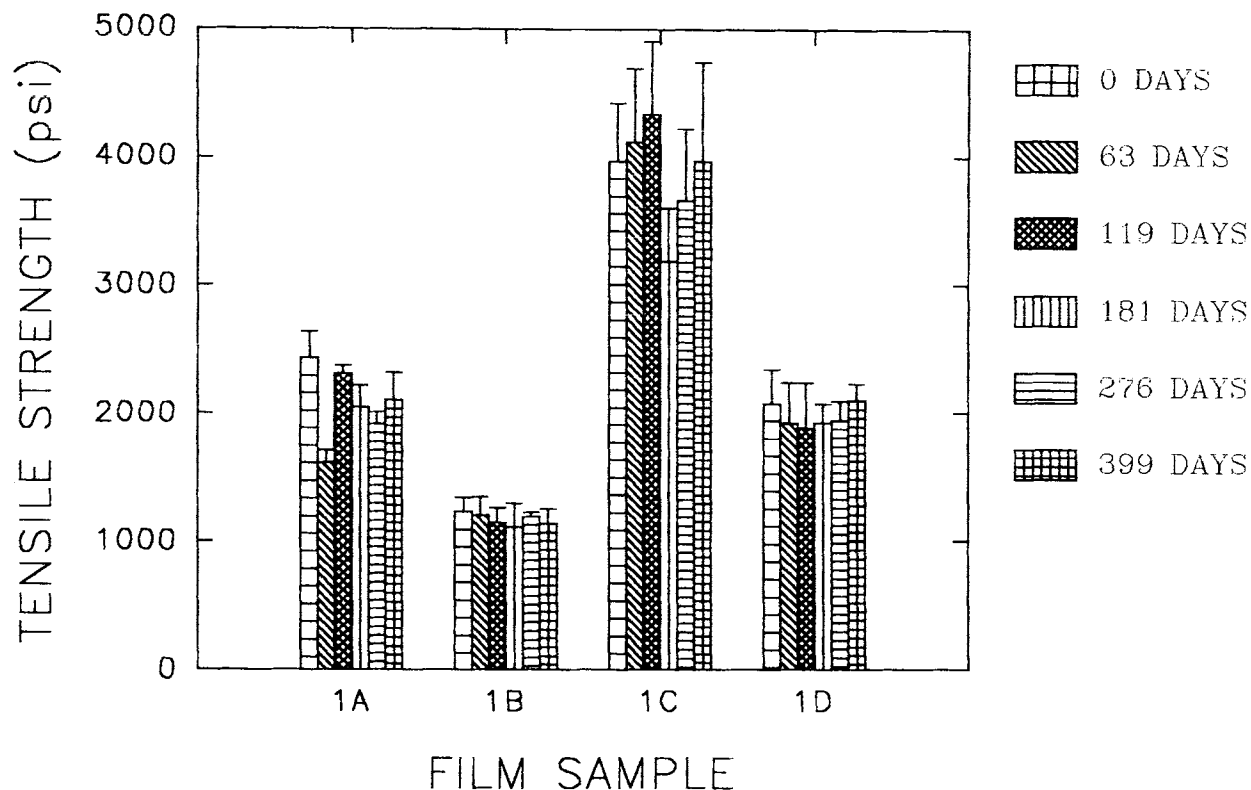


Figure 5 Variation in the tensile strength at break for films 1A, 1B, 1C, and 1D during 13 months sea water exposure.

strong set of C—O stretching bands in the 1090–980 cm^{-1} region (Fig. 12 and Table III).

Determination of Starch Loss from Starch-Polyethylene Composite Films

A decrease in the area of the C—O absorption region of 1090–980 cm^{-1} was observed in films retrieved from the strawline site (Fig. 13). The observed decrease in this absorbance region has served as the basis for the determination of starch loss from starch-polyethylene composite films by previous investigators.¹³ For this investigation, the change in the starch content of the films was estimated based on the decrease in the area of this absorbance region relative to the total absorbance of absorbance regions common to LDPE and LLDPE films. Changes in the absorbance regions common to LDPE and LLDPE were not observed following weathering. FTIR estimates of the relative starch content (RSC) of the starch-polyethylene composite films for this investigation was determined as follows:

$$\text{RSC}\% = \frac{A_{985}}{A_{2930} + A_{1463} + A_{1368} + A_{729} + A_{719}} \times 100$$

A = the integrated absorbance within the region specified in Table III.

Change in the relative starch content of starch-polyethylene composite LDPE and LLDPE films following placement was calculated as a percentage of the preplacement value according to

$$\begin{aligned} \% \text{ Starch remaining} &= [\text{RSC at time} \\ &= T (\%) / \text{RSC at time} = 0 (\%)] \times 100 \end{aligned}$$

T = 0, 61, 112, 179, 285, and 406 days.

Continuous decreases in the starch content of both LDPE and LLDPE starch-polyethylene composite films was observed for films placed in the strawline exposure site (Fig. 14). Starch-polyethylene composite LDPE showed a decrease of 34% in the starch content, whereas starch-polyethylene composite LLDPE showed a 32% decrease in the starch content after 13 months exposure at the strawline exposure site. The starch content of the 13-month LDPE and LLDPE starch-polyethylene composite films as determined using the chemical dissolution method were similar to the starch contents as determined by FTIR (Table IV).

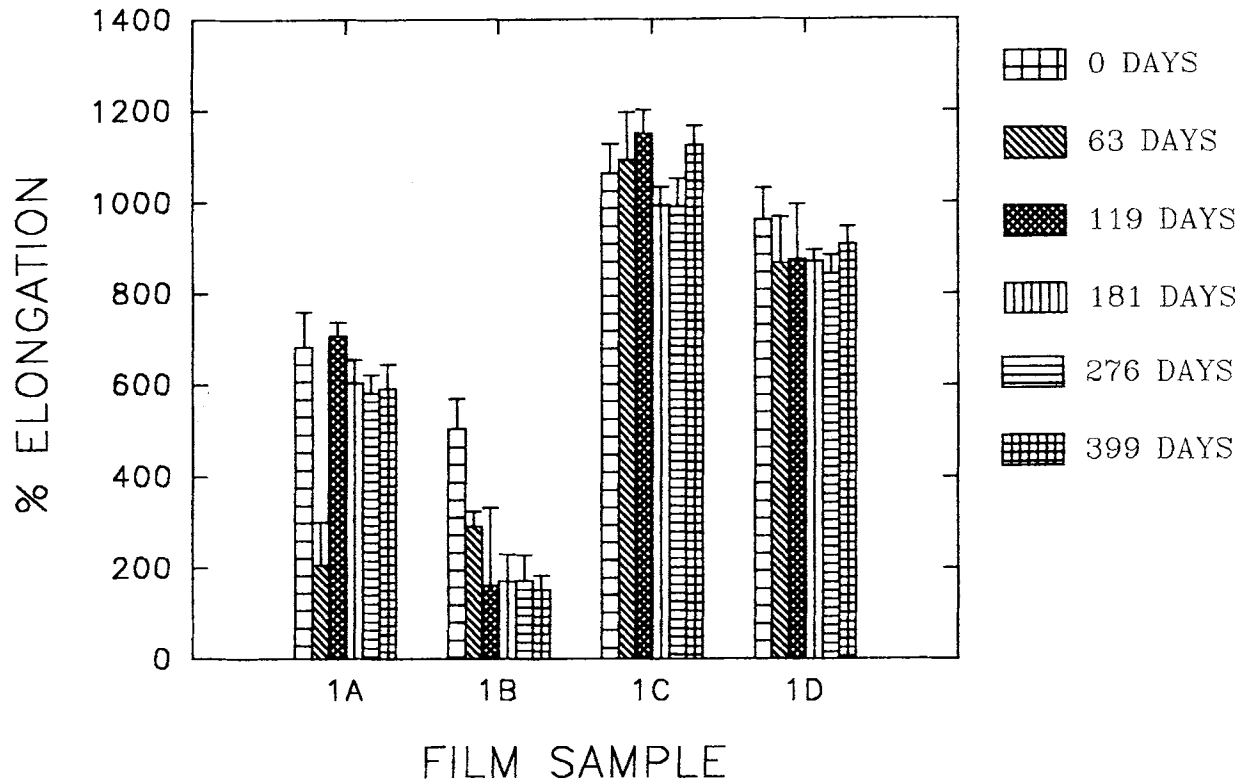


Figure 6 Variation in the ultimate % elongation for films 1A, 1B, 1C, and 1D during 13 months sea water exposure.

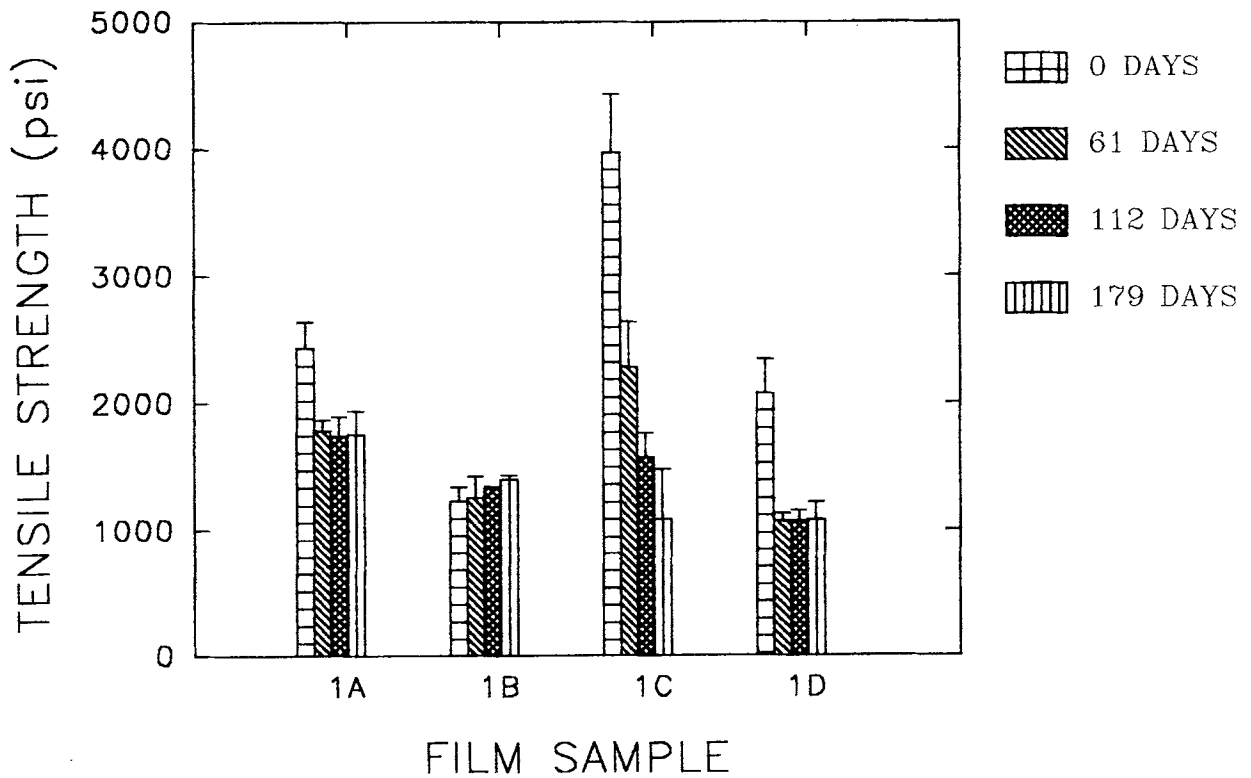


Figure 7 Variation in the tensile strength at break for films 1A, 1B, 1C, and 1D during 13 months strawline exposure.

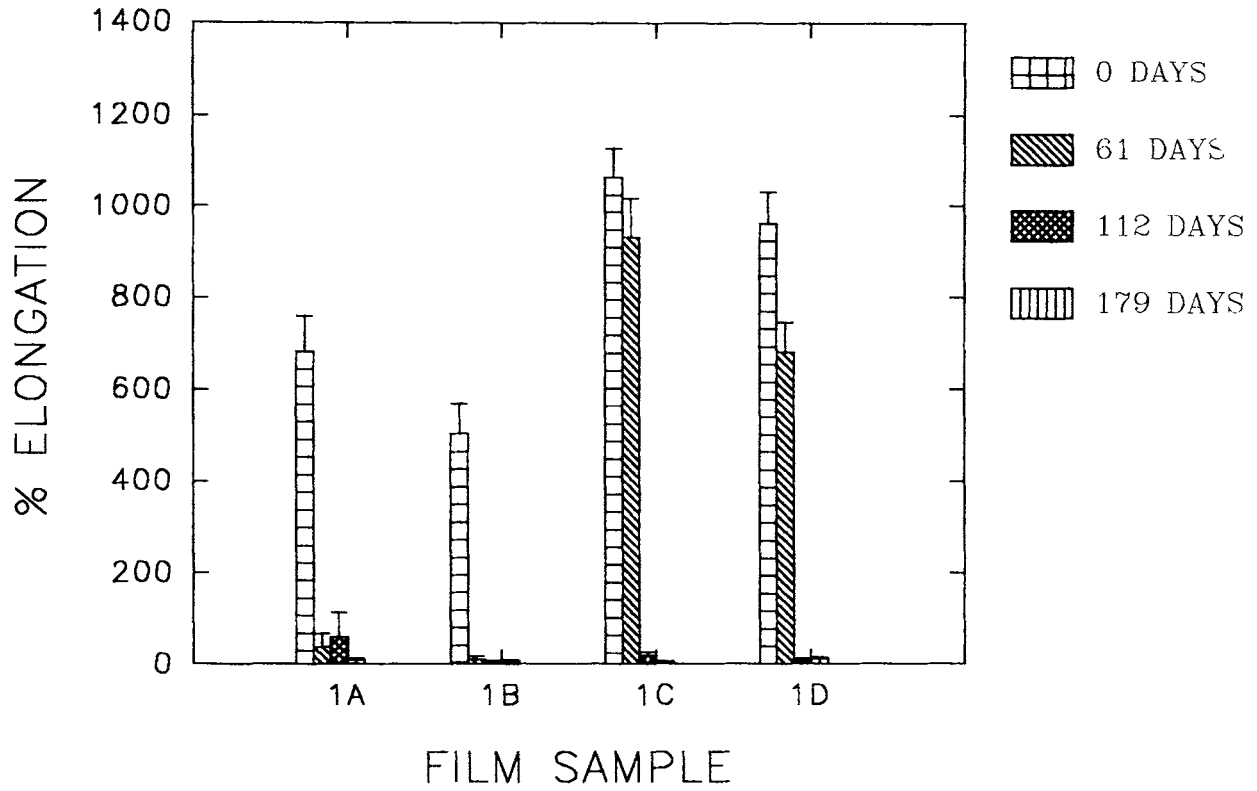


Figure 8 Variation in the ultimate % elongation for films 1A, 1B, 1C, and 1D during 13 months strawline exposure.

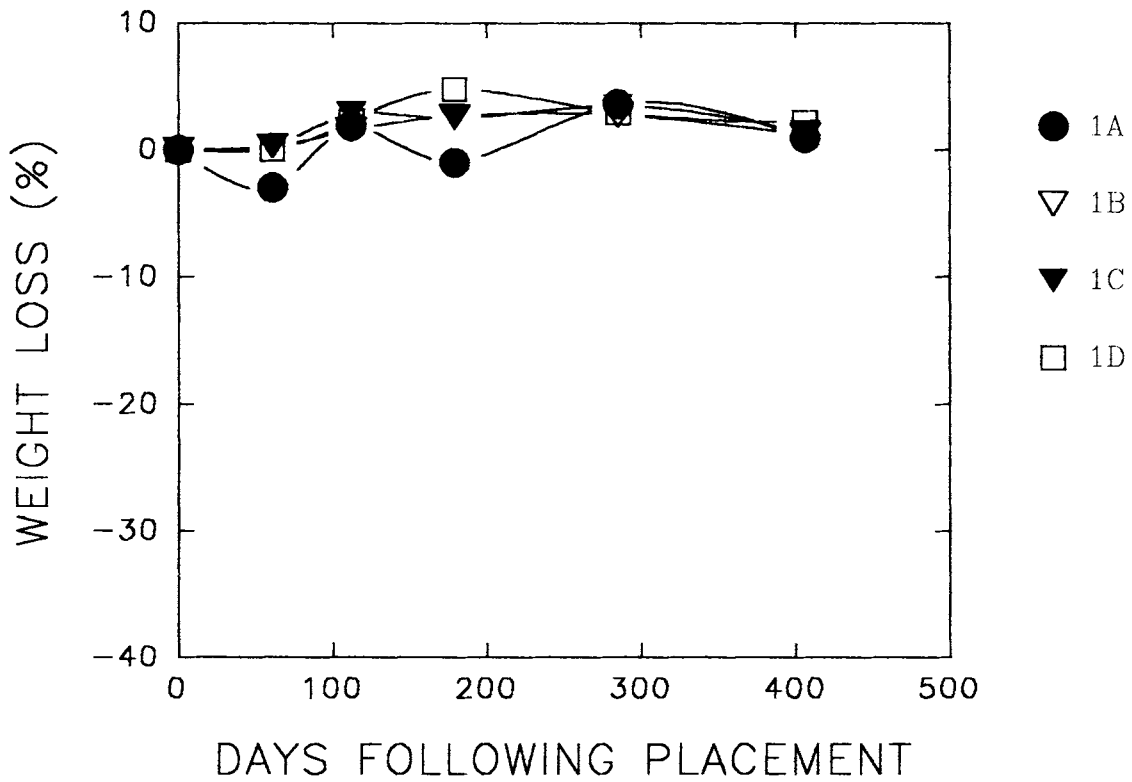


Figure 9 Weight loss for films 1A, 1B, 1C, and 1D during 13 months sea water exposure.

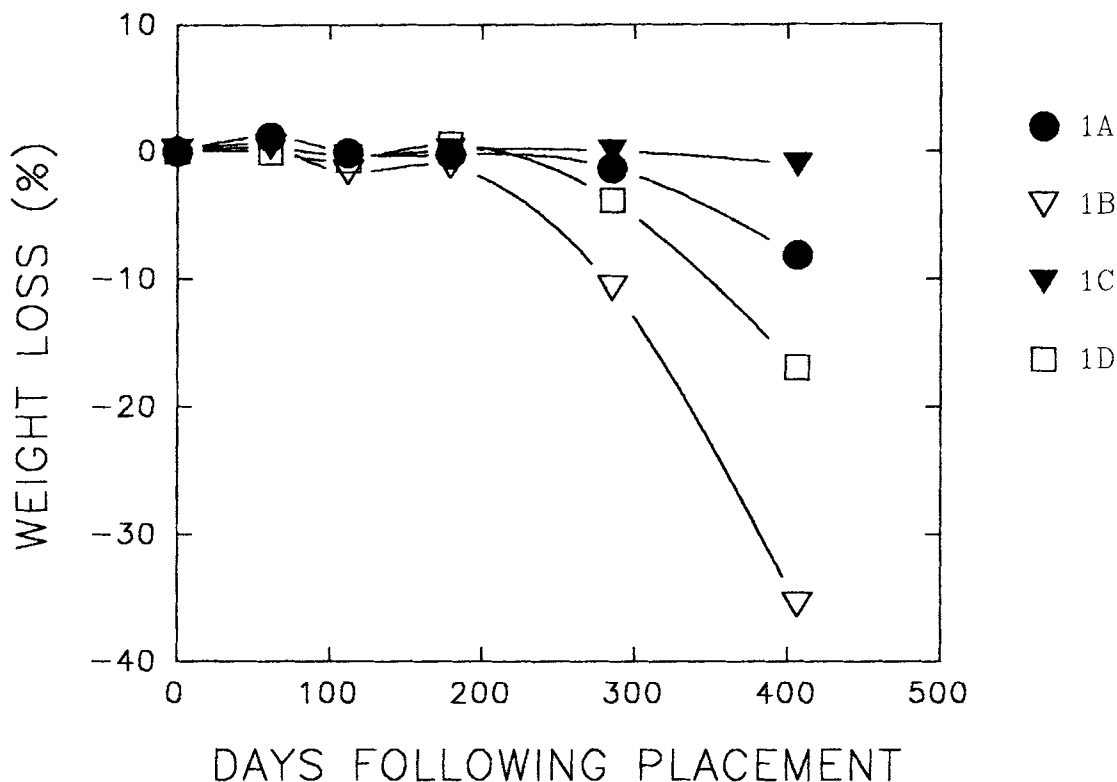


Figure 10 Weight loss for films 1A, 1B, 1C, and 1D during 13 months strawline exposure.

FTIR analysis of the starch content of starch-polyethylene composite LDPE and LLDPE seatable films was not possible due to the discoloration of weathered films. However, starch contents of the weathered films were determined using the chemical dissolution method.¹² The initial starch content of starch-polyethylene composite LDPE and LLDPE films was $6.6 \pm 0.2\%$. Results show that following 13 months seawater submersion starch losses of 15 and 8% were measured for starch-polyethylene composite LDPE and LLDPE films, respectively (Table IV).

Carbonyl Formation in Starch-Polyethylene Composite and Control Polyethylene Films

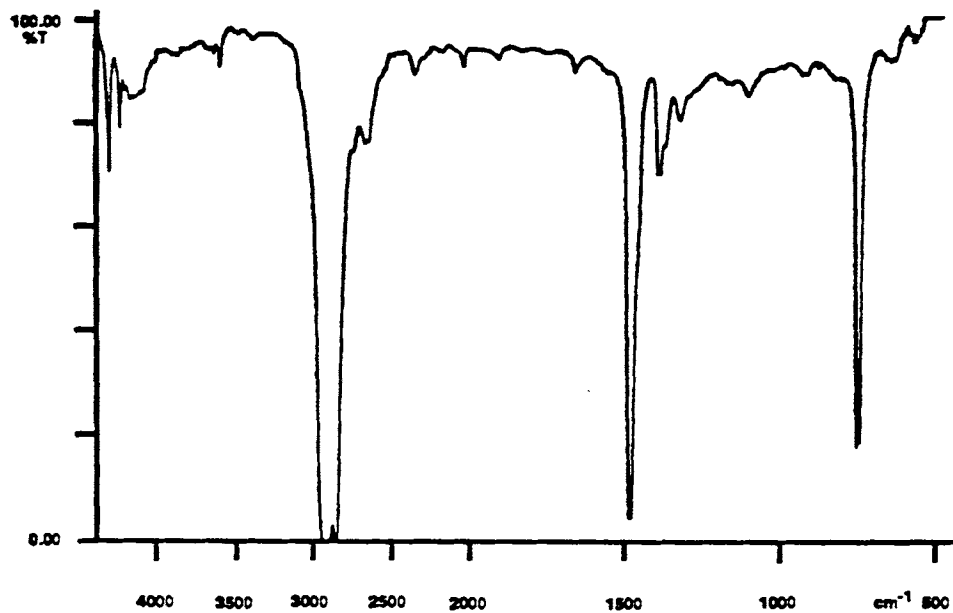
In addition to an observed decrease in the intensity of the starch peak, FTIR analysis of weathered LDPE and LLDPE starch-polyethylene composite and control films retrieved from the strawline site showed the presence of a new absorbance band centered at 1712 cm^{-1} , representing the carbonyl functional group (Fig. 13). FTIR determination of the

carbonyl index of starch-polyethylene composite and control polyethylene films was calculated as follows¹⁴:

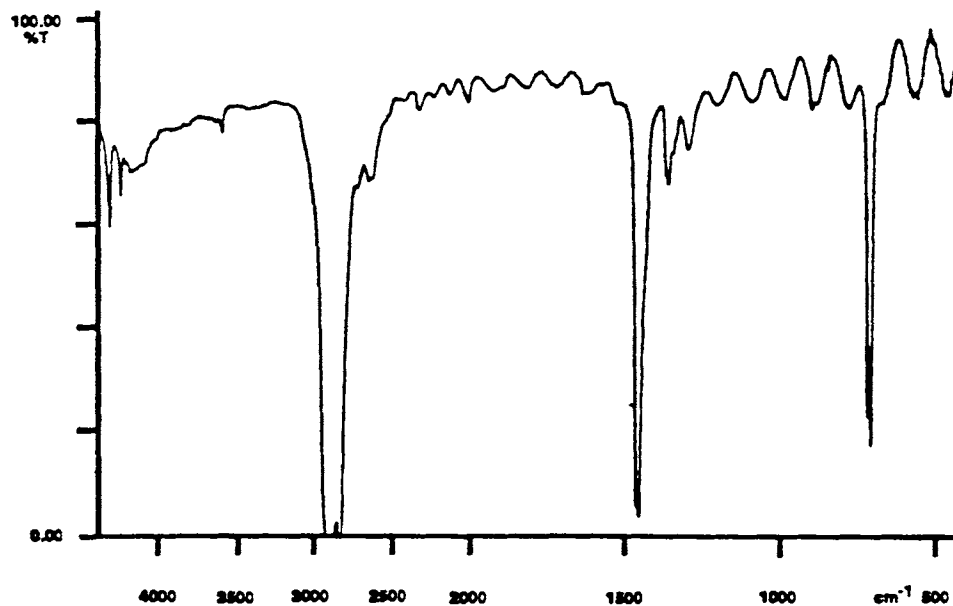
$$\text{Carbonyl index} = \frac{A_{1712}}{A_{1463}}$$

A = integrated absorbance within the region specified in Table III.

The carbonyl index of the starch-polyethylene and control LDPE and LLDPE films increased following exposure to increasing amounts of solar radiation. In general, the carbonyl index of the starch-polyethylene composite films was greater than the carbonyl index of the corresponding control film. The carbonyl index of starch-polyethylene composite films LDPE 1B and LLDPE 1D increased to 0.35 and 0.55, respectively, following exposure to 20.1 kilolangleys after 13 months in the strawline (Fig. 15). Shading due to extensive growth of the surrounding marsh grasses during spring 1990 may have reduced the total radiation received by the films.



(a)



(b)

Figure 11 FTIR spectra for (a) LDPE and (b) LLDPE control films.

DISCUSSION

Seatable Exposure Site

Low rates of deterioration were measured for both starch-polyethylene composite and control LDPE and LLDPE films weathered for 13 months in sea

water. Only starch-polyethylene composite LDPE film 1B showed a significant reduction in % elongation when compared to the corresponding control sample after 13 months seatable exposure (Fig. 6). In addition, high starch contents were measured for the starch-polyethylene composite films following 13 months weathering on the seatable (Table IV).

Table III FTIR Analysis of Starch-Polyethylene Composite and Control Polyethylene Films

Characteristic Group	Position or Region (cm ⁻¹)
O—H broad	3600–3200
C—H stretching	3000–2840
C=O Carbonyl	1720–1710
C—H bend (asymmetrical)	1465–1450
C—H bend (symmetrical)	1375–1365
C—O (starch region)	1090–980
C—H rock (out-of-plane bend)	740–719

The starch-polyethylene composite and control LDPE and LLDPE films, although discolored, remained intact throughout the 13-month exposure period. Several factors may act to influence the extent of degradation of the starch-polyethylene composite and control LDPE and LLDPE films weathered on the seatable (Table V).

Previous research has identified cool sea water temperatures as a factor in retarding the rate of deterioration of plastics in sea water.¹⁵ Seatable sea water temperatures varied from a low of 4.5°C to a high of 24°C during the 13-month exposure period (Fig. 4). Sea water temperatures were warm during the first 4 months of exposure. The average sea water temperature exceeded 20°C only during the first 4 months of exposure. During this exposure period, decreases in the % elongation of starch-polyethylene composite LDPE film 1B were observed. Following the initial 4 months, significant differences in the % elongation of starch-polyethylene composite films were not observed. Sea water temperatures following the initial 4-month exposure period averaged only 12°C. Low water temperatures would also limit the effectiveness of the transition metal prooxidant additive in the starch-polyethylene composite films in initiating the thermal oxidative degradation of the polymer.

The effect of solar radiation on the starch-polyethylene composite and control LDPE and LLDPE films was limited. The seatable was located within the Flax Pond laboratory building. Although the seatable was located adjacent to a window and exposed to direct sunlight for several hours each day, most of the damaging wavelengths of solar radiation are filtered out as it passes through glass. In addition, the surfaces of the films exposed to sea water were rapidly fouled by a variety of marine organisms. The growth of organisms completely covered the surfaces

of the films, further reducing the influence of solar radiation.

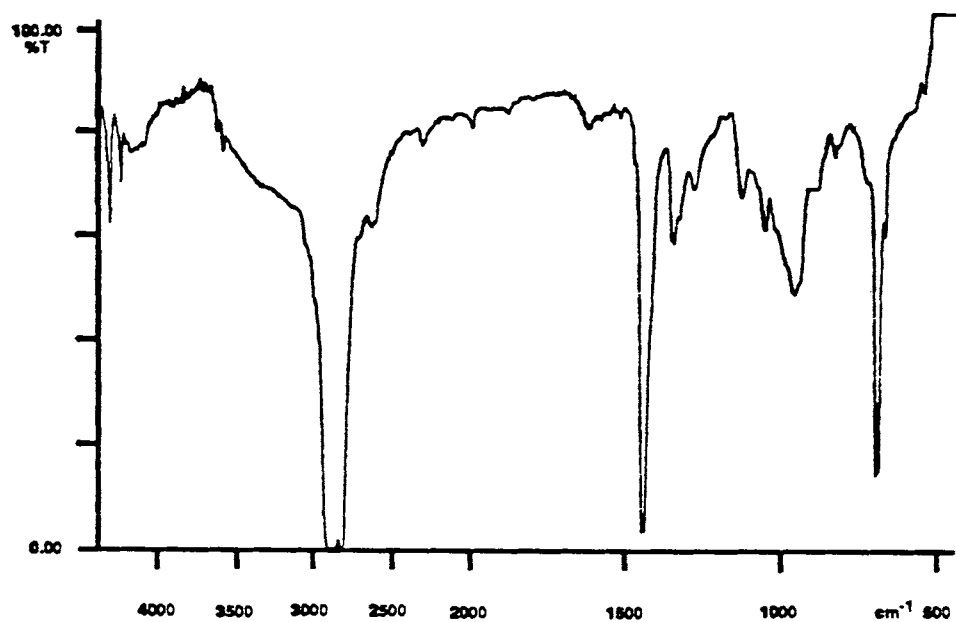
Biological activity on the seatable, as measured by the disappearance of cellophane sheets, was moderate. The cellophane sheets began to fragment following 2 months sea water exposure but did not completely disappear until the 4-month sampling event. Many of the marine organisms that fouled the surfaces of the films used the films as substrate and do not actively metabolize starch.

Measured starch contents of weathered films showed that only 8–15% of the starch content of the films was lost. Previous research has demonstrated that the starch within starch-polyethylene composite films is susceptible to biodegradation.^{13,16} However, recent research suggests that only a small fraction of the starch within the polyethylene matrix is available for biodegradation.¹⁷ In the absence of conditions causing further physical deterioration of the sample, i.e., photodegradation, thermal degradation, or physical abrasion, starch located within the polyethylene matrix will remain unavailable for biodegradation. As these additional physical and chemical forces were limited on the seatable, the deterioration of the starch-polyethylene composite films during the 13-month exposure period was most likely confined to the biodegradation of the surface-available starch.

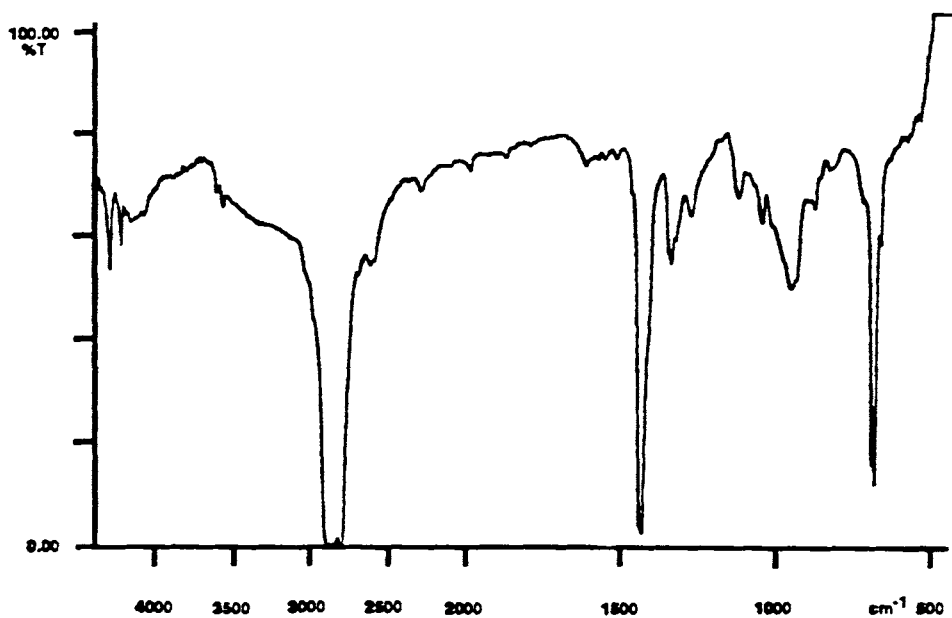
Strawline Exposure Site

Deterioration of the starch-polyethylene composite and control LDPE and LLDPE films placed in the strawline site occurred rapidly. Within 4–6 months of strawline exposure, the % elongation of control and starch-polyethylene composite films was less than 2% of their preplacement values. Initially, the starch-polyethylene composite LDPE and LLDPE films were found to deteriorate more rapidly than did their respective control films (Fig. 8). In addition, starch-polyethylene composite LDPE and LLDPE films were brittle following 4 months weathering and began to fragment following 6 months weathering in the strawline. Factors affecting the deterioration of the films placed in the strawline include solar radiation, temperature, biological activity, and starch loss (Table V).

The deterioration of the samples placed in the strawline site was primarily influenced by photodegradation. Photodegradation of polyethylene is initiated by the absorption of UV radiation, leading to radical formation. Oxygen is eventually absorbed



(a)

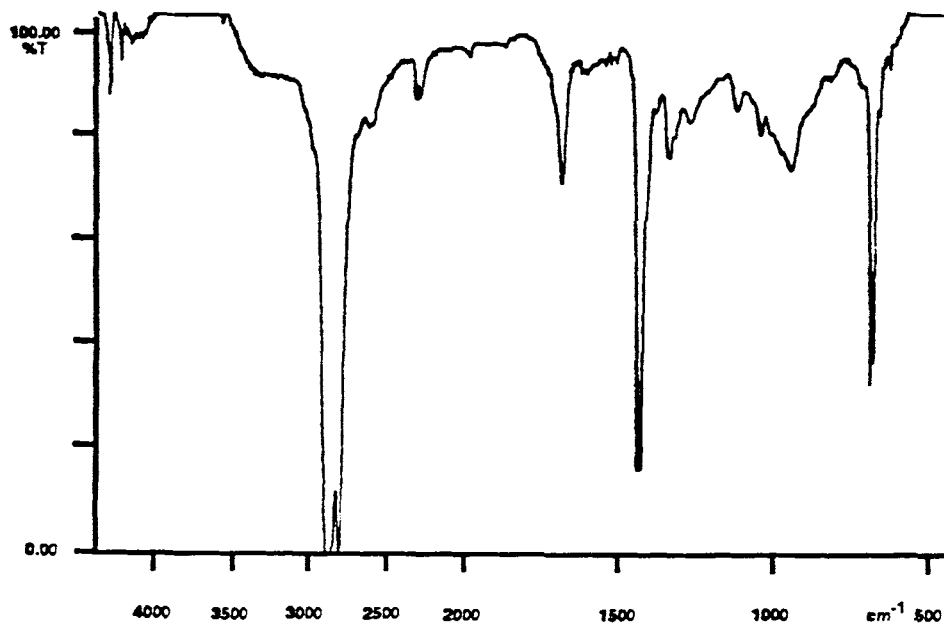


(b)

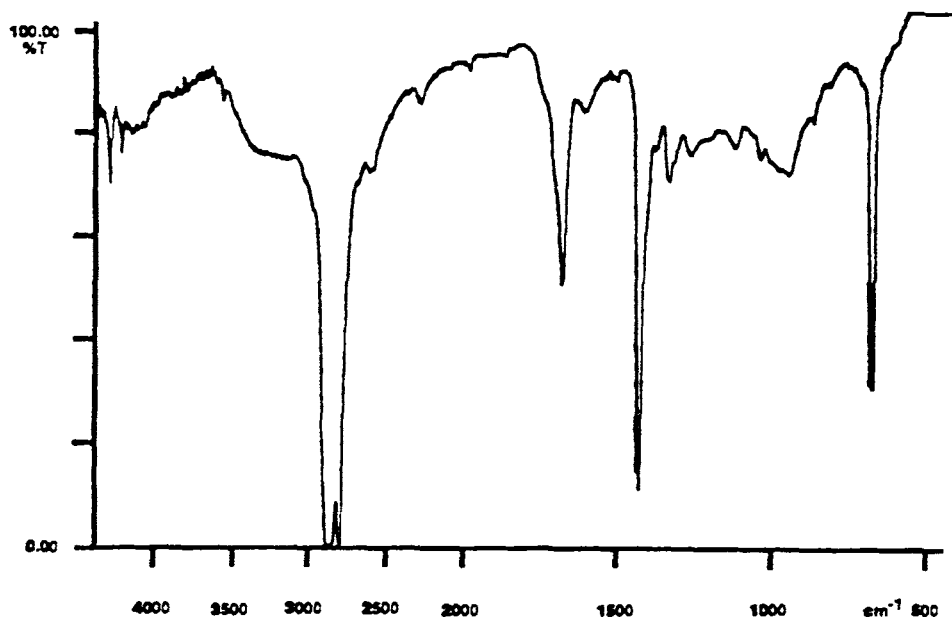
Figure 12 FTIR spectra for starch-polyethylene composite (a) LDPE and (b) LLDPE films.

and hydroperoxides are formed, resulting in the formation of carbonyl groups. FTIR analysis of films retrieved from the strawline exposure site showed an increase in the carbonyl index of the films as weathering progressed (Fig. 15). Initial increases in

the carbonyl index of the films correlated with the high intensity of the solar radiation during the first 4 months of film weathering (Fig. 2). Prolonged weathering of the films, however, did not result in continuous increases in the carbonyl index of the



(a)



(b)

Figure 13 FTIR spectra of starch-polyethylene composite (a) LDPE and (b) LLDPE films following 13 months exposure in the strawline of a marsh.

starch-polyethylene composite and control films.

The decrease in the % elongation of the films has been shown to be affected by the increase in the carbonyl index of the weathered plastic.¹⁸ UV degradation also results in increasing in the amount of low molecular weight material by breaking bonds

and increasing the surface area of the film through embrittlement.¹⁴

Other factors listed in Table V influence the rate of deterioration of starch-polyethylene composite and control LDPE and LLDPE films to a lesser degree. Biological activity at the strawline site did not

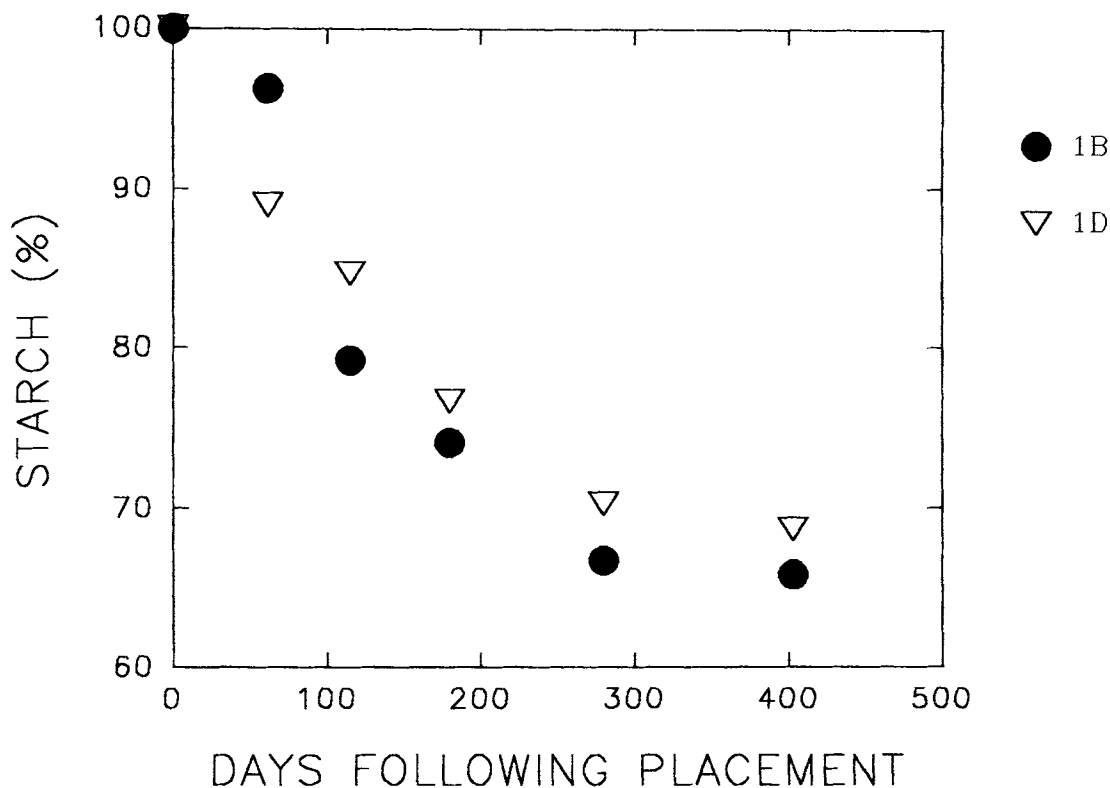


Figure 14 FTIR determination of starch loss for starch-polyethylene composite LDPE and LLDPE films retrieved during exposure in the strawline site.

appear to be an important factor since the cellophane sheets were present throughout the 13 months of weathering. Record rainfall and high seasonal temperatures occurred during the first 2-4 months when the majority of the sample deterioration occurred (Fig. 3). Average daily high temperatures exceeded 26°C, while a total of 64.5 cm of precipitation fell during the first 4 months of weathering

in the strawline. Normal rainfall for this period is about 36 cm. High temperatures contribute to the heat buildup, which may accelerate the deterioration of films weathered outdoors.¹⁵ The heat buildup in the starch-polyethylene composite films may result in an increase in the rate of thermal oxidation of the polyethylene catalyzed by the presence of the transition metal prooxidant additive.¹⁹

Table IV Comparison of % Starch Remaining as Determined by FTIR and the Chemical Method for the Analysis of Starch in Polyethylene following 13 Months Exposure

	% Starch Remaining LDPE Sample 1B		% Starch Remaining LLDPE Sample 1D	
	FTIR	Chemical Method ^a	FTIR	Chemical Method
Sea water	NA ^b	85 (1.8)	NA	92 (5.6)
Strawline	66 (0.06)	68 (3.5)	68 (0.07)	71 (4.3)

^a Nikolov.¹²

^b FTIR analysis for starch content was not conducted due to discoloration of the sea water samples.

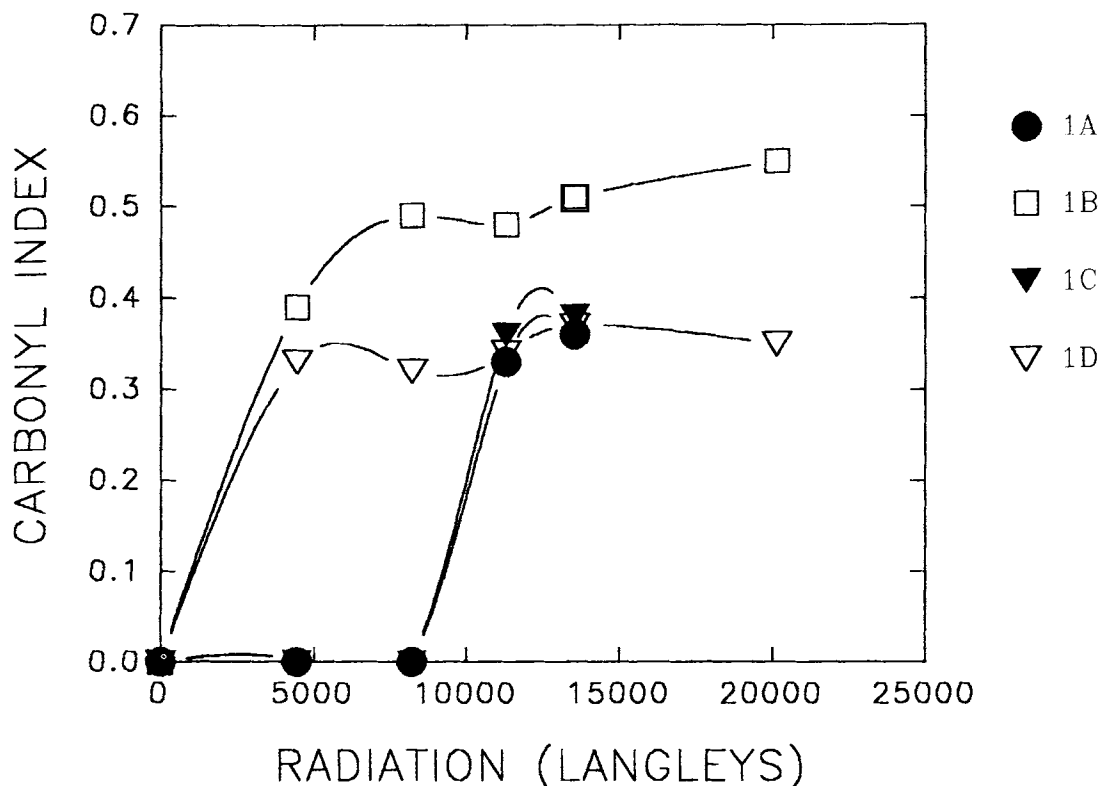


Figure 15 Carbonyl index of starch-polyethylene composite and control LDPE and LLDPE films during exposure in the strawline of a marsh.

Starch loss was higher for the films weathered in the strawline as compared to films weathered in sea water (Table IV). Although starch loss was observed throughout the exposure period, the rate of starch

loss was highest initially, with greater than 72% of starch loss occurring within the first 6 months of weathering (Fig. 14). The decrease in the rate of starch loss may be due to the lack of access to starch

Table V Factors Affecting Starch-Polyethylene Composite Film Degradation

Factor	Seatable	Strawline
Temperature	Seasonal (Fig. 4)	Seasonal (Fig. 3)
Solar radiation	Limited	Seasonal (Fig. 2)
Moisture	Seawater submersion	Rainfall tidal flooding
Biological activity ^a	Medium	Low
Starch loss ^b	8-15% (Table IV)	29-34% (Table IV)
Extent of degradation ^c	Low (Fig. 6)	High (Fig. 8)

^a Biological activity is defined by the rate of disappearance of the untreated cellophane sheets. Low biological activity is defined as the presence of cellophane sheets after 9 months. Medium biological activity is defined as the disappearance of the cellophane between 4 and 9 months. High biological activity is defined as the absence of the cellophane sheets within the first 2 months.

^b Starch loss for starch-polyethylene composite films LDPE 1B and LLDPE 1D as measured by FTIR and/or Nikolov¹² following 13 months exposure.

^c The extent of degradation is based on the decrease in % elongation of starch-polyethylene composite and control polyethylene films following 13 months exposure. The extent of degradation is considered high if the decrease in the % elongation of two or more films retrieved from the site exceeds 50% of their initial % elongation.

granules located within the polyethylene matrix. The initial high rate of starch loss seemingly conflicts with the low biological activity, as indicated by the presence of the cellophane sheets throughout 13 months exposure. Starch loss, however, may not be due to biological processes alone. The physical deterioration of the polyethylene caused by photodegradation may render the starch more accessible for removal by a combination of biological, chemical, and physical processes leading to lower starch contents of weathered films.

CONCLUSIONS

Differences in the rate of deterioration of starch-polyethylene composite and control LDPE and LLDPE films were measured for films weathered in sea water and the strawline of a marsh. However, starch-polyethylene composite LDPE film deteriorated more rapidly in both the strawline of a marsh and submerged in sea water as compared to a corresponding LDPE control film weathered under similar conditions. Deterioration of starch-polyethylene and control films in the strawline was rapid and primarily initiated by photodegradation. In contrast, lower rates of deterioration were measured for films weathered in sea water. Samples weathered in sea water experienced cool water temperatures, moderate biological activity, and reduced quantities of solar radiation, each factor contributing to the lower observed rate of deterioration.

Because of observed differences in the measured rates of deterioration for sea water and strawline exposure, the time required for the starch-polyethylene composite plastics to deteriorate in the marine environment will be influenced by several factors including residence time at sea, extent of biofouling, exposure to UV radiation, water temperature, and degree of physical abrasion. Although the starch-polyethylene composite LDPE and LLDPE polyethylene films are designed to deteriorate primarily through the action of microorganisms upon entering the environment, deterioration of these composites is actually due to the interaction of biological, chemical, and physical processes.

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