

Weathering of Polyethylene (LDPE) and Enhanced Photodegradable Polyethylene in the Marine Environment

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Synopsis

The outdoor weathering of polyethylene homopolymer under exposure in air and in sea water was studied. Rate of deterioration as indicated by the loss in mean ultimate extension was found to be slower when the material was weathered in sea water compared to that in air. The difference in rates is explained in terms of the lack of heat buildup in plastic material floating in sea water. A similar study on a commercially available ethylene-carbon monoxide copolymer indicated rapid photodegradation under both exposure conditions.

INTRODUCTION

Low density polyethylene is extensively used as a packaging material in a variety of applications, approaching a consumption of 2.8 billion lbs annually. The consequent increase in the plastics fraction of the municipal solid waste stream¹ and the associated urban plastic litter problem present serious disposal problems. A relatively recent concern is the presence of significant amounts of thermoplastic debris in the world's oceans.^{2,3} Aside from the undesirability of any litter in the marine environment, plastic materials in particular pose a hazard to marine life including several protected species.⁴

The hazardousness of plastics as waste material is associated with the excellent outdoor durability of thermoplastics which are resistant to hydrolysis and biodegradation in the environment. Properly compounded polyethylene is only moderately photodegradable and is relatively resistant to biodegradation than other types of marine debris (with the possible exception of glass).

Marine plastic debris consists of a predominant fishing-gear-related fraction⁵ and a smaller packaging-related fraction of plastics.⁶ The former consists of discarded or lost fishing gear (mainly netting and traps) made of polyethylene, polypropylene, or polyamides, while the composition of the latter parallels that in the municipal waste stream. Polyethylene is a major component in both categories. Hazardousness of the plastic debris to marine life has been discussed extensively. A growing body of data suggests that a wide range of species including sea birds,⁷ turtles,⁸ marine mammals,⁹ and even fish are affected. On encounter with the debris, the animal may either get entangled (in netting, ropes, six-pack rings) or ingest the material (plastic bags, rope, fragments, virgin plastic pellets), leading to serious impairment of growth, or even death.

Among the several approaches proposed to contain the problem is the wider

use of enhanced degradable plastics.^{10,11} These have a limited lifetime outdoors, measured in terms of time to embrittlement, and will therefore present only a very short period of time to act as a hazardous material. Once embrittled the plastic material is not perceived as litter either on land or at sea. Enhanced degradable polyethylene is used in agricultural mulch films and in the manufacture of six-pack ring holders. The latter product is extensively used in those states which require the use of rapidly degradable six-pack carriers exclusively.

In spite of the demonstrated success of the enhanced degradable polyethylenes in six-pack carrier application, the usefulness of this approach under marine exposure conditions has not been established. Adequate and timely degradation of the material under land exposure need not necessarily guarantee performance under marine conditions with the plastic material floating on sea water. While sunlight is available to the floating plastic material, fouling of the surface¹² may effectively shield some of the light or even cause the material to be submerged in water under the weight of macrofouling and entrapped debris (cutting the light off entirely). Furthermore, the material at sea is held at a fairly constant temperature very much lower than that experienced by a similar material exposed in air. In the latter case, the heat buildup in the sample may increase the temperature of the plastic material by as much as 30°C over that of surrounding air, leading to facile photodegradation.¹³⁻¹⁵

The primary objective of the present study is to determine if a selected enhanced photodegradable polyethylene material performs adequately under marine exposure conditions. A second objective is to establish any difference in the relative rates of weathering of polyethylene (regular LDPE polymer) when exposed on land and at sea.

ENHANCED PHOTODEGRADABLE POLYETHYLENE

Polyethylenes are rendered enhanced photodegradable either by the modification of the polymer chain to incorporate suitable chromophores in it or by using an appropriate additive in the formulation. The latter approach uses photosensitizing compounds and/or transition metal salts¹⁶⁻¹⁸ to initiate and accelerate the photodegradation. Six-pack carrier product relies on the former approach and uses a copolymer of ethylene and carbon monoxide.¹⁹ The copolymer so obtained contains low concentrations of ketone moieties randomly dispersed along the main chain of the polymer. These strongly absorb in the short wavelength ultraviolet B region of the solar spectrum and, via Norrish I and Norrish II mechanisms, lead to main chain scission of the polymer.²⁰ Under outdoor exposure conditions, Norrish type II reaction predominates. The overall reaction pathways obtained are generally similar to that obtained with unsensitized regular polyethylene where ketone groups are known to be a primary product of early photodegradation.

For a film containing 1% CO, the absorption maxima is at 279 nm,²¹ a wavelength much shorter than that typically found in terrestrial sunlight. As the photodegradation is effected merely by short wavelength "tail" of the solar spectrum, the copolymers are stable behind glass or under diffused light. The rate of photodegradation, however, depends markedly on the available

sunlight and may vary by as much as a factor of 10–12 or more depending on the geographic location.²² Ethylene carbon monoxide copolymers are also stable under high melt temperatures met with in processing.

EXPERIMENTAL

The LDPE sheets, both the regular and enhanced photodegradable, were provided by the HiCone division of ITW Company in Chicago, IL. All LDPE sheets used were of the same composition as the commercially available six-pack carriers. The material is a copolymer of ethylene containing approximately 1% of carbon monoxide as a comonomer.²³ Precut sample strips (6 × 0.5 in.) were exposed at two sites in a coastal location in Beaufort, NC during the winter of 1987. One set of samples was exposed on a wooden rack placed horizontally on the flat roof of a laboratory building. The other was exposed floating in a tank of sea water at the beach, with fresh sea water continuously flowing through the tank to maintain a depth of about 12–18 in. of water at all times. Exposure in the tank as opposed to directly at sea has several associated advantages.

In the preliminary experiments carried out with samples directly floating in an enclosed section of sea, the samples tended to accumulate mud and debris on the surface due to tidal action. Exposure within the tank ensured minimal accumulation of soil and other floating debris on the sample while providing a fresh, clear, biologically active sea water medium. The experiment thus simulates the conditions best suited for rapid photodegradation. The exposures were carried out for a 1-year period in the case of regular polyethylene samples and for a period of 15 weeks for the enhanced photodegradable polyethylene.

Sampling was carried out at weekly intervals in the case of enhanced photodegradable polyethylene and at 2-month intervals in the case of regular polyethylene films, for both sites. Samples from sea water exposure were dried in an air oven at about 50°C for a few hours and stored in the dark until testing.

Tensile property determinations were carried out using an Instron Universal Testing Machine Model 1122 equipped with pneumatic grips. A crosshead speed of 100 mm/min and a gauge length of 5 cm was used.

RESULTS AND DISCUSSION

Low Density Polyethylene Homopolymer

During the exposure period the samples exposed in air did not undergo any significant change in appearance except for a gradual loss in clarity. The samples exposed in sea water, however, underwent gradual fouling. A thin slimy biofilm developed within weeks of exposure and progressed into a thicker layer rich in green algae. After 3–4 months of exposure, the surface coating included even a few macrofoulants such as barnacles a centimeter or more in diameter.

Weathering of the polyethylene homopolymer in air was monitored over a 6-month period. The material gradually turned brittle, losing over 95% of its original ultimate extension at the end of 6 months. At this stage, the samples

were considered embrittled and the exposure was discontinued. The tensile strength of the material did not vary in a well-defined manner, possibly due to extensive crosslinking which accompany the weathering process. Ultimate elongation is generally a more sensitive measure of the extent of degradation than the tensile strength.²⁴ A valid comparison of the present data on weathering of LDPE with those reported in the literature cannot be made due to differences in the resin composition, thickness, processing conditions, and the exposure conditions.

Samples exposed floating on sea water, however, did not undergo a similar dramatic change in ultimate extension over a 1-year period of observation. At the end of 1 year, when the experiment was discontinued, the samples had lost a mere 12–17% of their initial mean ultimate extension. The mean tensile strength decreased only marginally. The data clearly show that, under the present experimental conditions, the photodegradation of polyethylene is markedly slower when the material is floating in sea water. It is reasonable to expect the same to hold true of samples exposed under open sea conditions as well.

TABLE I
Tensile Property Data on Weathered LDPE and Ethylene Carbon Monoxide
Copolymer Samples^a

Duration (weeks)	Enhanced photodegradable LDPE				Duration (months)	LDPE homopolymer					
	Tensile strength (kg/cm)		Ultimate extension (%)			Tensile strength (kg/cm)			Ultimate extension (%)		
	Mean	S.E.	Mean	S.E.		Mean	S.D.	S.E.	Mean	S.D.	S.E.
<u>Samples Exposed in Air</u>											
0	160.4	1.0	398	3.4	0	124.1	19.6	6.1	548	71	29
1	122.4	2.1	35.6	8.3							
2	128.0	2.4	21.0	4.4	2	143.1	9.9	4.4	541	38	17
3	134.1	2.4	16.8	1.4							
4	104.7	8.0	10.7	2.6	4	99.9	5.1	2.9	188	166	96
5	86.3	6.9	5.7	0.8							
					6	115.8	6.5	3.3	27	18	9
<u>Samples Exposed in Sea Water</u>											
0	160.4	1.0	398	3.4							
1	112.0	3.7	145.6	23.3							
2	112.3	1.0	42.4	3.3	2	139.5	17.1	7.7	613	133	59
3	115.1	0.8	42.3	5.4							
4	120.4	0.9	25.8	4.1	4	131.0	12.8	5.7	547	95	42
5	116.5	2.6	44.1	16.7							
6	120.2	1.6	19.1	1.0	6	132.3	23.6	13.7	601	197	114
7	122.9	0.8	21.0	3.1							
8	121.1	0.4	17.7	0.5	8	117.3	13.4	6.0	511	147	65
9	119.7	2.8	18.4	1.4							
10	122.6	0.5	18.1	0.6	10	117.8	7.3	2.9	550	106	46
11	122.8	0.5	22.6	5.1							
12	116.3	5.7	11.3	1.3	12	118.7	7.6	3.4	541	87	39
13	119.1	14.0	19.4	0.8							
14	73.77	21.8	13.9	2.2							
15	58.9	6.6	6.9	1.7							

^a Number of samples varies from 3 to 6; S.D. = standard deviation; S.E. = standard error.

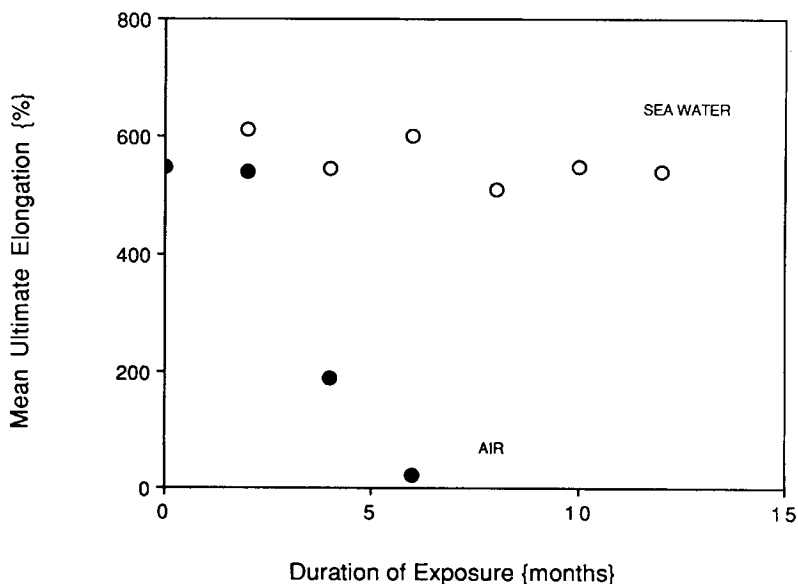


Fig. 1. The variation in the mean ultimate extension of polyethylene samples with the duration of exposure.

Table I gives the mean tensile properties for the two sets of samples, and the decrease in the mean ultimate extension with duration of exposure is illustrated in Figure 1. Slower rates of photodegradation under exposure on sea water might be attributed mainly to the differences in the temperature. Figure 2 shows the high and low water temperatures at the location and indicates the approximate temperature range in which the samples in sea water were maintained. Although the ambient air temperatures in the area during the period of exposure were known and indicated in Figure 2, the sample surface temperatures were not regularly monitored. The actual temperatures reached by the test samples in air possibly exceeded these ambient air temperatures, due to heat buildup. Furthermore, the samples exposed on land underwent diurnal temperature cycling probably conducive to faster degradation while those on sea water experienced a minimal diurnal variations.

On the basis of the present experiments, it is not clear if the light shielding by the foulant layer played a role in retarding the photooxidation in samples in sea water. Further experiments needed to establish the significance of fouling are in progress.

Enhanced Photodegradable Polyethylene (Ethylene Carbon Monoxide Copolymer)

As seen from the data in Table I, the weathering behavior of the enhanced photodegradable polyethylene was quite different from that of the polyethylene homopolymer sample (Fig. 3).

Samples exposed in air rapidly degraded, losing nearly 99% of the initial value of mean ultimate extension within 6 weeks of exposure. The tensile strength decreased more slowly, reaching about 50% of the initial value in the

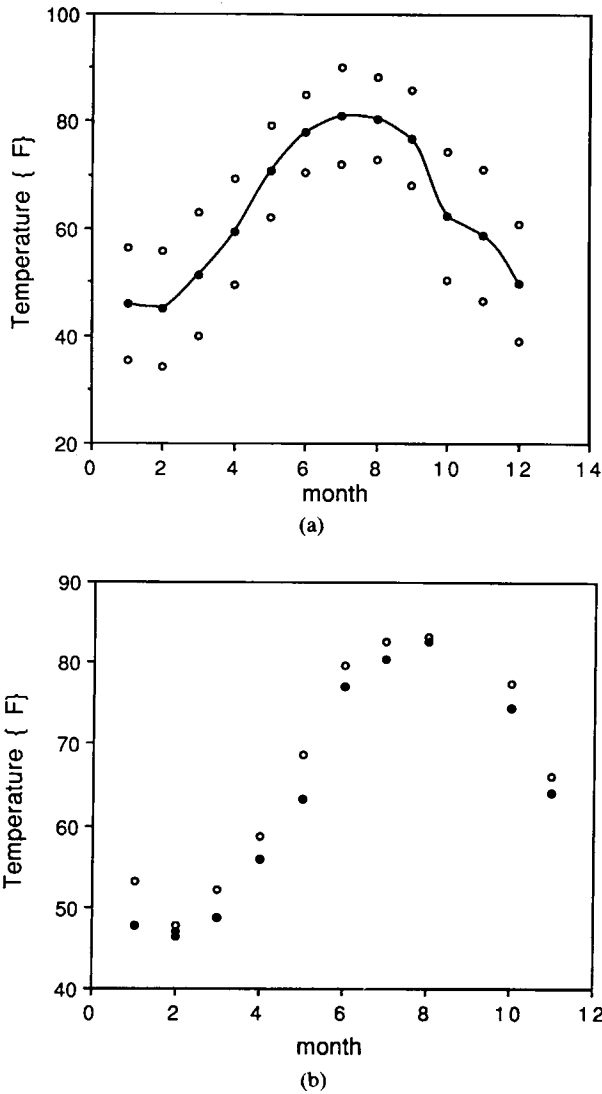


Fig. 2. (a) Monthly mean temperature (high, mean, and low) for 1987 for the Morehead City area. (b) The high and low sea-water temperatures at the test site on the first of each month in 1987. The filled symbols are for the lower temperature.

same period of exposure. At this stage, samples were embrittled and crumbled on handling.

The samples exposed in sea water also degraded rapidly on exposure, losing nearly 95% of the initial value of mean ultimate elongation in about 6 weeks. However, the material did not reach the same stage of final embrittlement obtained with samples in air, until after 14 weeks of exposure. The plateau in the mean extension values from about the sixth to 14th week of exposure is interesting but is of little practical consequence. It is clear that under the experimental conditions used in the study and under North Carolina climatic conditions, the enhanced photodegradable polyethylene performed satisfacto-

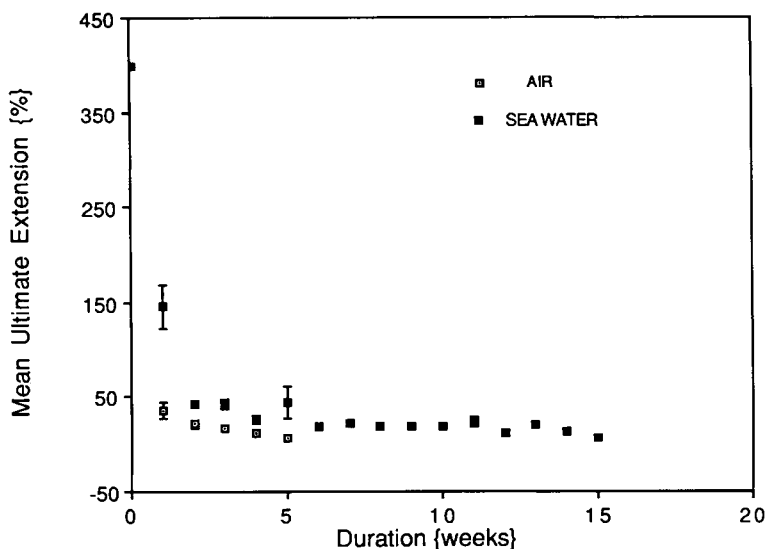


Fig. 3. The variation in the mean ultimate extension of [ethylene-carbon monoxide (~1%)] copolymer samples with the duration of exposure.

rily. The initial rates of decrease in both the mean ultimate extension as well as the mean tensile strength, with exposure, are somewhat slower than in the case of exposure on land. Slower initial rates might be attributed to lower temperatures and/or fouling as in the case of the polyethylene samples.

CONCLUSIONS

Photooxidative degradation of polyethylene films as monitored by changes in the tensile properties, particularly the mean ultimate extension, was markedly lower when the samples were exposed outdoors, floating on sea water, compared to those exposed in air. The slower rates of degradation in sea water were possibly due to the samples being maintained at a relatively lower and stable temperature in sea water compared to those exposed in air.

Commercially available enhanced photodegradable polyethylene was found to undergo rapid loss in ultimate tensile extension, even where the samples were exposed floating in sea water. The rate of degradation was marginally slower in sea water than in air, but the samples were embrittled in both cases.

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