ENVIRONMENTAL DEGRADATION OF PLASTICS UNDER LAND AND MARINE EXPOSURE CONDITIONS

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ABSTRACT

Several types of thermoplastic and latex rubber materials commonly encountered in marine plastic debris were weathered outdoors in air and while floating in seawater, under North Carolina climatic conditions. The degradation of the different samples was monitored by tensile property determination.

In general, the various materials exposed outdoors in seawater tended to weather at a slower rate than the materials exposed outdoors in air. This retardation of weathering is probably a result of lack of heat buildup in samples exposed in seawater. Also, surface fouling on samples in seawater may have shielded them from light to some extent.

INTRODUCTION

In spite of their short history, synthetic polymers, particularly plastics, have gained wide popularity as the material of choice in a wide range of packaging, building, and other applications. With the current consumption of plastics reaching around 27.5 million metric tons (MT) (50 billion lb) in the United States (Modern Plastics 1988), plastics will without doubt continue to replace conventional materials such as glass, metal, wood, and paper in a variety of additional uses. The projected production in the year 2000 is expected to be 41.3 to 55.1 million MT (75 to 100 billion lb).

The popularity of plastics in packaging and other applications is attributed to the unique, useful characteristics of the material. These include light weight, excellent mechanical strength (tensile properties, tear resistance, and impact resistance), readily controllable and superior optical properties (clarity, gloss, and color), biological inertness, easy processability, low cost, and outstanding durability. Because they are synthetic materials, plastic compositions might be "tailor made," within limits, to obtain specific useful characteristics. As a response to an historically consistent consumer demand for stronger and longer lasting plastics, the industry has continually improved the durability of plastics, especially for outdoor exposure conditions.

In R. S. Shomura and M. L. Godfrey (editors), Proceedings of the Second International Conference on Marine Debris, 2-7 April 1989, Honolulu, Hawaii. U.S. Dep. Commer., NOAA Tech. Memo. NMFS, NOAA-TM-NMFS-SWFSC-154. 1990.

The recent surge in the use of plastics as the material of choice in diverse applications is also reflected in uses of plastics at sea, particularly by the fishing industry. A very significant source of marine plastic debris is gear related. Introduction of plastics into the world's oceans started in the late 1940's with the changeover from natural fibers (jute, cotton, hemp) to synthetic polymer fibers in the construction of fishing gear (Uchida 1985). Today, nearly all the fishing gear used in developed countries is manufactured from durable synthetic materials (Klust 1973), and the commercial fishing industry is the prime source of plastics in the oceans.

In addition, passenger, freight, military, and research vessels, as well as beach users introduce plastic materials into the marine environment. Invariably, most of the non-gear-related plastic waste is discharged into the ocean as postconsumer waste from vessels or is washed into the ocean from the beach environment (Parker et al. 1987). The magnitude and the nature of this influx of plastics into the sea from such sources vary widely depending on the season of the year and the geographic region (Pruter 1987).

An inevitable consequence of increased usage of plastics, particularly in packaging applications, is the increased amounts of postconsumer plastic waste. The municipal waste stream (amounting to about >88,000 MT (160 million lb) annually in the United States) in urban areas now consists of about 7% postconsumer plastics, a figure that may increase to more than 9% by the year 2000 (Franklin Associates 1988). While accurate estimates of their lifetimes in the environment are not reliably known, plastics are perceived as being exceptionally persistent materials requiring hundreds of years of exposure to facilitate biodegradation.

Parallel estimates for the quantities of plastic waste in the world's oceans are not available. Estimates by several workers (Dahlberg et al. 1985; Pruter 1987), though probably very crude, allow an appreciation of the magnitude of waste at sea.

With a total annual world catch of about 45 million MT of fish (Parker et al. 1987), a substantial amount of plastic fishing gear is routinely introduced into the ocean. The estimates of worldwide losses of commercial gear vary from a low of about 750 MT tons annually (National Academy of Sciences (NAS) 1975) to as much as 75,000 MT/year (Merrell 1980). In addition to gear losses, fishing vessels also discharge "domestic" plastic waste. A 1986 estimate places the number of commercial vessels operating annually in the United States at 125,700 (Parker and Yang 1986). The world's fleet of fishing vessels is believed to discharge 23,000 tons of plastics annually into the sea (Horseman 1985).

A detailed discussion of the ecological concerns related to plastic debris at sea is beyond the scope of this paper. Several excellent reviews on the fate of plastic debris, the specific hazards posed by such debris in specific marine species, and the general impact of plastics on the populations of target species have been published (Day et al. 1985; Center for Environmental Education (CEE) 1987; Laist 1987).

Available evidence indicates entanglement by the debris and the ingestion of the debris to be the primary concerns with a variety of affected marine animals (including birds, turtles, marine mammals, and fish). These affected populations seem to seek out the debris (either mistaking it for prey or because of mere curiosity); such behavior leads to more fatalities than might be expected on the basis of random encounters with debris. The invariable association of either entangled fish or residual food in most of the plastic waste discharged into the sea also concentrates these species in the same geographic locations that have high incidences of plastic waste (Laist 1987). Recent declines in the natural populations of the Hawaiian monk seal, *Monachus schauinslandi*, by 4 to 8% per year have been attributed, at least in part, to entanglement in plastic waste (Fowler 1985, 1987).

PLASTICS AT SEA

Key Characteristics of Marine Plastic Waste

The potential negative impact of waste plastics on the marine resource depends upon the following key characteristics of the material.

- Geometry. Shape of the debris is important from the point of view of entanglement. Products such as six-pack rings and netting represent more of a potential hazard than an equivalent mass of the same polymer in the form of a laminate.

- Durability. The likelihood of encounter between a given item of marine debris and a marine animal depends upon the lifetime of the material. The duration available for the encounter is crucial in determining the potential hazard posed by the plastic material. Unfortunately, little information is available on the lifetime of plastics at sea. Lack of this information is a definite setback in the assessment of potential hazards posed by plastic waste.

- Strength. Strength of the debris material determines the likelihood that an entangled animal can escape. Alternatively, the possible obstruction of the gut in case of ingestion is less likely if the material is weak enough to mechanically fail during the ingestion process.

- Toxicity. Plastics, being undigestible macromolecules, cannot be absorbed through the gut lining. They are, therefore, not toxic materials. However, the plastics used in the fabrication of products may contain chemical additives which can be absorbed and assimilated.

Of these characteristics, lifetime is perhaps the most important. An attempt was therefore made in the present work to determine the relative lifetimes of some relevant debris items exposed on land and floating in seawater. The study will determine if the plastic materials floating on

seawater degrade at rates different from those exposed to the same natural weathering conditions, but in air.

Weathering of Plastics Under Marine Exposure Conditions

Sunlight-induced degradation is the principal mechanism of weathering of plastics outdoors. As sunlight is freely available to plastics floating in the sea, weathering might be expected to occur at sea at rates comparable to those on land. However, there are several reasons to expect the rate of degradation at sea to be different from that on land.

- High humidity is known to accelerate the rates of degradation of several classes of plastics (Davis and Sims 1983). This may be brought about by the "plasticizing" action of small quantities of sorbed water leading to increased accessibility of the matrix to atmospheric oxygen or by the leaching out of stabilizing additives from the formulation.

- Plastics exposed to sunlight outdoors undergo "heat buildup," a process which results in the plastic material reaching significantly higher temperatures than the surrounding air (Summers et al. 1983). The higher temperatures generally result in an acceleration of light-induced degradation and may even be high enough to induce significant thermooxidative degradation. Plastics at sea will not suffer from such heat buildup and may consequently undergo slower oxidative degradation and photodegradation.

- All materials exposed to the sea invariably undergo fouling (Fischer et al. 1984). In the initial stages of fouling, a biofilm forms on the surface of plastic. Gradual enrichment of the biofilm leads to a rich algal growth within it. Consequently, the biofilm becomes opaque, and the light available to the plastic for photodegradation is restricted. Thus, the rate of photodegradation at sea might be determined in part by the rate of fouling.

- Advanced stages of fouling are characterized by the colonization of the plastic surface by macrofoulants such as bryozoans. The weight of the macrofoulant and that of debris they entrap might even partially submerge the material. As the ultraviolet portion of sunlight is attenuated on passage through seawater, submerged plastics would necessarily undergo a slower rate of photodegradation. Microbe-rich foulant film may, however, also tend to accelerate the biodegradation process by providing a rich biotic population in contact with the plastic surface.

DEFINITIONS DEVELOPMENT

An important issue relating to the discussion of degradability and enhanced degradable plastics is that of definitions. The various terms are

used in a loose manner in the literature with no consistency. The need to develop adequate definitions has been pointed out recently by Andrady (1988) and others (General Accounting Office 1988). Definitions of the term "plastics" as it applies to the MARPOL Annex V Convention and the following terms relating to "degradability" are proposed as a starting point for further development.

For the purposes of MARPOL Annex V, the following definition of plastics has been proposed.

> Plastic: A solid material which contains as an essential ingredient one or more synthetic organic high polymer: and is formed (shaped) during either manufacture of the polymer or the fabrication into a finished product by heat and/or pressure.

The proposed definition includes both rubber and plastics (plastic products as well as virgin resin pellets). Inorganic polymers such as glasses are excluded along with low molecular weight polymers which are not "high" polymers or solids. The latter includes polymeric waxes, varnishes, and lubricants. The definition excludes any polymers produced by living organisms, including cellulose, natural rubber, and bacterial polyesters. In the case of a composite material where one component is a polymer, the material is excluded if the polymer itself is a minor component not essential to the formulation.

> Deterioration: Embrittlement and/or loss of physical integrity of a polymer regardless of the mechanism which brings about these changes.

The deterioration process might be the result of either a chemical or a physical process. Nonchemical deterioration of plastics plays an important role in environmental deterioration of plastics.

> Degradation: Deterioration which results from a chemical process.

Degradation might be further subdivided, based on the agency causing the chemical change. "Photodegradation" refers to degradation brought about by light. "Biodegradation" is that due to living organisms. Degradation due to slow oxidation of the plastic (especially at elevated temperatures) is "thermooxidative degradation," while that due to the chemical action of water is hydrolytic degradation or "hydrolysis." To be consistent with the definition for "degradation" proposed herein, it is necessary to show that a loss in property (in this case, tensile properties) occurred and that such loss is a result of a chemical reaction. The term "degradation" has been used throughout this paper without establishing that the loss was due primarily to a chemical change. However, the chemical nature of the processes which result in strength loss in plastics exposed to outdoor environments are well known.

The nonchemical deterioration processes might be similarly subdivided. "Dissolution" (or swelling in water), in which no chemical changes take

place, might be viewed as a deterioration of the plastic in water (or an aqueous solution). "Biodeterioration" can take place when the plastic is attacked by borers (at sea) and rodents: The net result is the breakdown of a larger piece of plastic into small fragments. In "physical deterioration" a plastic loses strength due to purely physical phenomena (for instance due to freeze-thaw cycles).

This proposed scheme allows a facile classification of the related processes and makes a clear distinction between degradation which tends to chemically break down plastics, and nonchemical deterioration processes, which merely reduce the particle size of the plastic. The distinction is of obvious importance from an environmental point of view.

EXPERIMENTAL

Materials

The following plastic products, selected on the basis of reported composition of beach debris (CEE 1987), were included in this study:

- Polyethylene film (low density). Representative of the plastic used in six-pack rings, plastic bags, etc.
- Polypropylene strapping tape. Commercially available.
- Trawl netting material (orange and blue-green color).
- Latex rubber balloons. Commercial sample.
- Foamed polystyrene sheet. Commercial sample.
- Rapidly degradable polyethylene. Commercial sample.

Polyethylene bags are a well-known component of marine debris. The threat to marine turtles via ingestion of plastic bags has been reported (Balazs 1985). While strapping bands (usually made of polypropylene or polyester) are not a major component of the debris, they present a particularly severe threat of entanglement to marine mammals (Laist 1987). Trawl webbing is a major component of floating plastic debris in some regions (Pruter 1987). A fraction of the latex rubber balloons released in promotional events may eventually reach the oceans, where their ingestion may present a threat to turtles and other species.

Weathering and Sampling

Experiments were carried out at the exposure facility at Duke Marine Laboratory in Beaufort, North Carolina. Figure 1 shows the ambient temperature of the seawater during the period of exposure and the air temperatures for the area as recorded by the National Weather Service.

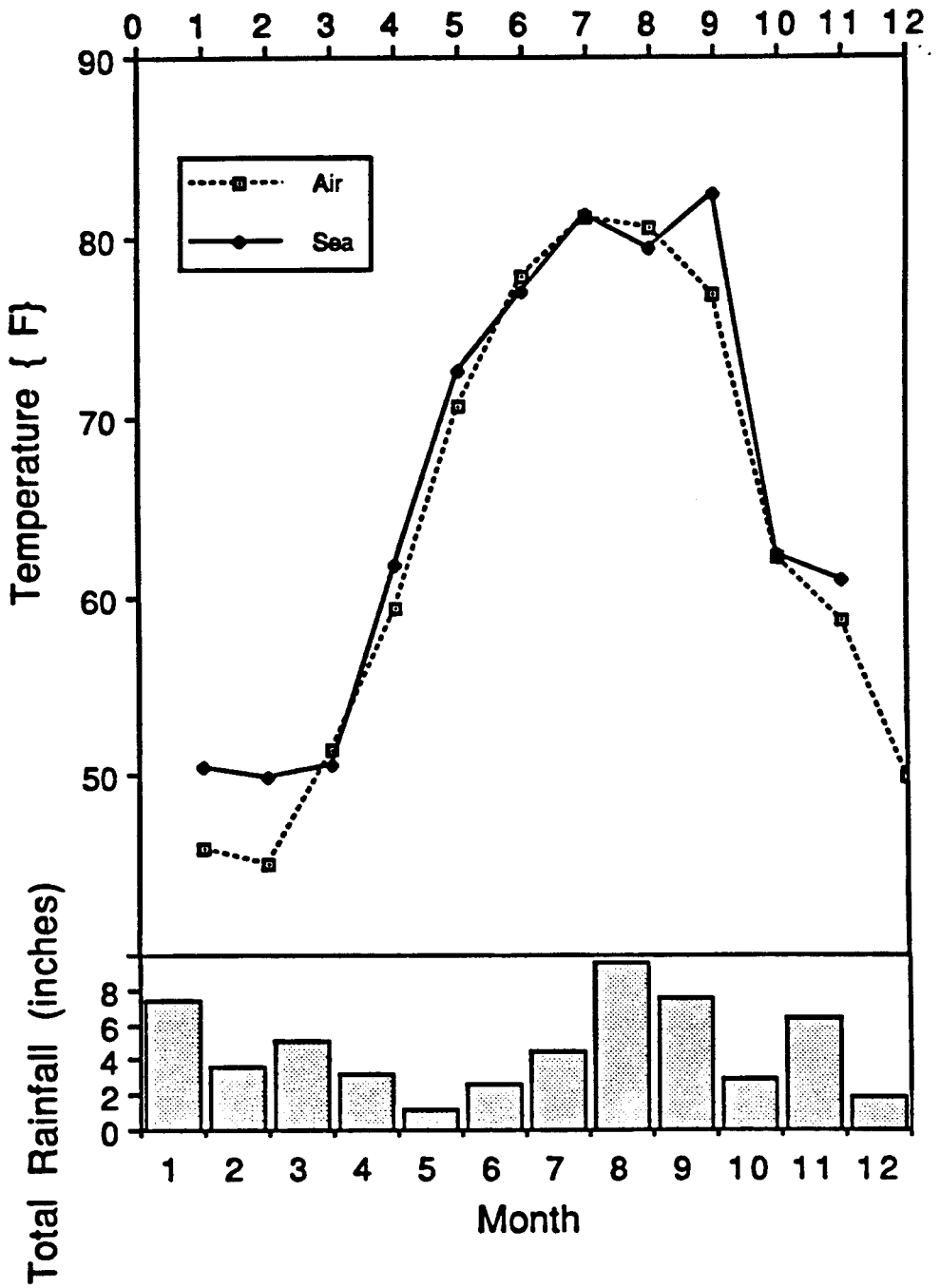

Figure 1.--Average monthly temperatures and rainfall for Morehead City, North Carolina for 1987.

The samples exposed on land were affixed with staples to a wooden platform and exposed horizontally on the flat roof of a laboratory building. These were backed by wood and were about 15.2 cm (6 in) from the roof surface. Another set of samples was exposed floating in a tank of seawater, with fresh seawater continuously flowing through the tank to maintain a depth of about 30.5-45.7 cm (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 seawater medium. The experiment thus simulates the conditions best suited for rapid photodegradation. The exposure was carried out for a period of 1 year.

Sampling was carried out at the end of every second month for all samples. The exposed samples were placed in a black plastic bag and transported to the Research Triangle Institute for measurement of tensile properties. The samples exposed at sea were dried for about 3 h in an air oven at 50°C and were stored in the dark at ambient temperatures.

Tensile Testing

Measurement of tensile properties was carried out with an Instron Mechanical Tester, Model 1122 generally in accordance with ASTM D 638 (American Society for Testing and Materials) Tensile Properties of Plastics. No further preconditioning of the samples was done prior to testing. Air-powered grips were used to hold the samples. Smooth grip faces were used with the polyethylene samples; for latex balloons and strapping tape, a serrated face had to be used to avoid slippage. Table 1 gives the test parameters for various types of samples tested. In the case of trawl webbing and strapping tape, where the fibrous nature and surface markings, respectively, made it difficult to determine the true area of cross section, the load to break is reported.

RESULTS AND DISCUSSION

Polyethylene Film

Table 2 summarizes the tensile property data for the polyethylene film samples exposed on land and at sea. Both the sea and air samples exhibit an increase in tensile strength after 2 months. This increase may be due in part to relaxation of stresses frozen into the sample during processing, a common occurrence during early exposure of processed thermoplastics.

Figure 2 shows the variation of ultimate extension with exposure time. Clearly, the samples exposed floating on seawater degraded at a much slower rate. The samples exposed at sea showed a 12% loss in ultimate extension after 12 months while the air-exposed samples lost 95% of the ultimate extension after only 6 months. Ultimate extension is considered a more

Test parameter[a]	A	B	C	D	E
Beam capacity (kg)	1,000	1,000	1,000	1,000	1,000
Full scale load (kg)	10	20,100	5	200	2/5
Crosshead speed (mm/min)	100	100	20	100	50
Gauge length (cm)	5	1.5	4	4	3
Clamp	Pneumatic	Pneumatic	Pneumatic	Pneumatic	Pneumatic
Jaw face size (in)	1 × 1.5	1 × 1.5	1 × 1.5	1 × 1.5	1 × 1.5

[a]A - Polyethylene film and degradable polyethylene, B - strapping tape, C - Styrofoam sheets, D - trawl netting, E - balloons.

appropriate parameter than tensile strength for measuring physical degradation since it reflects the brittleness and consequent tendency of the plastic to fragment. Statistical tests at the 0.05 level of significance showed no significant difference in mean ultimate extension values of the 2- and 12-month samples exposed at sea but did show a significant difference in mean ultimate extension of the 2- and 6-month samples exposed in air.

Polypropylene Tape

Table 3 gives the summary data relating to the weathering of polypropylene strapping tape. The formulation contained a filler and the material was highly anisotropic, easily tearing along its length. Material did not "neck" on extension but ruptured gradually. As the surface of the tape was not smooth enough (because of an embossed pattern on the surface) to obtain an accurate value for thickness, the maximum load rather than tensile strength is reported. Figure 3 illustrates the observed changes in ultimate extension. After 12 months, samples exposed on land had lost 90% of the initial ultimate extension, while samples exposed at sea had lost only 26% of the initial value. Thus, while some degradation does occur in samples exposed on seawater, it is much less pronounced than that for samples exposed in air for a comparable duration of exposure. This conclusion is further illustrated by testing for the statistical significance of differences in mean ultimate extensions at the 0.05 level. A significant difference exists in mean ultimate extension for the samples exposed in air for 0 and 12 months and for those exposed at sea for 0 and 12 months. As expected, a statistically significant difference was also found between the mean ultimate extensions of the 12-month samples exposed at sea and in air.

Trawl Netting

Tensile property data for net samples are given in Table 4. The data are reported as maximum load (kg), which often coincided with the ultimate load of the material, and ultimate extension.

Table 2.--Summary of data relating to weathering of low-density polyethylene film samples.

Duration (months)	Tensile strength (kg/cm^2)			Ultimate extension (%)			Number of samples
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
Samples exposed in air							
0	124.1	19.6	6.1	548	71	29	6
2	143.1	9.9	4.4	541	38	17	5
4	99.9	5.1	2.9	188	166	96	3
6	115.8	6.5	3.3	27	18	9	4
Samples exposed in seawater							
2	139.5	17.1	7.7	613	133	59	5
4	131.0	12.8	5.7	547	95	42	5
6	132.3	23.6	13.7	601	197	114	3
8	117.3	13.4	6.0	511	147	65	5
10	117.8	7.3	2.9	550	106	46	6
12	118.7	7.6	3.4	541	87	39	5

Table 3.--Summary of data relating to weathering of plastic strapping tape.

Duration (months)	Maximum load (kg)			Ultimate extension (%)			Number of samples
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
Samples exposed in air							
0	75.5	2.0	1.0	82	2	1	4
2	68.2	1.7	0.8	70	7	3	4
4	40.2	5.2	2.6	43	4	2	4
6	20.1	3.2	1.6	19	5	2	4
8	14.9	3.5	1.8	12	4	2	4
10	13.2	2.7	1.4	10	5	1	4
12	11.3	0.7	0.4	8	1	1	3
Samples exposed in seawater							
0	76.5	5.4	2.7	89	5	2	4
4	77.0	4.0	2.0	91	3	2	4
6	74.3	2.5	1.3	82	2	1	4
8	73.2	5.6	2.8	79	5	3	4
10	64.0	5.2	2.6	63	8	4	4
12	67.2	3.3	1.6	61	9	4	4

Note: Sample width was half the size of regular width of the tape.

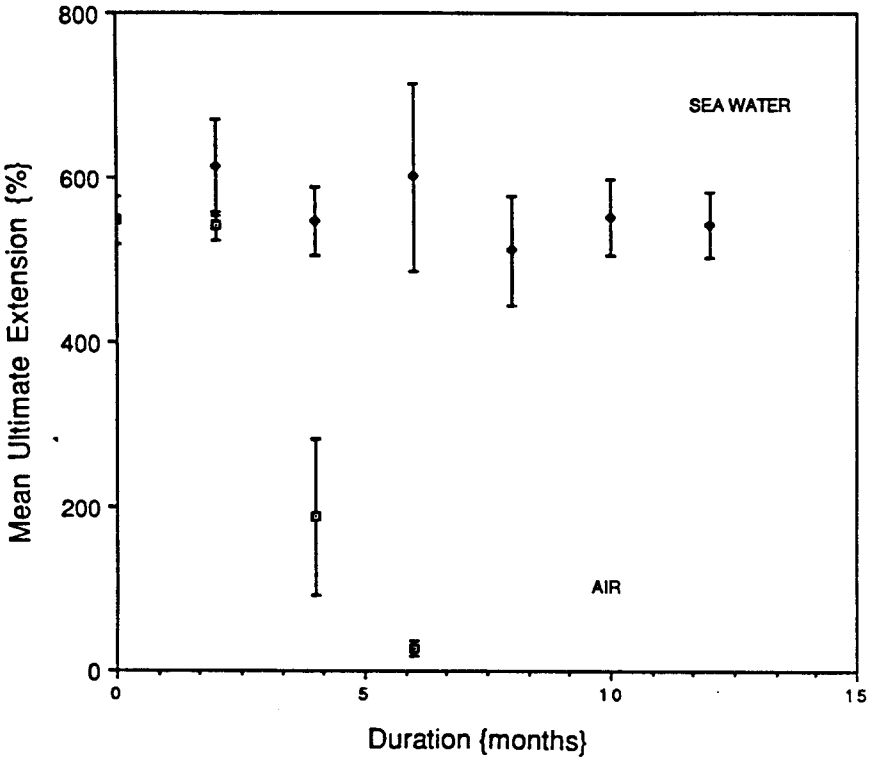

Figure 2.--The variation of the mean ultimate extension of polyethylene films with the duration of exposure.

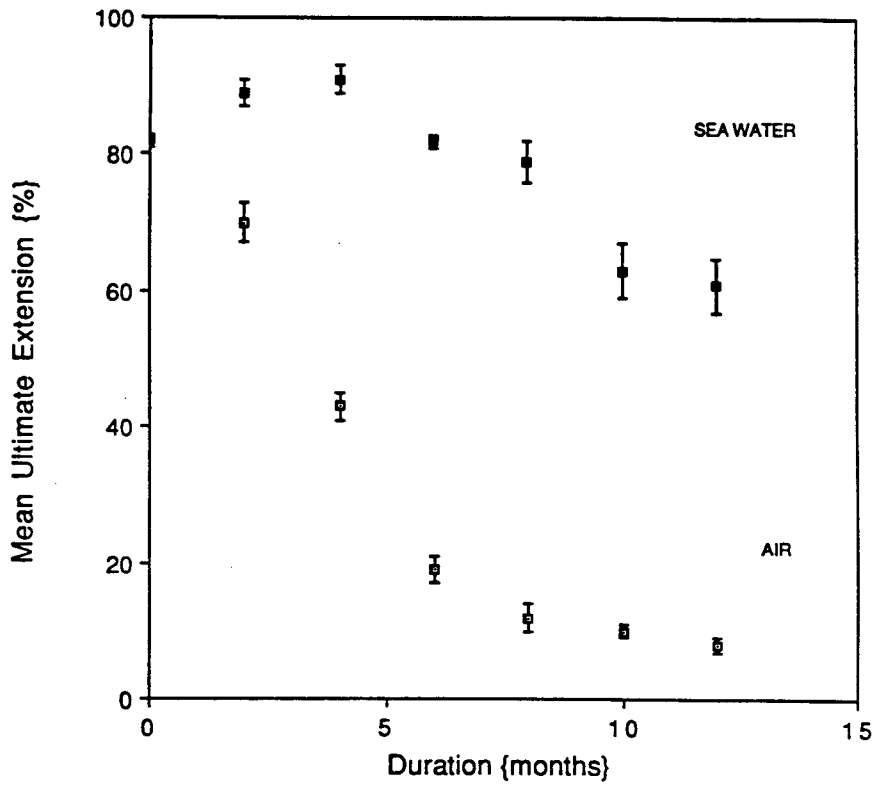

Figure 3.--The variation of the mean ultimate extension of polypropylene tapes with the duration of exposure.

Table 4.--Summary of data relating to weathering of trawl web material.

Duration (months)	Maximum load (kg)			Ultimate extension (%)			Number of samples
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
Orange-colored netting							
Samples exposed in air							
0	126	3.8	1.9	46.5	4.8	2.4	4
2	121	13.8	6.9	36.9	2.7	1.4	4
4	120	10.6	7.5	41.0	5.9	4.2	3
6	117	9.3	4.7	41.7	5.6	2.8	4
8	125	4.0	2.0	47.4	1.7	0.9	4
10	121	7.7	3.9	47.7	6.5	3.2	4
12	125	8.5	4.3	49.1	8.4	4.2	4
Samples exposed in seawater							
4	132	9.1	4.6	62.1	3.8	1.9	4
6	123	13.4	6.7	49.1	4.1	2.1	4
8	129	6.7	3.3	53.5	2.9	1.4	4
10	128	10.7	5.4	53.5	2.9	1.4	4
12	127	11.6	5.8	49.1	3.9	2.0	4
Blue-colored netting							
Samples exposed in air							
0	115	10.5	5.2	63.0	7.1	3.5	4
2	88	11.4	5.7	41.4	2.9	1.5	4
4	104	7.9	4.0	46.6	8.2	4.1	4
6	96	11.3	5.7	49.1	8.6	4.3	4
8	70	12.1	6.1	32.3	10.9	5.5	4
10	93	7.3	3.7	44.5	3.5	1.7	4
12	94	3.8	1.9	49.5	5.0	2.5	4
Samples exposed in seawater							
2	100	12.0	6.0	65.7	9.9	5.0	4
4	96	9.2	4.6	53.4	9.8	4.9	4
6	99	7.3	3.6	60.2	2.5	1.3	4
8	101	7.5	3.8	61.6	5.8	2.9	4
10	113	2.8	1.4	61.8	5.3	2.7	4
12	104	3.2	1.6	60.4	1.4	0.7	4

The changes in tensile properties obtained with trawl web samples on exposure in air and in seawater are less dramatic and are not shown in a figure. Netting intended for commercial fishing is compounded specifically for exceptional durability usually using hindered-amine and other light stabilizers. The data, however, did show that the blue netting is relatively more prone to outdoor degradation than is orange netting when exposed in air. While the difference is small, it is significant. On exposure in seawater, neither material underwent any significant change in maximum load up to 12 months of exposure (at which time the experiment was discontinued). The only conclusion that might be drawn from these samples is that they would persist longer in the environment, relative to the packaging materials and balloons tested.

Rubber Balloons

The strength and extensibility of the rubber balloons determine to a great extent the likelihood of the ingested material obstructing the air or gut passages of turtles. Retention of elasticity is of particular concern, as elastic materials are likely to be difficult to dislodge from the air passages or alimentary canals. Table 5 summarizes the tensile property data on balloons exposed under present experimental conditions. Figure 4 shows the variation of ultimate extension with duration of exposure. In air, the rubber lost 59% of its ultimate extension after only 2 months. For the same time at sea, the rubber lost only 11% of its ultimate extension. The balloons continued to retain their elasticity during exposure in seawater, with only a 48% loss after 12 months. In air, however, the balloons lost 94% of their ultimate extension after 6 months, beyond which time the samples were too weak and brittle to be tested. As with the plastic samples, the rate of degradation in seawater was much slower than that in air. The degree of hazard associated with a partially deteriorated balloon depends on the particle size which might be safely ingested by the target species. Such information on turtles and other relevant species is not available at the present time. However, the above results indicate that if the balloons do pose a hazard to marine life, they would, under present experimental conditions, be a threat for a relatively longer period of time at sea than on land.

Polystyrene Foam

In view of the abundance of polystyrene foam pieces in marine debris, the weathering behavior of polystyrene was particularly interesting. On exposure in air the foam underwent rapid yellowing, which apparently was a surface reaction. The sample exposed on seawater also underwent yellowing, although the algal fouling of the surfaces made it difficult to measure the extent of yellowing.

The yellowness index increased up to about the sixth month of exposure and decreased thereafter. However, the development of yellowness was also accompanied by embrittlement of the exposed surface. Over the exposure period of 1 year, a surface layer of up to half the original thickness became brittle enough to crumble on handling (and could be easily scraped out). Wind and rain are likely to remove at least some of the yellowed material during exposure. This may explain the reduction in the extent of yellowing at the longer exposure times.

Table 5.--Summary of data relating to weathering of latex rubber balloons.

Duration (months)	Tensile strength (kg/cm^2)			Ultimate extension (%)			Number of samples
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
Samples exposed in air							
0	96.7	7.2	3.6	986	100	50	5
2	3.6	1.9	0.9	405	184	92	4
4	1.9	--	--	140	--	--	2
6	1.4	--	--	63	--	--	2
[a]8	--	--	--	--	--	--	--
[a]10	--	--	--	--	--	--	--
Samples exposed in seawater							
2	22.7	3.4	1.5	874	107	48	5
4	21.5	5.4	2.4	727	75	34	5
6	16.0	3.1	1.5	611	69	34	4
8	14.0	3.6	1.8	600	87	44	4
10	18.3	3.5	1.7	719	74	37	4
12	9.1	1.0	0.6	513	26	15	3

[a]Too brittle or weak to be tested.

The yellowness index of the degraded polystyrene foam correlates well ($r = 0.90$) with the tensile strength of the degraded material up to 6 months of exposure in air. Lack of such a correlation at longer exposure times is also possibly due to loss of embrittled yellow surface material (from rain, wind).

In fact, the thickness of the degraded (removable) yellow surface layer increased with duration of exposure for both sets of samples. The reduced thickness of the samples after the embrittled layer was scraped off is given below.

Duration Months)	Thickness of lower layer (cm)	
	Air	Seawater
0	0.418	0.418
2	0.349	0.221
4	0.308	0.164
6	0.234	0.168
8	0.217	0.229
10	0.214	0.155

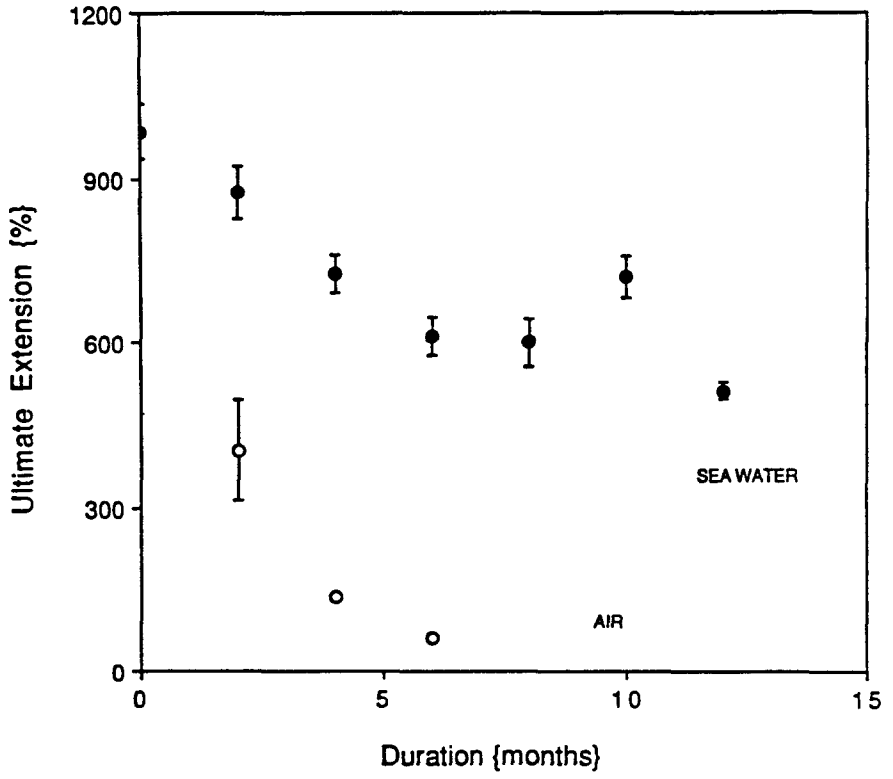

Figure 4.--The variation of mean ultimate extension of latex rubber balloons with the duration of exposure.

The tensile strength can thus be calculated in two ways: based on original thickness, and based on the thickness of the unembrittled layer. Table 6 summarizes the tensile property data. If the oxidative degradation process was restricted to the yellowed brittle surface layer, the tensile strength of the underlying polystyrene would yield about the same tensile strength regardless of the duration of exposure. However, as seen in the table and in Figure 5, the tensile strength based on reduced thickness of the material also decreases with the duration of exposure. The lower unembrittled region is apparently accessible to the free radicals generated during the photo reaction.

Expanded polystyrene was the only type of plastic material tested where the rate of deterioration (of tensile properties) was faster at sea than on land. In air, the material requires an exposure of at least a year to decrease its tensile strength by 40%. Exposure in seawater reduces the tensile strength by over 60% in 4 months!

Under the present exposure conditions, the polystyrene foam material deteriorates relatively rapidly when exposed outdoors on seawater. This would lead to the breaking up of the material into smaller pieces fairly easily. Unlike most other plastic debris items, pieces of foamed polystyrene are not capable of entanglement. They might, however, be ingested by a variety of species, especially when covered with foulants. Effects of ingestion of weathered polystyrene foam material are not known.

Table 6.--Summary of data relating to weathering of expanded-extruded polystyrene.

Duration (months)	Tensile strength[a] (kg/cm^2)			Tensile strength[b] (kg/cm^2)			Ultimate extension (%)			Number of samples
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
Samples exposed in air										
0	3.89	0.50	0.21	3.89	0.50	0.20	3.9	1.70	0.07	6
2	4.31	0.34	0.17	5.16	0.40	0.20	3.5	0.29	0.14	4
4	3.46	0.59	0.29	4.70	0.80	0.40	3.9	0.32	0.16	4
6	2.45	0.27	0.19	4.37	0.48	0.24	2.9	0.13	0.06	4
8	2.39	0.27	0.19	4.60	0.52	0.26	3.2	0.24	0.12	4
10	2.61	0.14	0.07	5.09	0.27	0.14	3.2	0.24	0.12	4
12	2.37	0.27	0.19	4.53	0.51	0.25	3.3	0.32	0.16	4
Samples exposed in seawater										
2	2.88	0.21	0.09	5.45	0.40	0.18	4.6	0.80	0.36	5
4	1.13	0.71	0.36	5.50	1.82	0.91	4.1	1.60	0.80	4
6	1.09	0.17	0.09	3.20	0.44	0.22	2.2	0.88	0.44	4
8	1.22	0.29	0.13	2.22	0.54	0.25	1.9	0.29	0.13	5
10	0.69	0.09	0.04	2.13	0.22	0.11	1.6	0.24	0.12	4

[a]Tensile strength calculated using the initial area of cross section.
[b]Tensile strength calculated using the area of cross section based on residual unembrittled layer.

Enhanced Photodegradable Polyethylene (Ethylene Carbon Monoxide Copolymer)

The weathering behavior of the enhanced degradable polyethylene was quite different from that of the polyethylene homopolymer sample (Table 7). As might be expected, the samples exposed in air rapidly degraded, losing nearly 99% of the initial value of mean ultimate extension within 6 weeks of exposure (Fig. 6). The tensile strength decreased slowly reaching to about 50% of the initial value in the same period of exposure. At this stage samples were embrittled and too weak to be tested.

The samples exposed in seawater 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 mechanism leading to a plateau in the mean extension values from about the sixth to fourteenth week of exposure is not understood. But it is of little practical consequence. It is clear that under the experimental conditions of the study, the enhanced photodegradable polyethylene performs

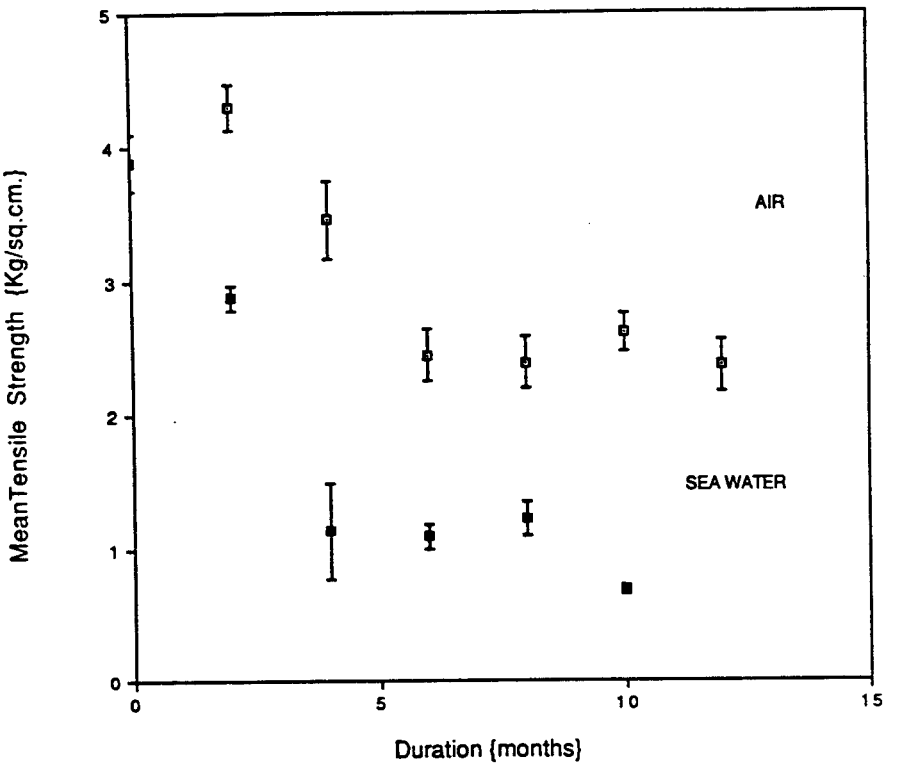

Figure 5.--The variation of mean tensile strength of expanded extruded polystyrene with the duration of exposure.

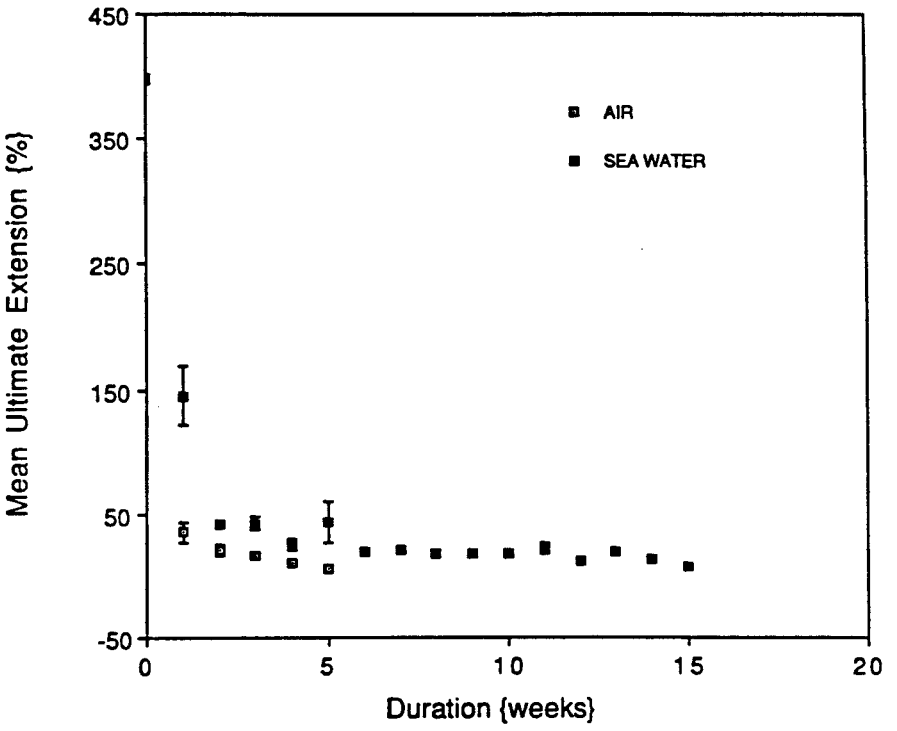

Figure 6.--The variation of mean ultimate extension of enhanced degradable polyethylene sheets with the duration of exposure.

Table 7.--Summary of data on outdoor weathering of enhanced photodegradable six-pack ring material (LDPE).

Duration (weeks)	Tensile strength (kg/cm^2)		Ultimate extension (%)	
	Mean	S.E.	Mean	S.E.
Exposure in air				
0	160.4	1.0	398	3.4
1	122.4	2.1	35.6	8.3
2	128.0	2.4	21.0	4.4
3	134.1	2.4	16.8	1.4
4	104.7	8.0	10.7	2.6
5	86.3	6.9	5.7	0.8
Exposure in seawater				
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
3	115.1	0.8	42.3	5.4
4	120.4	0.9	25.8	4.1
5	116.5	2.6	44.1	16.7
6	120.2	12.6	19.1	1.0
7	122.9	0.8	21.0	3.1
8	121.1	0.4	17.71	0.5
9	119.7	2.8	18.4	1.4
10	122.6	0.5	18.1	0.6
11	122.8	0.5	22.6	5.1
12	116.3	5.7	11.3	1.3
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

satisfactorily at sea for all practical purposes. The initial rates of decrease in the mean tensile properties obtained with exposure in seawater, are somewhat slower than those obtained with exposure on land.

SUMMARY FINDINGS

Table 8 illustrates the general findings of the exposure study by a comparison of tensile properties before and after exposure in air and in seawater for the different samples. Data relating to a single duration of exposure are shown to illustrate the general trend observed. Except for the netting, rates of degradation for the samples in seawater were much

Table 8.--Comparison of weathering data for exposure on land and at sea.

Sample	Duration of exposure (months)	Percent decrease in the mean value of tensile property			
		Air		Seawater	
		Strength[a]	Extension	Strength[a]	Extension
Polyethylene film	6	6.6	95.1	No change	No change
Polypropylene tape	12	85.0	90.2	11.0	31.5
Latex balloons	6	98.6	93.6	83.5	38.0
Expanded polystyrene	10	32.9	18.0	82.3	65.2
Netting	12	No change	No change	No change	No change
Rapidly degradable polyethylene	1.25	46.2	98.6	27.1	88.9

[a]The percentages reported as based on the maximum load in the case of netting and polypropylene type materials.

slower than the degradation rates on land. Netting material did not show any significant variation in tensile properties due to the type or duration of exposure. Enhanced degradable polyethylene six-pack ring material degraded in about the same time scale under both air and seawater exposure.

The marked retardation of the weathering process observed in some types of plastic materials floating in seawater might be attributed to: (a) differences in heat buildup and (b) fouling of samples in seawater.

A significant fraction of the sunlight impinging on a plastic surface is absorbed by the material as heat. Depending on the nature of the plastic, the velocity of the air around it, and the temperature difference between the plastic and the surroundings, this absorbed energy maintains the plastic at a temperature higher than that of the surrounding air (Summers et al. 1983). Plastics exposed in air undergo heat buildup easily. The effect is even more pronounced in the present samples, which were exposed on a thermally insulating wood surface. Under such conditions, the heat buildup is likely to be higher than for the case of exposure on soil, thus simulating weathering under "worst case" conditions and accelerating the degradation process in the samples exposed in air. Samples exposed in seawater, however, are held at near ambient temperature leading to slower rates of degradation.

Samples floating on seawater underwent extensive fouling during the exposure. Foulants were mostly algae except for several *Balanus* sp. found on samples exposed for over 8 months. The experimental method used in the present study (containment of samples in a shallow tank) is likely to have reduced the extent of fouling and prevented the settlement of debris (or

"silting") on the sample surface. Fouling retards the photodegradation by restricting the light available to the plastic.

CONCLUSIONS

Under present experimental conditions, low density polyethylene film, polypropylene tape, and latex rubber balloon samples were found to significantly degrade when exposed in air outdoors. Marked decreases in ultimate extension were obtained in 1 year of exposure. Similar samples exposed at the same site, but floating on seawater, degraded at a significantly slower rate during the same period of time.

The lower rates of degradation might primarily be attributed to lack of heat buildup in samples exposed on seawater. Biofouling of sample surface leading to reduced light availability may also have decreased the rate of weathering.

Foamed polystyrene degraded at a faster rate in seawater than in air when exposed outdoors.

Enhanced degradable six-pack ring polyethylene degraded at nearly the same rate when exposed in air and in seawater.

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