



**Northwest and  
Alaska Fisheries  
Center**

**National Marine  
Fisheries Service**

**U.S. DEPARTMENT OF COMMERCE**

## **NWAFC PROCESSED REPORT 88-19**

# **Experimental Demonstration of Controlled Photodegradation of Relevant Plastic Compositions under Marine Environmental Conditions**

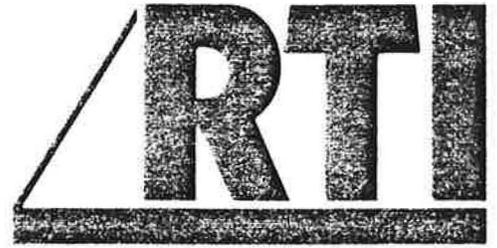
**September 1988**

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Experimental Demonstration of Controlled Photodegradation of  
Relevant Plastic Compositions under Marine Environmental Conditions

Final Report

Covering the Period

September 1986 to May 15, 1988

Prepared for:

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## 1.0 Introduction

### 1.1 Background

An increasing body of scientific data suggests consistently increasing levels of plastic debris in the world's oceans. While the information on occurrence of plastic debris is limited and incomplete, the phenomenon is undoubtedly a global one, as indicated by the reports of plastics in the marine environment from regions as diverse as the North Pacific (Dahlberg and Day, 1985), Southern Oceans (Gregory, 1978), Arctic beaches (Wong, 1976), South Atlantic (Morris, 1980b), Lisianski Islands (Hawaiian archipelago) (Henderson, 1983), Lebanese beaches (Shiber, 1979), Malta (Morris, 1980a), etc. Plastic, a unique cost-effective material well suited for a variety of applications, is extensively used worldwide. It is very likely that the future usage of plastics will grow at even a faster rate as conventional materials (wood, paper, glass, etc.) continue to be replaced by plastics in numerous applications.

Plastics in the ocean environment might be traced back to several sources. Commercial fishing activity is the primary source of plastic litter at sea, and gear-related debris is often an important component of beach debris in regions near commercial fisheries. Since the change-over from fishing gear constructed from natural fibers to those made from synthetic materials (plastics), increasing amounts of plastic gear have been used by fishing vessels. The OECD countries [Organization for Economic Corporate Development, consisting of 21 member countries including USA] alone in 1985 reported a world fishing fleet of over 600,000 vessels. On the basis of reported data (Uchida, 1985) over 21,000 km of drift net is used nightly in the North Pacific salmon and squid fisheries alone! A small fraction of this gear is inevitably lost

(or deliberately discarded) at sea each year and ends up as persistent marine debris. Attempts at quantifying such losses are underway.

Significant amounts of plastics are also discarded into the oceans from other vessels such as cargo vessels, passenger vessels, military vessels, and small pleasure craft. The plastic debris associated with these vessels is often the plastic component of domestic waste stream generated on board and depends more on the population aboard than on the size of the vessel. While some estimates are available (Parker et al., 1987), quantitative information on the extent of plastic waste disposal at sea from vessels remains sketchy.

Among the land-based sources of plastic debris which eventually finds its way to the sea, beach litter left behind by the users of the beaches is likely to be the most significant. Consisting mostly of packaging materials designed for single use, the plastic debris on beaches is readily carried into the ocean. Land-based litter is transported into the oceans via rivers and water-borne municipal waste and sewage as well.

Plastics in general have outstanding durability and are persistent in the environment for extended periods of time. The lifetime at sea of even the more common commodity plastics is not known with any degree of reliability. However, there is little doubt that such lifetimes must be very much longer than those of natural fibers, wood, and metal. Persistence of plastic debris at sea poses several hazards to marine life, commercial fisheries and users of the sea.

The gear-related debris such as net fragments, lengths of monofilament line, rope, and traps (as well as packing bands and six-pack carriers) have been observed to cause the entanglement of marine animals. The entanglement of marine mammals is perhaps the best studied (Laist,

1987). In fact, entanglement is suspected to be the cause of recent decline in the population of northern fur seals in the Pribilof Islands (Fowler, 1985, 1987).

Ingestion of plastic fragments by several species of marine animals has also been reported. In some instances such as with turtles, the ingestion of plastics may result in severe damage or death, while in others such as with sea birds, the effect of plastics ingested is not as yet fully understood (Fry et al., 1987). Anecdotal accounts of fish ingesting inedible objects have been reported since the 1920's (Gudger 1928, 1929). Unlike the case of entanglement of fish in plastic gear (i.e. "ghost fishing"), the ingestion of plastics by fish has not been studied in much detail. While plastics are generally non-toxic (some of the compounding ingredients such as plasticizers therein might be toxic), the material may obstruct the alimentary tracts of animals.

As might be expected, plastic debris at sea tends to concentrate along coastal areas, commercial fisheries and vessel routes, the same areas likely to be affected by plastic debris. Current activity may, however, carry some of the debris into other regions. The various marine species generally susceptible to entanglement unfortunately spend a significant portion of their life cycle in coastal areas, increasing chances of encounter. Marine animals, particularly young animals, are attracted by colored debris (as well as active fishing gear) at sea. Ingestion of plastics, at least in some species (sea birds, turtles, etc.), is due to the plastic closely resembling food items such as insects, fish eggs and larvae, and jelly fishes.

Thus, the process of entanglement/ingestion is not necessarily a result of chance encounter between a potential victim and an item of plastic debris. As it is likely to result from active encounter, the

hazard presented by even a limited amount of persistent debris can be substantial.

## 1.2 Factors Affecting Hazard Levels of Plastic Debris

The degree of hazard posed by an item of debris at sea is determined by several factors:

### (a) Geometric Features

Netting, six pack rings, etc., capable of entangling would obviously present more of a hazard to the appropriate marine species than more simply-shaped debris, such as short fragments of thick rope or plastic bottles.

### (b) Life-time

The lifetime of the item at sea determines the period of time the plastic material will be available for encounter with marine animals. Furthermore, an item's lifetime also determines how long it retains the capability for entanglement, as opposed to becoming an ingestible embrittled material.

### (c) Physical Properties

The two most important determinants of the hazardousness of plastic debris are specific gravity and strength. The former determines if the threat is limited to the benthic environment (if the plastic is negatively buoyant in sea water) or to the surface environment, and the latter property decides which species (and even which age class in a population) might remain entangled after an encounter with the debris. With at least some of the material, particularly the partly weathered plastic debris, the strength might be low enough to allow some species to escape and survive entanglement.

(d) Toxicity

Most plastics, being resistant to hydrolysis, cannot be digested to yield molecular fragments small enough to be absorbed into the body. Consequently, the high molecular weight plastic itself is not toxic by ingestion.

However, the compounding ingredients used in the process of fabrication of various plastics products may, in adequate concentrations, be toxic by ingestion. Examples include alkyl phthalate plasticizers (NTIS 1988) used in flexible PVC packaging films, some inorganic pigments used as opacifiers or fillers (Fry, 1987), and possibly antioxidants used in polyolefins. On ingestion, the plastic is in contact with gut fluids at a relatively lower pH than the sea water. Depending on the nature of the compound, some of it may leach out of the polymer and be absorbed through the stomach/gut lining. Neither the leaching process nor absorption into body tissue of such additives has been experimentally demonstrated for any plastic/marine animal combination.

Another, as yet undemonstrated, contention is that the plastic debris picks up toxic compounds such as PCB's and DDT from water and transfers them to sea birds via ingestion (Carpenter et al., 1972).

1.3 Definition of Lifetimes

Of the above factors, the lifetime of the plastic material is clearly the most important factor as it alone determines the duration of the threat. The definition of a "lifetime" requires the selection of a criterion for "degradation" (i.e. the lifetime would be the duration between the introduction of the debris into the environment and the time when the material is degraded to such an extent that it is no longer considered as plastic debris). As a number of ways of defining "degradation" can be suggested, the identification of "lifetime" becomes a

difficult task. The sequence of events which leads to the degradation of a plastic material outdoors might be described in several stages, as follows:

(a) Loss of Strength

Mainly due to the action of sunlight, moisture, and microbial action (in the case of some polymers), plastics undergo slow weakening. Of these factors, sunlight is the most important. Eventually, the strength might be reduced to a point where any movement due to wind or attempted entanglement may result in the brittle plastic material breaking up into several smaller pieces. At this stage, the plastic is embrittled and is too weak to pose a threat via entanglement.

(b) Breakdown Into Large Fragments

The larger pieces of plastics formed during the slow embrittlement will continue to break down to progressively smaller fragments. Depending on the particle size, ingestion of the plastic material might lead to blockage of the digestive tract in a variety of animals. Small enough fragments of plastic, however, may pass through the digestive tract of animals without any seriously ill effects. For a given species, a narrow range of particle sizes (irrespective of the type of plastic material involved) which can be ingested without serious consequences might be identified.

(c) Conversion to Minute Plastic Fragments

The minute plastic fragments (or dust) formed during the above stage do not pose a threat via ingestion to the larger species. The plastic is, however, as yet not degraded from a chemical standpoint. The long chain structure typical of polymeric materials still persists in the powdery products of degradation. With the decrease in particle size and consequent increase in the surface area, the plastic becomes

progressively more amenable to microbial degradation (Albertsson, 1986). A combination of photodegradation and this slow microbial process eventually breaks down the long chain-like structure of the plastic into smaller molecules.

(d) Breakdown of Products into Simple Compounds

In the strictest chemical sense, the degradation is not complete until these products of degradation are in turn broken down into chemically simpler compounds such as carbon dioxide and water.

Neither the exact sequence nor the time scale for any of the stages of deterioration of plastics in the marine environment is reliably known.

1.4 Assessment of Relative Lifetimes at Sea and on Land

A crucial question relating to plastic debris at sea is that of the lifetime of key plastic types in the ocean environment. It is a question that needs to be addressed in the short-term to allow a realistic assessment of the hazard posed by plastic waste at sea. The research effort required consists of three tasks: (1) identification of key plastic product types in the waste stream, (2) the development of appropriate criteria of degradation along with suitable test methods for their evaluation, and (3) accelerated weathering under simulated marine conditions and monitoring the consequent degradation of the plastic.

The intent of the present work is to initiate study on this general topic by addressing the related preliminary question of relative rates of degradation of plastic debris at sea and on land. Specifically, the study will determine if plastic floating on sea water degrades at a rate different from that exposed to the same natural weathering conditions, but in air.

There are several reasons to believe that the rate of degradation at sea might be different from that on land. Some of these are as follows:

- (a) High humidity is known to accelerate the rates of degradation of several classes of plastics. 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.

Being in contact with sea water may thus have an accelerating effect on the degradation of some types of plastic materials.

- (b) Plastics exposed to sunlight outdoors undergo "heat buildup", a process which results in the plastic material exposed to sunlight reaching significantly higher temperatures than the ambient air. The higher temperatures generally result in an acceleration of light-induced degradation and may even be high enough to induce significant thermo-oxidative degradation.

Plastics at sea will not suffer from such heat build-up due to heat transfer and may consequently undergo slower oxidative and photodegradation.

- (c) Coastal sea water is often rich in microbial flora. Compared to those on land, plastics at sea are constantly accessible to a diverse concentrated population of microbes. This will tend to accelerate the biodegradation of the material at sea.

(d) All materials exposed to the sea invariably undergo fouling. The initial stages of fouling result in the formation of a biofilm 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 sea water (Sverdrup et al., 1942), submerged plastics would necessarily undergo a slower rate of photodegradation.

If the rate of degradation of plastics at sea is found to be significantly slower than that on land due to several of the above factors, the finding would have a direct impact on the assessment of the hazardousness of plastic waste. On the other hand, if the rates are faster relative to those on land, the threat might be regarded as being somewhat overstated.

Enhanced degradable plastics have been suggested as a possible means of controlling plastics waste in general. Recent legislation, in fact, requires that this technology be studied for its potential as a means of litter control. While the enhanced plastic technologies are well known to perform under terrestrial exposure conditions, their performance under marine exposure conditions has not been reported. As a

part of the present investigation, a preliminary experiment was undertaken to determine if a selected enhanced photodegradable polyethylene performs satisfactorily when exposed floating in sea water, under North Carolina coastal conditions. The selected material was a commercially available rapidly photodegradable polyethylene six-pack material manufactured by the HiCone Division of ITW Company. This product is the highest volume photodegradable packaging product in the US today.

A secondary goal of the study is to determine if the by-products of plastics degradation at sea are likely to be toxic to marine life. Experimental studies on the isolation, purification, and identification of products from plastics degradation in the marine environment are complex, time consuming, and beyond the scope of the present study. Assuming that the basic photo and thermooxidative mechanisms of degradations operate at sea as well as on land, the research literature will be examined to identify the nature of the degradation products.

## 2.0 Scope of Investigation

### 2.1 Sample Selection

Detailed quantitative information on the composition of plastic debris at sea is not available. However, on the basis of the various known modes of influx of plastic materials into the oceans, certain types of plastic products likely to be associated with marine plastic debris might be readily identified. These consist of products used in the fishing industry and as packaging materials.

The beaches, an important component of the marine environment, often suffer higher levels of plastic pollution than the ocean itself. Not only are they littered regularly by the users, but the floating plastic debris originating from vessels at sea may eventually end up at the beaches. Thus a study of the beach debris represents a convenient and valid method of qualitative identification of the composition of plastic waste in the marine environment.

The list of plastic products to be included in the present investigation was based on the above considerations. Several recent beach clean-up exercises where the composition of collected debris was reported were invaluable in developing the list, which is given below:

1. Trawl netting material (orange color). Sample provided by Jeff Short, Auk Bay Laboratory, NOAA.
2. Trawl netting material (blue-green color). Origin - Jeff Short, Auk Bay Laboratory, NOAA.
3. Foamed polystyrene laminates. Commercially available trays for packing fish/meat at retail outlets.
4. Polypropylene strapping tape. Commercially available Wilton Brand strapping tape.
5. Polyethylene film (low density). Representative of the plastic used in six-pack rings, plastic bags, etc. Sample provided by ITW HiCone Division, Itasca, IL.

6. Latex rubber balloons. Commercial sample of balloon.
7. Enhanced degradable polyethylene material. The material used in rapidly photodegradable six-pack ring carriers, provided by the manufacturer, ITW HiCone Division, Itasca, IL.

Trawl webbing is a major component of floating plastic debris and the two colors selected are particularly popular in the Pacific Northwest fisheries. Samples were obtained from a NOAA laboratory rather than a commercial source because the same material was used in an ongoing beach exposure study in the Auk Bay Laboratory (NOAA) in Alaska. Use of identical plastic compositions allows the comparison of data from the two studies, which may lead to a better understanding of the geographic factors in the weathering of plastics in the marine environment. (Samples of trawl webbing aged to different extents in air and water, collected at the two locations, will be exchanged for further study at a future date.)

Expanded polystyrene foam is widely used as floatation devices (e.g. gill net floats) and as packaging material (e.g. bait boxes and cups). Several studies of plastics floating at sea (Colton, 1974; Morris, 1980a; Dahlberg, 1985), as well as numerous beach debris studies, indicate polystyrene foam to be the principle or a major component of plastic debris. Extruded, expanded polystyrene (thermoformed) is used in food trays.

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. The polypropylene strapping is widely used in packing cargo.

Polyethylene bags are a well known component of marine debris. The threat to marine turtles via ingestion of plastic bags has been reported.

A fraction of the rubber balloons released in promotional events may eventually reach the oceans where their ingestion may present a threat to turtles and other species.

## 2.2 Weathering and Sampling

Preliminary exposure studies were carried out in Miami, Florida, where one set of samples was exposed horizontally on sample racks at a location close to beach and a duplicate set exposed floating at sea. The latter samples were fixed with monofilament to a wooden pier at the marine exposure site and were able to freely float in the water.

Detailed experiments were carried out at the exposure facility at Duke Marine Laboratory in Beaufort, NC. The Florida location had the advantage of warmer conditions and therefore higher rates of degradation within the limited (1 year) period of observation, but the facility at North Carolina was more secure and could be monitored closely on a daily basis.

The set of samples exposed on land at North Carolina was affixed with staples to a wooden platform and exposed horizontally on the flat roof of a laboratory building. The samples were backed by wood and were about 6 inches from the roof surface. Polystyrene foam tray samples were likely to be dislodged by heavy winds, rains, and birds. A thin gauge metal mesh was therefore placed above the tray samples to prevent such losses. Sunlight was not cut down to any significant extent by this mesh.

Samples exposed at sea were fixed onto monofilament line and allowed to float in sea water off a wooden ramp. However, within the first two months of exposure, water at the sample location was observed to be often muddy. Depending on tidal movement, mud and debris often settled on the samples and tended to sink them in water. Such silting

and turbidity is probably not typical under deep ocean conditions. In any event, the samples exposed under the experimental conditions received only partial and intermittent sunlight, the main factor bringing about the degradation. Rather than proceeding with the exposure experiments under such "worst case" conditions, the exposure protocol was changed at the end of the second month of exposure to obtain the full impact of available sunlight.

In this latter arrangement, the samples were exposed within a large fiberglass reinforced plastic tank placed at the beach. Sea water was continuously circulated through the tank to maintain about 12-18 inches height of fresh sea water at all times in the tank. The tank was of sufficiently large area to accommodate the full set of floating samples and the flow of water was rapid enough to ensure that the water temperature in the tank was the same as that of the sea even under hot summer conditions. This arrangement allowed the samples to be exposed on clear water and without the danger of samples entrapping debris and mud.

The samples probably received a marginally lower dosage of sunlight than in the open sea, due to the sides of the tank shielding the samples at low sun angles.

Sampling was carried out at the end of every second month for all samples except the enhanced photodegradable polyethylene material which was sampled once every week. The exposed samples were placed in a black plastic bag and transported to the Research Triangle Institute. The samples exposed at sea were dried for about 3 hours in an air oven at ~40°C and were stored in the dark at ambient temperatures.

## 2.3 Testing and Evaluation

### 2.3.1 Tensile Properties

Measurement of tensile properties was carried out in an Instron Mechanical Tester, Model 1122, generally in accordance with ASTM D 638, 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 all samples except net samples, latex balloons and strapping tape, where a serrated face had to be used to avoid slippage.

Table 2.1 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.

### 2.3.2 Yellowness Measurement of Polystyrene

Yellowness measurements were carried out within 10 days of exposure using a Macbeth 1500 Colorimeter with an integrating sphere. The specular component of light was excluded and the ultraviolet portion included in the measurements. A white ceramic standard tile was used as the backing material. The ASTM yellowness indices are calculated on the basis of the CIE standard illuminant C (CIE = 1931 2° standard observer viewing) and are expressed as:

$$YI = [100 (128 x -1.06 z)]/y$$

where  $x$ ,  $y$ , and  $z$  are tristimulus values of the sample with reference to source C. Several values of YI, obtained from different parts of the sample, were generally used to obtain an average value of the yellowness index. Reproducibility of the measurements with this technique is better than  $\pm 0.25$  units.

Table 2.1. Tensile Properties Test Method Specification.

Test Parameter	A	B	C	D	E
<b>Preliminary Tests</b>					
Beam Capacity (lbs)	100	1,000	100	1,000	-
Full Scale Load (lbs)	20/50	500	10	500	-
Crosshead Speed (in/min)	20	2	0.5	10	-
Gauge Length (in)	2	4	5	10	-
Clamp	Pneumatic	Flat	Flat	Flat	-
Jaw Face Size (in)	1 x 1.5	3 x 2	3 x 2	3 x 2	-
<b>Detailed Tests</b>					
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 x 1.5				

A = Polyethylene film  
 B = Strapping tape  
 C = Styrofoam sheets  
 D = Trawl netting  
 E = Balloons

### 2.3.3 Spectroscopy

Reflectance spectra of weathered polystyrene foam surfaces were measured in a Cary spectrophotometer. The infra-red spectra of the same sample in solution was obtained using an Analect FX-6200 FTIR instrument.

### 2.4 Climatic Data

The ambient temperature of the sea water at the location covering most of the period of exposure is shown in Figure 2.1. Air temperatures for the area are those recorded by the National Weather Service for the Beaufort area.

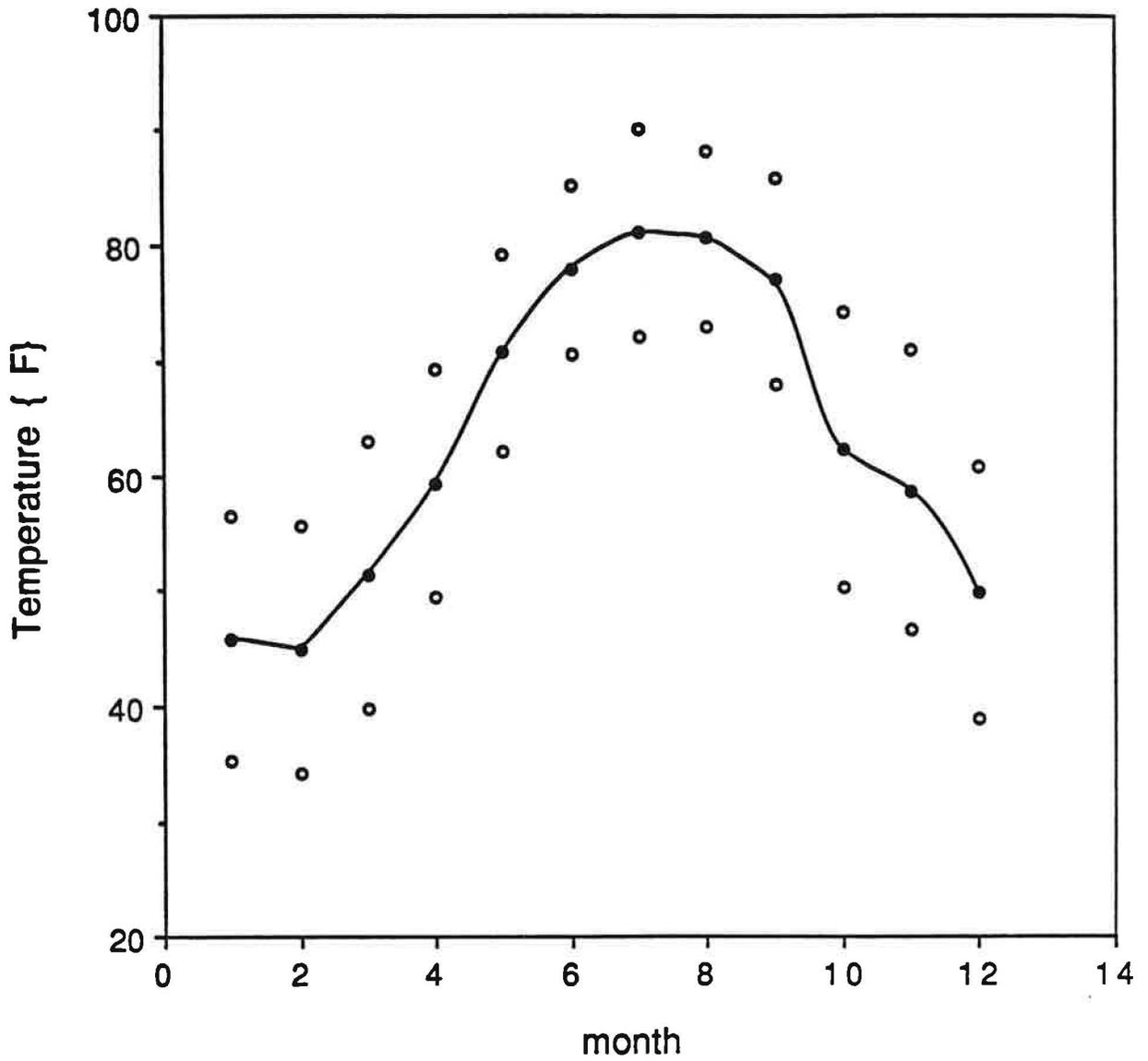


Figure 2.1a. Average Monthly Temperatures (Low, High, and Mean) for Morehead City, NC for 1987.

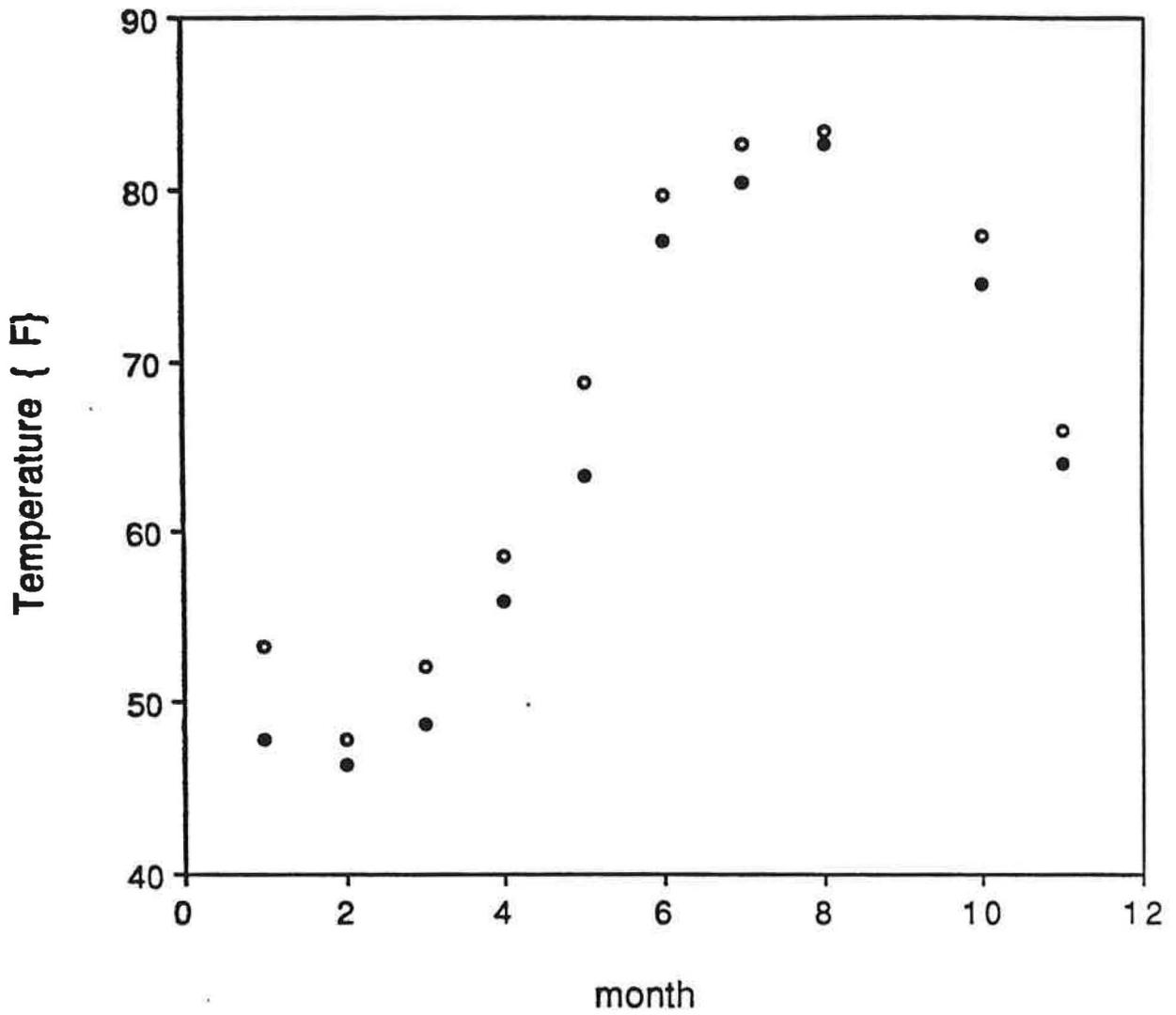


Figure 2.1b. Sea Water Temperature (Low and High) on the First Day of the Month at the Exposure Site.

### 3.0 Results and Discussion

#### 3.1 Preliminary Data

The data included in this section are from exposure experiments conducted in Miami, Florida. Data are available only for a period of one month for most samples and served merely to determine a suitable sampling period for the study.

Table 3.1 gives the tensile properties for the various samples before and after one month's exposure at sea and on land in the Miami area. The sample dimensions used in the calculation of tensile strengths are indicated below the table.

The data indicates that the one month interval for sampling is too short even under Florida exposure conditions in air. The values for the key tensile properties remained essentially unchanged during the month. The small increase in tensile strength on exposure observed for some of the samples may, at least in part, be due to relaxation of stresses frozen into the sample while processing. Processed thermoplastic material often exhibits such "stiffening" during early exposure outdoors.

On the basis of this observation, a two-month sampling interval yielding six samples for each type of sample over the one-year period of exposure was selected for the detailed study.

The data relating to enhanced photodegradable samples exposed during the preliminary study is shown in Table 3.2. As the sampling period selected in this study was two weeks, two sampling periods were included in the one-month experiment. An additional preliminary exposure was carried out under coastal North Carolina conditions to confirm the appropriate sampling interval and for comparison purposes.

The enhanced degradable samples underwent rapid deterioration losing a significant fraction of the original tensile strength during

**Table 3.1. Preliminary Tensile Property Data on Samples Exposed for Zero and One Month.**

Sample Type	Tensile Strength (psi)	Ultimate Elongation (%)	Yield Strength (psi)	Tensile Modulus (psi) x 100
<b>Samples Exposed in Sea Water</b>				
<b>(A) PE Film</b>				
0 month	2613	509	1676	206
1 month	2625	520	1653	211
<b>(B) Strapping</b>				
0 month	28600	122	28600	1530
1 month	28400	124	28400	1320
<b>(C) Foamed PS</b>				
0 month	71	4	71	0.29
1 month	83	6	83	0.24
<b>(D) Trawl web I*</b>				
0 month	32	34	279	162
1 month	30	35	243	147
<b>(E) Trawl web II*</b>				
0 month	26	41	282	100
1 month	30	35	278	144
<b>(F) Balloons</b>	Not tested in preliminary experiment			

Table 3.1. (continued)

Sample Type	Tensile Strength (psi)	Ultimate Elongation (%)	Yield Strength (psi)	Tensile Modulus (psi) x 100
Samples Exposed in Air				
(A) PE Film				
0 month	2613	509	1676	206
1 month	2641	506	1681	214
(B) Strapping				
0 month	28600	122	28600	1530
1 month	28300	124	28300	1210
(C) Foamed PS				
0 month	71	4	71	0.29
1 month	67	3	68	0.30
(D) Trawl web I*				
0 month	32	34	279	162
1 month	30	39	247	161
(E) Trawl web II*				
0 month	26	41	282	100
1 month	27	40	275	102
(F) Balloons Not tested in preliminary experiment				

\* NOTE: In the case of trawl web material which is a braided twine made up of several strands of multifilament fiber, the true area of cross section cannot be easily determined. The tensile strength and modulus is replaced by Breaking Tenacity (gf/tex) and Initial Modulus (gf/tex) for these two samples.

Table 3.1 (continued)

Breaking Tenacity is the tensile force per unit linear density of the unstrained sample. The linear density in "tex" expresses the mass in grams of a kilometer of the twine material.

Sample Type	A	B	C
Sample Thickness (in.)	0.016	0.025	0.194
Sample Width (in.)	0.50	0.447	0.500
Area of Crossection (sq. in.)	0.008	0.011	0.097

The samples D and E had linear densities of 5435 tex and 5523 tex, respectively.

**Table 3.2 Preliminary Tensile Property Data on Enhanced Photodegradable PE Samples Exposed for Zero, Two and Four Weeks.**

Duration (weeks)	Tensile Strength (psi)	Ultimate Elongation (%)	Yield Strength (psi)	Tensile Modulus (psi) x 100
Florida Exposure Conditions (November- December, 1986)				
(a) Samples Exposed in Sea Water				
0	2282	398	1672	198
2	1860	99	1860	231
4	1888	69	1888	236
(b) Samples Exposed in Air				
0	2283	398	1672	198
2	2072	32	2072	229
4	1613	9	1613	250
North Carolina Exposure Conditions (March-April, 1987)				
(a) Samples Exposed in Sea Water				
0	2282	398	-	-
4	1437	16	-	-
6	1392	16	-	-
(b) Samples Exposed in Air				
0	2282	398	-	-
4	1346	8	-	-
6	822	4	-	-

the first week of exposure. Preliminary data strongly suggested the enhancement to take place in samples floating on sea water as well. The sampling period of two weeks appeared to be too long, particularly where the exposure is carried out during the warmer months of the year. For enhanced degradable polyethylene, a weekly sampling period was selected on the basis of the above data.

### 3.2 Weathering Under North Carolina Coastal Conditions

#### 3.2.1 Polyethylene Film Material

The summary of tensile property data for polyethylene samples is given in Table 3.3. Clearly, the samples exposed in sea water degrade at a much slower rate than those exposed in air. The latter set of samples was exposed on a wooden (insulating) backing material. Under such conditions, the heat build-up in the plastic films is likely to be higher than for the case of exposure on soil. The land exposure thus simulated conditions close to weathering under "worst case" conditions.

The average tensile strength of even the samples exposed for one-year floating on sea water showed no statistically significant difference from the average value of the starting (unexposed) polyethylene (t - test,  $t = 5.68$  at  $f=11$ ). This was true also for the ultimate extension values.

Figure 3.1 shows the variation of the average ultimate elongation of polyethylene samples with exposure time for exposures in air and on sea water.

Data on the polyethylene films clearly show that in the one-year period of observation, the samples at sea were virtually unaffected, while the samples exposed in air at the same general location lost nearly 20 percent of the tensile strength and over 95 percent of the ultimate extension over a six-month period.

Table 3.3 Summary of Data Relating to Weathering of Low-Density Polyethylene Film Samples.

Duration (months)	Tensile Strength (kg/cm <sup>2</sup> )			Ultimate Extension (%)			n*
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
<b>(a) Samples Exposed in Air</b>							
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
<b>(b) Samples Exposed in Sea Water</b>							
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

S.D. = Standard Deviation  
 S.E. = Standard Error  
 n\* = Number of Samples

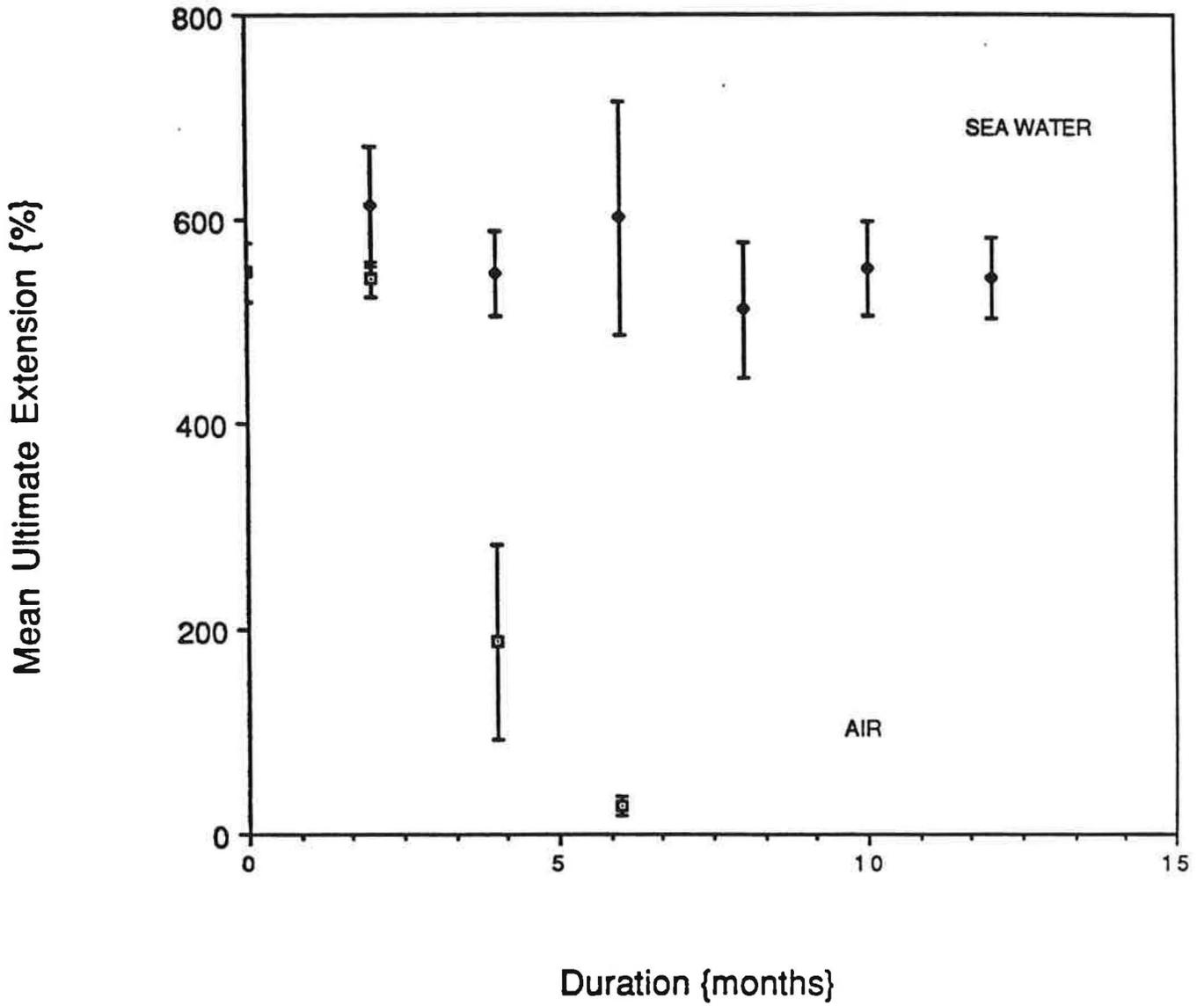


Figure 3.1 The Variation of the Mean Ultimate Extension of Polyethylene Films With the Duration of Exposure.

### 3.2.2 Polypropylene Tape

Table 3.4 gives the summary data relating to the weathering of polypropylene strapping tape under North Carolina exposure conditions. The formulation contained a filler and the material was highly anisotropic, easily tearing along its length. Material did not "neck" on extension, i.e., did not exhibit a sharp reduction in cross-sectional area in one section of the sample, as generally obtained with polyolefins, but ruptured gradually. The ultimate extensions quoted do not correspond to complete rupture of the sample to two sections but to a point of partial rupture. Further extension of the sample after this stage did not change the value of maximum load. As the surface of the material 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. The point of rupture was determined consistently by setting the control parameters in the Instron testing machine.

Samples exposed on land lost over 85 percent of the initial tensile load and over 90% of the initial ultimate extension during a one year period. Those exposed on sea water, however, deteriorated to a minimal extent, retaining almost 75 percent of the original ultimate extension and 89 percent of the original load after a comparable duration of exposure. Figure 3.2 (a & b) illustrates the observed changes in ultimate extension and maximum load.

### 3.2.3 Expanded Polystyrene Foam Material

In view of the abundance of polystyrene foam pieces in marine debris, the weathering behavior of polystyrene is particularly interesting. On exposure in air, the foam underwent rapid yellowing which apparently was a surface reaction. The sample exposed on sea water

Table 3.4 Summary of Data Relating to Weathering of Plastic Strapping Tape.

Duration (months)	Maximum Load (kg)			Ultimate Extension (%)			n*
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
(a) 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
(b) Samples Exposed in Sea Water							
2	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

\* = number of samples

S.D. = Standard Deviation

S.E. = Standard Error

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

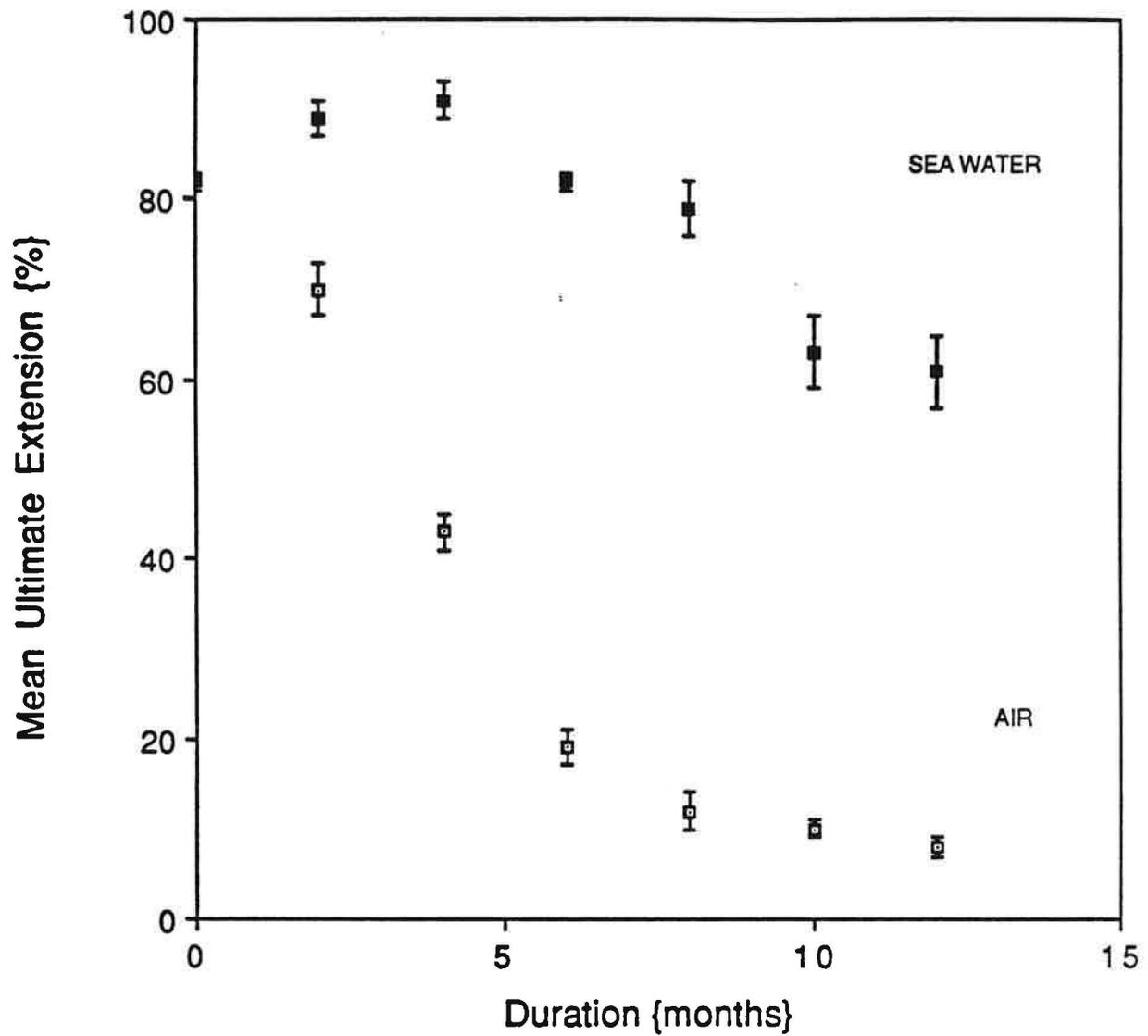


Figure 3.2a. The Variation of the Mean Ultimate Extension of Polypropylene Tapes With the Duration of Exposure.

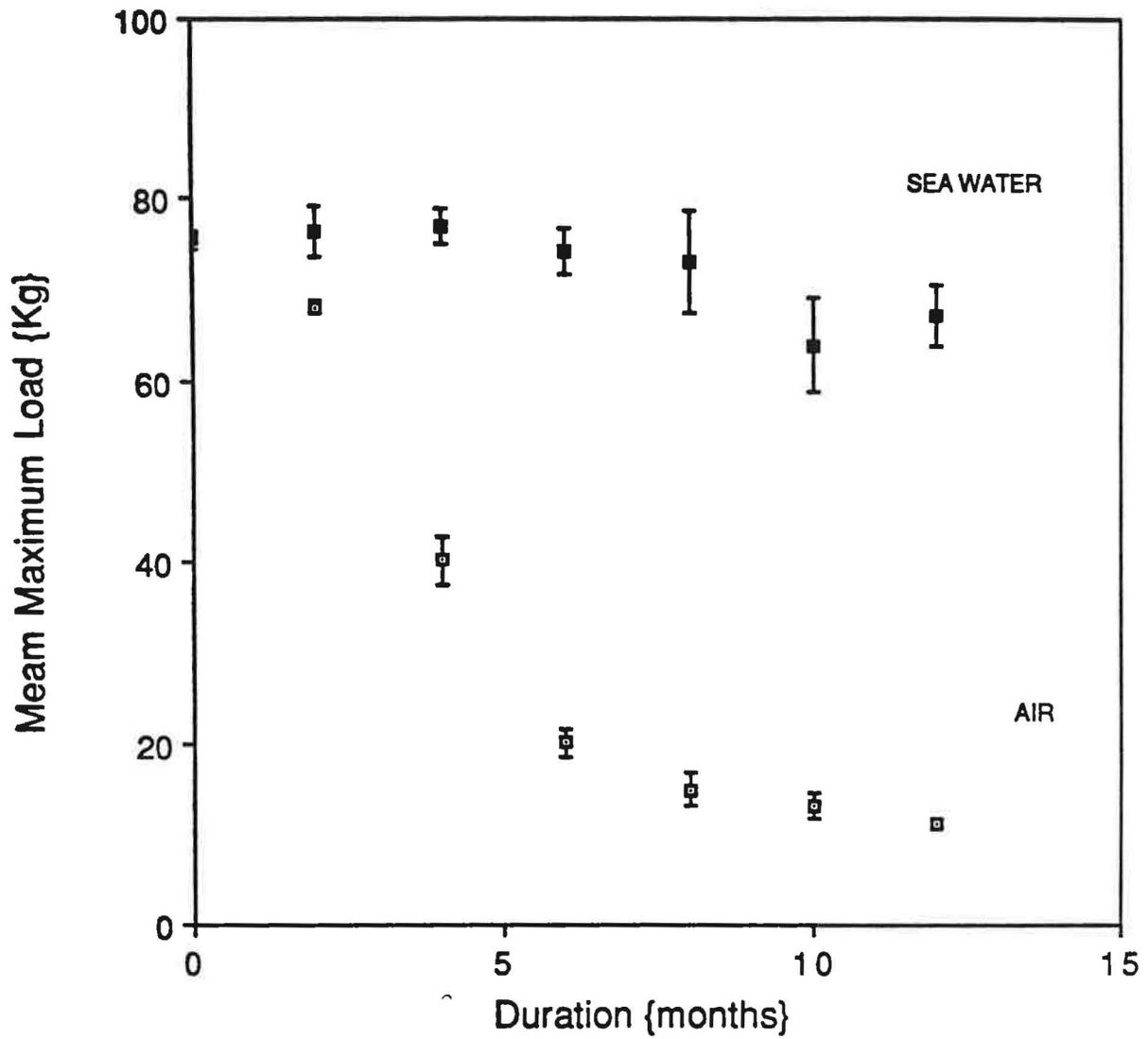


Figure 3.2b The Variation of the Mean Maximum Load of Polypropylene Tapes With the Duration of Exposure.

also underwent yellowing although the algal fouling of the surfaces made it difficult to measure the extent of yellowing. An attempt was made to quantify the extent of yellowing in the case of the samples exposed in air. Colorimetric measurements of the surfaces yielded ASTM Yellowness Index values for samples weathered for different periods of time; L, a, and b are tristimulus color coordinates for lightness, red/green and yellow/blue, respectively. .

Duration (months)	<u>L</u>	<u>a</u>	<u>b</u>	Yellowness Index
0	92.7	-0.08	-0.13	-0.01
2	88.57	-2.99	12.59	23.11
	88.29	-3.11	13.01	23.93
	88.77	-3.13	13.31	24.40
4	89.04	-3.78	14.99	27.16
	88.33	-3.79	1.56	28.49
	88.88	-3.74	15.14	27.54
6	87.23	-3.83	17.26	32.29
	89.18	-3.96	16.24	29.46
	88.19	-3.73	16.11	29.71
10	87.2	-3.50	13.64	25.19
	86.53	-3.30	12.56	23.34
	87.53	-3.42	13.03	23.93
12	83.94	-3.03	14.06	27.46
	84.62	-3.03	13.00	25.00
	84.77	-2.99	13.56	26.17

The yellowness index increases up to about the sixth month of exposure and decreases thereafter. However, the development of yellowness is accompanied by embrittlement of the exposed surface. Over the exposure period of one year, a surface layer of up to half the original thickness becomes brittle enough to crumble on handling (and be easily scraped out). Wind and rain are likely to remove at least some of the yellowed material during exposure.

This may explain, at least in part, the reduction in the extent of yellowing at the longer exposure times.

The tensile strength of the degraded polystyrene foam correlates well ( $r = 0.90$ ) with the Yellowness Index 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, etc.).

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	Thickness of Lower Layer (cm)	
	Air	Sea Water
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

The tensile strength can thus be calculated in two ways, based on original thickness and based on the thickness of the unembrittled layer. Table 3.5 summarizes the tensile property data. The data shows two interesting features.

If the oxidative degradation process was restricted to the yellowed brittle surface layer, the tensile strength of the underlying polystyrene should yield about the same value as that of unexposed starting material regardless of the duration of exposure. However, as seen in

**Table 3.5. Summary of Data Relating to Weathering of Expanded-Extruded Polystyrene.**

Duration (months)	Tensile Strength <sup>a</sup> (kg/cm <sup>2</sup> )			Tensile Strength <sup>b</sup> (kg/cm <sup>2</sup> )			Ultimate Extension (%)			n <sup>a</sup>
	Mean	S.D.	S.E.	Mean	S.D.	S.E.	Mean	S.D.	S.E.	
<b>(a) Samples Exposed in Air</b>										
0	3.89	0.50	0.21	3.89	0.50	0.20	3.9	1.70	0.70	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
<b>(b) Samples Exposed in Sea Water</b>										
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

<sup>a</sup> Tensile strength calculated using the initial area of cross-section.

<sup>b</sup> Tensile strength calculated using the area of cross-section based on residual unembrittled layer.

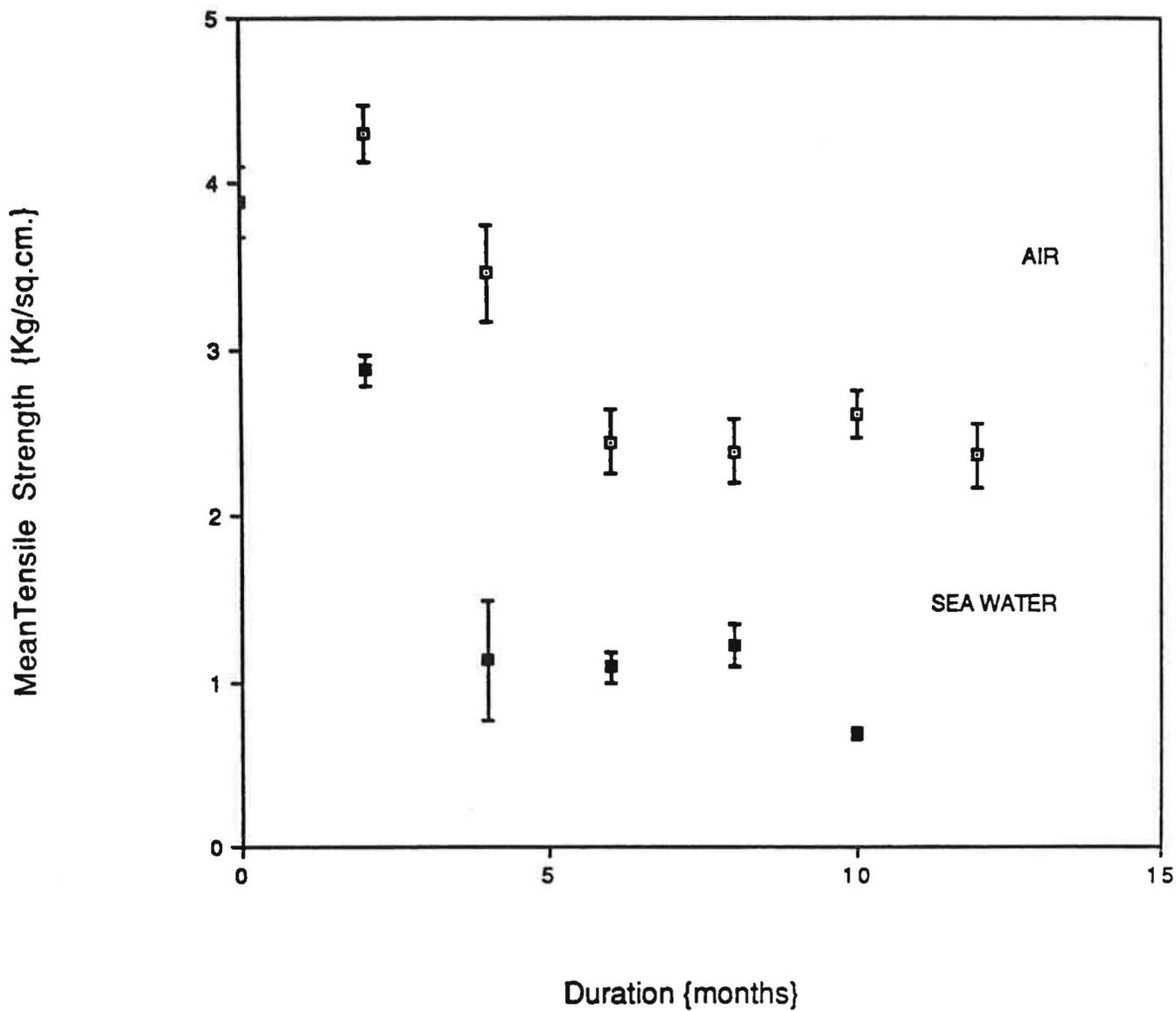


Figure 3.3 The Variation of Mean Tensile Strength of Expanded Polystyrene With the Duration of Exposure.

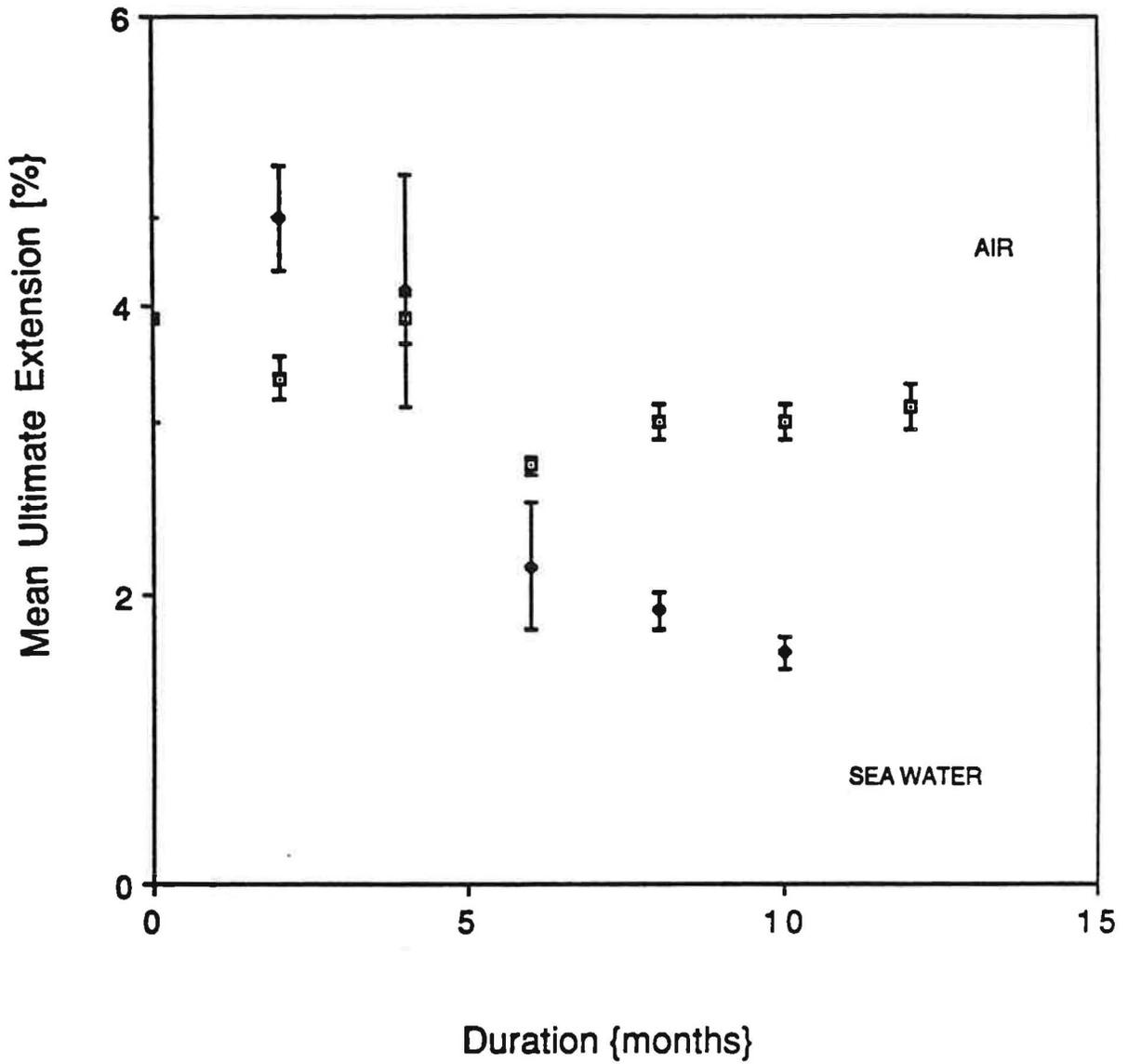


Figure 3.4 The Variation of Mean Ultimate Extension of Expanded Extruded Polystyrene With the Duration of Exposure.

Table 3.5, the tensile strength based on reduced thickness of the material also decreases with the duration of exposure in sea water. The lower unembrittled region is apparently accessible to the reactive species generated during the photo reaction in the case of weathering in sea water but not in air.

Expanded polystyrene is the only type of plastic material tested where the rate of deterioration (of tensile properties) was found to be faster in sea water than on land. In air, the material required an exposure of at least one year to decrease its tensile strength by 40 percent. Exposure in sea water reduced the tensile strength by over 60 percent in four months! In fact, the water-swollen material (the foam absorbs about 1% by weight of water) is likely to be considerably weaker.

This phenomenon is likely to be in part due to the cellular nature of the material. If water enters the void spaces and promotes fouling within them the strength would decrease rapidly in sea water. As the hydrophilicity of the surface layers increase as a result of the photo-oxidation process, the wetting, water sorption and, consequently, the fouling will also increase.

The yellow surface layer formed during photodegradation absorbs highly in the UV region of the spectrum. Consequently, it acts as a protecting filter for lower layers of the polymer. In sea water, however, this layer is likely to be removed continuously, exposing more of the lower layers to photodegradation. This is consistent with the finding that the undergraded layer is thinner for samples exposed in sea water than for those exposed in air, for the same duration of exposure.

In any event, under the present exposure conditions the polystyrene foam material deteriorates relatively rapidly when exposed outdoors on

sea water. This would lead to the breaking up of the material to smaller pieces fairly easily. Unlike in the cases of most other plastic debris items, pieces of foamed polystyrene are not capable of entanglement. They might be ingested by a variety of species especially when covered with foulants. Effects of ingestion of weathered polystyrene foam material are not known.

#### 3.2.4 Rubber Balloons

Latex rubber balloons are considered a hazard, via ingestion, particularly to marine turtles. The strength and extensibility of the rubber balloons determine to a great extent the likelihood of the material obstructing the air or gut passages of turtles. Retention of elasticity is of particular concern, as elastic materials are difficult to dislodge from the air passages or alimentary canals of an animal.

Table 3.6 summarizes the tensile property data on balloons exposed under present experimental conditions. Figure 3.5 (a and b) shows the variation of tensile properties with duration of exposure.

The tensile strength of the rubber quickly falls to about 4 percent of the initial value on exposing for only two months in air. Exposure for a comparable period in sea water achieved a more modest decrease, with the tensile strength falling to about 23 percent of the starting value. Thereafter, the deterioration is slower under both exposure conditions. In the case of exposure in air, the balloons become weak and non-rubbery within six months of exposure. In sea water, however, the balloons retain their elastic nature much longer. The average tensile properties (ultimate strength and extension) of those exposed in

Table 3.6. Summary of Data Relating to Weathering of Latex Rubber Balloons.

Duration (Months)	Tensile Strength (kg/cm <sup>2</sup> )			Ultimate Extension (%)			N*
	Mean	S.D	S.E	Mean	S.D	S.E	
<u>Samples Exposed in Air</u>							
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
8	too brittle/weak to be tested						
10	too brittle/weak to be tested						
<u>Samples Exposed in Sea Water</u>							
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

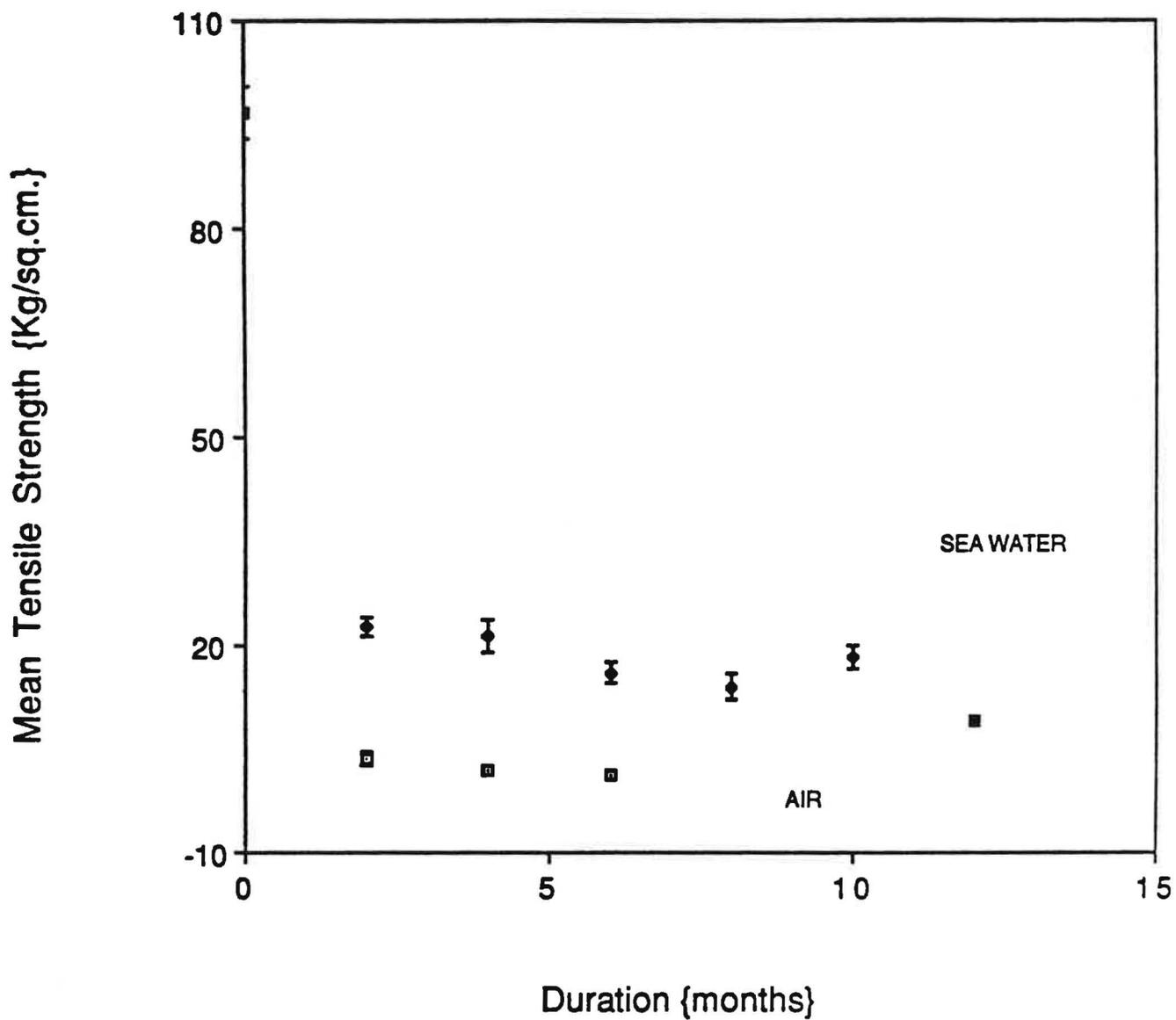


Figure 3.5a The Variation of Mean Tensile Strength of Latex Rubber Balloons With the Duration of Exposure.

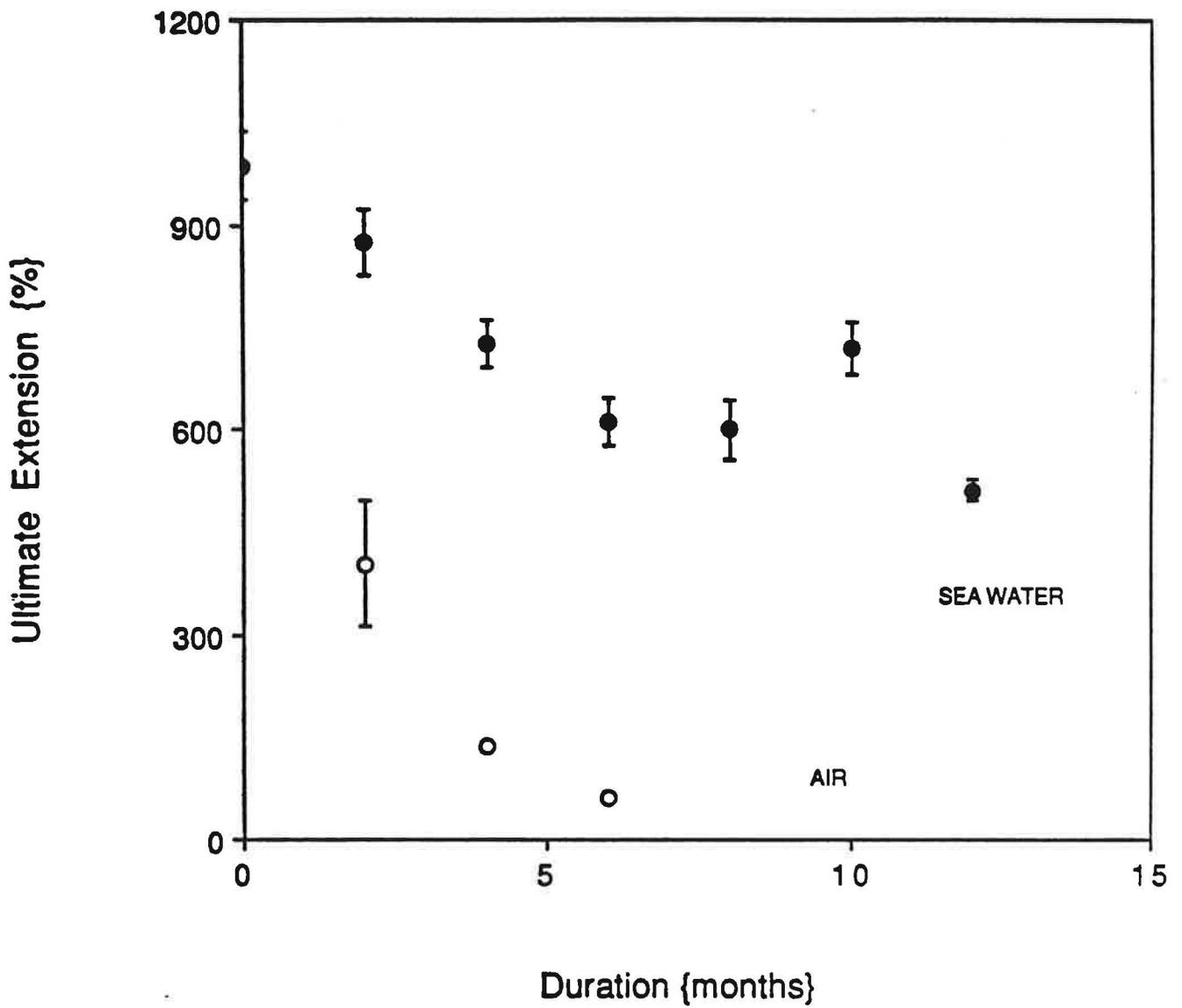


Figure 3.5b The Variation of Mean Ultimate Extension of Latex Rubber Balloons With the Duration of Exposure.

sea water for a year are still much higher than those exposed in air for only two months!

Figure 3.6 shows balloons from both exposure sites and indicates the retention of almost the original physical shape by those exposed in sea water. Heavy fouling by algae and some barnacles is also apparent.

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 pose a hazard to marine life, they would be a threat for a relatively longer period of time at sea than on land, under present experimental conditions.

### 3.2.5 Trawl Netting

Tensile property data for net samples is given in Table 3.7. As explained in an earlier section, tensile data is reported as maximum load (kg), which often coincided with the ultimate load of the material. Ultimate extensions reported are the extensions at which the rupture process began, as detected by the test instrument, and does not correspond to total rupture of the sample.

The data on the netting samples do not show any significant trend in the variation of tensile properties over the one-year period of exposure. As the material is compounded with adequate light stabilizers and designed to endure outdoor exposure, the period of exposure was quite inadequate to even begin to see the changes due to environmental degradation. 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.

Table 3.7. Summary of Data Relating to Weathering of Trawl Web Material.

Duration (Months)	Maximum Load (kg)			Ultimate Extension (%)			N*
	Mean	S.D	S.E	Mean	S.D	S.E	
<b>Orange-Colored Netting</b>							
<u>Samples Exposed in Air</u>							
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
<u>Samples Exposed in Sea Water</u>							
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
<b>Blue-Colored Netting</b>							
<u>Samples Exposed in Air</u>							
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
<u>Samples Exposed in Sea Water</u>							
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

Figure 3.6 Rubber Latex Balloons Exposed Outdoors in Air and in Sea Water for Varying Periods of Time.

					<b>AIR</b>
					
<b>0</b>	<b>2</b>	<b>6</b>	<b>10</b>	<b>12</b>	
<b>MONTHS</b>					



It is suggested that laboratory accelerated weathering studies be carried out to determine the relative rates of degradation for this type of sample in future studies.

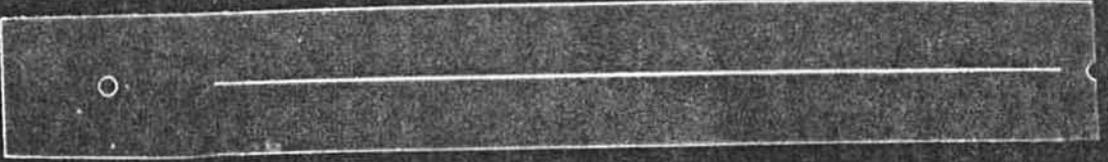
### 3.3 Possible Reasons for Slower Degradation in Exposure on Sea Water

The marked retardation of the weathering process observed in some types of plastic materials floating in sea water might be attributed to: (a) differences in heat build-up; and (b) fouling of samples in sea water.

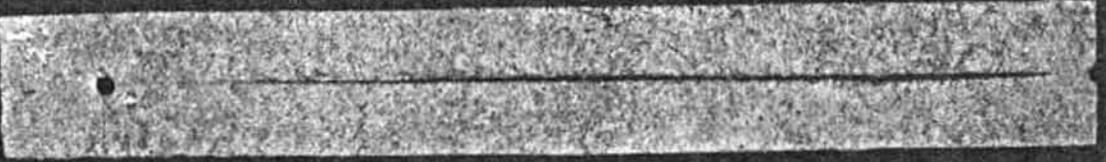
A significant fraction of the sunlight impinging on a plastic surface is absorbed by the material as heat. Depending on the nature of the plastic, the velocity of the air around it, and the temperature difference between the plastic and the surroundings, this absorbed energy maintains the plastic at a temperature higher than that of the surrounding air. As was pointed out earlier, the effect is even more pronounced in the present samples which were exposed on a thermally insulating wood surface. Increased temperatures tend to accelerate the degradation process.

Samples floating on sea water underwent extensive fouling during the exposure. Figure 3.7 illustrates the extent of fouling observed on polyethylene samples. No attempt was made to identify the foulant species involved. 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 involved the containment of samples in a shallow tank. This is likely to have reduced the extent of fouling and prevented the settlement of debris (or "silting") on the sample surface.

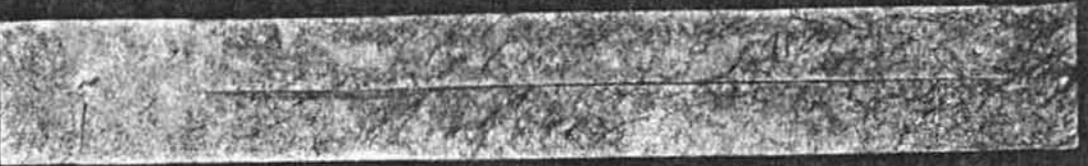
Figure 3.7 Fouling of Polyethylene Strips on Exposure to Sea Water.



0  
Months



2  
Months



4  
Months



The determination of the relative importance of the two factors (heat build-up versus fouling) in retardation of photodegradation of plastics at sea is important but beyond the scope of the present study. This key piece of information will indicate if the degradation of plastics at sea is affected significantly by biological factors (such as the occurrence of an algal "bloom").

#### 3.4 Enhanced Degradable Polyethylene

Enhanced photodegradable low density polyethylene, based on carbon monoxide-ethylene copolymers, is currently commercially available through several suppliers. The ketone moiety might be incorporated also as a side chain using vinyl ketone instead of carbon monoxide as the comonomer. Ketones absorb in the ultraviolet region of the solar spectrum and undergo facile photolysis via Norrish type I and type II mechanisms, with the latter often predominant at ambient temperatures (Guillet et al., 1972). The chemical pathways involved are similar to those in polyethylene homopolymer or other saturated hydrocarbons, where the formation of ketone groups during early oxidation and their role as chromophores is well known. Several studies indicate that the partially photodegraded ethylene copolymer of reduced molecular weight might be more susceptible to biodegradation in the soil.

The rate at which light-induced deterioration of the polymer takes place will depend mainly on the available direct or scattered ultraviolet light and the temperature. A primary obvious requirement for enhanced photodegradability at sea is, therefore, that the material float in sea water, as even a few meters of water strongly attenuate ultraviolet light. Availability of light for the photoreaction, however, might be restricted by rapid biofouling of plastic surfaces at

sea. Within hours of immersion, a microbial film covers the immersed surfaces. Within a few weeks of coastal exposure, depending on the season of the year, a moderate to heavy growth of algae becomes apparent. The process may continue with eventual colonization of the surface by macrofoulants, such as barnacles. Fouling gradually restricts the light available for photodegradation. The net effect of the fouling process on enhanced photodegradation at sea will depend eventually on the relative rates of the two processes. It is not unusual to observe plastic debris, such as films and tapes, eventually sinking under the weight of the foulants and the other debris they entrap.

The tensile strength of the enhanced degradable LDPE rapidly decreased during early exposure, falling by nearly 25 percent of its initial value in one week of exposure in both air and in water. Figure 3.8 shows the change in the average tensile strength with time. Within five weeks of exposure, the samples exposed in air were embrittled to the point that handling and attempted testing resulted in brittle failure. Samples floating on sea water, however, had to be exposed for nearly 15 weeks to obtain about the same degree of embrittlement. The tensile strengths in the latter case stay remarkably constant over a period of 2-3 months before eventually decreasing. The numerical values are given in Table 3.8.

The ultimate extension data shown in Figure 3.9 shows a very sharp drop in ultimate strength after only a week's exposure in air and on sea water, indicating the material to lose most of its extensibility during the early photooxidation. While the data does indicate that the loss of extensibility is marginally more rapid in air, there is little doubt that the enhanced degradation process did take place in sea water under the present exposure conditions. Unlike the samples exposed in air,

Table 3.8: Summary of Data on Outdoor Weathering of Enhanced Photodegradable Six-pack Ring Material (LDPE).

Duration (Weeks)	Tensile Strength (kg/sq. cm)		Ultimate Extension (%)	
	Mean	S.E	Mean	S.E
<u>Exposure in Air</u>				
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
<u>Exposure 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
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	1.6	19.1	1.0
7	122.9	0.8	21.0	3.1
8	121.1	0.4	17.7	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

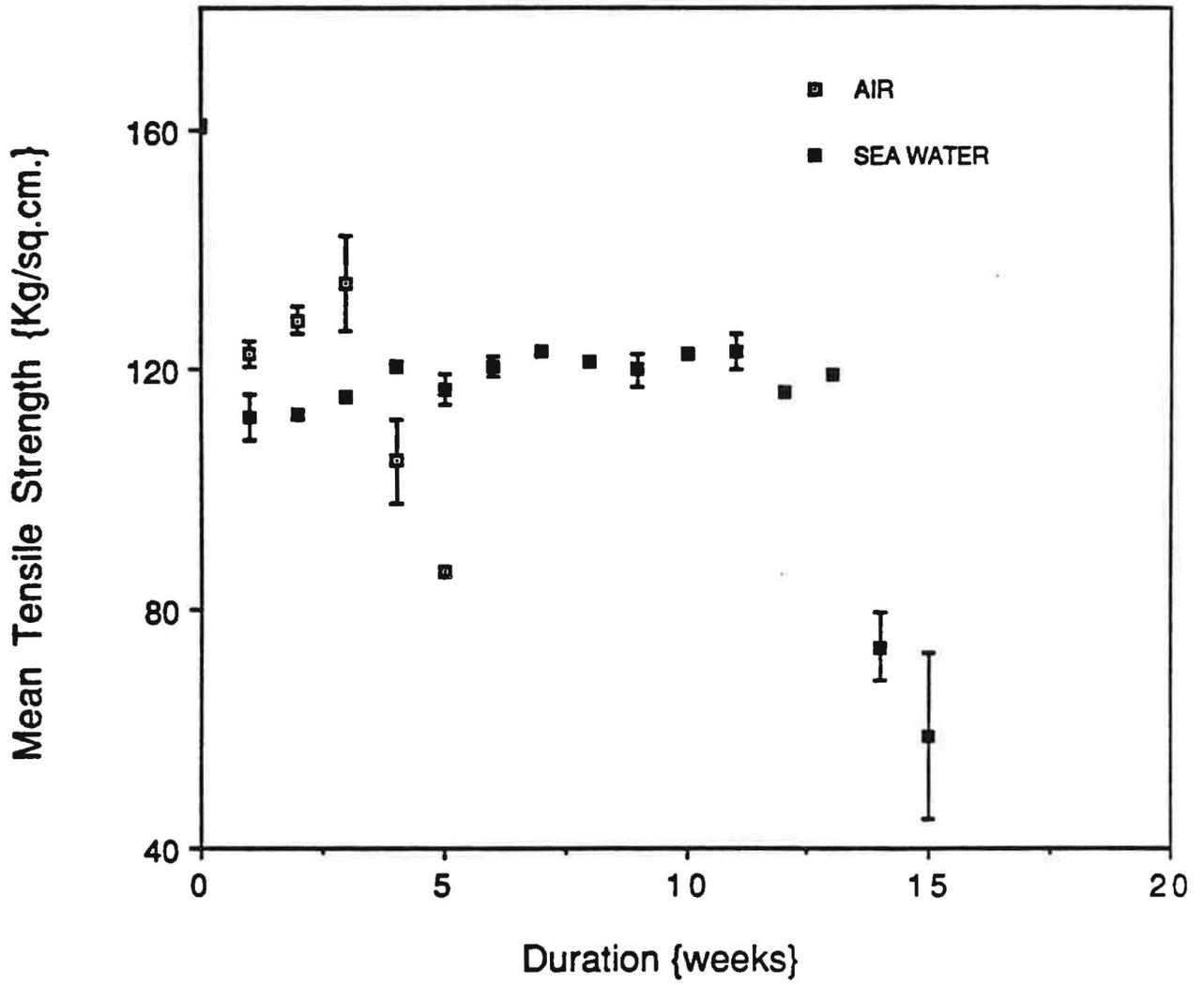


Figure 3.8 The Variation of Mean Tensile Strength of Enhanced Degradable Polyethylene Sheets With the Duration of Exposure.

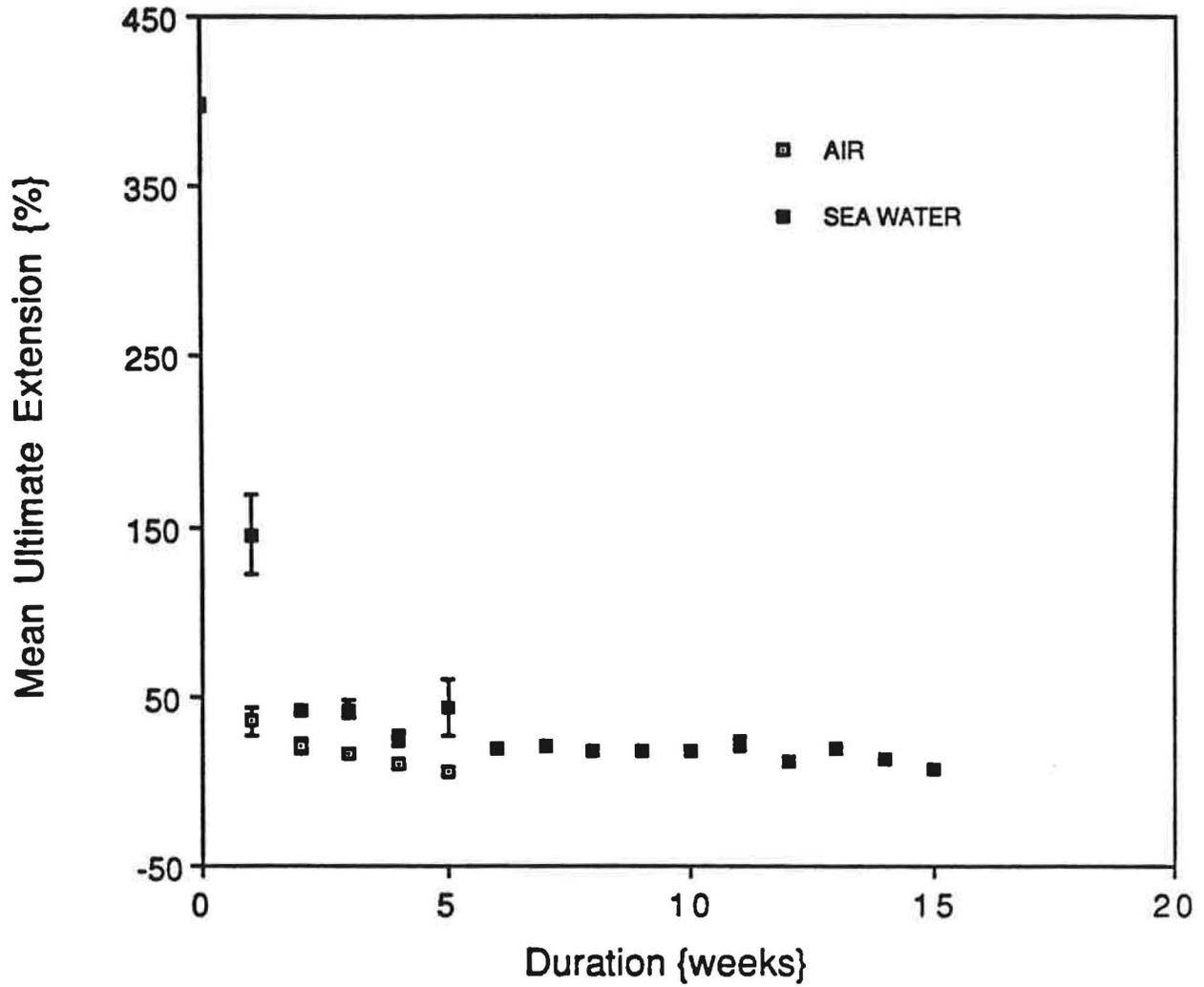


Figure 3.9 The Variation of Mean Ultimate Extension of Enhanced Degradable Polyethylene Sheets With the Duration of Exposure.

those on water survived for a longer period of time (allowing sampling up to 15 weeks), possibly due to the algal covering on their surfaces which added to their physical integrity. The polyethylene in water may also have absorbed very small amounts of moisture due to the accumulation of polar oxidation products within the matrix. Consequent plasticization of the film may also have reduced its brittleness and fragility.

Tensile strength (measured in uniaxial extension) alone is not a good indicator of the fragility of the plastic. Bending or twisting of even the moderately degraded polyethylene material was found to result in rupture in spite of the moderate extents of retention of tensile strength. Where the six-pack rings pose a threat of entanglement of marine or other animals, the degree of severity of the threat depends upon the ease of escape of the animal, presumably via rupture of the plastic film. The stresses involved are complex and do not necessarily resemble those associated with uniaxial extension.

The results illustrate this particular technique to perform well for polyethylene sheets floating in sea water under North Carolina exposure conditions. It is prudent to carry out additional outdoor exposure tests and accelerated weathering studies, to determine the extent to which climatic/ biological factors affect such performance, before generalizing the result to other geographical locations.

### 3.5 Summary of Exposure Studies

Table 3.9 illustrates the general findings of the exposure study by a comparison of tensile properties before and after exposure in air and in sea water. Data relating to a single duration of exposure (usually the largest) is shown and is sufficient to illustrate the trend.

Table 3.9: Comparison of Weathering Data for Exposure on Land and at Sea.

Sample	Duration of Exposure	Percent Decrease in the Mean Value of Tensile Property			
		Air		Sea Water	
		Strength#	Extension	Strength#	Extension
Polyethylene Film	6 months	6.6	95.1	no change	no change
Polypropylene Tape	12 months	85.0	90.2	11.0	31.5
Latex Balloons	6 months	98.6	93.6	83.5	38.0
Expanded Polystyrene	10 months	32.9	18.0	82.3	65.2
Netting	12 months	no change	no change	no change	no change
Rapidly Degradable Polyethylene	1.25 months	46.2	98.6	27.1	88.9

\*The percentages reported are based on the maximum load in the case of netting and polypropylene tape materials.

In four of the six types of material tested, rates of degradation for the samples in sea water were much slower than the degradation rates on land. The differences were quite marked. Expanded polystyrene was the exception, degrading faster in sea water than on land. Netting material did not show any significant variation in tensile properties due to the type or duration of exposure.

#### 4.0 Environmental Degradation of Relevant Plastic Materials

Polyolefins and polystyrene have been identified as the major classes of plastics associated with marine debris. The following are some products made from these plastics and reported as components of debris:

Polystyrene: Expanded polystyrene pieces  
Floats (gill nets)  
Cups made from expanded polystyrene  
Plastic cutlery

Polyolefins: Trawl webbing  
Plastic strapping  
Six-pack carriers  
Plastic bags  
Tampon applicators

Polyolefins of particular interest are the polyethylenes and polypropylenes. The term "polyethylene" merely identifies the chemical nature of the polymer but does not uniquely specify the material. There are, for instance, a variety of polyethylenes differing in density, physical properties, and cost. Three main classes of polyethylenes, based on the differences in density (a consequence of the macromolecular structure), are as follows:

<u>Type</u>	<u>Symbol</u>	<u>Density</u>
Low density	LDPE	0.915 - 0.930
Linear low density	LLDPE	0.915 - 0.940
High density	HDPE	0.960 - 0.970

Low density polymer (LDPE) is mostly used in the fabrication of packaging films, refuse bags, six-pack rings, etc. Packaging film accounts for about 2/3 of the US market for low-density polyethylene. Some LLDPE is also used in the manufacture of films.

The main chemical pathways involved in the photodegradation of these polymers and the products formed from the various degradation reactions will be reviewed in this section.

#### 4.1 Polyethylene and Polypropylene

Several excellent reviews on the photodegradation of polyolefins have been published (Carlsson & Wiles, 1976, McKellar and Allen, 1979, Winslow, 1977, and Allen, 1983).

Oxidative degradation of polyethylene, as well as polypropylene, is a free radical, autocatalytic process. The free radicals formed mainly by the unimolecular or bimolecular decomposition of hydroperoxides act as initiators. The peroxy radicals are able to abstract labile hydrogens from the macromolecular chain. The resulting alkyl radicals react with available oxygen to form peroxy radicals. In the presence of oxygen and hydrocarbon polymer, this propagation sequence can be repeated numerous times, often associated with a chain-scission reaction. Termination occurs by radical pair interaction occurring in a fast reaction.

The initial photo or thermal oxidation reactions result in the chemical modification of the polymer chain itself. During the latter stages of oxidation, particularly at high temperatures (e.g., 150°C-280°C), a variety of volatile compounds have been observed. As the concentration of volatile products generated during ambient temperature thermo-oxidative degradation is very low, identification of such products often requires high-temperature oxidation experiments. However, the mechanisms of oxidation reactions at ambient temperatures may not be very different from those obtained at moderate temperatures. Therefore, at least qualitatively, Table 4.1 (Hoff et al., 1982) indicates the general nature of degradation products of thermooxidation of polyethylene. The data is in agreement with those reported earlier by Matveeva et al., 1963.

The most abundant group of compounds found were fatty acids, followed by aldehydes (formaldehyde and acetaldehyde, in that order). In

Table 4.1: Volatile Products from Thermooxidation of Polyethylene.

Product	$\mu\text{mol/g}$ of polymer at 280°C in 4 mins.	
	LDPE	HDPE
<u>Aldehydes</u>		
Formaldehyde	59.3	88.3
Acetaldehyde	44.3	30.7
Propanal	6.4	5.3
Butanal	9.7	7.5
Pentanal	6.3	6.5
Acrolein	5.0	6.4
<u>Ketones</u>		
Acetone	4.3	4.6
Methylethylketone	4.4	8.9
2-Pentanone	3.4	7.2
<u>Acids</u>		
Formic	75.0	106.5
Acetic	23.3	30.0
Propionic	9.4	9.7
<u>Lactones</u>		
Butyrolactone	3.4	5.3

Taken from Hoff et al., 1982.

contrast to these data on oxidation at 280°C, that for milder oxidation at 150°C is reported to yield aldehydes, especially acetaldehyde, as the (or one of the) major volatile products (Spore et al., 1972; Barabas et al., 1976). Some of the discrepancies might be explained in terms of limitations imposed by the different analytical techniques used in the three studies, but the conditions under which the oxidation was carried out also probably played an important role in determining the course of the chemical reactions involved. The mechanism of formation of different products is discussed elsewhere (Hoff et al., 1981).

Polypropylene thermooxidation pathways are not too different from those for polyethylene. Thus, not surprisingly, the volatile products evolved are also similar. The data for the polymer oxidation at 220-280°C for 2 minutes are given in Table 4.2 (Frostling et al., 1984). Aldehydes are clearly the main class of volatiles, with acetaldehyde as the major product. Ketones, the second major group of volatiles at these relatively high temperatures, may, in fact, be the major class of volatile products under lower temperature oxidation conditions at 120-140°C (Barabas et al., 1978).

Shimura (1978) studied the products of outdoor weathered polypropylene by vacuum distillation of weathered samples at 100°C to obtain the residual volatiles (most, such as the low molecular weight aldehydes, would have volatilised during exposure). His technique yielded acetic acid, propionic acid, and formic acid as the major products.

#### 4.2 Polystyrene

The products of thermooxidative degradation of polystyrene are also reported for oxidation at relatively high temperatures of >200°C. Hoff et al., 1982, reported benzaldehyde, styrene, benzoic acid and acetophenone to be the major volatile products, as shown in Table 4.3.

Table 4.2: Volatile Products from the Thermooxidation of Polypropylene.

Compound	mg/kg of Volatile Product At:	
	220°C	280°C
<u>Aldehydes</u>		
Formaldehyde	480	12,100
Acetaldehyde	1,100	22,900
Methylacrolein	390	8,820
<u>Ketones</u>		
Acetone	700	12,350
Acetylacetone	600	5,500
2-pentanone	120	2,800
<u>Acids</u>		
Formic	-	2,600
Acetic	560	12,800
<u>Alcohols</u>		
Methanol	-	230
2-methyl-2-propen-1-ol	-	200
<u>Water</u>	48,600	954,000

Only the major products are indicated in the table. (Taken from Frostling et al., 1984.)

Table 4.3: Volatile Products from Thermooxidation of Polystyrene.

Product	$\mu\text{g/g}$ Of Products Formed During 10 Minutes	
	250°C	197°C
<u>Aldehydes</u>		
Benzaldehyde	2300	130
Acrolein	-	50
Cinnamaldehyde	55	-
<u>Acids</u>		
Benzoic acid	570	-
<u>Ketones</u>		
Acetophenone	380	450
<u>Alcohols</u>		
2-phenyl-2-propanol	-	700
Phenol	120	-
<u>Oligomers</u>		
Dimer	110	-
<u>Aromatic Hydrocarbons</u>		
Styrene	740	7800
Isopropyl benzene	<10	190
Alpha methylstyrene	29	120
Ethylbenzene	24	56
<u>Other Hydrocarbons</u>		
4-vinyl-1-cyclohexene	-	82

NOTE: Only those products which exceeded a yield of 50  $\mu\text{g/g}$  of polymer are indicated in the table. (Taken from reference Hoff et al., 1982.)

The reported data are in agreement with those of Shimura (1978) who found benzaldehyde and acetophenone to be the primary volatiles from photodegraded polystyrene. Since the latter samples were analyzed after photoexposure in a weatherometer, the lower molecular weight volatiles were not detected in the analysis (presumably lost via volatilization during exposure).

#### 4.3 Significance of Reported Data

A review of the literature shows that the information available on the volatile products of thermooxidation of polymers is somewhat limited. In contrast, compositional changes of the polymer molecule itself, resulting from thermooxidation, are emphasized in research literature. In most applications, the changes caused to the polymer by photooxidation are of greater interest than the volatiles evolved during the reaction. Furthermore, trapping and identifying the very low levels of volatiles generated during ambient temperature polymer oxidation is a difficult task. Consequently, even the few reports on the subject are based on higher-than-ambient temperature thermooxidation, where the types and the yields of products might be somewhat different than those obtained under ambient conditions.

In fact, some of the data presented above illustrate such differences. While under ambient conditions, in thin sections of polymer, the oxygen diffusion is not the rate determining step, the process might become diffusion controlled at higher temperatures where the rates of oxidation are rapid. This can easily lead to chemical pathways and products not typical of ambient temperature oxidation.

The generation of secondary products from thermooxidation of the primary volatiles also presents a major source of error in all these studies. Products from thermooxidation, including those functional

groups bound to the polymer, are often more readily oxidized than the original polymer itself. Thus, especially at high temperatures, these secondary oxidation reactions probably contribute heavily to the product stream.

In contrast to the virgin polymers, the post consumer plastic debris is compounded and processed. The presence of various compounding ingredients in the formulation may alter the chemical pathways.

Finally, the reported data specifically relates to oxidation under terrestrial exposure conditions. Studies relating to marine exposure are virtually nonexistent. At least in the case of plastics floating on water, the photo and/or thermal oxidation takes place at lower temperatures relative to exposure on land. In the latter case, the plastics reach higher-than-ambient temperatures due to heat build up. To be useful in marine ecological studies, low-temperature oxidation conditions must be maintained.

In view of the variability in reported data and the above considerations, an exhaustive compilation of the literature data, relating to the products, was considered unnecessary. There is a clear lack of useful data on ambient or low-temperature oxidation products for the plastics under study.

## 5.0 Conclusions

1. In general, the plastic/rubber materials, with the exception of netting samples and the foamed polystyrene sheets, were found to deteriorate much slower in sea water than on land during one year of exposure under North Carolina conditions. The netting material showed no significant change in either air or sea water exposure during the one-year period. The extruded, expanded polystyrene samples, in fact, showed a faster rate of degradation in sea water than on land during one year of exposure under North Carolina conditions.
2. Enhanced photodegradable six-pack ring material currently marketed was found to perform effectively when the material is exposed on land as well as on sea water, under North Carolina conditions.
3. While the scientific literature indicates the nature of primary volatile products formed during oxidation of commodity thermoplastics, these data are of limited relevance to oxidation under marine exposure conditions.

### 5.1 Suggestions for Future Studies

Currently, available analytical techniques are capable of identifying low-level volatiles typical of those reported for polymer thermo-oxidation. Even under low temperature conditions, such analysis should be feasible, particularly for catalysed systems. In the case of photo-oxidation studies, increased light availability at even ambient temperatures should generate sufficient concentrations of volatile products to allow a reliable analysis to be carried out.

1. A study of the volatile products formed and leached out into water during the photooxidation of typical plastic materials

under marine conditions is proposed. The study should address both the regular and enhanced degradable plastics. Toxicological studies relating to the volatiles in question, reported in the literature, are generally not suited for use in sea-related studies. Since most reported work relates to occupational health of plastic industry employees, the toxicological screening is based on terrestrial species. Parallel studies employing marine species are not available.

2. A determination of the toxicology of selected organic compounds, based on the above study, with emphasis on marine biota, is proposed.

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