WEATHERABILITY OF ENHANCED-DEGRADABLE PLASTICS

by

Anthony L. Andrady
Research Triangle Institute
Research Triangle Park, NC 27709

Contract No. 68-02-4544

Work Assignment Manager

Walter E. Grube, Jr.
Waste Minimization, Destruction and Disposal Research Division
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

DISCLAIMER

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions,

The Risk Reduction Engineering Laboratory is responsible for planning, implementing and managing research, development and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the research and the user community

This publication is a result of co-funded research between the Office of Research and Development and the Office of Solid Waste. The purpose of this project was to assess the performance of several enhanced degradable plastic materials under a variety of different exposure conditions.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

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ABSTRACT

The main objective of this study was to assess the performance and the asociated variability of several selected enhanced degradable plastic materials under a variety of different exposure conditions. Other objectives were to identify the major products formed during degradation and to assess the preliminary toxicity of such products, and to determine the effect of the enhanced degradable plastic material on the quality of recycled products.

Several commercially available materials, including both photodegradable and biodeteriorable plastics were chosen for inclusion in this study. Exposure scenarios consisted of outdoor direct exposure, soil burial, and marine and freshwater exposure. Laboratory exposure scenarios consisted of accelerated weathering and lab accelerated soil burial.

Results of this study showed the elongation at break and the energy to break to be the test parameters most sensitive to weathering induced changes.

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ACKNOWLEDGEMENT

SECTION 1.0

INTRODUCTION

1.1 BACKGROUND

The use of plastics in packaging and in other consumer applications invariably leads to a growing fraction of post-consumer plastic waste in the municipal solid waste stream and in urban litter. The United States presently generates about 160 million tons of municipal solid waste annually, of which about 8 percent by weight is plastics [Franklin Associates, 1988; USEPA, 1991]. On a volume basis, however, the value is higher, about 20-25 percent [Modern Plastics, April 1990]. Since litter is generally perceived more readily in terms of volume, the latter figure is probably of greater relevance. The proliferation of plastic waste is related to the useful lifetimes (or the periods of utility) of the consumer plastic products. Disposable plastic products with short useful lives, such as packaging, therefore constitute nearly one third of the plastic waste in the municipal solid waste stream [USEPA, 1990]. The large fraction of packaging materials designed for single use (fast food containers, plastic cups, plastic bags, food wrappers, beverage bottles and bottle caps) further exacerbates the situation. Even those packaging products designed for multiple use do not have useful lifetimes comparable to those of durable plastic goods.

The present interest in plastic waste is driven not merely by aesthetic considerations but also by ecological and economic concerns. The available volume of landfill space is rapidly depleting in most regions of the country [USEPA, 1988; USEPA, 1989]. Landfilling is by far the primary means of solid waste disposal, and the growing shortage of available volume of landfills in the United States will have a serious effect on future waste disposal practices. A particularly visible fraction of post-consumer plastic waste is urban litter. The unacceptability of litter, particularly the plastic litter, on purely aesthetic grounds has been discussed since the early seventies when the problem of waste plastics first surfaced [Guillett, 1973; Jensen et al., 1974].

Over the recent years a growing body of scientific data suggesting that plastic waste may be hazardous to wildlife has been gathered. This is especially true in marine environments where many instances of entanglement of several species in plastic debris such as netting and six-pack rings have been reported. Sea lions [Loughlin, 1986] and fur seals [Henderson, 1985; Bonner,1982] are particularly susceptible to entanglement in plastic waste. Not only do these species concentrate about vessel routes (possibly because of food waste discharged from ships), but the young animals are specifically attracted by floating colored plastic material, increasing the probability of encounter with debris [Laist, 1987].

Entangled animals may on occasion free themselves, but the episode, at least in some species, may result in changes in feeding habits and slower growth rates [Feldkamp, 1985]. Entanglement can also be permanent, with the animal swimming about with a "collar" of plastic restricting its growth and eventually leading to its death by asphyxiation.

At least fifty species of marine birds are known to ingest plastics [Day, 1980]. While the effects of ingesting plastic waste, including virgin resin pellets, are not definitely known, ingestion is believed at least to reduce the urge to feed. Turtles [Balazs, 1985], too, ingest plastic, particularly floating plastic bags probably mistaken for jellyfishes, a staple of these species. Large amounts of plastics have been observed in the stomach contents of turtles drowned and washed ashore.

1.2 RATIONALE FOR ENHANCED DEGRADABLE PLASTICS AND IMPACT ON WASTE MANAGEMENT

Plastics are perceived to be persistent and non-degradable unlike other constituents of the solid waste stream, particularly nature's own polymers such as cellulose, chitin, and proteins. Rates of degradation of natural materials such as plant and animal tissue might be a reasonable guide to ecologically "acceptable" rates of environmental degradation. If synthetic thermoplastic materials can be designed to break down into innocuous products in the environment at rates matching or exceeding the rates for naturally occurring polymeric materials, the synthetic material would presumably be equally environmentally acceptable.

Enhanced degradable plastics technology strives to accelerate the breakdown of plastic material by chemical modification of the polymer, synthesis of new thermoplastics which are environmentally degradable, and incorporation of additives into commodity plastic materials to achieve faster breakdown. Several different classes of such plastics have evolved over the years, and these claim enhanced degradability in sunlight, under soil, in sea water (or marine sediment), and under composting conditions.

From a practical standpoint this category of materials might be expected to have the following impacts on solid waste management.

(a) Litter reduction. The lifetime of litter will be reduced, thus reducing the cost of litter collection and disposal. In this role the degradable plastics can bring about the same benefits as source reduction, if the lifetime of litter will be shortened to an extent to make collection unnecessary.

(b) Marine plastic waste. There is no mechanism by which plastic waste is removed from the marine/estuarine environments. Collection and disposal is often impractical. In the absence of alternative strategies, the degradable plastics might play a role in addressing this need.

(c)   Composting. Mechanical sorting of the solid waste prior to composting is both costly and time consuming. If plastic films and containers can be left in the composting stream, it represents a substantial cost saving. Enhanced degradable plastics may therefore be desirable in a composting operation. The same is true of anaerobic digestion processes as well.

(d)   Landfills and sewers. These essentially anaerobic environments do not affect plastics. Consequently even natural products such as food wastes and yard wastes as well as cellulosics undergo very slow breakdown under landfill conditions (Rathje, 1987). Containment of organic waste capable of ready degradation in an enhanced degradable plastic material might in some instances hasten the plastic's breakdown in a landfill.

Figure 1.2.1 summarizes the fate of plastics waste and the impact of Enhanced Degradable Plastics on current solid waste management practices. The present emphasis in the area of municipal solid waste disposal is heavily placed on landfilling. Mainly due to economic factors, future disposal strategies are likely to rely more heavily on incineration, composting, and anaerobic treatment. Recycling, while certainly a helpful strategy, is essentially a means of extending the useful lifetime of the plastic by a limited extent and is not a means of disposal. It may, however, move the plastic material from the packaging category into one which has a longer period of utility, easing the burden on the waste stream. Success in recycling depends to a great extent, unfortunately, on large-scale, consistent public participation as well as on identification of markets of adequate size for the recycled product.

1.3   BARRIERS TO WIDER ACCEPTANCE OF ENHANCED DEGRADABLE PLASTICS

While several enhanced-degradable plastic formulations are currently available in the market, their use in large-volume applications remains limited. The six-pack ring material made of (ethylene - carbon monoxide) copolymer and the agricultural mulch films using different photodegradable polymer technologies are about the only large-volume applications at the present time.

The slow growth and acceptability of the technology might be directly attributed to lack of information on the nature, performance, and limitations of this technology. Specifically, there are several key issues which have not been fully resolved. In most cases, their resolution requires scientific information not as yet available from either the manufacturer or from other sources. Due to the limited resources of smaller companies, and also to the perceived small market size for their degradable plastics products, the manufacturers often

cannot afford to carry out the studies required to fully explore this technology. These issues are listed below.

Issue I: Confusions in Terminology

There is no consistent terminology to accurately describe a given category of enhanced degradable plastics. The technical literature on the subject often uses inaccurate and make-shift descriptive terms. Manufacturer's trade literature does the same, using terms which may potentially mislead the consumer.

A primary concern is the extent to which the environmental disintegration of a product needs to be accelerated before the plastic material may appropriately be described as being enhanced degradable (or controlled lifetime). For instance, even the addition of regular compounding ingredients and the processing of the resin itself can (and often do) increase its degradability. Such cursory increases, however, should not qualify the material as an enhanced-degradable plastic. A well defined enhancement factor for different types of enhanced-degradable plastics, compared to a control plastic, needs to be eventually established to adequately define the term.

The related issue is that of classification. The main confusion seems to arise from the inconsistent use of the "bio" and "photo" prefixes and careless use of the term "degradation". The naming of a given technique is best based on the primary, predominant mechanism and not on the resulting secondary processes. (Thus, the rapidly disintegrating six-pack yokes currently in use are correctly called enhanced photodegradable materials. On extensive photodegradation, the polyethylene might be rendered increasingly biodegradable. Since this is incidental and secondary, a "bio" or even "photo/bio" prefix is not appropriate.)

Issue II: Performance: Litter and Municipal Solid Waste

Adequate performance of degradable plastics must invariably be defined in terms of enhancement of degradation relative to that of a typical stabilized compound of the same plastic. The two key aspects of performance are: (a) the degree of enhancement achieved with a given degradable plastic in a specific product under given exposure conditions, and (b) the variability of actual lifetimes (relative to the average controlled lifetime) that might be expected during field performance. Fear of premature failure is perhaps a key factor which stands in the way of transferring degradable plastics technology to most applications. This concern needs to be completei_ .ressed before any large-scale use of degradable plastics might be expected.

Enhanced degradable plastics may show both geography-dependent and seasonal variations in performance. Claims made for some degradable polyethylenes of continued degradation in landfills following an initial exposure to light have not been verified. Rates and variability of environmental deterioration of starch-containing systems need to be verified and completely investigated.

It is also important for the user to be assured that a pre-determined controlled lifetime will not overlap with the useful life of the product leading to premature failure during use. Some degree of variability is to be expected in the controlled average lifetimes. However, such scatter must not only be manageable and small, but the average lifetime selected must be sufficiently longer than the maximum expected useful life of the product.

Issue III: Performance: Marine Environment

Any strategy adopted to address the plastic waste problem must also address the marine/estuarine environment as well. While recent legislative developments, such as United States ratification of MARPOL Annex V, may discourage the discharge of plastics into the world's oceans, a significant amount of discharge might still be expected due to non-compliance, accidental gear losses, and input from land-based sources [CMS, 1990]. This is particularly true of regions with high levels of maritime activity.

None of the currently available enhanced degradable plastics, however, have been demonstrated to perform equally well under both outdoor (land) and marine/estuarine conditions. Except for some preliminary data on enhanced photodegradable six-pack material made of (ethylene-carbon monoxide) copolymer, no relevant data exists in the technical literature.

Adequate performance of a given enhanced degradable plastic material under outdoor weathering need not necessarily guarantee similarly acceptable performance under marine exposure. Plastics at sea are maintained at lower temperatures compared to those on land, in spite of severe solar irradiation, and can become progressively shielded from sunlight due to surface fouling. Unique microbial environments experienced by plastics at sea (both floating and submerged) might be expected to modify any biodegradation behavior of plastics as well. Thus both classes of degradable plastics (photo- and biodegradable) may perform differently on exposure at sea compared to that on land. These differences, where they exist, must be established for different classes of products.

Issue IV: Toxicity of Degradation Products

While there is little chemical basis upon which to expect the majority of products of enhanced degradation to be significantly different from those of regular plastic products,

the issue has not been completely addressed. In the case of enhanced photodegradable plastics, the small amounts of additives (or low levels of matrix modification) may lead to some degradation products not typically found in the case of regular polymers.

The rates and extents at which these additional products are released into the environment during weathering and their toxicities are not known at this time. Furthermore, even the usual breakdown products common to both enhanced degradable and regular plastics will be generated at a faster rate by the enhanced degradable plastic material. The consequent effects of higher levels of such chemical products on the soil microenvironments have not been studied.

Issue V: Effect of Degradable Plastics on Recycling

The recycling of post-consumer plastics is expected to become increasingly important as a future solid waste management strategy. Reusable plastic resin for low-value applications can be derived from uniform, high-volume, easily separable post-consumer plastic products. Polyester soft-drink bottles as well as polyethylene milk jugs are currently recycled successfully. While the recycling of commingled post-consumer plastics is technically feasible, a remarketable base resin cannot often be cost-effectively obtained. The mix can, however, be extruded into profile which might be used as synthetic lumber, auto-stops, and other specific products.

Inadvertent mixing of low levels of enhanced degradable plastic items into a recycling stream of well-identified products (such as soda bottles) is extremely unlikely. Bottles for carbonated beverages are currently not rendered enhanced degradable. Even if a degradable plastic bottle does enter the market, the chances are that it will be easily identifiable and separated during the pre-cleaning operation. The product would probably be designed in such a manner that it would be easily identified as a degradable plastic product.

The same is not true of commingled streams of plastics where cleaning of individual items is too expensive, and some degradable material may easily find its way into the recycling stream. Reliable estimates of the fraction of degradable plastics likely to be found in the municipal waste stream are not available.

The key question is - does the inclusion of degradable plastics in a commingled stream significantly affect the weatherability of the extruded recycled product (usually synthetic lumber posts and panels)? Technical literature does not show any experimental data either supporting or refuting the claim sometimes made that even a small amount of degradable plastic will be disastrous to the quality of re-extruded material.

However, it must be pointed out that the recycled extruded products from commingled plastics tend to be very thick and dark colored material. Environmentally degradable

plastics generally cannot function in products other than thin films or laminates. Light - induced enhanced degradation of such a thick product is likely to be minimal and will be limited exclusively to surface layers.

1.4 GOALS AND THE SCOPE OF WORK

The basic objectives (a major goal A and three minor goals) of this research program effort might be summarized as follows.

A. To study the performance and the associated variability of several selected Enhanced Degradable Plastic [EDP] materials under a variety of different expo- sure conditions.

B. To better understand the underlying factors governing enhanced degradability in EDP systems.

C. To study the major products formed during the enhanced degradation of EDP materials and to assess the preliminary toxicity of such products.

D. To study the effects of including small fractions of partially degraded EDP materials in a recycling stream on the quality of recycled products.

These broad objectives cover a wide area of experimentation which cannot be exhaustively studied within the period of performance and the available resources. The dif- ferent goals shown above have all been achieved, though to different extents. The state- ment of work, given below, identifies the specific research areas addressed during the pre- sent effort.

1.4.1 Goal A

(a) To determine the relative rates of disintegration of different types of Enhanced Degradable Plastics [EDP] on exposure to outdoor environments at different geographic locations in the US.

(b) To determine the relative rates of disintegration of selected EDP materials exposed outdoors in air and at sea.

(c) To determine the relative rates of disintegration of enhanced biodegradable plas- tics under exposure to soil.

(d) To determine the rate of disintegration of selected EDP materials under acceler- ated laboratory exposure conditions.

(e) To study the improvement of outdoor exposure methodology with the develop- ment of "Duplicate Exposure" protocol.

1.4.2 Goal B

(a) To study activation spectra of the enhanced photodegradable plastics to identify the spectral regions most effective in bringing about light-induced degradation.

(b) To study the temperature dependence of photodegradation in enhanced photodegradable polymers.

(c) To develop a rapid method for determining the starch content in starch/LDPE blend materials.

(d) To study the effect of enhanced degradation on the water vapor and gas permeability of selected EDP materials.

1.4.3 Goal C

(a) To determine the volatile photodegradation products formed on exposure of enhanced photodegradable polymers to light.

(b) To carry out a preliminary assessment of any toxicity related to degradation products formed on exposure of selected EDP plastics to the outdoor environment.

(c) To study the effect of photodegradation on possible changes in leachability of metal components from the polymer matrices.

1.4.4 Goal D

To carry out preliminary experiments to determine the range of mix compositions to be considered in a future recycling study.

1.5 REVIEW OF DEFINITIONS

The research and technical literature on Enhanced Degradable Plastics [EDP's] shows a variety of definitions for terms such as "photodegradability", "biodegradability," and "degradable plastics". These definitions are inconsistent and sometimes vague, resulting in conclusions which are not clear. Unfortunately, most work carried out on degradable plastics therefore tends to be somewhat poorly defined and not standardized, making it difficult to make inter-laboratory comparisons of data.

The need for good definitions is also felt by those attempting to develop various pieces of legislation relating to plastics solid waste management. A recent GAO report [GAO, 1988] highlighted this lack of agreement on definitions of the basic terms and standard test procedures for assessing enhanced degradability and found the federal government and the private sector to be making only limited efforts to develop the required standards for EDP materials.

Definitions in the most recent literature include those currently under development and approval by the ASTM Committee D-20, subcommittee on "Environmentally Degradable

Plastics", D20.96. The subcommittee is currently in the process of drafting definitions and test procedures for "Degradable Plastic" materials. The definitions developed thus far include the following key terms. Each term has two definitions: a broader general definition and a specific definition.

Degradable Plastic --

(General) *Plastic materials that disintegrate under environmental conditions in a reasonable and demonstrable period of time.*

(Specific) *Plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological, and/or physical forces in the environment at a rate which is reasonably accelerated, as compared to a control, and which leads to fragmentation or disintegration of the plastic.*

Related terms such as "photodegradable plastics" and "biodegradable plastics" also have such pairs of definitions. These definitions have not as yet been adopted by the ASTM.

Andrady [Andrady, 1991] has proposed a set of working definitions for these terms which allow the demarcation between EDP materials which chemically degrade as opposed to those where the plastic component physically breaks down. This set of definitions is adequate for the purpose of this study and is given below.

Definitions Used in the Study

The term "Degradable Plastics" is strictly a misnomer suggesting the existence of non-degradable plastics; all polymers are of course environmentally degradable. In the case of most synthetic organic polymers, the rate of biologically-mediated degradation in the environment is too slow to be of any practical consequence. It is more appropriate to use the term "enhanced degradable plastics" or "rapidly degradable plastics" for those plastics designed (or selected) for relatively faster breakdown in the environment.

It is convenient to first define "Disintegration" as a broad overall description of the loss in properties and embrittlement of plastic materials exposed to the environment. This is consistent with the general usage of the term as well as with its use in the ASTM general definition of Degradable Plastics given above.

Disintegration: The loss of integrity, embrittlement, or breakdown of a material on exposure to the environment.

The term "deterioration" is next defined rather narrowly as a sub-set of "disintegration", to mean breakdown primarily due to non-chemical causes. This term has unfortunately been used in the literature to mean different phenomena [Eggins et al., 1980].

Deterioration: Disintegration of a material predominantly due to physical changes.
(e.g.. damage to materials due to freeze-thaw cycles, damage from thermal expansion, dissolution, damage from rodents, and insect attack on plastics)

A second sub-set of "disintegration" is "degradation" as defined below. The two classes of disintegrations are mutually exclusive as defined. However, both processes could occur concurrently. In any event the primary, predominant process is used for the purpose of definition.

Degradation: Disintegration of a material predominantly due to chemical processes.
(light-induced degradation of polymers, hydrolysis, microbial attack on polymers.)

Note that degradation alters the chemical nature of the polymer while deterioration does not. A degraded polymer will generally show an altered average molecular weight and changes in functional group chemistry, while in a deteriorated polymer, the individual fragments after disintegration retain about the initial intrinsic properties of the original polymer. The reader is cautioned that the above terms are used rather loosely and in a widely different sense from above in the literature [Modern Plastics, 1990; Barenberg et al., 1990]. Both Deterioration and Degradation might be further classified according to the agency bringing about the disintegration. Table 1.5.1 illustrates the use of the above terminology with the various types of breakdown. Some of the more important ones are discussed below.

1. Photodegradable polymers: The primary predominant mechanism of **degradation** on exposure to the environment is via light-induced (chemical) processes. Two classes of such polymers are widely used: (a) Polymers such as (ethylene-carbon monoxide) copolymer which use the absorbed solar radiation primarily for direct bond scission reactions (direct photolysis); and (b) polymer systems where light initiates thermo-oxidative reactions.
   This latter group of plastics is classified as "photodegradable " under the present scheme, but light is used merely to initiate the degradation process.

2. Biodegradable polymers: The **degradation** is brought about by the activity of microorganisms. Polymers such as poly(ε-caprolactone) fall into this category. The biodegradation process may occur in several stages: biotransformation of polymer to oligomeric species or small molecules, consequent biotransformation of non-polymer products into simple chemical compounds, and finally mineralization of these compounds into carbon dioxide, ammonia, and water.

3. Biodeteriorable material: The plastic material undergoes **deterioration** as a result of microbial activity on the material. Starch/LDPE blends are an example of

this class of material. On exposure to a biotic environment, the microorganisms degrade the starch component but do not utilize or chemically affect the polymer fraction. Weakening of the material due to loss of the starch component eventually causes embrittlement of the composite material.

Table 1.5.1. Proposed Definitions of Environmental Breakdown Processes and Enhanced Degradable Plastics.

	Examples	Product
DEGRADATION — A disintegration caused predominantly by chemical changes → **PHOTODEGRADATION** Light-induced	a	Ecolyte ECO resin
	b	Plastigone
BIODEGRADATION Brought about by living animals, plants, particularly microbes	c	Biopol - ICI
OXIDATIVE DEGRADATION Caused by thermooxidative reactions	d	--
HYDROLYSIS Caused by reaction with water	e	--
DISINTEGRATION Breakdown (size reduction) of material into small fractions, including embrittlement		
DETERIORATION — A disintegration caused predominantly by physical changes → **BIODETERIORATION** Brought about by living animals and plants	f	ADM, Ecostar
DISSOLUTION (Hydrodeterioration) Brought about by water	g	PCL/PE - Union Carbide
THERMAL DETERIORATION Caused by freeze-thawing or thermal cycling forces		Belland

a   Polymers with ketone groups in main chain or as a side chain.

b   Metal-compounds additives for PE

c   Poly(hydroxybutyrate valerate)

d   Metal-compounds and inorganic pigments in polyolefins

e   Acid catalyzed hydrolysis of cellulose

f   Starch-polymer composites; biodegradable polymer - other polymer composites

g   Soluble acrylic copolymers; soluble poly(vinyl alcohol) films

4.   Water soluble plastics: Plastics such as soluble poly(vinyl alcohols) do not represent a case of "degradation," as sometimes incorrectly stated, but only a water-induced **deterioration**.

1.6   SUMMARY OF CURRENTLY COMMERCIALIZED ENHANCED DEGRADABLE (EDP) TECHNOLOGIES

A variety of techniques described in the patent and scientific literature fall under the definition of "Enhanced Degradable Plastics" as defined above. However, all such systems have not been commercialized or have not been successful after commercialization. The intent of this section is not to present a technical review of the research literature on degradable plastics but to provide a general description of the mechanisms responsible for enhanced degradability (or enhanced deteriorability) in some of the common EDP systems.

Discussion is limited to those EDP systems selected for the experimental part of this study. A description of the actual EDP film materials used in the study is provided in Section 2.1.

1.6.1   Ethylene-carbon Monoxide Copolymers (PHOTODEGRADABLE)

Copolymerization of ethylene with carbon monoxide allows the introduction of low levels of ketone functionalities into the main chain of the polymer [Hartley and Guillet, 1968; Heskins and Guillet, 1968; Heskins and Guillet, 1970; Guillet, 1972]. The product, a low density polyethylene containing usually 1 percent of the ketone repeat unit, is generally referred to as ECO copolymer and is able to absorb ultraviolet radiation in sunlight and undergo photolysis reactions. Enhancement of the degradation is obtained due to the presence of a significant amount of carbonyl chromophores in the form of keto groups in the polymer. The photooxidation of regular polyethylene on exposure to sunlight also results in the formation of ketone functionalities. However, the main mechanism of chain scission is different for ECO copolymers and regular polyethylene material.

Success of the ECO copolymer system is due to the ability of these ketones to undergo n-π^* transitions absorbing relatively long wavelength solar radiation (313 nm) [Hartley and Guillet, 1968]. The chain scission process occurs via classical Norrish I and Norrish II mechanisms [Guillet and Norrish, 1955], though the Type II reaction predominates under ambient temperatures [Hartley and Guillet, 1968]. At ambient temperatures the difference between the quantum yield of the Type II and Type I reactions is about 100-fold [Guillet, 1973]. The Type II reaction, an intramolecular elimination reaction with a low activation energy of about 1 kcal/mole, results in chain scission yielding a methyl ketone and vinyl unsaturated chain end. Norrish I and II reactions for ethylenes with ketone functionalities in the main chain as well as on a side chain are shown below.
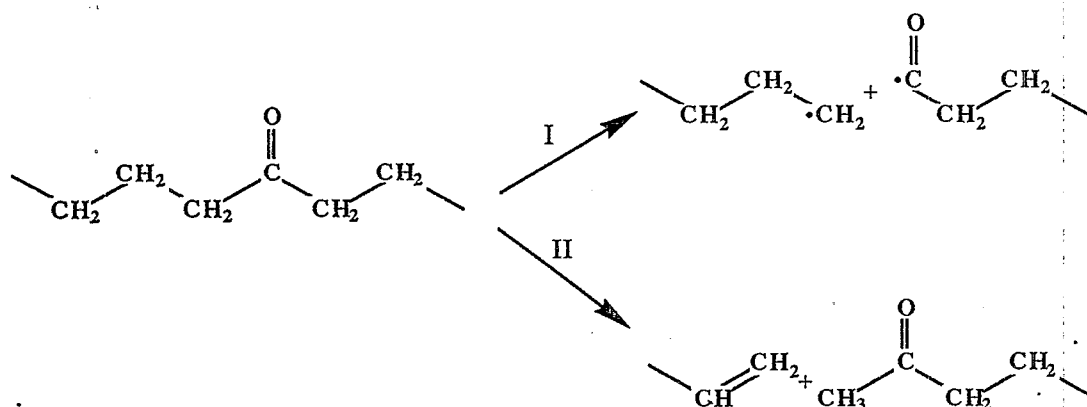
Norrish I and II Reactions Leading to Degradation of Polymer

ECO copolymers are manufactured in the U. S. by several resin manufactures and are almost exclusively used in the fabrication of six-pack ring connectors in the packaging industry. The success of this particular application as a large-volume user of photodegradable plastics is to a large extent due to regional legislation in more than seventeen states requiring photodegradability in six-pack carriers. Public Law 100-556, Degradable Plastic Ring Carriers Law, will encourage even stronger growth for this material. ITW-HiCone Division trade literature on photodegradable carrier material claims a loss of approximately 75 percent of its structural integrity within days and embrittlement in a matter of weeks. The manufacturer has carried out several exposure studies, both in the United States and in Europe, which show the ECO copolymer used in six-pack rings to embrittle within a 5-8 week period.

1.6.2 Polymers with Ketone Functionality on a Side Chain [PHOTODEGRADABLE]

(a) Polyethylene

Ketone groups on a side chain of the polymer can also be effective as chromophores in bringing about Norrish I and II photolysis of polymers. Copolymerization with vinyl ketone has been extensively used to synthesize enhanced degradable polyethylenes [Li and Guillett, 1980], polystyrene [Heskins et al., 1976], and other polymers [Amerik and Guillet, 1971].

With the carbonyl group located on the side chain, only the Norrish II type reaction causes chain scission, while the Type I reaction yields a free radical on the macromolecule. This radical may, however, initiate oxidation via reaction with oxygen followed by hydrogen abstraction. While the quantum yield for the Type II reaction in ethylene/methylvinyl ketone polymers is not high, the material is claimed to undergo facile embrittlement on

exposure to light. Generally , a small number of scission events cause a large decrease in the strength of the polymer. The approach has been demonstrated for polystyrene as well.

This technique has been developed to the point of commercialization, and a masterbatch compound of the modified polymer (containing 2 - 5 percent ketone content) is available for use in polyethylene and polystyrene resins. Appropriate amounts of the masterbatch blended (in a ratio of 1:9 to 1:20) with the base unmodified resin render the blends enhanced photodegradable. The extent of such enhancement depends on the level of masterbatch incorporated into the resin and also on the level of pigment, if any, in the formulation.

(b)   Polystyrene

Vinyl ketone/styrene copolymers undergo photodegradation in a manner similar to the ethylene copolymers discussed above. The general mechanism [Heskins et al., 1976] and the quantum yield [Dan and Guillet, 1973] have been reported for such systems.

1.6.3   Low Density Polyethylene Containing Added Metal-compound Pro-oxidants

> [PHOTODEGRADABLE] (A polymer which undergoes catalyzed
> photoinitiated oxidative degradation)

The ability of transition metals to accelerate both thermal autoxidation and photoinitiated autoxidation of polyolefins is well known [Alter, 1960; Reich and Stivala, 1971]. The mechanism primarily involves the catalysis of the hydroperoxide dissociation reaction which initiates the oxidation. Some likelihood of the metal ion participating in the propagation/termination steps also exists.

Particularly interesting is the use of transition metal thiolates, particularly dithiocarbamates. Some of these, such as the nickel complex, show outstanding antioxidant effects, while others, such as the iron complex, are unstable and act as prooxidants in polyolefins. The difference in stabilizer activity of metal dithiocarbamates is due mainly to their invariable light stability [Scott, 1984]. Some of the metal dithiocarbamates act as thermal stabilizers (or act as neutral additives) during processing and as antioxidants during early exposure to light but thereafter are themselves photodegraded into pro-oxidant species. This results in polyethylene/MX systems (where MX refers to dithiocarbamate or other organic compound of iron or manganese) which, when exposed to light, undergo enhanced photodegradation after a delay or a "lag time". During processing, shelf life, use,

1-15

Termination: radical combination

and the lag-time, the metal dithiocarbamate is believed to stabilize the polymer by reacting with hydroperoxides in a reaction yielding non-radical products [Gilead and Scott, 1982]. Early weathering photodegrades the dithiocarbamate, liberating the metal, which can catalyze the initiation by hydroperoxide decomposition.

This reaction produces ferric ions which are efficient hydroperoxide decomposers in an initiating reaction. The redox catalysis [Amin and Scott, 1974] reaction involved is well known. This latter reaction can occur in the absence of light and is probably the basis of the manufacturer's claim that, once initiated, the degradation process will continue in the dark in air [Gilead et al., 1981; Gilead, 1978].

$$Fe^{2+} + ROOH \longrightarrow Fe^{3+} + RO\bullet + OH^-$$

$$Fe^{3+} + ROOH \longrightarrow Fe^{2+} + RO_2\bullet + H^+$$

The delay period can be altered, and therefore controlled to some extent, by changing the amount of metal dithiocarbamate used in the polymer. A later improvement of the technology uses a second, more stable, metal dithiocarbamate as an additional additive. Varying the relative proportion of the pair of dithiocarbamates is claimed to allow close control of the outdoor lifetime of the film [Gilead, 1984]. The commercial product, in the form of a plastic film containing the relevant metal compounds, has been successfully used in agricultural mulch films [Gilead, 1978; Gilead, 1990].

1.6.4 LDPE/starch Systems With or Without Added Pro-oxidants

[BIODETERIORABLE] or [PHOTODEGRADABLE/BIODETERIORABLE]

(a) Starch/Polyethylene Blends

Biodegradation of polyethylene under soil exposure is well known to be extremely slow, and the reported evidence for any biodegradation at all is based on radiotracer studies indicating a breakdown of a few percent over several years [Albertsson, 1978; Albertsson and Banhidi, 1980]. Incorporating starch grains as an organic filler into a polyethylene or other polymer matrix was observed to enhance the breakdown of the polymer in biotic environments as early as 1974, when the first patent was issued to Griffin [Griffin, 1974]. The plastic material so prepared was essentially a very slowly biodegradable thermoplastic material filled with a readily biodegradable naturally occurring polysaccharide. Starch consists of 17-21 percent amylose fraction, a linear polysaccharide consisting of up to 1000 glucose residues, and 73-82 percent amylopectin, a branched chain polysaccharide fraction. Blending in a hydrophilic filler (and an unsaturated fatty acid) at levels high enough to obtain a significant difference in disintegration rates, without sacrificing the mechanical properties of the filled polymer, is the major challenge in this approach. This is generally achieved by using a small enough particle size of starch to optimize dispersion and a novel silicone (or other polymeric) treatment of the starch grains to improve the starch/polymer interphase properties. The addition of an unsaturated vegetable oil which readily autoxidizes is claimed to further enhance the disintegration of the system, particularly under warm exposure conditions such as compost environments.

On exposure to a biotic environment, the starch fraction of the composite material can readily undergo ready biodegradation. This would depend on the accessibility of the starch to soil microbes and/or extracellular amylases secreted by the microbes. Biodegradation of starch creates voids within the plastic matrix which weaken and deteriorate the plastic film. The matrix may contain a readily auto-oxidizable hydrocarbon blended with the polyolefin.

The above approach was first described by Griffin [Griffin, 1978] and is marketed by St. Lawrence Starch Company. A modified version of this technology is marketed under the trade names Polygrade II and Polygrade III. The modified approach based on technology licensed from Archer Daniels Midland Company uses untreated starch and a proprietary prodegradent compound. Manufacturers often add metal compound pro-oxidants into the mix to make the material more photodegradable, thereby making it more versatile. The pro-oxidant promotes photoinitiated autoxidation as mentioned earlier and also catalyzes the thermooxidative breakdown of plastics under the higher temperatures found in composting. Where both biological and light-initiated processes work simultaneously, the latter mechanism is expected to work relatively faster.

The original concept for this type of material was patented by Griffin [Griffin, 1978], and both manufacturers currently marketing the product use the same general composition. The main difference between the two commercially available product lines appears to be in the choice of additives which cause rapid autoxidation.

(b)   Starch Chemically Bonded to Polyethylene

The loss of useful mechanical properties of the blend at even moderate levels of starch in the polymer limits the use of the above approach. This can be avoided to some extent by more intimate mixing of the starch with polymer and even possible partial reaction of the two materials. A varient of the starch/polymer blend technology developed in USDA laboratories by Otey [Otey, et al., 1977] uses a copolymer of polyethylene containing pendent carboxylic acid groups which are able to react with starch molecules. The starch itself is pregelatinized, intimately mixed, and partially reacted with the polymer. The resulting 'blend" is claimed to be processable into films and molded objects which display a high degree of biodeteriorability due to the relatively high levels of starch that can be incorporated into the matrix.

While the idea has been patented [Otey, 1979]and some developmental work is under way, the product has not as yet been commercialized.

1.6.5 Polyethylene/ ε-Polycaprolactone Blends [BIODETERIORABLE]

This approach is essentially similar to that discussed under 1.6.4 above in that it uses a blend of a non-degradable polymer and a degradable polymer. In place of starch, which is a biopolymer, this system uses polycaprolactone, a readily biodegradable synthetic polymer. Unlike starch, polycaprolactone can be easily blended with polyethylene and polypropylene without affecting the mechanical properties of the blend.

Environmental degradability of ε-polycaprolactone under biotic conditions has been reported by Potts [Potts et al., 1972] and others [Fields, et al. 1974; Benedict et al., 1983]. Fungi in particular are able to fully degrade this polymer [Benedict et al., 1983]. For instance, Penicillin species acting on a polycaprolactone sample of $M_n = 25,000$ reduced the organic carbon content of the growth medium to near zero in 15 days under laboratory exposure conditions [Tokiwa et al., 1976].

The manufacturer's trade literature on Tone P-767 polycaprolactone shows tensile test data for film samples 0.125 in. in thickness. Under aerobic soil burial exposure, the test samples embrittled (elongation at break< 5 percent) within 4 months and lost 42 percent of weight within 12 months. The temperature for the exposure is unspecified. The literature also shows data on marine degradation [based on Andrady, 1989] of polyethylene/polycapro-lactone blends. Film samples of 10 or 20 percent by weight of ε-polycaprolactone in polyethylene lost 70-80 percent of initial elongation at break on exposure to marine sediment at a coastal Miami location for a 9 month period. As in the case of starch/polymer composites, the deterioration of these blends is controlled by the accessibility of the polycaprolactone to the relevant enzymes.

1.6.6 Biopol Thermoplastic Biopolymer

Under certain growing conditions, bacteria and algae are known to synthesize polyesters which are stored in the form of granules within the cell and utilized as a source of energy as needed by the microrganism. The aliphatic polyester, poly(3-hydroxy-butyrate), is an example of such a polyester.

By controlling the feedstock and growth conditions closely, ICI researchers were able to induce a common soil bacterium, *Alcaligenes eutrophus,* to produce up to 80 percent (of dry biomass weight) of the polyester, which could be easily extracted to obtain a biodegradable thermoplastic material [Lloyd, 1987]. Incorporation of a valerate comonomer (5-20 %) reduces the crystallinity of the polyester, leading to improved properties. An aqueous extraction process is used to obtain a copolymer with moderate molecular weights.

While the material cost is high at the present time, given high levels of production, this polymer might be available at a cost comparable to that of engineering thermoplastics.

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POST-CONSUMER PLASTIC WASTE MANAGEMENT OPTIONS
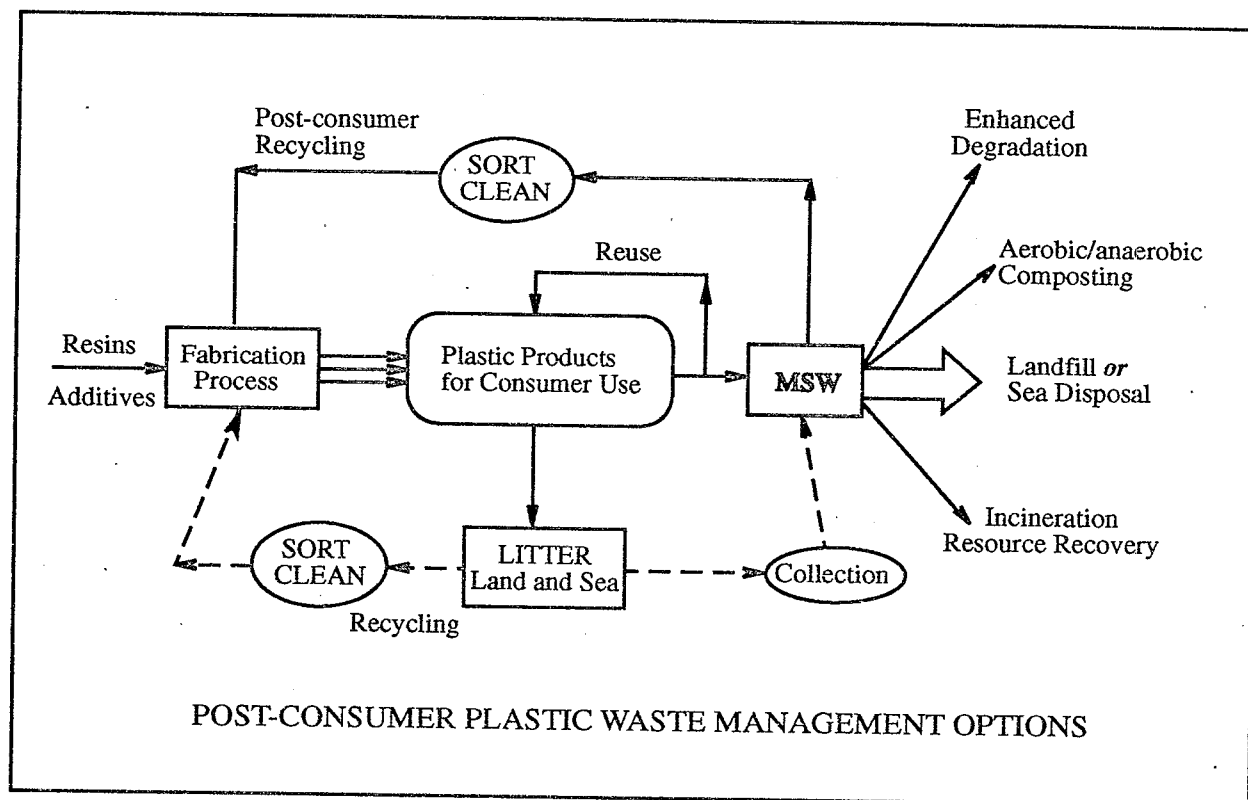
Andrady, 1991

Figure 1.2.1.   A flow chart for consumer plastic products: production, use, and disposal
(MSW: Municipal Solid Waste).

SECTION 2.0

EXPOSURE METHODS

2.1 SAMPLE SELECTION AND ACQUISITION

The number of different types of degradable plastics investigated in this study was limited by the available resources. As such, a representative set of sample types had to be selected from the commercially available (or fully developed) technologies. The following criteria were used in making the selections.

(a) The most-used consumer packaging material which utilizes enhanced degradable plastics technology is the six-pack ring holder. State level legislation and anticipated national legislative interest in the product also made it a key material to be included in the study.

(b) Given the time scale of the study, which included less than six months of exposure duration, enhanced photodegradable materials are likely to be the more profitable class of enhanced degradable plastics to study. Therefore the main selections included three photodegradable plastics, one photodegradable/biodeteriorable plastic, and one which was biodeteriorable. On the basis of literature data, photodegradable materials were expected to be more likely to undergo measurable changes in mechanical properties during the short duration of exposure.

(c) An attempt was made to include different classes of resins as well as different technologies for imparting enhanced degradability in the study. Therefore, both polyethylene and polystyrene were included. The latter was expanded extruded polystyrene foam widely used in single-serve food and packaging applications.

(d) Polymer/starch blends are an important class of enhanced degradable plastics which have drawn public as well as technical interest. The photo/bio-disintegrating material was included in the study, as it represented a plastic/starch blend and in addition claimed photodegradability, which allowed both processes to be studied.

Based on these considerations the following test materials were selected for the study. In each case the manufacturer of the material and/or the relevant packaging product was contacted. In the case of polyethylenes, including blends, approximately 1 mil thick films were requested for use in the study. In the case of six-pack ring material and polystyrene foam material, however, thicker sheets of the material typically used in the product were requested. The samples were labelled with the appropriate code and stored at ambient temperature. A list of the sample types is given below.

1. (Ethylene-carbon monoxide) copolymer containing ~ 1 percent of the CO comonomer units. The sample was obtained as sheets (some sheets partially cut into sample strips).

   Classification: [Enhanced photodegradable plastic material]
   Source: Illinois Tool Works (HiCone Division).
   Code: 6P
   Control: Low density polyethylene of comparable thickness. Code : 6PC

2. Polystyrene blended with (styrene - vinyl ketone) copolymer, as an expanded, extruded sheet. The amount of the photoactive copolymer in the blend was approximately 10 percent.

   Classification: [Enhanced photodegradable plastic material]
   Source: Polysar Inc., Leominister, MA
   Code: PS
   Control: Sheets of regular expanded extruded polystyrene. Code: PSC

3. Low density polyethylene containing metal prooxidant compounds.

   Classification: [Photodegradable film]

                        Note: Photoinitiated thermooxidation is the degradation mechanism.
   Source: Plastigone Company, Miami, FL
   Code: PG
   Control: Low density polyethylene sheet with no prooxidant additive.
                       Code: PGC

4. Low density polyethylene/starch (6 percent) blends containing metal compound prooxidants.

   Classification: [Biodeteriorable /Photodegradable film]

   Note: Photoinitiated thermooxidation is the degradation mechanism. Some biodeterioration due to loss of starch is also expected.
   Source: Archer-Daniels Midland Company
   Code: ADM

Control: Low density polyethylene film with no prooxidant additive.
                  Code: ADMC

5.   Linear low density polyethylene/polycaprolactone (20 percent) blends.
     Classification: [Biodeteriorable film]
     Source: Union Carbide Company
     Code: PCL
     Control: Linear low density polyethylene film. Code: LLDPE

6.   Poly(hydroxybutyrate valerate) film.
     Classification: [Biodegradable film]
     Source: ICI Americas Co.
     Code: BP
     Control: None used
     NOTE: This sample type was used only in a limited number of exposures
                       due to cost and sample limitations.

2.2   SAMPLE CONTROL AND IDENTIFICATION

The various types of plastics for the study, their manufacturers, and the code names used to identify them are listed in Table 2.2.1. The samples will be referred to by their code names, e.g., 6P for (ethylene-carbon monoxide) copolymer, throughout this report. These samples were dispatched from RTI to various locations for the different types of exposure required by the study: direct weathering, marine floating and marine sediment exposure, and laboratory-accelerated weathering (Weather-Ometer®). Outdoor and laboratory-accelerated soil burial were conducted at RTI.

The large numbers of samples exposed at the various outdoor weathering sites necessitated the development of a sample tagging system able to withstand severe outdoor exposure to identify each sample to prevent inadvertent mislabeling by the exposure service. Small metal punches of various shapes were used to stamp the plastic films before sending them for exposure. Each sample type and each exposure location were represented by a different shape. Conventional labels were also used, allowing two independent means of sample identification.

Samples were returned to RTI as soon as possible after each sampling interval. Upon receipt of a sample, the punch code was checked to see if it had been properly labeled. Each sample was then assigned a code which identified the material type (code names from Table 2.2.1); type of exposure (O = outdoor direct weathering, F = marine floating, M = marine sediment, FW = freshwater, S = soil burial, W = Weather-Ometer®, LA = lab accelerated soil burial); exposure site; and duration of exposure. The exposure logs are

Table 2.2.1. Identification, Sources, and Code Names of Plastic Film Materials Used in the Study.

Description of Material	Manufacturer	Code Name
Ethylene/carbon monoxide copolymer with 1% CO-monomer (Used in 6-pack rings for beverage cans)	Illinois Tool Works HiCone Division, IL	6P
Polyethylene 6-pack ring material (Control for 6P)	Illinois Tool Works HiCone Division, IL	6PC
Low density polyethylene films containing proprietary metal compounds	Plastigone Company, FL	PG
Low density polyethylene film (Control for PG)	Plastigone Company, FL	PGC
Low density polyethylene film containing 6-7% by weight cornstarch, and proprietary metal compounds	Archer Daniels Midland Company, IL	ADM
Low density polyethylene film (Control for ADM)	Archer Daniels Midland Company, IL	ADMC
Expanded, extruded polystyrene foam with ketone groups (10%)	Polysar, Inc., MA	PS
Expanded, extruded polystyrene foam	Polysar, Inc., MA	PSC
Linear low density polyethylene/polycaprolactone (20%) blend	Union Carbide Company, NY	PCL
Linear low density polyethylene film (Control for PCL)	Union Carbide Company, NY	LLDPE
Biopol film (polyhydroxybutyl valerate)	Imperial Chemical Industries	BP

given in Appendices A, B, and C and show a complete record of the information pertaining to sample exposure. These logs were also used to keep a record of the tensile testing performed on the exposed samples.

2.3 FIELD EXPOSURE METHODS

2.3.1 Rationale for Use of Duplicate Exposures

Outdoor exposure under natural weathering conditions is best suited for studying permanence properties of plastics to the extent that it is typical of the exposure received by the material in use. Attempts at acceleration of weathering in the laboratory by resorting to higher temperature, more intense light, spectrally altered light , and cycling result in very large deviations from the actual outdoor conditions. Consequent uncertainty as to the similarity of underlying chemical processes resulting in degradation of the exposed material in outdoor and accelerated conditions can often make the latter data difficult to interpret. The more the exposure condition deviates from natural outdoor conditions, the higher is the likelihood that the mechanisms are not typical of those taking place under natural exposure, and therefore less reliable is the test data.

The main difficulty associated with natural weathering is of course the very long durations of exposure required to collect meaningful data for most commodity plastics. In the case of enhanced degradable plastic materials, however, the duration of exposure to embrittlement is relatively short, and, unlike the case of regular plastics, data can easily be obtained from natural weathering studies. The main drawbacks are the large variations in temperature, sunlight, and rainfall generally obtained with natural weathering. The non-uniformity of outdoor exposure conditions is well known to lead to variability in weathering test results. Unlike the case of establishing permanence properties of regular plastic films, the outdoor exposure of enhanced degradable plastic films requires a much shorter period of exposure, often 2-3 weeks outdoors. As such, the short term (day to day) fluctuation in key factors such as average temperature, rainfall, and the available sunshine, is likely to affect the variability of test data to a greater extent in the case of exposures of a few weeks compared to longer exposures of months or years. In an attempt to overcome this difficulty a "duplicate exposure" protocol was developed during this work. This protocol, however, was only used in selected exposure sites due to cost constraints.

Figure 2.3.1 illustrates the basis of the "duplicate exposure" procedure. An exposure experiment is initiated with a set of n samples exposed outdoors. Essentially, each time a sample is removed from the original set of plastic films, it is replaced by a fresh sample of the identical plastic film. Thus, two complete sets of samples are available for testing at the

end of the test period; one with $1, 2, \ldots\ldots n^{th}$ week of exposure and another with n^{th}, $(n-1)^{th}, \ldots\ldots 1^{st}$ week of exposure. Thus for any given duration of n weeks of exposure, the procedure yields two samples collected in chronologically reverse order. With no drastic changes in weathering conditions both sets should yield very similar data. Inconsistent data between the two sets would suggest non-uniform exposure conditions during the short duration of exposure.

SET 1	ADD	n	0	0	0	• • •	0	0	0
	REMOVE	0	1	1	1	• • •	1	1	1
	TOTAL	n	n-1	n-2	n-3	• • •	2	1	0
SET 2	ADD	1	1	1	1	• • •	1	1	0
	REMOVE	0	0	0	0	• • •	0	0	n-1
	TOTAL	1	2	3	4	• • •	n-3	n-2	n-1
	EXPOSURE TIME	0	1	2	3	• • •	n-2	n-1	n

Weeks

Figure 2.3.1   Duplicate exposure protocol for an exposure for *n* weeks with weekly sampling of set 1.

While this duplicate exposure protocol is straightforward, its novelty made it difficult to implement in the field. In several of the sample sets, the exposure procedure was not correctly carried out by the field technicians. However, in the cases where the protocol was properly followed, good data showing little or no drastic changes in the factors responsible for weathering were obtained.

2.3.2   Outdoor Exposure

The following samples were exposed outdoors at five geographic locations:
(a)   (ethylene-carbon monoxide) copolymer (6P),
(b)   low density polyethylene/MX (PG),
(c)   low density polyethylene/starch/MX (ADM), and
(d)   expanded polystyrene foam (PS).

(MX represents proprietary metal complexes.) The five locations were Cedar Knolls, NJ; Chicago, IL; Miami, FL; Seattle, WA; and Wittmann, AZ. In addition, samples of polycaprolactone/linear low density polyethylene blend (PCL) and poly(hydroxybutyl

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valerate) (BP) were exposed outdoors in Miami, FL. Control samples of plastic films were exposed simultaneously with the degradable materials in most exposure experiments. Table 2.3.1 shows the sample matrix for outdoor direct weathering, as well as for marine and soil burial exposures. Data for daily average, minimum, and maximum temperature, daily rainfall, and total global and UV radiation for the exposure sites are reported in Appendices D through H.

Outdoor exposure studies were carried out from June 19 to September 30, 1990 in general accordance with ASTM G7. The samples were exposed on racks to direct sunlight facing 45° south and were backed with unpainted plywood. The exposed samples were placed in opaque paper envelopes and returned to RTI from the exposure service as quickly as possible after sampling for testing. The samples were not exposed to any light in the interim period between exposure and testing. To prevent any misidentification, samples were coded using small punches of various shapes prior to sending them to the exposure services.

In certain cases, duplicate sample sets were exposed. Duplicate exposure was carried out by replacing a sample from the original set with one from the duplicate set at each sampling interval. Upon removal of the final sample from the orginal set, the entire duplicate set was removed. A detailed discussion of the rationale for exposing duplicate sets is given in Section 2.3.1. Table 2.3.2 identifies the sample materials, locations, duplicate sets, and scheduled sampling intervals for outdoor exposure. Actual sampling intervals are shown in Appendix A.

2.3.3 Marine Exposure

Two types of marine exposure were utilized for the degradable plastic materials; photodegradable materials were exposed floating in sea water, while biodegradable materials were exposed to bottom sediment at a depth of about 10 feet. The two locations for marine exposure were Miami (Biscayne Bay), FL, and Seattle (Puget Sound), WA. For floating exposures, the rectangular samples were attached by nylon monofilament lines to a plastic frame attached to styrofoam floats so that sample level was unaffected by tidal conditions. Water depth was always at least 15 feet. Excess nylon line was provided so that the samples were always freely floating. Biodegradable samples were affixed to 8" x 12" fiberglass-reinforced polyester frames, which kept the samples flat. The frames were bolted to plastic piping and placed on the bottom of about 10 feet of water at a coastal exposure site. After sampling, the plastic pieces were wrapped in newspaper, enclosed in a plastic bag, and returned to RTI for testing. Prior to testing at RTI, the wet samples were dried at ambient temperature under a fume hood for at least 24 hours.

Table 2.3.1 Sample Exposure Matrix for Natural Weathering.

Material	Code	Location Cedar Knolls, NJ	Chicago, IL	Miami, FL	Seattle, WA	Wittmann, AZ	Kerr Lake, VA	RTP, NC
(Ethylene-carbon monoxide) copolymer	6P	O	O	O, F	O, F	O	FW	
LDPE/MX	PG	O	O	O, F	O, F	O	FW	
LDPE/Starch/MX	ADM	O	O	O, F, M	O, F, M	O		S
Polystyrene Foam	PS	O	O	O, F	O, F	O		
LLDPE/PCL Blend	PCL			O, M	M		FW	S
Biopol	BP			O, M			FS	S

O = Outdoor direct weathering
F = Marine floating exposure
M = Marine sediment exposure
FW = Freshwater floating exposure
FS = Freshwater sediment exposure
S = Soil burial exposure

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Table 2.3.2 Sample Identification for Outdoor Exposure.

Code	Location	Sample Set	Initial Number Samples		Sampling Frequency	
			Degradable	Control	Degradable	Control
6P	Cedar Knolls, NJ	Original	15	10	3 days	6 days
6P	Chicago, IL	Original	15	10	3 days	6 days
6P	Miami, FL	Original	15	10	3 days	6 days
		Duplicate	15	10	3 days	6 days
6P	Seattle, WA	Original	20	10	Twice/week 1st 4 weeks; then every 7 days	7 days
6P	Wittmann, AZ	Original	15	10	3 days	6 days
PG	Cedar Knolls, NJ	Original	20	10	3 days	6 days
		Duplicate	20	10	3 days	6 days
PG	Chicago, IL	Original	20	10	3 days	6 days
		Duplicate	20	10	3 days	6 days
PG	Miami, FL	Original	20	10	3 days	6 days
		Duplicate	20	10	3 days	6 days
PG	Seattle, WA	Original	20	10	Twice/week 1st 4 weeks; then every 7 days	7 days
PG	Wittmann, AZ	Original	20	10	3 days	6 days
		Duplicate	20	10	3 days	6 days
PS	Cedar Knolls, NJ	Original	20	10	7 days	14 days
		Duplicate	20	10	7 days	14 days
PS	Chicago, IL	Original	20	10	7 days	14 days
		Duplicate	20	10	7 days	14 days
PS	Miami, FL	Original	20	10	7 days	14 days
		Duplicate	20	10	7 days	14 days
PS	Seattle, WA	Original	20	10	7 days	14 days
PS	Wittmann, AZ	Original	20	10	7 days	14 days
		Duplicate	20	10	7 days	14 days

- continued-

Table 2.3.2 (continued)

Code	Location	Sample Set	Initial Number Samples		Sampling Frequency	
			Degradable	Control	Degradable	Control
ADM	Cedar Knolls, NJ	Original	15	10	3 days	6 days
		Duplicate	-	10	-	6 days
ADM	Chicago, IL	Original	15	10	3 days	6 days
		Duplicate	-	10	-	6 days
ADM	Miami, FL	Original	15	10	3 days	6 days
		Duplicate	15	10	3 days	6 days
ADM	Seattle, WA	Original	15	i .	Twice/week 1st 4 weeks; then every 7 days	7 days
ADM	Wittmann, AZ	Original	15	10	3 days	6 days
		Duplicate	-	10	-	6 days
PCL	Miami, FL	Original	20	10	7 days	14 days
BP	Miami, FL	Original	12	-	7 days	-

Pertinent weather conditions for marine exposure, i.e., air and water temperatures, are included in Appendices F and G. Table 2.3.3 identifies the samples and conditions for marine exposure.

2.3.4 Freshwater Exposure

Exposure to a fresh water environment was carried out at Kerr Lake in Boydton, VA at the United States Army Corps of Engineers maintenance facility.

Floating samples were exposed affixed to a floating platform fabricated of PVC pipes and held afloat by two plastic buoys. Samples were attached in a manner to allow them to freely float on water at all times. The depth of water at the exposure location was about 8-10 feet. Test samples exposed to the lake bottom environment were mounted on fiberglass frames which held the film flat and allowed an area of approximately 6" x 8" to be exposed to the water/sediment. Frames were attached to several nylon ropes in such a way as to allow the frames to be placed flat on the lake bottom.

Samples (identified in Table 2.3.4) were removed at appropriate intervals, placed in plastic bags, and transported to RTI for testing. All samples were dried under ambient conditions prior to tensile testing.

2.3.5 Soil Burial Exposure

Samples to be tested for biodegradability (or biodeteriorability) were exposed to field soil burial conditions at Research Triangle Institute (NC). The exposure site was an aboveground wooden enclosure, approximately 3 feet in depth and 15' x 15' in area, filled with unfumigated, unfertilized standard sieved soil. The soil mixture could drain freely from the enclosure into the ground. The entire area was enclosed by fence to prevent animals from interfering with the exposure. Rectangular sample pieces were buried vertically in numbered plots, with the top of the material at least one inch below the surface of the soil. The soil burial was carried out in triplicate, using three separate blocks of the soil burial enclosure. Samples were randomized within each block. The material codes and sampling frequencies for soil burial exposure are given in Table 2.3.5. Climatic data for the Raleigh-Durham, NC area are given in Appendix I.

2.4 LABORATORY EXPOSURE METHODS

2.4.1 Weather-Ometer® Exposure

Accelerated weathering studies were carried out in general accordance with ASTM G 26 (Operating Light-Exposure Apparatus (Xenon-Arc Type) With and Without Water

Table 2.3.3 Sample Identification for Marine Exposure.

Code	Location	Sample Set	Initial Number Samples		Sampling Frequency	
			Degradable	Control	Degradable	Control
6P	Miami, FL	Floating	20	10	3 days	6 days
6P	Seattle, WA	Floating	20	10	7 days	14 days
PG	Miami, FL	Floating	20	10	3 days	6 days
PG	Seattle, WA	Floating	20	10	7 days	14 days
PS	Miami, FL	Floating	20	10	7 days	14 days
PS	Seattle, WA	Floating	10	10	7 days	7 days
ADM	Miami, FL	Floating	15	10	3 days	6 days
ADM	Seattle, WA	Floating	15	8	7 days	14 days
ADM	Miami, FL	Sediment	15	10	7 days	14 days
ADM	Seattle, WA	Sediment	15	8	7 days	14 days
PCL	Miami, FL	Sediment	20	10	14 days	28 days
PCL	Seattle, WA	Sediment	15	8	Every 2 weeks until 9 weeks; then weekly	Every 4 wks until 10 wks; then every 2 wks
BP	Miami, FL	Sediment	12	-	1 day	-

Table 2.3.4 Sample Identification for Freshwater Exposure at Kerr Lake, VA.

Sample Code	Exposure Type	Initial Number Samples		Sampling Frequency	
		Degradable	Control	Degradable	Control
6P	Floating	7	-	4 days	-
PG	Floating	9	3	2 days	7 days
PCL	Floating	4	-	14 days	-
BP	Sediment	5	-	2-3 days	-

Table 2.3.5 Sample Identification for Soil Burial Exposure at Research Triangle Institute.

Sample Code	Initial Number Samples		Sampling Frequency	
	Degradable	Control	Degradable	Control
ADM	30 (10x3)	30 (10x3)	14 days	28 days
PCL	60 (20x3)	30 (10x3)	14 days	28 days
BP	45 (15x3)	-	7 days	-

for Exposure of Nonmetallic Materials). Samples (rectangular films or sheets) of (ethylene-carbon monoxide) copolymer (6P), low density polyethylene/MX (PG), low density polyethylene/starch/MX (ADM), and expanded polystyrene foam (PS) were exposed for durations of 50, 100, 150, 200, and 250 hours. (MX refers to transitional metal compound pro-oxidants.) Controls for each sample type (with the exception of 6P) were exposed for 100, 200, and 250 hours. The following conditions were used:

Apparatus:	Xenon Arc Weather-Ometer®
Black Panel Temperature:	63 +/- 3°C
Cycle:	102 minutes light/18 minutes light and water spray
Relative Humidity:	50 +/- 5%

Prior to exposure, samples were conditioned for a minimum of 24 hours at 23°C and 50%   lative humidity. After exposure, samples were returned to RTI for testing.

To study the effects of temperature, the four sample types (6P, PG, ADM, and PS) were exposed for a constant time (50 hours) at several temperatures under the following conditions:

Test Method:	ASTM G 26
Apparatus:	HERAEUS XENOTEST® 1200
Light Source:	Xenon Arc
Black Panel Temperature:	65, 70, 75, 80, and 85°C
Duration:	50 hours
Cycle:	102 minutes light/18 minutes light and water spray
Relative Humidity:	50 +/- 5%
Filter:	Borosilicate Natural Sunlight Suprax
Radiation:	14.5 MJ/m^2 (300-400 nm)

2.4.2 Accelerated Laboratory Soil Exposure

The biodeteriorable samples (PCL and ADM) and corresponding controls were subjected to accelerated soil burial under controlled laboratory conditions. Rectangular pieces of film approximately 8" x 10" in size were placed in a specially prepared soil mixture contained in Rubbermaid® plastic containers. Each box contained approximately 3.2 kg soil, and four film samples were initially placed into each container. A total of 8 sheets each of PCL and ADM were exposed, along with 4 sheets of each control. Thus, a total of 6 plastic containers were necessary for the experiment. For consistency, one large batch of soil mixture containing additives to provide microbes and nutrients was made up and divided among the six containers. The contents of the mixture were:

1. "Black Kow" Brand Topsoil - (6 x 3155) g
2. Garden soil (source: outdoors at RTI) - 1% of weight of topsoil
3. Urea - 0.1% of total weight of plastic samples
4. K_2HPO_4 - 0.05% of total weight of plastic samples
5. Water - 20% of the saturation value of the topsoil (in this case, 1735 mL)

The containers were incubated in a controlled-temperature room at 37°C. The initial sampling intervals were every 3 days for the degradable films and every 6 days for the controls, but testing of the inital samples showed that longer exposure durations would be needed to achieve measurable degradation. The actual sampling frequencies are given in Appendix C.

2.4.3 Evaluation of Spectral Sensitivity: Determination of the Activation Spectrum of a Material by the Sharp Cut-on Filter Technique

(a) Filter Set

The set of filters covering the ultraviolet region consisted of 12 or 13 glass filters with cut-on wavelengths (5% transmittance) ranging from 265 nm to 375 nm. The filters were normally 2" x 2", but other sizes up to 6" x 6" can be used. A combination of Hoya and Schott filter glasses were used to fabricate filters with the required transmission characteristics. The spectral transmittance curves of the first six filters in the set are shown in Figure 2.4.1.

In fabricating the filters, types of glass which provide a spectral shift between filter pairs of approximately 10 nm at 40% transmittance when ground to appropriate thicknesses are generally selected. The exact thickness to which each filter is ground is governed by
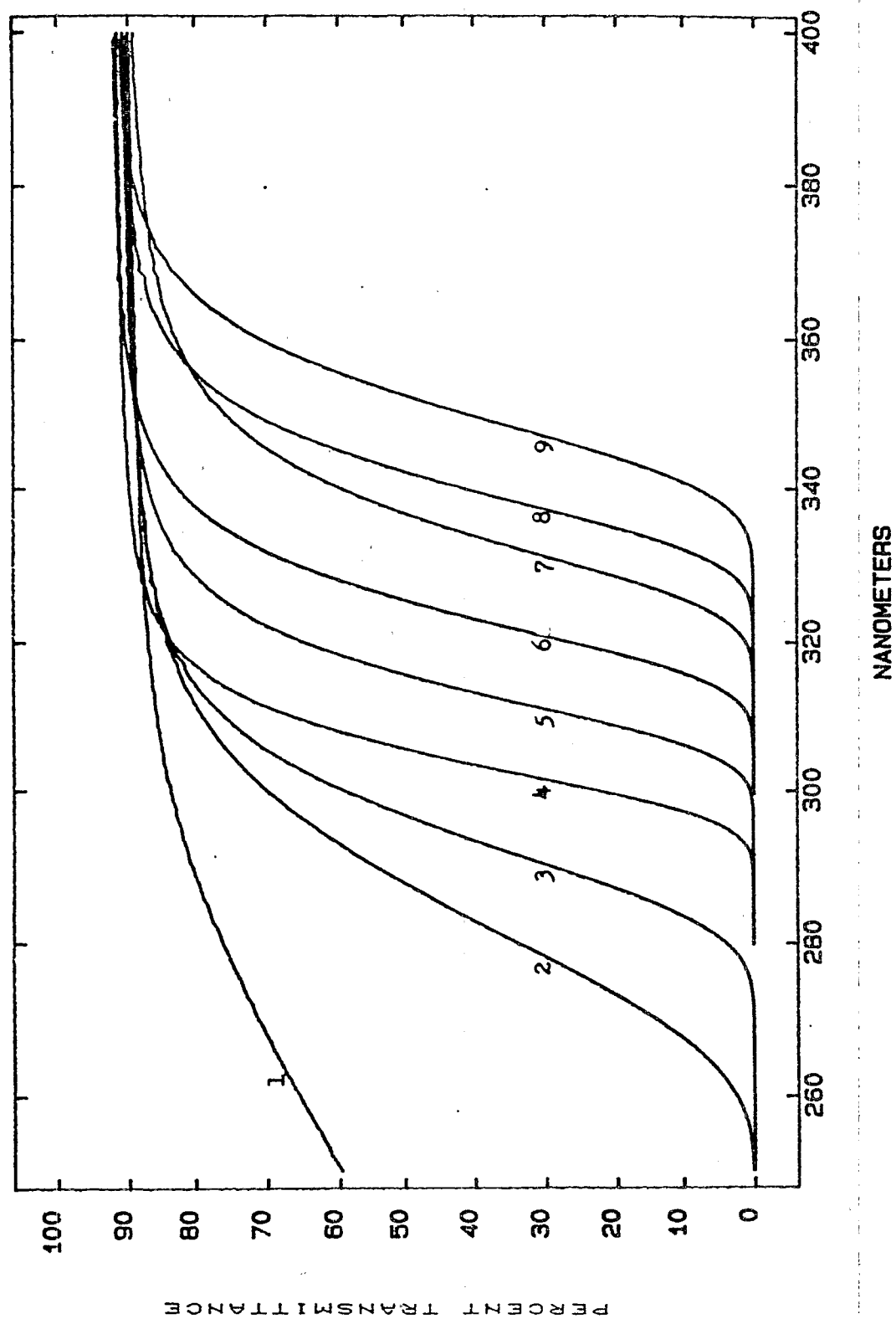
Figure 2.4.1. Spectral transmittance of sharp-cut filters.

the incremental ultraviolet transmitted by the shorter wavelength filter of the pair. The thicknesses are adjusted so that the incremental ultraviolet is nearly the same for all filter pairs. Because of the large tolerance in transmission characteristics of each glass type necessitated by variations in the melt, the thickness required for each type varies with the melt.

(b)   Determination of Incremental Ultraviolet Between Filter Pairs

The area in Figure 2.4.1 between the curves of filters 5 and 6 represents the additional portion of the ultraviolet transmitted by filter 5 compared with that transmitted by filter 6. The spectral curve in Figure 2.4.2 is a plot of Δ% transmittance for the filter pair. Similar spectral curves spaced about 10 nm peak to peak were obtained for the other pairs of filters.

The area of the spectral curve above Δ 10% transmittance is referred to as the incremental ultraviolet (Figure 2.4.2). This is the radiation transmitted by filter 5 which is mainly responsible for the incremental degradation in the specimen exposed behind filter 5 compared with the degradation in the specimen exposed behind filter 6. The area can be determined from transmission spectra by any suitable technique such as by the use of a planimeter, by counting squares if plotted on grid paper, or by cutting out the area and weighing it. The measured areas of the spectral curves of the different filter pairs above Δ 10% transmittance are used to determine the normalization factors.

(c)   Normalization Factors

Although the filter thicknesses are adjusted to provide nearly equal areas above the Δ 10% transmittance level for all filter pairs, the areas are not identical. Therefore, normalization factors are used to adjust the measured incremental degradation caused by each spectral region so that the activation spectrum represents the relative effect of equal spectral portions of the ultraviolet.

The normalization factor for each filter pair is calculated by dividing the average of the measured areas by the area measured for each filter pair. Since degradation is usually not a linear function of radiant exposure, the filter set is designed so that the maximum adjustment required is less than 15%.

(d)   Activation Spectrum

The activation spectrum is a plot of the relative extent of degradation caused by different spectral portions of the radiation of the source. In the sharp cut filter technique, the adjusted incremental degradation of the pairs of specimens exposed behind each pair of adjacent filters in the set is plotted in bar graph form versus the spectral band pass of the filter pair.
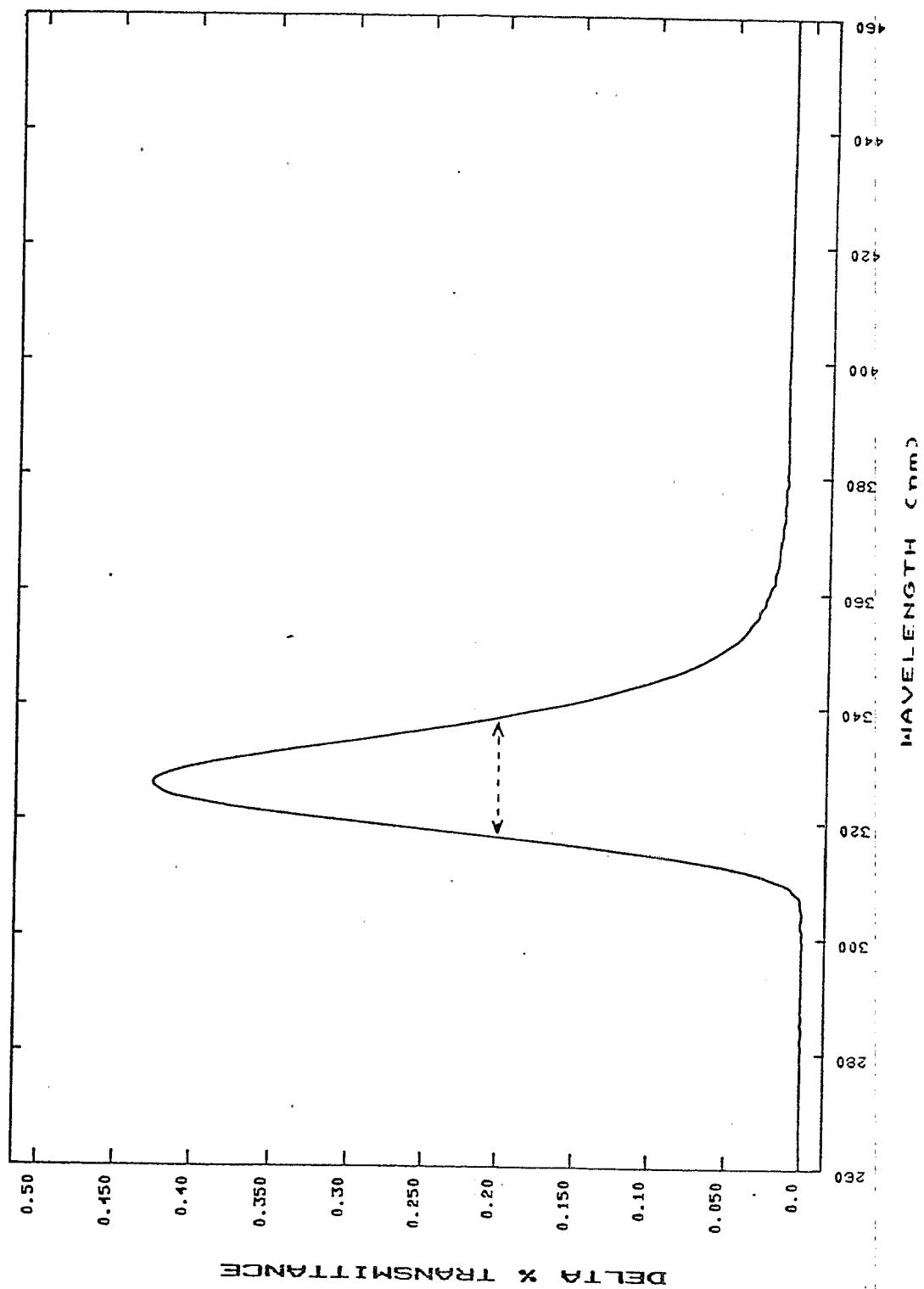
Figure 2.4.2 Spectral band for incremental UV of filters 5 and 6.

The spectral band pass defined by a pair of filters is the spectral range at Δ 20% transmittance, approximately half the maximum Δ% transmittance. Thus, for the filter pair 5-6 of the set illustrated in Figures 2.4.1 and 2.4.2, the maximum Δ% transmittance is 42% at 326 nm and the spectral range at Δ 20% transmittance is from 317 to 337.

(e) Exposure

Samples were exposed in an Atlas 6500 watt borosilicate-filtered xenon arc Weather-Ometer® using the filter sets described above. Several preliminary exposures using a variety of filters were carried out for each sample type, and the information was used to select the proper exposure times for activation spectra determination. Figure 2.4.3 schematically illustrates the specimen arrangement during exposure.
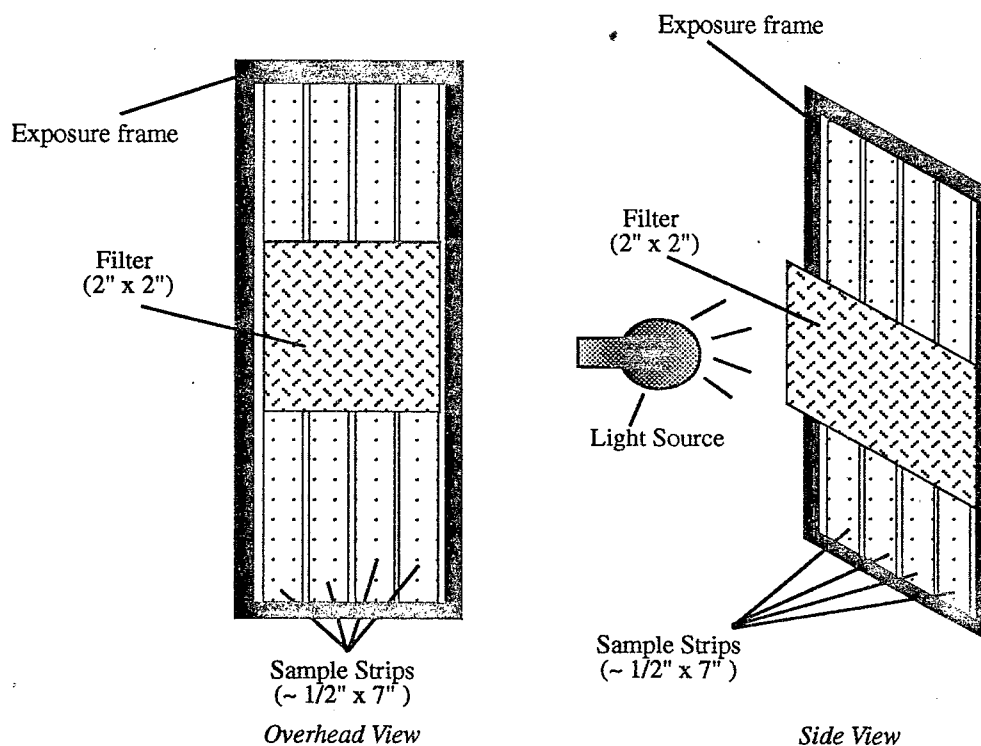
Figure 2.4.3. Specimen arrangement for Weather-Ometer® exposure of activation spectra samples.

(f) Testing

With the exception of polystyrene foam, all exposed samples were tested on an Instron Model 1122 using a crosshead speed of 500 nm/min and a gauge length of 40 mm. Yellowness Indices of exposed polystyrene foam were measured according to ASTM D1925 using a Macbeth 1500 colorimeter with integrating sphere for reflectance

2-19

measurements. The specular component of light was excluded and the ultraviolet component included in the measurements. The specimens were backed with white ceramic tile. On the basis of CIE standard illuminant C, Yellowness Index (YI) was calculated from the tristimulus values X, Y, and Z using the equation below (see also Section 2.5.2):

$$YI = \frac{100\ (1.28X - 1.06Z)}{Y} \tag{2-1}$$

2.5 OTHER TEST METHODS

2.5.1 Tensile Properties

Tensile testing of plastic films after field, Weather-Ometer®, and lab accelerated soil burial exposure was carried out according to ASTM D882 (Tensile Properties of Thin Plastic Sheeting). Method A of the test procedure, which employs a constant rate of grip separation, was used. The instrument used was an Instron Model 1122 connected to a computerized data acquisition system with a Sintech Testworks software package to allow for statistical analysis of the data. At least five test pieces of each sample type were tested unless deterioration of the film due to exposure did not allow five pieces to be cut. To prepare test pieces, films were cut into 1/2-inch strips using a TMI Twin-Blade Cutter Model 22-34-03. Thickness values (to the nearest 0.001 mm) of films were obtained prior to exposure using a Digitrix II Digital Micrometer. Thickness values are reported in Appendices J and K, which summarize all tensile data obtained. Instron parameters for the various sample types are shown in Table 2.5.1. As per the test method, test parameters were chosen based on the properties of each sample material.

Tensile testing for determination of activation spectra of 6P, PG, and PCL was carried out as described above except that gauge length was 4.0 cm instead of 5.0 cm.

2.5.2 Yellowness Index

Yellowness Index (YI) and L, a, b, values for polystyrene foam samples were determined in accordance with ASTM standard D1925-70 by reflectance measurements using an X-Rite 968 colorimeter. A standard calibration tile, whose percent reflectance was measured between wavelength 400 nm and 700 nm against CPPA calibrated Japanese Opal Glass EW-24 with the exclusion of specular light, was used as the white standard. Both for the opal glass standard and for the test samples, the UV component of the incident light (98%) was included but the specular component of the reflected light was excluded during

Table 2.5.1. Instron Test Parameters Used for Testing Exposed Samples.

Material	Test Parameter				
	Full Scale Load (kg)	Crosshead Speed (mm/min)	Gauge Length (mm)	Clamp	Jaw Face Size (in)
6P 6PC	20	500	50	Pneumatic; 50PSI	1 x 1.5
PG PGC	2	500	50	Pneumatic; 50PSI	1 x 1.5
ADM ADMC	2	500	50	Pneumatic; 50PSI	1 x 1.5
PCL LLDPE	2	500	50	Pneumatic; 50PSI	1 x 1.5
BP	2	50	100	Pneumatic; 50PSI	1 x 1.5

the measurement. The yellowness index (YI) was based on CIE standard illuminant D_{60} and CIE 10° standard observer viewing (CIE-SO) and was obtained from the tristimulus values of X, Y and Z relative to the source C using the equation 2-1.

$$YI = \frac{100\ (1.28X - 1.06Z)}{Y} \qquad (2\text{-}1)$$

"L", "a", and "b" parameters were also calculated from the tristimulus values. The following equations were used for the purpose.

$$L = 116\ (\frac{Y}{Y_n})^{1/3} - 16 \qquad (2\text{-}2)$$

$$a = 500\ [\ (\frac{X}{X_n})^{1/3} - (\frac{Y}{Y_n})^{1/3}\ ] \qquad (2\text{-}3)$$

$$b = 200\ [\ (\frac{Y}{Y_n})^{1/3} - (\frac{Z}{Z_n})^{1/3}\ ] \qquad (2\text{-}4)$$

The tristimulus values X_n, Y_n, and Z_n define the color of normally white object-color stimulus. This is given by the spectral radiant power of a standard illuminant (C.I.E. illuminant C, in this case) reflected into the observer's eye by the perfectly reflecting diffuser. Under these conditions, X_n, Y_n, and Z_n are the tristimulus values of the standard illuminant with Y_n equal to 100.

Several values of YI obtained from different sections of exposed sheet were used to obtain the mean value of yellowness index. Reproducibility of measurement was generally better than ±0.50 units.

2.5.3 Tumbling Friability

For polystyrene foam samples exposed outdoors, degradation was measured in general accordance with the Test Method for Tumbling Friability of Degradable Polystyrene Foams, which is currently under consideration by subcommittee D20.96 as a standard ASTM test method. This method determines the mass loss of a foam sample as a result of the abrasion and impact produced by a laboratory tumbling device. It was suitable for the samples subjected to outdoor weathering and to laboratory-accelerated weathering, but it could not be used for samples exposed to marine conditions, where fouling caused by marine growth greatly affected sample weight.

The tumbling apparatus was a cubical box of oak wood (3/4 in thick) with inside dimensions of 190 x 197 x 197 mm. One of the 190 x 197-mm faces was a hinged lid

which was gasketed to prevent passage of dust. One of the 197 x 197-mm faces was attached to an axis (the axis was normal to the center of the face) which allowed rotation of the box at 60 ± 2 rpm. Two sets of 24 cubes (3/4 ± 1/32 in) of white oak wood were prepared. Each set of cubes was preconditioned by tumbling for 6000 revolutions. The two sets were numbered from 1 to 24 so that at the end of each test, a given cube could be removed and replaced with the correspondly-numbered cube from the other set. In this way, the cubes were continually rotated, and cube wear was eliminated as a variable.

Each test required 12-1" x 1" squares cut from the foam sample. All cut samples were conditioned overnight at 50% relative humidity in a dessicator at 23°C before testing. The humidity level in the dessicator was maintained by a saturated KSCN solution.

Since all the unexposed polystyrene foam samples were of uniform thickness, initial values (before exposure) of mass of a 1" x 1" square were determined for both the degradable and the control PS foam by cutting and weighing 50 squares of each. These averages were used in all tumbling friability calculations as initial mass. For degradable foam, a 1" x 1" square weighed 0.1031 g with a standard deviation of 0.0018 g; a square of the control material weighed 0.1039 g with standard deviation of 0.0039 g.

Before each day's testing, the apparatus was calibrated by setting the speed control and counting the number of revolutions per 60 seconds. (This calibration was done with the 24 wooden cubes in the box.) The count was repeated twice and the three values entered in the calibration log book. For an average speed above or below 60 ± 2 rpm, the speed was readjusted and calibration repeated. Based on the average speed, the time required to give exactly 600 revolutions was calculated and used for all testing for that day.

For each test, 24 wooden blocks and 12 foam test squares were placed into the box and the lid secured. The box was rotated for 600 revolutions, after which the wooden cubes were removed and the polystyrene emptied onto a 1/4" mesh screen placed over a collection pan. The screen was gently tapped to cause dust and large particles to pass through, and all large pieces which did not pass the screen were collected and weighed to the nearest 0.0001 g.

Mass loss was calculated with the following equation:

$$\text{Mass Loss } (\%) = [(M_1 - M_2)/M_1] \times 100 \qquad (2\text{-}5)$$

where M_1 was the original mass before exposure (equals 12 x the initial values discussed above) and M_2 was the weight recorded after the tumbling friability test.

2.5.4 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to obtain molecular weight measurements for selected foamed polystyrene sheets (PS) and polycaprolactone/ polyethylene

blend films (PCL). Chloroform solutions (0.2% w/w) of PS samples were prepared directly from the exposed samples. For PCL samples, the polycaprolactone fraction was extracted by stirring the film in chloroform at ambient temperature for at least 24 hours. The chloroform solutions of polycaprolactone were then diluted to give the required concentration for GPC analysis. All solutions (particularly those of the marine floating samples, which were covered with foulants) were filtered prior to injection into the GPC.

The chromatography system used consisted of a Waters Associates pump (Model M-6000A), a Waters Associates differential refractometer (Model R401), and five Ultra-sytragel® columns (Millipore) with pore sizes of 500, 10^3, 10^4, 10^5, and 10^6 Å. The mobile phase was HPLC-grade chloroform at a flow rate of 0.9 mL/min. The attenuation setting on the refractometer was 2X. Eight monodisperse polystyrene standards were used in calibration.

Data from the chromatograms were entered into a computer program which calculated molecular weights and molecular weight distribution based on the coefficients for each polymer for the Mark-Houwink equation and on the elution volume of the polystyrene standards.

GPC results were obtained for the following PS samples: outdoor exposure in Chicago and Miami, marine floating exposure in Miami and Seattle, and Weather-Ometer® exposure. For PCL, GPC results were obtained for outdoor soil burial exposure and for marine sediment exposure in Miami.

2.5.5   Water Vapor Transmission

The area of exposed film samples available for the water vapor transmission rate [WVTR] determination was small, so a smaller area than the standard sample area of at least 3000 sq.mm (ASTM E 96) was used in the test. The methodology described is therefore a modified test method.

Measurements of WVT were made using a modified "cup method", where the film sample was attached over the mouth of a cylindrical glass dish (5.0 cm diameter and 58 ml in volume) containing about 20 g of calcium oxide (Aldrich Chemicals), using a rubber o-ring. The weight of the dish with attached film was accurately determined with a balance readable to 0.1 mg. Two to four replicate dishes were used for each determination. The weighed dishes were placed in a dessicator containing deionized water and kept in an air oven at 37°C. Figure 2.5.1 depicts the experimental set-up for WVTR measurements. At appropriate intervals the dishes were removed, cleaned free of adhering water droplets on the outside, and weighed. Samples were generally weighed every 2-4 days for a period of 10 days. Thicknesses of the films were measured using a recording micrometer (Digitrix

II, Japan Micrometer Manufacturing Co.). The slope of a plot of the weight gain versus the duration of exposure to saturated water vapor yielded the WVTR of the film.

In the case of samples exposed outdoors for long periods of time, the material was too brittle to be folded over the outside rim of the glass dish and secured with the o-ring. This led to development of micro-cracks along the fold. For these samples, a smaller dish with a diameter of 2.1 cm was used and the film sample was glued on to the mouth of the

37°C Oven
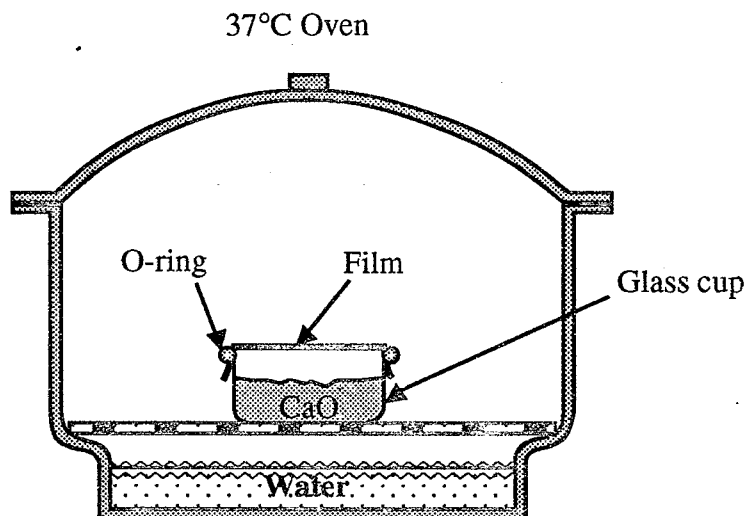
Figure 2.5.1   Experimental set up for WVTR measurements.

dish using rubber cement. Weight gains of photodegraded plastic film samples were monitored for a period of 22 - 25 days.

2.5.6 Thermogravimetry

A thermogravimetric method was developed for rapid determination of the starch content of polyethylene/starch blends.

A Perkin Elmer model TGS-2 Thermogravimetric System, with a 4-system microprocessor temperature control unit and a TADS data station, was used. The samples of plastic films were cut into discs (5 mm in diameter). Several discs cut from different areas of the film sample were placed together in an aluminum sample pan and set in the sample holder of the equipment. Initial weight of the sample was recorded and generally found to be 6 - 10 mg. The sample in the pan was heated from 50°C to 450°C in a helium atmosphere at a heating rate of 10°C/min. The weight of sample (with pan) was monitored as a function of temperature.

Under these conditions a distinct loss in weight was obtained at about 280°C - 340°C that was attributed to degradation of starch. The loss in weight and the initial sample weight were then used to determine the percent starch in the sample. In the case of samples exposed in soil environments, the film was washed free of surface debris and dried prior to being tested.

2.5.7 Gas Transport Properties

A gravimetric sorption technique was used to obtain transport parameters for the plastic films. A recording electrobalance (Cahn 2000, Cahn Instruments Inc.) was used to monitor the increase in weight of a sample placed in a carbon dioxide atmosphere due to sorption of the gas by the polymer previously held *in vacuo*. The weight increases were directly recorded on floppy disc using a simple data acquisition system consisting of an A-D board and an IBM XT computer. The balance assembly was insulated, protected from air current, and maintained at constant temperature $30 \pm 2°C$ in a lagged wooden box.

A sample of the film material (approximately 200 mg for PG samples and 170 mg for 6P material) was placed in an aluminum pan and placed in the sample holder of the microbalance. The sample chamber was evacuated to 0.01 torr and maintained under vacuo for 24 hours to remove any dissolved gas from the polymer matrix. Dry carbon dioxide at a pressure of 760 mm Hg was introduced into the chamber, and the data collection was carried out at the rate of a reading every 5 or 10 seconds. Sensitivity of the balance was 0.5 µg. Data collection was continued until a constant weight was recorded.

Sorption data obtained in the above described experiments can be conveniently plotted as amount of gas absorbed by the plastic versus time. Solubility, S, is calculated using the equilibrium weight gain at t_∞, M_∞, as follows.

$$S = \frac{(M_\infty/M_W) \times 29.47}{(w_0/\rho)} \qquad (2\text{-}6)$$

where M_W is the molecular weight of carbon dioxide (44 g/mole), ρ is the density of film (0.93 g/cc for LDPE), w_0 is the weight of film sample, and P is the applied pressure of gas. M_∞ is the final maximum weight of the sample after gas sorption. During initial stages of gas sorption the time dependence of the weight gain by the sample was given by the following equation.

$$\frac{M_t}{M_\infty} = \frac{4}{\ell}\sqrt{\frac{Dt}{\pi}} \qquad (2\text{-}7)$$

where ℓ is the thickness of the sample, and D is the diffusion coefficient of carbon dioxide in the film sample. The diffusion coefficient was calculated from the initial slope, k, of the plot of (M/M_∞) versus square root of time.

$$D = \frac{k^2 \ell^2 \pi}{16} \qquad (2\text{-}8)$$

Permeability constant P was obtained as the product of solubility and diffusivity

$$P = S * D \qquad (2\text{-}9)$$

2.6 TOXICITY METHODOLOGY

2.6.1 Extraction Procedures

Thin plastic sheets such as (ethylene-carbon monoxide) copolymer, the Plastigone material, and the ADM plastic material were ground by a Wiley mill and passed through 0.032-in mesh. The grinding was facilitated by dipping the plastic sheets in liquid nitrogen. The foamed polystyrene sample was ground by a blender. The ground plastics were leached by the water extraction procedure as follows:

1. Add 80 g of ground plastic to a container,
2. Add 4 L of deionized water,
3. Measure and record initial pH of the plastic/water mixture,
4. Stir the mixture continuously for 24 hours at 18 to 27°C,
5. Filter the extract with porcelain funnel using Whatman Filtering Paper No. 1,
6. Measure and record the pH of the filtrate,
7. Test filtrate for toxicity.

2.6.2 General Laboratory Toxicity Testing Procedures

1. Prior to mixing toxicity test dilutions, dissolved oxygen (DO), pH, total residual chlorine, conductivity, and salinity of the sample were measured and recorded. For DO values of an extract sample <40% saturation, the sample was aerated with single-bubble aeration until the DO was >40% saturation. Aeration rate and duration were recorded. For pH values below 6.0 or above 9.0, the pH was generally adjusted to pH 7.0 with base or acid. The type, strength, and volume of acid or base added were recorded.

2. For cases where dechlorinated water was used as diluent, the total residual chlorine was measured as nondetectable prior to using a given batch for testing.

3. All containers, glassware, and materials coming into contact with the test solution were cleaned and dried. Each test container and other glassware were labeled as to the test concentration, replicate number, and test identifier or experiment ID number.

4. For definitive tests at least 5 test concentrations and a control were tested. Ideally, the test concentrations should produce extreme effects in the high concentrations (assuming the sample is toxic), moderate or partial effects in the intermediate concentrations, and no effects in the low concentrations. At least 2 replicates for each test concentration were used.

5. Appropriate volumetric glassware was used for preparing the test concentrations (Class A volumetric flasks, graduated cylinders, and pipets). The total volume of the glassware used was not more than 2 times the volume being measured. The glassware used and volumes of effluent/stock solution and diluent measured for each test concentration were recorded.

6. Prior to introducing the test organisms, temperature, pH, and conductivity (and salinity for saltwater testing) of (at a minimum) the control, intermediate, and high test concentrations were measured. Dissolved oxygen was measured in one replicate of all concentrations. These parameters were measured at least every 24 hours for the test duration, more frequently (hourly) for a low initial DO of the high concentration. For tests in which the DO of any container fell below 40% saturation for warm water species or 60% saturation for cold water species, all test chambers were provided single-bubble aeration (approximately 100 bubbles/min.) for the remainder of the test. Alkalinity and hardness were measured in the control and high concentration prior to test initiation.

7. Test organism re randomly assigned to the test containers. One to five test organisms were seq atially placed in each container starting with the control and ending with the highest concentration. This was repeated until the appropriate number of test organisms were added to each container. During transfer, organisms were released under the surface of the water, and the volume of culture water transferred with the organism was minimal (<0.5 ml).

8. All containers were checked for the proper number of organisms and to ensure that the organisms were not harmed in the transfer process.

9. The number of live organisms in each test container was recorded every 24 hours for the test duration. Dead organisms were removed when noted. General behavior of the organisms was also noted.

2.6.3 Static or Static Renewal (48 or 96 H) Fathead Minnow Toxicity Tests

1. The test temperature was $20 \pm 2°C$.
2. All test fish were 1-90 days old at the start of the test. The range of ages in each test did not exceed 3 days.
3. The test volume and test chamber size was based on test organism size. Organism loading did not exceed 0.8 g/L.
4. Steps 1 through 9 in General Laboratory Toxicity Test Procedures (G.1) were followed.
5. All test solutions were renewed at 48 hours: A duplicate set of chambers was used, fresh solutions prepared, and organisms carefully transferred to corresponding test chambers just as when initiating the test.
6. U. S. EPA computer program for analysis of acute toxicity test data was used.

2.6.4 H.1 *Ceriodaphnia dubia* Survival and Reproduction Test

1. The test temperature was $25 \pm 1°C$.
2. The test chambers were 30 ml plastic beakers, and the test volume was 15 ml.
3. The samples were filtered through a 60 μm plankton net.
4. Neonate *Ceriodaphnia dubia* <24 hours old and released during the same 8 hour period were used as test organisms.
5. Generally 6 or 7 test concentrations, including a control, were used. Ten organisms were exposed to each concentration, one per test chamber. The test consisted of 60 or 70 beakers.
6. Stock solutions (200 ml) of each test concentration were prepared using the appropriate volumetric glassware. BMI *Ceriodaphnia* culture water (20% DMW mixed with a pond water) was used as diluent. All stock solution containers were labeled with concentration and test I.D.#.
7. The temperature of the stock solutions was adjusted to $25\pm1°C$. Temperature, dissolved oxygen, conductivity, and pH in the control, low, intermediate, and high concentration stock solutions were recorded. Dissolved oxygen concentration of any stock solution of less than 40% saturation necessitated the aeration of all stock solutions prior to the start of the test. Alkalinity and hardness of the control and high concentration were measured.
8. Test chambers were labeled with concentration, test I.D.#, and replicate #. Stock solutions were distributed to appropriate test chambers (15 ml each chamber). *Ceriodaphnia dubia* food (0.1 ml) was added to each chamber along with 0.05 ml *Selenastrum* food .

Table 2.6.1   Test Conditions for Acute Fathead Minnow (*Pimephales promelas*) Toxicity Tests.

1.	Temperature (°C)	20°C ± 2°
2.	Light quality:	Ambient laboratory illumination
3.	Light intensity:	50-100 foot candles (ft c) (ambient laboratory levels)
4.	Photoperiod:	16 h light/24 h
5.	Size of test vessel:	500-1000 ml
6.	Volume of test solution:	500-1000 ml
7.	Age of fish:	1-90 days
8.	No of fish/rep.	10 (not to exceed 0.8 g fish per liter of test solution)
9.	No. of replicate test vessels per concentration:	2
10.	Total no. organisms per concentration:	20
11.	Feeding regime:	None
12.	Aeration:	None, unless DO concentration falls below 40% of saturation, at which time single-bubble aeration should be started.
13.	Dilution water:	Dechlorinated water or other approved water.
14.	Test duration:	Definitive test 48 or 96 h (static or static renewal test)
15.	Effect measured:	Mortality - no movement (LC50)

9. One organism was transferred to the 0% "A" replicate test chamber using a polyethylene disposable pipet (bore size 3 mm). During transfer, the organism was released below the surface of the test solution and as little culture water as possible was transferred with the organism (less than 0.3 ml).

10. One organism from a given brood was transferred to each "A" replicate test chamber as described above (one pipet was used to transfer control animals only). When all "A" test chambers contained one organism, organisms from another brood were transferred to the "B" replicates. Organisms were transferred in this manner until all test chambers contained one organism. Each test chamber contained one organism from a brood size greater than 8.

11. Replicates of each concentration were randomly placed in rows.

12. Test solutions were renewed daily with the appropriately collected and mixed samples. Two-hundred ml stock solutions were prepared, their temperature adjusted, and water chemistry analyses performed. Starting with the control (0%), organisms were transferred to clean beakers containing 15 ml of fresh test solution containing 0.1 ml

Ceriodaphnia food and 0.1 ml *Selenastrum* food (only adults were transferred, offspring were discarded after counting). The number of living adults and the number of offspring produced by each female were then recorded. Water chemistry analyses were performed after organisms were counted and transferred in one randomly selected chamber from the control, low, intermediate, and high test concentrations (this was recorded as "before renewal").

13. The test ended at 7 days or when 60% of the control organisms had had 3 broods, and each female must have averaged ≥ 15 offspring.

14. Seven day NOEC and LOEC values for survival and reproduction were calculated using computer programs for analysis of chronic toxicity test data as per EPA/600/4-89/001.

Toxicity testing was carried out by Biological Monitoring, Inc. of Blacksburg, VA, using water extracts of plastics prepared at Research Triangle Institute.

Table 2.6.2   Test Conditions for *Ceriodaphnia dubia* Survival and Reproduction Test
(Conforming to EPA/600/4-89/001).

1.	Test Type:	Static renewal
2.	Temperature (°C)	$25 \pm 1°°C$
3.	Light quality:	Ambient laboratory illumination
4.	Light intensity:	10-20 $\mu E/m^2/2$, or 50-100 ft c (ambient laboratory levels)
5.	Photoperiod:	16 h light, 8 h darkness
6.	Size of test vessel:	30 ml
7.	Volume of test solution:	15 ml
8.	Renewal of test concentrations:	Daily (for N. Carolina Methodology, 2X)
9.	Age of test organism:	<24 h; and all released with an 8 hour period
10.	No. of test organisms per chamber:	1
11.	No. of replicate chambers per treatment:	10
12.	Feeding regime:	Feed 0.1 ml each of food suspension Selenastrum per test chamber daily.
13.	Aeration:	None
14.	Dilution water:	Moderately hard standard water, 20% DMW receiving water, other surface water, or ground water with hardness similar to receiving water.
15.	Dilution factor:	Approximately 0.3 or 0.5.
16.	Test duration:	7 days or until 60% of the controls have 3 broods.
17.	Effects measured:	Survival and reproduction
18.	Effluent concentrations:	Minimum of 5 and a control for definitive tests.
19.	Test acceptability:	80% or greater survival and an average of 15 or more young/surviving females in the control solutions. At least 60% of surviving females in controls should have produced their third brood.
20.	Sampling requirements:	For on-site tests, samples are collected daily, and used within 24 hours. For off-site tests, a minimum of 3 samples are collected. Maximum time to first use of a sample is 36 hours.

2.7 PRELIMINARY RECYCLING STUDY

2.7.1 Sample Preparation

Four of the degradable materials were chosen for the recycling study: (ethylene-carbon monoxide) copolymer (6P), low density polyethylene/MX (PG), low density polyethylene/starch/MX (ADM), and expanded polystyrene foam (PS). Samples of these degradable plastics were pre-exposed to outdoor weathering in Miami, FL, for selected exposure durations and were then mixed with virgin resin to extrude new films. Pre-exposure was carried out in general accordance with ASTM G7 (direct sunlight, samples backed on racks at 45° South), with exposure dates given in Table 2.7.1 below:

Table 2.7.1 Pre-Exposure of Degradable Plastics for Recycling Study

Sample Code	# of Sample Pieces*	Exposure Duration (days)	Exposure Dates	Total Solar Radiation (MJ/m^2)	Total Solar UV Radiation- 300 -385 nm (MJ/m^2)
6P	27	5	8/2-8/7/90	61	3
6P	27	9	8/2-8/11/90	114	6
6P	27	15	8/2-8/17/90	190	9
PG	66	5	7/19-7/24/90	74	4
PG	66	9	7/19-7/28/90	153	8
PG	66	14	7/19-8/2/90	225	11
ADM	56	5	8/2-8/7/90	61	3
ADM	56	9	8/2-8/11/90	114	6
ADM	56	15	8/2-8/17/90	190	9
PS	10	5	7/19-7/24/90	74	4
PS	10	9	7/19-7/28/90	153	8
PS	10	14	7/19-8/2/90	225	11

*These were the number of sample pieces required to give 80-100 g of sample for each exposure duration.

To prepare for extrusion, the exposed films were ground (6P, ADM) or chopped (PG, PS) into small pieces. Grinding was done using a Wiley mill; the samples were mixed with dry ice to keep them brittle enough to be cut by the blades of the mill. PG samples were too thin and flexible to be ground by this method; they were cut into small pieces with a paper cutter. PS samples were made into an aqueous slurry and chopped into small pieces using a household blender.

2.7.2 Extrusion

Various levels of the pre-exposed samples were blended with virgin resin and extruded into thin films. The compositions of the extruded films are given in Table 2.7.2. The virgin resin used for 6P, PG, and ADM was a medium density polyethylene powder (particle size <0.032") with melt index of 0.54; for PS, crystal polystyrene of melt flow 1.7 was used. The polystyrene virgin resin was in pellet form and had to be ground to pass 40 mesh prior to extrusion.

All pre-exposed films were micro-pelletized prior to extrusion using a single strand pelletizing die 0.062" in diameter. A Micro-pelletizer was used to make pellets roughly 0.02" in diameter and 0.02" long.

Blends (50 g) of virgin resin and exposed material were prepared according to the ratios given in Table 2.7.2. Extrusion was carried out using a Microtruder of 1/4" 24:1 L/D ratio with a 1/2 HP DC drive and digital temperature controllers. The feed section was water cooled, and screw RPM varied from 20 to 175. Temperatures were:

Barrel Zone 1:	300°F
Barrel Zone 2:	375°F
Barrel Zone 3:	425°F
Die:	425°F

A slit die was used to extrude films 2" wide and approximately 1.5 mils thick.

2.8 QUALITY OF DATA

Figure 2.8.1 shows the typical sample flow for all types of weathering experiments, both natural and accelerated exposures. Various steps were taken at each stage of sample handling to insure the highest possible data quality. These steps included proper sample identification and record-keeping, care in handling and preparing samples for exposure and testing, use of standard test protocols when at all possible, and statistical analysis of the data to determine its significance. An internal audit was conducted by the RTI Quality Assurance Officer, Doris Smith; her report is shown in Exhibit A.

(a) Sample Identification and Record-Keeping

When received from the manufacturer, all plastic materials (both enhanced degradable and controls) were assigned a code name generally consisting of several letters. These codes have been identified in Sections 2.1 and 2.2 of this report. These code names were consistently used throughout the study to refer to the samples. To prevent inadvertent mislabeling by the exposure service, small metal punches of various shapes were used to

Table 2.7.2. Composition of Extruded Films Prepared for Preliminary Recycling Study.

Film Code	Percent of Pre-exposed Material	Amount of Virgin Resin * (g)	Amount of Pre-exposed Material (g)	Exposure Time for Pre-exposed Material** (days)
6P-0	0	50.0	0.0	-
6P-1	5	47.5	2.5	0
6P-2	10	45.0	5.0	0
6P-3	20	40.0	10.0	0
6P-4	5	47.5	2.5	5
6P-5	10	45.0	5.0	5
6P-6	20	40.0	10.0	5
6P-7	5	47.5	2.5	9
6P-8	10	45.0	5.0	9
6P-9	20	40.0	10.0	9
6P-10	5	47.5	2.5	15
6P-11	10	45.0	5.0	15
6P-12	20	40.0	10.0	15
PG-0	0	50.0	0	-
PG-1	5	47.5	2.5	0
PG-2	10	45.0	5.0	0
PG-3	20	40.0	10.0	0
PG-4	5	47.5	2.5	5
PG-5	10	45.0	5.0	5
PG-6	20	40.0	10.0	5
PG-7	5	47.5	2.5	9
PG-8	10	45.0	5.0	9
PG-9	20	40.0	10.0	9
PG-10	5	47.5	2.5	14
PG-11	10	45.0	5.0	14
PG-12	20	40.0	10.0	14
ADM-0	0	50.0	0.0	-
ADM-1	5	47.5	2.5	0
ADM-2	10	45.0	5.0	0
ADM-3	20	40.0	10.0	0
ADM-4	5	47.5	2.5	5
ADM-5	10	45.0	5.0	5
ADM-6	20	40.0	10.0	5
ADM-7	5	47.5	2.5	9
ADM-8	10	45.0	5.0	9
ADM-9	20	40.0	10.0	9
ADM-10	5	47.5	2.5	15
ADM-11	10	45.0	5.0	15
ADM-12	20	40.0	10.0	15

- continued -

Table 2.7.2. (continued)

Film Code	Percent of Pre-exposed Material	Amount of Virgin Resin* (g)	Amount of Pre-exposed Material (g)	Exposure Time for Pre-exposed Material** (days)
PS-0	0	50.0	0.0	-
PS-1	5	47.5	2.5	0
PS-2	10	45.0	5.0	0
PS-3	20	40.0	10.0	0
PS-4	5	47.5	2.5	5
PS-5	10	45.0	5.0	5
PS-6	20	40.0	10.0	5
PS-7	5	47.5	2.5	9
PS-8	10	45.0	5.0	9
PS-9	20	40.0	10.0	9
PS-10	5	47.5	2.5	14
PS-11	10	45.0	5.0	14
PS-12	20	40.0	10.0	14

*   Virgin resin for 6P, PG, and ADM films was medium density polyethylene and for PS was crystal polystyrene.

**   Outdoor exposure was carried out at 45° South in Miami, Florida.
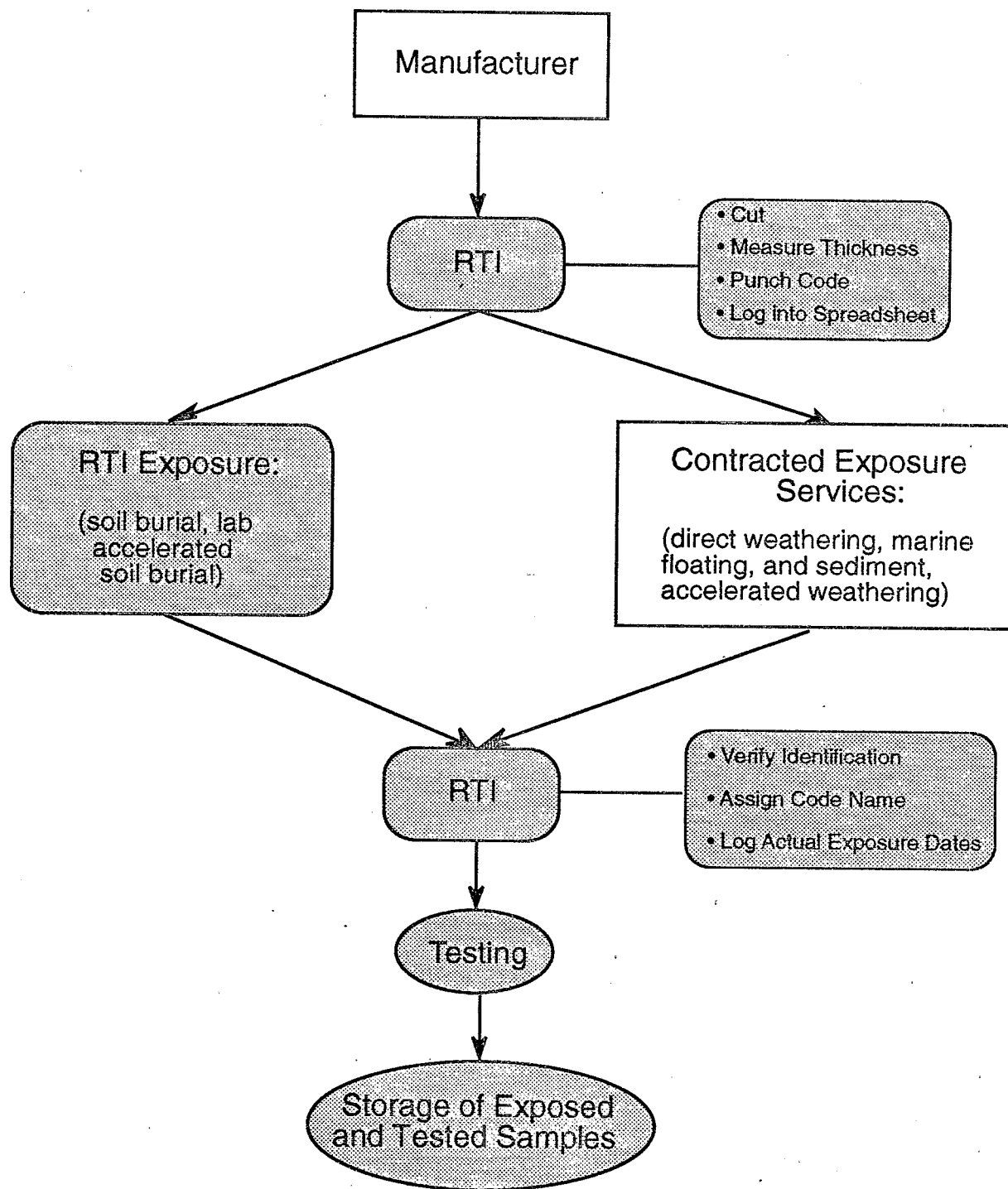
Figure 2.8.1 Typical sample flow.

TO: Shri Kulkarni

FROM: Doris Smith

DATE: July 19, 1990

Systems Audit Report: Exposure Assessment Work Assignment Number II-60.
Accelerated Environmental Exposure, Laboratory Testing, and
Recyclability of Photo/Bio-degradable Plastics.

The QAPP for this work assignment states that four major study
components will be reviewed during this study:

      -Results of preliminary studies,
      -Sample exposure in the field,
      -Measurement systems, and
      -Data processing.

A systems audit was conducted July 10 and July 19, 1990 to review the
first 2 study areas. A checklist was prepared and used for the systems
audit. The participants were

      Dr. A. L. Andrady, Preliminary Experiments and Subtask 1,
Literature Review,
      Dr. J. Pegram, Subtask 2, Outdoor Exposure.

The review focus was determining that the objectives of the preliminary
experiments and literature review were met, and reviewing the sample
documentation and custody records for outdoor exposure experiments.

Results:

The recordkeeping for this work assignment is excellent, and samples are
tracked using a computer spreadsheet system designed for this study.
Dr. Pegram is responsible for sample custody and tracking, and she
reviews all data from the samples. I suggested that she record her
reviews in some manner, such as initialing data sheets, or adding the
review to the spreadsheet.

The preliminary experiments fulfilled the objective of providing data to
determine the timing of the outdoor exposure experiments. Corrective
action was required in only one case where an experimental material was
found to have an unexpectedly short shelf life.

No data were reviewed as a part of this audit.

Copy:
Dr. A. L. Andrady

stamp the plastic films before sending them for exposure. Each sample type and each exposure location were represented by a different shape. These shapes were identifiable even after weathering of the sample. As samples were removed from field exposure racks, field sites, or from Weather-Ometers®, each sample was labeled. A paper label was stapled onto dry samples. Wet samples were placed in a plastic bag which was labeled on the outside with a marker pen.

After exposure, each sample was assigned a name which included the material code; type of exposure (O = outdoor direct weathering, F = marine floating, M = marine sediment, FW = freshwater, S = soil burial, W = Weather-Ometer®, LA = lab accelerated soil burial); exposure site; and duration of exposure. An example of a sample name would be 6P/O-Mi/3DY, which completely identifies the material with respect to type, location, and duration of exposure: (ethylene-carbon monoxide) copolymer exposed to outdoor direct weathering in Miami for three days.

Computer spreadsheets were used to keep a record of the number of samples sent for exposure, the dates samples were sent and received, actual dates of exposure, and testing of the exposed samples. These spreadsheets were updated each time a sample was received from the exposure service. Notes of any abnormalities were also entered into the spreadsheets. Back-up copies of the spreadsheets were kept on separate disks. Printouts of the spreadsheets are given in Appendices A, B, and C.

(b) Exposure

Samples were prepared for exposure at RTI by cutting the plastic films into approximately 8" x 10" sheets (except for 6P samples, which were received from the manufacturer in sheets which could be easily cut into 3-1/2" x 6" pieces which contained 6 1/2" strips of material). All sample pieces were consistently cut with the machine direction of the film along the 8" side so that strips for tensile testing would all be parallel to the machine direction and thus be comparable for a given material at various exposure times. The material and exposure location for each individual piece were then identified using the punch code system. Average thickness measurements of each type of material were taken prior to exposure and the values used for all subsequent stress-strain calculations. It was necessary to use unexposed thicknesses because marine exposure causes build-up of a foulant layer on the surface of the film and makes it impossible to obtain accurate thickness values. Thickness measurements were made to the nearest 0.001 mm using a digital Digitrix II micrometer connected to an EDP-1000 QC printer with statistical capabilities. At least ten measurements were taken for each average value determined.

To determine suitable sampling intervals, preliminary exposures were carried out at one location (Miami) for direct weathering for four of the sample types and for marine sediment exposure for two of the sample types. Results for tensile testing of the exposed materials were used to choose sampling frequencies and intervals for the main exposure experiment. In all cases, at least fifteen unexposed sample pieces were included in each set to be exposed to given conditions at each exposure site.

During the exposure, each of the three testing services carrying out outdoor and marine exposures were visited by either Dr. Andrady or Dr. Pegram. During these visits, the exposure set-ups were inspected to insure their adherence to the ASTM standard (G7) for outdoor exposure. In the case of marine floating and marine sediment exposures, no ASTM standards exist, so the set-ups were checked to insure that the conditions described in Sections 2.3.3 and 2.3.4 were provided.

Upon receipt of the exposed samples, each was checked to see that it had been properly identified by the test service. The code name was then assigned and the sample information concerning exposure logged into the computer spreadsheet. All paperwork provided by the test service concerning exposure dates for each sample, measured solar radiation, and exposure procedure was kept on file at RTI.

In some cases, particularly for marine and for soil burial exposure, photographs of exposed samples were made. The photographs were taken to show growth of marine foulants, partial loss of sample due to physical deterioration, or small holes in the sample matrix (noted for soil burial exposure). Color slides were made by staff photographers at RTI as soon as possible after receipt of the samples from the testing service. In most cases, the marine samples had not been dried before the photograph was taken. Complete computer records were kept of which samples were photographed and the date on which the photographs were made.

Climatic data for all the exposure sites were either provided by the testing service or were obtained from the National Climatic Data Center or other outside sources. Environmental data and the sources from which they were obtained are given in the appendices to this report.

Exposed samples were tested as soon as possible after their receipt at RTI from the testing service. Marine samples, which were received wet, were dried under a fume hood at ambient temperature before testing. Care was taken to cover the samples to prevent their exposure to light during drying. All samples were stored in brown envelopes until testing. Untested samples were stored separately from tested samples.

(c)   Testing

While different tests might have been carried out by several researchers, sample custody was handled by a single person (Dr. Pegram). All samples, before and after exposure as well as after testing, were managed by her.

Two major types of testing were carried out to determine degradation/deterioration of exposed samples: tumbling friability for polystyrene foam and determination of tensile properties by Instron for all other sample types. As described in Section 2.5.3, the procedure for tumbling friability testing is currently under consideration by an ASTM subcommittee for acceptance as a standard test method. The proposed draft procedure, kindly provided by the subcommittee, was followed for this test. The test apparatus was constructed according to the instructions in the method, using the specified materials. It was calibrated daily to determine the proper time to give the exact number of rotations per test. A computer log of the daily calibration was kept on record at RTI. Data summaries for tumbling friability, as well as a record of which samples had been tested, were kept on computer spreadsheets, including back-up files.

Tensile properties of the plastic films were measured according to ASTM D882, Tensile Properties of Thin Plastic Sheeting. This method applies to materials less than 1.0 mm in thickness. Method A of the procedure, Static Weighing - Constant-Rate-of-Grip Separation Test, was followed. As stated previously, the average thickness of each material prior to exposure was used for stress-strain calculations. Test pieces 1/2" in width were cut after exposure using a TMI twin-blade cutter which gave smooth, consistent edges and sample widths. Cut edges of the samples were routinely examined, and those which were not perfectly smooth were discarded. All samples were cut so that machine direction of the film was parallel to the direction of pull on the Instron. Samples were conditioned for 24 hours prior to testing in the standard laboratory atmosphere of 23 °C and 50% relative humidity. Instron testing was also conducted under these conditions. The hydrophobicity of these plastic samples minimized the effects of conditioning on the test results.

The Instron machine was calibrated daily using a 2-kg weight to set the load range. Gauge length was also checked before each use of the machine. Conditions for gauge length and rate of separation of the grips were determined according to the test method. As per the test method, at least five pieces were tested for each sample except in those cases where embrittlement or sample loss due to deterioration did not allow five pieces to be cut. Observations were made during testing as to whether the sample gave a clean break, tore, broke at the grip, or showed abnormal behavior. In most cases, samples which broke at the grip gave similar tensile results to those which broke between the grips, so these data were retained. (See Section 8.3 of ASTM D882.) Those data points which were abnor-

mally low due to tear failure, holes, or other anomalies were marked to be excluded from the statistical analysis. Computer printouts of the complete tensile data showing all individual results, comments, omitted data points, and statistical analyses of data were too voluminous to be included in this report but are on file at RTI. The data are also stored on floppy disks.

(d)   Tested Samples

After testing, samples were stored under dark conditions at ambient temperatures at RTI. The samples were identified by code name and were available for additional testing, e.g., Yellowness Index measurements and GPC for polystyrene foam, TGA, toxicity testing, and other methods discussed in this report.

All the exposed samples will be retained for a reasonable period of time at RTI.

(e)   Statistical Analysis of Data

As stated above, at least five pieces of each sample were tested for all Instron work except where loss of sample prevented it. Based on values for percent elongation at break, data points were omitted in cases of extremely low values, which were attributed to failure at a tear or hole in the sample and thus were not indicative of the tensile properties of the polymer material. Values for mean, standard deviation, and the number of test pieces included in the analysis are given in the summaries of tensile data in Appendix K. These numbers can be used to calculate confidence intervals for the mean values and thus determine whether significant differences exist between enhanced degradable and control materials for comparable conditions at a given duration of exposure. Relatively large values for standard deviation are inherent in the testing of exposed plastic materials due to the variability of the polymer material itself as well as to variations in exposure conditions within a given film sample, especially in marine exposure due to fouling.

For soil burial exposure, where the profile of the microbial population can vary widely even at the same geographic location, a randomized block experiment was carried out in which triplicate samples were buried in each of three different blocks. Analysis of variance of the data for soil burial showed the block effects to be insignificant and the treatment effects (variation of exposure times) to cause significant differences in values for elongation at break.

In conclusion, the basic methodologies proposed in the Quality Assurance Project Plan of January 1990 were closely followed. System audits relating to (a) preliminary studies, (b) field exposure, (c) measurement systems, and (d) data processing were carried out as proposed in Section 4.2 of the QA plan. In the case of Subtask 3, Degradation of Products of Plastics, the actual work carried out was less than planned due to resource

limitations. The proposed protocol for trapping and concentrating volatiles on Tenax cartridges was not used.

SECTION 3.0

SPECTRAL SENSITIVITY OF ENHANCED PHOTODEGRADABLE PLASTICS

3.1 ACTIVATION SPECTRA

The activation spectrum of a material identifies the wavelengths in a specific light source responsible for its photodegradation. A specially designed set of sharp cut-on filters was used to determine the relative effect of various spectral regions in the ultraviolet portion of the white light spectrum, between about 270 to 400 nm, on polymer degradation. Each spectral region was defined by the difference in transmittance of a pair of cut-on filters.

A separate sample of the same material was exposed behind each of the filters in the set for the same duration of time. The extent of degradation of the exposed material was then defined using an appropriate test method. The degradation caused by each of the spectral regions was based on the difference in degradation in the two samples exposed behind each pair of filters that defined a spectral region. It was plotted in bar graph form versus the spectral band pass of each filter pair to give the activation spectrum.

3.1.1 <u>Ethylene-Carbon Monoxide Copolymer (ECO Copolymer - Code 6P)</u>

Data were obtained for a set of ECO copolymer film samples exposed for 117 hours behind filters in a preliminary experiment. The temperature of these samples during exposure was maintained at 77°C (set 1). Table 3.1.1 shows the data summary for percent elongation at break for these samples. (Detailed results on tensile testing of all activation spectra samples are given in Appendix J.) Only the elongation at break is considered, as this measure was found to be the most sensitive tensile property to degradation.

Separate results are shown for the inner two strips of the exposed specimens to study the possibility that the outer positions (strips A & D in Figure 2.4.3) may have been shielded by the edge of the frame; however, no difference in wavelength sensitivity was noted when the inner position data was evaluated separately. However, the scatter in data is significantly lower for the later set of data (see Figure 3.1.1 compared to 3.1.2).

An activation spectrum was not plotted for data on ECO copolymer samples because extensive degradation occurred within a very narrow spectral region of the borosilicate-filtered xenon arc radiation. Based on percent elongation at break, the data suggested that wavelengths below 330 and 340 nm were mainly responsible for the degradation.

Differences in elongation at break among samples exposed behind filters #9 through #16 appeared to be within experimental variation. The lower elongation-at-break in these specimens compared with the unexposed specimens indicates some photodegradation even

Table 3.1.1 Photodegradation Data for (ethylene-carbon monoxide) Copolymer [6-Pack Rings (6P)] Exposed 117 Hours (Set 1) at 77°C.

| Filter No. | 5% Transmittance (nm) | Percent Elongation at Break | | | |
| | | Inner Strips Only | | All Strips | |
		Average	Standard Deviation	Average	Standard Deviation
Unexposed (3 specimens)				922	21
00	238.2	155	9	132	28
2	262.5	175[1]	–	165[2]	15
3	280.2	54	10	57[2]	9
4	295.0	125	5	100	31
5	303.5	48	50	55	52
6A	313.2	101	27	113	31
6B	318.0	214	4	166	56
7	322.5	162	63	107	10
8	328.1	214	22	175[2]	70
9	337.9	593	94	612	70
10	339.7	632	59	460	202
11	352.4	693	5	640	72
12	359.1	626	58	493[2]	234
13	360.5	513	32	525[2]	31
14	367.5	459	149	504[2]	131
15	373.0	734	131	738	80
16	406.8	281[3]	207	369[3]	210

Exposure Filter Set A Only - 4 strips behind each filter; no air space between filters and specimens. The latter were backed with black paper and cardboard.

1   Only one sample available for testing.
2   Three samples only.
3   The data for filter #16 was omitted because of abnormally low % elongation.

at these wavelengths. A further indication that this radiation had little effect on these samples is that most of them failed at the clamp during tensile testing. In contrast, those specimens exposed to shorter wavelength radiation failed in the section exposed to the radiation. There was a slight increase in degradation with decreasing wavelength of irradiation by wavelengths shorter than about 330 nm (the wavelength at 10% transmittance of filter 8). It was noted that nearly all samples behind filters #9 through #16 failed at the clamp indicating that the central portion which was exposed to the radiation was not extensively degraded by it.

The value of percent elongation at break used for the long-wavelength, flat part of the curve is the average of data for filters #9 through #15, which is 606% for the inner strips only and 567% for the inner and outer strips taken together. The data for inner strips only was evaluated because of the possibility that a small portion along the edge of some of the outer strips may not have been fully exposed to the source. However, the wavelength sensitivity is the same as when combined data for the inner and outer strips are used.

Reduction in elongation at break was due almost entirely to the shorter wavelength ultraviolet transmitted by filter #8 compared with the ultraviolet transmitted by filter #9. Although the spectral band pass (at Δ 20% transmittance) for this filter pair was between 334 and 354 nm, the actinic wavelengths were probably at the short wavelength end of this spectral band. Although filter #9 transmits a significant amount of radiation between 344 and 354 nm, the specimen exposed behind filter #9 was not degraded by the radiation it transmits.

Figure 3.1.1 shows percent elongation at break as a function of short wavelength cut-off for the 117-hour exposure data. The short wavelength cut-off is the wavelength corresponding to 5% transmittance of the filter. Figure 3.1.2 is similar except that it is based on the inner strips only. The curves in the two figures are very similar, indicating that the specimens did not receive uneven exposure.

The data in Figure 3.1.2 clearly identify the transition from relatively low-damage to high damage for samples exposed at $\lambda < (344-354)$ nm and $\lambda > (354)$nm. However, the data is based on a maximum of 4-5 sample strips in each wavelength range. Further exposures were carried out to confirm these findings.

Two series of cut-on filters were used in a second experiment where ECO copolymer films were exposed for 219 hours at 60°C; these data are summarized in Table 3.1.2 (set 2). Because of the large standard deviations among replicate specimens, the activation

Table 3.1.2   Photodegradation Data for (ethylene carbon-monoxide) Copolymer
[6-Pack Rings (6P)] Exposed 219 Hours (Set 2) at 60°C.

| Filter No. | 5% Trans. (nm) | Percent Elongation at Break | | | | | |
| | | Filter Set A | | Filter Set B | | Filter Sets A + B | |
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Unexposed (5 specimens)		774	174	774	174	774	174
00	238.2	73	78	-	-	73	78
2	262.5	15	4	7	0	11	5
3	280.2	170	22	6	2	88	91
4	295.0	141	26	40	48	91	65
5	303.5	49	41	78	35	63	38
6A	313.2	72	41	92	7	82	29
6B	318.0	73	9	148	8	103	42
7	322.5	63	19	170	16	117	60
8	328.1	275[1]	173	932[1]	16	604[2]	376
9	337.9	812	41	900	36	856	59
10	339.7	95	19	-	-	95[2]	19
11	352.4	190	72	992[3]	42	591[2]	443
12	359.1	97	19	919[3]	56	506[2]	449
13	360.5	877	38	950	50	913	56
14	367.5	887[3]	21	169	44	528[2]	395
15	373.0	369	433	68	5	219[2]	320
16	406.8	384	174	112	11	248[2]	186

1   The averages for Filter Sets A and B were plotted separately instead of combining them because the two averages were very different and the standard deviation of the combined data was large.

2   These data points for the combined averages were not plotted.

3   The average for Filter Set B was plotted for filters #11 and #12, and the average for Filter Set A was plotted for Filter #14.

spectrum could not be plotted as a bar diagram, and the wavelength sensitivity was evaluated on the basis of the percent elongation at break values as in the previous experiment. Figure 3.1.3 shows a plot of the data. The percent elongation at break used for the long wavelength flat part of the curve is the average of data obtained for filters #9 through #14, i.e. 913%. Table 3.1.2 indicates the data points which were combined averages for the two filter sets and those which were plotted separately. Data from all exposure experimens taken together clearly show a narrow, critical wavelength interval below which extensive photodegradation of ECO copolymer occurs. The values of average ultimate extension obtained for samples exposed at wavelengths in the critical region show a drastic and consistent change. Based on the three sets of data (Set 1, Set 2 - Filter Sets A & B) this transition in photodegradation was determined to occur at 328-338 nm and 323-328 nm. Samples exposed to filters with 5 percent transmission at these pairs of wavelength for equal duration showed a more than 5-fold difference in average ultimate extension.

Both experiments also indicated a moderate fall (compared to unexposed material) in elongation at break, suggesting increased photodegradation at wavelengths greater than 373 nm (5 percent transmission). As the degradation process in (ethylene-carbon monoxide) copolymer under ambient conditions is relatively insensitive to temperature (see Section 4.2.1.2), this might be due to a secondary minimum in the activation spectrum. Further work is needed to establish this effect.

The sunlight spectrum, filtered through window glass, is not totally devoid of UV radiation. Figure 3.1.4 shows such a spectrum. It is clear that small amounts of light in the region between 320 nm and 345 nm are transmitted through clear float glass commonly used in residential and store front glazing. Therefore, the data does not allow the assumption that these materials will not degrade during behind-glass exposure. Since the thickness and quality of glass, as well as spectral qualities of sunlight at a given location, influence behind-glass degradability, exposure studies are needed to establish the performance of degradable plastics in this regard.

3.1.2   Low Density Polyethylene Containing Added Metal Compound Pro-oxidants (PG)

Plastigone material (PG or LDPE/MX) was exposed for 94.5 hour behind one set of filters as a preliminary experiment and for 295 hours behind two sets of filters. The data for percent elongation at break for these exposure times are summarized in Tables 3.1.3 and 3.1.4.

Figure 3.1.5 shows the data from the preliminary exposure experiment. Unlike the case of (ethylene-carbon monoxide) copolymer samples, which were 16 mils in thickness, the LDPE/MX samples were thin and flimsy (1 mil thick). The outer sample strips adjacent

Table 3.1.3   Photodegradation Data for Plastigone Material (PG) Exposed 94.5 Hours at 77°C..

Filter No.	5% Transmittance (nm)	Number of Samples	Percent Elongation at Break Inner Strips Only	
			Average	Standard Deviation
Unexposed		4	398	112
00	238.2	2	52	19
2	262.5	4	41	12
3	280.2	2	8	2
4	295.0	4	92	29
5	303.5	3	92	37
6A	313.2	4	61	11
6B	318.0	3	81	8
7	322.5	2	162	66
8	328.1	3	124	19
9	337.9	4	138	21
10	339.7	3	150	48
11	352.4	3	314	88
12	359.1	2	393	93
13	360.5	2	176	60
14	367.5	2	412	54
15	373.0	1	374	-
16	406.8	0	-	-

Exposure Filter Set A Only - 4 strips behind each filter; no air space between filters and specimens. The latter were backed with black paper and cardboard.

[1] Data for specimens that broke at the clamp, in most cases, was abnormally low. Data for such samples was not included in the table.

Table 3.1.4 Photodegradation Data for Plastigone Material (PG) Exposed 295 Hours at 77°C.

Filter No.	5% Trans. (nm)	Percent Elongation at Break					
		Filter Set A		Filter Set B		Filter Sets A + B	
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Unexposed		398	112	398	112	398	112
00	238.2	51	11	-	-	51	11
2	262.5	50	11	42	13	46	12
3	280.2	60	13	53	12	56	12
4	295.0	59	23	63	22	61	20
5	303.5	59	20	101	12	80	27
6A	313.2	96	6	91	9	93	8
6B	318.0	131	5	156	22	141	18
7	322.5	109	18	136	24	122	25
8	328.1	181	28	136	32	158	36
9	337.9	273	44	332	122	302	88
10	339.7	347[1]	-	-	-	347[1]	-
11	352.4	287	217	290	29	289	139
12	359.1	355	81	329	81	342	74
13	360.5	494[2]	-	319[2]	-	406[2]	123
14	367.5	310[3]	146	344[3]	145	327[3]	72
15	373.0	-	-	329[1]	123	329[4]	123
16	406.8	-[5]					

[1] Data for inner strips only.

[2] Data for only one of the outer strips was used from each of the two sets. The inner and one outer strip of each of the sets had scratches and smudges and an opaque section.

[3] Data used for 2 strips from each of the sets. The strip that had the lowest percent elongation at break in each set was eliminated. In set B, one of the outer strips had white, opaque marks on the edge and a lengthwise scratch.

[4] Only the outer strips of Set B were used for filter #15.

[5] Data excluded.

to the edges of the exposure frame and filter were easily marred, wrinkled, and stained. The data shown was calculated using inner film samples exclusively.

The data shows a gradual increase in elongation at break with wavelength region of exposure expressed as the 5 percent transmission levels of the relevant filter pair. While not as sharp as that obtained with (ethylene-carbon monoxide) copolymer, there is a well-defined transition wavelength above which the elongation at break remains close to that for unexposed material. The percent elongation at break value used for the long-wavelength, flat part of the curve is the average of the data for the total of four strips used for filters #12 and #14, i.e., 403%. The data for filter 13 was too low to be included and the single data point accepted for filter #15 was also not included. For the preliminary set of data, the transition occurred in the 340-352 nm interval. The average elongation at break for films exposed behind the relevant pair of filters varied by a factor of two. The gradual increase in degradation in the wavelength region 260 nm - 352 nm is interesting. Significant levels of photodegradation are obtained in a broad range of wavelengths in this region. Unlike the ECO copolymer, where the light-absorbing chromophore (i.e. $>C=O$ group) is well-defined, the LDPE/MX system uses light as an initiating agent. Hydroperoxide photolysis may occur over a wider range of wavelengths compared to carbonyl group excitation. Hence the gradual increase is not surprising.

Figure 3.1.6 shows the data from repeat exposures using two different sets of filters (A & B). Note that the temperature for the 295 hour exposure is 77°C (as opposed to 60°C for the 95 hour exposure). For a metal-compound catalyzed system, the oxidation might be photo- and/or thermally initiated. Higher temperatures can contribute to increased sample degradation. This might explain the slight shift of the curve in Figure 3.1.6 toward longer wavelengths. The percent elongation at break used for the long wavelength flat part of the curve is the average of the data used for filters 9 through 15, i.e., 335%.

As with the ECO polymer, the LDPE/MX system shows maximum photodegradation near the 340 nm band of the solar spectrum.

3.1.3 Foamed Polystyrene with Carbonyl Functionalities (PS)

An activation spectrum for yellowing of polystyrene foam was obtained for foam samples exposed 189 hours. Table 3.1.5 summarizes the data. Table 3.1.6 shows the L, a, b values from which Yellowness Indices were calculated.

The activation spectrum (Figure 3.1.7) shows that yellowing by the borosili-cate-filtered xenon arc radiation is due mainly to wavelengths between about 310 nm and 345 nm. Wavelengths longer than 350 nm cause very little yellowing, while wavelengths

Table 3.1.5 Yellowness Data for Polystyrene Foam (PS) Exposed 189 Hours in Atlas 6500 Watt Borosilicate Filtered Xenon Arc Weather-Ometer® at 60°C.[1]

Filter No.	Transmittance[2] (nm)			YI[3]	Filter Pair	ΔYI	Normalization Factor	ΔYI Adjusted	Spectral Band Pass at Δ20% Transmittance
	5%	10%	40%						
00	238.2	245.5	269.8	26.6	00-2	-0.6	0.99	-0.6	258.0-282.5 nm[4]
2	262.5	266.7	282.3	27.3	2-3	-2.6	1.10	-2.9	273.5-294 nm
3	280.2	282.9	293.0	29.8	3-4	1.3	1.02	1.3	287.5-305.5 nm
4	295.0	296.7	302.9	28.5	4-5	4.5	0.92	4.1	300-320 nm
5	303.1	305.0	312.5	24.0	5-6A	6.1	1.00	6.1	308.5-327.5 nm
6A	313.2	315.2	322.5	17.9	6A-7	6.6	0.94	6.2	319-339.5 nm
7	322.4	324.5	332.6	11.3					
6B[5]	318.0	320.1	327.6	15.0	6B-8	6.6	0.95	6.3	324-344 nm
8	328.2	330.3	338.1	8.4	8-9	5.3	0.94	5.0	334-354.5 nm
9	337.9	340.4	349.3	3.1					
10	339.7	342.2	352.2	2.8	10-11	1.2	1.19	1.4	346.5-365 nm
11	352.7	354.8	362.6	1.6	11-13	0.2	0.93	0.2	359-381.5 nm
13	360.6	363.1	372.6	1.4					
12[5]	359.2	361.6	371.3	1.8	12-14	0.4	1.16	0.5	367.5-387 nm
14	367.3	370.1	381.5	1.4	14-15	0.1	1.02	0.1	379-403 nm
15	373.0	377.1	393.3	1.3					
Unexposed				0.8					

1 Specimens were exposed with shiny side facing source.
2 The repeatability of measurement is about 0.3 nm.
3 YI = Yellowness Index of Polystrene foam. The numbers are an average of two measurements for each of the specimens. Repeatability of measurement is about 0.2.
4 This was not plotted because the source emits some energy only at the longest wavelength end of this spectral band.
5 These are out of sequence in order to show the data for the pairs of filters in close proximity to each other.

Table 3.1.6. L, a, and b Values for Polystyrene Foam Samples.

Filter	YI	L	a	b
00	26.6	88.10	-4.21	14.73
2	27.2	87.84	-4.19	15.02
3	29.8	87.66	-4.36	16.30
4	28.5	87.38	-4.23	15.60
5	24.0	88.15	-3.89	13.31
6A	17.9	88.91	-3.24	10.14
6B	15.0	89.95	-2.95	8.81
7	11.3	89.92	-2.27	6.50
8	8.4	90.36	-1.72	4.81
9	3.1	91.03	-0.66	1.71
10	2.8	90.88	-0.55	1.48
11	1.6	91.38	-0.28	0.79
12	1.8	91.41	-0.27	0.85
13	1.4	91.59	-0.26	0.67
14	1.4	91.50	-0.21	0.67
15	1.4	91.34	-0.23	0.63
Unexposed	0.8	91.69	-0.19	0.34

shorter than about 300 nm tended to bleach the yellow color formed under longer wavelength radiation.

3.1.4 LDPE/Starch Systems

The marked temperature-sensitivity of this material caused it to become embrittled at even short exposure times; it was therefore not possible to determine its wavelength sensitivity. Trial exposures resulted in extremely low values for percent elongation at break which could not be differentiated with respect to the wavelength of radiation transmitted.

3.1.5 Polycaprolactone/Polyethylene Blend

This sample type is a biodeteriorable material which has no additives (or chemical modification) to render it photodegradable. However, even the biodeteriorable or biodegradable packaging can also end up as litter. It was therefore thought desirable to investigate its activation spectrum as well. The samples of linear low density polyethylene blended with 20% polycaprolactone (PCL) were exposed for 129 hours behind 2 sets of filters. Again, large standard deviations between replicates prevented determination of an actual activation spectrum in the form of a bar diagram. Data for percent elongation at break are summarized in Table 3.1.7; graphs are shown in Figure 3.1.8. All of the average percent elongation at break values for specimens exposed behind filters #9 through #16 are within the range of values of the unexposed specimens. Therefore, wavelengths longer than about 338 nm (the 5% transmittance of filter #9) do not appear to cause photodegradation. The destructive effect of the xenon arc radiation appears to be due primarily to wavelengths between about 328 nm and 338 nm. The percent elongation decreases from an average of 545 to an average of 164 in this wavelength region. Wavelengths shorter than the 5% transmittance of filter #8 contribute only a little more than 20% to the total destructive effect of the UV radiation. The average percent elongation at break of the 6 specimens exposed behind filter #9 (545%) is the same as the average for all the specimens exposed behind filters #9 and #11-#16, i.e., 542%, the value used for the long wavelength flat part of the curve. The data for filter #10 was omitted from the average because only 3 specimens were exposed and their average appears to be out of line with the other points on the graph. The curve shows the activation region to be between 328 and 338 nm.

3.1.6 Summary of Results

For polystyrene, the activation spectrum based on Yellowness Index measurements showed maximum yellowing to be due to radiation between 320 and 345 nm. For the other samples, activation spectra could not be obtained in the form of a bar diagram (conventional

Table 3.1.7　Photodegradation Data for Polycaprolactone/LLDPE (PCL) Exposed 129 Hours at 60°C.

Filter No.	5% Trans. (nm)	Filter Set A			Filter Set B			Filter Sets A + B	
		Average	Standard Deviation	Range	Average	Standard Deviation	Range	Average	Standard Deviation
Unexposed (12 specimens)		505	136	287-778	505	136	287-778	505	136
2	262.5	16	15	7-34	34	16	23-52	25	17
3	280.2	65	50	12-111	51	73	8-136	58	57
4	295.0	52	10	44-64	64	18	43-76	58	14
5	303.5	29	30	8-64	55	39	11-87	42	35
6A	313.5	108	77	28-183	59	23	40-85	84	58
6B	318.0	132	104	18-219	71	12	63-79	107	81
7	322.5	99	30	65-123	173	113	64-289	136	84
8	328.1	237	79	167-323	91	60	30-150	164	102
9	337.9	737	210	505-917	353	88	266-442	545	255
10	339.7	342	132	259-494	-	-	-	342	132
11	352.4	494	93	426-599	635	53	582-688	565	103
12	359.1	527	51	474-576	658	43	611-695	593	82
13	360.5	632	162	446-741	526	132	409-669	579	144
14	367.5	425	219	189-621	438	36	415-480	432	140
15	373.0	539	149	378-672	568	101	451-630	554	115
16	406.8	529	103	428-601	532	115	425-654	530	93

Percent Elongation at Break

Exposure: Two sets of activation spectra filters (A and B) were used to expose 6 specimens behind each type of filter (3 specimens behind each filter) at the same time in the 6500 W B/B Xenon Arc Weather-Ometer®.

representation for activation spectra) due to large standard deviations for elongation at break between replicate samples. Spectral sensitivities were thus evaluated based on elongation at break as a function of short wavelength cut-off (5% transmittance of the filter). Nevertheless, with all three types of samples examined, the change from relatively low levels to high levels of light-induced damage was marked and occurred over a narrow range of wavelengths. It is of interest to note that the main actinic region for the different types of enhanced degradable plastics is essentially the same. The results are summarized in Table 3.1.8.

Table 3.1.8.   Spectral Sensitivity of Plastic Materials.

Material	Temperature	Main Actinic Region	Additional Actinic Effects
PCL	60°C	>328-338 nm	>310-328 nm
6P	60°C[1]	>323-328 nm	
	77°C[1,2]	>328-338 nm	>310-328 nm
	77°C[1,3]	>328-338 nm	>310-328 nm
PG	60°C[1]	>328-338 nm	>300-328 nm
	77°C[1]	>340-360 nm	>300-340 nm
PS	-	320-345 nm	-

[1] The temperature is based on measurement of the surface of specimens using Omega label temperature monitor strips during exposure.
[2] Inner strips only (of 4 strips in sample holder, the 2 inner strips)
[3] Inner and outer strips

In the case of LDPE/MX material, a temperature-dependent shift in the actinic wavelength region was observed. The higher temperature shifted the actinic region to longer wavelengths. This can probably be explained by the fact that the longer wavelength, lower energy, radiation is more effective in causing degradation when the energy supplied by heat is greater. Previous studies on polycarbonate and aromatic polyesters have not exhibited a shift in wave-length sensitivity with temperature; this behavior has only been observed with the above samples.

Window glass may transmit as much as 54% of 330 nm and 75% of 340 nm radiation incident on its surface. The activation spectra obtained in this study do not rule out the possibility that the three types of photodegradable plastics studied undergo at least a small amount of degradation in behind-the-glass exposure. The practical significance of such amounts of disintegration must be established by experiment.
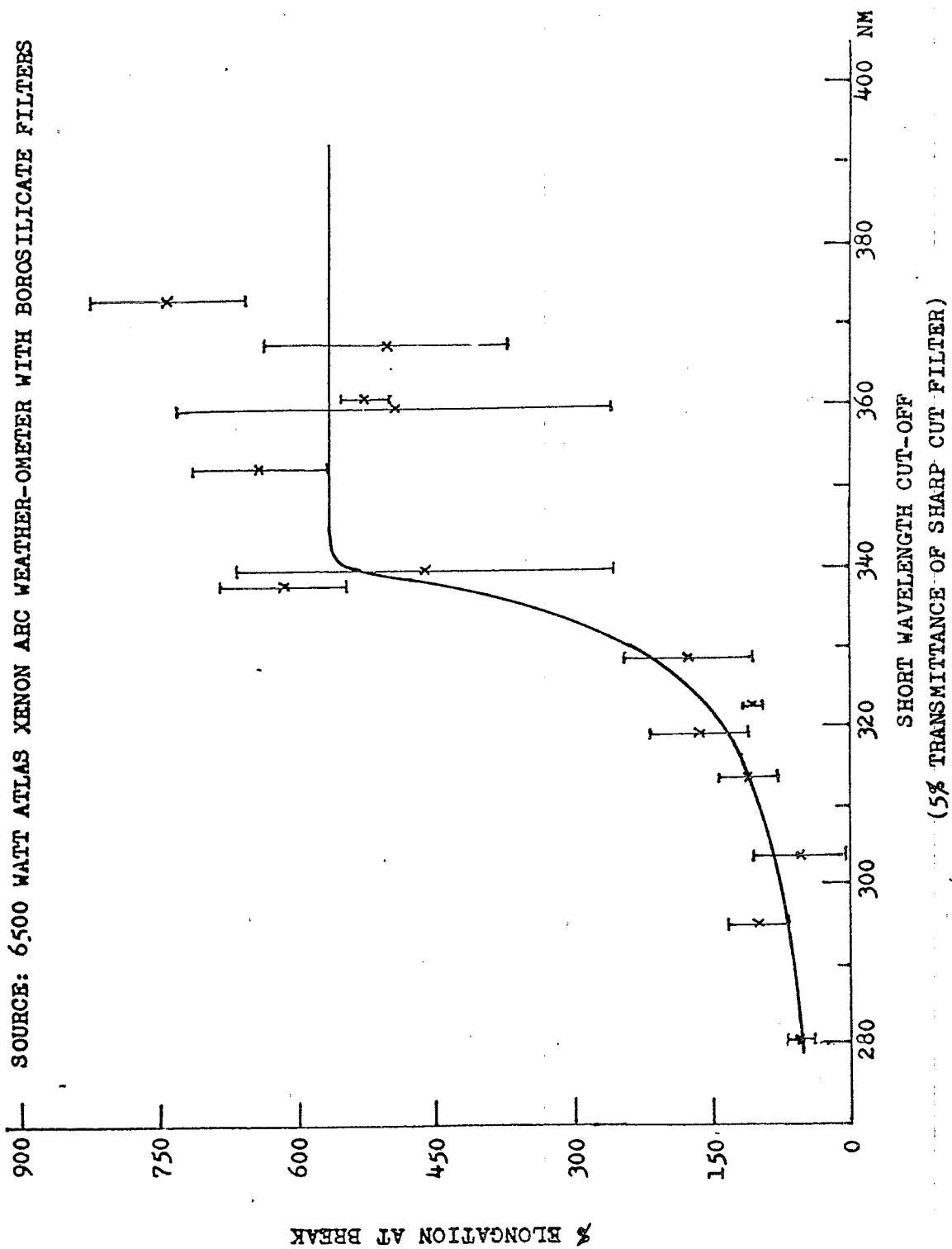
Figure 3.1.1 (Ethylene carbon monoxide) copolymer (6P): percent elongation at break as a function of short wavelength cut-off-Set 1 - 77°C - inner plus outer strips.

Figure 3.1.2 (Ethylene carbon monoxide) copolymer (6P): percent elongation at break as a function of short wavelength cut-off-Set 1 - 77°C - inner strips only.

Figure 3.1.3 (Ethylene carbon monoxide) copolymer (6P): percent elongation at break as a function of short wavelength cut-off-Set 2 - 60°C.
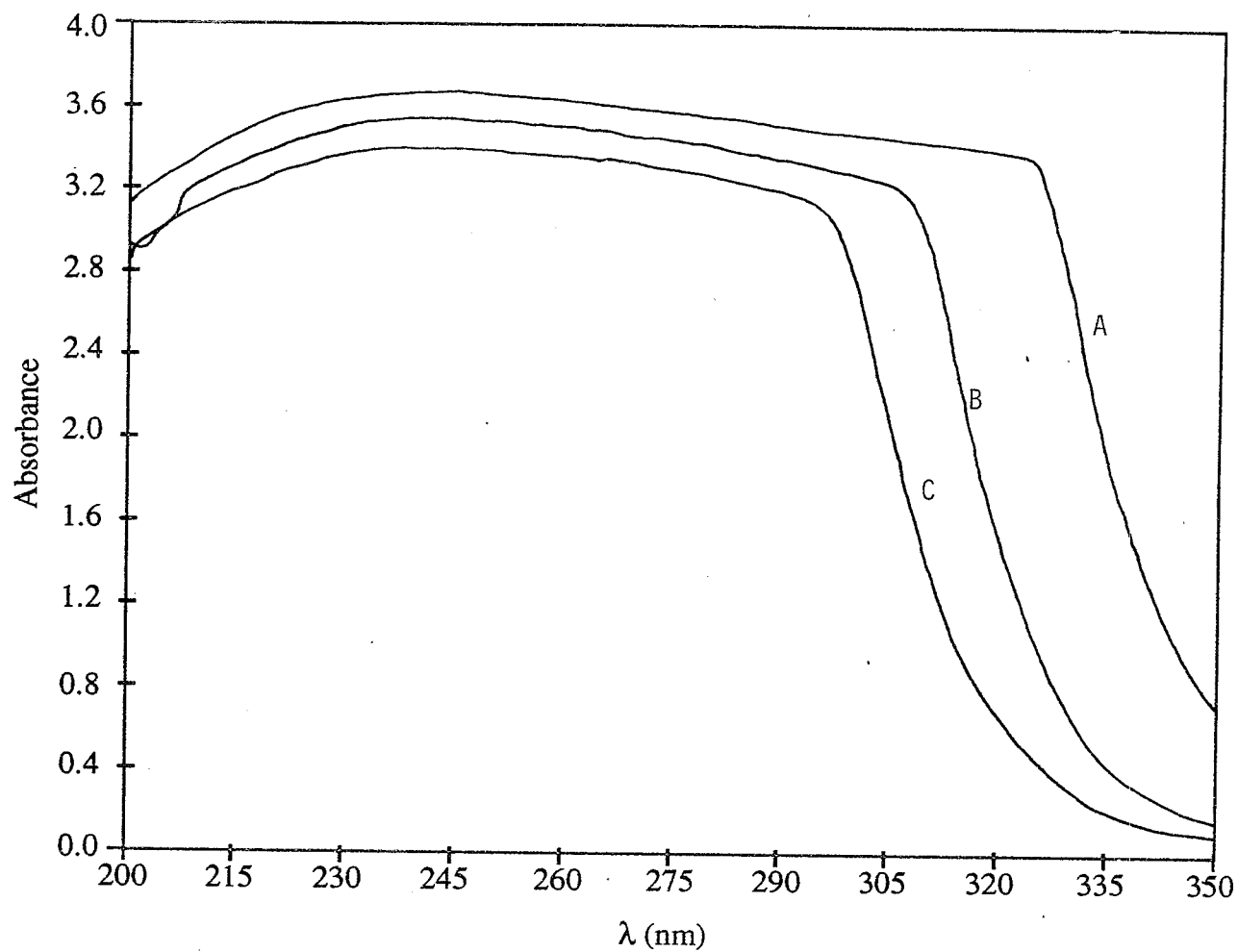
Figure 3.1.4. UV absorbance spectrum of window glass. (A = Float glass - 1/4" - Grey; B = Float Glass - 1/4" - Clear; C = Float Glass - 1/16" - Clear).

Figure 3.1.5 Low density polyethylene containing added metal compound prooxidants (PG): percent elongation at break as a function of short wavelength cu ~ preliminary exposure.
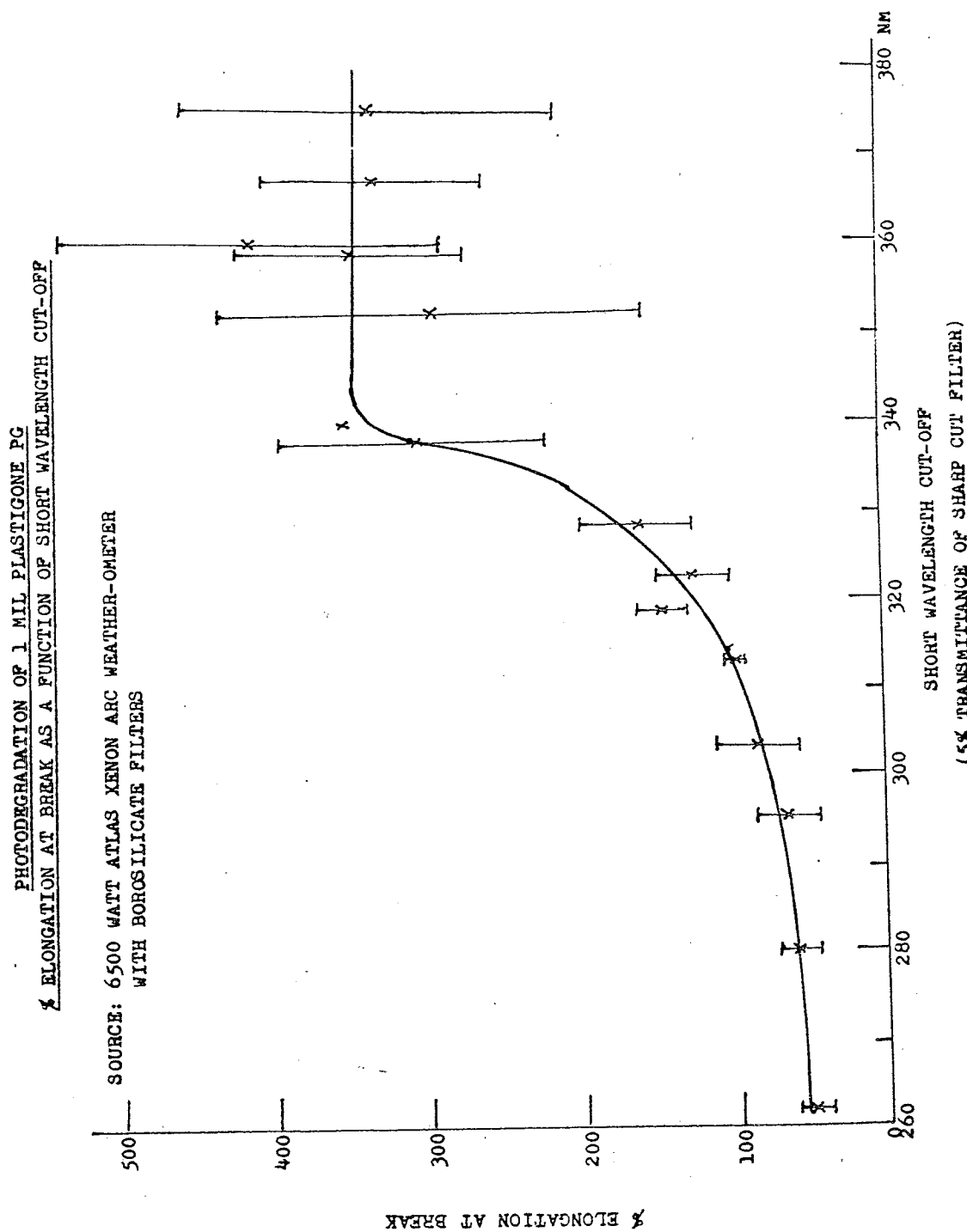
Figure 3.1.6   Low density polyethylene containing added metal compound prooxidants (PG): percent elongation at break as a function of short wavelength cut-off - 295 hours - filter sets A and B

ACTIVATION SPECTRUM OF POLYSTYRENE FOAM
(SHARP CUT FILTER TECHNIQUE)

SOURCE: 6500 WATT ATLAS XENON ARC WEATHER-OMETER WITH BOROSILICATE FILTERS

SPECTRAL REGIONS OF IRRADIATION
(BAND PASS AT DELTA 20% TRANSMITTANCE)

CHANGE IN YELLOWNESS INDEX
FOR EQUAL SPECTRAL BAND AREAS

Figure 3.1.7   Activation spectrum for yellowing of polystyrene foam.

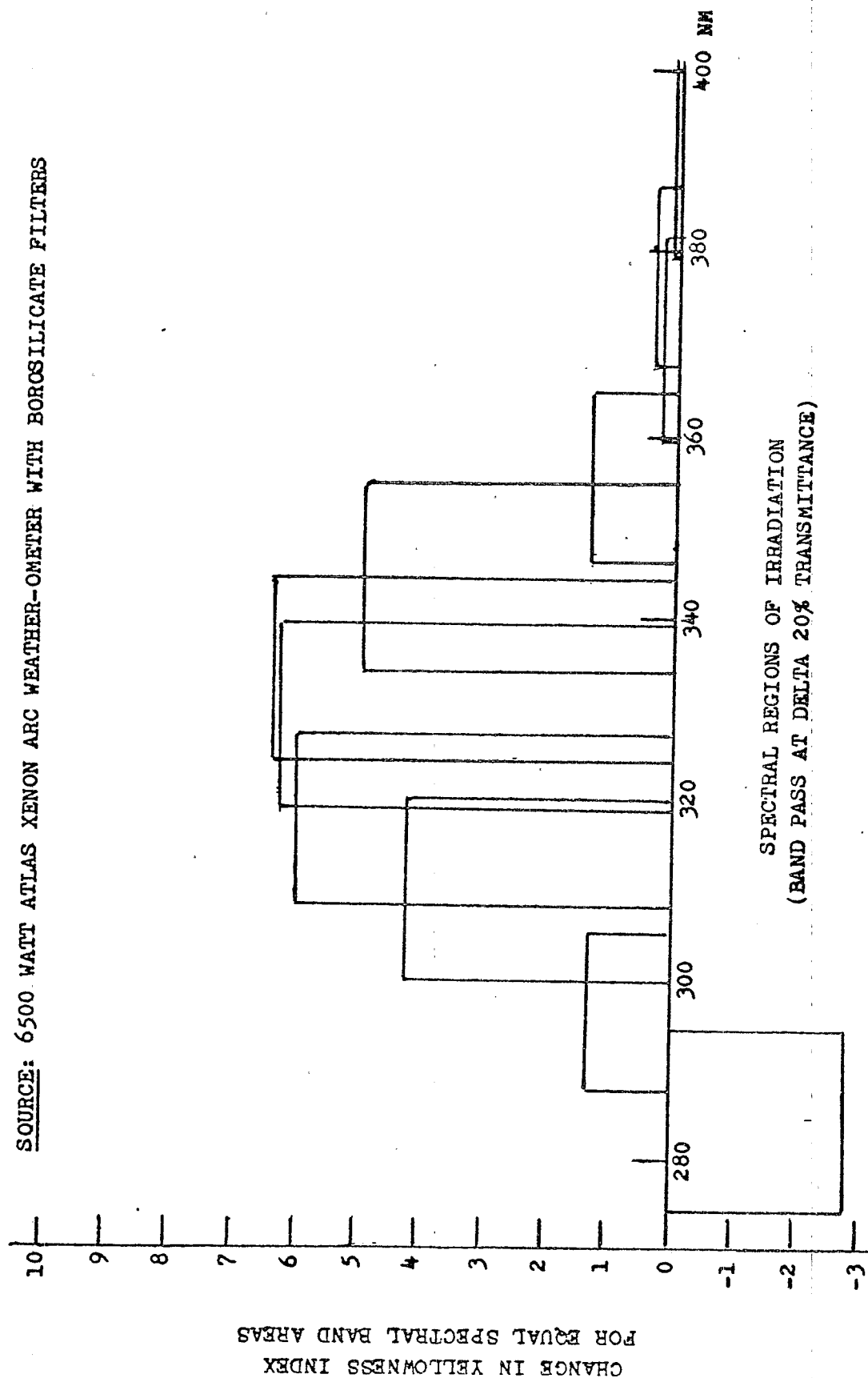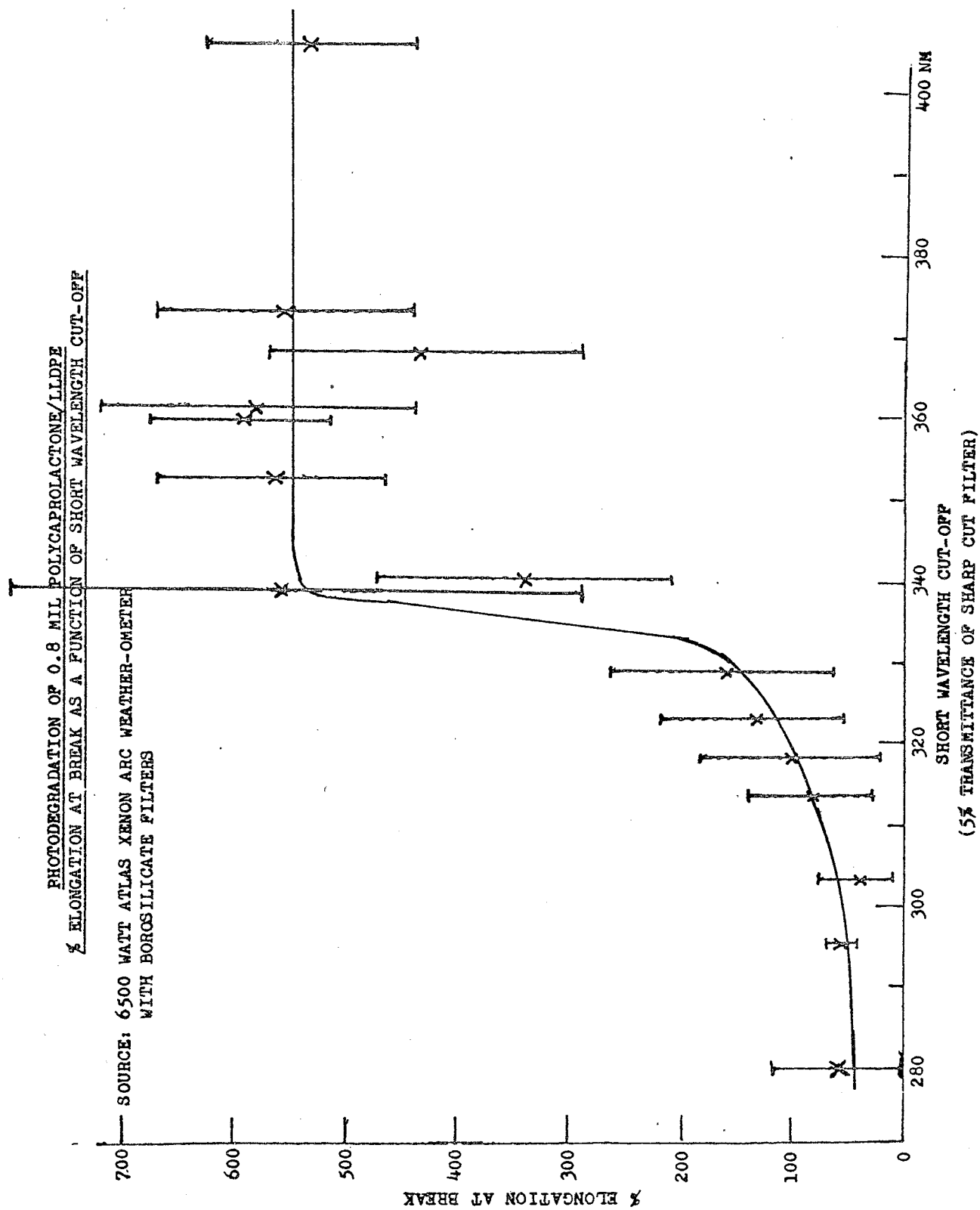Figure 3.1.8 Polycaprolactone/LLDPE (PCL): percent elongation at break as a function of short wavelength cut-off of filter.

SECTION 4.0

WEATHERING OF ENHANCED DEGRADABLE PLASTICS

4.1   NATURAL WEATHERING

For the purpose of this study, natural weathering refers either to direct weathering (outdoor exposure at 45° facing South), marine floating exposure, marine sediment exposure, freshwater exposure, or outdoor soil burial. Not all of the plastic types tested were exposed to all types of natural weathering; in general, the photodegradable samples were exposed to direct weathering and to marine and freshwater floating environments, while the biodegradable samples were exposed to marine sediment and soil burial conditions (see Table 2.3.1).

4.1.1   Outdoor Duplicate Exposure

The rationale for exposing duplicate sample sets at selected locations has been discussed in Section 2.3.1. Duplicate exposures were carried out only for direct weathering. Figures 4.1.1, 4.1.2, and 4.1.3 show plots of the tensile elongation at break (4.1.1, 4.1.2) or tumbling friability mass loss (4.1.3) for the samples versus exposure time for duplicate sets of selected materials and exposure sites. Figure 4.1.1 illustrates tensile test data for duplicate exposure of sample 6P in Miami, FL, and shows good agreement between the original data and that for the duplicate set, especially for the degradable material (Figure 4.1.1.a). For the control material, the duplicate samples were inadvertently exposed for longer durations than the original set, but the duplicate data continues the trend established by the original data, as seen in Figure 4.1.1.b.

Figures 4.1.2.a and 4.1.2.b illustrate exposure of sample PG in Chicago, IL and show some disagreement in elongation at break at comparable times for the two sets. This may in part be explained by the fact that for short exposure durations, the equivalent time intervals for the two sets (original and duplicate) occurred at different months of the year; e.g., the three-day sample from the original set was exposed in June, but the three-day sample from the duplicate set was exposed in August. Values for solar radiation and temperature would be different, especially in Chicago, for these two time intervals. The data does in fact show that for the period of 6/19 to 6/22/90, total radiation (45°S) was 37.9 MJ/m^2 and for 8/3 to 8/6/90 was 48.7 MJ/m^2. In general, however, the data points for the original and duplicate sets follow the same trend.

Duplicate exposure results for PS and PSC in Cedar Knolls, NJ, are shown in Figures 4.1.3.a and 4.1.3.b. The degradation parameter shown in the figure is the frac-

tional mass of sample remaining after the tumbling friability test. The data show excellent agreement between original and duplicate sample sets, indicating no drastic changes in weather during the period of exposure and thus good reliability of the results.

4.1.2 Comparison of Various Tensile Parameters

Tensile testing of the plastic films (See 2.5.1.) resulted in values for breaking load and elongation, stress at break (load divided by cross-sectional area of the sample), strain at break (elongation divided by gauge length), modulus (initial slope of stress-strain curve), and energy to break (total area under load-elongation curve). The computerized data acquisition system connected to the Instron test machine enabled quick, accurate determination of the above parameters and others. It was, however, necessary to choose a single parameter which could be used consistently to characterize degradation for all the types of plastic films. Percent elongation (or strain) at break, a measure of brittleness, has been used in previous studies [Andrady, 1990; Pegram and Andrady, 1989] as an indicator of film embrittlement and consequent tendency to break into small pieces. For the present study, one goal of which was to formulate a mathematical model for rates of disintegration of materials exposed to various conditions and locations, a parameter which was convenient to obtain and was well suited for facile mathematical treatment was required. The four candidate parameters studied were stress at break, percent elongation at break, energy to break, and initial modulus.

Figure 4.1.4 shows semi-logarithmic plots of these four tensile parameters versus exposure time for outdoor exposure of two sample types, 6P and PG, and the relevant controls in Miami, FL and Seattle, WA. The data could best be fitted by an equation of the form:

$$\log P = \log A - Bt \tag{4-1}$$

where P is the tensile parameter, t is the duration of exposure in days, and A and B are constants. Table 4.1.1 summarizes the gradient (B) values and correlation coefficients for the four sets of data. Both elongation at break and energy to break tended to have higher values for correlation coefficient than the other two parameters, especially for the degradable plastics. The ratio of parameter B for the degradable material to that of the control material is also shown in the table. This ratio was especially useful in choosing a single parameter for data analysis; it was consistently higher for elongation at break and energy to break, suggesting these parameters to be the more sensitive to weathering-related changes in the plastic.

Table 4.1.1   Table of Slopes Based on Plots of Selected Tensile Parameters of 6P and PG Exposed Outdoors in Miami, FL and Seattle, WA, According to Equation 4-1.

Polymer	Location	Parameter	Degradable Polymer		Control Polymer		B_d/B_c
			$B (\times 10^3)$	r*	$B (\times 10^3)$	r*	
6P/6PC	Miami, FL	Stress (kg/cm^2)	10.3	0.837	3.38	0.939	3.05
		Elongation (%)	69.2	0.925	11.0	0.826	6.29
		Energy (kg-mm)	91.7	0.942	11.4	0.807	8.04
		Modulus (kg/cm^2)	-6.90	0.563	-4.61	0.859	1.50
6P/6PC	Seattle, WA	Stress (kg/cm^2)	5.25	0.892	3.06	0.880	1.72
		Elongation (%)	32.1	0.857	7.59	0.765	4.23
		Energy (kg-mm)	40.3	0.902	8.65	0.785	4.66
		Modulus (kg/cm^2)	-3.59	0.634	-3.82	0.846	0.94
PG/PGC	Miami, FL	Stress (kg/cm^2)	9.34	0.791	4.36	0.702	2.14
		Elongation (%)	73.0	0.959	18.4	0.864	3.97
		Energy (kg-mm)	86.3	0.959	23.6	0.909	3.65
		Modulus (kg/cm^2)	-9.94	0.951	-5.18	0.860	1.92
PG/PGC	Seattle, WA	Stress (kg/cm^2)	10.3	0.827	3.71	0.742	2.78
		Elongation (%)	53.5	0.960	13.6	0.834	3.93
		Energy (kg-mm)	62.1	0.961	15.9	0.896	3.91
		Modulus (kg/cm^2)	-6.81	0.823	-3.87	0.873	1.76

Equation: log (Parameter) = Log A - Bt ; where t = exposure time in days.

* r is the correlation coefficient

B_d and B_c are the values of B for degradable and control plastic films, respectively.

Modulus is an indication of a material's stiffness and may in fact generally increase to a certain extent as a material degrades. For 6P samples exposed in Seattle,WA, this increase was greater for the control material than for the enhanced degradable material. Similarly, breaking stress or tensile strength sometimes increases slightly in the initial stages of degradation due to crosslinking reactions or crystallization which may occur as longer chains break down into lower molecular weight chains. This effect is observed in Figures 4.1.4.a, e, i, and m. Although stress at break eventually does decrease at longer exposure durations, this parameter does not show as great a relative change as energy to break or elongation at break.

In terms of correlation coefficient and values for B ratio, both the energy to break and percent elongation at break were equally sensitive parameters, but consideration of the ease of obtaining values for the parameter would favor percent elongation at break. Determination of energy at break would require measurement of the entire area under the stress-strain curve, which would be very difficult to carry out without an automated data collection set-up. Percent elongation at break is simple to obtain directly from the load-elongation or stress-strain curve. Therefore, percent elongation at break was chosen as the tensile parameter to characterize the extent of degradation.

4.1.3 Discussion of Outdoor, Marine Floating, and Marine Sediment Exposure by Sample Type

4.1.3.1 Rate Parameters Based on Elongation at Break --

As discussed in 4.1.2, the degradation of all samples under exposure was characterized using values for percent elongation at break. This included all samples except expanded polystyrene foam, which was characterized by tumbling friability, Yellowness Index measurements, and GPC. These results for polystyrene will be discussed in 4.1.3.2.

Figures 4.1.5.a through 4.1.5.gg illustrate the data for percent elongation at break plotted against exposure time. Separate plots are shown for each exposure location, with the degradable material and its corresponding control plotted on the same graph. In cases where duplicate exposures were carried out, these data points are also included. Figures 4.1.6.a through 4.1.6.gg show the same data plotted on a semi-logarithmic scale with curve fitting based on the equation:

$$\log E = \log A - Bt \tag{4-2}$$

B_d and B_c are B values for the degradable and control materials, respectively. The magnitude of B_d/B_c is a measure of the effectiveness of enhanced-degradable polymer in bringing about accelerated disintegration and is called the "enhancement factor". Based on Figures 4.1.5 and 4.1.6 and on Table 4.1.2, each sample material will be discussed separately.

(a)   (Ethylene-carbon monoxide) Copolymer - 6P

For (ethylene-carbon monoxide) copolymer (6P) samples, comparison of raw data for percent elongation at break versus exposure time showed a very significant difference in degradation rate between the degradable and the LDPE control film. This is evidenced by the values for B_d/B_c shown in Table 4.1.2. The data are illustrated by Figures 4.1.6 (a) - 4.1.6 (h). The photodegradable plastic material showed extensive disintegration on exposure at all locations. With control samples, however, the 2-3 month exposure was often too short to obtain a marked change in elongation at break. Good correlation between elongation at break and duration of exposure was obtained at all exposure sites, especially for the enhanced degradable material. Low values for correlation coefficient were obtained at some exposure sites for the control material, but in these cases percent elongation at break changed very little with increased exposure time. The only exposure sites where measurable degradation of the control material occurred were Miami, FL, and Wittmann, AZ, where average daily temperature and/or solar radiation would have been relatively high.

Comparison of rate parameters (Table 4.1.2) for 6P at various sites showed that the samples exposed in Wittmann, AZ, degraded at the fastest rate followed by those exposed in Chicago, IL. Samples exposed outdoors at the other locations all showed similar degradation rates which were significantly lower than that for the Wittmann, AZ site.

Samples exposed floating in sea water experienced much slower degradation rates (comparison of B values) than samples exposed to direct weathering at the same location. Both the enhanced-degradable and the control samples showed a decreased rate of disintegration probably related to lower temperature of samples exposed floating in sea water. The enhancement factors (B_d/B_c values) were greater for samples exposed floating in sea water than for samples exposed to direct weathering.

(b)   Plastigone Films (LDPE/MX) - PG

For PG samples, the degradation rate of the enhanced degradable material was consistently 3 to 4 times greater than that of the LDPE control material. The curve-fitting lines in Figures 4.1.6 (i) - 4.1.6 (p) represent regression applied to the data points from the original data set; points for duplicate sets are shown on the graphs, but separate regression equations were obtained for the duplicates, as seen in Table 4.1.2. The B values show

4.1.2 Table of Regression Coefficients (Slopes and Intercepts) Based on Plots of Tensile Elongation at Break Data for Outdoor Exposure Experiment.

Equation: log (% elongation) = log (A) - Bt where t = exposure time in days

Sample Code	Exposure Type	Location	Degradable Polymer		Control Polymer		ΔB (x 10³)	Bd/Bc
			A	B (x 10³)	A	B (x 10³)		
6P/6PC	Outdoor	Cedar Knolls, NJ	139	52	708	0.95	51	-
		Chicago, IL	246	87	648	0.43	87	-
		Miami, FL	184	69	953	14	55	4.9
		Miami, FL*	182	65	810	13	52	5
		Seattle, WA	96.7	40	823	4.2	35.8	9.5
		Wittmann, AZ	550	257	1047	25	232	10
	Marine Floating	Miami, FL	157	45	665	0.5	44.5	-
		Seattle, WA	70.1	11	648	-	10.7	-
	Fresh Water Floating	Kerr Lake, VA	356	39	-	-	-	
PG/PGC	Outdoor	Cedar Knolls, NJ	1033	50	613	12	38	4.2
		Cedar Knolls, NJ*	1015	49	794	12	37	4.1
		Chicago, IL	1091	49	742	13	36	3.7
		Chicago, IL*	615	53	828	14	39	3.8
		Miami, FL	960	72	917	22	50	3.3
		Miami, FL*	704	59	670	20	39	3.0
		Seattle, WA	1004	54	587	16	38	3.4
		Wittmann, AZ	885	122	607	33	89	3.7
		Wittmann, AZ*	791	115	505	22	93	5.2
	Marine Floating	Miami, FL	859	27	632	4.2	22.8	6.4
		Seattle, WA	352	18	383	2.4	15.6	7.5

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Table 4.1.2 (continued)

Sample Code	Exposure Type	Location	Degradable Polymer		Control Polymer			
			A	B (x 10³)	A	B (x 10³)	ΔB (x 10³)	Bd/Bc
PG/PGC (cont.)								
ADM/ADMC	Fresh Water Floating	Kerr Lake, VA	938	7.5	739	1.2	6.3	6.3
	Outdoor	Cedar Knolls, NJ	65.9	137	340	6	131	23
		Cedar Knolls, NJ*	-	-	459	12	-	-
		Chicago, IL	67.5	148	354	11	137	13
		Chicago, IL*	-	-	321	8.4	-	-
		Miami, FL	41.4	129	371	9.1	119.9	14
		Miami, FL*	-	-	508	17	-	-
		Seattle, WA	53.7	102	395	10	92	10
		Wittmann, AZ	89.2	391	300	25	366	16
		Wittmann, AZ*	-	-	212	12	-	-
	Marine Floating	Miami, FL	89.2	386	252	8.1	377.9	48
		Seattle, WA	42	64	283	3.9	60.1	16
	Marine Sediment	Miami, FL	53	19	170	2.2	16.8	8.6
		Seattle, WA	47.7	18.2	131	3.7	14.5	4.9
ADM Repeat	Fresh Water Floating	Kerr Lake, VA	178	4.7	256	-0.1	4.8	-
	Outdoor	Cedar Knolls, NJ	194	77	-	-	-	-
		Chicago, IL	176	67	-	-	-	-
		Miami, FL	180	85	-	-	-	-
		Wittmann, AZ	176	140	-	-	-	-

- continued -

Table 4.1.2 (continued)

Sample Code	Exposure Type	Location	Degradable Polymer		Control Polymer		ΔB (x 10^3)	B_d/B_c
			A	B (x 10^3)	A	B (x 10^3)		
PCL/LLDPE	Outdoor	Miami, FL	1034	27.3	1223	21.5	41	1.3
	Marine Sediment	Miami, FL	500	1.2	605	5.4	-	-
		Seattle, WA	474	1.7	497	2.7	-	-
	Fresh Water Floating	Kerr Lake, VA	664	7.1	-	-	-	-
BP	Outdoor	Miami, FL	61.5	3.1	No control used			
	Marine Sediment	Miami, FL	34.9	102	-	-	-	-
	Fresh Water Sediment	Kerr Lake, VA	29.7	48	-	-	-	-

* duplicate sample sets

good agreement between duplicate sets of test samples for all exposure sites. As with 6P samples, exposure in Wittmann, AZ, produced the fastest degradation rate in the PG films. The other locations produced comparable rates for direct weathering.

PG material also behaved similarly to 6P with regard to marine and freshwater floating exposure; B values were lower for floating exposures than for direct weathering, but B_d/B_c ratios were generally higher for floating exposures.

(c)   Archer Daniels Midland Co. Films (LDPE/Starch/MX) - ADM

Figures 4.1.6 (q) - 4.1.6 (z) show the semi-logarithmic plots of data for ADM samples. In addition to its enhanced photodegradability, this material was also heat sensitive and underwent slight degradation even when stored in darkness at ambient temperatures in the laboratory. Tensile testing carried out on unexposed samples which had been stored in darkness at ambient temperature for three months showed a decrease in percent elongation at break from 89% to 33%. The original lot of ADM samples had been dispatched for exposure approximately two months after receipt from the manufacturer and therefore had probably degraded somewhat before actual exposure. For this reason, a second lot of identical composition was requested from the manufacturer for repeat direct weathering at selected outdoor exposure sites. The repeat exposures are shown as "Set II" in the figures. The original samples (Set I) are also included for comparison with the floating and marine sediment exposures, as these could not be repeated with fresh material.

Due to the extremely rapid degradation rate of ADM samples, duplicate exposures could not be carried out on the enhanced degradable material; however, duplicates were exposed for the control material at several sites. Comparison of B_d values for the original and duplicate sets showed fair agreement.

Values for B_d for Set II were generally somewhat lower than B values for Set I but were still much higher than the B_c values for the LDPE control material. Values for B_d/B_c for Set I exposure are shown in Table 4.1.2 and are generally higher than the ratio for both the 6P and PG materials. For Sets I and II of the enhanced degradable material, direct weathering in Wittmann, AZ resulted in the highest rate parameters for disintegration.

The B value for floating exposure in Miami, FL could not be obtained due to lack of a sufficient number of data points but appears to be high based on the two data points available. For exposure in Seattle, WA, the B_d/B_c ratio for marine floating exposure was similar to the ratio obtained for direct weathering.

In addition to being extremely sensitive to light and heat, the ADM material also exhibited some degree of enhanced biodeterioration. A comparison of the B_d values for marine-floating and marine-sediment exposure of the ADM films suggests the principal mechanism of disintegration to be photodegradation rather than biodeterioration. However,

the rates of disintegration of the films under sediment exposure are significantly faster than those of control films indicating a small contribution to disintegration by the biodeterioration mechanism. ADM film samples exposed to marine sediment conditions in Miami and Seattle were found to disintegrate 5 to 9 times faster than the control material (See B_d/B_c values in Table 4.1.2.), although the B values themselves were lower for marine sediment exposure than for direct weathering or floating exposure for both the enhanced degradable and control materials.

(d) Polycaprolactone Blends (LLDPE/PCL) - PCL

Exposure of the polycaprolactone/LLDPE blend (PCL) was carried out under marine sediment conditions in Miami, FL and Seattle, WA and under direct weathering in Miami, FL. Plots of the tensile test data according to equation 4-1 are shown in Figures 4.1.6 (aa) - 4.1.6 (dd). PCL was slightly more degradable than the control for direct weathering, but for marine sediment conditions, values for B_d/B_c were slightly less than one, indicating no significant acceleration in disintegration during this time scale. The PCL fraction of the blend (20%) is known to be biodegradable; however, it may not biodegrade within the exposure durations reported here. In addition, the polyethylene matrix may have limited the access of microorganisms to the polycaprolactone domains.

(e) Biopol Films

Biopol [poly(hydroxybutyrate) films] showed very low degradability under direct weathering but showed high values for B when exposed to sediment conditions in both marine and freshwater (Figures 4.1.6 (ee)-4.1.6 (gg). There was no control material data for Biopol for comparison of degradation rates; however, comparison of B_d values with B_c values for polyethylene under marine sediment exposure suggests an enhancement factor of about 20.

4.1.3.2 Rate Parameters Based on Yellowness Index, Tumbling Friability, or GPC --

Three tests were used to characterize the degradation of expanded polystyrene foam; two methods, tumbling friability testing and measurement of Yellowness Index, were used for samples exposed to direct outdoor weathering. These methods were unsuitable, however, for samples exposed to marine environments. Accumulation of marine foulant species on the surface of foam sheets interfered with color measurements (Yellowness Index) and mass determinations (required for tumbling friability testing). Marine floating samples could, however, be characterized by gel permeation chromatography (GPC).

Table 4.1.3 shows the Yellowness Index values obtained for PS samples exposed to direct weathering. Visual examination of the exposed samples showed the formation of a brittle, yellow surface layer on the surface of sample exposed to sunlight. In general,

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Yellowness Index (YI) increased with exposure time for both the enhanced degradable and control samples of polystyrene foams, with YI for the degradable material higher than for the control for the same exposure duration. For longer exposure durations, YI leveled off or even decreased. This was attributed to loss of the brittle yellow layer due to abrasion or removal by wind or rain.

A study of the change in color might be attempted based on values of the parameters "L", "a", and "b" (see Section 2.5.2). Typically, outdoor exposure did not drastically affect the lightness, L, of the styrofoam. The parameters "a" and "b" both changed with exposure, the former becoming more negative and the latter increasing with exposure time. During early periods of exposure, "a" and "b" are almost linearly correlated. The change in these parameters suggests a gradual change from light blue-white color of sample to a progressively darker yellow color. After a deep yellow color is achieved, the value of "b" increases further with exposure time (with that of "a" remaining almost the same), indicating increased redness in color.

Interestingly, the same trend was observed with data for samples exposed in a Weather-Ometer®. Both control and degradable polystyrene foam samples showed the same behavior in Weather-Ometer® exposure as in a typical outdoor exposure site such as Cedar Knolls, NJ. In both instances, "a" changed from about 0 to -4 and "b" from about 0 to 25. This agreement essentially supports the assumption that the chemical processes giving rise to the colored species must be the same in both types of exposure.

The partial loss of the embrittled layer due to wind, rain, and abrasion, especially in samples exposed for an extended period of time, precluded a detailed study of the development of coloration on exposure.

Tumbling friability testing resulted in values for percent mass loss for the samples exposed to direct weathering. These values are given in Table 4.1.4 and show a general increase in mass loss with exposure duration, with the effect more pronounced for the enhanced degradable material than for the control. Mass loss values were converted to percent mass remaining after tumbling friability, and these values were used to obtain the plots in Figure 4.1.7. Data for duplicate exposures are also shown on these graphs and tend to overlap the data from the original exposures. The graphs in Figure 4.1.7 illustrate the existence of a "lag time" for the onset of measurable degradation by tumbling friability. This lag time was always greater for the control material. The significance of this "lag time" and the mechanism giving rise to it are not clear at this time.

Table 4.1.3 Yellowness Index and L, a, b Values for Polystyrene Foam Exposed Outdoors.

Exposure Site	Exposure Duration (days)	PHOTODEGRADABLE PS FOAM					CONTROL PS FOAM				
		Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Unexposed	0	F	91.76	0.22	1.51	3.07	F	90.10	0.21	1.60	3.38
		B	92.97	0.24	1.42	3.01	B	92.88	0.14	1.64	3.21
Cedar Knolls, NJ	7	B	91.83	-1.31	6.01	10.57					
	14	B	91.19	-2.32	9.66	16.70	B	92.26	-0.49	3.34	6.13
	22	B	90.62	-3.06	12.92	22.26					
	29	B	89.62	-3.30	14.88	25.41	F	88.34	-1.64	7.64	14.02
	36	B	89.25	-3.66	17.39	29.61					
	43	B	89.19	-3.88	19.50	33.09	F	88.10	-2.73	12.27	21.42
	50	F	86.27	-3.69	19.33	33.65					
	58	F	88.18	-3.90	23.17	38.96	F	88.22	-3.20	16.94	29.24
	64	F	87.59	-3.64	25.67	43.95					
	71	F	87.88	-3.76	25.98	44.35	B	88.44	-3.34	19.44	33.57
	85	F	85.14	-3.22	27.51	47.35	B	85.90	-3.16	22.52	39.05
	99	B	88.51	-3.66	24.61	42.93	B	88.82	-3.55	20.63	35.47
	104		85.16	-3.52	27.60	47.30		86.95	-3.16	24.47	42.05
Cedar Knolls, NJ (duplicates)	5		92.54	-0.42	3.61	6.57		92.26	-0.07	2.31	4.52
	12		91.42	-1.33	6.17	10.77					
	19		91.16	-1.84	8.10	14.17		91.61	-0.42	3.45	6.39
	26		90.77	-2.35	10.05	17.25					
	33		90.14	-3.62	12.97	22.32		91.31	-1.66	7.26	12.75

- continued -

Table 4.1.3 (continued).

Exposure Site	Exposure Duration (days)	PHOTODEGRADABLE PS FOAM					CONTROL PS FOAM				
		Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Cedar Knolls, NJ											
Duplicates (cont.)	40		89.61	-3.51	15.81	26.81					
	47		89.52	-3.66	17.02	28.62		90.49	-2.31	10.09	17.41
	54		88.08	-3.82	19.74	33.67					
	61		88.18	-4.04	21.96	36.98		89.11	-3.06	14.58	25.23
	68		87.61	-3.97	23.66	39.99					
	75		87.11	-3.88	24.47	41.40		88.64	-3.36	17.27	29.69
	82		86.93	-3.75	26.54	45.01					
	90		86.43	-3.68	27.25	46.18		87.42	-3.44	20.46	35.67
	97		85.79	-3.64	27.52	46.89					
	104		85.49	-3.42	28.01	48.67		87.61	-3.65	22.84	39.20
Chicago, IL	7	B	91.68	-1.06	5.50	9.85					
	14	B	91.00	-2.17	9.30	16.01	B	91.35	-0.60	3.95	7.21
	22	B	90.25	-3.00	13.12	22.44					
	29	B	89.81	-3.35	15.14	25.99	B	91.04	-1.75	7.89	13.76
	36	B	85.98	-3.60	15.25	27.34					
	43	B	86.40	-3.81	17.32	30.03	B	88.06	-2.32	10.18	18.43
	50	B	86.47	-3.90	20.46	35.15					
	57	B	85.31	-3.77	20.53	36.58	B	88.68	-2.93	15.60	25.42
	64	F	86.67	-3.49	26.31	44.80					
	71	F	85.75	-3.57	26.89	46.39	B	85.90	-2.75	20.15	35.65

- continued -

Table 4.1.3 (continued).

Exposure Site	Exposure Duration (days)	PHOTODEGRADABLE PS FOAM					CONTROL PS FOAM				
		Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Chicago, IL (continued)	78	F	83.73	-3.03	27.96	49.46					
	85	F	83.22	-2.86	28.27	49.80	B	84.21	-2.61	20.96	37.71
	92	F	84.89	-3.06	27.22	47.49					
	99	F	84.43	-3.17	28.09	48.39	B	84.91	-2.94	21.72	38.61
	106		85.01	-3.34	25.70	45.65					
	113		84.92	-3.09	24.63	42.75		85.02	-3.22	20.48	36.51
Miami, FL	7	F	90.33	-1.34	6.23	11.14	F	89.53	-0.53	3.52	6.59
	14	F	90.22	-2.40	9.92	17.09					
	21	F	89.56	-3.16	13.94	23.89					
	28	F	88.55	-3.48	16.46	28.29	F	88.78	-1.78	7.77	13.90
	35	F	89.53	-3.62	17.86	29.34					
	42	F	88.78	-3.92	20.93	35.12	F	87.64	-2.82	12.97	22.95
	49	F	85.27	-3.59	21.37	38.04					
	56	F	87.03	-3.64	21.03	36.58**	B	87.38	-2.78	12.93	22.69
	63	B	92.02	-3.45	15.47	24.92					
	70	B	91.11	-0.35	16.81	28.63	B	91.14	-2.85	12.95	21.83
	77	B	90.04	-3.90	21.27	35.74					
	84	B	89.82	-3.97	23.56	38.02	B	90.24	-3.56	17.86	29.34
	91	B	91.12	-3.61	18.45	30.88					
	98	B	91.13	-3.72	18.95	30.45	B	90.86	-3.39	16.44	27.21

- continued -

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Table 4.1.3 (continued).

Exposure Site	Exposure Duration (days)	PHOTODEGRADABLE PS FOAM Side of Sample Exposed*	L	a	b	Yellowness Index	CONTROL PS FOAM Side of Sample Exposed*	L	a	b	Yellowness Index
Miami, FL (cont.)	103		88.94	-3.85	26.03	42.37**		89.28	-3.62	21.80	37.66
Miami, FL *Duplicates*	5		90.68	-1.41	6.20	10.91		90.03	-0.10	2.52	4.79
	12		90.33	-2.23	9.27	16.21					
	19		89.70	-3.04	12.74	21.71		89.76	-0.87	4.73	8.79
	26		88.93	-3.60	16.31	27.90					
	33		88.40	-3.93	19.41	32.68		88.40	-2.34	10.38	18.29
	40		87.57	-3.95	21.60	37.14					
	47		87.68	-3.95	23.19	39.71		86.92	-3.16	15.39	27.15
	54		88.63	-3.90	22.45	37.13**					
	61		87.91	-3.75	24.72	42.14**		87.50	-3.47	18.60	31.95
	68		86.74	-3.59	26.23	44.34**					
	75		87.94	-3.71	26.72	45.35**		89.07	-3.52	19.11	32.73
	82		87.09	-3.48	27.09	46.84**					
	89		88.07	-3.55	27.45	45.39**		88.53	-3.54	22.28	38.56
	96		87.98	-3.56	27.45	43.82**					
Seattle, WA	7	F	91.09	-1.25	5.88	10.55					
	14	F	90.71	-2.32	8.99	15.62	B	92.23	-0.63	3.70	6.86
	21	F	90.25	-3.18	12.94	22.05					
	28	-	-	-	-	-	B	91.40	-2.27	9.36	15.94
	35	F	88.43	-3.94	21.03	35.79					

-- continued --

Table 4.1.3 (continued).

Exposure Site	Exposure Duration (days)	PHOTODEGRADABLE PS FOAM					CONTROL PS FOAM				
		Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Seattle *(continued)*	42	F	85.65	-3.92	21.83	37.42	B	88.84	-2.94	12.72	22.13
	45	F	86.56	-3.89	21.18	36.97					
	52	F	85.37	-3.82	23.20	39.77	B	87.36	-3.25	15.25	27.02
	59	F	84.53	-3.39	24.64	42.72					
	66	B	87.59	-3.09	25.78	44.36	B	86.97	-2.87	22.90	39.84
	73	B	89.63	-3.69	21.55	36.93					
	79	B	88.55	-3.55	24.99	42.94	B	87.70	-3.52	23.39	40.16
	87	B	88.54	-3.46	24.43	42.87					
	94	B	87.16	-3.16	27.02	46.55	F	86.34	-3.12	25.46	44.33
	101		82.31	-1.18	31.87	55.85**	B	86.57	-2.68	24.92	43.93
Wittmann, AZ	7	B	91.86	-2.33	9.54	16.40					
	14	B	91.01	-3.53	14.85	24.81	B	91.48	-1.62	6.83	11.69
	22	B	89.85	-4.04	19.58	32.36					
	29	-	-	-	-	-	B	90.36	-3.22	14.91	25.51
	36	B	88.40	-3.94	25.28	42.57					
	43	B	85.37	-4.06	25.72	43.91	B	87.30	-3.50	19.20	33.30
	50	B	85.71	-3.58	25.95	44.91					
	57	B	84.55	-2.91	25.45	44.78**	B	87.08	-3.30	20.79	35.91
	64	B	86.30	-2.55	27.77	47.89					
	71	B	88.03	-2.32	20.87	39.62					

- continued -

Table 4.1.3 (continued).

		PHOTODEGRADABLE PS FOAM					CONTROL PS FOAM				
Exposure Site	Exposure Duration (days)	Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Wittmann, AZ (continued)	78	B	91.93	-1.98	12.75	26.32					
	85	B	91.93	-2.83	15.24	27.20	B	87.79	-3.30	26.32	44.50
	92	B	88.40	-2.02	20.03	34.74					
	99						.B	86.69	-2.43	27.74	48.57
	113		88.76	-2.69	18.45	32.73		86.39	-3.90	27.87	46.82
	120		83.29	-2.14	30.61	51.51		85.48	-3.54	29.04	49.66
Wittmann, AZ (Duplicates)	7		90.65	-1.31	5.61	9.94		91.31	-0.12	2.26	4.32
	14		90.62	-2.22	8.57	14.75					
	21		89.88	-3.23	12.71	21.66		90.73	-1.25	5.82	10.41
	28		89.19	-3.77	15.96	27.10					
	35		88.46	-4.23	19.32	32.65		89.91	-2.77	11.85	20.00
	42		87.89	-4.27	21.94	37.56					
	49		87.43	-4.21	22.41	37.46		89.03	-3.38	15.76	26.81
	56		86.32	-4.20	26.72	45.02					
	63		86.04	-4.14	28.36	47.91		87.15	-3.81	22.79	38.96
	70		85.94	-4.07	28.70	48.72					
	77							86.68	-3.92	24.15	41.06
	84		85.83	-3.92	29.83	50.38					
	91							86.37	-3.98	25.84	44.13
	98		86.09	-3.49	29.11	49.20					

- continued -

Table 4.1.3 (continued).

| Exposure Site | Exposure Duration (days) | PHOTODEGRADABLE PS FOAM | | | | | CONTROL PS FOAM | | | |
		Side of Sample Exposed*	L	a	b	Yellowness Index	Side of Sample Exposed*	L	a	b	Yellowness Index
Wittmann, AZ	106		83.77	-2.43	30.05	52.81		85.73	-3.84	27.38	46.16
Duplicates (*cont.*)	113		84.18	-2.45	32.03	55.40					
	120		81.38	-0.95	30.57	54.70					

* F = front (smooth side of sample); B = Back side of sample
  For samples exposed for longer times, it was difficult to discern the front and back sides; in these cases it is not noted.

** Some loss of yellow layer possibly due to abrasion

Table 4.1.4. Tumbling Friability Results for Polystyrene Foam Samples Exposed Outdoors.

Exposure Site	Exposure Duration (days)	Mass Loss (%)	
		Photodegradable PS Foam	Control PS Foam
Unexposed	0	0.00	0.00
Cedar Knolls, NJ	7	0.00	
	14	0.00	0.00
	22	7.26	
	29	24.71	0.00
	36	28.58	
	43	35.75	1.15
	50	42.93	
	58	46.29	12.03
	64	44.15	
	71	46.31	16.22
	85	46.14	17.31
	99	48.63	22.51
	104	54.44	25.09
Cedar Knolls, NJ (duplicates)	5	0.00	
	12	0.00	
	19	0.00	0.00
	26	0.00	
	33	20.60	0.00
	40	34.50	
	47	38.05	0.00
	54	42.66	
	61	47.08	6.50
	68	44.88	
	75	46.94	15.32
	82	45.24	
	90	47.91	21.69
	97	49.05	
	104	48.62	25.14
Chicago, IL	7	0.00	
	14	0.00	0.00
	22	12.30	
	29	25.06	0.00
	36	29.12	
	43	36.55	8.25
	50	35.17	
	57	39.05	21.40
	64	44.47	
	71	46.10	26.15
	78	43.53	
	85	47.37	22.57
	92	46.19	
	99	49.65	25.47
	106	48.70	

- continued -

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Table 4.1.4.   (continued).

Exposure Site	Exposure Duration (days)	Mass Loss (%)	
		Photodegradable PS Foam	Control PS Foam
Chicago, IL (cont.)	113	47.74	26.86
	120	47.73	
	127	52.40	26.97
	134	55.67	
	141	55.01	28.30
Chicago, IL (duplicates)	28	0.49	
	35	0.00	
	42	0.00	0.00
	49	16.01	
	56	32.05	0.00
	63	36.15	
	70	41.21	0.00
	77	48.09	
	84	47.23	6.29
	91	47.03	
	98	47.98	19.92
	105	47.46	
	112	47.73	22.09
	119	51.01	
	127	-	22.49
	134	52.49	
Miami, FL	7	0.00	
	14	0.00	0.00
	21	17.00	
	28	24.19	0.00
	35	33.96	
	42	40.10	4.32
	49	41.06	
	56	41.43	23.08
	63	46.10	
	70	52.59	35.52
	77	51.41	
	84	64.18	35.70
	91	57.28	
	98	58.96	36.99
	103	63.82	40.63
Miami, FL (duplicates)	5	0.00	
	12	0.00	
	19	8.92	5.57
	26	30.79	
	33	33.40	0.73
	40	40.80	
	47	38.91	10.47
	54	41.66	

- continued -

Table 4.1.4.   (continued).

Exposure Site	Exposure Duration (days)	Mass Loss (%)	
		Photodegradable PS Foam	Control PS Foam
Miami , FL Duplicates (continued)	61	42.64	14.00
	68	52.13	
	75	56.02	26.67
	82	57.19	
	89	59.66	36.41
	96	66.82	
Seattle, WA	7	0.00	
	14	0.07	7.02
	21	-	
	28	6.25	0.49
	35	35.91	
	42	38.36	3.82
	45	36.76	
	52	42.28	13.69
	59	44.04	
	66	43.03	27.51
	73	43.97	
	79	47.72	23.86
	87	46.92	
	94	45.07	31.66
	101	47.92	24.26
Wittmann, AZ	7	0.00	
	14	24.51	0.00
	22	33.80	
	29	-	0.00
	36	47.58	
	43	46.99	17.70
	50	48.55	
	57	49.63	30.77
	64	57.06	
	71	53.52	
	78	55.21	
	85	57.27	36.80
	92	56.49	
	99		42.56
	113	74.39	35.15
	120	72.69	42.49
Wittman, AZ (duplicates)	7	0.00	0
	14	0.00	
	21	19.32	0
	28	37.85	
	35	47.03	0
	42	50.16	
	49	48.69	18.17
	56	52.72	

Table 4.1.4.   (continued).

Exposure Site	Exposure Duration (days)	Mass Loss (%)	
		Photodegradable PS Foam	Control PS Foam
Wittman, AZ			
Duplicates (continued)	63	55.56	31.44
	70	56.79	
	77	-	35.27
	84	55.09	
	91	-	38.29
	98	59.94	
	106	66.20	40.46
	113	63.93	
	120	70.47	42.08

Figure 4.1.8 shows curve-fitting for the tumbling friability data. The equation used was the same as for the data based on percent elongation at break:

$$\log M = \log A - Bt \tag{4-3}$$

where M is fractional mass remaining after tumbling friability, t is the duration of exposure in days, and A and B are constants. To obtain the best straight lines, the points for exposure durations less than the "lag times" discussed above were omitted. Good correlation coefficients were obtained for all the polystyrene data. Values for the rate parameter, B, show good agreement for duplicate data sets with the exception of Chicago, IL. As with tensile test data, the rate parameter (B) values obtained for control samples were always smaller than those obtained for photodegradable foam material.

Marine floating samples exposed in Miami, FL and Seattle, WA, as well as samples from selected outdoor exposure sites (Miami, FL and Chicago, IL), were characterized by gel permeation chromatography (GPC). The molecular weights (number average) from GPC are shown in Table 4.1.5. Molecular weight determinations are the best indicator of degradation at a molecular level since they show actual breakdown of the polymer chains. For example, tumbling friability data for direct weathering in Chicago, IL showed a "lag time" of about 14 days before measurable mass loss, whereas GPC data showed over 50% reduction in molecular weight after only 7 days of exposure. Brittleness of surface layer apparently developed after significant molecular level degradation had taken place.

Analysis of GPC data was accomplished by converting molecular weight values to degree of polymerization (DP) and using the following equation [Jellinek, 1967]:

$$1/DP_t - 1/DP_0 = A + Ht \tag{4-4}$$

where t is the duration of exposure in days. The value of H would increase for increasing degradation rate. These plots are shown in Figure 4.1.9 and show good fit for all data sets. The constant A should have a value of zero and was approximately zero for the control material but was somewhat higher for the degradable material. It is possible that the degradable material at zero exposure time is already degraded to a slight extent due to "shelf aging".

Table 4.1.6 summarizes the degradation rates obtained by both GPC and tumbling friability for polystyrene foam. Comparison of the ratio of B values (from tumbling friability data) for degradable and control materials (B_d/B_c) showed the degradation rate during direct weathering to be approximately twice as fast for the degradable material. The enhancement factor was slightly larger (3-4 times) for marine floating exposure.

Table 4.1.5   Number Average Molecular Weight of Polystyrene Foam Exposed Outdoors, as Determined by Gel Permeation Chromatography.

Exposure Site	Exposure Type	Exposure Duration (days)	Molecular Weight x 10^{-3}	
			Degradable PS Foam	Control PS Foam
Unexposed		0	125	144
Chicago, IL	Outdoor	7	51.1	
		14	45.6	102
		22	43.7	
		29	35.2	72.1
		36	32.6	
		43	29.2	63.2
		50	29.4	
		57	31.0	52.5
		64	27.9	
Miami, FL	Outdoor	7	66.7	
		14	45.5	95.3
		21	45.7	
		28	40.4	81.7
		35	38.3	
		42	45.4	59.6
		49	34.4	
		56	40.0	74.5
		63	36.4	
		70	32.0	
Miami, FL	Marine Floating	7	64.2	-
		29	35.6	-
		35	33.9	-
		43	-	72.3
		58	-	68.9
Seattle, WA	Marine Floating	7	70.7	126
		14	71.3	120
		21	51.9	103
		28	50.3	96.1

Table 4.1.6   Table of Regression Coefficients (Slopes and Intercepts) Based on Plots of Tumbling Friability and GPC Data for Polystyrene Foam Exposed Outdoors.

Location	Test Method**	Degradable Polymer			Control Polymer			B_d/B_c#	ΔB (x 10^3)#
		t_o (days)	A	B (x 10^3)#	t_o (days)	A	B (x 10^3)#		
OUTDOOR EXPOSURE									
Cedar Knolls, NJ	TF	20	0.897	2.9	44	1.13	1.7	1.7	1.2
Cedar Knolls, NJ*	TF	25	0.927	2.9	51	1.28	2.2	1.3	0.7
Chicago, IL	TF	15	0.868	2.2	36	0.98	1.1	2.0	1.1
Chicago, IL*	TF	36	1.04	2.9	75	1.38	2.1	1.4	0.8
Miami, FL	TF	15	0.955	4.1	38	1.16	3.0	1.4	1.1
Miami, FL*	TF	15	0.995	4.6	40	1.31	3.4	1.4	1.2
Seattle, WA	TF	14	0.841	2.4	37	1.08	1.9	1.3	0.5
Wittmann, AZ	TF	7	0.808	3.8	31	1.03	2.2	1.7	1.6
Wittmann, AZ*	TF	12	0.836	3.7	35	1.10	2.6	1.4	1.1
OUTDOOR EXPOSURE									
Chicago, IL	GPC	-	0.719	38.7	-	0.011	22.1	1.8	16.6
Miami, FL	GPC	-	0.675	25.2	-	0.12	14.3	1.8	10.9
MARINE FLOATING									
Miami, FL	GPC	-	0.166	62.8	-	0.021	14.3	4.4	48.5
Seattle, WA	GPC	-	0.135	43.0	-	0	13.0	3.3	30.0

*   duplicate sample

** For tumbling friability (TF): equation used was: log (M_t/M_0) = log (A) - Bt where M_t/M_0 = fractional mass remaining after tumbling friability and t = exposure time in days. In some cases, the lag time, t_o, for the onset of degradation (as detected by the tumbling friability method) results in an extrapolated A value >1. This lag time is also reported. For 0<t<t_o; M_t/M_0 is 1.
For GPC: equation used was: (1/DP_t - 1/DP_0) = A + Ht, where DP is degree of polymerization as calculated from number average molecular weight determined by GPC and t is exposure time in days. H_d/H_c is listed as B_d/B_c.

\#   Note: The parameter H from GPC studies is listed in this table in the B column; however these two parameters cannot be directly ared with each other.

4.1.3.3 Comparison of Marine and Freshwater Exposure to Land Exposure (Direct Weathering --

As discussed previously, samples placed in marine environments became fouled, or covered with various types of marine foulant species, during exposure. The fouling is illustrated in Figures 4.1.10 through 4.1.15, which show photographs of various sample types after marine exposure. Fouling occurred on both photodegradable and control film samples. In general, the presence of surface foulants shields the sample from UV radiation and slows the degradation rate. However, such shielding occurs unevenly due to the non-uniform foulant layer on the sample surface. This unevenness in photodegradation is a primary cause of the high scatter in tensile property data obtained with marine-exposed samples. Various plastic materials have been shown [Pegram and Andrady, 1989] to degrade more slowly in seawater than on land due to the cooling effect of the water and to the shielding of foulants.

In agreement with previous studies, comparison of B values (Table 4.1.2) for direct weathering to those for marine and freshwater floating shows slower rates in water for both control and degradable materials for 6P, PG, and ADM samples. Values for B_d/B_c, however, are higher for floating samples than for samples exposed to direct weathering, indicating the enhancement effect to be greater in water than for direct weathering. The higher values for this ratio for marine samples are attributed to extremely low degradation rates of control materials (B_c) in water. While the degradation rates of both the control and degradable plastic films slowed, as expected, in sea water, that of the latter slowed to a relatively lesser extent. Polystyrene foam also shows higher values for the B ratio for floating exposure as compared to direct weathering.

4.1.4 Effect of Geographic Location of Exposure on Rate Parameters

In all figures discussed, the elongation at break has been plotted versus the duration of exposure in order to determine degradation rates. This is based on the assumption that the samples receive a fairly constant average daily radiation at each exposure site. Figure 4.1.16 shows a plot of total solar radiation versus exposure duration for each location. The plots are, in fact, linear, with the slope of each line a measure of each location's average daily total solar radiation (All referrals to radiation measurements in this section are to radiation received at a tilt angle of 45° South). Thus, for the period of exposure for this study, degradation parameters may be plotted against either time or total radiation. The average daily radiation would be expected to change from month to month for a given location; the graphs in Figure 4.1.16 do appear to slightly decrease in slope toward the end of

the study period (September), particularly for Chicago, IL; Cedar Knolls, NJ; and Seattle, WA.

From the values of gradients in Figure 4.1.16, the locations can be ranked as follows in order of average daily total radiation (high to low): Wittmann, AZ; Seattle, WA; Chicago, IL; Miami, FL; and Cedar Knolls, NJ. To determine the correlation of degradation rate with radiation received, values for B (Table 4.1.2) were plotted versus average daily total radiation, and also versus average daily temperature, at each location. Where more than five points are shown on a graph, duplicate exposures were included. These graphs are shown in Figure 4.1.17 and show a somewhat better correlation of degradation rate with temperature than with radiation. For example, the degradation rate of 6P in Seattle, WA was lower than for any of the other sites, and even though Seattle, WA had a high value for average daily total radiation, it had the lowest average daily temperature. This is somewhat surprising in view of the fact that the 6P material, which is an (ethylene-carbon monoxide) copolymer, photodegrades via a Norrish II pathway under ambient conditions. Rates of Norrish II reactions are not particularly sensitive to temperature. Miami, FL exposure, which generally resulted in relatively high degradation rates, received lower average daily radiation than most sites but had a higher average daily temperature. Apparently the rate of disintegration is influenced by a combination of the two factors of temperature and radiation.

Figure 4.1.18 shows a composite semi-log plot of percent elongation at break versus total radiation for the exposure duration for all exposure sites for each plastic material. Using the same equation for modeling as for Figure 4.1.6, moderately good correlation coefficients were obtained for all materials. The data points which showed the poorest fit to the equation were those for Miami, FL and Seattle, WA, where, as discussed above, the effect of temperature should not be discounted. For example, in Figure 4.1.18.b, the data for Seattle, WA could be shifted to the left (and therefore closer to the line predicted by the equation) if the lower temperatures were accounted for by effectively decreasing the values for total radiation. Similarly, the data points for Miami, FL could be shifted to the right by effectively increasing radiation values to account for the higher average temperature in Miami, FL.

4.1.5 Outdoor Soil Burial

Outdoor soil burial was carried out at Research Triangle Institute from March to September, 1990. Samples expected to be enhanced-biodegradable/biodeteriorable, i.e., ADM, PCL, and BP, were exposed to these conditions. Tensile elongation at break was used to characterize the extent of disintegration of the materials. As described in Section

2.3.5, exposure was carried out in triplicate by randomly distributing samples in each of three different blocks at the soil burial testing site. This type of experimental design would show whether differences in extent of degradation could be attributed solely to exposure time or whether the effects of soil conditions, e.g., microbe population distribution, moisture content, growth of vegetation, etc., significantly affected degradation. These latter factors will be referred to as block effects. Tables 4.1.7.a through 4.1.7.e show an analysis of variance for each plastic material in which the sources of variation for percent elongation at break are broken down into treatments (exposure times), blocks, and error. Hypothesis testing for each material showed the block effects to be insignificant in each case, with exposure time being the only significant variable. Average values for percent elongation at break were therefore obtained from the three block values for each exposure duration. These values were used to obtain the plots shown in Figure 4.1.19. Each page shows a linear as well as a semi-log plot.

Values for B (empirical disintegration rate) are summarized in Table 4.1.8. Of the three enhanced biodegradable materials, BP showed the highest degradation rate. Figure 4.1.20 shows photographs of BP samples taken after various durations of soil burial exposure; tiny holes caused either by chemical degradation due to microbial action or by the physical deterioration caused by insects, etc., are evident even in the early stages of exposure. All BP samples were too weak for tensile testing by 29 days of exposure.

Based on comparison of B values, ADM was approximately twice as biodeteriorable under soil burial conditions as its corresponding control material; PCL blend material, however, was not significantly more deteriorated than the control. As discussed previously, the LLDPE matrix surrounds the polycaprolactone domains, limiting the PCL's access to enzymes required for biodegradation (or to microbes themselves) in the short time-scale of observation.

4.1.6 Comparative Extents of Degradation

The rate of disintegration of a plastic film or sheet material is an important parameter which characterizes the effectiveness of the material as an enhanced degradable plastic. However, in screening a material for enhanced degradability and in analysis of limited amounts of data which do not allow for the determination of such a rate, it is convenient to refer to degradability (or disintegration) in terms of "time to embrittlement". Here the term "embrittlement" is taken to mean the reduction of the tensile elongation at break to a value of 5 perce or less. While a figure of 2 percent is sometimes used in the literature with most types of common plastic films, the standard error associated with measuring the

Table 4.1.7 (a). Analysis of Variance for ADM Soil Burial Samples.

Analysis of variance for tensile data: Randomized complete block design
Parameter used: Percent elongation at break
k = Number of treatments (exposure times) = 10
b = Number of blocks = 3

Equations:

$$SST = \Sigma\Sigma y_{ij}^2 - T_{..}^2/bk \qquad s_1^2 = SSA/(k-1) \qquad SSA + SSB + SSE = SST$$

$$SSA = \Sigma T_{i.}^2/b - T_{..}^2/bk \qquad s_2^2 = SSB/(b-1) \qquad f_1 = s_1^2/s^2$$

$$SSB = \Sigma T_{.j}^2/k - T_{..}^2/bk \qquad s^2 = SSE/(b-1)(k-1) \qquad f_2 = s_2^2/s^2$$

Exposure Time (weeks)	Blocks			Total ($T_{i.}$'s)
	1	2	3	
0	89.2	89.2	89.2	267.6
2	67.3	70.0	71.0	208.3
4	50.3	56.3	51.6	158.2
6	65.1	57.6	58.6	181.3
8	52.3	62.3	56.7	171.3
10	23.1	25.9	20.5	69.5
12	28.7	36.0	32.7	97.4
14	19.4	24.1	25.1	68.6
16	13.1	21.1	20.3	54.5
18	11.1	7.0	7.3	25.4
20	-	-	-	
Total ($T_{.j}$'s)	419.6	449.5	433.0	1302.1 ($T_{..}$)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Exposure Times	18443.74	9	2049.30	210.89
Blocks	44.86	2	22.43	2.31
Error	174.91	18	9.72	
Total	18663.51	29		

Critical values of f:

Exposure times: $F_1 = F_\alpha[k-1,(k-1)(b-1)]$

Blocks: $F_2 = F_\alpha[b-1,(k-1)(b-1)]$

Let $\alpha = 0.05$

For Blocks:

H_0: $\beta_1 = \beta_2 = \beta_3 = 0$ (block effects zero)
Critical region: $F > f_{.05}(2,18)$
$\qquad\qquad\qquad F > 3.55$
Computed f = 2.31; $\therefore$ .. accept H_0

For Exposure Times:

H_0: $\alpha_1 = \alpha_2 = ... = \alpha_k = 0$
Critical region: $F > f_{.05}(9,18)$
$\qquad\qquad\qquad F > 2.46$
Computed f = 210.89, $\therefore$. reject H_0

Table 4.1.7 (b). Analysis of Variance for ADMC Soil Burial Samples.

Analysis of variance for tensile data: Randomized complete block design
Parameter used: Percent elongation at break
k = Number of treatments (exposure times) = 8
b = Number of blocks = 3

Equations:

$$SST = \sum\sum y_{ij}^2 - T_{..}^2/bk \qquad s_1^2 = SSA/(k-1) \qquad SSA + SSB + SSE = SST$$

$$SSA = \sum T_{i.}^2/b - T_{..}^2/bk \qquad s_2^2 = SSB/(b-1) \qquad f_1 = s_1^2/s^2$$

$$SSB = \sum T_{.j}^2/k - T_{..}^2/bk \qquad s^2 = SSE/(b-1)(k-1) \qquad f_2 = s_2^2/s^2$$

Exposure Time (weeks)	Blocks			Total $(T_{i.}$'s$)$
	1	2	3	
0	331.7	331.7	331.7	995.1
4	108.9	82.7	131.3	322.9
8	94.8	97.4	105.2	297.4
12	159.5	117.1	165.5	442.1
16	50.5	107.0	96.0	253.5
20	84.5	62.7	73.9	221.1
24	84.5	77.5	91.3	253.3
28	218.4	69.6	85.0	373.0
Total $(T_{.j}$'s$)$	1132.8	945.7	1079.9	3158.4 $(T_{..})$

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Exposure Times	149296.21	7	21328.03	18.87
Blocks	2325.60	2	1162.80	1.03
Error	15827.27	14	1130.52	
Total	167449.08	23		

Critical values of f:

Exposure times: $F_1 = F_\alpha[k-1,(k-1)(b-1)]$

Blocks: $F_2 = F_\alpha[b-1,(k-1)(b-1)]$

Let $\alpha = 0.05$

For Blocks:

H_0: $\beta_1 = \beta_2 = \beta_3 = 0$ (block effects zero)
Critical region: $F > f_{.05}(2,14)$
$\qquad\qquad\qquad F > 3.74$
Computed $f = 1.03$; $\therefore$ accept H_0

For Exposure Times:

H_0: $\alpha_1 = \alpha_2 = ... = \alpha_k = 0$
Critical region: $F > f_{.05}(7,14)$
$\qquad\qquad\qquad F > 2.76$
Computed $f = 18.87$, $\therefore$ reject H_0

Table 4.1.7 (c). Analysis of Variance for PCL Soil Burial Samples.

Analysis of variance for tensile data: Randomized complete block design
Parameter used: Percent elongation at break
k = Number of treatments (exposure times) = 15
b = Number of blocks = 3

Equations:

$$SST = \Sigma\Sigma y_{ij}^2 - T_{..}^2/bk$$

$$SSA = \Sigma T_{i.}^2/b - T_{..}^2/bk$$

$$SSB = \Sigma T_{.j}^2/k - T_{..}^2/bk$$

$$s_1^2 = SSA/(k-1)$$

$$s_2^2 = SSB/(b-1)$$

$$s^2 = SSE/(b-1)(k-1)$$

$$SSA + SSB + SSE = SST$$

$$f_1 = s_1^2/s^2$$

$$f_2 = s_2^2/s^2$$

Exposure Time (weeks)	Blocks			Total ($T_{i.}$'s)
	1	2	3	
0	717.3	717.3	717.3	2151.9
2	466.5	504.7	456.9	1428.1
4	508.3	483.3	332.6	1324.2
6	468.6	519.3	522.3	1510.2
8	433.4	493.6	412.5	1339.5
10	511.6	444.2	449.9	1405.7
12	501.4	471.2	467.9	1440.5
14	417.4	378.0	469.2	1264.6
16	441.3	396.3	401.0	1238.6
18	553.8	431.9	450.7	1436.4
20	354.8	460.2	347.5	1162.5
22	352.9	319.9	402.1	1074.9
24	359.3	336.6	323.6	1019.5
26	389.0	359.2	447.6	1195.8
28	466.7	377.0	374.1	1217.8
Total ($T_{.j}$'s)	6942.3	6692.7	6575.2	20210.2 ($T_{..}$)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Exposure Times	325086.45	14	23220.46	10.99
Blocks	4685.97	2	2342.99	1.11
Error	59144.85	28	2112.32	
Total	388917.28	44		

Critical values of f:

Exposure times: $F_1 = F_\alpha[k-1,(k-1)(b-1)]$ Blocks: $F_2 = F_\alpha[b-1,(k-1)(b-1)]$

Let $\alpha = 0.05$

For Blocks:
H_0: $\beta_1 = \beta_2 = \beta_3 = 0$ (block effects zero)
Critical region: $F >$ $f_{.05}$ (2,28)
                     $F >$ 3.34
Computed f = 1.11; ∴ accept H_0

For Exposure Times:
H_0: $\alpha_1 = \alpha_2 = ... = \alpha_k = 0$
Critical region: $F >$ $f_{.05}$ (14,28)
                     $F >$ 2.06
Computed f = 10.99, ∴ reject H_0

Table 4.1.7 (d). Analysis of Variance for LLDPE Soil Burial Samples.

Analysis of variance for tensile data: Randomized complete block design
Parameter used: Percent elongation at break
k = Number of treatments (exposure times) = 8
b = Number of blocks = 3

Equations:

$$SST = \Sigma\Sigma y_{ij}^2 - T_{..}^2/bk \qquad s_1^2 = SSA/(k-1) \qquad SSA + SSB + SSE = SST$$

$$SSA = \Sigma T_{i.}^2/b - T_{..}^2/bk \qquad s_2^2 = SSB/(b-1) \qquad f_1 = s_1^2/s^2$$

$$SSB = \Sigma T_{.j}^2/k - T_{..}^2/bk \qquad s^2 = SSE/(b-1)(k-1) \qquad f_2 = s_2^2/s^2$$

Exposure Time (weeks)	Blocks			Total ($T_{i.}$'s)
	1	2	3	
0	698.1	698.1	698.1	2094.3
4	368.9	395.3	694.8	1459.0
8	375.7	387.9	391.3	1154.9
12	488.4	476.8	520.3	1485.5
16	156.7	367.2	341.7	865.6
20	301.6	312.9	314.9	929.4
24	302.1	341.5	412.9	1056.5
28	330.1	363.4	357.1	1050.6
Total ($T_{.j}$'s)	3021.6	3343.1	3731.1	10095.8 ($T_{..}$)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Exposure Times	382543.63	7	54649.09	11.16
Blocks	31554.02	2	15777.01	3.22
Error	68564.25	14	4897.45	
Total	482661.90	23		

Critical values of f:

Exposure times: $F_1 = F_\alpha[k-1,(k-1)(b-1)]$ Blocks: $F_2 = F_\alpha[b-1,(k-1)(b-1)]$

Let $\alpha = 0.05$

For Blocks:
H_0: $\beta_1 = \beta_2 = \beta_3 = 0$ (block effects zero)

Critical region: $F >$ $f_{.05}$ (2,14)
                  $F >$ 3.74
Computed f =3.22; : .. accept H_0

For Exposure Times:
H_0: $\alpha_1 = \alpha_2 = ... = \alpha_k = 0$

Critical region: $F >$ $f_{.05}$ (7,14)
                  $F >$ 2.76
Computed f = 11.16, : . reject H_0

Table 4.1.7 (e). Analysis of Variance for BP Soil Burial Samples.

Analysis of variance for tensile data: Randomized complete block design
Parameter used: Percent elongation at break
k = Number of treatments (exposure times) = 8
b = Number of blocks = 3

Equations:

$$SST = \Sigma\Sigma y_{ij}^2 - T_{..}^2/bk \qquad s_1^2 = SSA/(k-1) \qquad SSA + SSB + SSE = SST$$

$$SSA = \Sigma T_{i.}^2/b - T_{..}^2/bk \qquad s_2^2 = SSB/(b-1) \qquad f_1 = s_1^2/s^2$$

$$SSB = \Sigma T_{.j}^2/k - T_{..}^2/bk \qquad s^2 = SSE/(b-1)(k-1) \qquad f_2 = s_2^2/s^2$$

Exposure Time (days)	Blocks			Total ($T_{i.}$'s)
	1	2	3	
0	60.0	60.6	60.6	181.2
7	20.3	8.0	12.8	41.1
14	11.6	6.4	10.6	28.6
20	8.5	4.3	4.8	17.6
22	3.7	11.2	4.0	18.9
24	5.9	3.1	4.5	13.5
27	3.7	4.2	4.7	12.6
29	3.8	4.6	3.5	11.9
Total ($T_{.j}$'s)	117.5	102.4	105.5	325.4 ($T_{..}$)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Exposure Times	7751.52	7	1107.36	121.04
Blocks	15.90	2	7.95	0.87
Error	128.08	14	9.15	
Total	7895.50	23		

Critical values of f:

Exposure times: $F_1 = F_\alpha[k-1, (k-1)(b-1)]$

Blocks: $F_2 = F_\alpha[b-1, (k-1)(b-1)]$

Let $\alpha = 0.05$

For Blocks:

H_0: $\beta_1 = \beta_2 = \beta_3 = 0$ (block effects zero)
Critical region: $F > f_{.05}(2,14)$
$F > 3.74$
Computed $f = 0.87$; $\therefore$ accept H_0

For Exposure Times:

H_0: $\alpha_1 = \alpha_2 = ... = \alpha_k = 0$
Critical region: $F > f_{.05}(7,14)$
$F > 2.76$
Computed $f = 121.04$, $\therefore$ reject H_0

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Table 4.1.8   Table of Regression Coefficients (Slopes and Intercepts) Based on Plots of Tensile Elongation at Break Data for Soil Burial Exposure.

Equation: $\log (\% \text{ elongation}) = \log (A) - Bt$ where t = exposure time in days

Polymer Code	Degradable Polymer		Control Polymer		ΔB (x 10^3)	B_d/B_c
	A	B (x 10^3)	A	B (x 10^3)		
ADM/ADMC	98.0	7.0	213	3.5	3.5	2.0
PCL/LLDPE	544	0.9	571	1.3	-0.4	0.7
BP	41.0	38.3	-	-	-	--

elongation at break of a near-embrittled material is too high to allow a clear distinction between values of 2 and 5 percent.

With enhanced photodegradable film materials 6P, PG, and ADM, the durations of exposure used were long enough to obtain embrittlement of the samples. After a certain number of weeks, each exposure location reported samples too embrittled to be collected for testing. Table 4.1.9 shows the time scale to embrittlement for the different exposure locations as the exposure duration. In the case of 6P samples, for instance, Wittmann, AZ exposure resulted in embrittlement after one week of exposure, while in Seattle, WA, the same material required an exposure as long as 8.5 weeks for embrittlement. In fact, the different locations might be ranked in terms of the length of exposure to embrittlement. For the three materials assessed on the basis of elongation at break, the following rankings were obtained:

6P   AZ > IL > FL > NJ > WA

PG   AZ > IL > NJ > FL > WA

ADM   AZ > IL > NJ > FL > WA

The rankings are very similar for all materials, unlike the rankings based on the rate parameter B.

In the case of marine and freshwater exposures, the process of degradation is generally slower, and the samples were not always embrittled at the maximum duration of exposure. These durations were estimated on the basis of a few preliminary experiments and were not long enough to obtain embrittlement of all samples exposed. Each of the sample types embrittled in the marine floating exposure conducted in Miami, FL, with the ADM material degrading the fastest. However, only the ADM film reached the embrittlement point in the Seattle, WA exposure. PG and 6P samples had extensibilities of 11 and 14 percent, respectively after a maximum of about 14 weeks of exposure. Freshwater lake exposures were of a limited duration, and the samples did not reach embrittlement.

Of the enhanced biodegradable and biodeteriorable samples, BP degraded extensively in the time scale of observation. The BP films were embrittled at the end of the test period in both soil and marine sediment environments. While embrittlement was not obtained in the nearly 2 weeks of exposure in fresh water, the sample had an elongation at break of only 14 percent at the end of this period. While not designed for enhanced photodegradability, the BP film did break down well under outdoor exposure as well and yielded an elongation at break of 18 percent within 8.5 weeks of exposure.

None of the PCL (polycaprolactone/LLDPE blend) samples embrittled in the time scale of observation. The disintegration of these samples evidently requires longer times and could not be observed.

Table 4.1.9 Extents of Degradation for Natural Weathering.

Material Code	Exposure Type[1]	Exposure Location	Exposure Duration (days)	Initial Percent Elongation	Final Percent Elongation	Embrittled?[2]
6P	O	Cedar Knolls, NJ	37	775	3	yes
		Chicago, IL	22	775	5	yes
		Miami, FL	30	775	3	yes
		Seattle, WA	66	775	2	yes
		Wittmann, AZ	6	775	22	yes
	MF	Miami, FL	35	775	4	yes
		Seattle, WA	94	775	14	no
	FF	Kerr Lake, VA	32	775	40	no
PG	O	Cedar Knolls, NJ	31	796	6	yes
		Chicago, IL	22	796	93	yes
		Miami, FL	34	796	4	yes
		Seattle, WA	42	796	4	yes
		Wittmann, AZ	9	796	52	yes
	MF	Miami, FL	49	796	63	yes
		Seattle, WA	101	796	11	no
	FF	Kerr Lake, VA	21	796	578	no
ADM	O	Cedar Knolls, NJ	9	89	4	yes
		Chicago, IL	9	89	3	yes
		Miami, FL	13	89	1	yes
		Seattle, WA	14	89	3	yes
		Wittmann, AZ	3	89	6	yes
	MF	Miami, FL	3	89	6	yes
		Seattle, WA	14	89	11	yes
	MS	Miami, FL	65	89	3	yes
		Seattle, WA	14	89	10	yes
	SB	RTI	126	89	8	yes
PCL	O	Miami, FL	63	717	24	yes
	MS	Miami, FL	147	717	359	no
		Seattle, WA	101	717	327	no
	FF	Kerr Lake, VA	56	717	358	no
	SB	RTI	196	717	406	no

- continued -

Table 4.1.9 (continued).

Material Code	Exposure Type[1]	Exposure Location	Exposure Duration (days)	Initial Percent Elongation	Final Percent Elongation	Embrittled?[2]
BP	O	Miami, FL	58	61	18	no
	MS	Miami, FL	12	61	2	yes
	FS	Kerr Lake, VA	12	61	14	no
	SB	RTI	29	61	4	yes

1 O = Outdoor; MF = Marine floating; FF = Freshwater floating; MS = Marine sediment; SB = Soil burial; FS = Freshwater sediment

2 Embrittled: "Yes" indicates that the exposure duration given is the maximum for which samples could be tested. Beyond this duration, the remaining samples were either retrieved in pieces too small and brittle to be tested or could not be retrieved at all. "No" indicates either that the entire sample set initially exposed could be retrieved and tested or that the deadline for ending the exposure period was reached before the entire set was sampled.

4.2 LABORATORY-ACCELERATED WEATHERING

4.2.1 Weather-Ometer® Exposure

All enhanced photodegradable plastic materials (6P, PG, ADM, and PS) were exposed to laboratory-accelerated weathering in a Xenon-Arc type Weather-Ometer® with both exposure time and black panel temperature varied. The corresponding control samples were also exposed under identical conditions. With the exception of PS foam samples, which were subjected to tumbling friability testing, all exposed materials were tested by Instron to determine percent elongation at break.

4.2.1.1 Rate Parameters --

Rate parameters for the samples exposed to accelerated weathering were determined by using the same curve-fitting equation as for outdoor weathering. Figures 4.2.1 (a) through 4.2.1 (c) show the linear and semi-log plots of the data, along with the curve-fitting equations. For accelerated exposure of 6P, the enhanced degradable material was inadvertently submitted for exposure in place of the control material, so values for elongation at break after Weather-Ometer® exposure for the control material were obtained from literature supplied by the manufacturer of this product. Literature values from the same source for the degradable material were found to overlap with the experimental values obtained in this study; the literature values for control samples were therefore considered acceptable substitutes for experimental values. These data points are shown in Figure 4.2.1 (a). Data shown in Figure 4.2.2 is based on the tumbling friability results for polystyrene foam.

Rate parameters for Weather-Ometer® exposure based on these plots are summarized in Table 4.2.1. The enhancement factors (B_d/B_c), shown in Table 4.2.1, are similar to those given in Table 4.1.2 for 6P, PG, and ADM and in Table 4.1.6 for PS. These B values are hourly rates, and should be converted into daily rates for direct comparison with the outdoor degradation rates. The B values based on elongation at break can be compared to those for outdoor exposure in Table 4.1.2 to determine the acceleration factor for Weather-Ometer® exposure. (For PS accelerated rate parameter can be compared to the values in Table 4.1.6.) Weather-Ometer® rate parameters were from 2-5 times greater than outdoor rate parameters for 6P, PG, and ADM for all exposure locations except Wittmann, AZ, which had similar values to those for accelerated exposure. The following table (4.2.2) shows values for the ratio of B_w (Weather-Ometer® rate parameter) to B_0 (outdoor rate parameter) for the enhanced degradable materials. These values shall be referred to as

Table 4.2.1. Table of Regression Coefficients (Slopes and Intercepts) Based on Plots of Tensile Elongation at Break and Tumbling Friability Data for Weather-Ometer® Exposure.

Polymer Code	Type of Test[1]	Degradable Polymer		Control Polymer		ΔB (x 10^3)	B_d/B_c
		A	B (x 10^3)	A	B (x 10^3)		
6P/6PC	T	235	8.7	903	1.7	7.0	5.1
PG/PGC	T	927	6.3	599	0.9	5.4	7.0
ADM/ADMC	T	195.0	8.1	144	1.1	7.0	7.4
PS/PSC	TF	1.2	2.0	1.6	1.1	0.9	1.8

1 T = Tensile Test; TF = Tumbling Friability

For Tensile Test, equation used was: $\log(\% \text{ elongation}) = \log(A) - Bt$ where t = exposure time in hours

For Tumbling Friability, equation used was: $\log(M_t/M_0) = \log(A) - Bt$ where M_t/M_0 = fractional mass remaining after tumbling friability and t = exposure time in hours.

acceleration factors. Rate parameters for Set II of ADM outdoor exposure were used in the calculations, as this was the material used in Weather-Ometer® exposure. The acceleration of the rate of degradation in the Weather-Ometer® was much more pronounced for polystyrene foam than for the other materials. Since the intensity and spectral quality of light in the Weather-Ometer® (borosilicate-filtered xenon source) were not too different from that encountered outdoors, this phenomenon must be attributed to higher temperature, cycling, and/or humidity. Of these, temperature is likely to be a major factor. The temperature-dependence of embrittlement times for polystyrene foam is not known. Perhaps a high temperature dependence of the surface embrittlement phenomenon leads to the observed dramatic acceleration of degradation under laboratory conditions compared to that obtained outdoors. All samples collected during the experiment were not degraded to an extent to preclude testing (or embrittled), although formation of an embrittled yellow surface layer did occur during Weather-Ometer® exposure, as evidenced by the values for Yellowness Index in Table 4.2.3.

Table 4.2.2. Acceleration Factors Obtained for Weather-Ometer® Exposures as Compared to Outdoor Exposures.

	Cedar Knolls, NJ	Chicago, IL	Miami, FL	Seattle, WA	Wittmann, AZ
6P	4.0	2.4	3.0	5.2	0.8
PG	3.0	3.1	2.1	2.8	1.2
ADM	2.5	2.9	2.3	-	1.4
PS	17	22	12	20	17

4.2.1.2   Temperature Dependence --

Figures 4.2.3 and 4.2.4 show the effect of increasing black panel temperature in the Weather-Ometer® on the rate parameters of 6P, PG, and ADM for an exposure time of 50 hours. ADM appears to be the most temperature sensitive material at this exposure duration. 6P was relatively unaffected by temperature changes, although exposure for 50 hours at even the lowest temperature (65°C) resulted in a breaking elongation value much lower than for the unexposed material. This is not surprising, as the (ethylene-carbon monoxide) copolymers are known to photolyze predominantly via Norrish II reaction, which is not sensitive to temperature. Nevertheless, secondary oxidation of photolysis products, as

Table 4.2.3. Polystyrene Foam Yellowness Index Values for Weather-Ometer® Exposure.

Exposure Duration* (hours)	Degradable PS Foam				Control Material			
	L	a	b	Yellowness Index	L	a	b	Yellowness Index
0	92.97	0.24	1.42	3.01	92.88	0.14	1.64	3.21
50	90.37	-1.94	7.51	13.05				
100	89.22	-3.19	11.52	20.31	90.50	-1.23	5.40	9.42
150	88.42	-3.82	15.46	26.73				
200	88.05	-4.21	19.81	34.20	89.49	-2.98	11.82	19.61
250	86.77	-4.20	23.60	40.21	88.50	-3.80	16.67	28.16

* All samples were exposed on the back (duller) side of the foam sheet.

well as any concurrent, low levels of Norrish I reactions, will initiate free radical reaction sequences which can be sensitive to changes in temperature.

Based on evaluation by tumbling friability, PS material did not significantly degrade when exposed for 50 hours in the temperature range studied. This exposure duration was apparently not sufficient to overcome the "lag time" for the onset of measurable (by tumbling friability) degradation discussed in Section 4.1.3.2. Had longer exposures been carried out, the material was likely to have shown markedly high rates of breakdown based on data discussed in Section 4.2.1.1.

4.2.2 Laboratory-Accelerated Soil Burial

The enhanced biodegradable plastic samples ADM and PCL were exposed to soil burial under laboratory-controlled conditions at 37°C. Values for percent elongation at break were measured and are reported in Table 4.2.4. These results show little change in breaking elongation during the exposure, which was carried out for up to 70 days, and tend to confirm the results of the outdoor exposure. Evidently, modifications to the accelerated exposure procedure will be necessary in order to achieve measurable degradation within this time scale. Such modifications may include raising the temperature, seeding the soil with a higher or different microbial population, improving soil aeration, or changing conditions of moisture and pH. However, changes to exposure environment cannot be so drastic as to induce biological/chemical processes not typical of outdoor, field exposure.

Table 4.2.4 Tensile Test Data for Laboratory Accelerated Soil Burial Samples.

Material Code	Exposure Time (days)	Average Stress at Break (kg/cm^2)	Stress Std. Dev. (kg/cm^2)	Average Elongation at Break (%)	Elongation Std. Dev. (%)	Number of Samples
ADM	0	119	8	176.3	22.0	16
ADM	3	123	5	139.2	20.5	5
ADM	7	114	5	160.1	13.6	7
ADM	10	127	4	156.9	17.9	7
ADM	15	119	4	165.5	15.6	6
ADM	22	118	6	199.4	18.2	8
ADM	36	117	3	178.3	23.1	6
ADM	70	134	2	168.2	9.9	5
ADMC	0	220	21	183.5	41.2	11
ADMC	7	149	7	171.8	35.0	5
ADMC	15	216	15	167.8	43.5	4
ADMC	36	241	6	169.9	23.7	6
ADMC	70	201	28	107.7	59.5	6
PCL	0	333	100	717.3	92.2	10
PCL	3	287	40	664.0	41.3	5
PCL	7	353	64	683.7	57.2	6
PCL	10	176	48	406.4	68.9	8
PCL	15	162	25	449.0	71.3	5
PCL	22	343	55	748.1	41.9	7
PCL	36	337	51	761.4	63.7	6
PCL	70	244	80	678.3	91.0	6
LLDPE	0	257	67	698.1	79.1	8
LLDPE	7	156	73	422.9	165.8	9
LLDPE	15	62	4	323.4	36.3	6
LLDPE	36	240	112	670.8	164.5	7
LLDPE	70	108	5	366.7	50.0	5

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J. E. Pegram and A. L. Andrady, Outdoor Weathering of Selected Polymeric Materials under Marine Exposure Conditions, Polymer Degradation and Stability, 26, 333-345 (1989).

H.H.G. Jellinek, Appl. Polym. Symp., 4, 41-54 (1967).
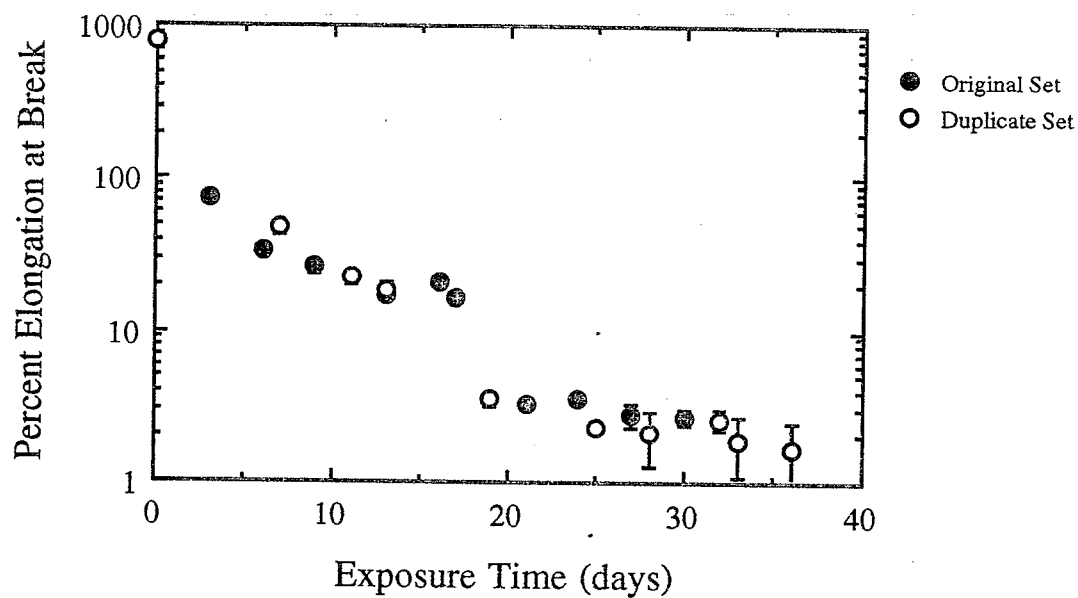
Figure 4.1.1 (a)   Elongation at break vs. exposure time for duplicate exposures of 6P samples outdoors in Miami, FL - Enhanced degradable material.
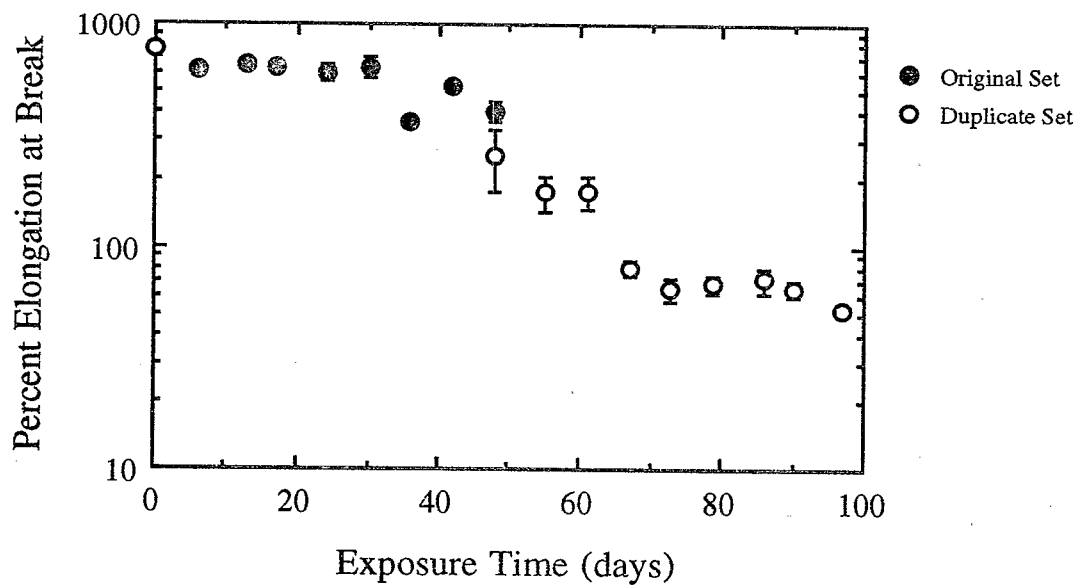
Figure 4.1.1 (b)   Elongation at break vs. exposure time for duplicate exposures of 6P samples outdoors in Miami, FL - Control material.
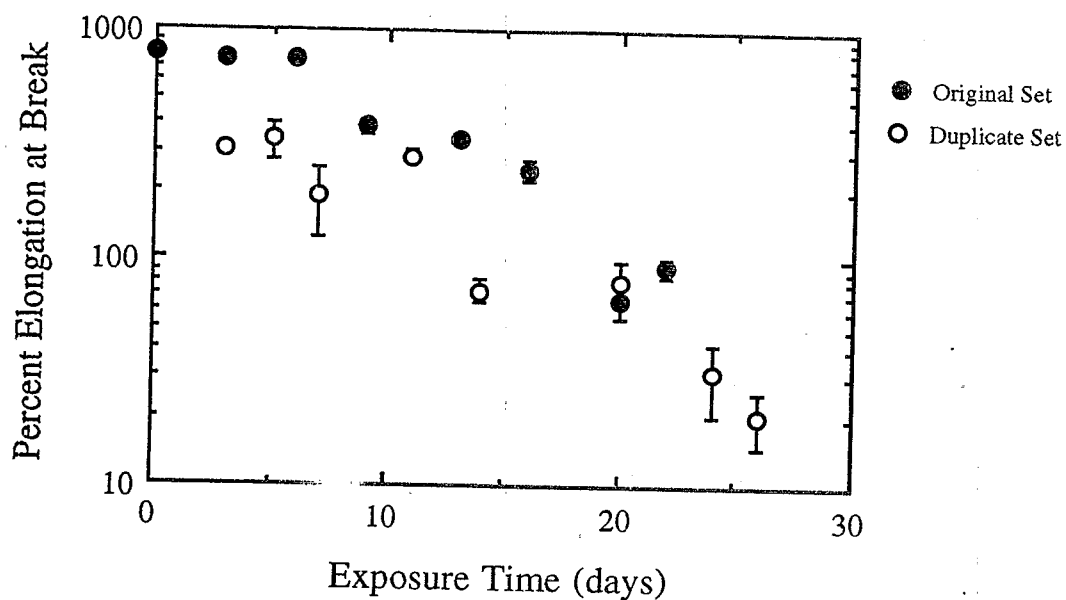
Figure 4.1.2 (a)   Elongation at break vs. exposure time for duplicate exposures of PG samples outdoors in Chicago, IL - Enhanced degradable material.
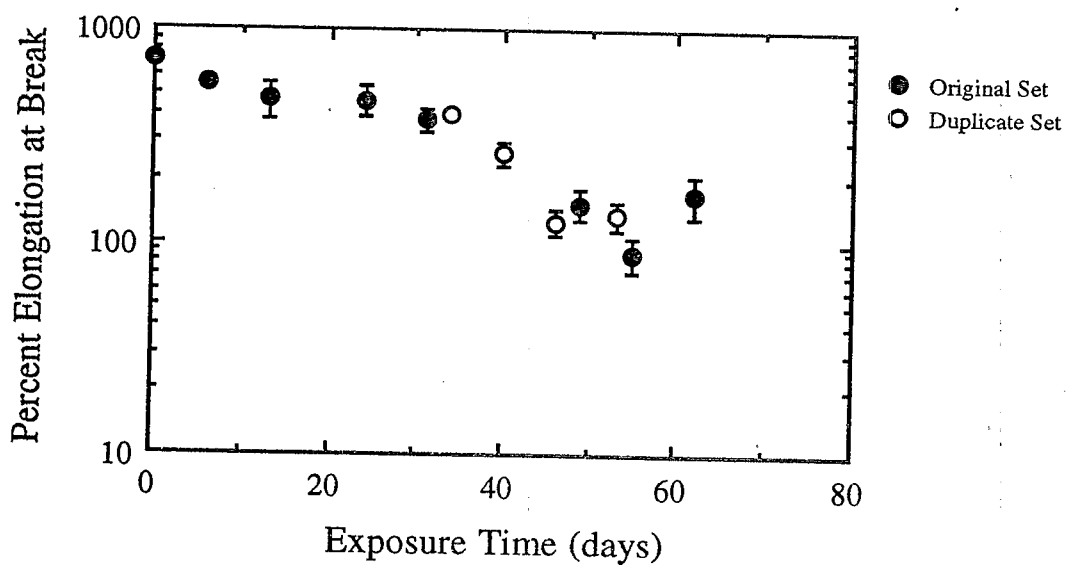
Figure 4.1.2 (b)   Elongation at break vs. exposure time for duplicate exposures of PG samples outdoors in Chicago, IL - Control material.
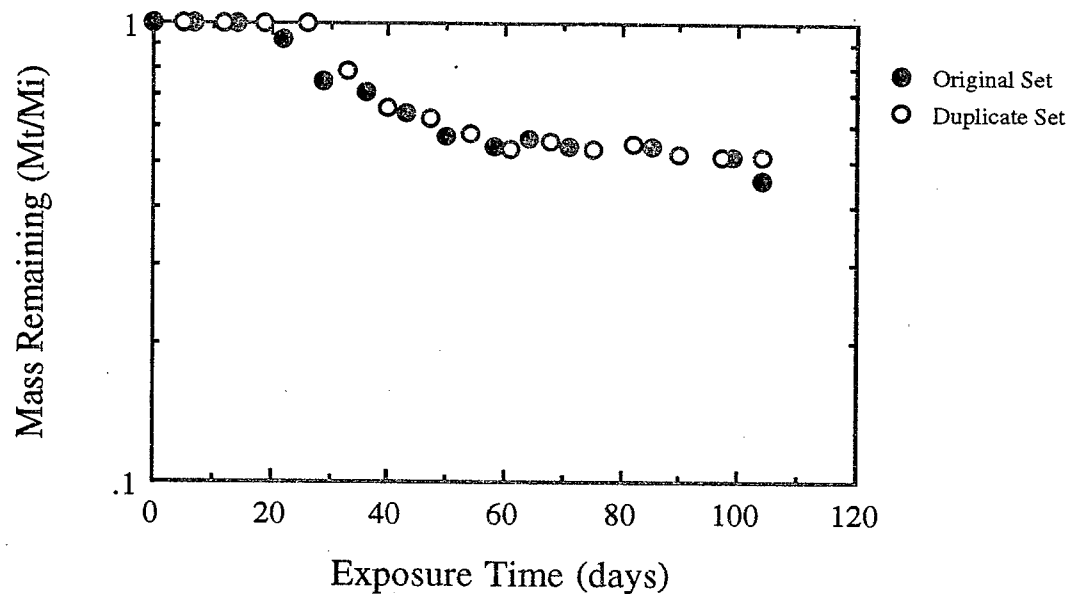
Figure 4.1.3 (a)   Change in mass after tumbling friability test vs. exposure time for duplicate exposures of PS foam outdoors in Cedar Knolls, NJ - Enhanced degradable material.
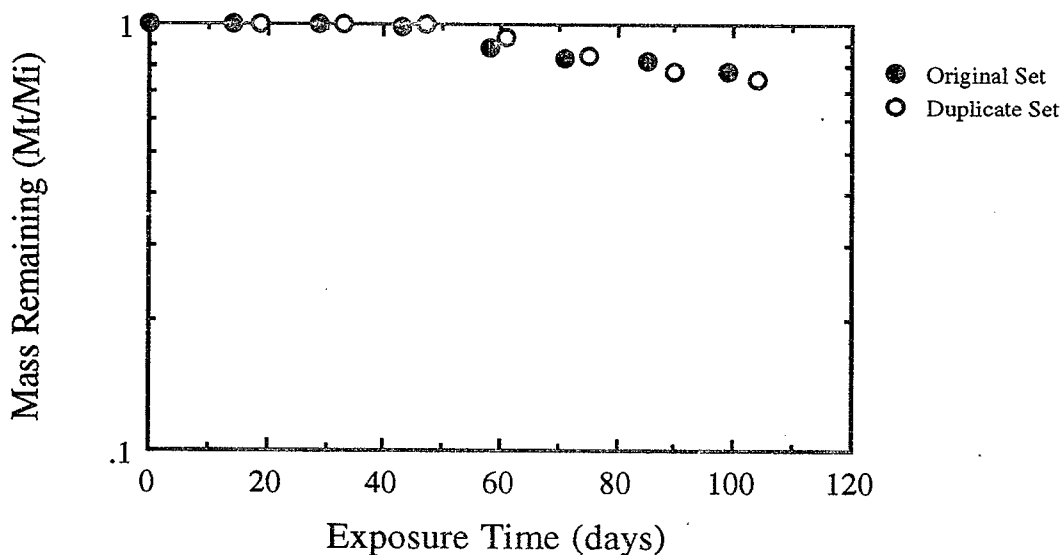
Figure 4.1.3 (b)   Change in mass after tumbling friability test vs. exposure time for duplicate exposures of PS foam outdoors in Cedar Knolls, NJ - Control material.
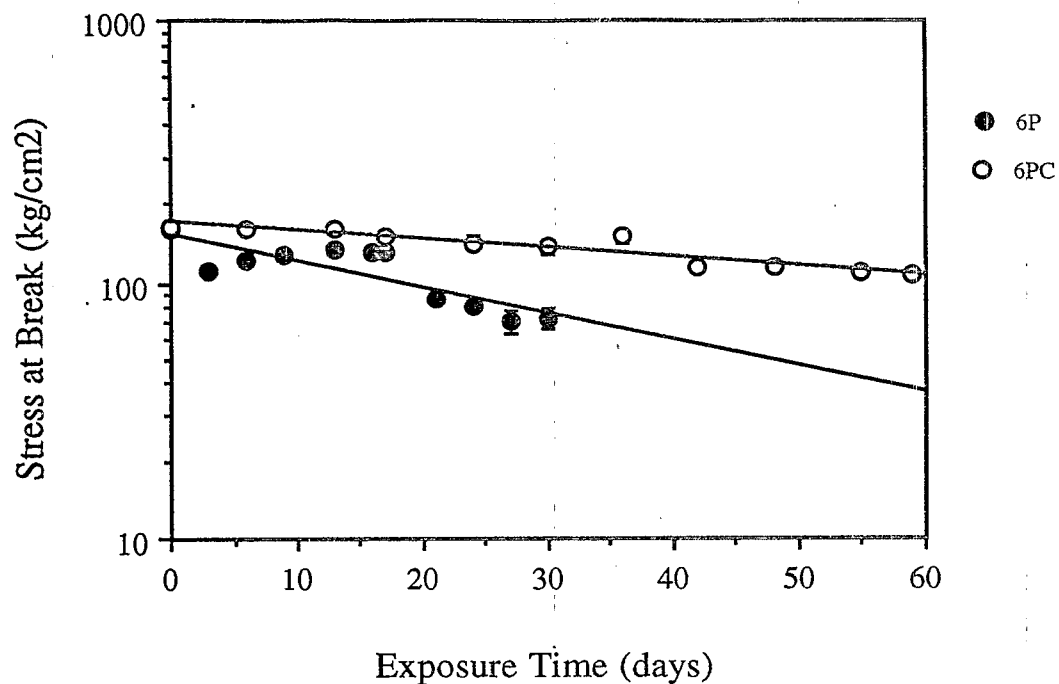
Figure 4.1.4 (a)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Miami, FL - stress at break).
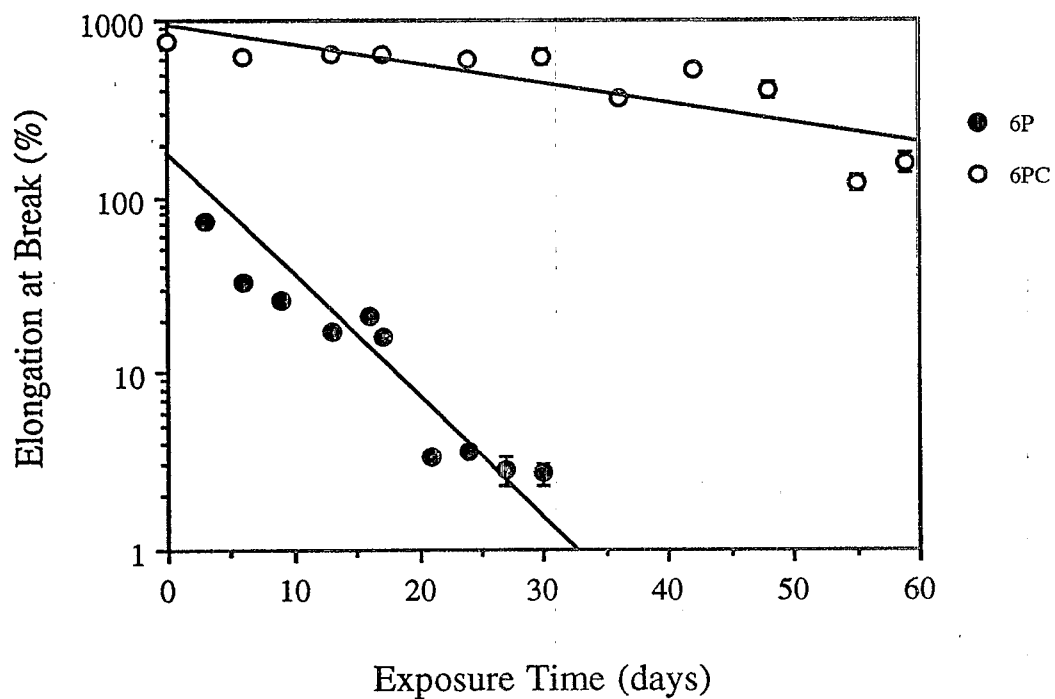
Figure 4.1.4 (b)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Miami, FL - elongation at break).
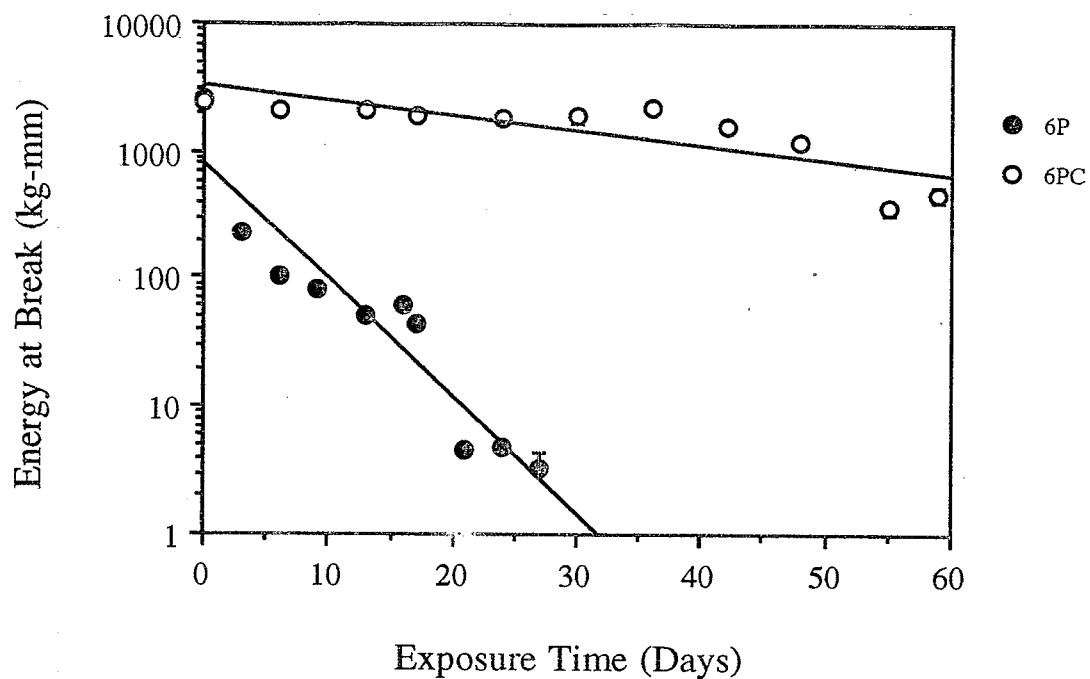
Figure 4.1.4 (c)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Miami, FL - energy to break).
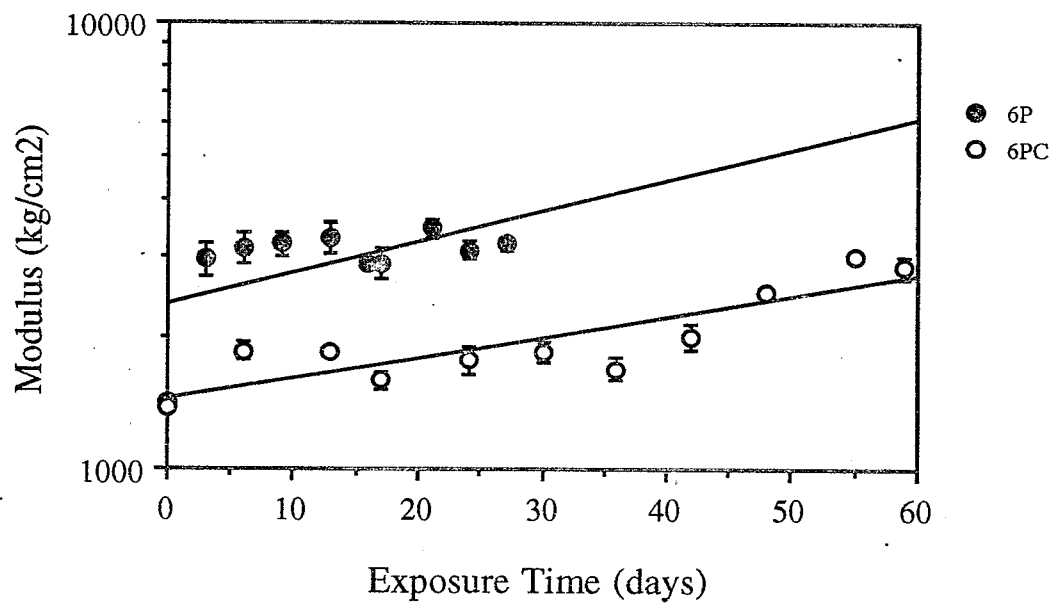
Figure 4.1.4 (d)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Miami, FL - modulus).
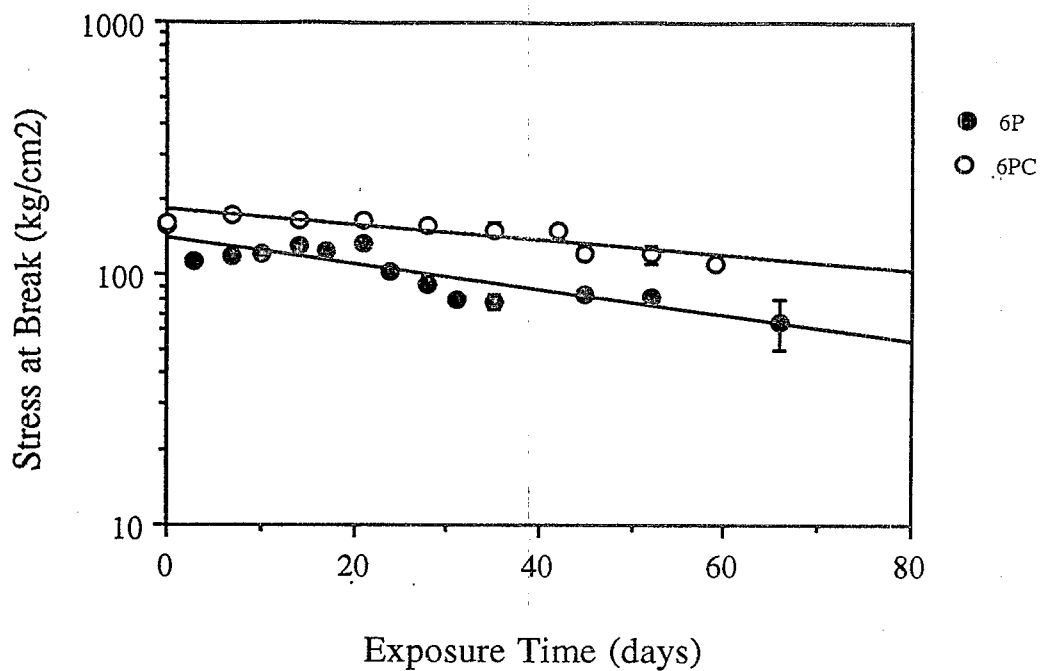
Figure 4.1.4 (e)   Variation of selected tensile parameters with duration of exposure for
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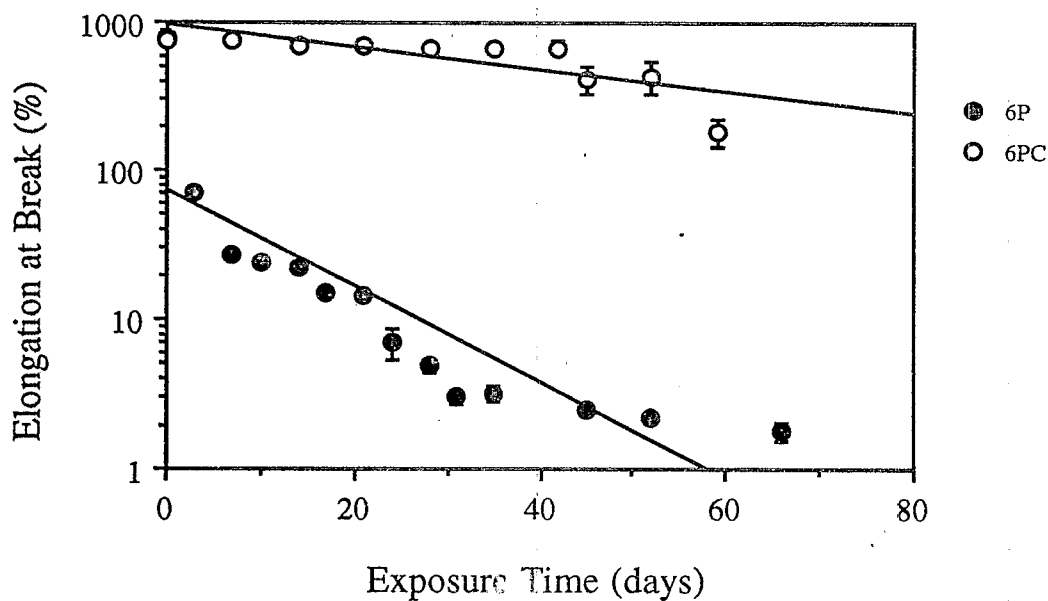
Figure 4.1.4 (f)   Variation of selected tensile parameters with duration of exposure for
outdoor exposure (6P - Seattle, WA - elongation at break).
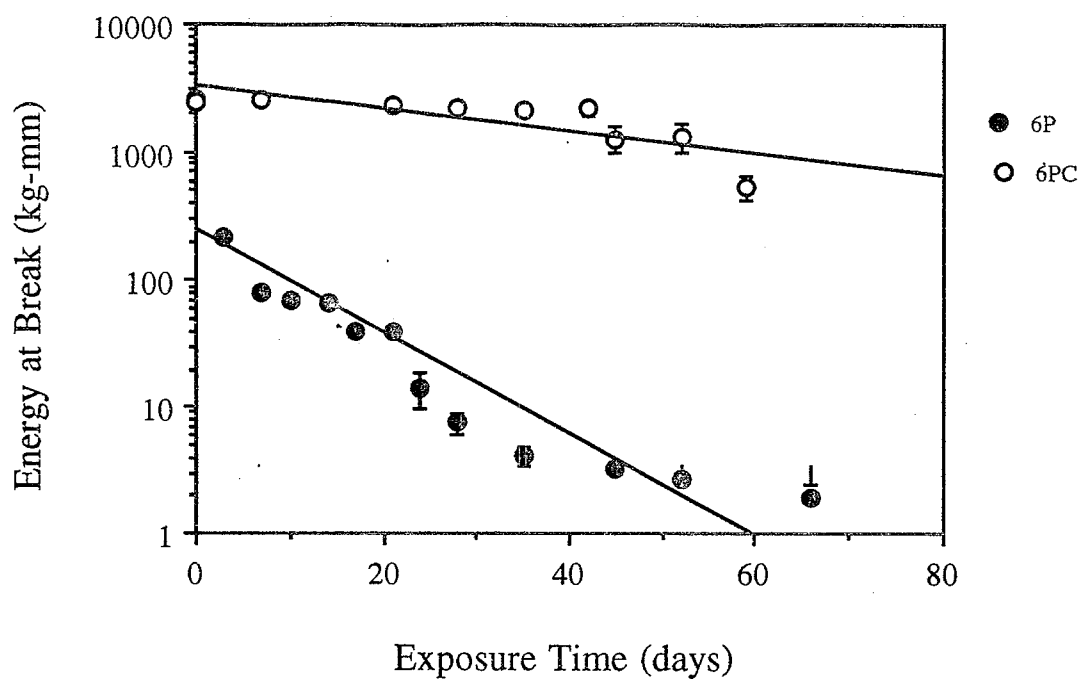
Figure 4.1.4 (g)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Seattle, WA - energy to break).
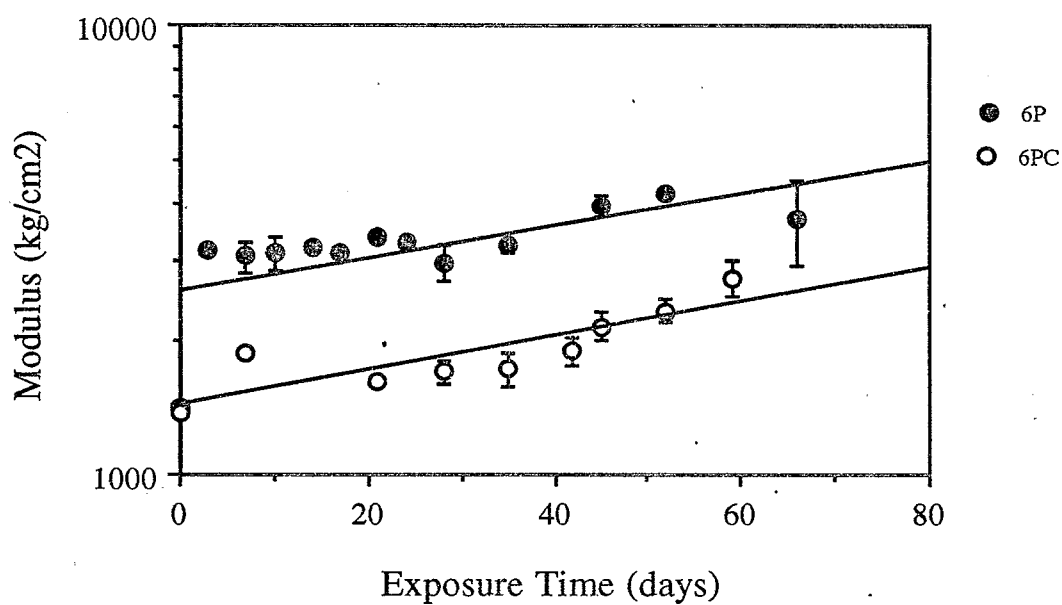
Figure 4.1.4 (h)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (6P - Seattle, WA - modulus).
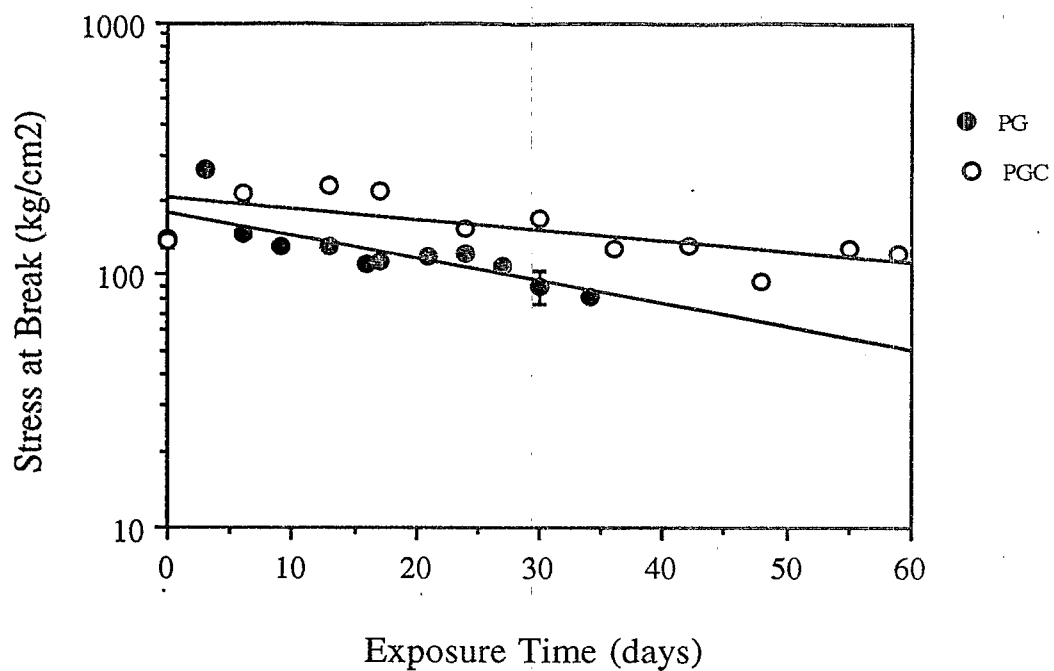
Figure 4.1.4 (i)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Miami, FL - stress at break).
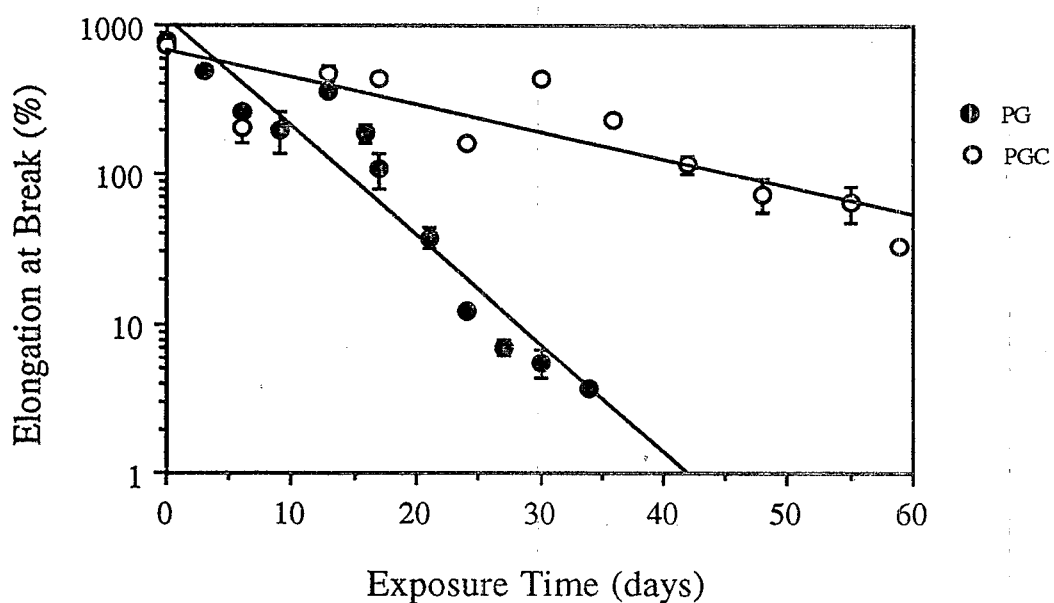
Figure 4.1.4 (j)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Miami, FL - elongation at break).
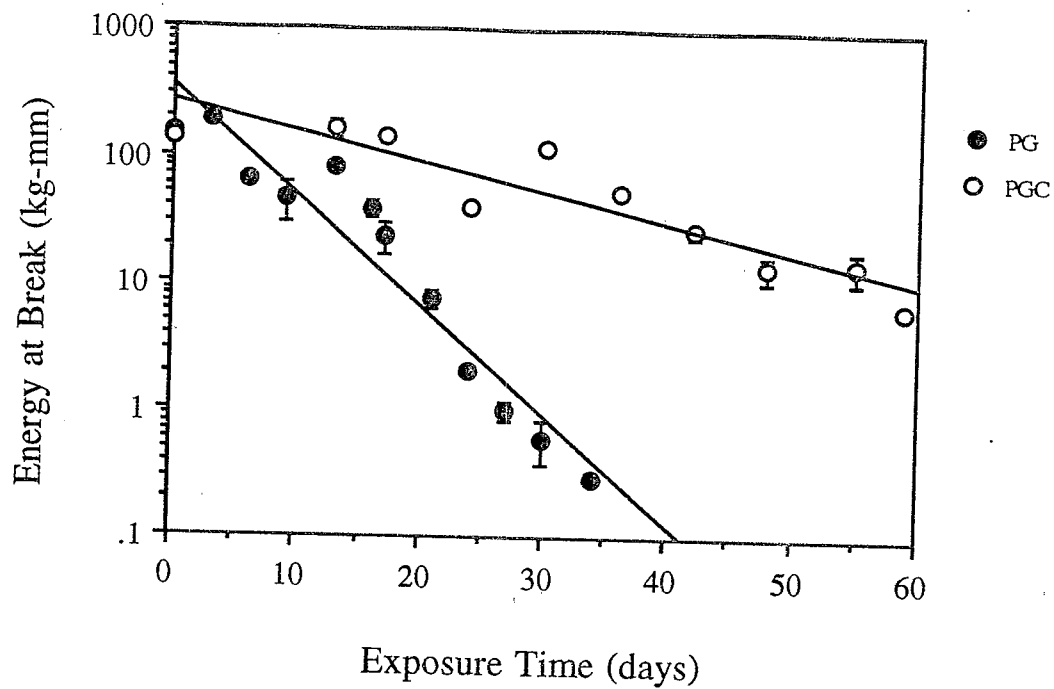
Figure 4.1.4 (k)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Miami, FL - energy to break).
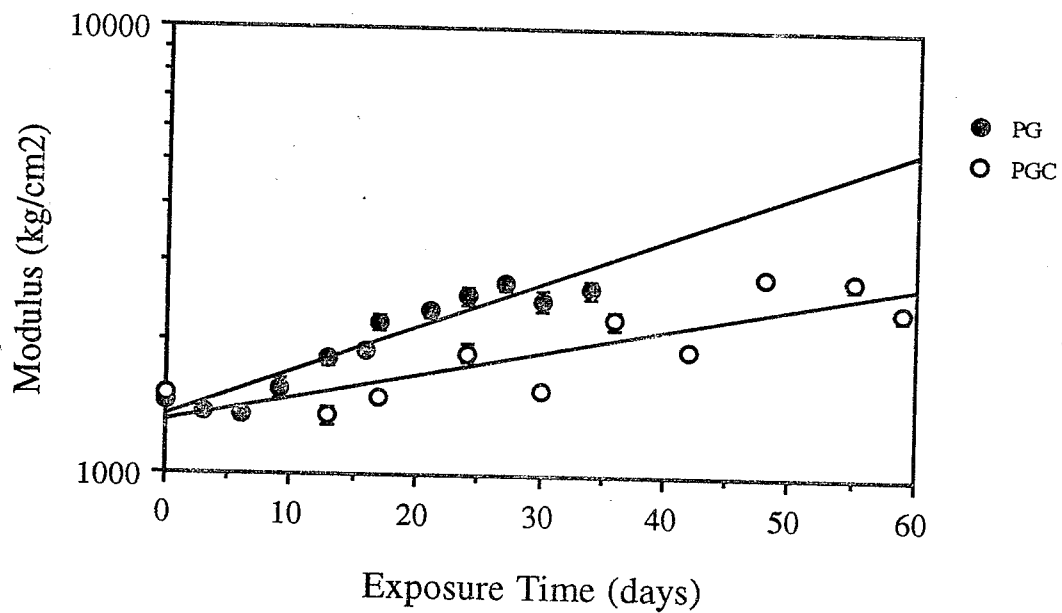
Figure 4.1.4 (l)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Miami, FL - modulus).
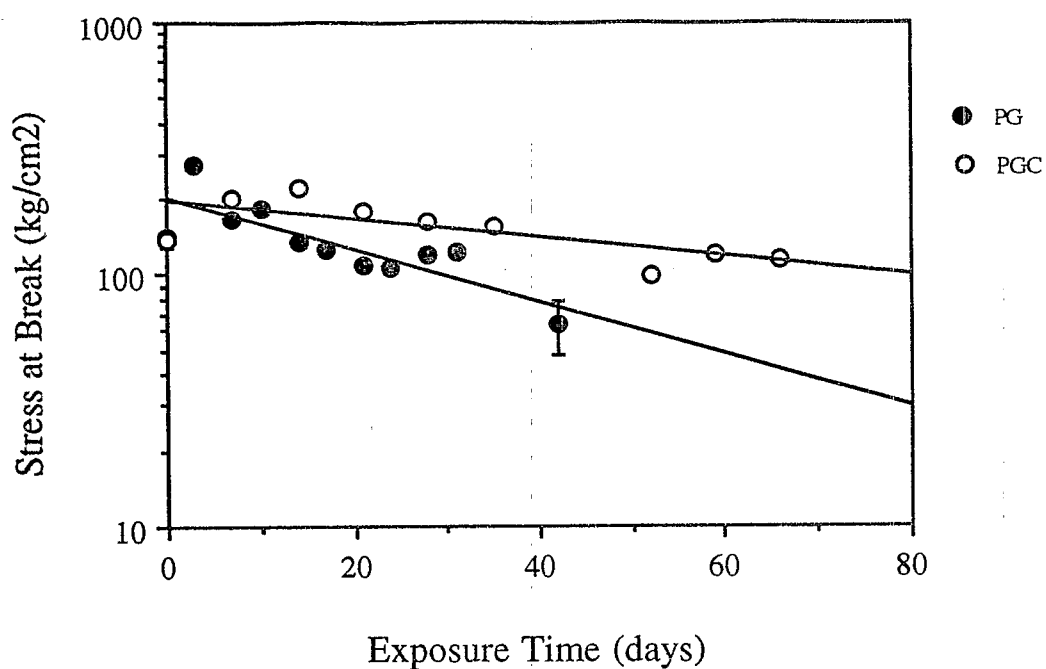
Figure 4.1.4 (m)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG- Seattle, WA - stress at break).
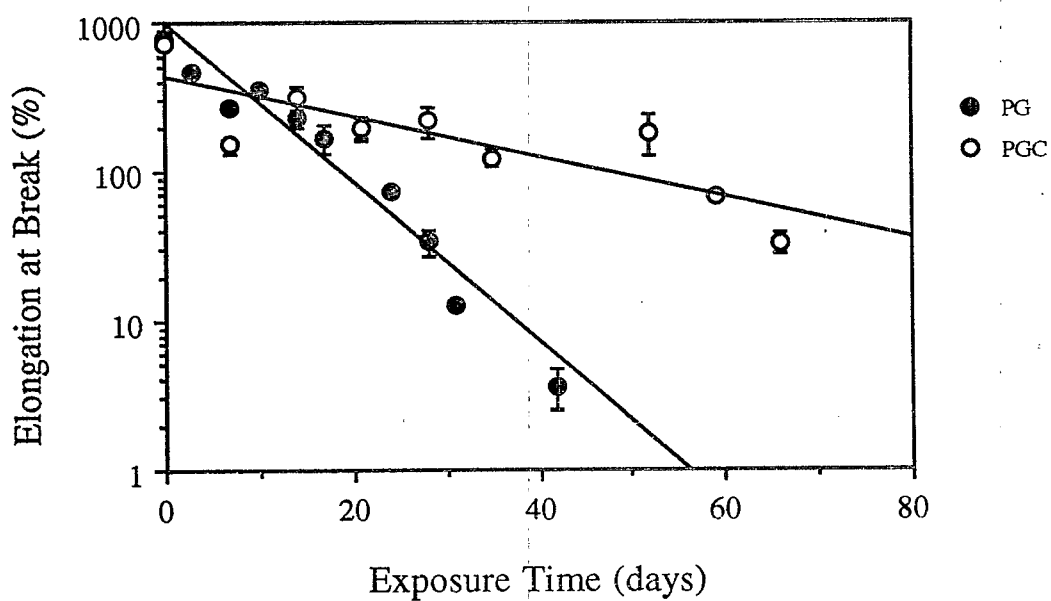
Figure 4.1.4 (n)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Seattle, WA - elongation at break).
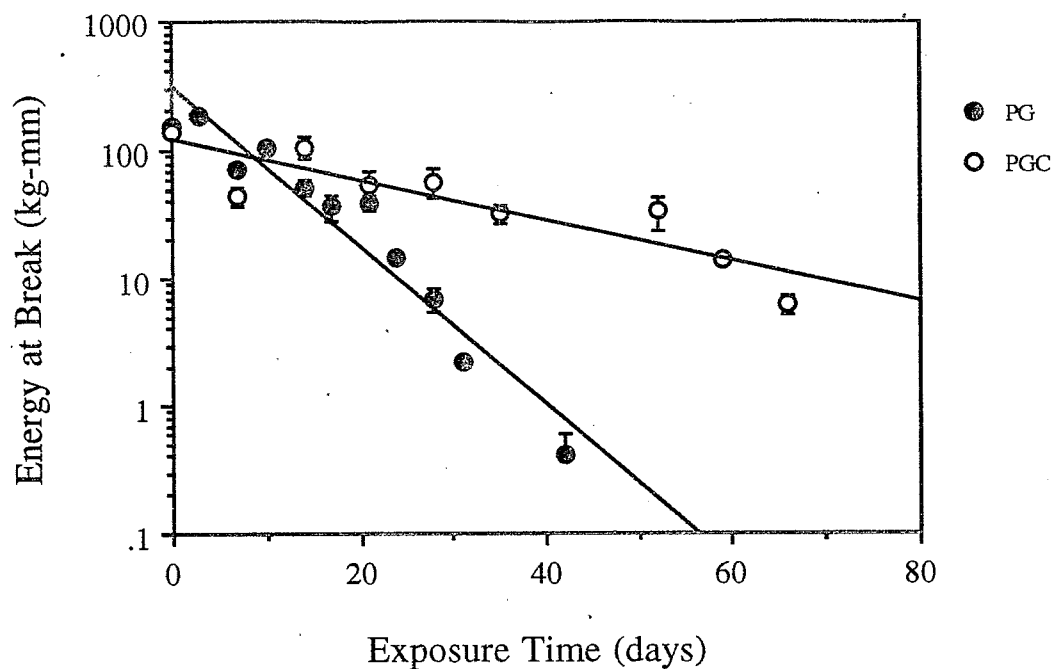
Figure 4.1.4 (o)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Seattle, WA - energy to break).
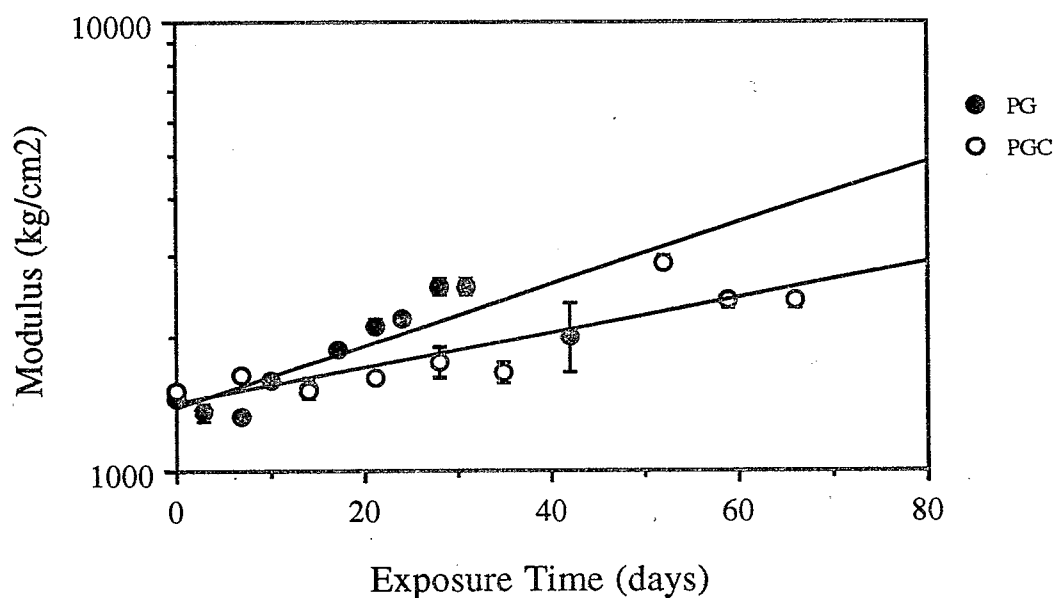
Figure 4.1.4 (p)   Variation of selected tensile parameters with duration of exposure for outdoor exposure (PG - Seattle, WA - modulus).

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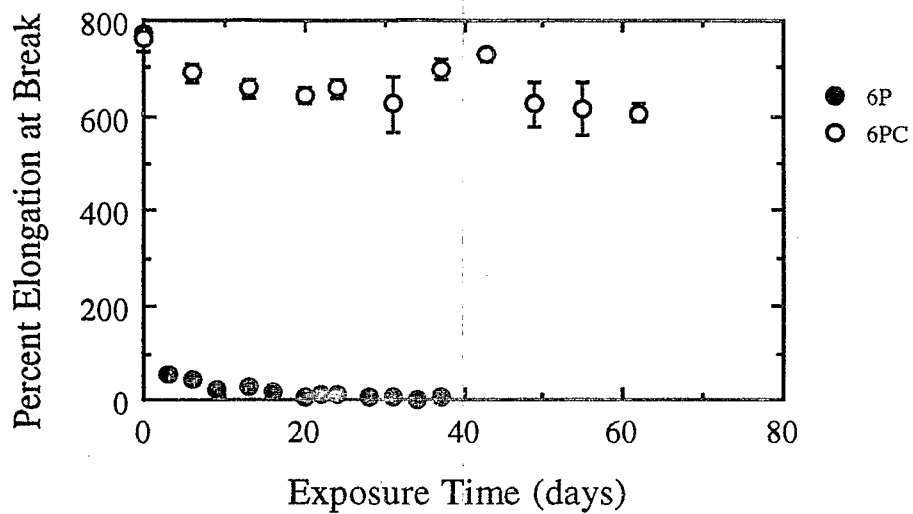
Figure 4.1.5 (a)   Elongation at break vs. exposure time. (6P - Cedar Knolls, NJ - outdoor exposure).
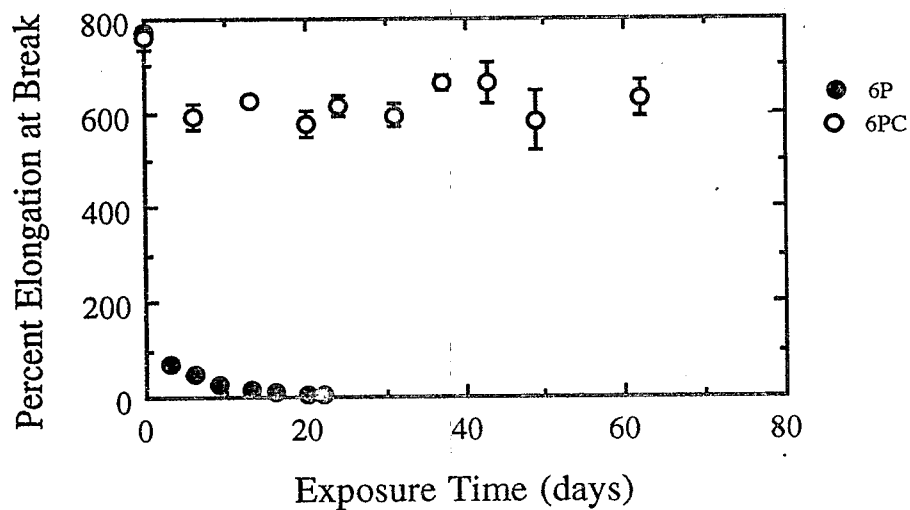
Figure 4.1.5 (b)   Elongation at break vs. exposure time. (6P - Chicago, IL - outdoor exposure).
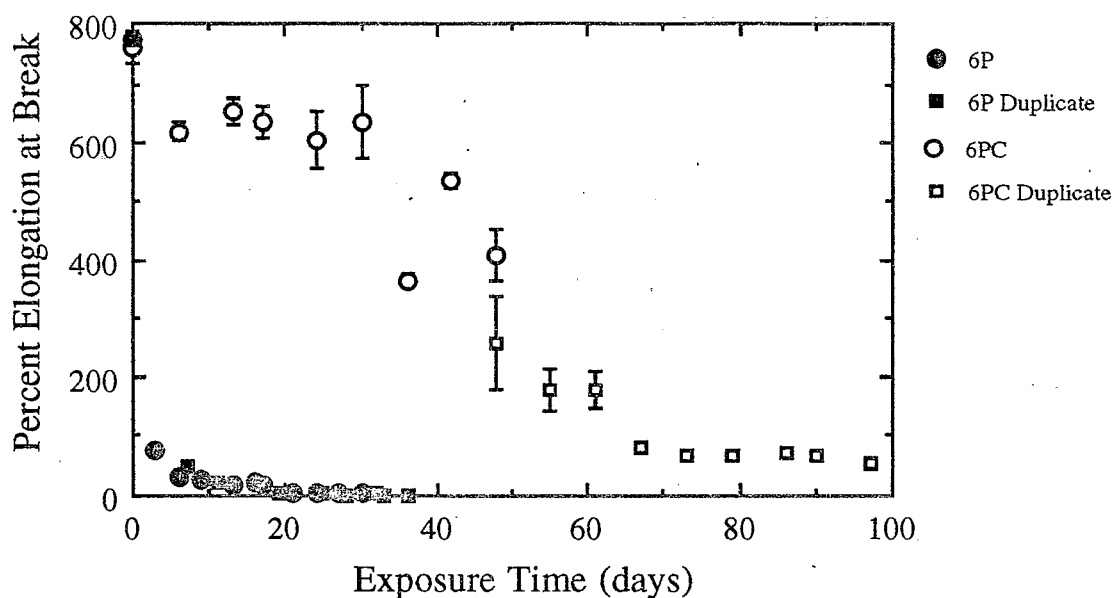
Figure 4.1.5 (c)   Elongation at break vs. exposure time. (6P - Miami, FL - outdoor exposure).
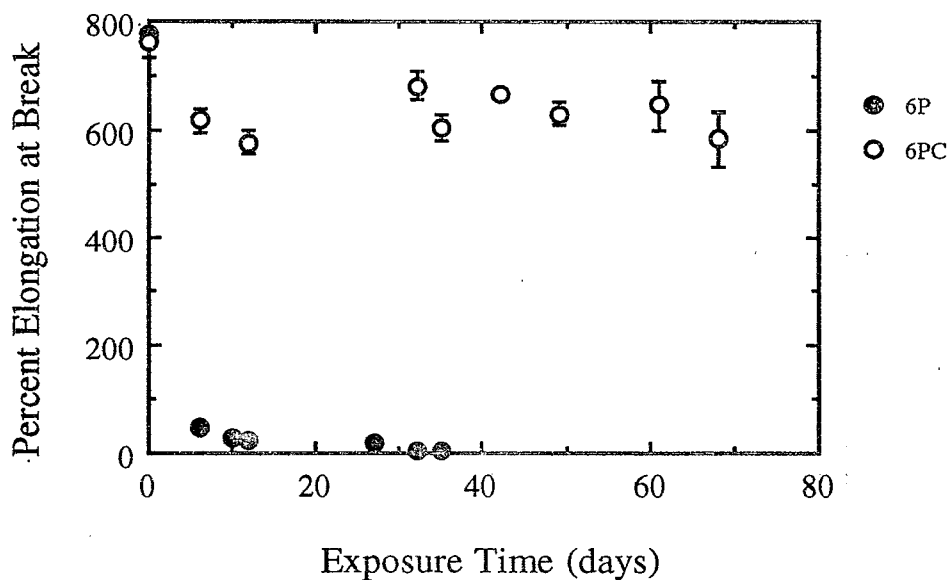
Figure 4.1.5 (d)   Elongation at break vs. exposure time. (6P- Miami, FL - marine floating exposure) .
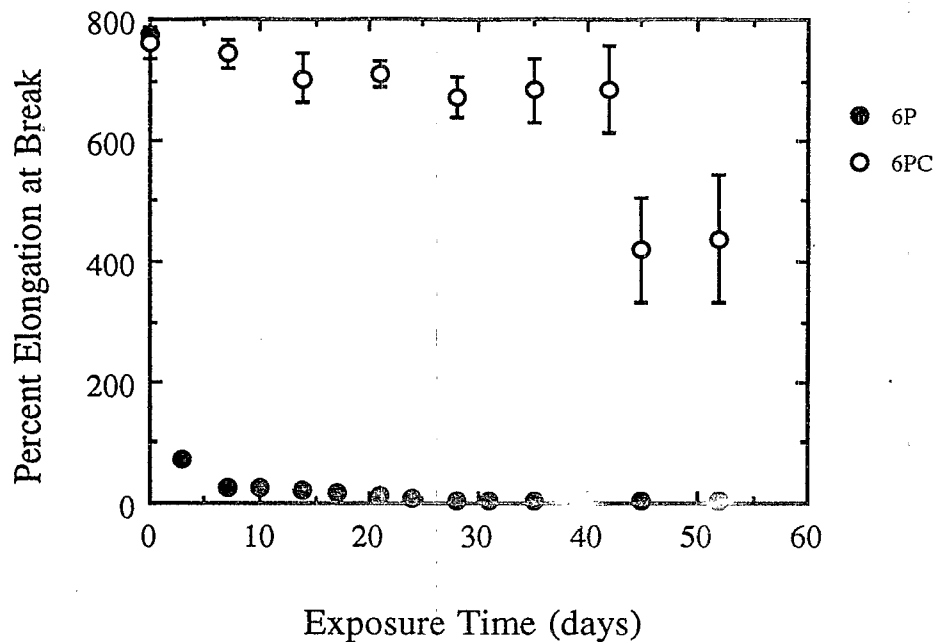
Figure 4.1.5 (e)   Elongation at break vs. exposure time. (6P - Seattle, WA - outdoor exposure).
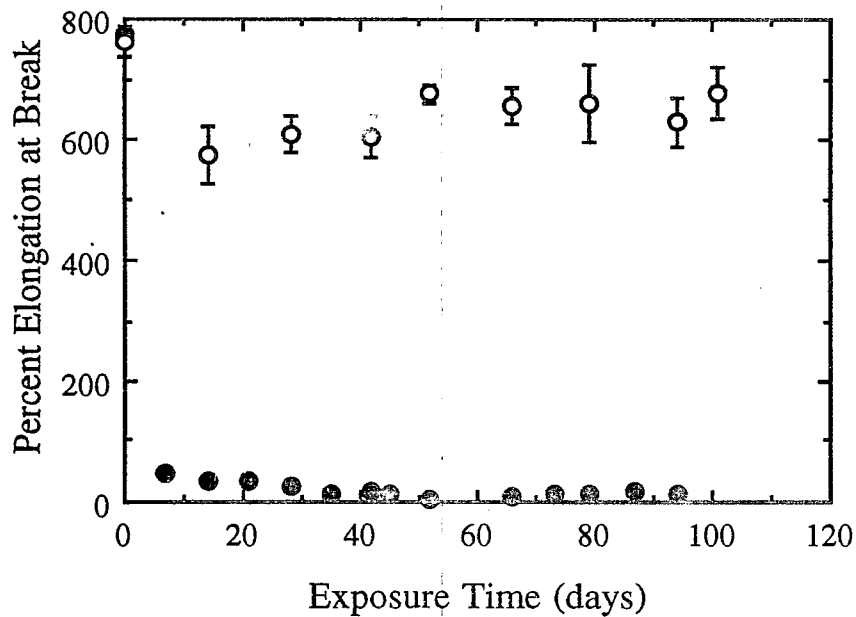
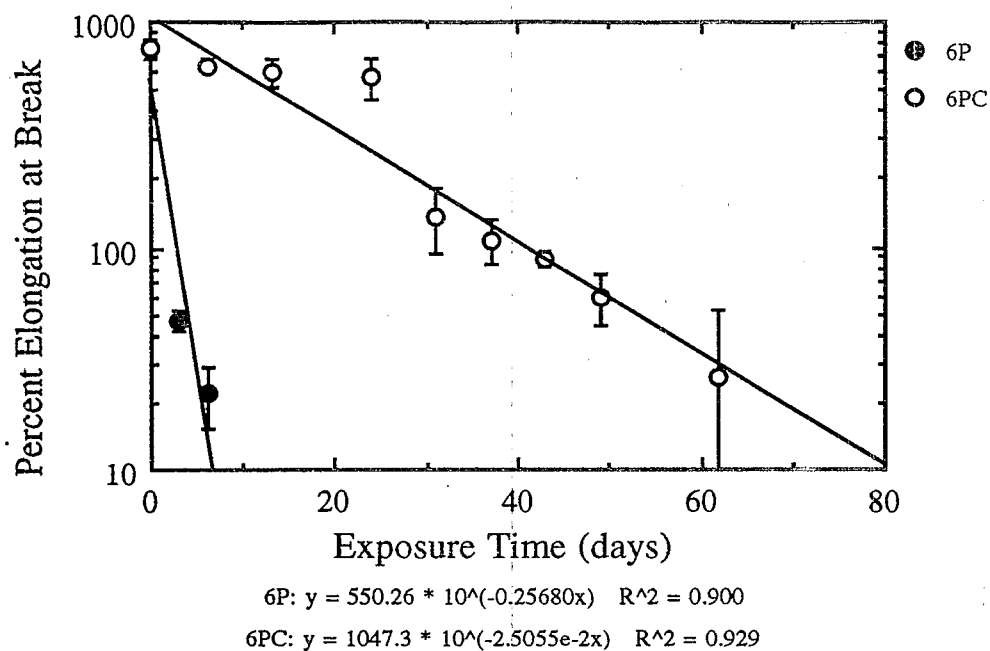Figure 4.1.5 (f)   Elongation at break vs. exposure time. (6P - Seattle, WA - marine floating exposure).
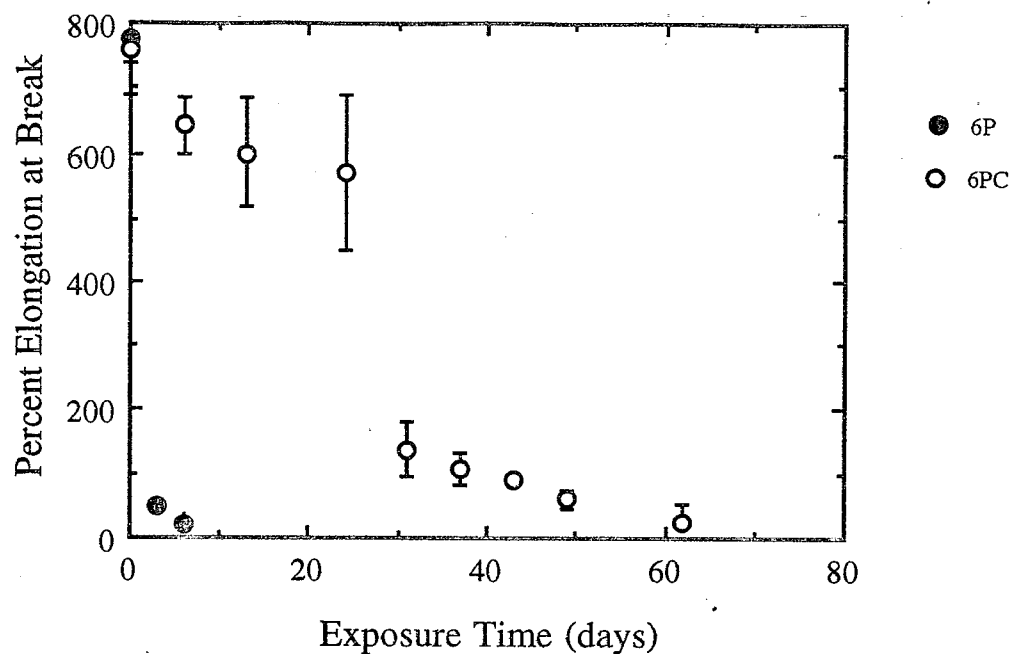
Figure 4.1.5 (g)   Elongation at break vs. exposure time. (6P - Wittmann, AZ - outdoor
exposure).
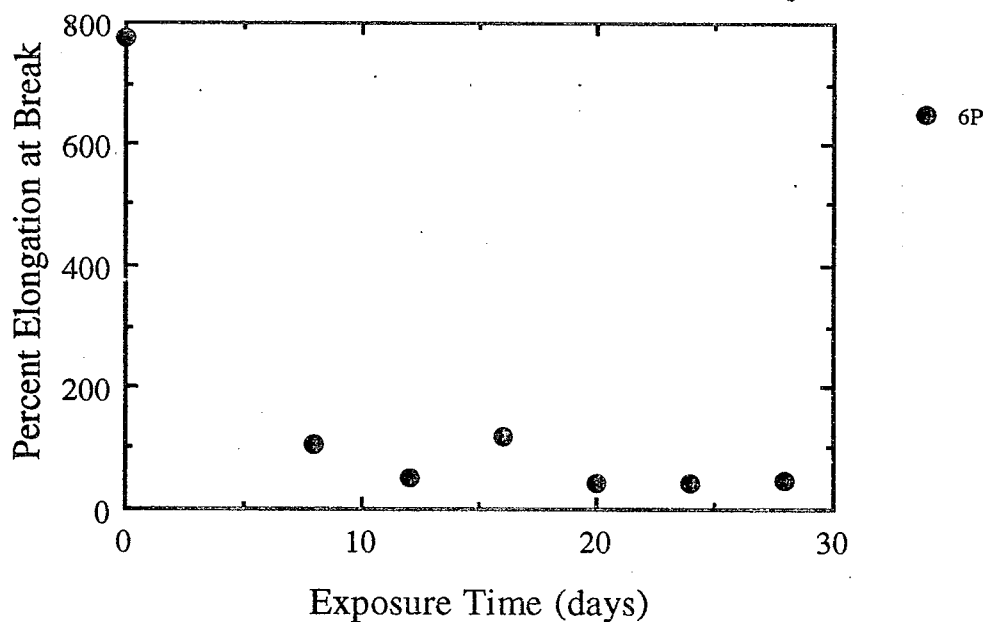
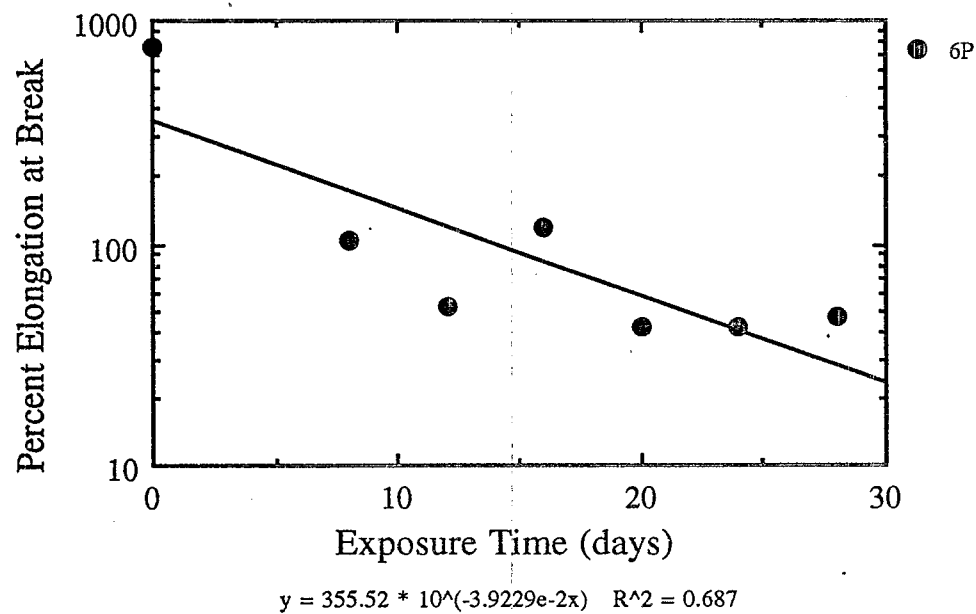Figure 4.1.5 (h)   Elongation at break vs. exposure time. (6P - Kerr Lake, VA - fresh water
floating exposure).
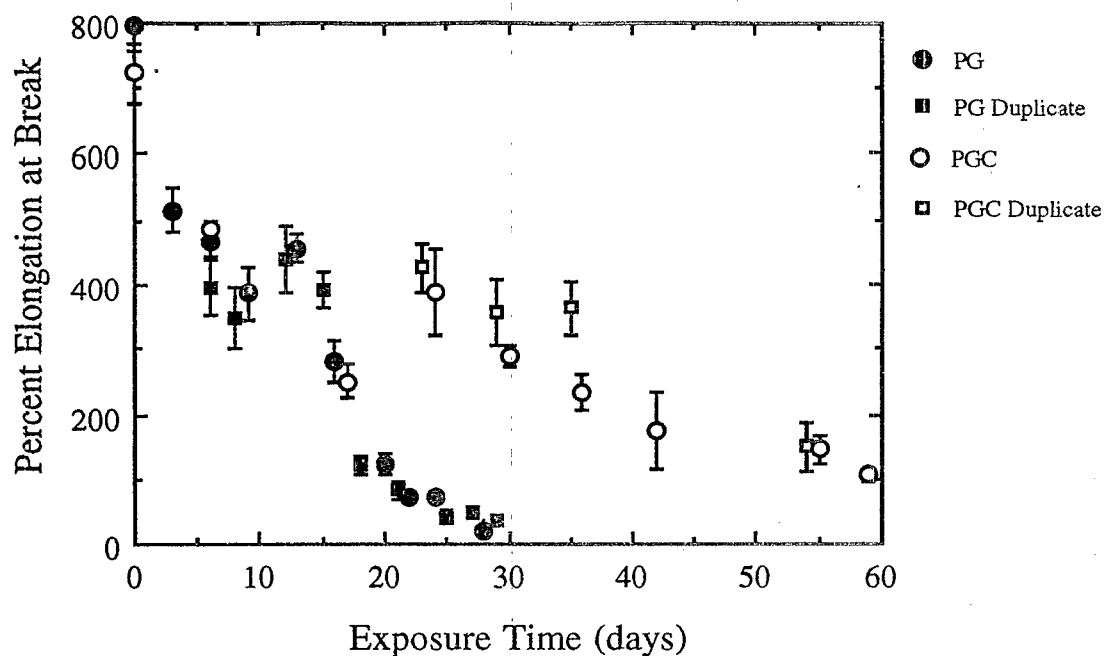
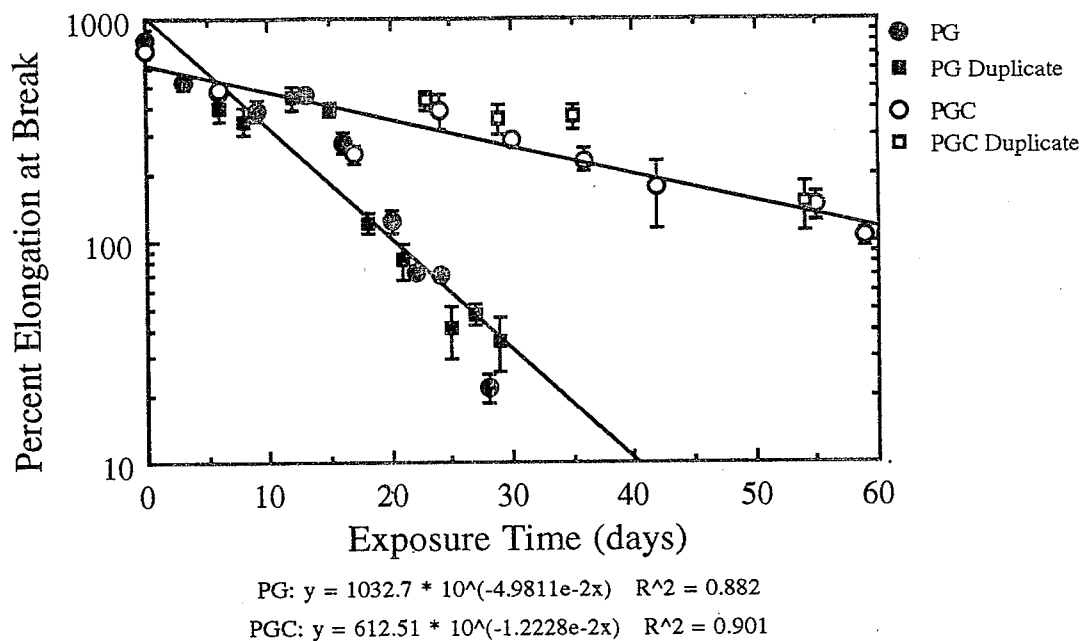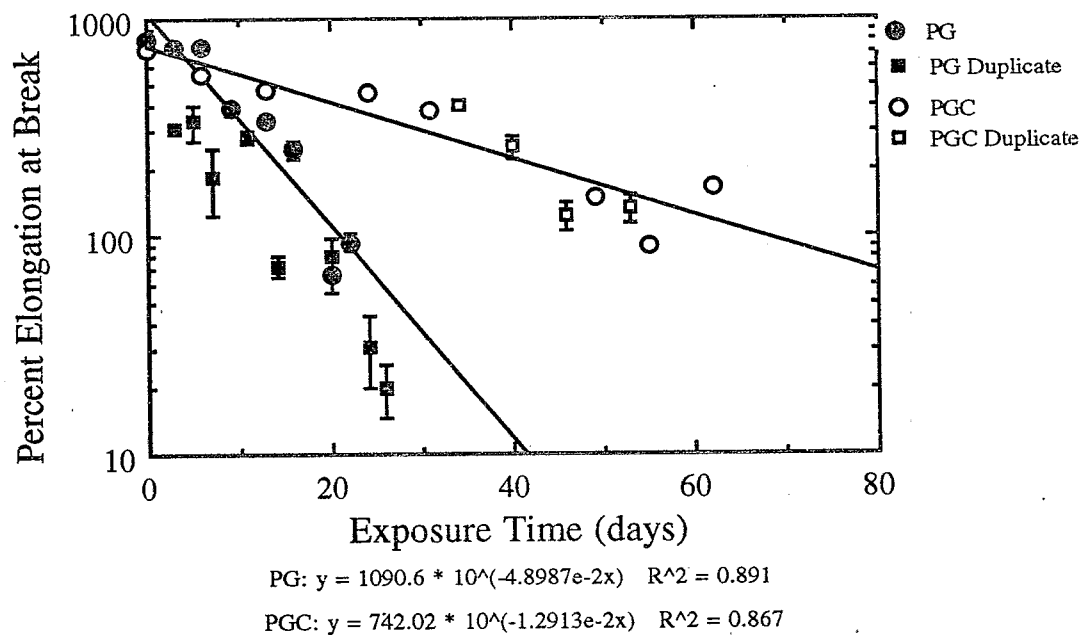Figure 4.1.5 (i)   Elongation at break vs. exposure time. (PG - Cedar Knolls, NJ - outdoor exposure).
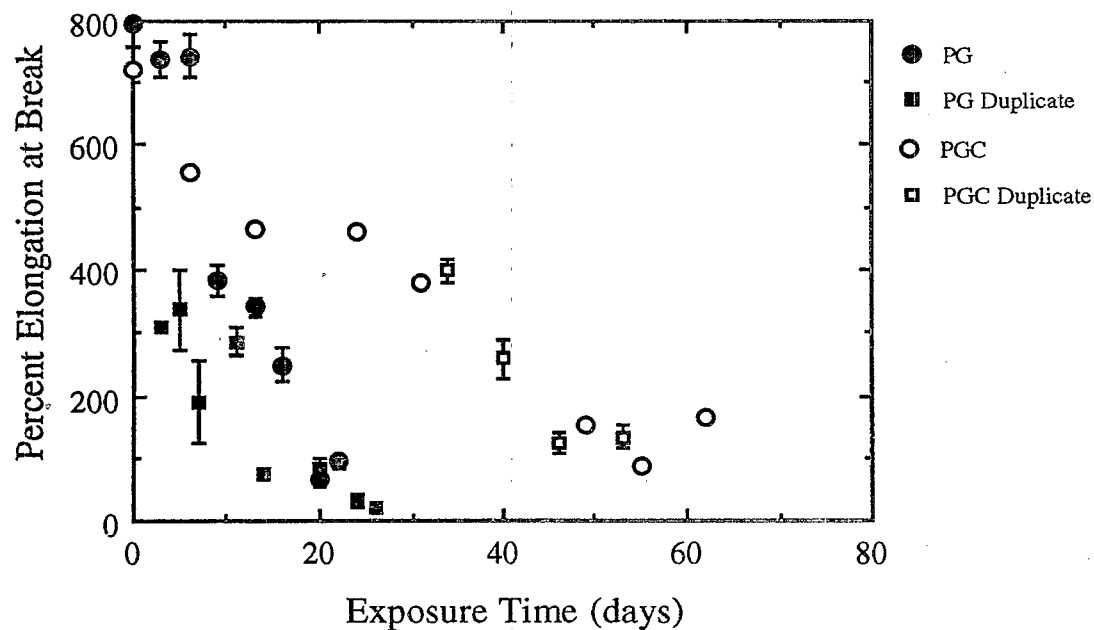
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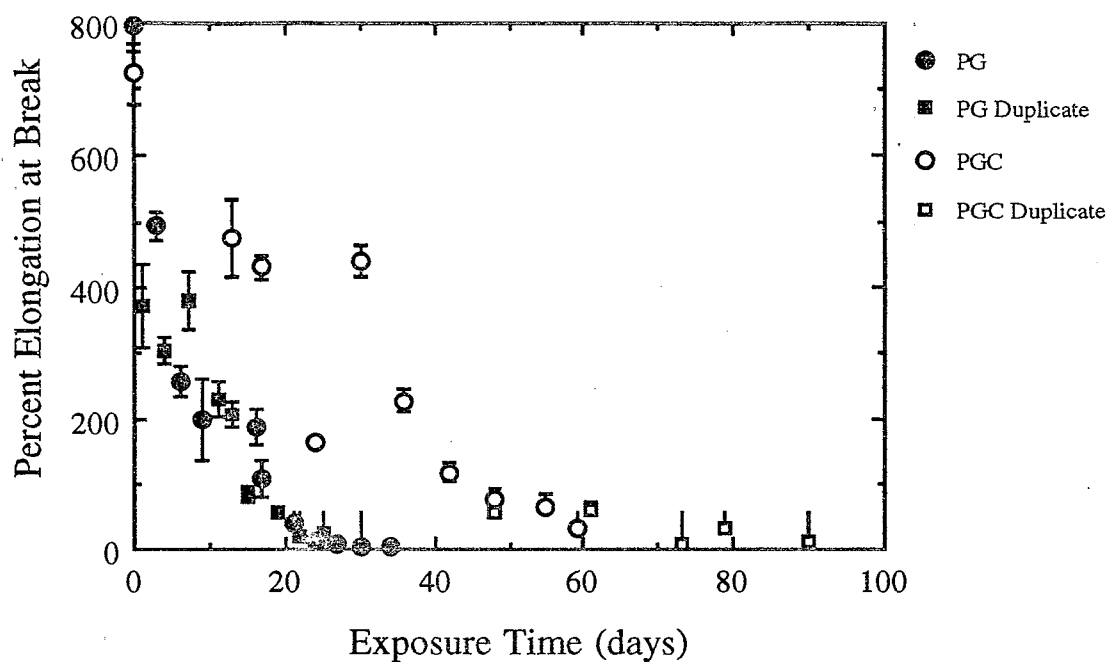
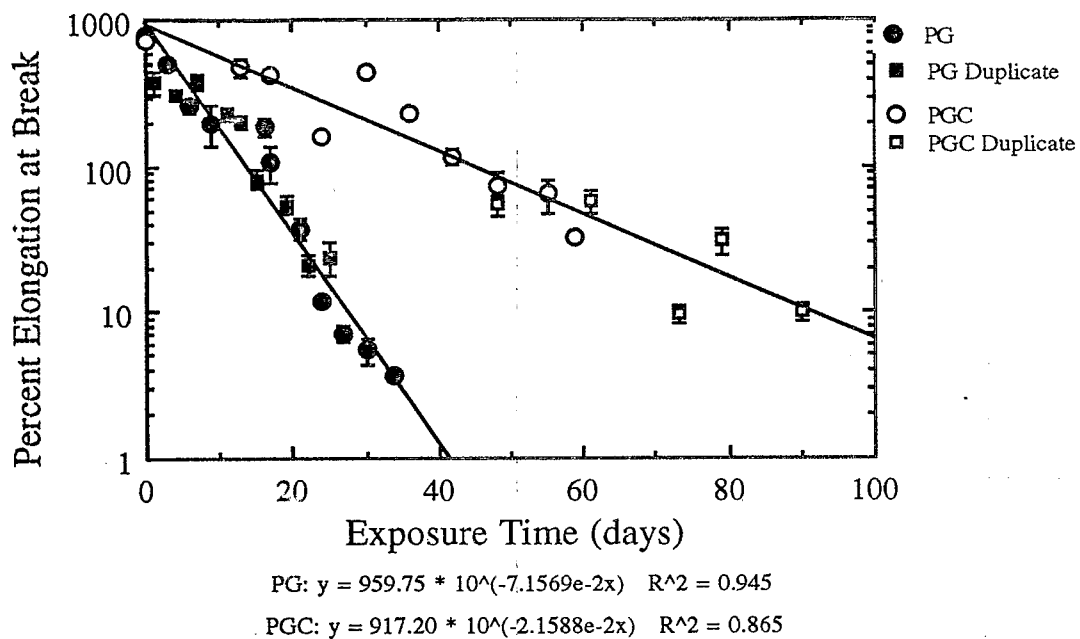Figure 4.1.5 (k)   Elongation at break vs. exposure time. (PG - Miami, FL - outdoor exposure).
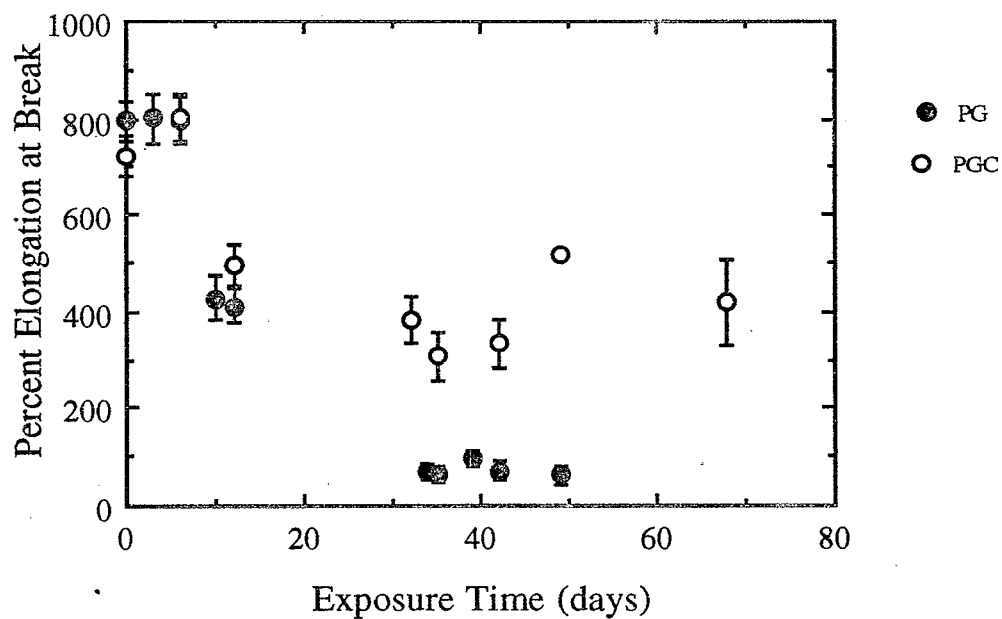
Figure 4.1.5 (l)   Elongation at break vs. exposure time. (PG - Miami, FL - marine floating exposure).
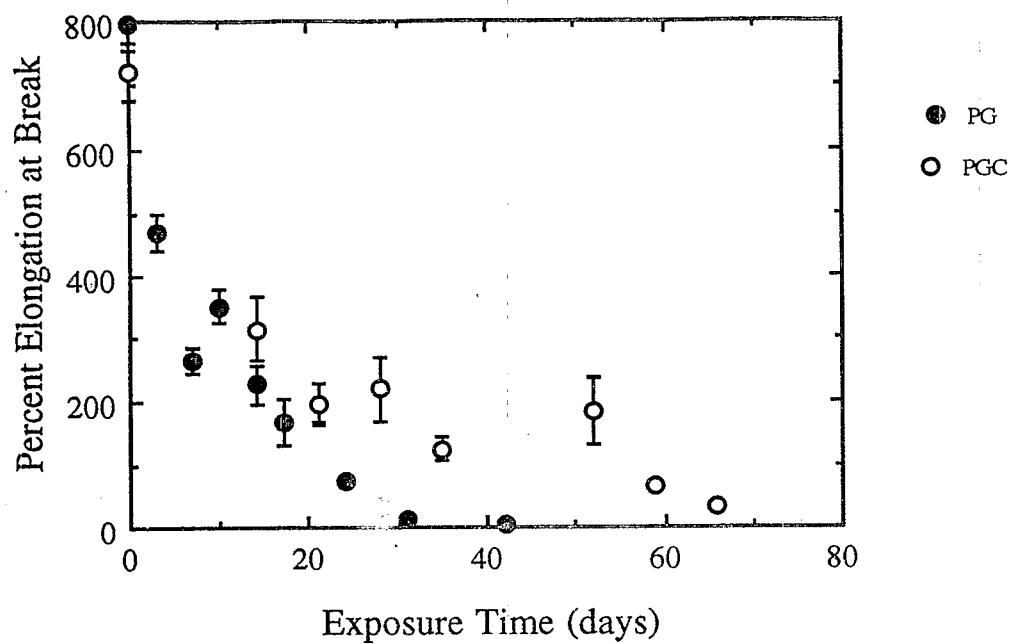
Figure 4.1.5 (m)   Elongation at break vs. exposure time. (PG - Seattle, WA - outdoor exposure).
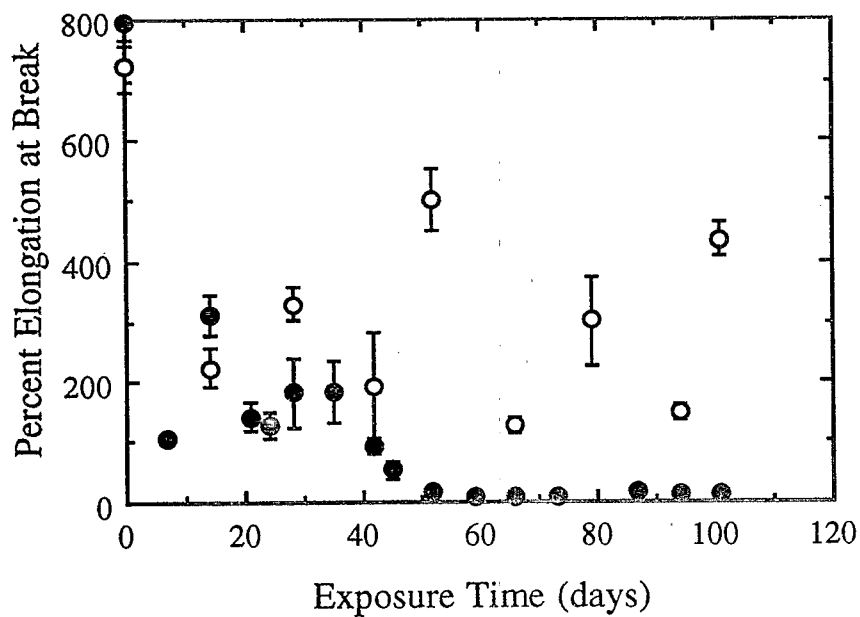
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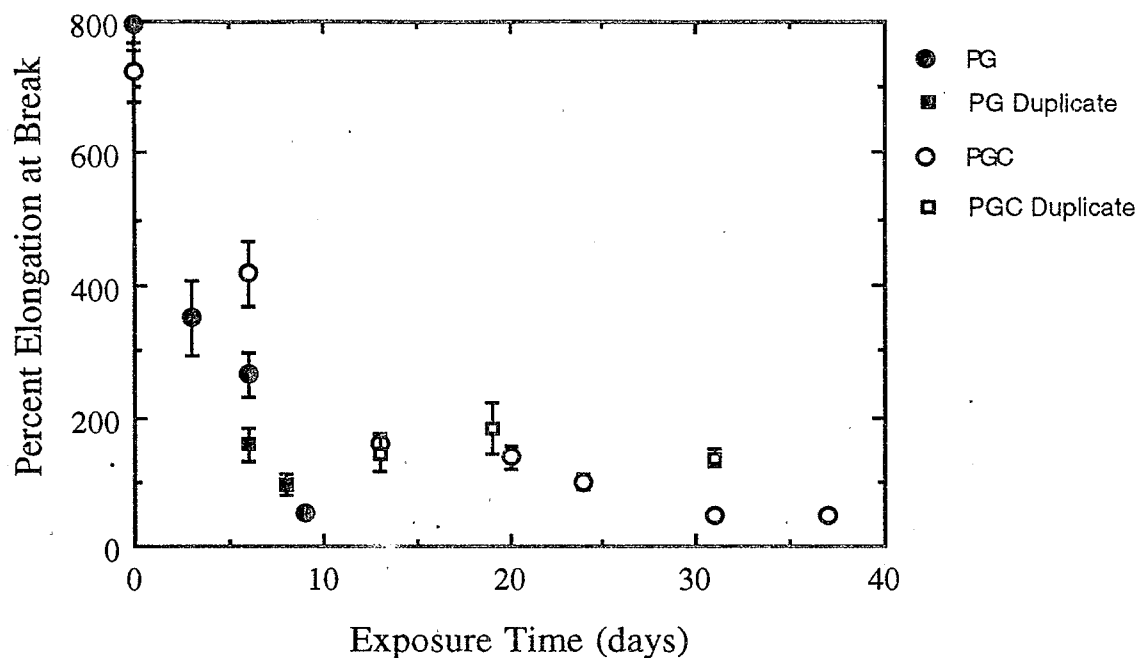
Figure 4.1.5 (o)   Elongation at break vs. exposure time. (PG - Wittmann, AZ - outdoor exposure).
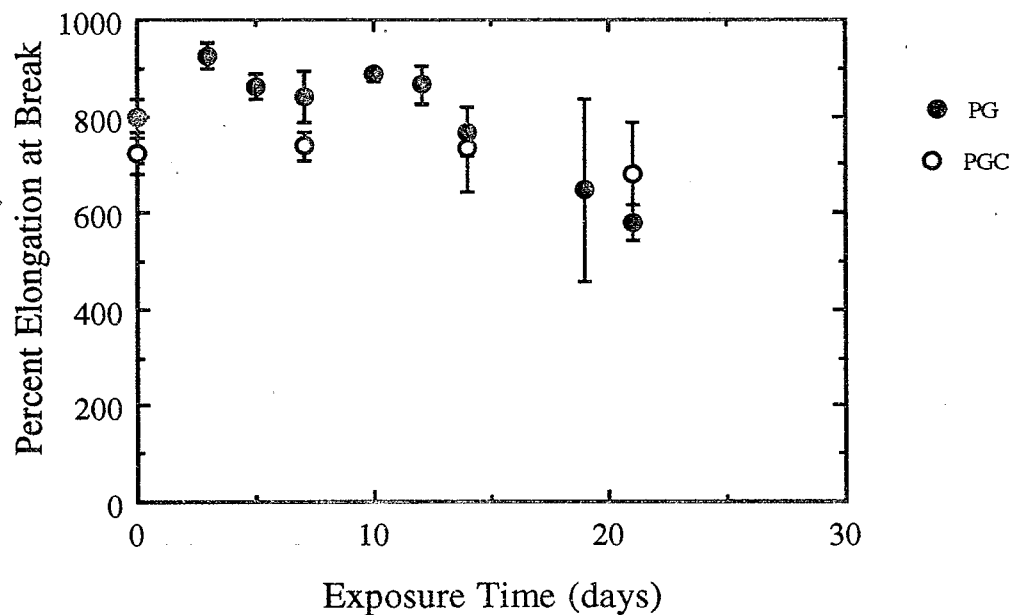
Figure 4.1.5 (p)   Elongation at break vs. exposure time. (PG - Kerr Lake, VA - fresh water floating exposure).

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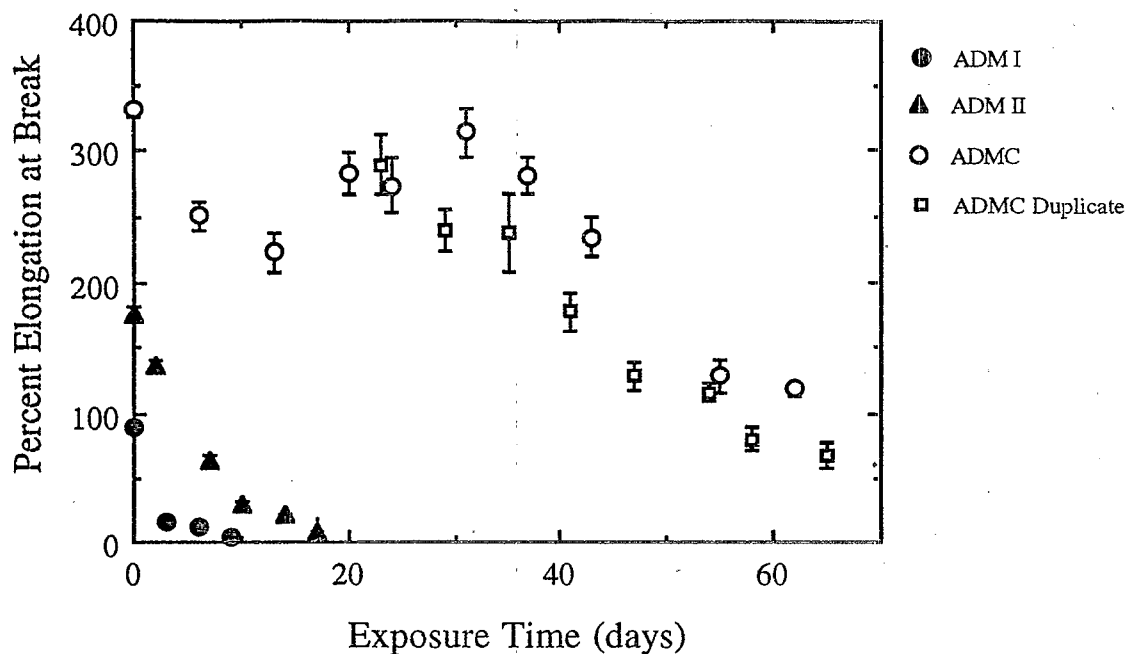
Figure 4.1.5 (q)　Elongation at break vs. exposure time. (ADM - Cedar Knolls, NJ - outdoor exposure).
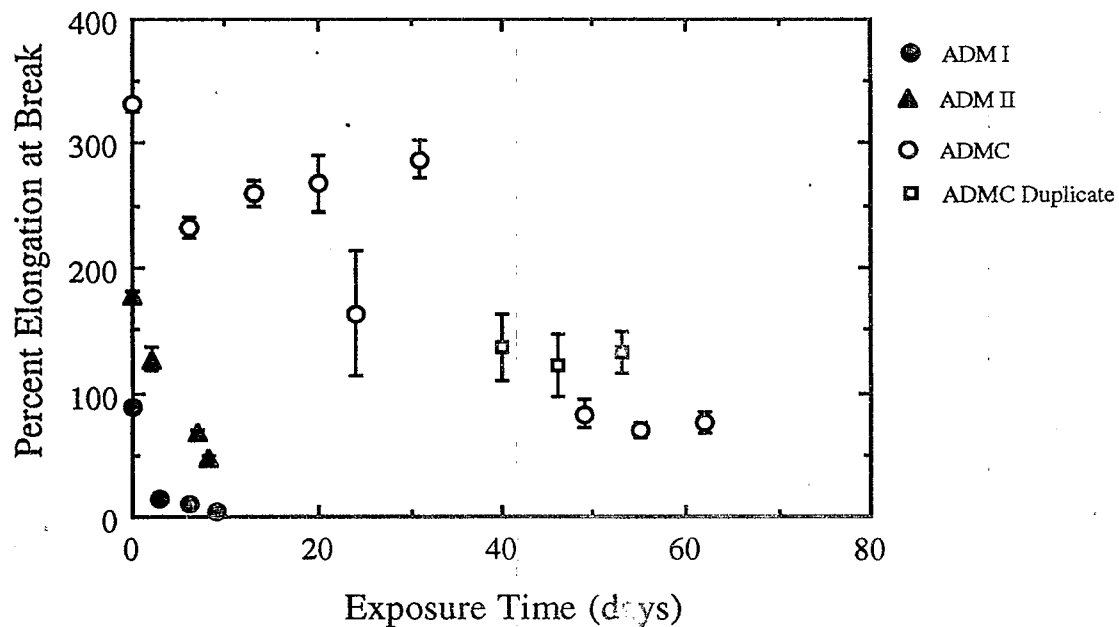
Figure 4.1.5 (r)　Elongation at break vs. exposure time. (ADM - Chicago, IL - outdoor exposure).
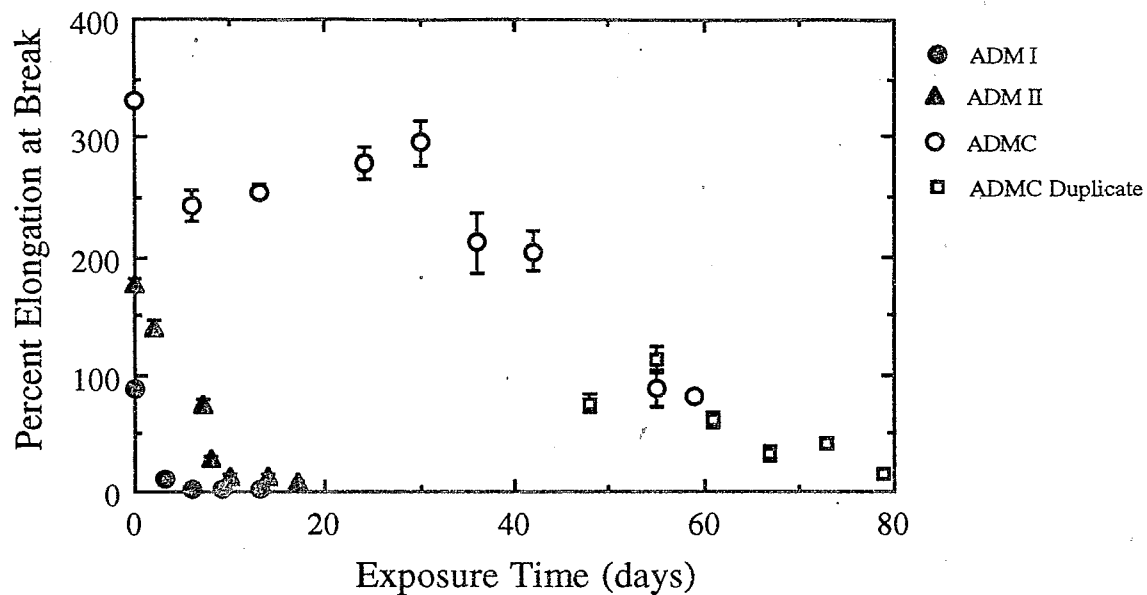
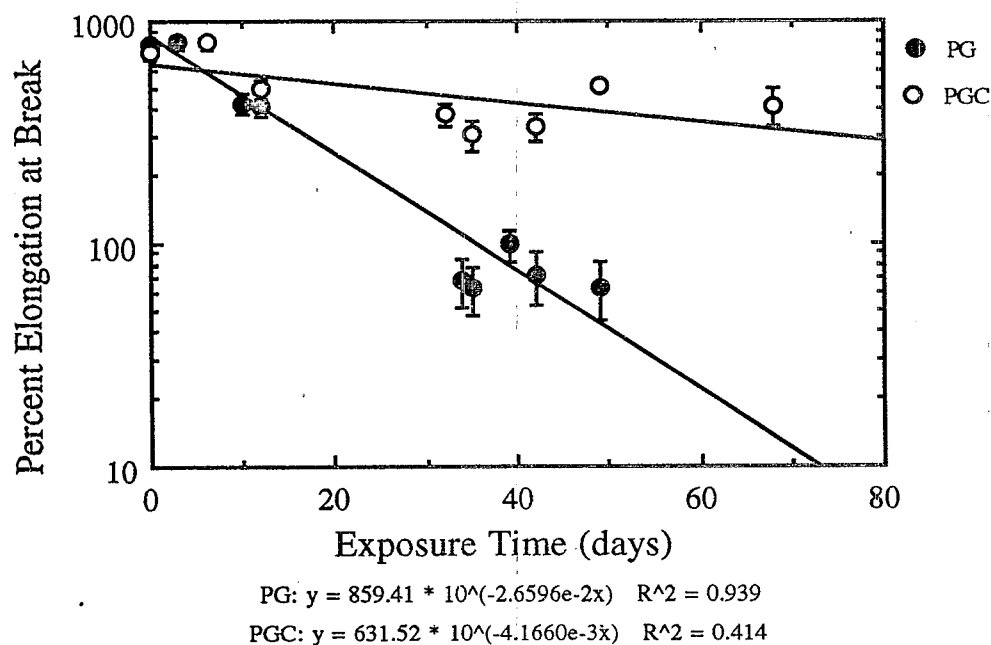Figure 4.1.5 (s)   Elongation at break vs. exposure time. (ADM - Miami, FL - outdoor exposure).
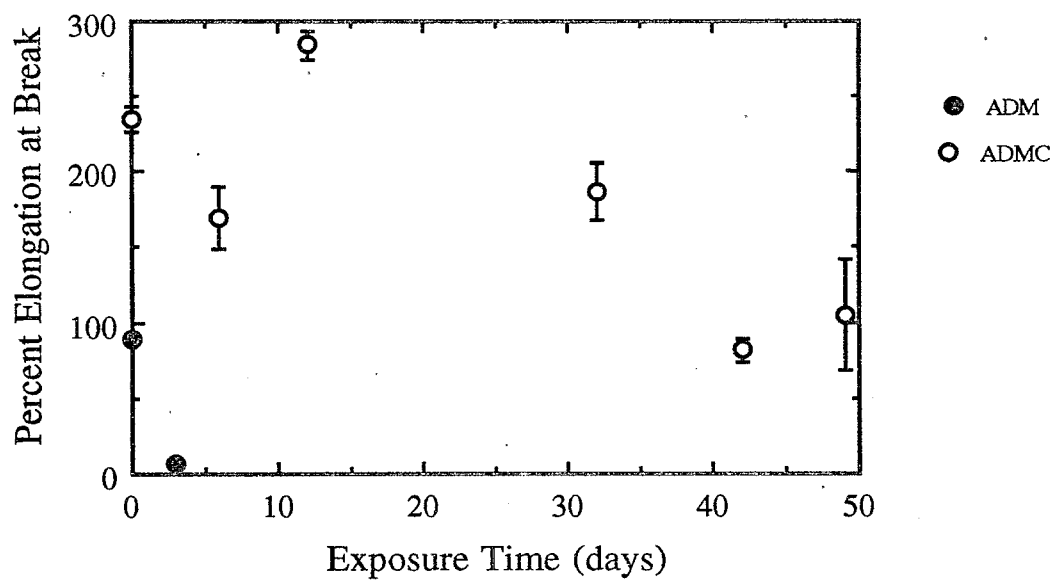
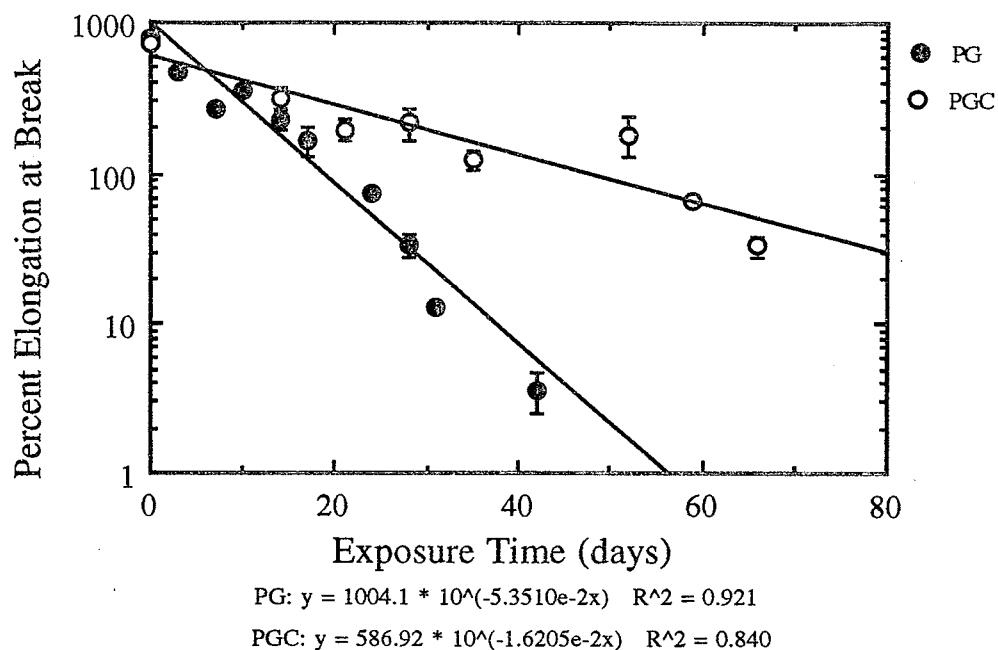Figure 4.1.5 (t)   Elongation at break vs. exposure time. (ADM - Miami, FL - marine floating exposure).
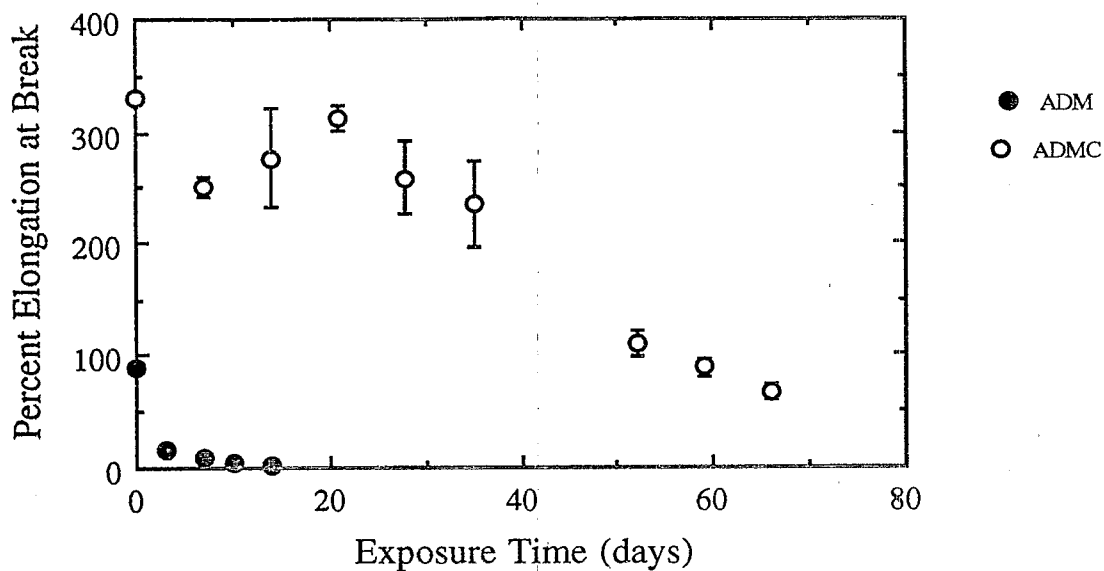
Figure 4.1.5 (u)   Elongation at break vs. exposure time. (ADM - Seattle, WA - outdoor exposure).
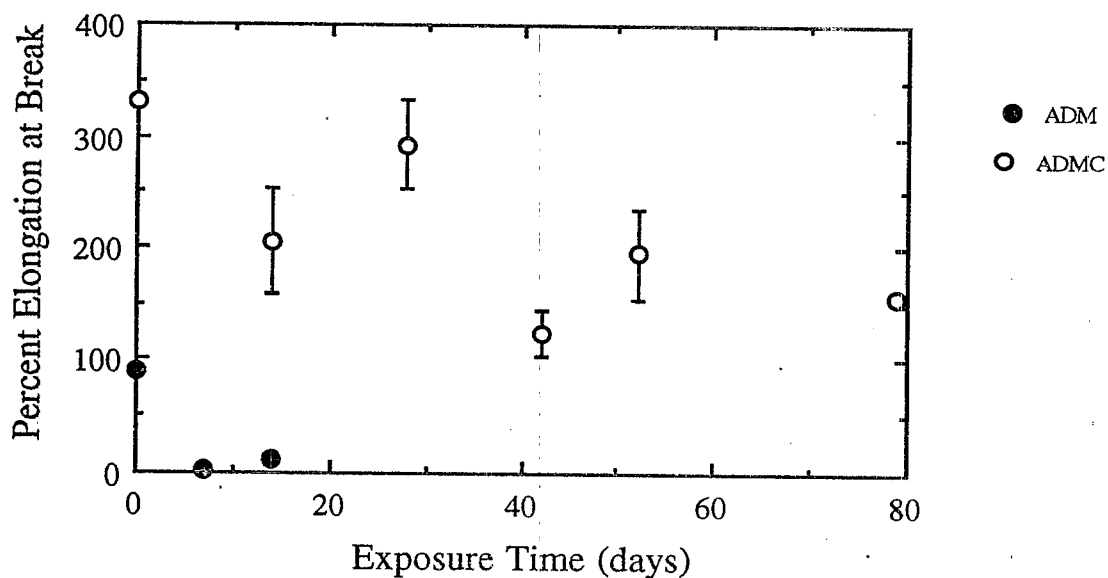
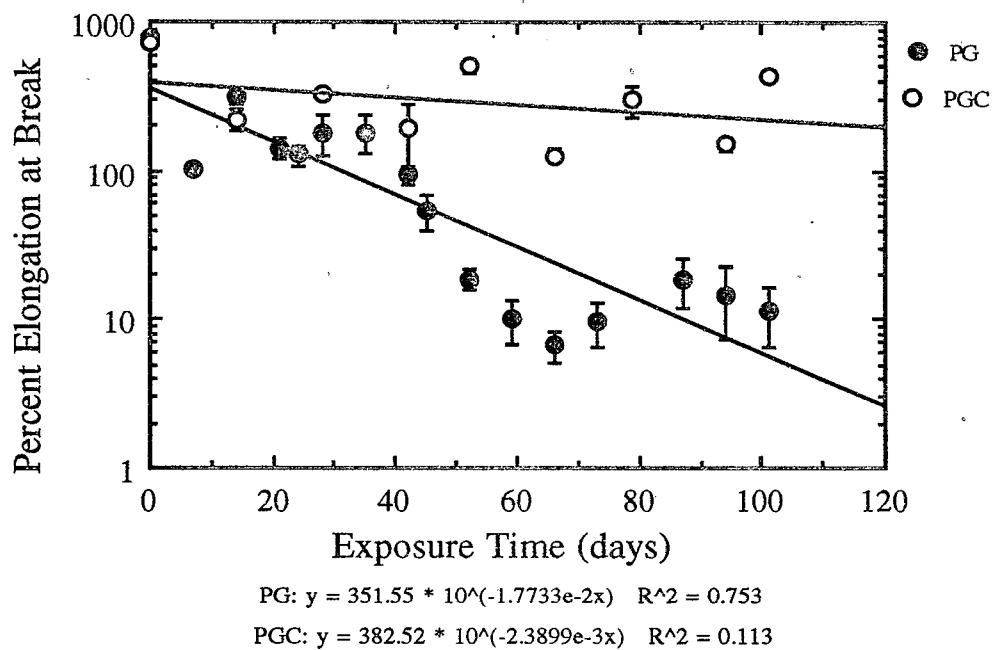Figure 4.1.5 (v)   Elongation at break vs. exposure time. (ADM - Seattle, WA - marine floating exposure).
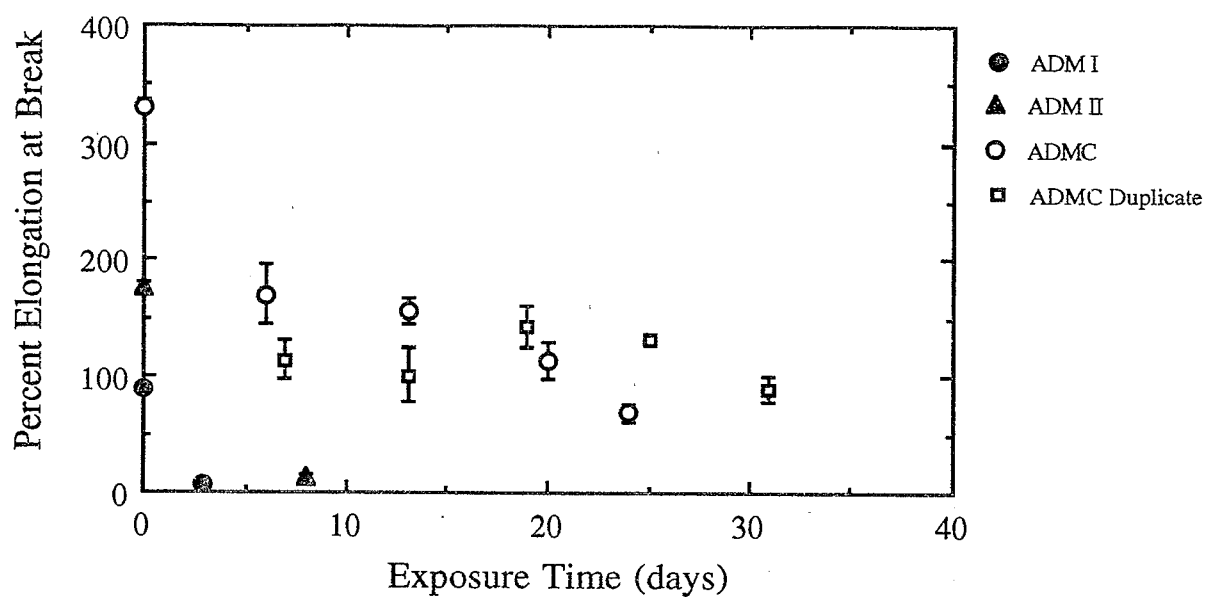
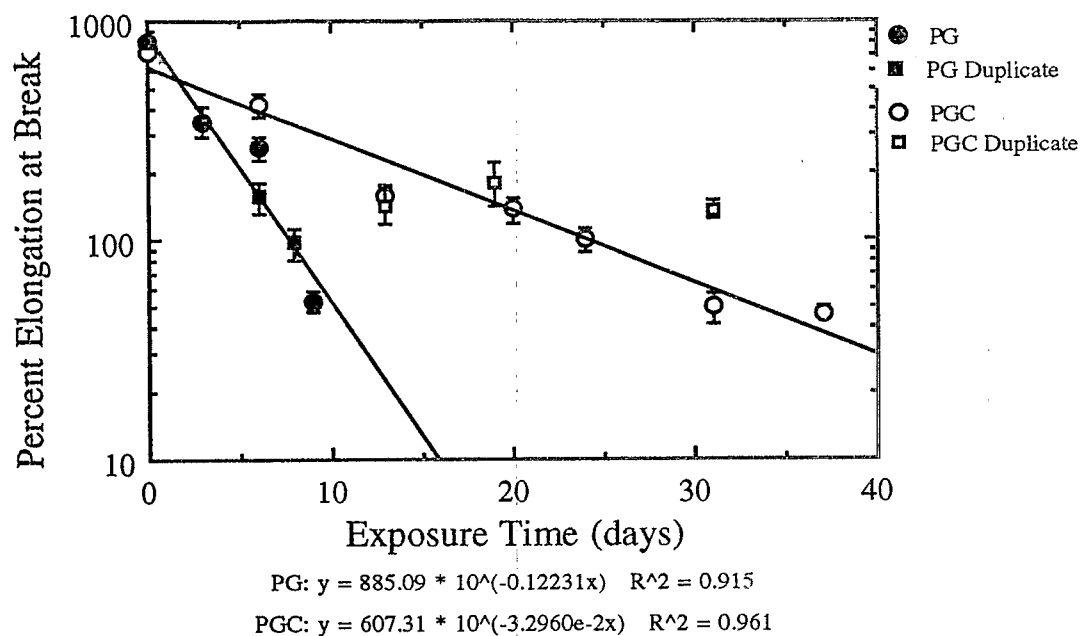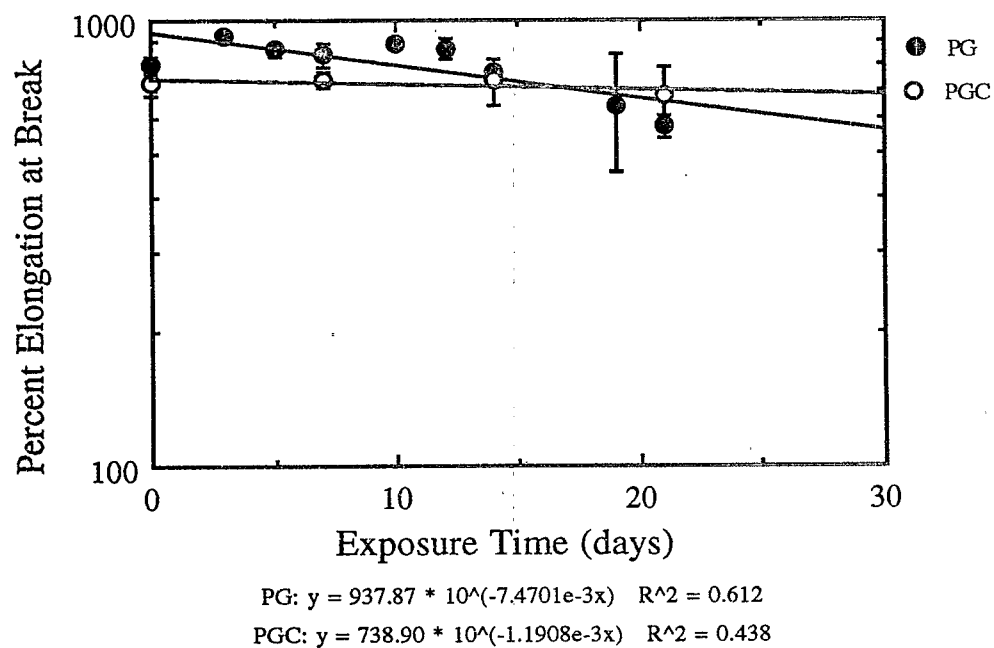Figure 4.1.5 (w)   Elongation at break vs. exposure time. (ADM - Wittmann, AZ - outdoor exposure).
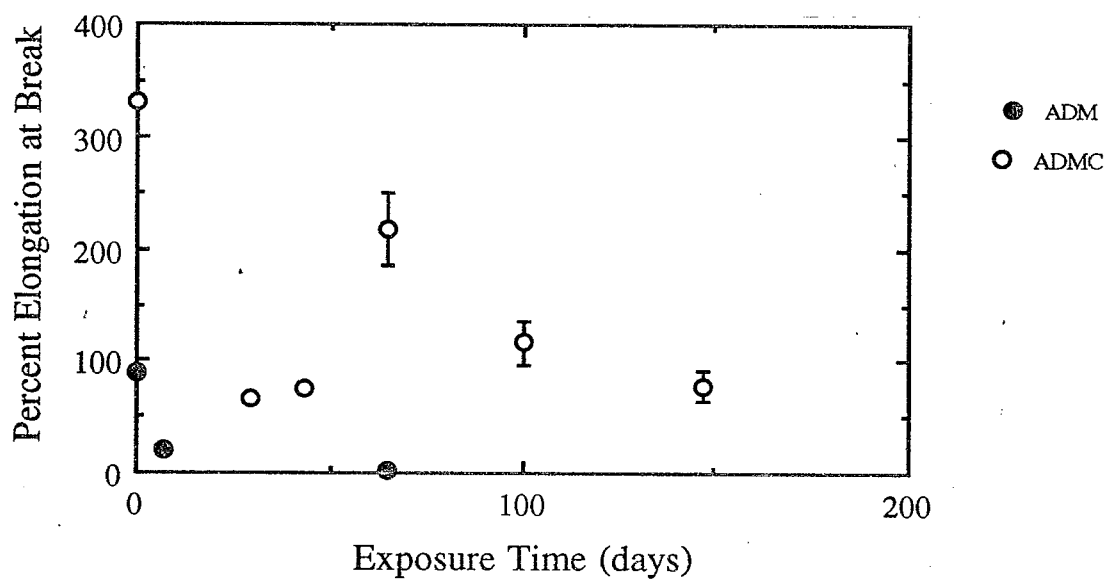
Figure 4.1.5 (x)   Elongation at break vs. exposure time. (ADM - Miami, FL - marine sediment exposure).
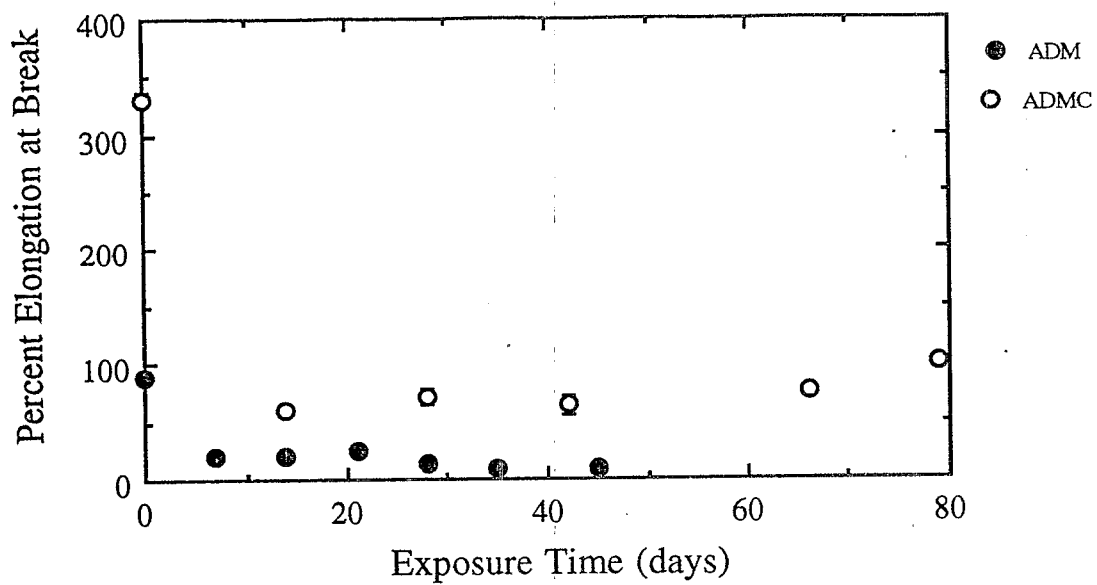
Figure 4.1.5 (y)   Elongation at break vs. exposure time. (ADM - Seattle, WA - marine sediment exposure).
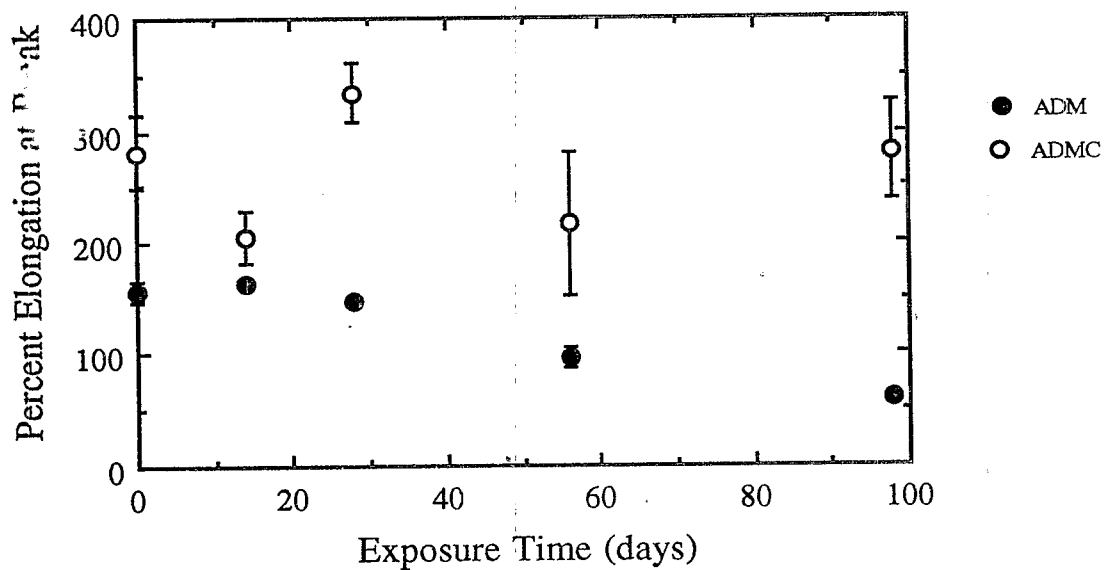
Figure 4.1.5 (z)   Elongation at break vs. exposure time. (ADM - Kerr Lake, VA - fresh water floating).
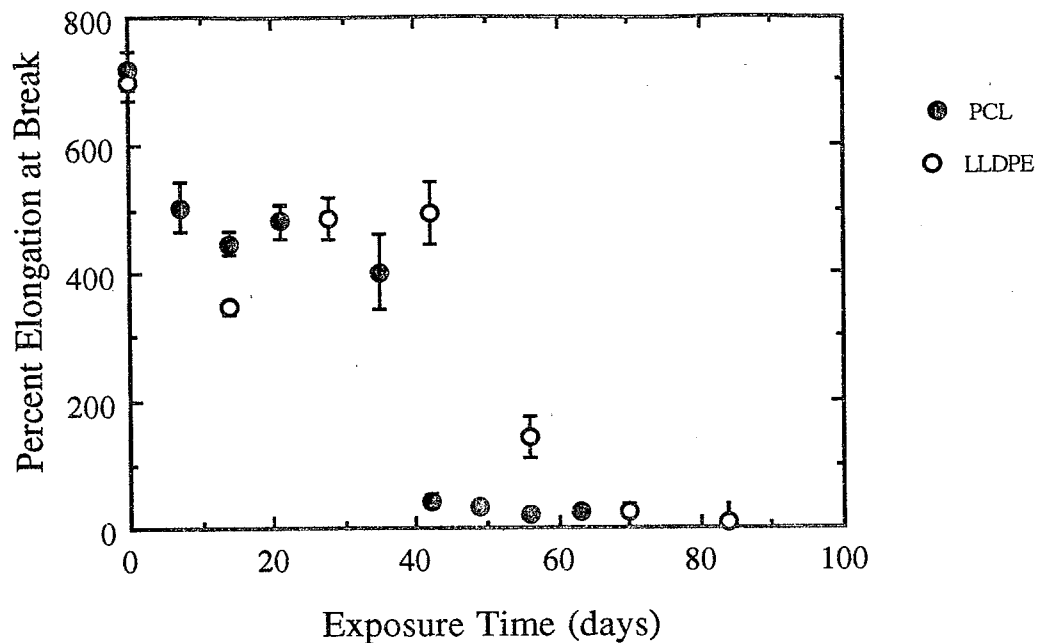
Figure 4.1.5 (aa)   Elongation at break vs. exposure time. (PCL - Miami, FL - outdoor exposure).
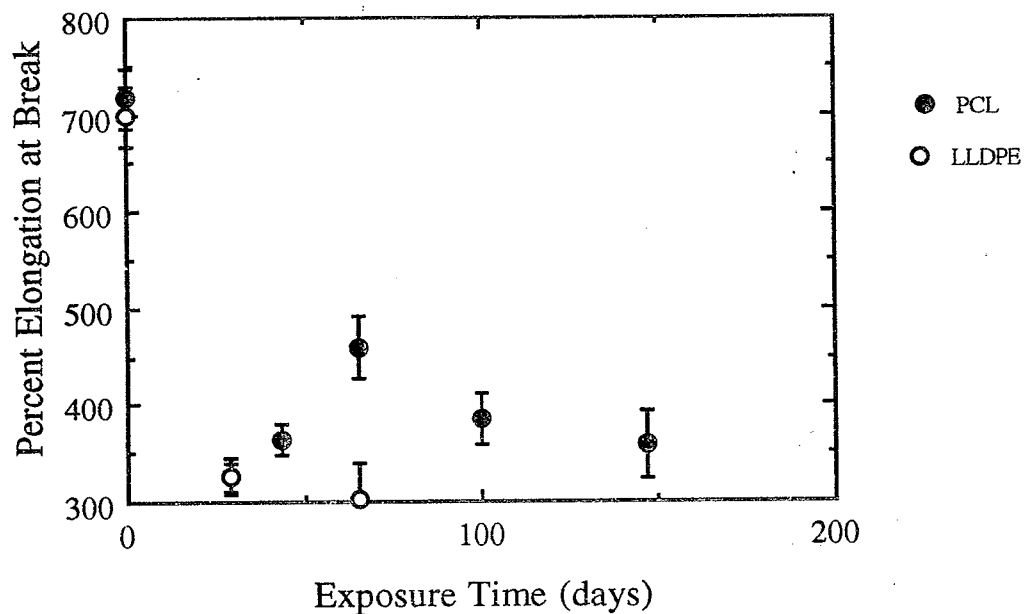
Figure 4.1.5 (bb)   Elongation at break vs. exposure time. (PCL - Miami, FL - marine sediment exposure).
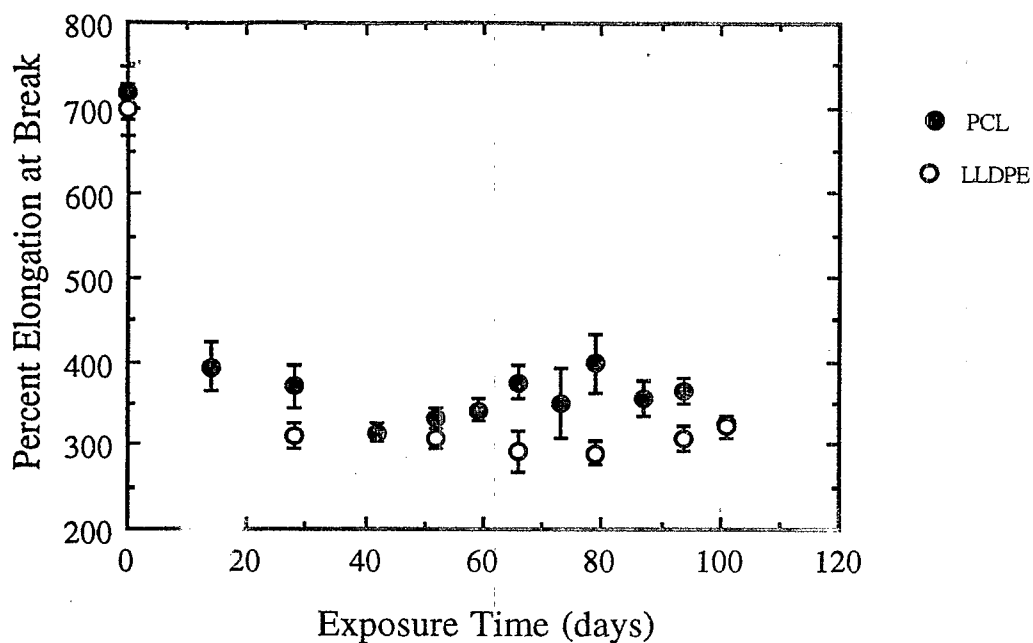
Figure 4.1.5 (cc)   Elongation at break vs. exposure time. (PCL - Seattle, WA - marine sediment exposure).
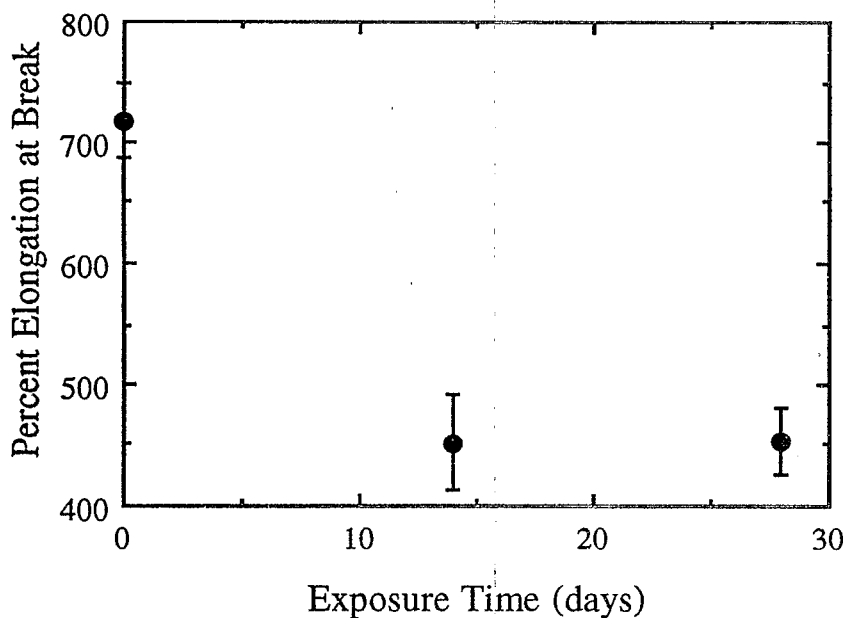
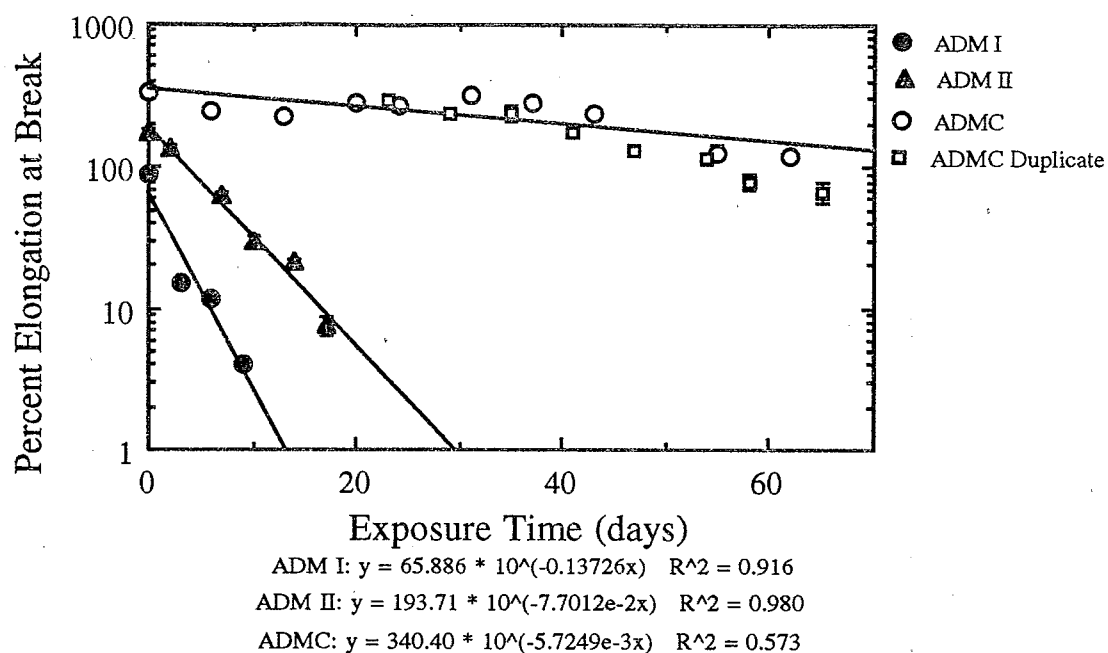Figure 4.1.5 (dd)   Elongation at break vs. exposure time. (PCL - Kerr Lake, VA - fresh water floating exposure).
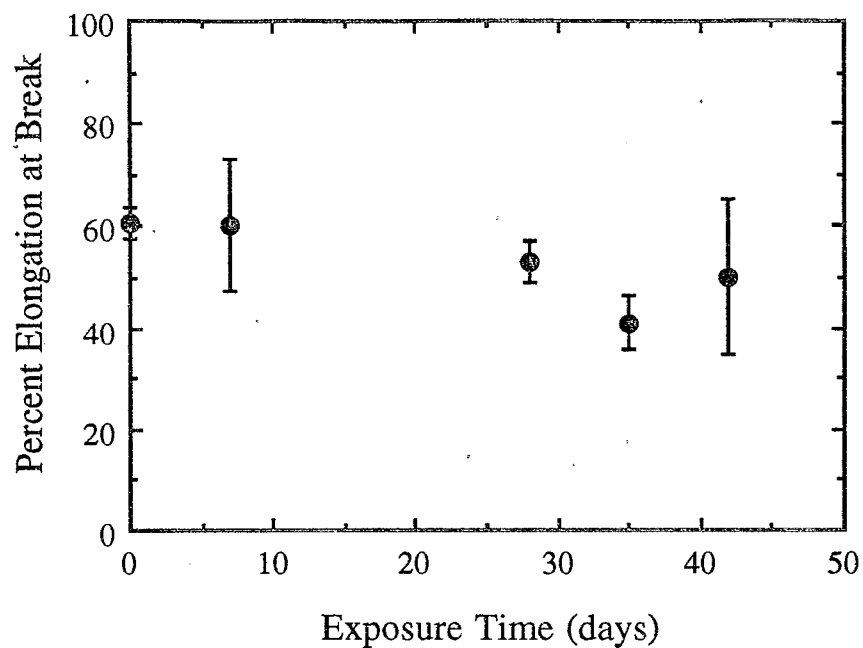
Figure 4.1.5 (ee)   Elongation at break vs. exposure time.   (BP - Miami, FL - outdoor exposure).
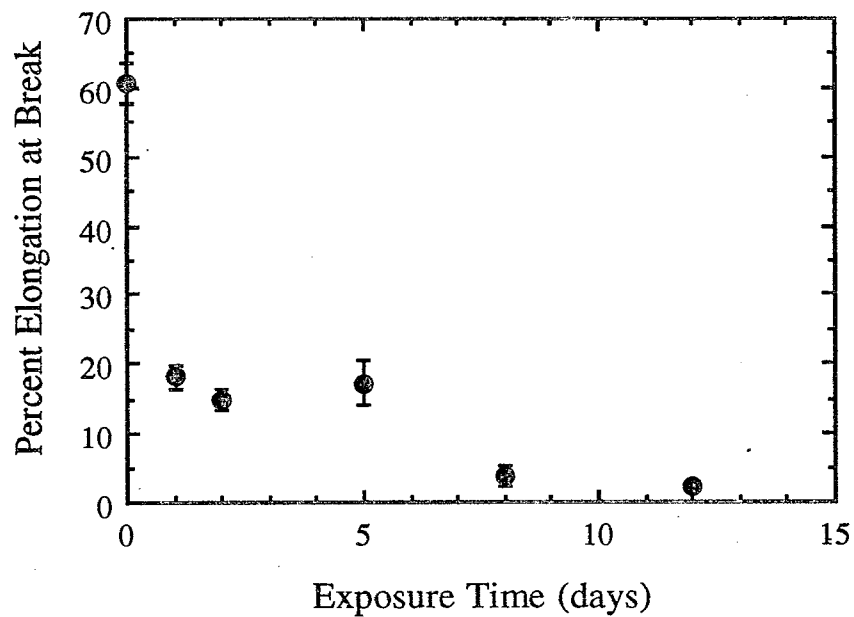
Figure 4.1.5 (ff)   Elongation at break vs. exposure time. (BP - Miami, FL - marine sediment exposure).
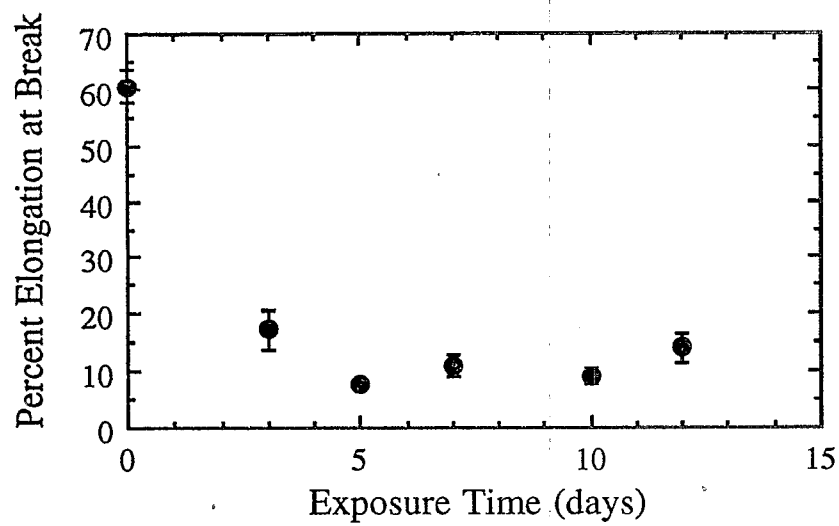
Figure 4.1.5 (gg)   Elongation at break vs. exposure time. (BP - Kerr Lake, VA - fresh water sed̃ nt exposure).

6P: y = 139.21 * 10^(-5.2012e-2x)   R^2 = 0.826

6PC: y = 708.26 * 10^(-9.5306e-4x)   R^2 = 0.367
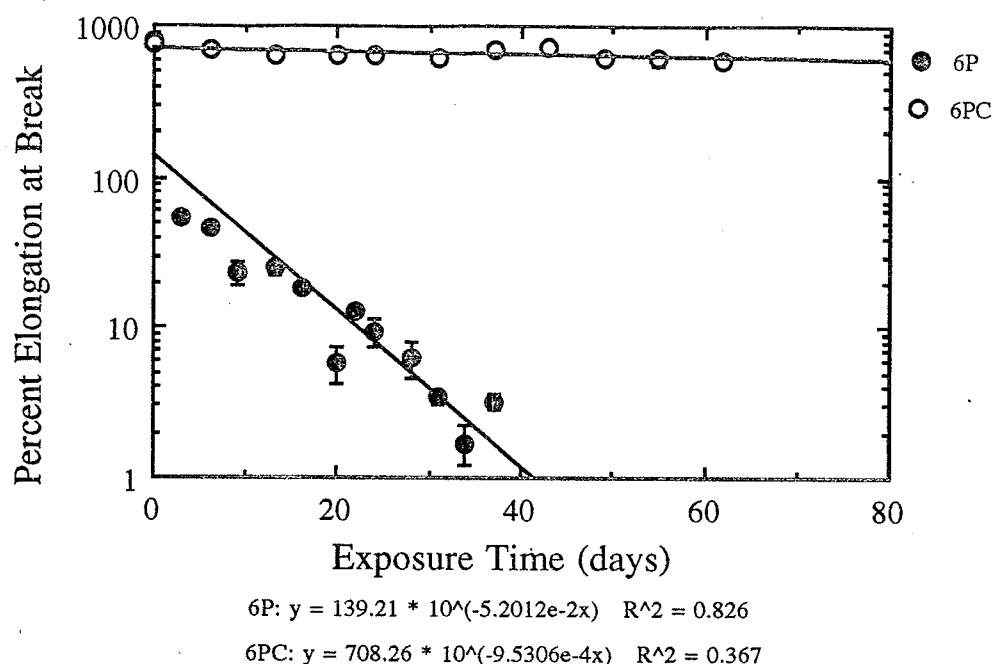
Figure 4.1.6 (a)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P -Cedar Knolls, NJ - outdoor exposure).

6P: y = 246.43 * 10^(-8.7294e-2x)   R^2 = 0.886

6PC: y = 647.89 * 10^(-4.3002e-4x)   R^2 = 0.056
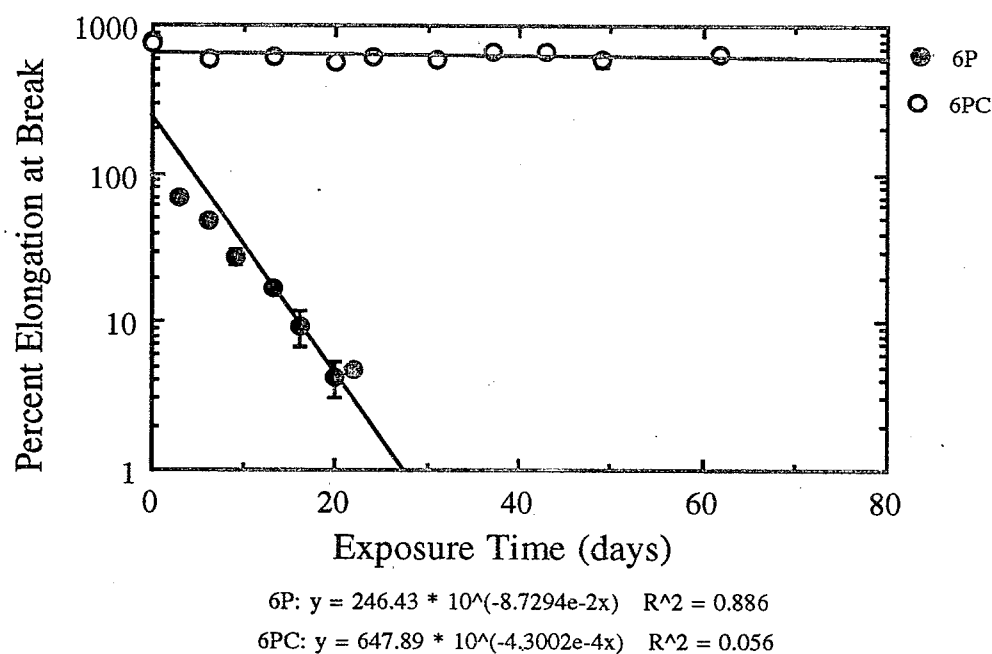
Figure 4.1.6 (b)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Chicago, IL - outdoor exposure).
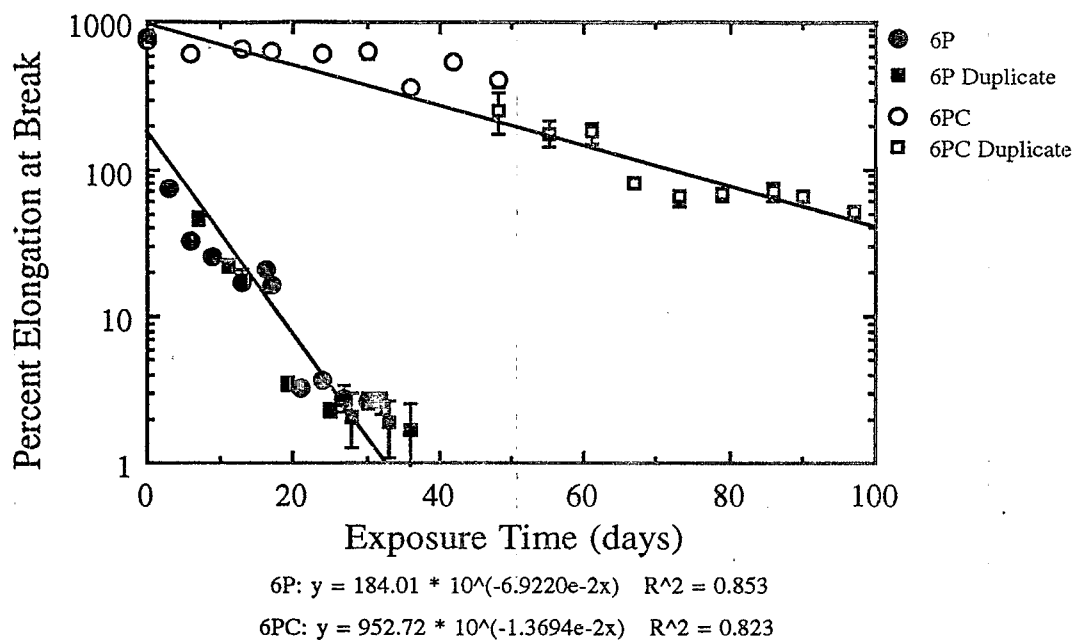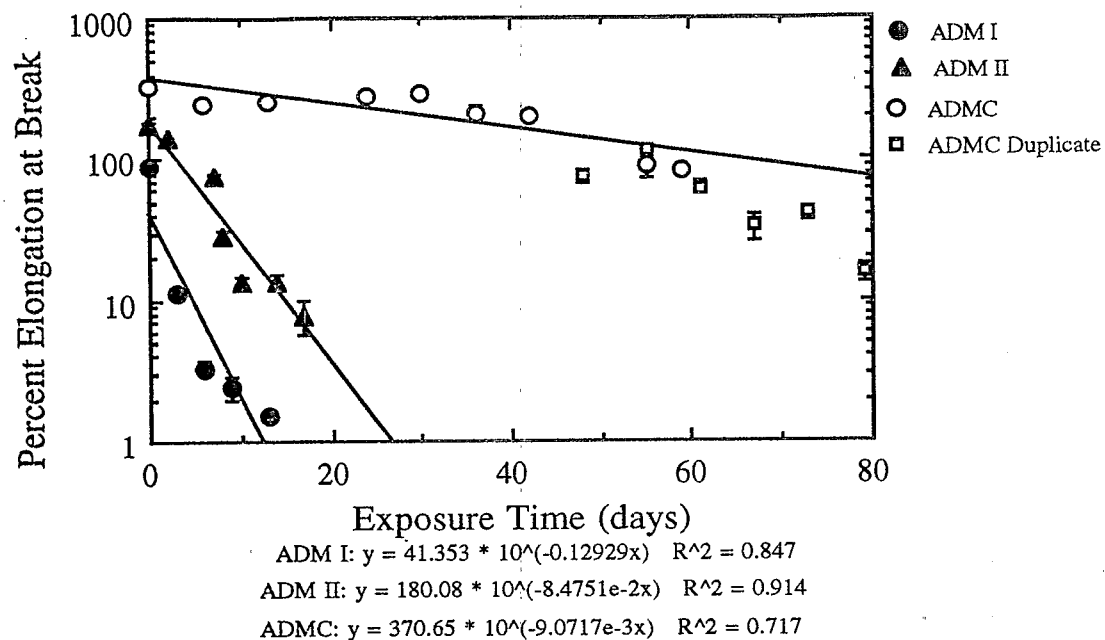
Figure 4.1.6 (c)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Miami, FL - outdoor exposure).
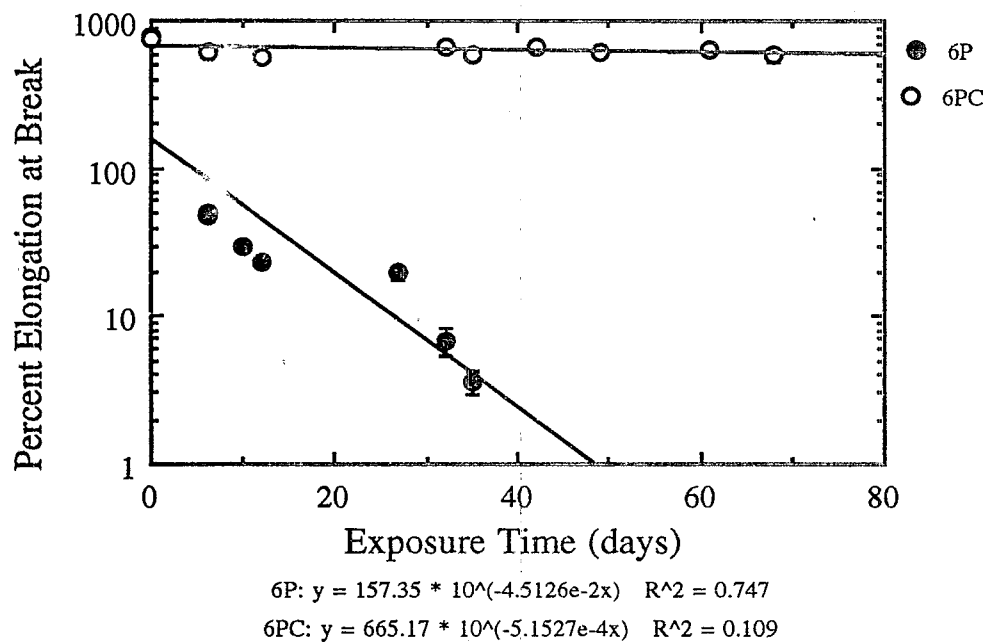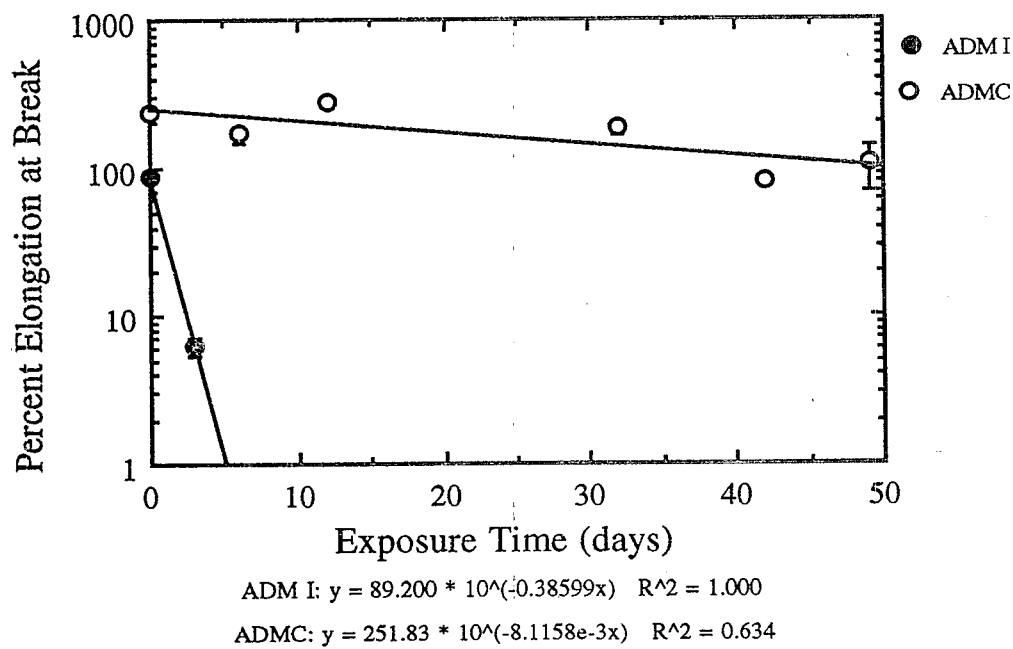

Figure 4.1.6 (d)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Miami, FL - marine floating exposure).
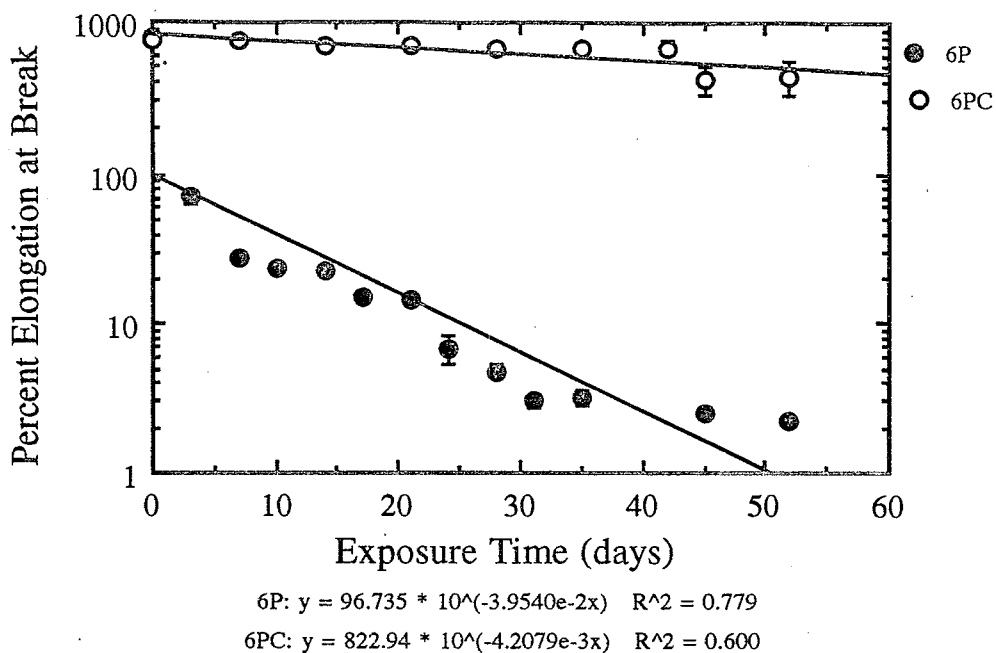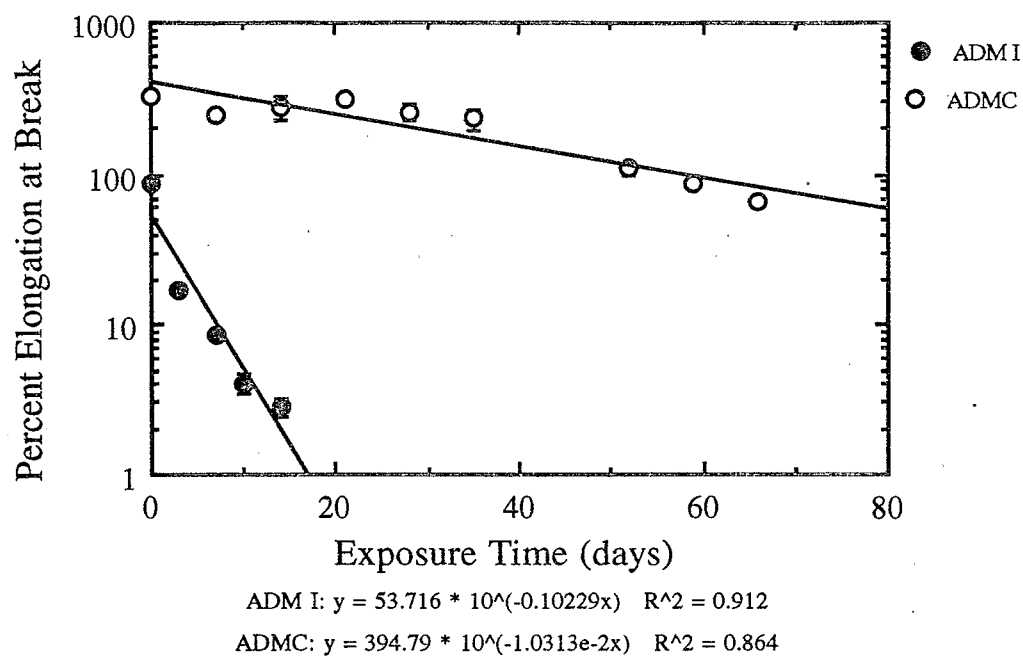
Figure 4.1.6 (e)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Seattle, WA - outdoor exposure).
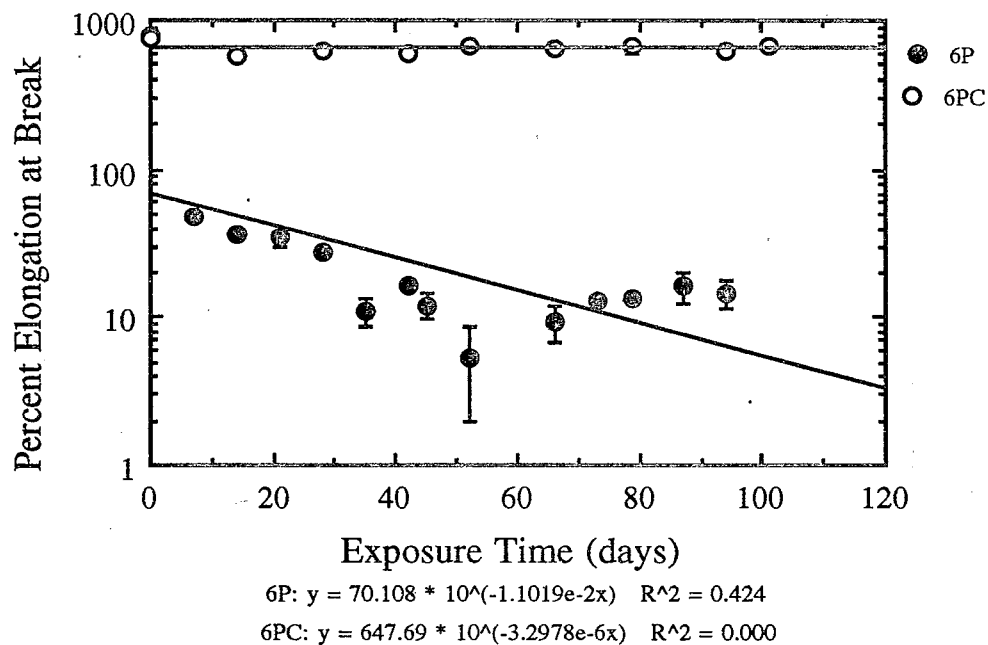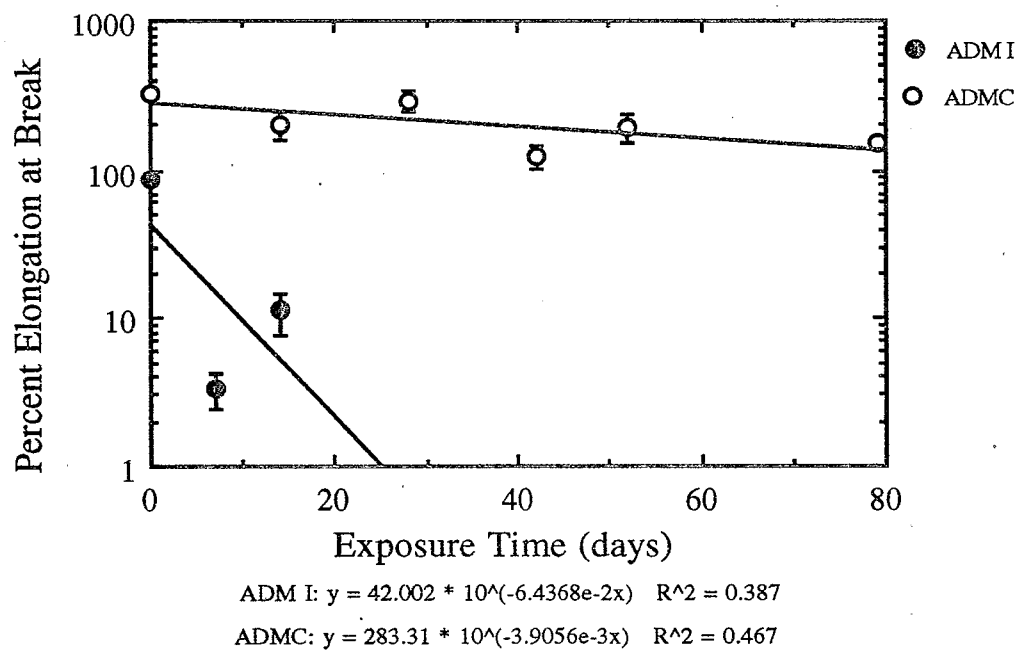

Figure 4.1.6 (f)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Seattle, WA - marine floating exposure).
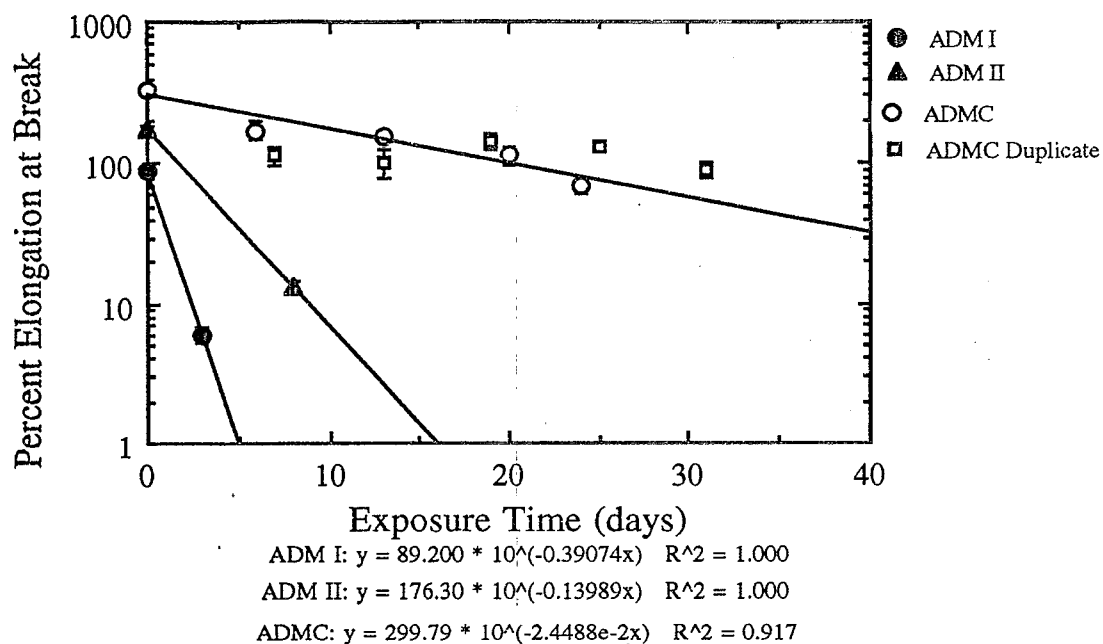
6P: y = 550.26 * 10^(-0.25680x)   R^2 = 0.900

6PC: y = 1047.3 * 10^(-2.5055e-2x)   R^2 = 0.929

Figure 4.1.6 (g)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Wittmann, AZ - outdoor exposure).

y = 355.52 * 10^(-3.9229e-2x)   R^2 = 0.687

Figure 4.1.6 (h)   Semi-logarithmic plot of elongation at break vs. exposure time. (6P - Kerr Lake, VA - fresh water floating exposure).

PG: y = 1032.7 * 10^(-4.9811e-2x)   R^2 = 0.882

PGC: y = 612.51 * 10^(-1.2228e-2x)   R^2 = 0.901

Figure 4.1.6 (i)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Cedar Knolls, NJ - outdoor exposure).

PG: y = 1090.6 * 10^(-4.8987e-2x)   R^2 = 0.891

PGC: y = 742.02 * 10^(-1.2913e-2x)   R^2 = 0.867

Figure 4.1.6 (j)   Semi-logarithmic plot of elongation at break vs. exposure time. PG - Chicago, IL - outdoor exposure).

PG: y = 959.75 * 10^(-7.1569e-2x)   R^2 = 0.945

PGC: y = 917.20 * 10^(-2.1588e-2x)   R^2 = 0.865

Figure 4.1.6 (k)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Miami, FL - outdoor exposure).

PG: y = 859.41 * 10^(-2.6596e-2x)   R^2 = 0.939

PGC: y = 631.52 * 10^(-4.1660e-3x)   R^2 = 0.414

Figure 4.1.6 (l)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Miami, FL - marine floating exposure).

PG: y = 1004.1 * 10^(-5.3510e-2x)   R^2 = 0.921

PGC: y = 586.92 * 10^(-1.6205e-2x)   R^2 = 0.840

Figure 4.1.6 (m)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Seattle, WA - outdoor exposure).

PG: y = 351.55 * 10^(-1.7733e-2x)   R^2 = 0.753

PGC: y = 382.52 * 10^(-2.3899e-3x)   R^2 = 0.113
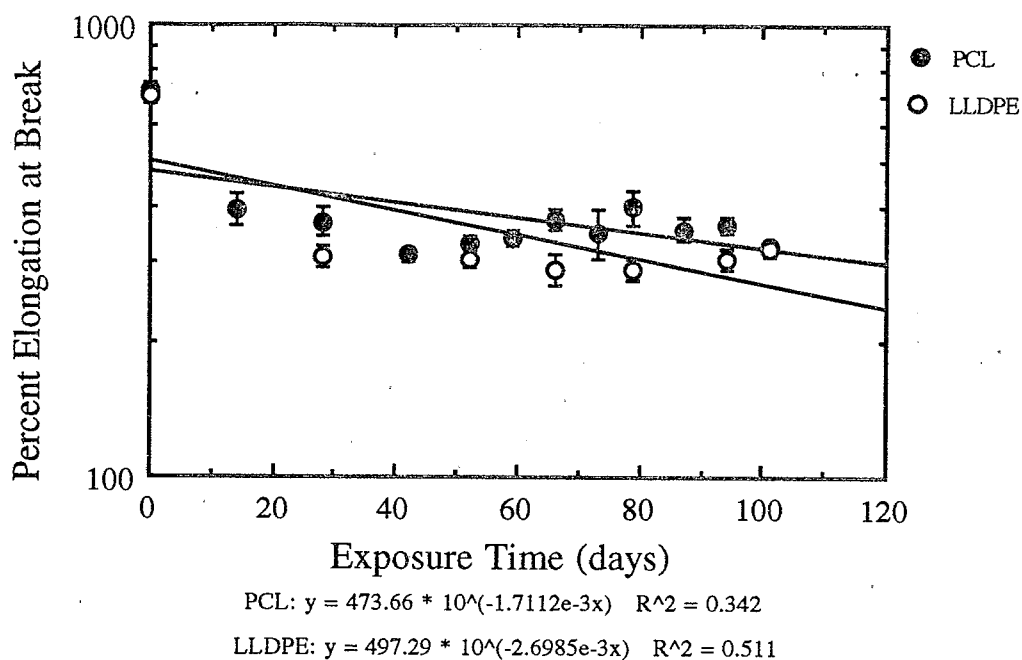
Figure 4.1.6 (n)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Seattle, WA - marine floating exposure).

PG: y = 885.09 * 10^(-0.12231x)   R^2 = 0.915

PGC: y = 607.31 * 10^(-3.2960e-2x)   R^2 = 0.961

Figure 4.1.6 (o)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG-Wittmann, AZ - outdoor exposure).

PG: y = 937.87 * 10^(-7.4701e-3x)   R^2 = 0.612
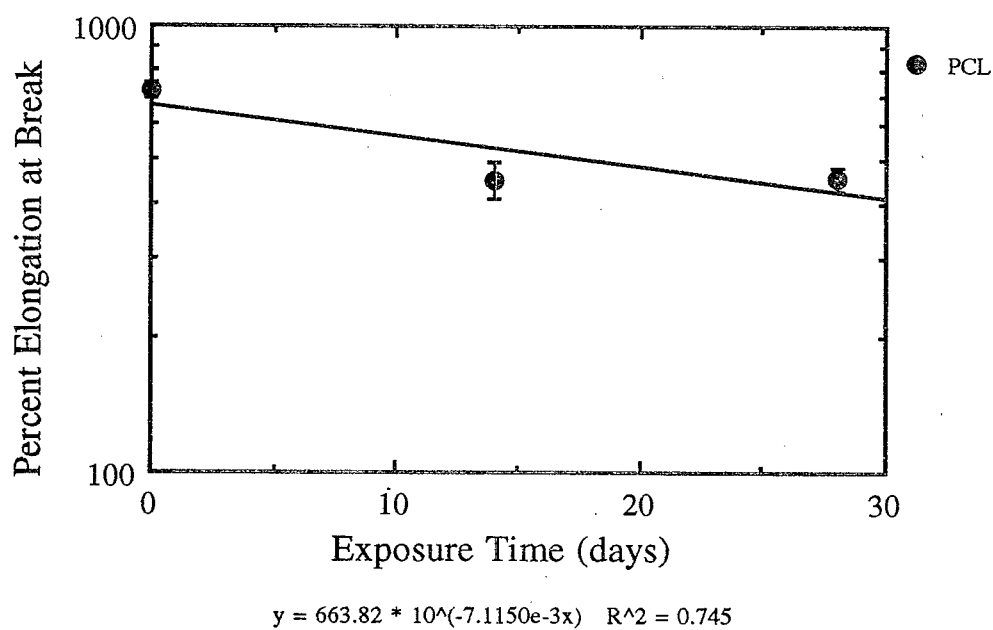
PGC: y = 738.90 * 10^(-1.1908e-3x)   R^2 = 0.438

Figure 4.1.6 (p)   Semi-logarithmic plot of elongation at break vs. exposure time. (PG - Kerr Lake, VA - fresh water floating exposure).

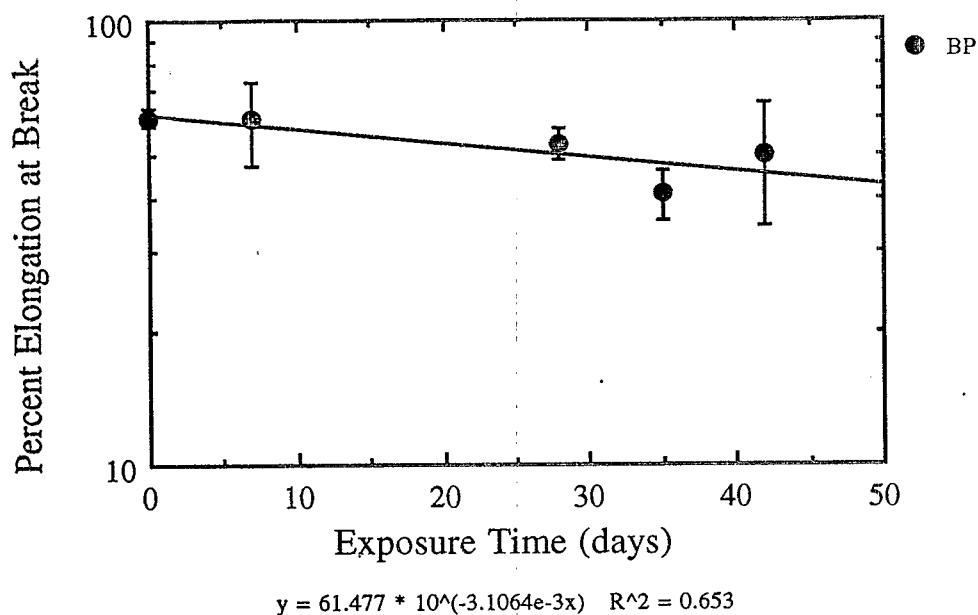Figure 4.1.6 (q)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM-Cedar Knolls, NJ - outdoor exposure).

ADM I: y = 65.886 * 10^(-0.13726x)   R^2 = 0.916

ADM II: y = 193.71 * 10^(-7.7012e-2x)   R^2 = 0.980

ADMC: y = 340.40 * 10^(-5.7249e-3x)   R^2 = 0.573

ADM I: y = 67.514 * 10^(-0.14776x)   R^2 = 0.940

ADM II: y = 176.15 * 10^(-6.6930e-2x)   R^2 = 0.978

ADMC: y = 354.16 * 10^(-1.1136e-2x)   R^2 = 0.816
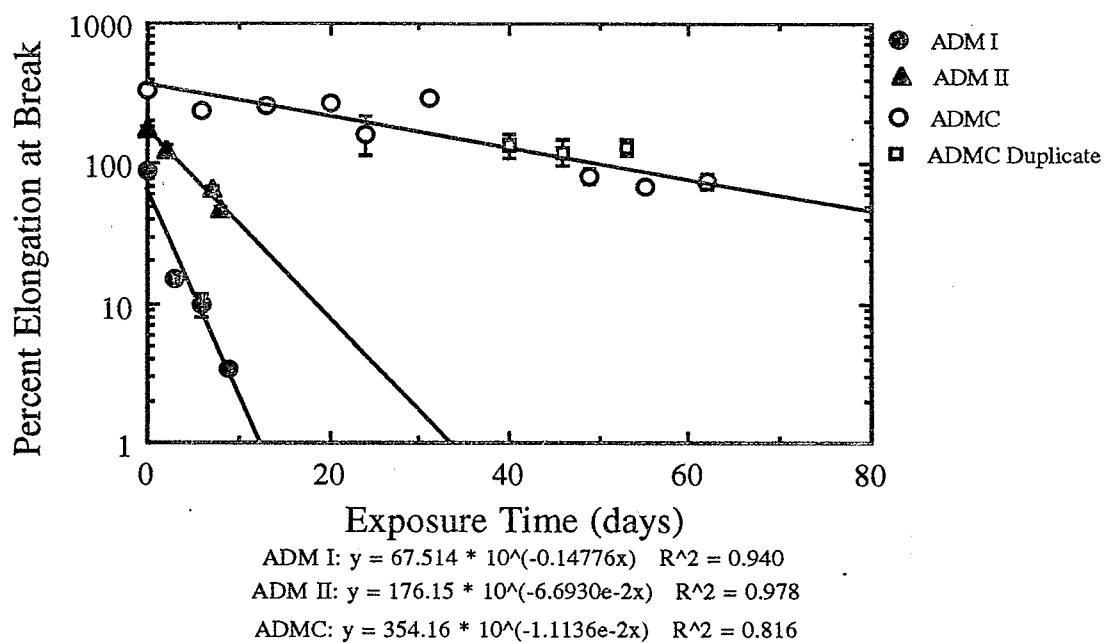
Figure 4.1.6 (r)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Chicago, IL - outdoor exposure).

Figure 4.1.6 (s)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Miami, FL - outdoor exposure).
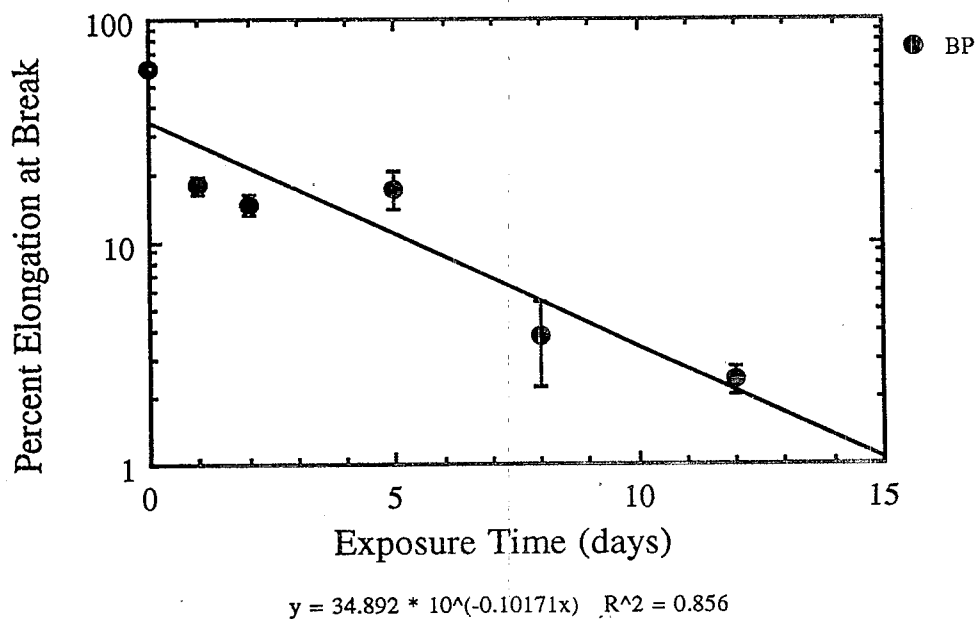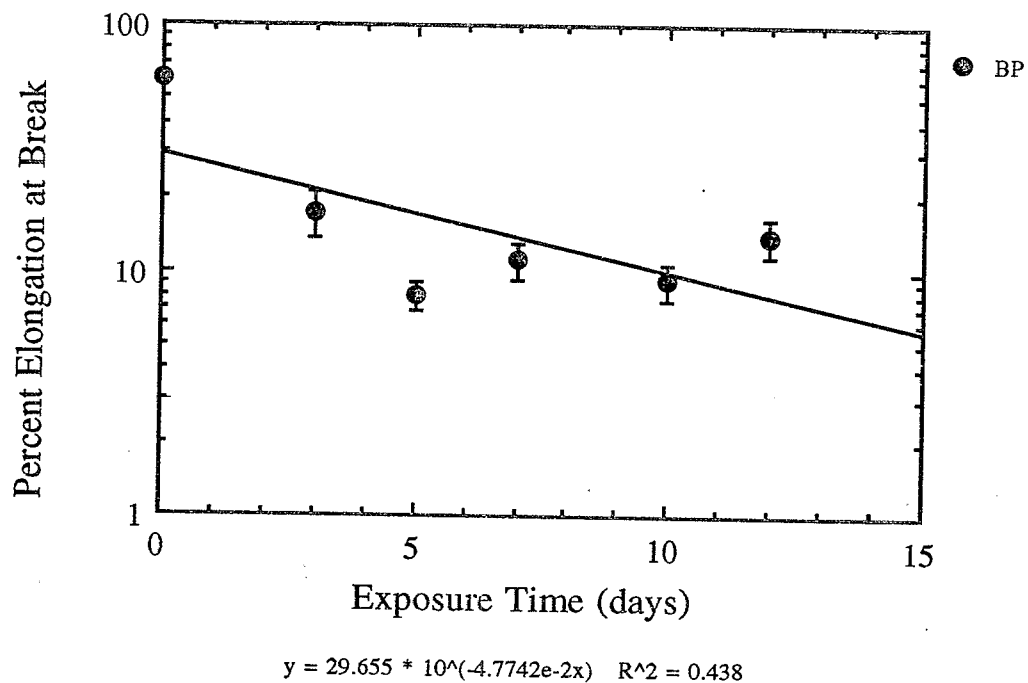

Figure 4.1.6 (t)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Miami, FL - marine floating exposure).

Figure 4.1.6 (u)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Seattle, WA - outdoor exposure).

Figure 4.1.6 (v)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Seattle, WA - marine floating exposure).

ADM I: y = 89.200 * 10^(-0.39074x)   R^2 = 1.000

ADM II: y = 176.30 * 10^(-0.13989x)   R^2 = 1.000

ADMC: y = 299.79 * 10^(-2.4488e-2x)   R^2 = 0.917

Figure 4.1.6 (w)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Wittmann, AZ - outdoor exposure).

ADM I: y = 53.021 * 10^(-1.8972e-2x)   R^2 = 0.888

ADMC: y = 169.70 * 10^(-2.2124e-3x)   R^2 = 0.171
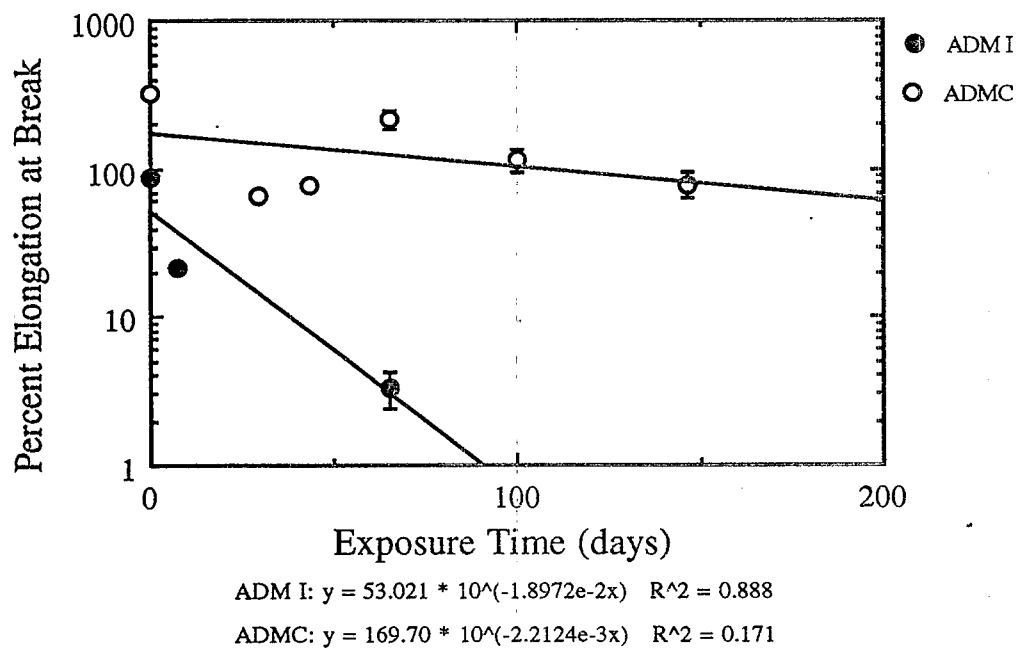
Figure 4.1.6 (x)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Miami, FL - marine sediment exposure).
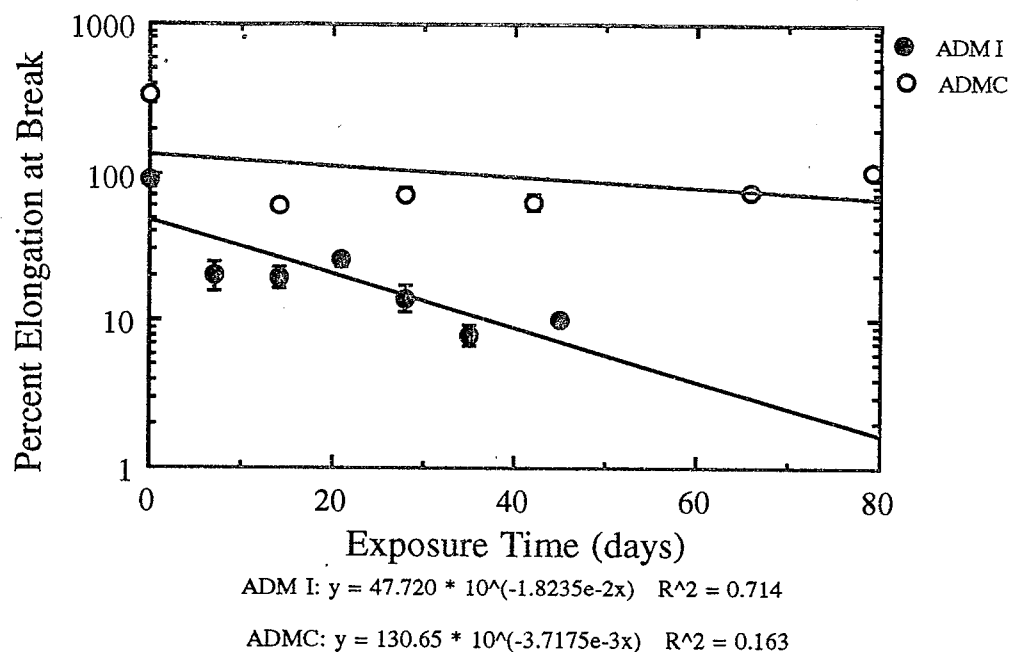
Figure 4.1.6 (y)   Semi-logarithmic plot of elongation at break vs. exposure time. ADM - Seattle, WA - marine sediment exposure).
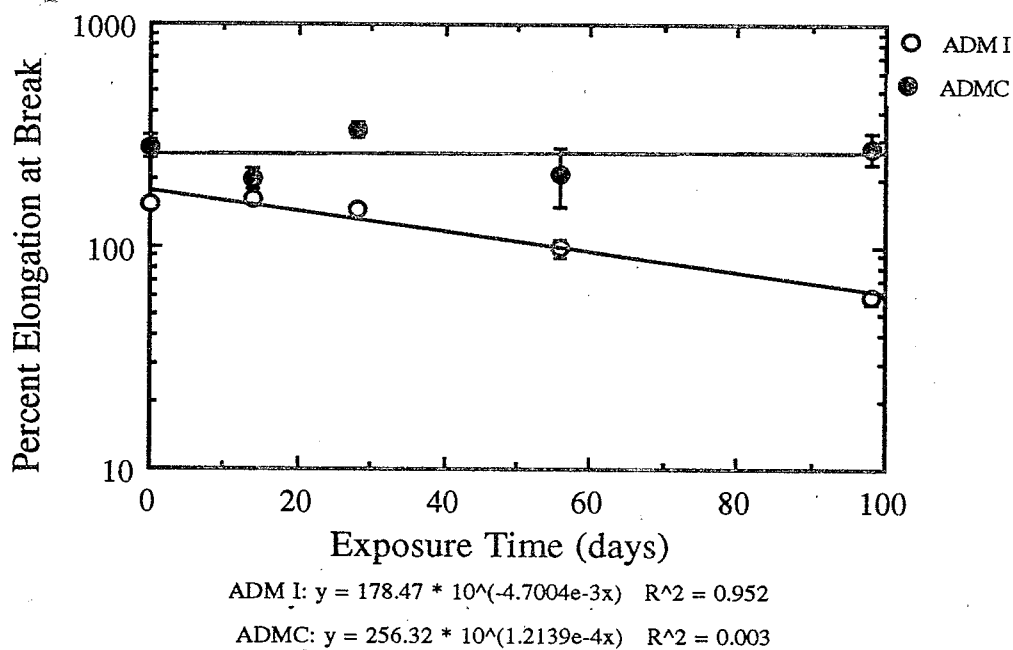
Figure 4.1.6 (z)   Semi-logarithmic plot of elongation at break vs. exposure time. (ADM - Kerr Lake, VA - fresh water floating exposure).

PCL: y = 1034.3 * 10^(-2.7304e-2x)   R^2 = 0.849

LLDPE: y = 1223.1 * 10^(-2.1475e-2x)   R^2 = 0.802
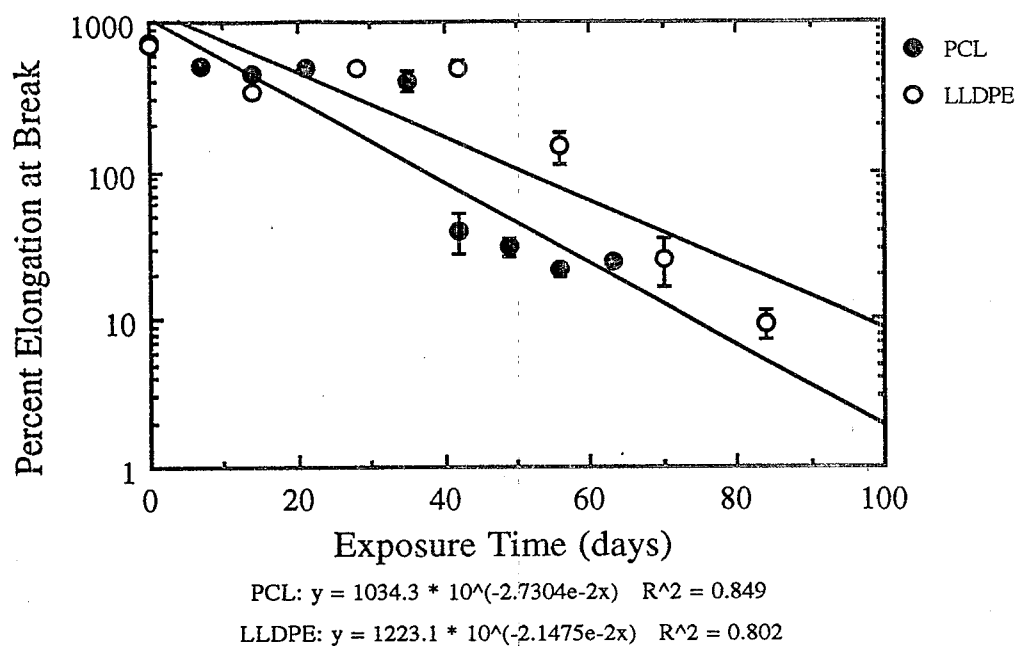
Figure 4.1.6 (aa)   Semi-logarithmic plot of elongation at break vs. exposure time. (PCL - Miami, FL - outdoor exposure).

PCL: y = 499.50 * 10^(-1.1951e-3x)   R^2 = 0.257

LLDPE: y = 604.84 * 10^(-5.3880e-3x)   R^2 = 0.764
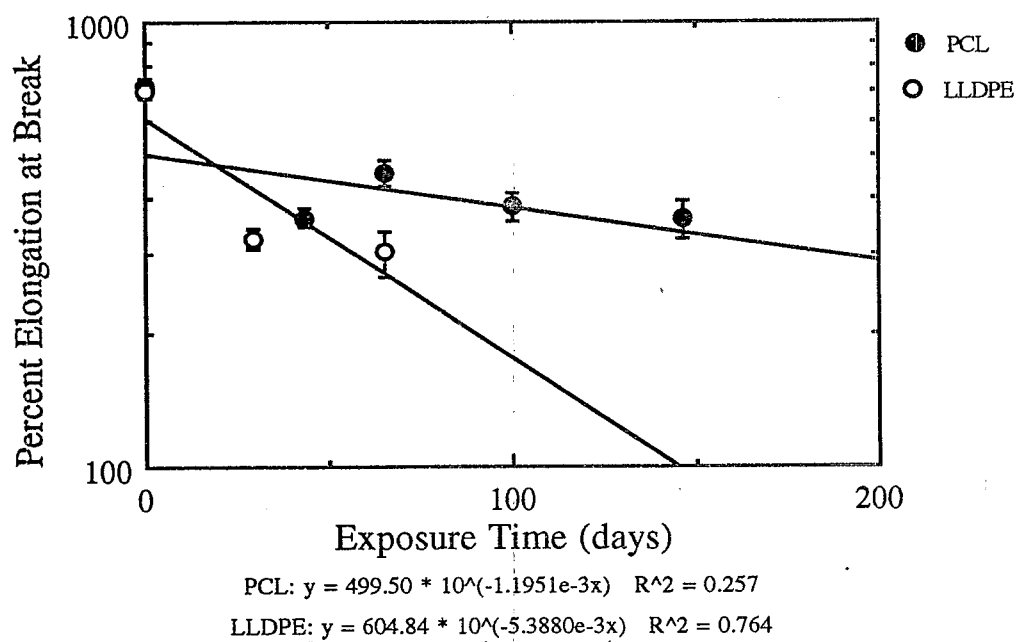
Figure 4.1.6 (bb)   Semi-logarithmic plot of elongation at break vs. exposure time. (PCL - Miami, FL - marine sediment exposure).

PCL: y = 473.66 * 10^(-1.7112e-3x)   R^2 = 0.342

LLDPE: y = 497.29 * 10^(-2.6985e-3x)   R^2 = 0.511

Figure 4.1.6 (cc)   Semi-logarithmic plot of elongation at break vs. exposure time. (PCL - Seattle, WA - marine sediment exposure).

y = 663.82 * 10^(-7.1150e-3x)   R^2 = 0.745

Figure 4.1.6 (dd)   Semi-logarithmic plot of elongation at break vs. exposure time. (PCL - Kerr Lake, VA - fresh water floating exposure).

$$y = 61.477 * 10\char`\^(-3.1064e\text{-}3x) \quad R\char`\^2 = 0.653$$

Figure 4.1.6 (ee)   Semi-logarithmic plot of elongation at break vs. exposure time. (BP - Miami, FL - outdoor exposure).

$$y = 34.892 * 10\char`\^(-0.10171x) \quad R\char`\^2 = 0.856$$

Figure 4.1.6 (ff)   Semi-logarithmic plot of elongation at break vs. exposure time. (BP - Miami, FL - marine sediment exposure).

$$y = 29.655 * 10^{(-4.7742e-2x)} \quad R^2 = 0.438$$

Figure 4.1.6 (gg) Semi-logarithmic plot of elongation at break vs. exposure time. (BP - Kerr Lake, VA - fresh water sediment exposure).
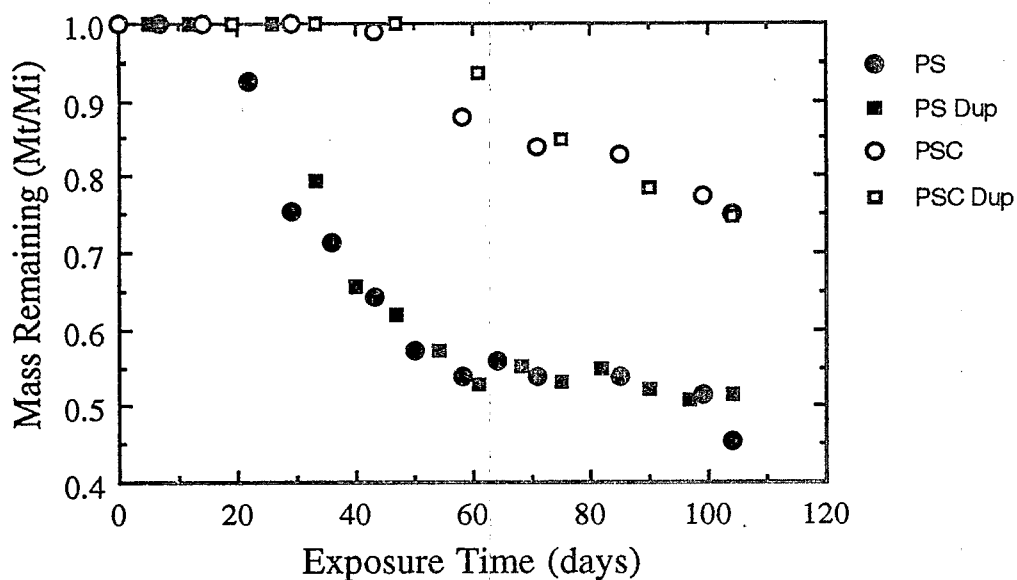
Figure 4.1.7 (a)   Change in mass (as measured by tumbling friability) with duration of exposure for polystyrene foam exposed outdoors - (Cedar Knolls, NJ).
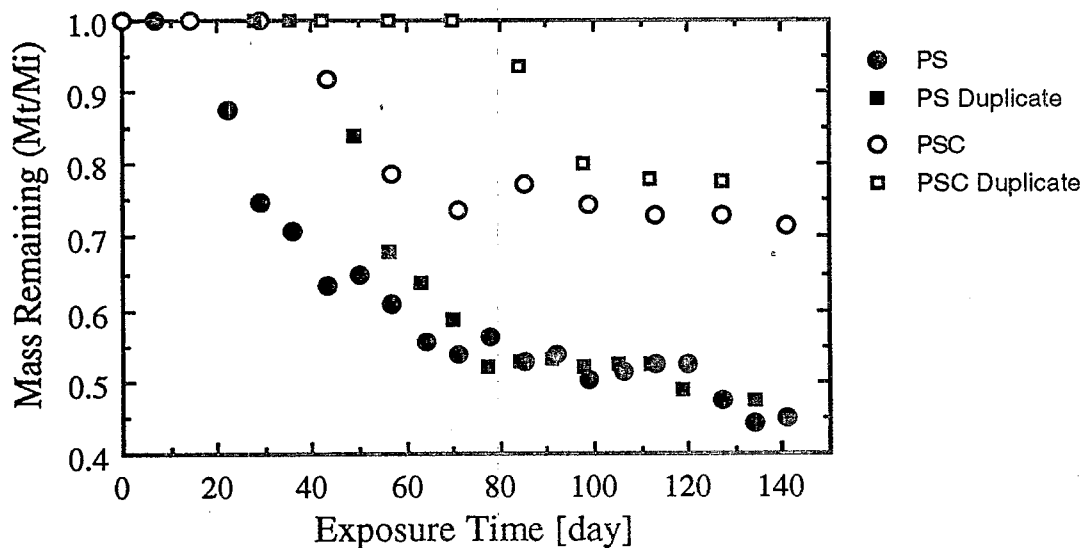
Figure 4.1.7 (b)   Change in mass (as measured by tumbling friability) with duration of exposure for polystyrene foam exposed outdoors - (Chicago, IL).
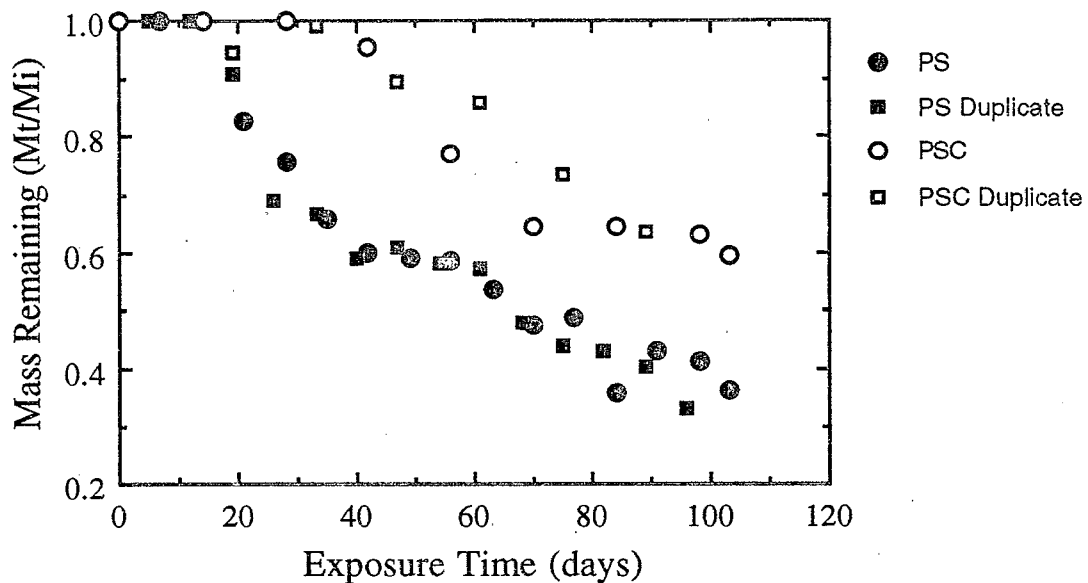
Figure 4.1.7 (c)   Change in mass (as measured by tumbling friability) with duration of exposure for polystyrene foam exposed outdoors - (Miami, FL).
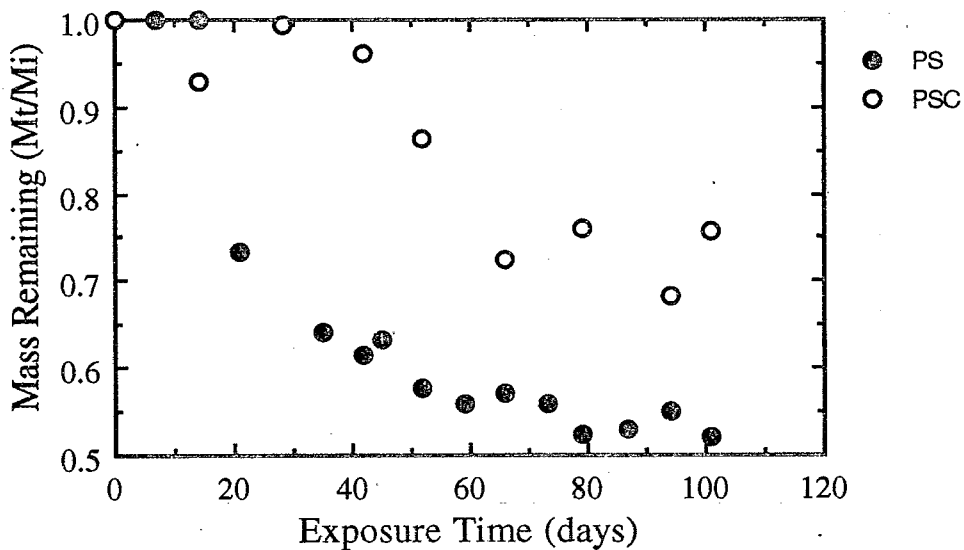
Figure 4.1.7 (d)   Change in mass (as measured by tumbling friability) with duration of exposure for polystyrene foam exposed outdoors - (Seattle, WA).
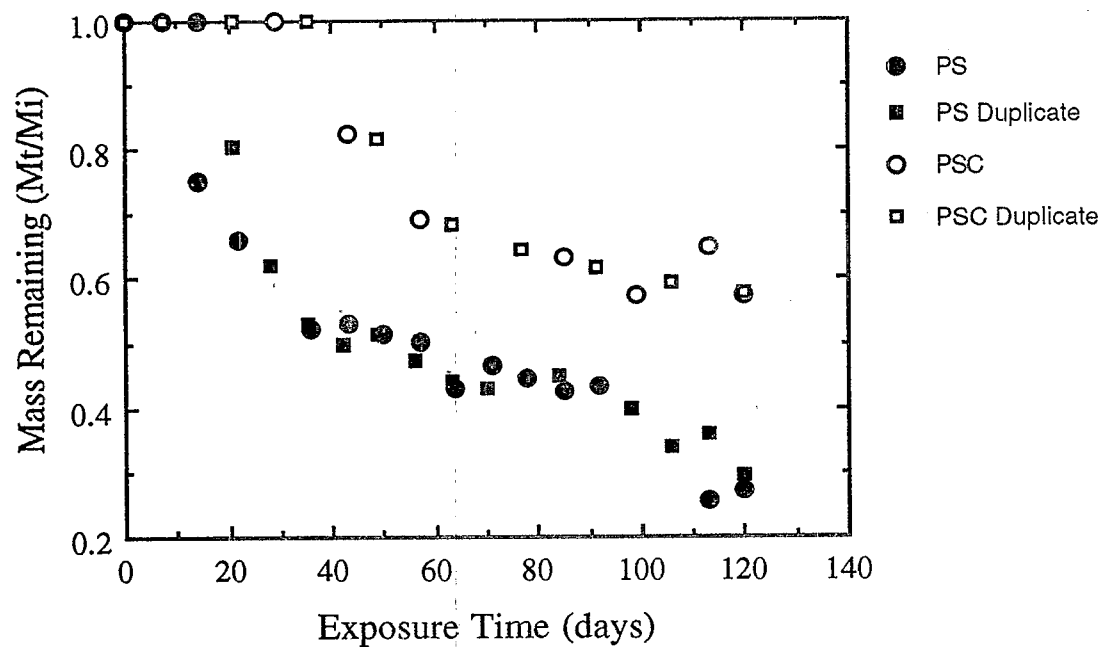
Figure 4.1.7 (e)   Change in mass (as measured by tumbling friability) with duration of exposure for polystyrene foam exposed outdoors - (Wittmann, AZ).

PS: y = 0.89728 · 10^(-2.8935e-3x)   R^2 = 0.803

PS Dup: y = 0.92676 * 10^(-2.9269e-3x)   R^2 = 0.700

PSC: y = 1.1287 * 10^(-1.6861e-3x)   R^2 = 0.963

PSC Dup: y = 1.2780 * 10^(-2.2969e-3x)   R^2 = 0.987
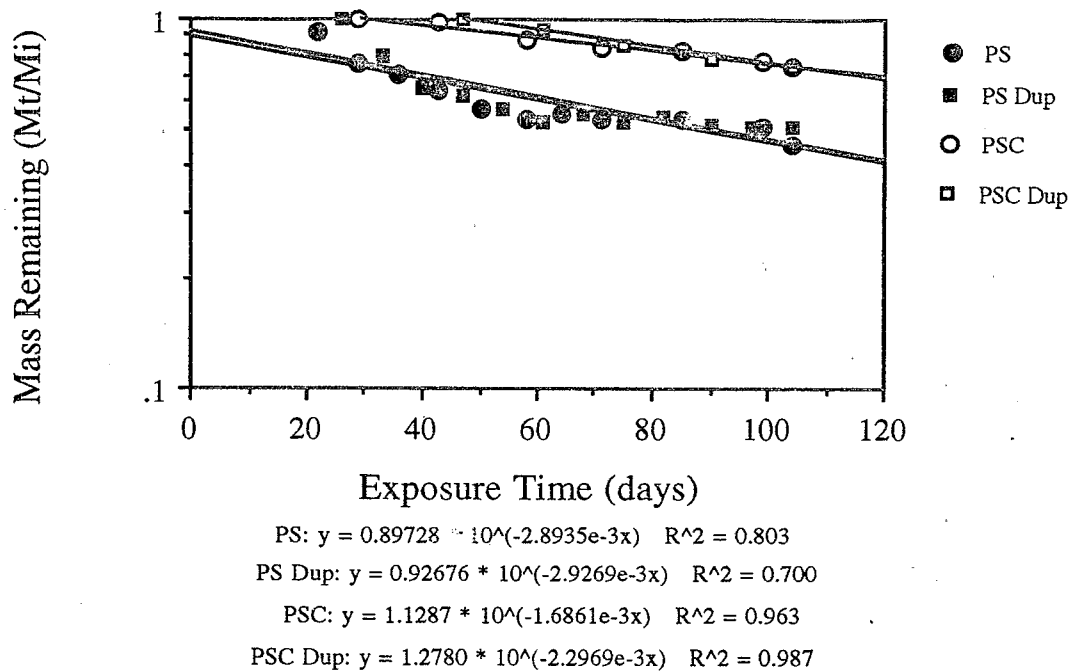
Figure 4.1.8 (a)   Semi-logarithmic plot of tumbling friability data versus duration of exposure for polystyrene foam exposed outdoors - (Cedar Knolls, NJ).


PS: y = 0.86780 * 10^(-2.1989e-3x)   R^2 = 0.845

PS Dup: y = 1.0408 * 10^(-2.9193e-3x)   R^2 = 0.733

PSC: y = 0.98004 * 10^(-1.1117e-3x)   R^2 = 0.715

PSC Dup: y = 1.3766 * 10^(-2.1135e-3x)   R^2 = 0.861
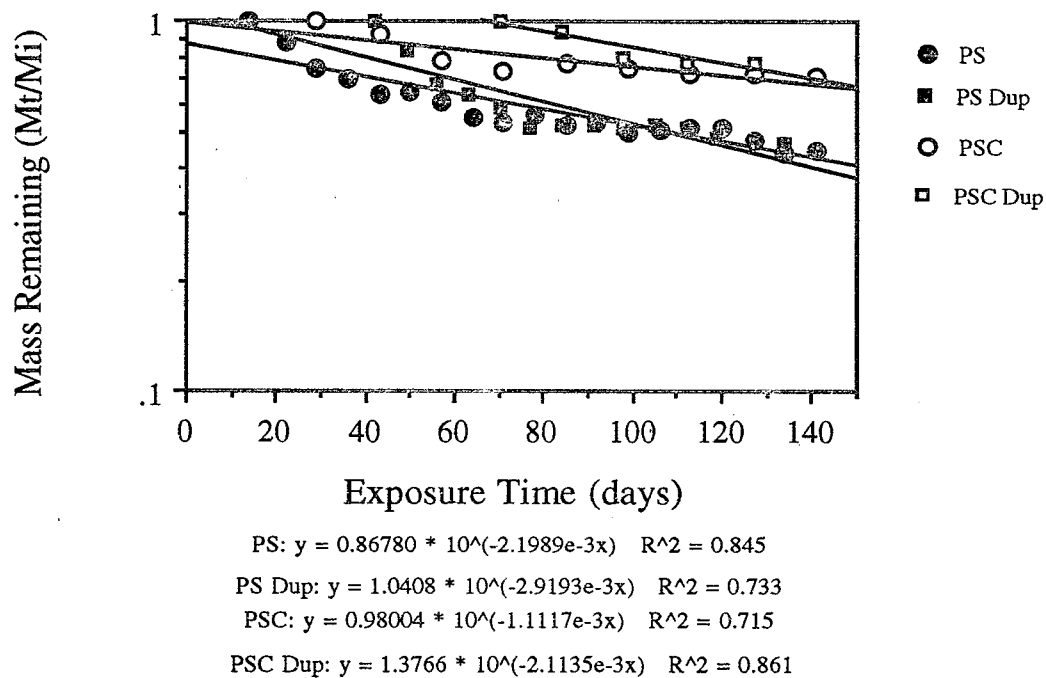
Figure 4.1.8 (b)   Semi-logarithmic plot of tumbling friability data versus duration of exposure for polystyrene foam exposed outdoors - (Chicago, IL).

PS: y = 0.95497 * 10^(-4.1068e-3x)   R^2 = 0.926

PS Dup: y = 0.99516 * 10^(-4.6193e-3x)   R^2 = 0.938

PSC: y = 1.1630 * 10^(-2.9494e-3x)   R^2 = 0.834

PSC Dup: y = 1.3083 * 10^(-3.3825e-3x)   R^2 = 0.964
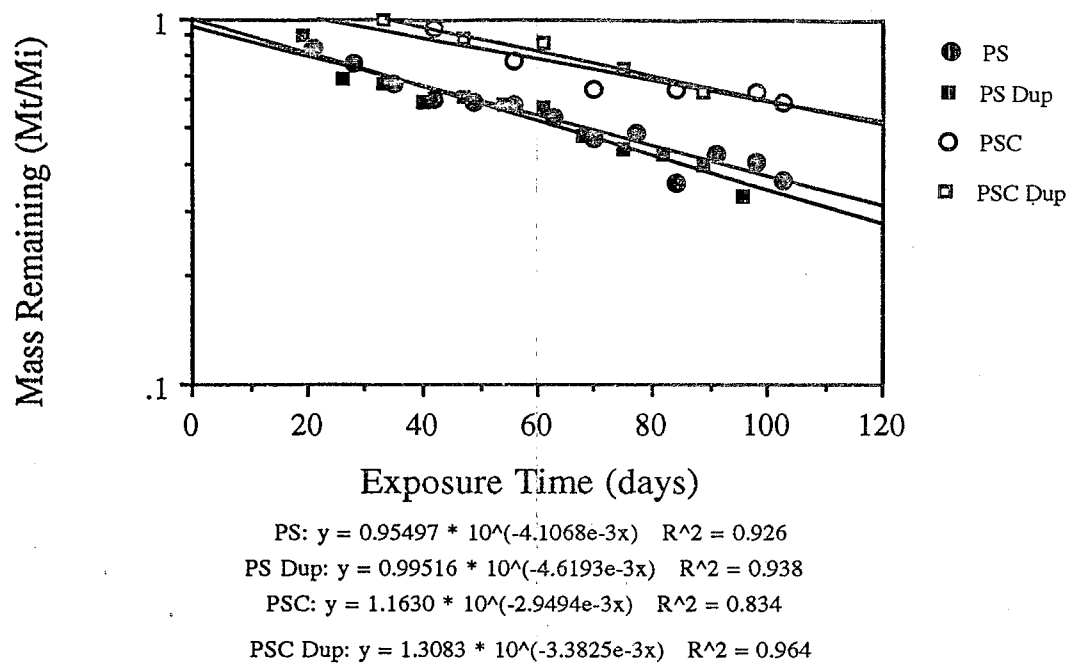
Figure 4.1.8 (c)   Semi-logarithmic plot of tumbling friability data versus duration of exposure for polystyrene foam exposed outdoors - (Miami, FL).

PS: y = 0.84067 * 10^(-2.4004e-3x)   R^2 = 0.717

PSC: y = 1.0786 * 10^(-1.8944e-3x)   R^2 = 0.661
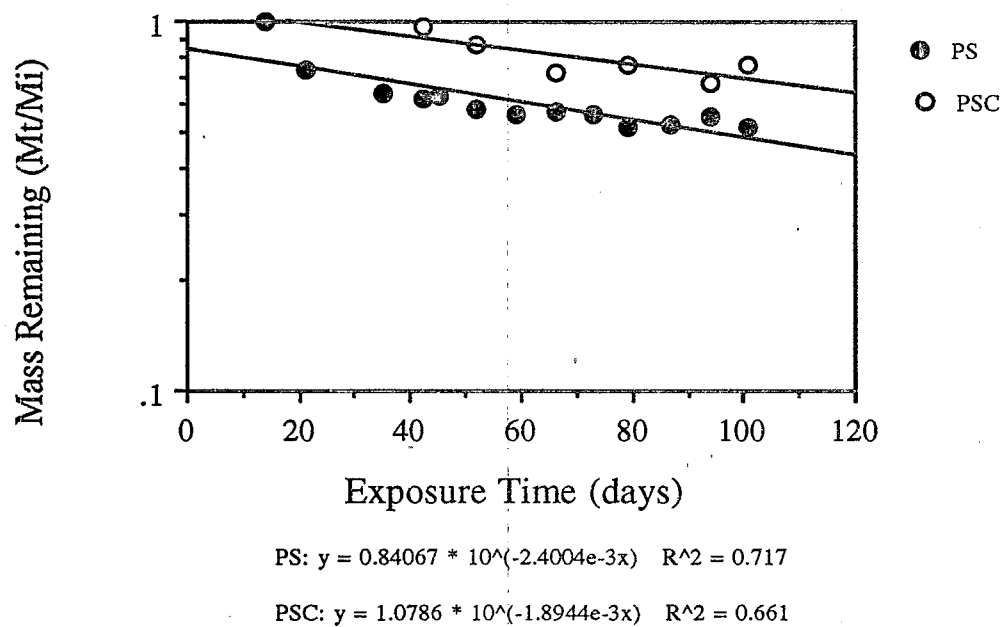
Figure 4.1.8 (d)   Semi-logarithmic plot of tumbling friability data versus duration of exposure for polystyrene foam exposed outdoors - (Seattle, WA).
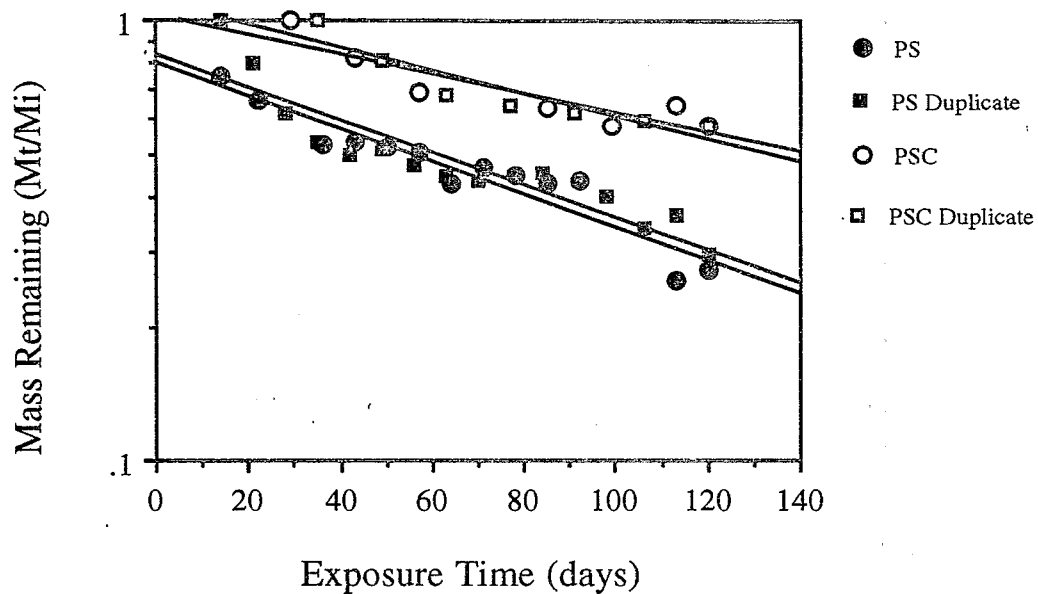
PS: y = 0.80825 * 10^(-3.7587e-3x)   R^2 = 0.897

PS Dup: y = 0.83593 * 10^(-3.6807e-3x)   R^2 = 0.838

PSC: y = 1.0347 * 10^(-2.2277e-3x)   R^2 = 0.804

PSC Dup: y = 1.1010 * 10^(-2.5958e-3x)   R^2 = 0.854

Figure 4.1.8 (e)   Semi-logarithmic plot of tumbling friability data versus duration of exposure for polystyrene foam exposed outdoors - (Wittmann, AZ).

PS: y = 0.71872 + 3.8665e-2x   R^2 = 0.844

PSC: y = 1.0811e-2 + 2.2063e-2x   R^2 = 0.993
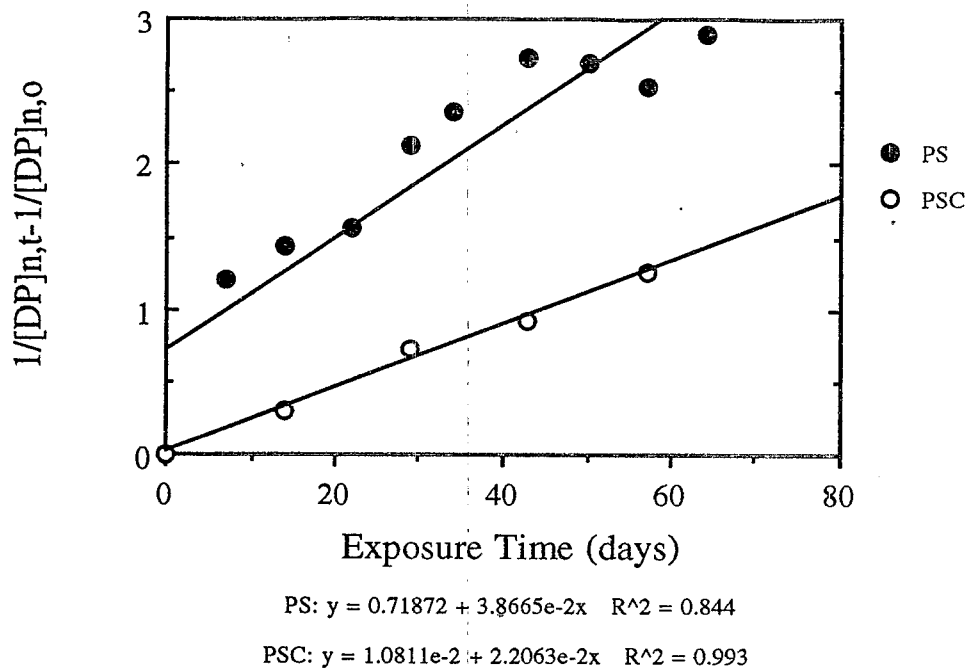
Figure 4.1.9 (a)   GPC data for PS plotted as reciprocal degree of polymerization vs. duration of exposure - (Outdoor - Chicago, IL).

PS: y = 0.67541 + 2.5237e-2x   R^2 = 0.730

PSC: y = 0.12389 + 1.4315e-2x   R^2 = 0.703
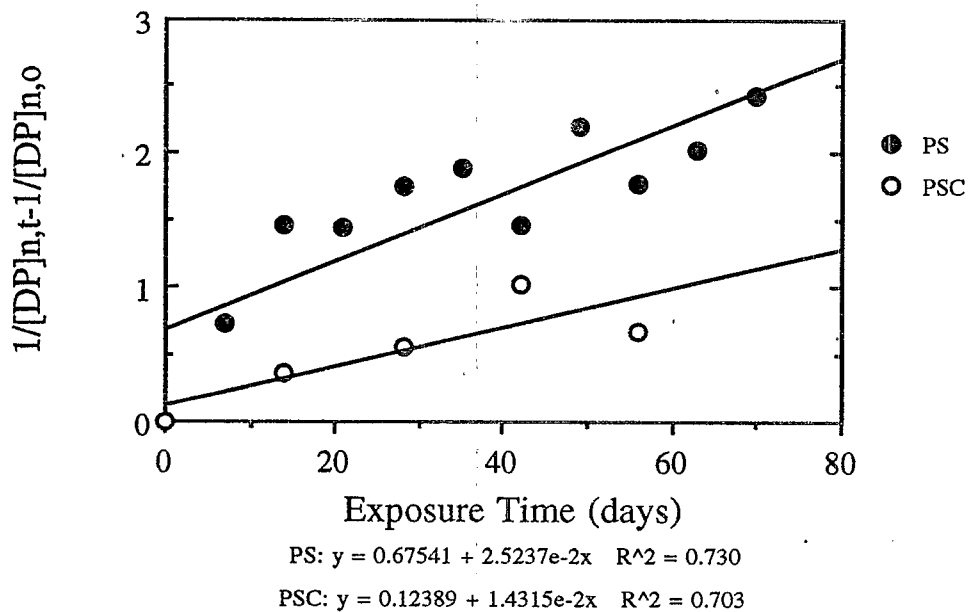
Figure 4.1.9 (b)   GPC data for PS plotted as reciprocal degree of polymerization vs. duration of exposure - (Outdoor - Miami, FL).

PS: y = 0.16602 + 6.2791e-2x   R^2 = 0.975

PSC: y = 2.1521e-2 + 1.4294e-2x   R^2 = 0.971
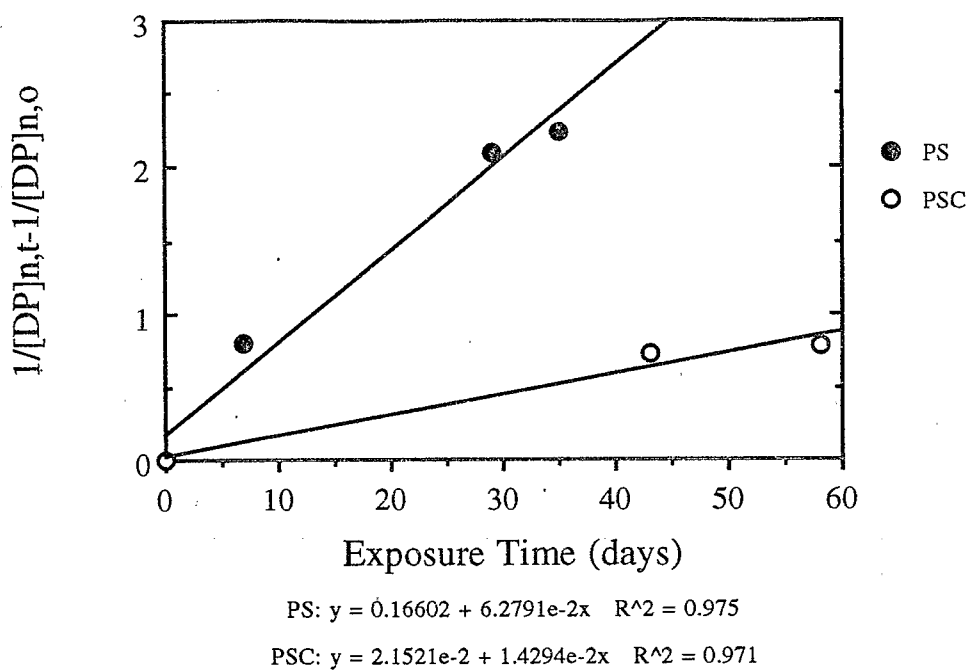
Figure 4.1.9 (c)   GPC data for PS plotted as reciprocal degree of polymerization vs. duration of exposure - (Marine floating - Miami, FL).

PS: y = 0.13528 + 4.3049e-2x   R^2 = 0.899

PSC: y = - 1.8654e-4 + 1.2972e-2x   R^2 = 0.979
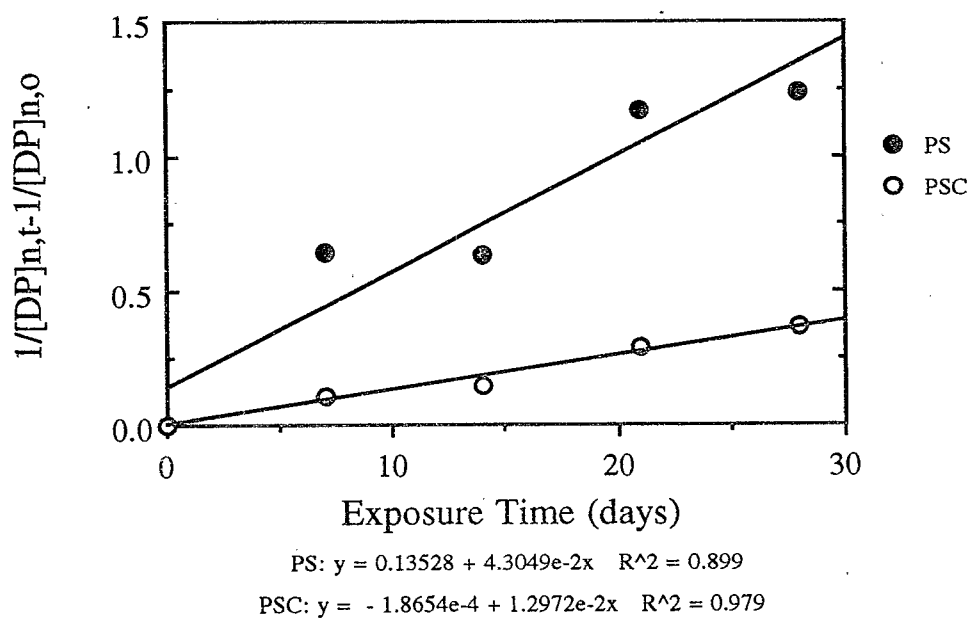
Figure 4.1.9 (d)   GPC data for PS plotted as reciprocal degree of polymerization vs. duration of exposure - (Marine floating - Seattle, WA).

6-PACK RINGS
MARINE FLOATING EXPOSURE AT
MIAMI, FL
35 DAYS: 6/1/90-7/6/90
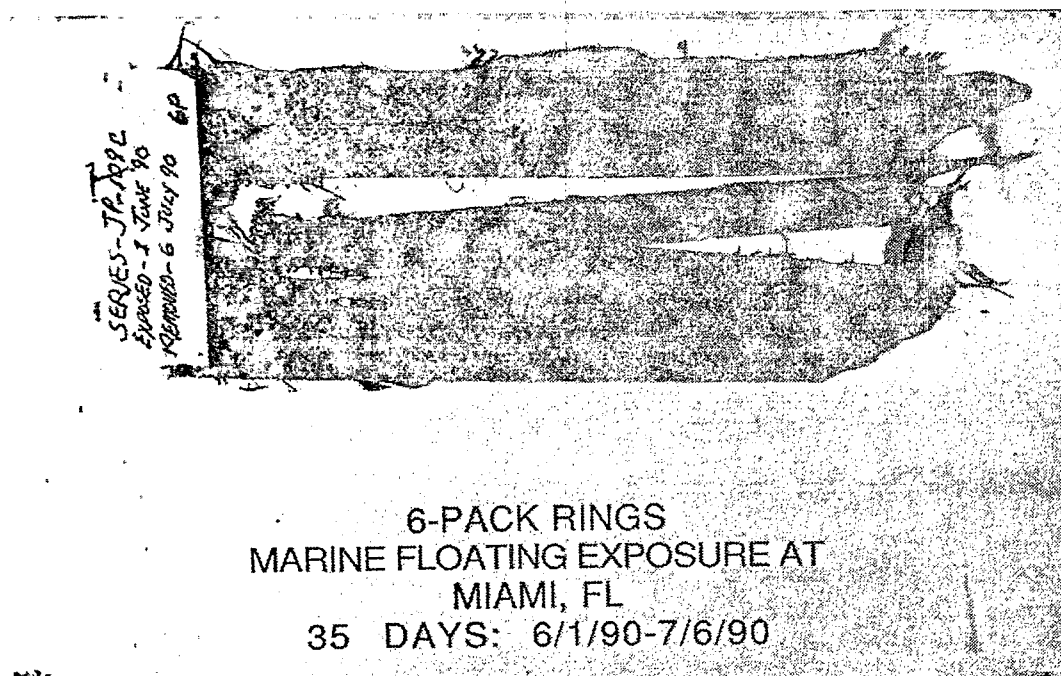
Figure 4.1.10 (a)   Marine-floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Miami, FL - (6P - 35 days).
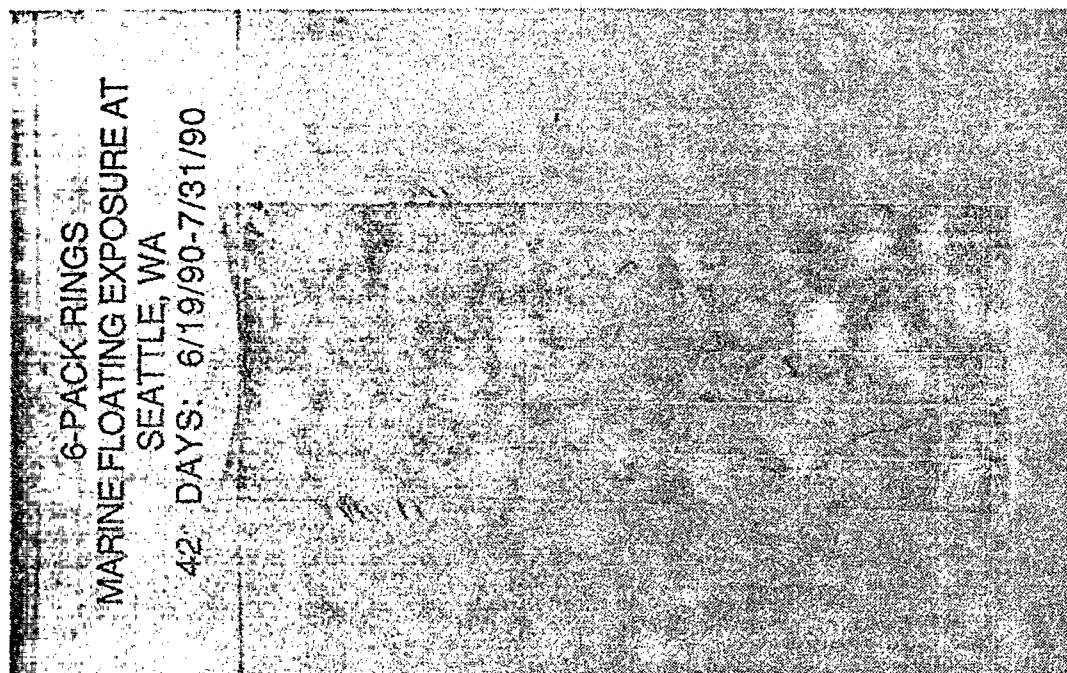

6-PACK CONTROL
MARINE FLOATING EXPOSURE AT
MIAMI, FL
35 DAYS: 6/1/90-7/6/90
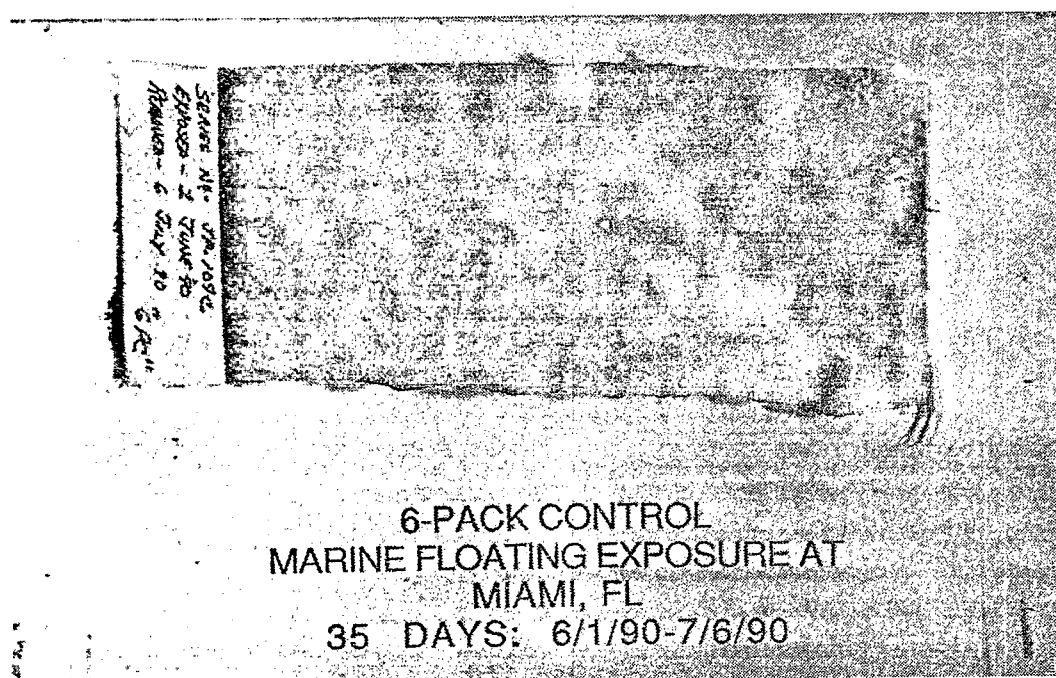
Figure 4.1.10 (b)   Marine-floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Miami, FL - (6PC - 35 days).

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6-PACK CONTROL
MARINE FLOATING EXPOSURE AT
MIAMI, FL
49 DAYS: 6/1/90-7/20/90

Figure 4.1.10 (d)   Marine-floating exposure of LDPE control and ethylene-carbon monoxide) copolymer in Miami, FL - (6PC-49 days).

6-PACK RINGS
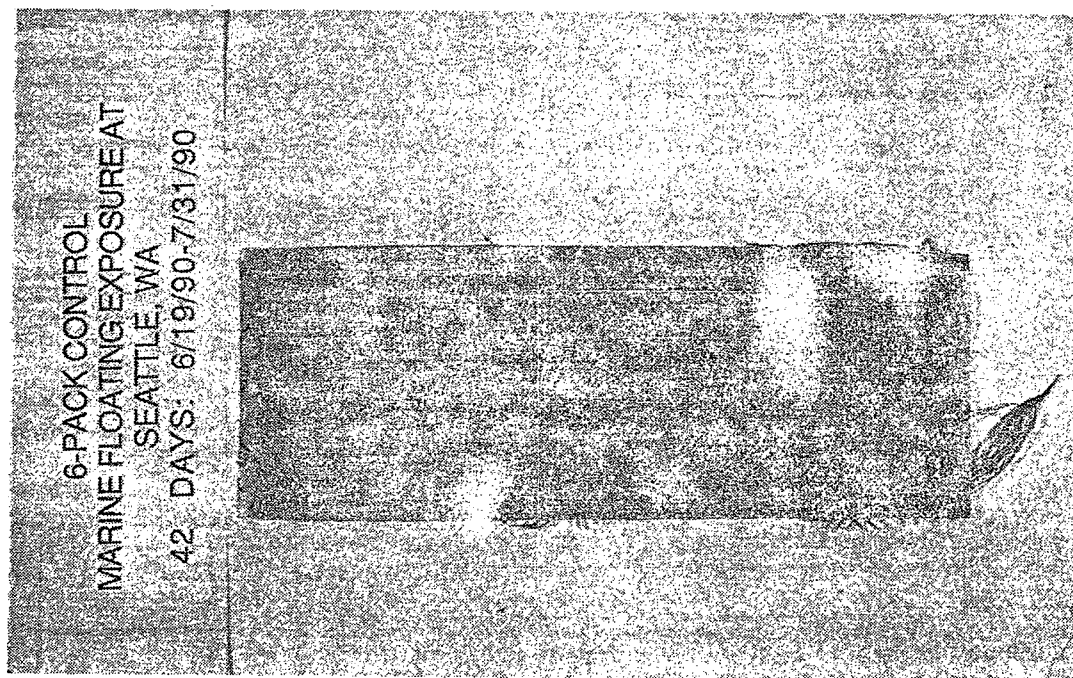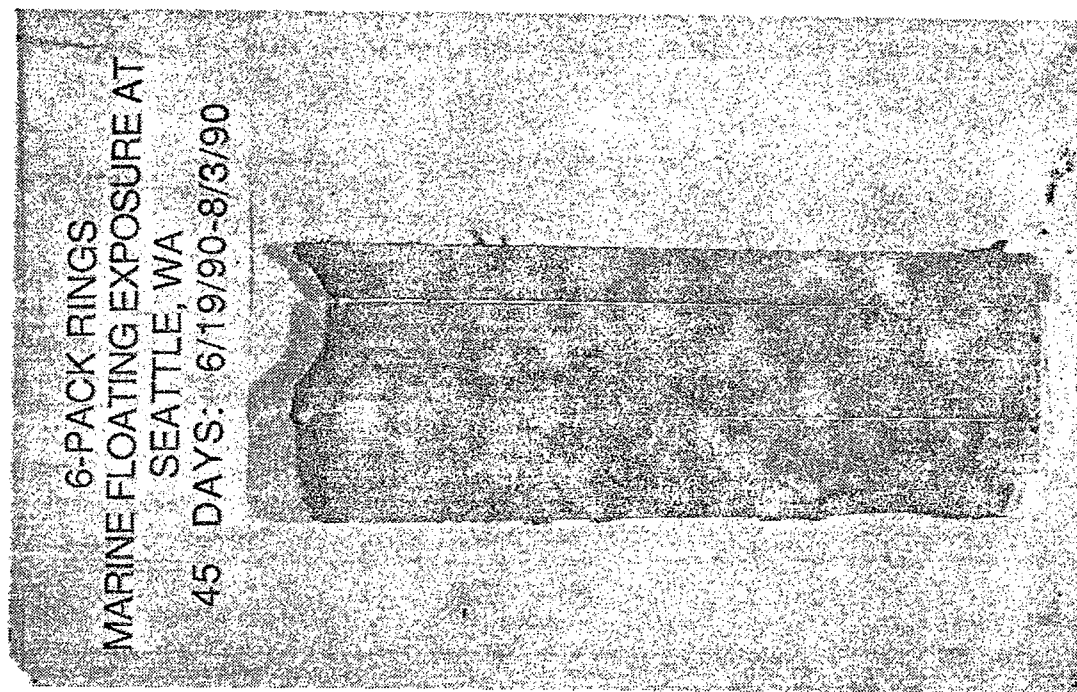MARINE FLOATING EXPOSURE AT
MIAMI, FL
49 DAYS: 6/1/90-7/20/90
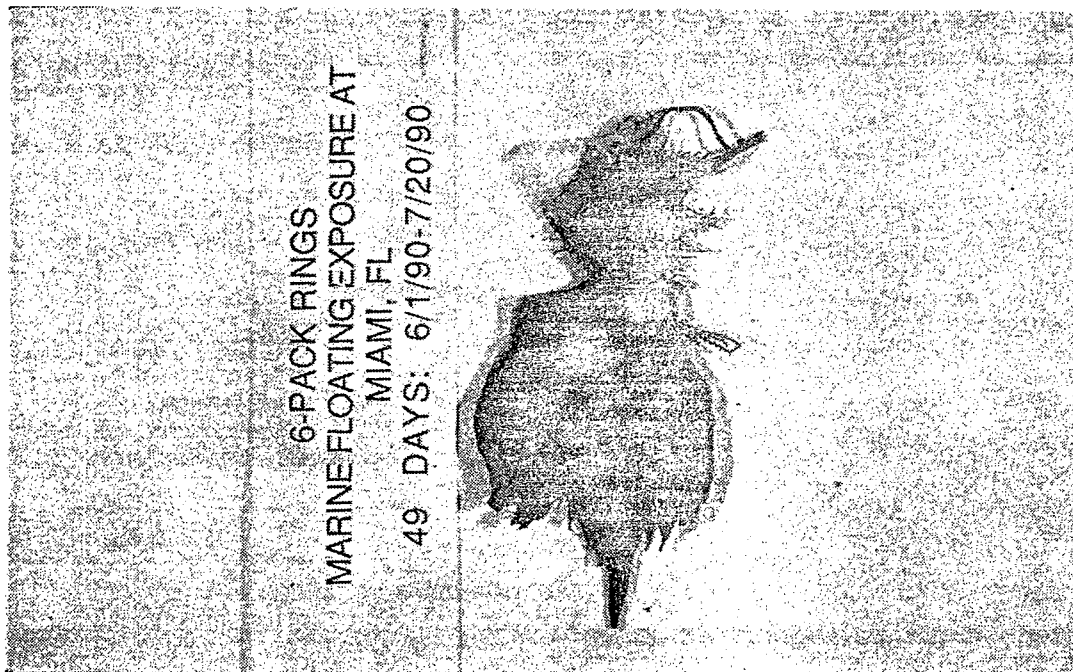
Figure 4.1.10 (c)   Marine-floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Miami, FL - (6P - 49 days).
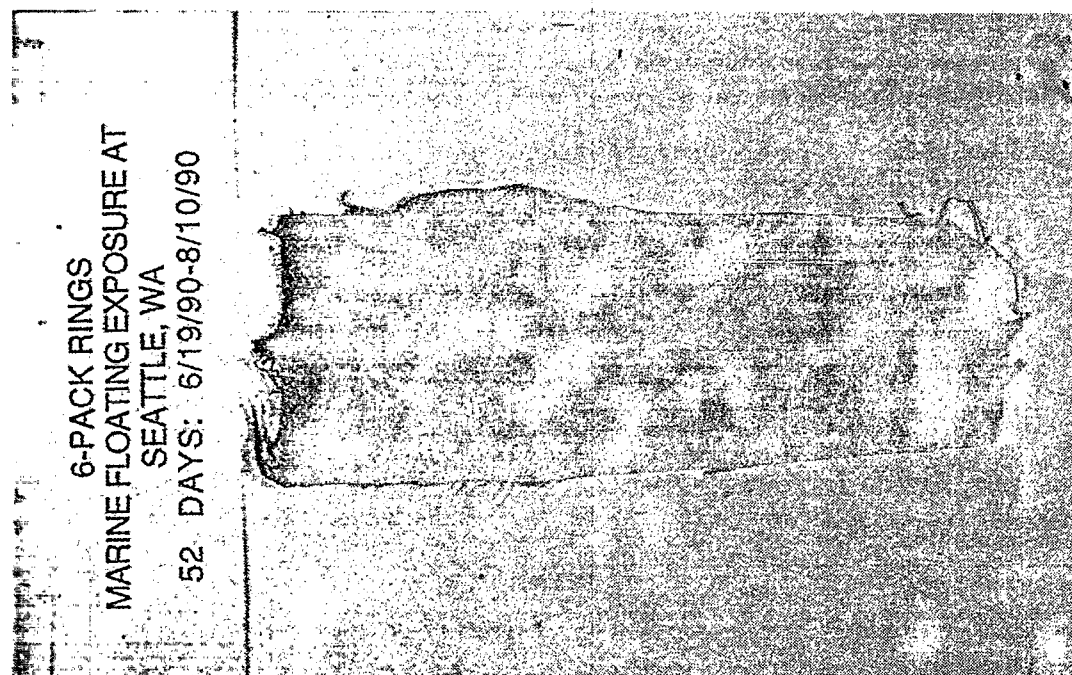
Figure 4.1.11 (b)   Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6P - 42 days).
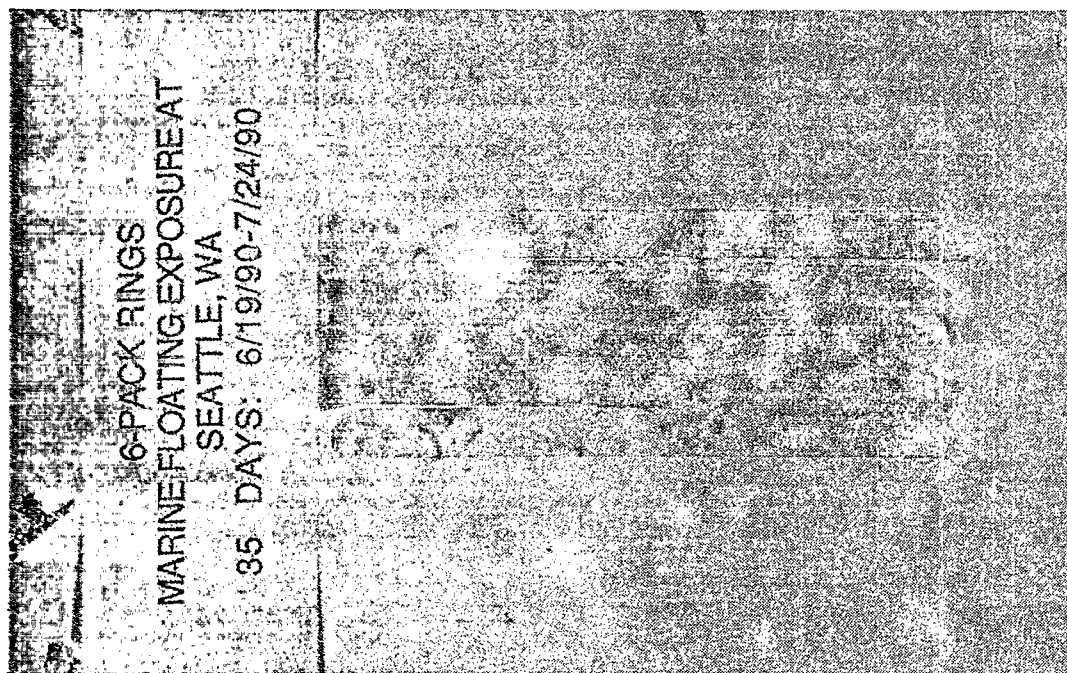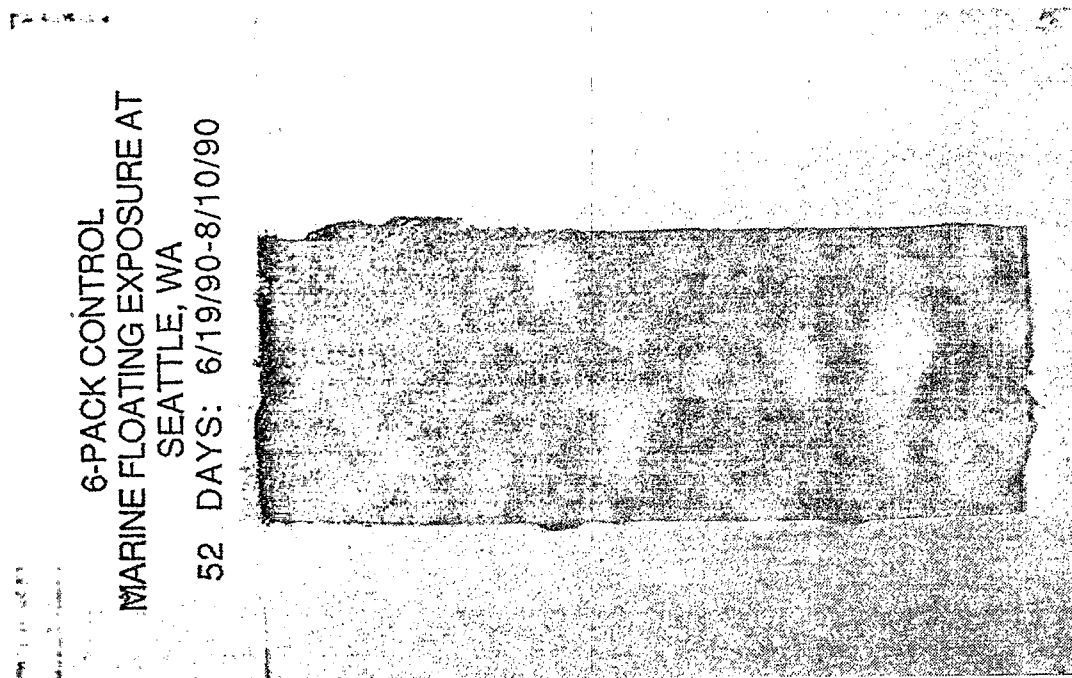

Figure 4.1.11 (a)   Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6P - 35 days).

6-PACK RINGS
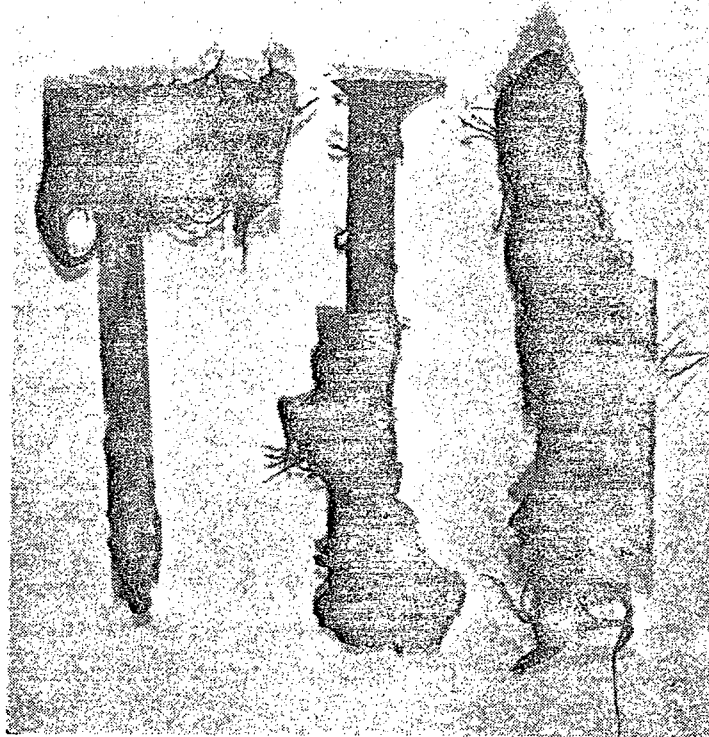MARINE FLOATING EXPOSURE AT
SEATTLE, WA
45 DAYS: 6/19/90-8/3/90

Figure 4.1.11 (d) Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6P - 45 days).

6-PACK CONTROL
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
42 DAYS: 6/19/90-7/31/90

Figure 4.1.11 (c) Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6PC - 42 days).

6-PACK CONTROL
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
52 DAYS: 6/19/90-8/10/90

Figure 4.1.11 (f)   Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6PC - 52 days).

6-PACK RINGS
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
52 DAYS: 6/19/90-8/10/90

Figure 4.1.11 (e)   Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA - (6P - 52 days).

**6-PACK RINGS
MARINE FLOATING EXPOSURE
AT SEATTLE, WA
59 DAYS: 6/19/90-8/17/90**

Figure 4.1.11 (g)   Marine floating exposure of LDPE control and (ethylene-carbon monoxide) copolymer in Seattle, WA.- (6P - 59 days).

PG - PLASTIGONE
MARINE FLOATING EXPOSURE AT
MIAMI, FL
39 DAYS: 6/1/90-7/10/90
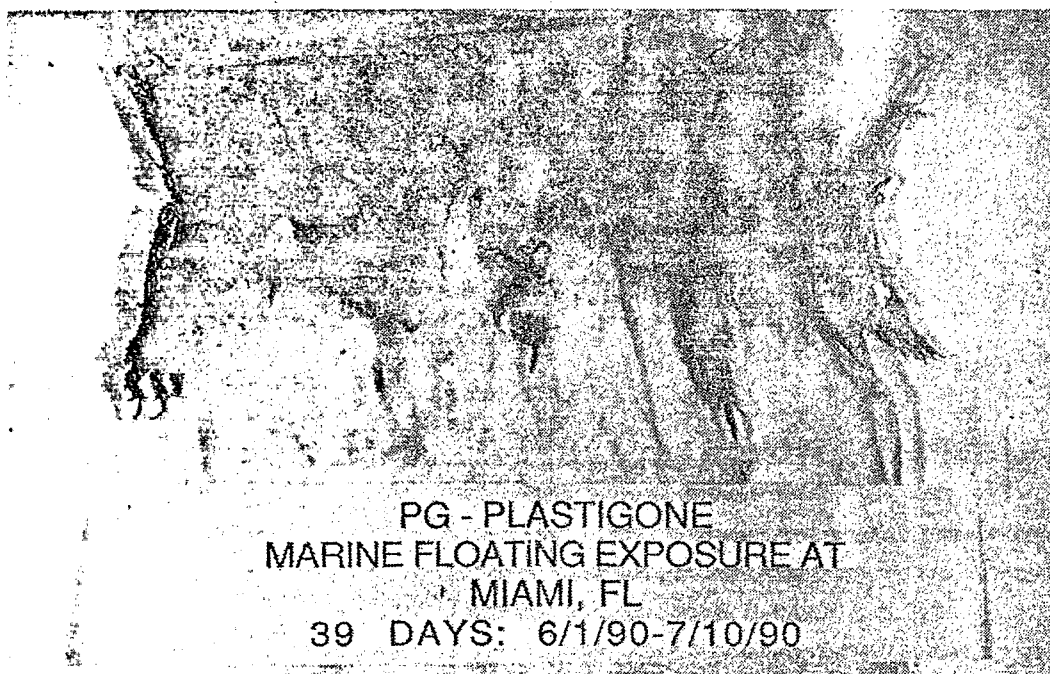
Figure 4.1.12 (a) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PG - 39 days).
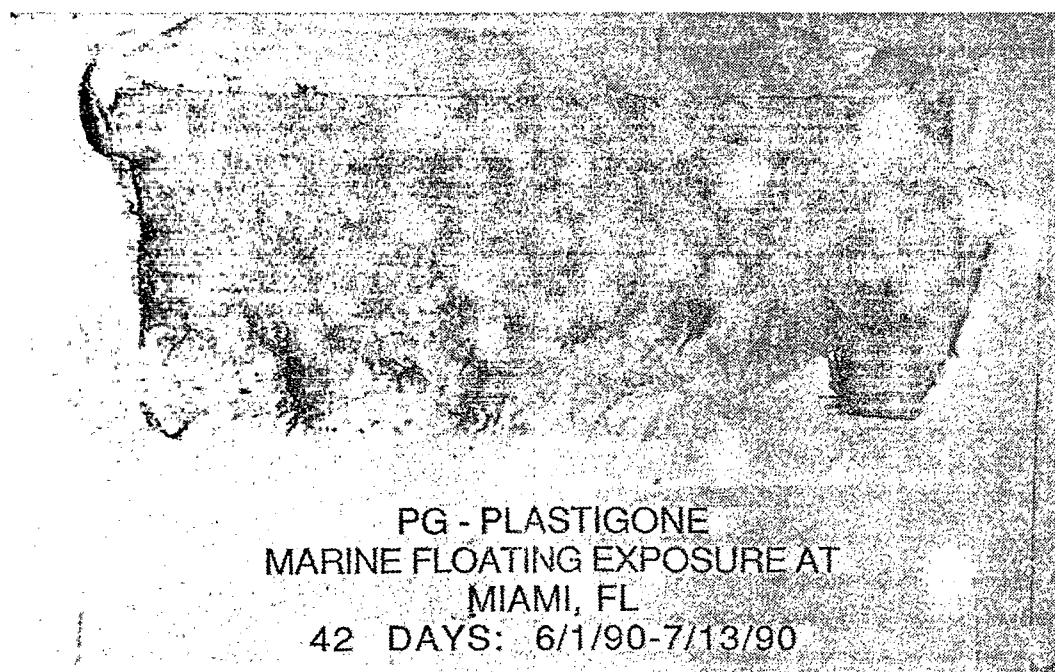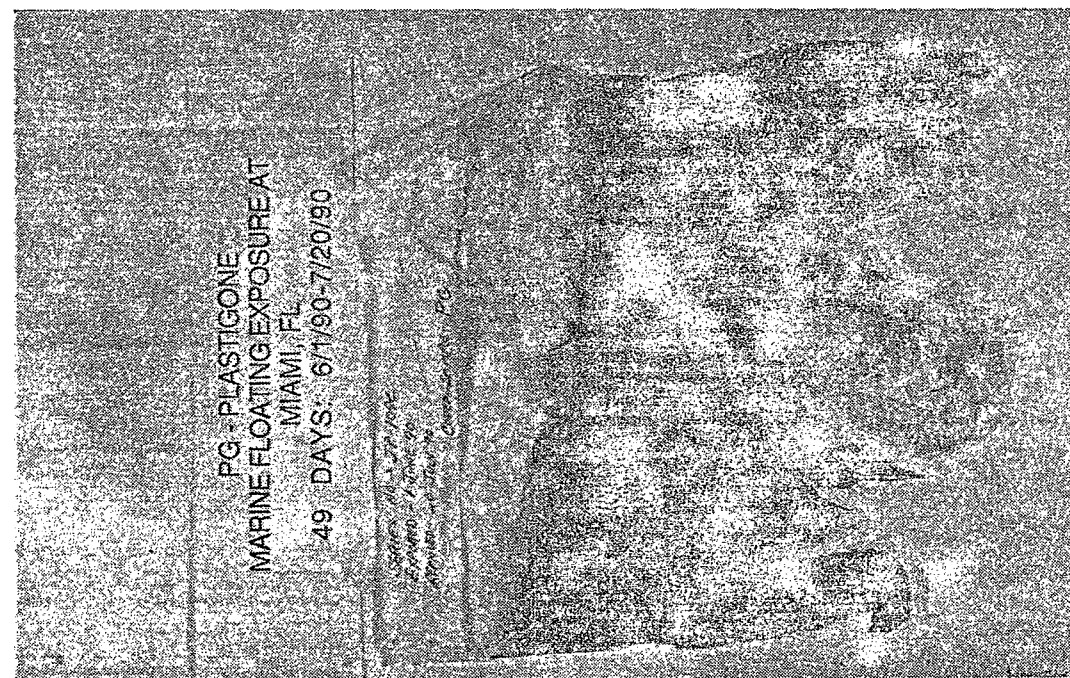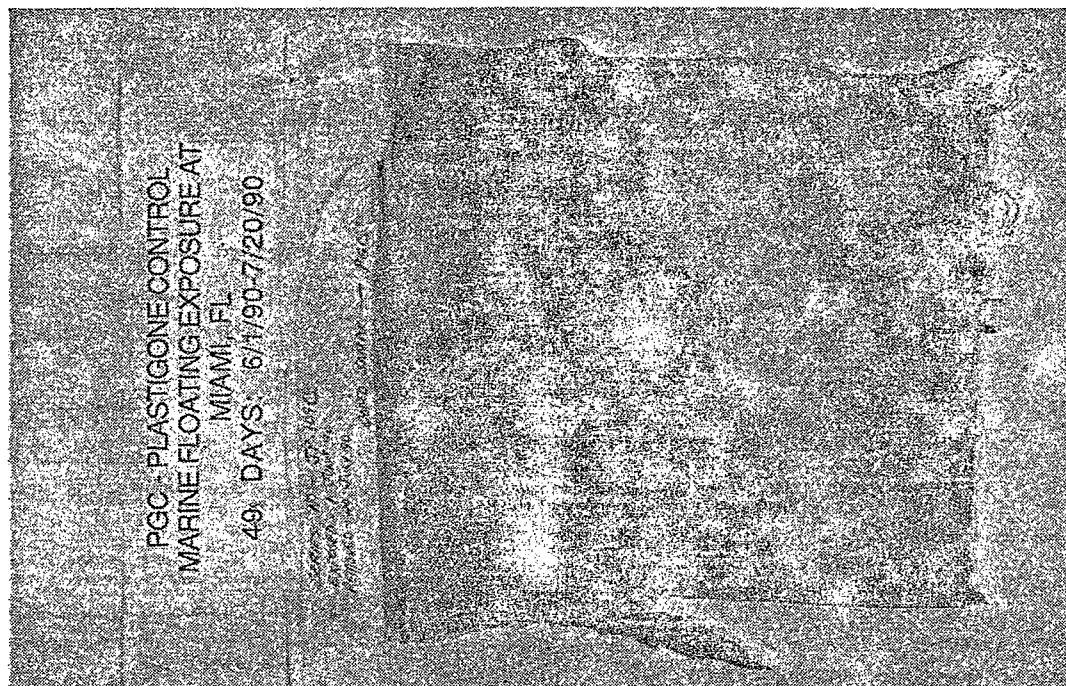

PG - PLASTIGONE
MARINE FLOATING EXPOSURE AT
MIAMI, FL
42 DAYS: 6/1/90-7/13/90

Figure 4.1.12 (b) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PG - 42 days).
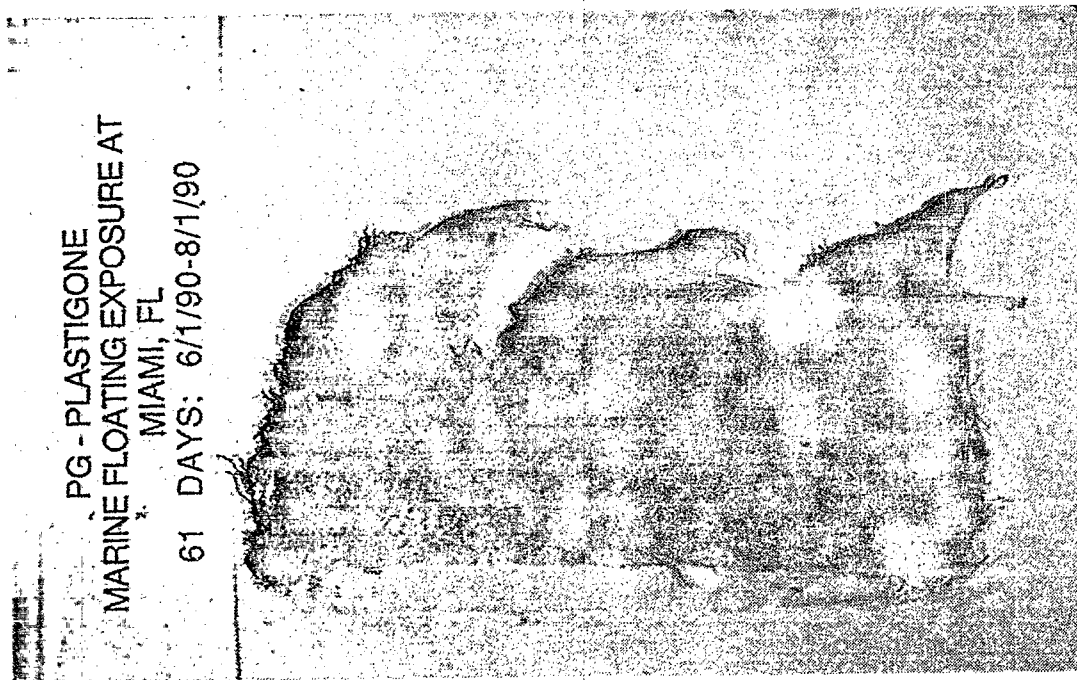
PGC - PLASTIGONE CONTROL
MARINE FLOATING EXPOSURE AT
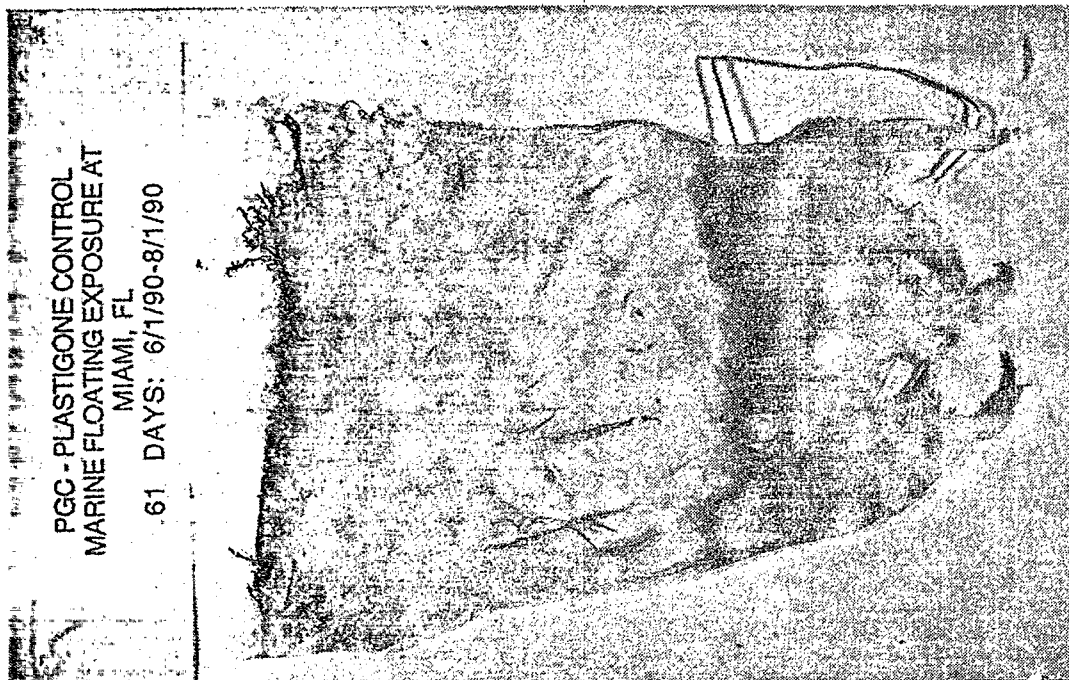MIAMI, FL
49 DAYS 6/1/90-7/20/90

Figure 4.1.12 (d) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PGC - 49 days).

PG - PLASTIGONE
MARINE FLOATING EXPOSURE AT
MIAMI, FL
49 DAYS: 6/1/90-7/20/90

Figure 4.1.12 (c) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PG - 49 days).

PGC - PLASTIGONE CONTROL
MARINE FLOATING EXPOSURE AT
MIAMI, FL
61 DAYS: 6/1/90-8/1/90

Figure 4.1.12 (f) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PGC - 61 days).

PG - PLASTIGONE
MARINE FLOATING EXPOSURE AT
MIAMI, FL
61 DAYS: 6/1/90-8/1/90

Figure 4.1.12 (e) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PG - 61 days).

Figure 4.1.12 (g)   Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Miami, FL - (PG - 68 days).
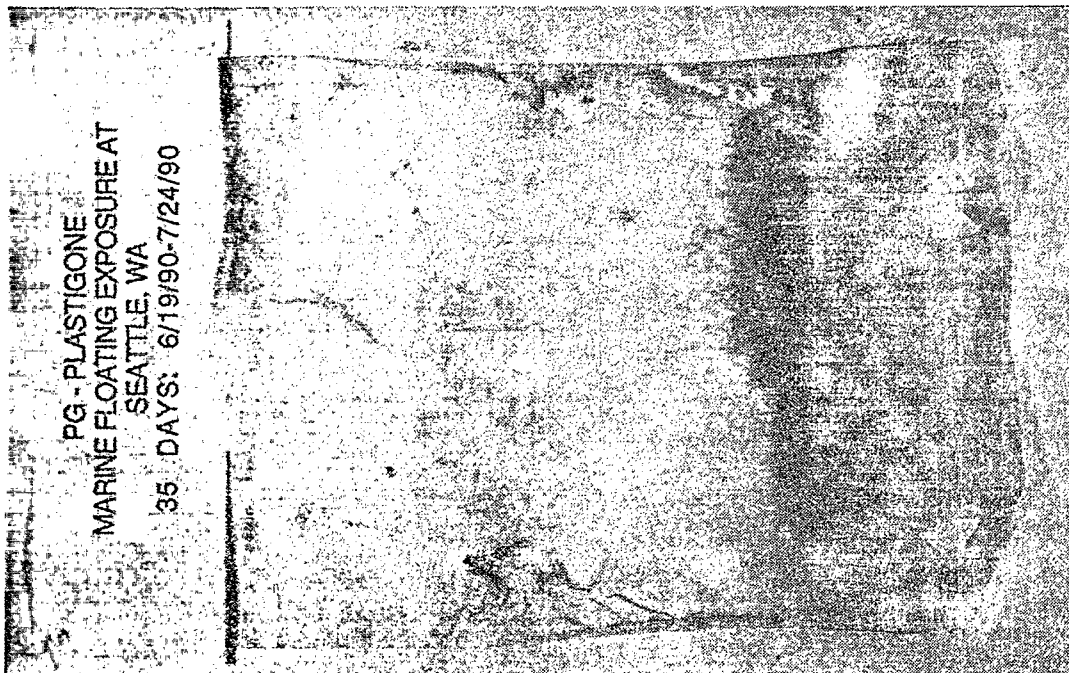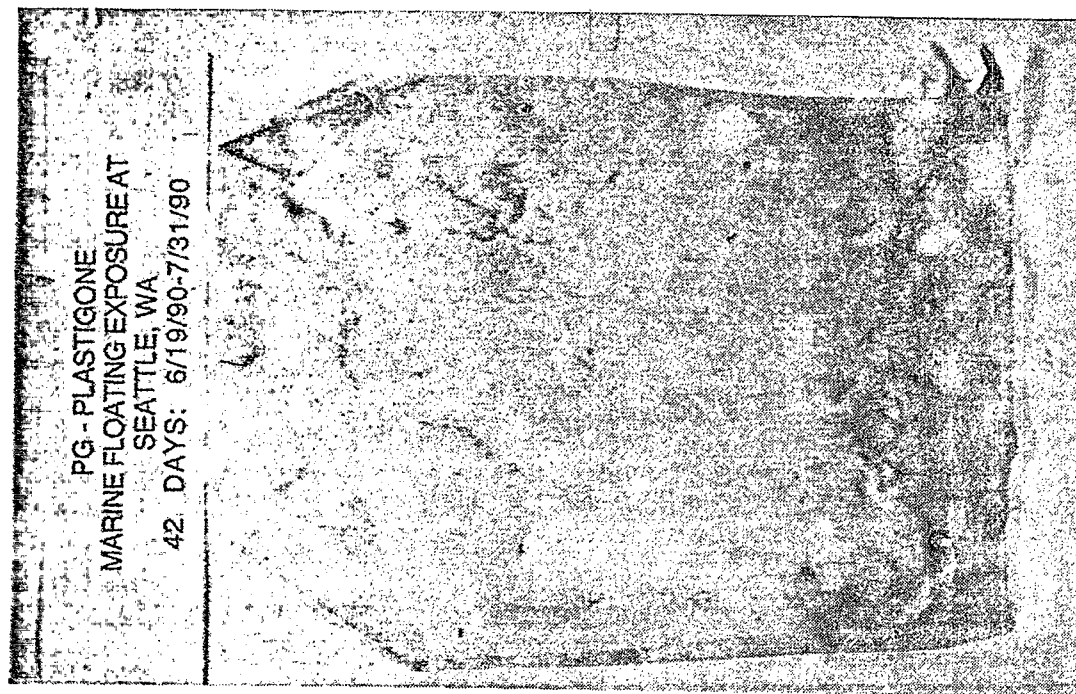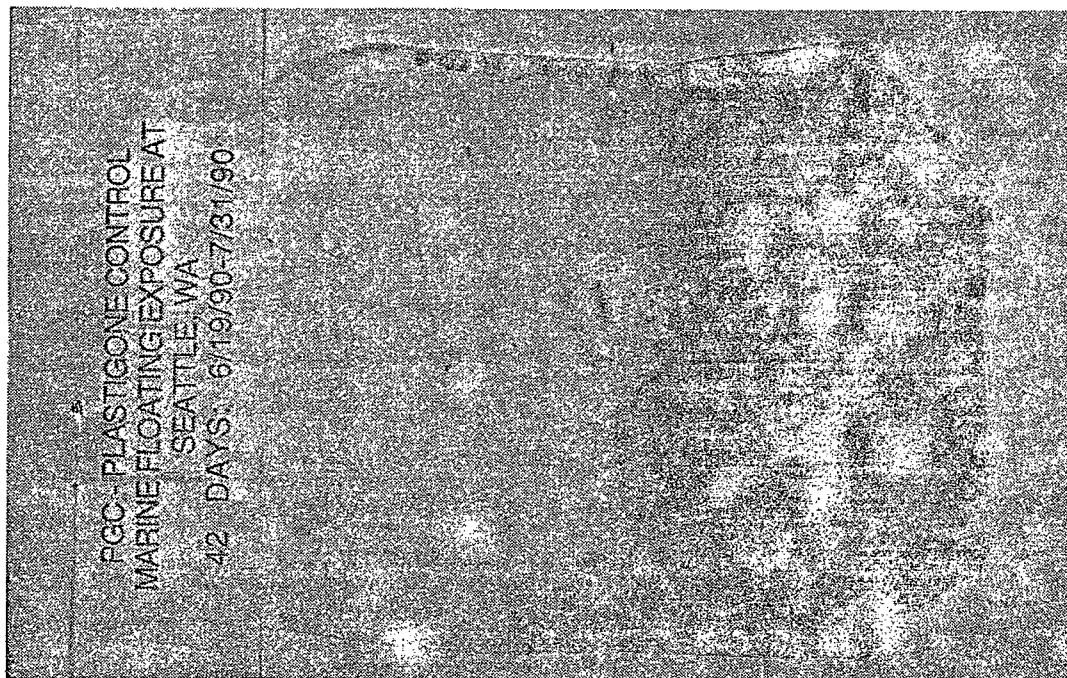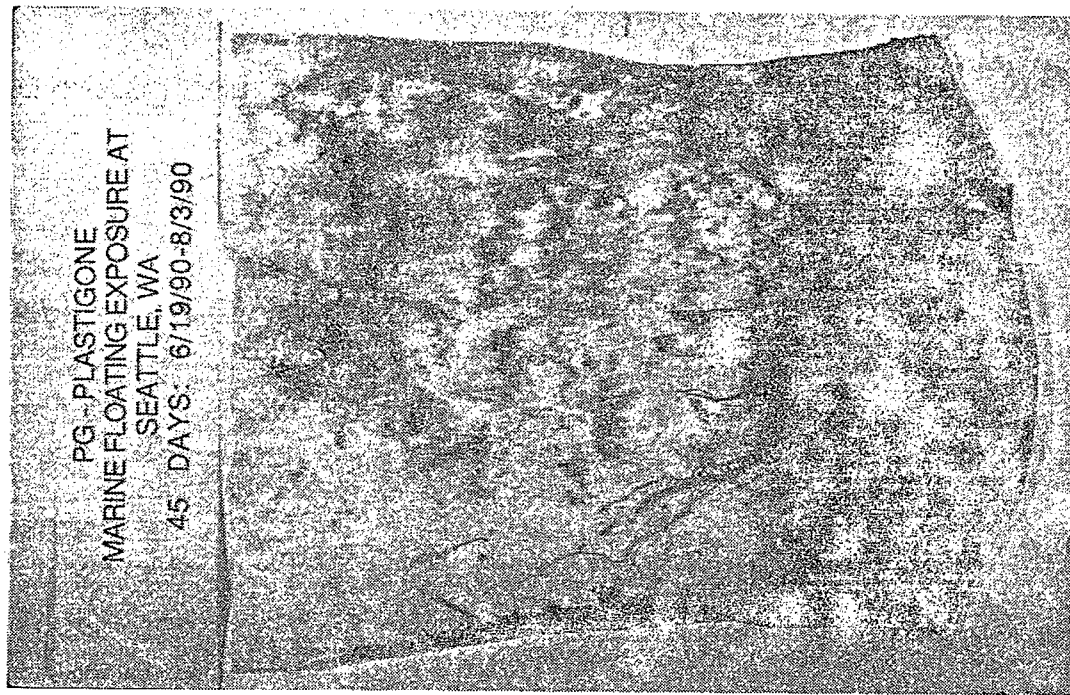
Figure 4.1.13 (b) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PG - 42 days).

Figure 4.1.13 (a) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PG - 35 days).

PG- PLASTIGONE
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
45 DAYS: 6/19/90-8/3/90

Figure 4.1.13 (d) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PG - 45 days).

PGC- PLASTIGONE CONTROL
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
42 DAYS: 6/19/90-7/31/90

Figure 4.1.13 (c) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PGC - 42 days).

PGC - PLASTIGONE CONTROL
MARINE FLOATING EXPOSURE AT
SEATTLE, WA
52 DAYS: 6/19/90-8/10/90

Figure 4.1.13 (f) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PGC - 52 days).

PG - PLASTIGONE
MARINE FLOATING EXPOSURE AT
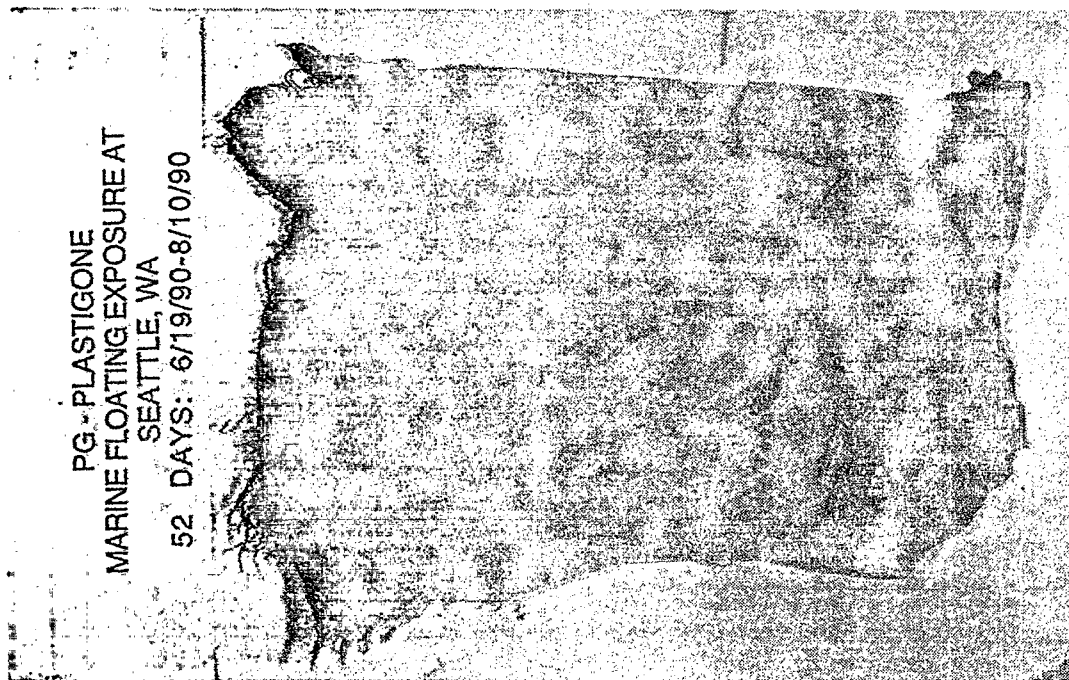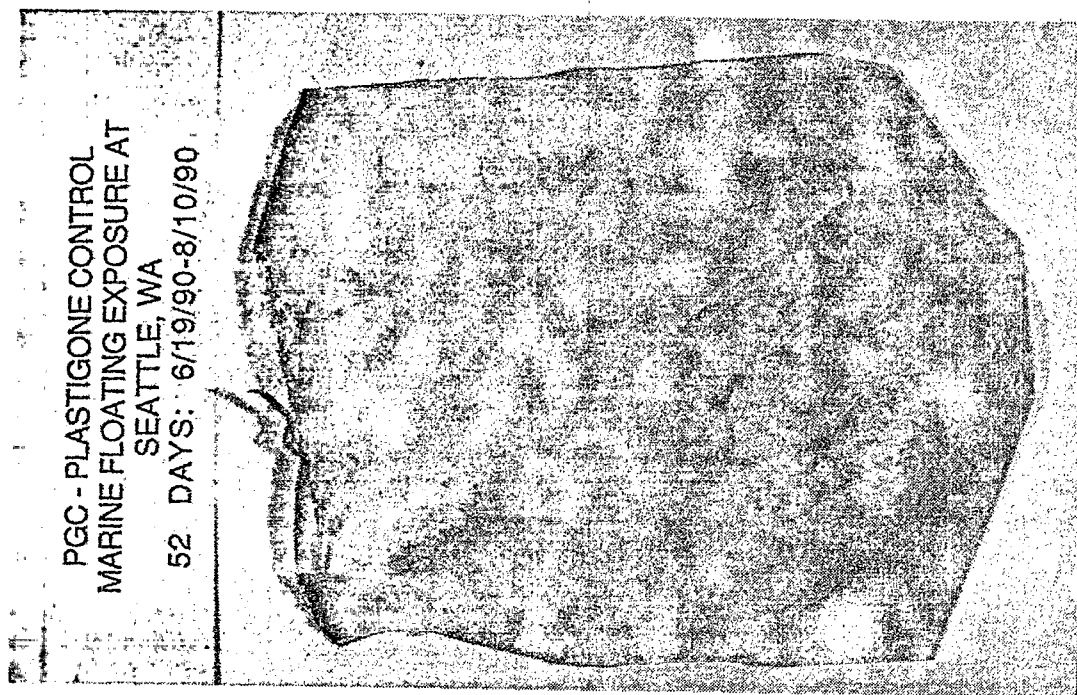SEATTLE, WA
52 DAYS: 6/19/90-8/10/90

Figure 4.1.13 (e) Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PG - 52 days).
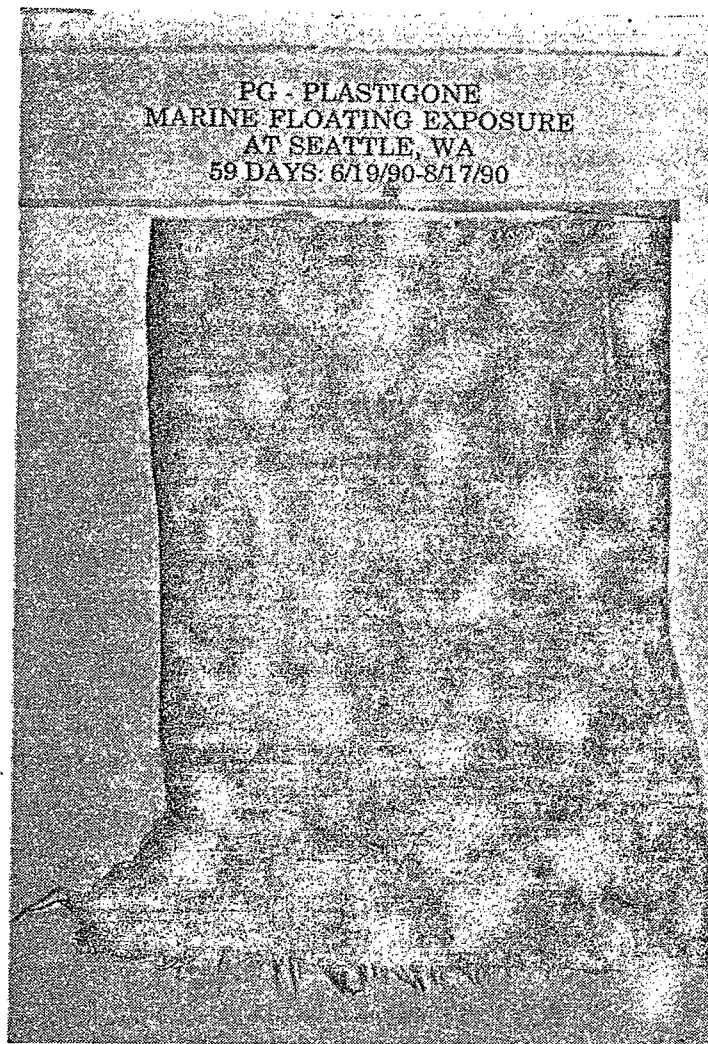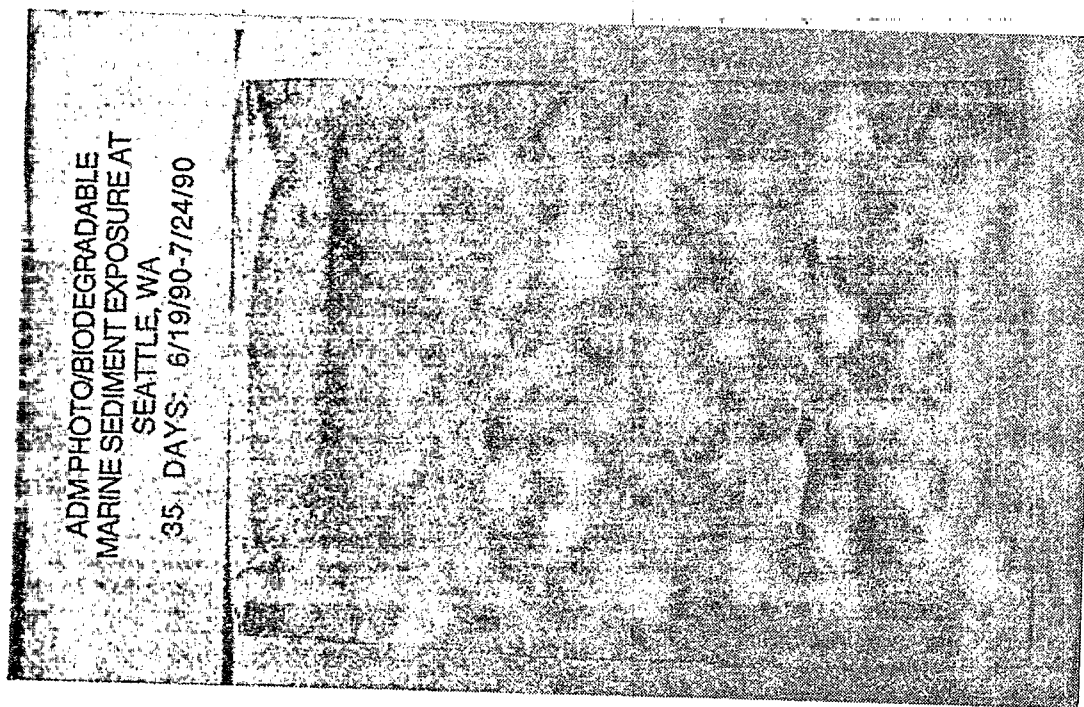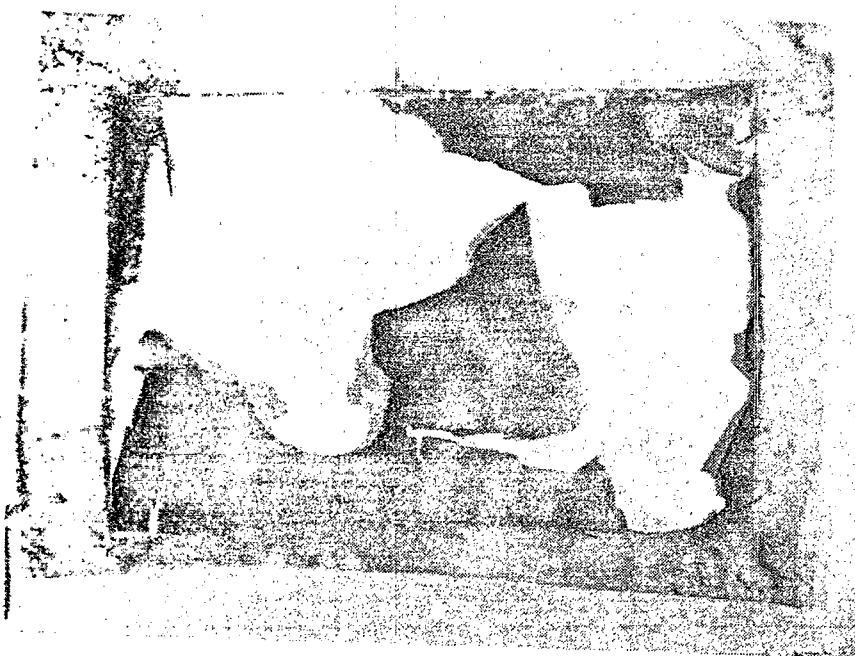
Figure 4.1.13 (g)   Marine floating exposure of LDPE control and Plastigone (LDPE/MX) material in Seattle, WA - (PG - 59 days).

ADM PHOTO/BIODEGRADABLE
MARINE BOTTOM EXPOSURE AT
SEATTLE, WA
42 DAYS: 6/19/90-7/31/90

ADM PHOTO/BIODEGRADABLE
MARINE SEDIMENT EXPOSURE AT
SEATTLE, WA
35 DAYS: 6/19/90-7/24/90

Figure 4.1.14 (b) Marine sediment exposure of LDPE control and ADM (LDPE/starch/MX) material in Seattle, WA - (ADM - 42 days).

Figure 4.1.14 (a) Marine sediment exposure of LDPE control and ADM (LDPE/starch/MX) material in Seattle, WA - (ADM - 35 days).

ADM PHOTO/BIODEGRADABLE
MARINE BOTTOM EXPOSURE AT
SEATTLE, WA
59 DAYS:6/19/90-8/17/90

Figure 4.1.14 (d) Marine sediment exposure of LDPE control and ADM (LDPE/starch/MX) material in Seattle, WA - (ADM - 59 days).

ADMC ADM CONTROL
MARINE BOTTOM EXPOSURE AT
SEATTLE, WA
42 DAYS: 6/19/90-7/31/90

Figure 4.1.14 (c) Marine sediment exposure of LDPE control and ADM (LDPE/starch/MX) material in Seattle, WA - (ADMC - 42 days).
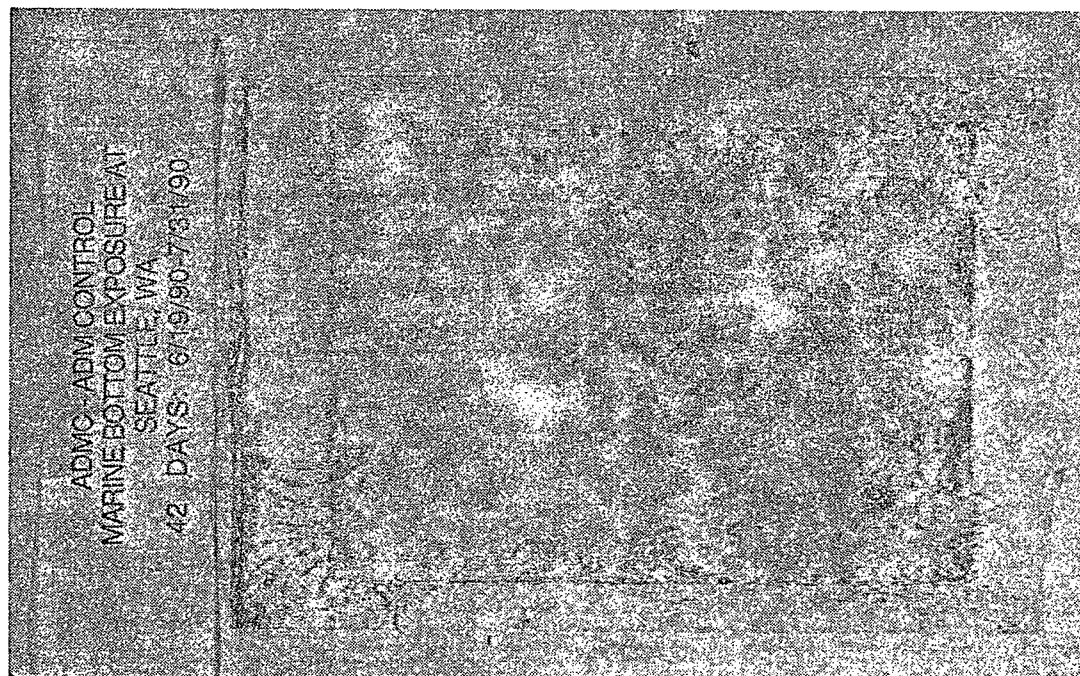
PS-POLYSTYRENE FOAM
MARINE FLOATING EXPOSURE
AT SEATTLE, WA
14 DAYS: 8/3/90-8/17/90

PSC-POLYSTYRENE FOAM
CONTROL
MARINE FLOATING EXPOSURE
AT SEATTLE, WA
14 DAYS: 8/3/90-8/17/90

Figure 4.1.15 (a)   Marine floating exposure of polystyrene foam and photodegradable polystyrene foam in Seattle, WA - (PS - 14 days).
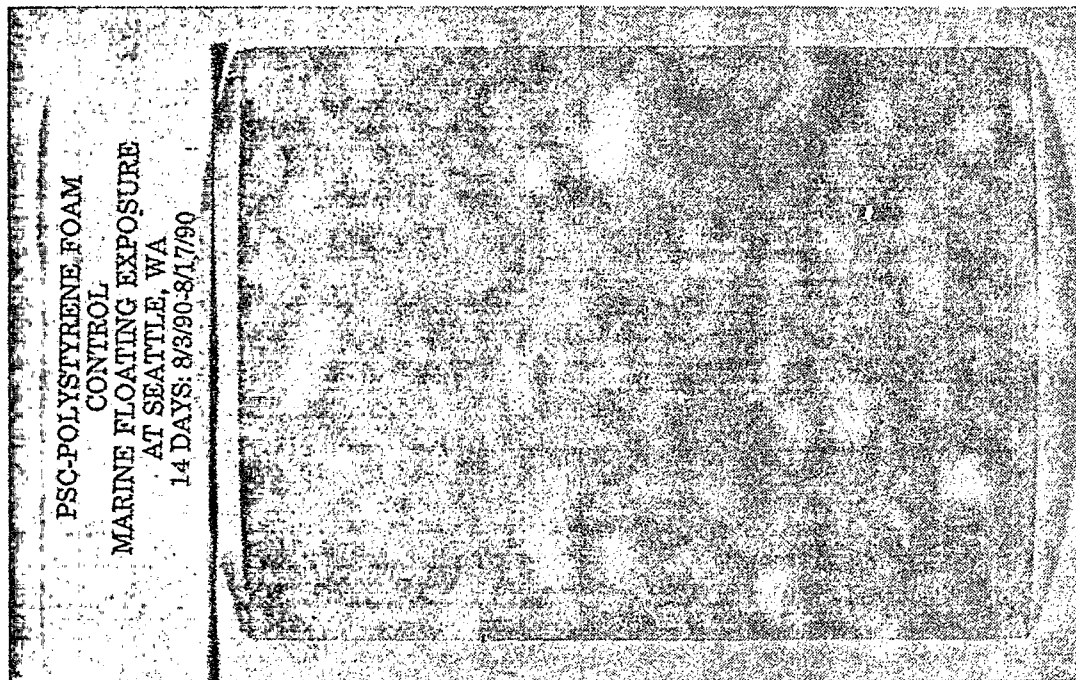
Figure 4.1.15 (b)   Marine floating exposure of polystyrene foam and photodegradable polystyrene foam in Seattle, WA - (PSC - 14 days).

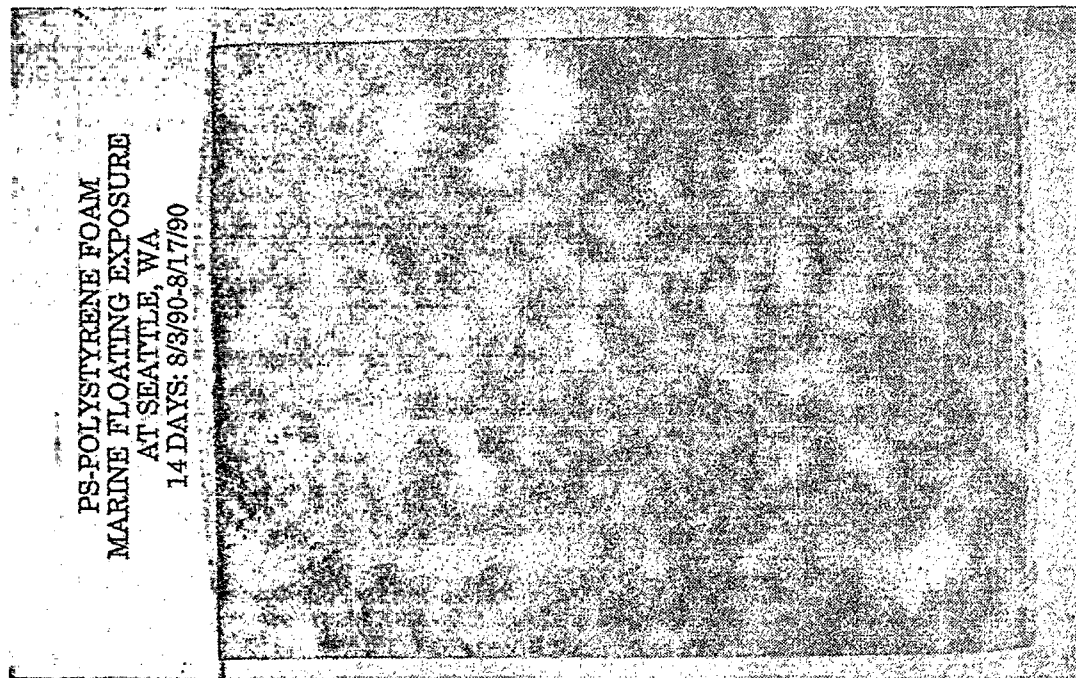$$y = 41.102 + 14.456x \quad R^2 = 0.996$$

Figure 4.1.16 (a)   Total solar radiation (45° south) versus the duration of exposure - (Cedar Knolls, NJ).

Total Global: y = - 8.1630 + 16.511x   R^2 = 0.998

TUVR: y = 2.0811 + 0.62485x   R^2 = 0.994
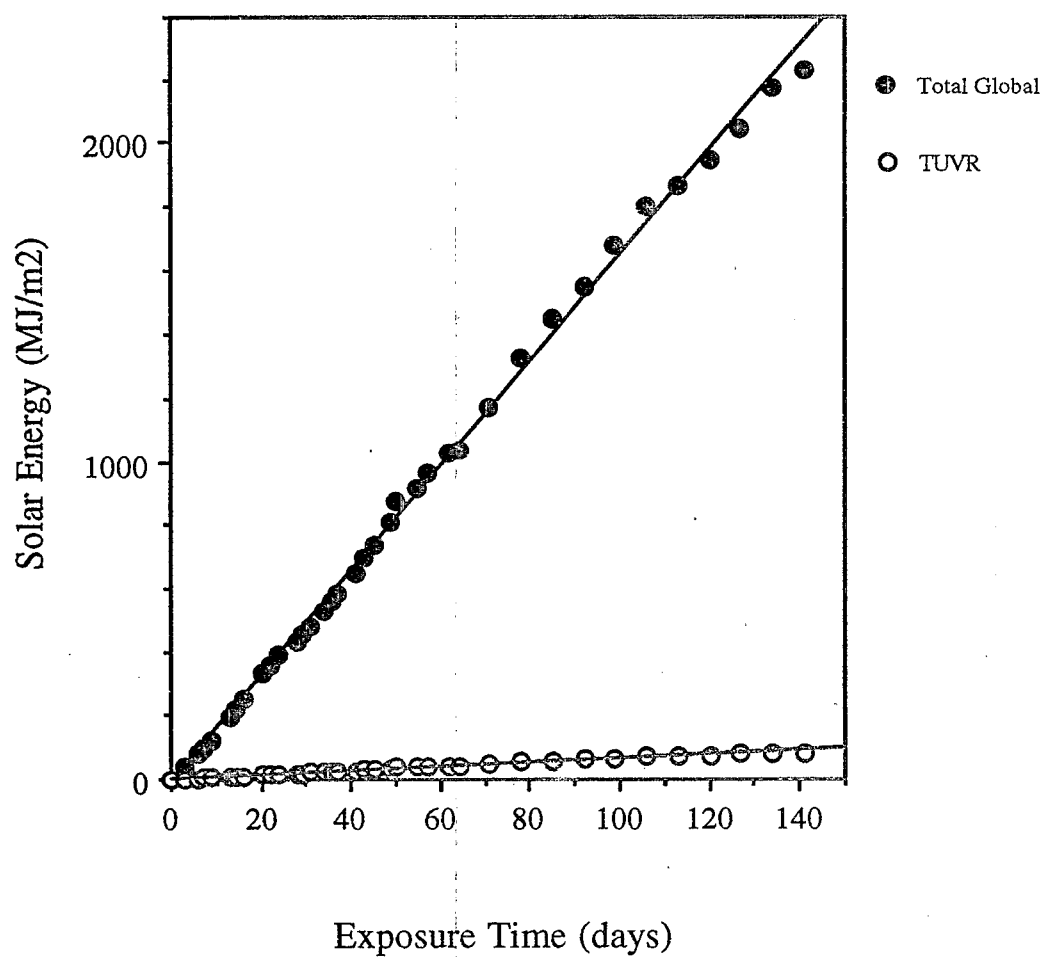
Figure 4.1.16 (b)   Total solar radiation (45° south) versus the duration of exposure -
(Chicago, IL).
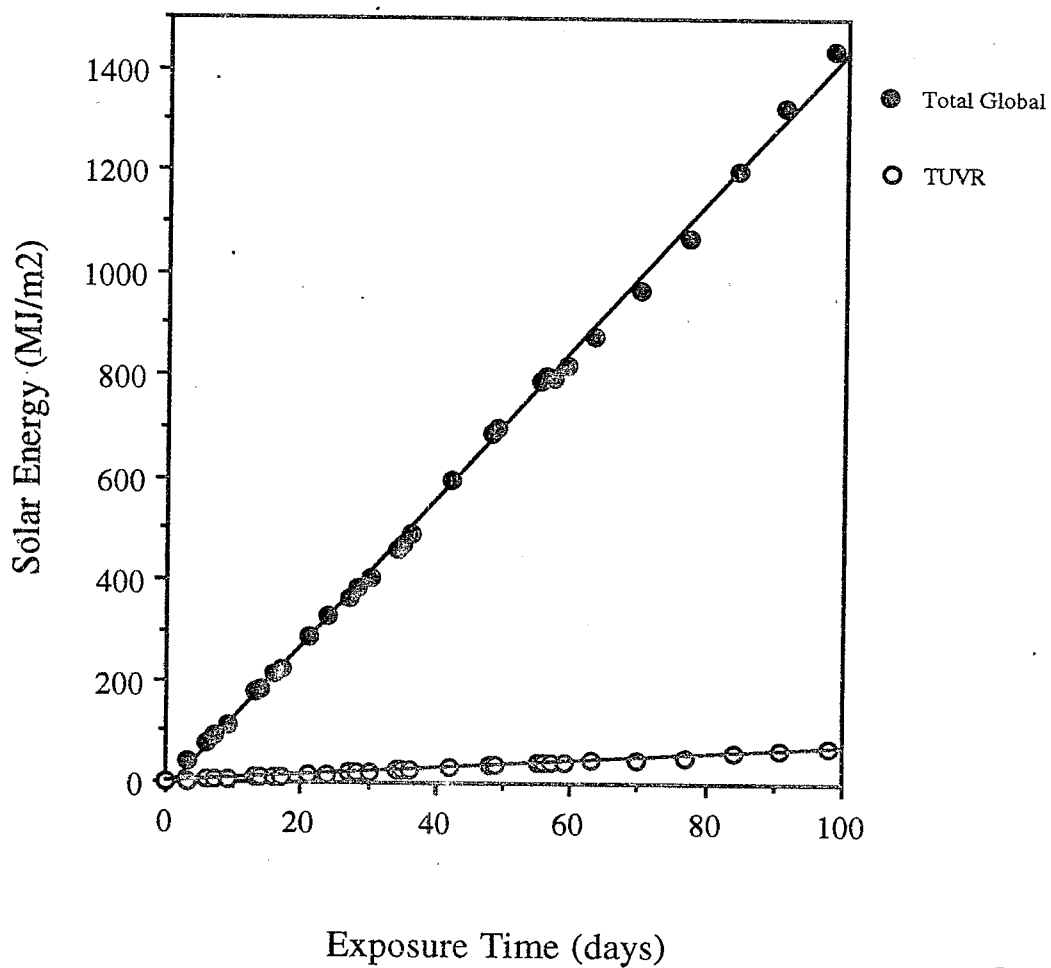
Total Global: y = - 19.254 + 14.498x   R^2 = 0.999

TUVR: y = - 0.42290 + 0.70222x   R^2 = 0.999

Figure 4.1.16 (c)   Total solar radiation (45° south) versus the duration of exposure - (Miami, FL).

Figure 1.16 (d) Total solar radiation (45° south) versus the duration of exposure - (Seattle, WA).

$y = 25.129 + 18.273x$ $R^2 = 0.993$

Total Global: y = - 18.727 + 21.855x   R^2 = 0.998
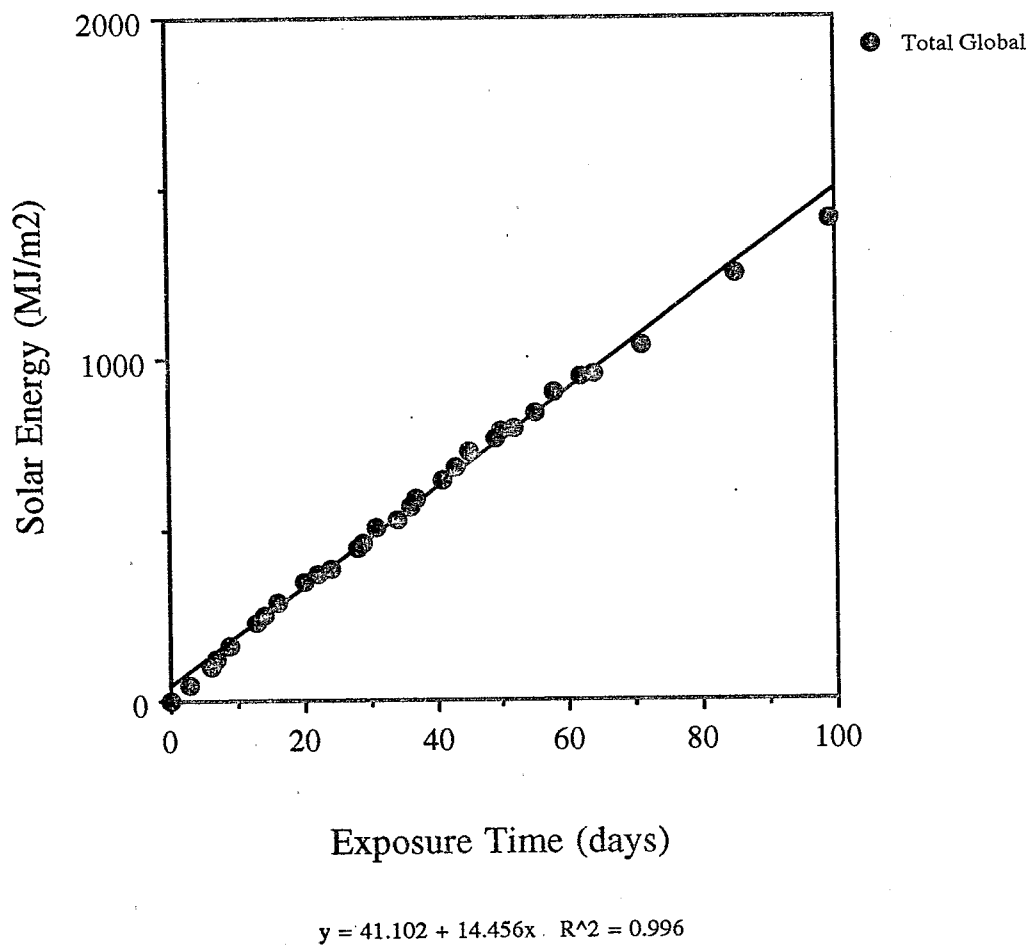
TUVR: y = 0.49238 + 0.97707x   R^2 = 0.999

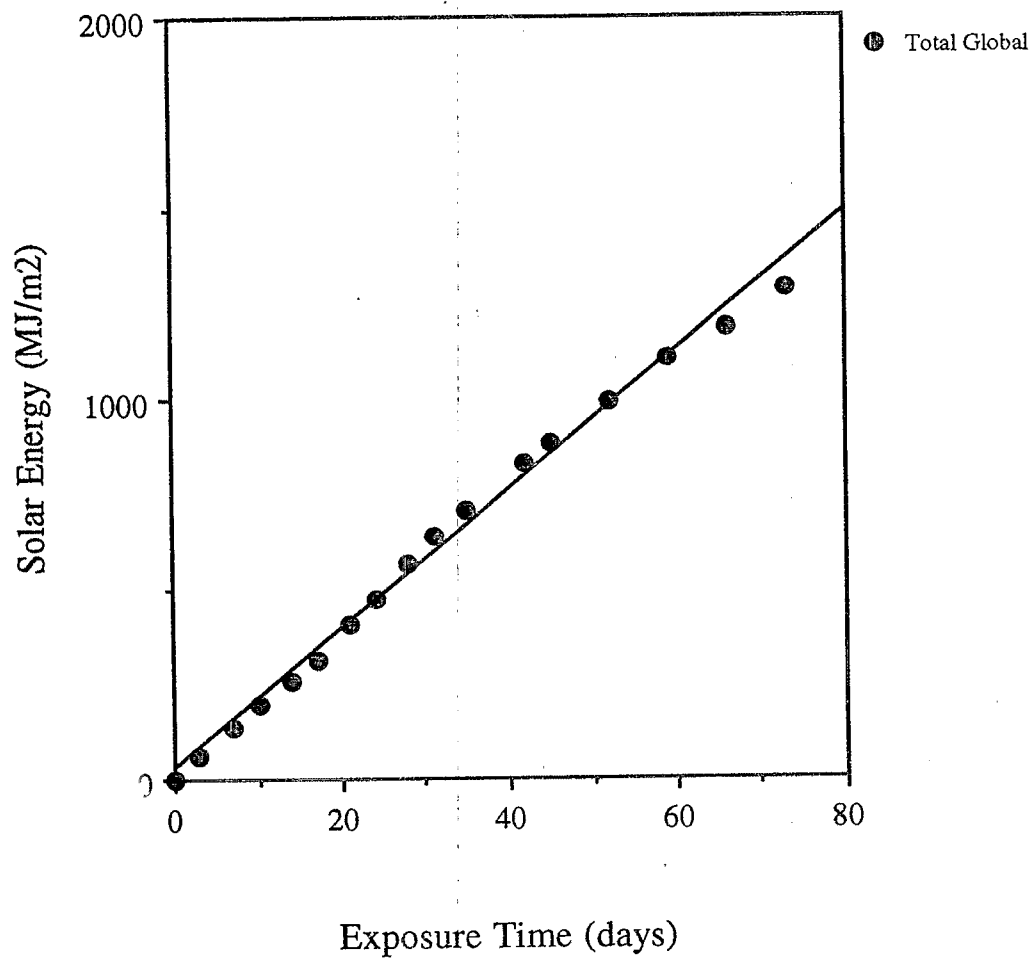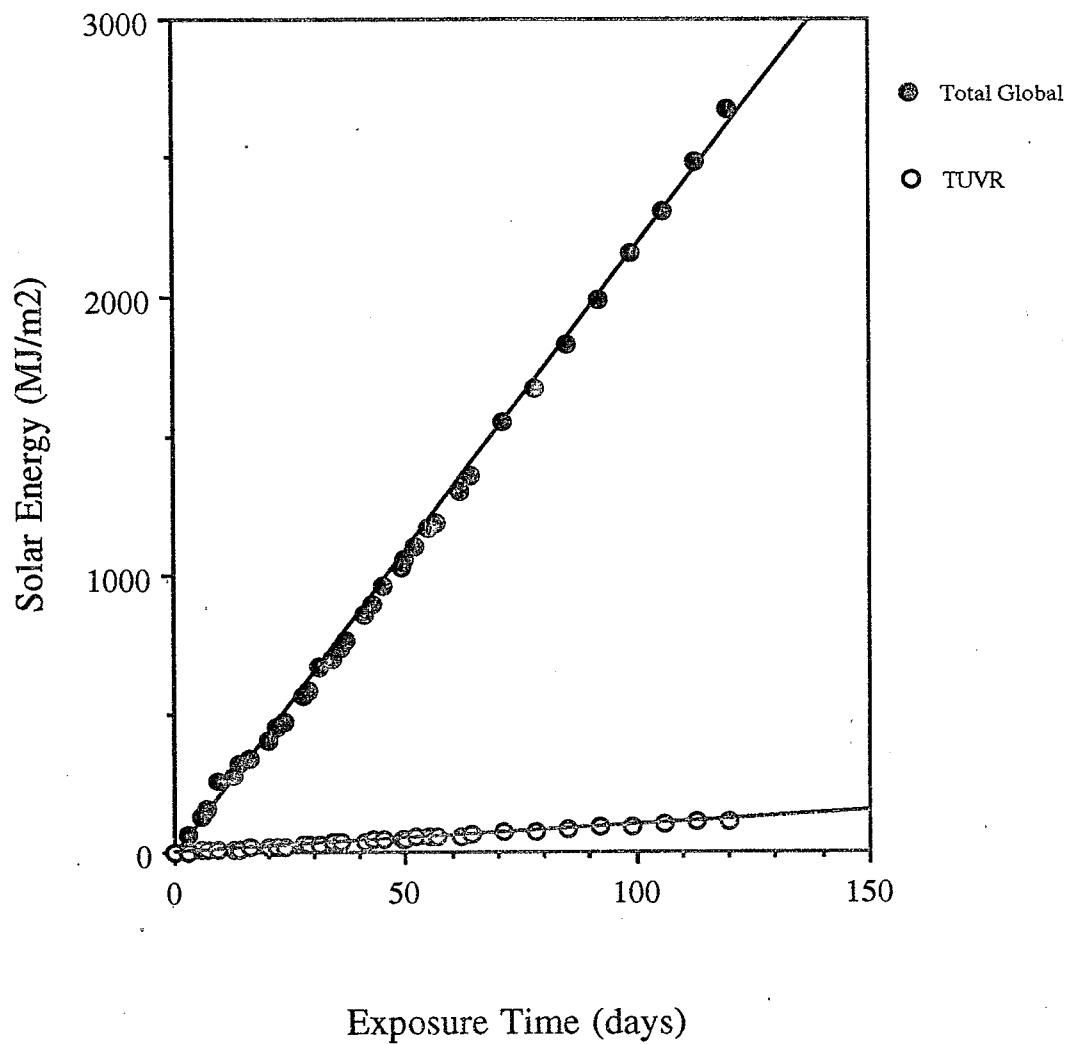Figure 4.1.16 (e)   Total solar radiation (45° south) versus the duration of exposure -
(Wittmann, AZ).
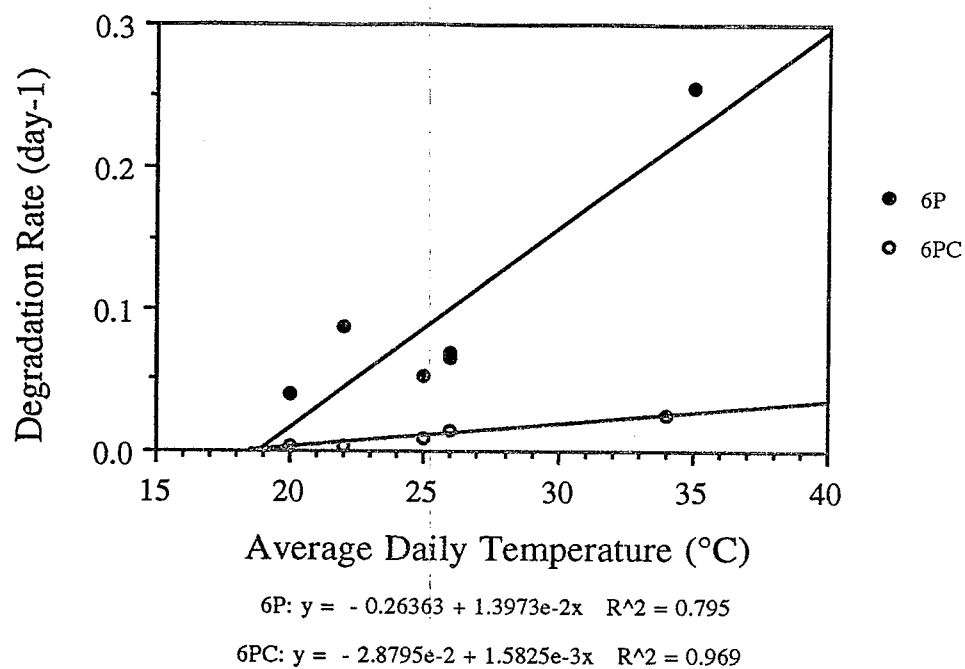
Figure 4.1.17 (a) Degradation rate versus the average temperature and average solar radiation at exposure site - ([Ethylene-carbon monoxide] copolymer).

PG: y = - 5.2742e-2 + 4.6752e-3x   R^2 = 0.842

PGC: y = - 1.7802e-2 + 1.4136e-3x   R^2 = 0.699

PG: y = - 1.6167e-2 + 4.6426e-3x   R^2 = 0.708

PGC: y = - 1.2776e-2 + 1.8805e-3x   R^2 = 0.345
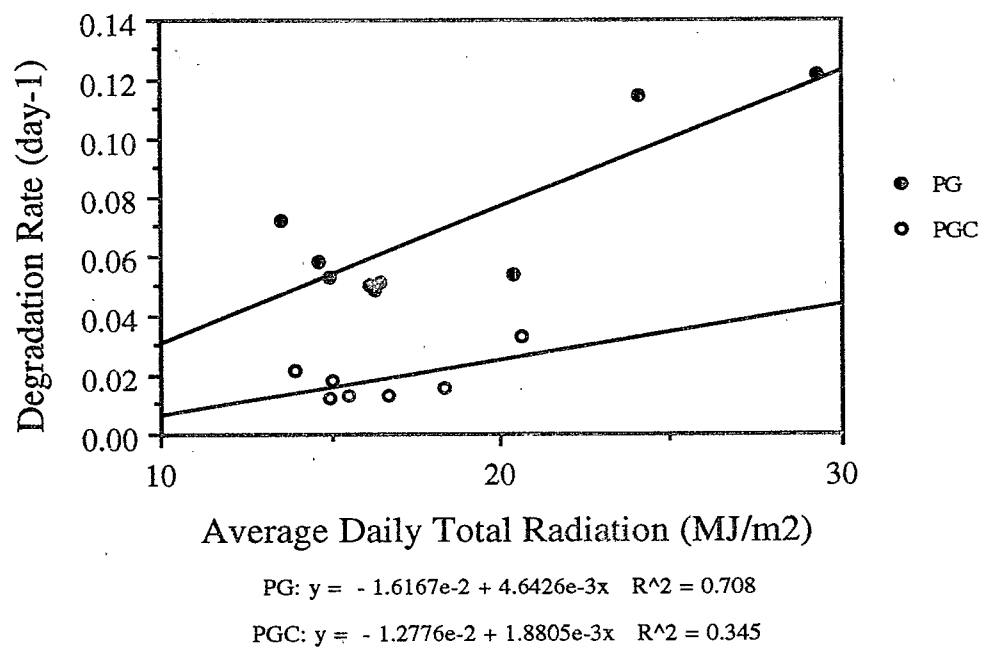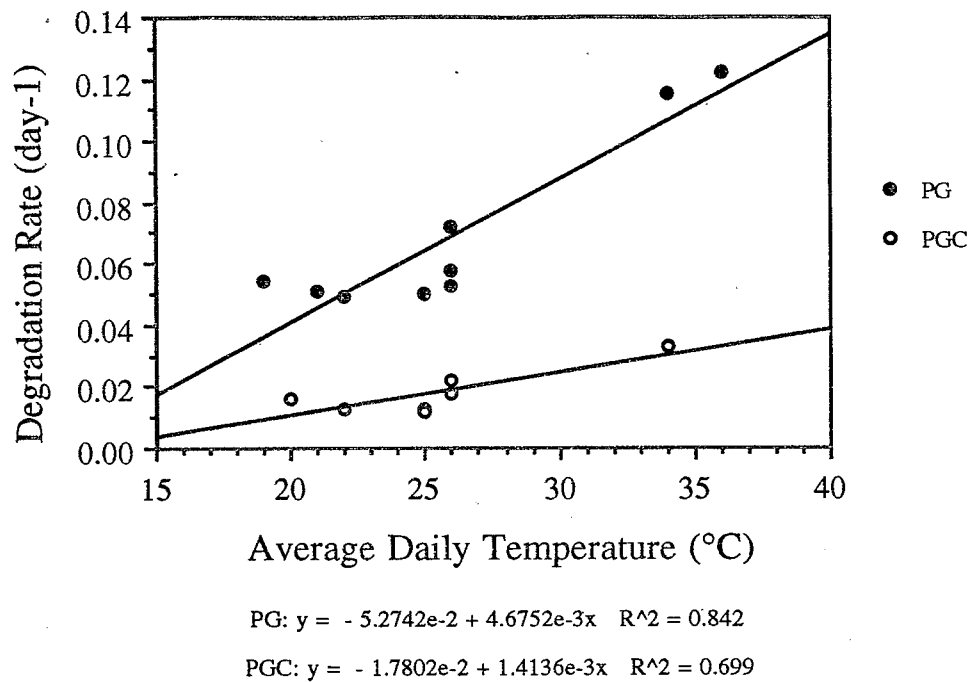
Figure 4.1.17 (b)   Degradation rate versus the average temperature and average solar radiation at exposure site - (Plastigone [LDPE//MX] film).
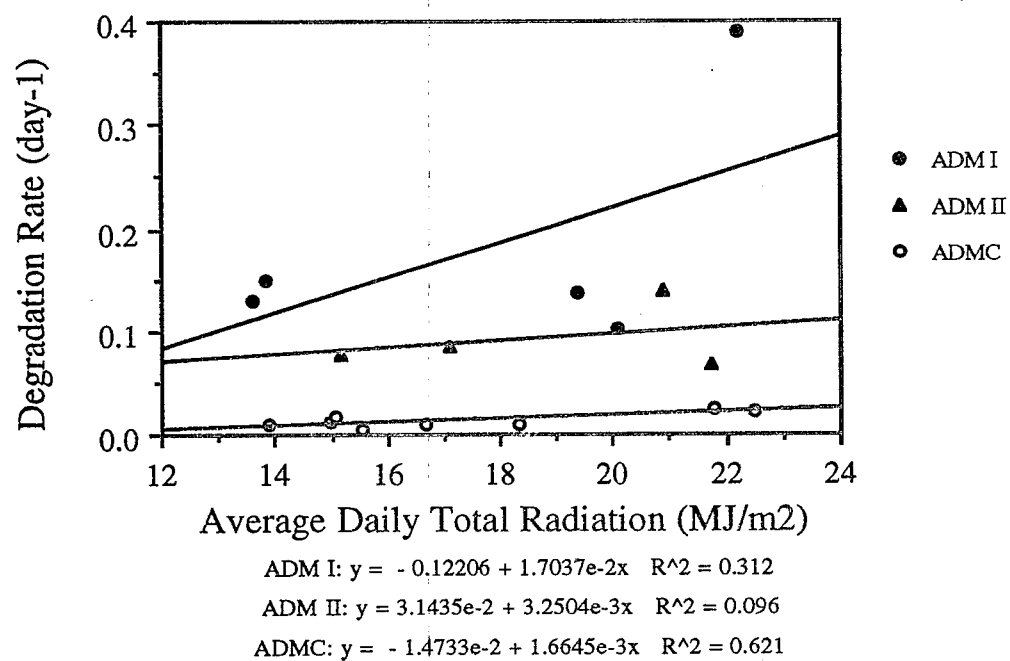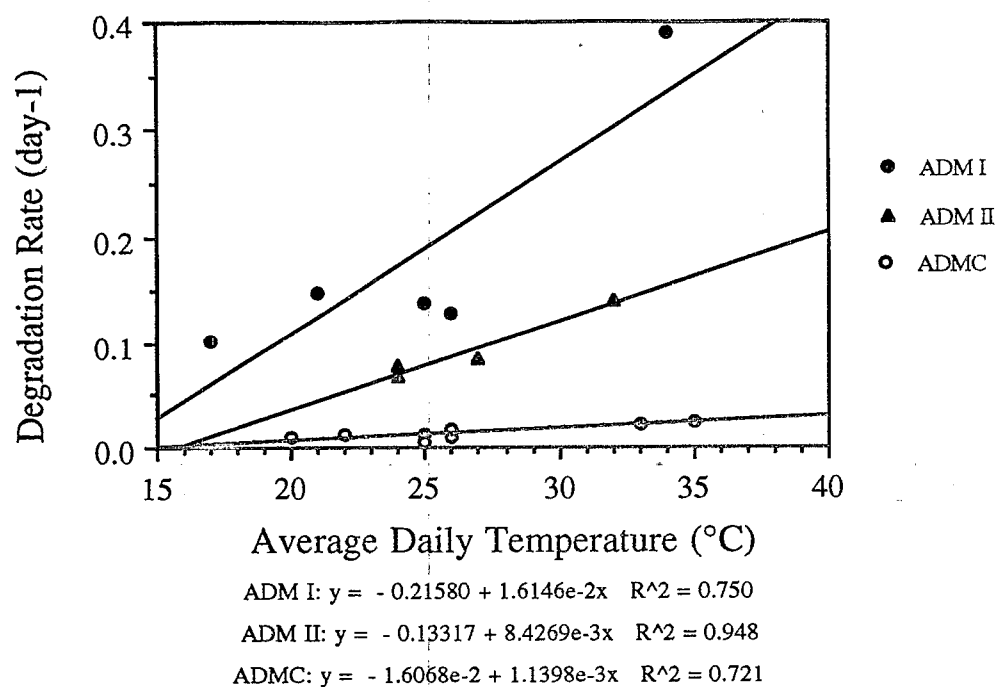
Figure 4.1.17 (c)   Degradation rate versus the average temperature and average solar radiation at exposure site - (ADM [LDPE/Starch/MX] film).

PS: y = 4.4024e-4 + 1.1778e-4x   R^2 = 0.409

PSC: y = 1.1392e-3 + 4.9866e-5x   R^2 = 0.120

PS: y = 2.5149e-3 + 5.1942e-5x   R^2 = 0.051

PSC: y = 2.1411e-3 + 8.7154e-6x   R^2 = 0.002
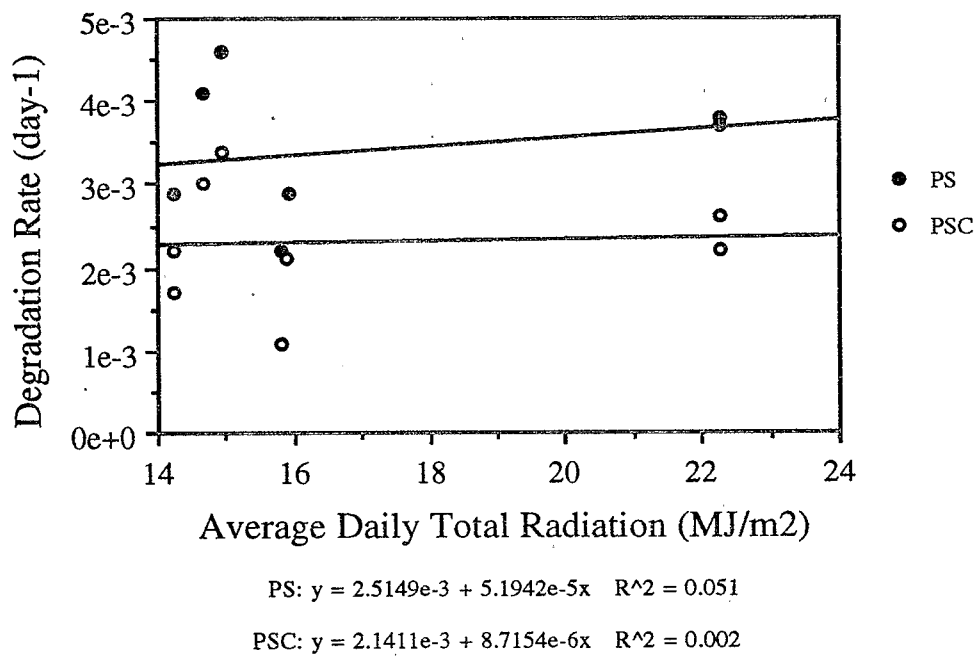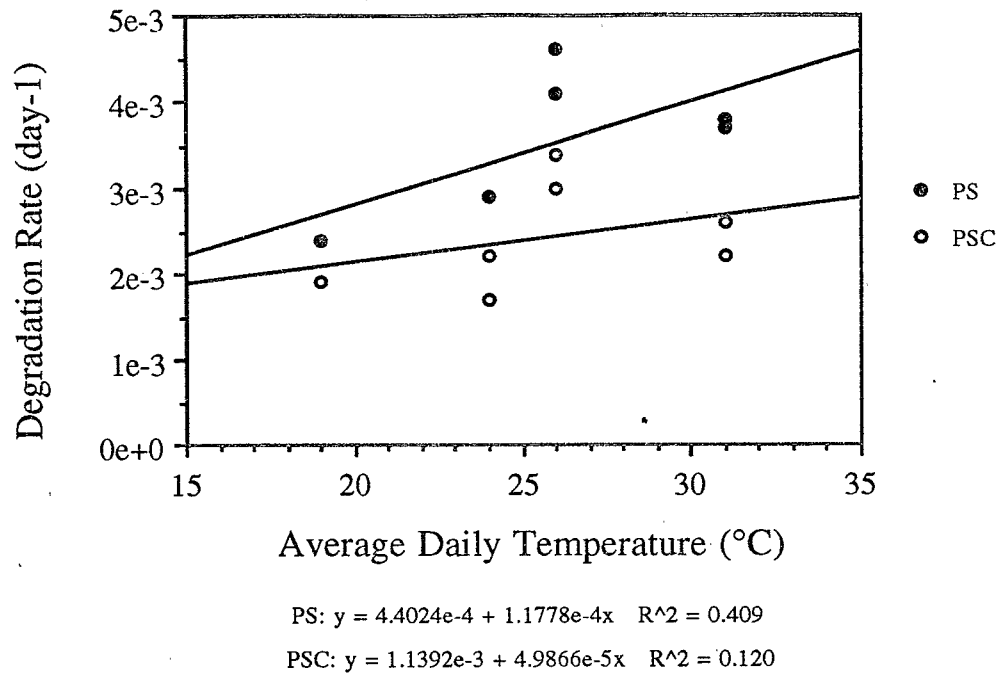
Figure 4.1.17 (d)   Degradation rate versus the average temperature and average solar radiation at exposure site - (Expanded polystyrene foam [Polysar material]).

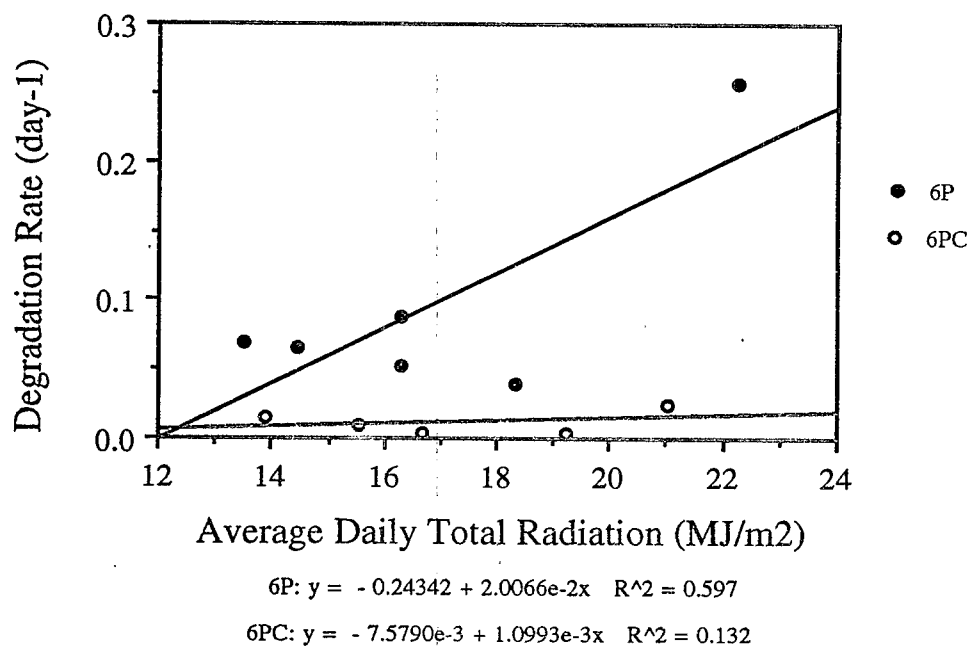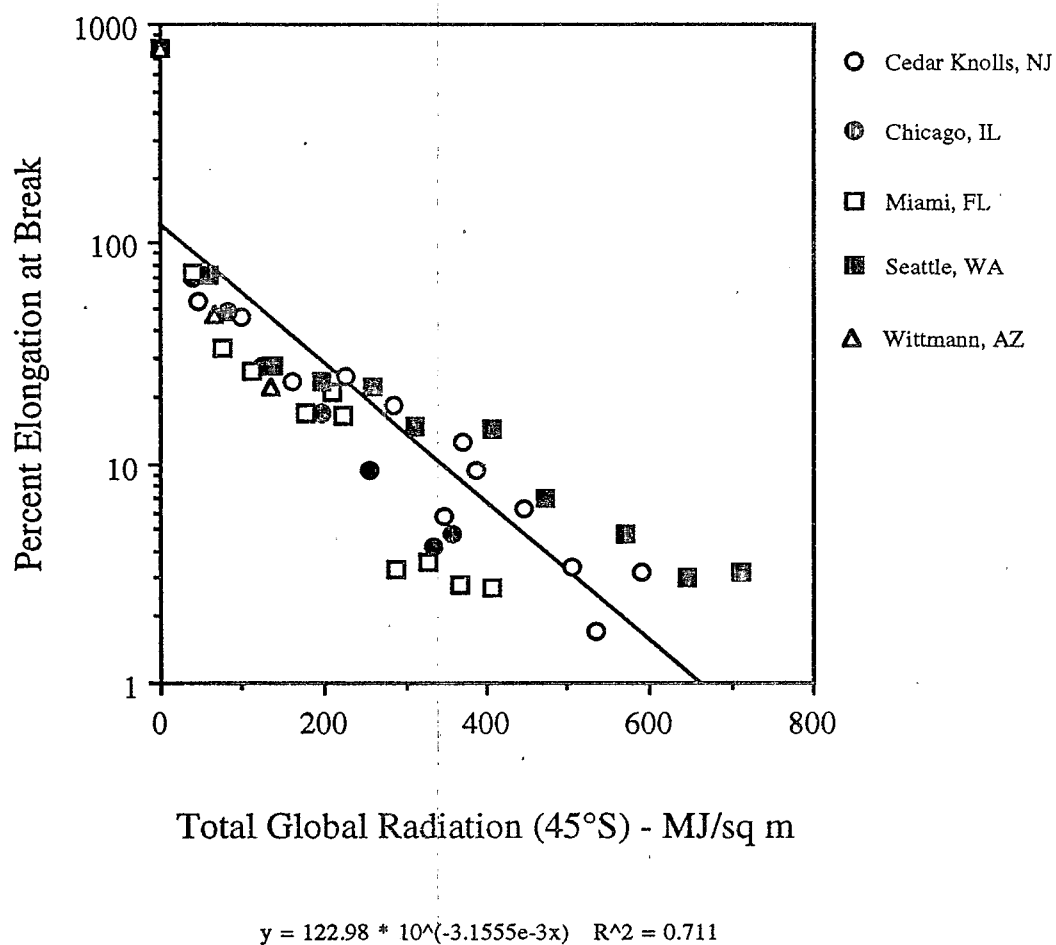Figure 4.1.18 (a)   Semi-logarithmic plot of elongation at break versus the total radiation at
exposure site: composite data for all outdoor locations ([Ethylene-carbon
monoxide] copolymer).

y = 751.61 * 10^(-3.0182e-3x)   R^2 = 0.717
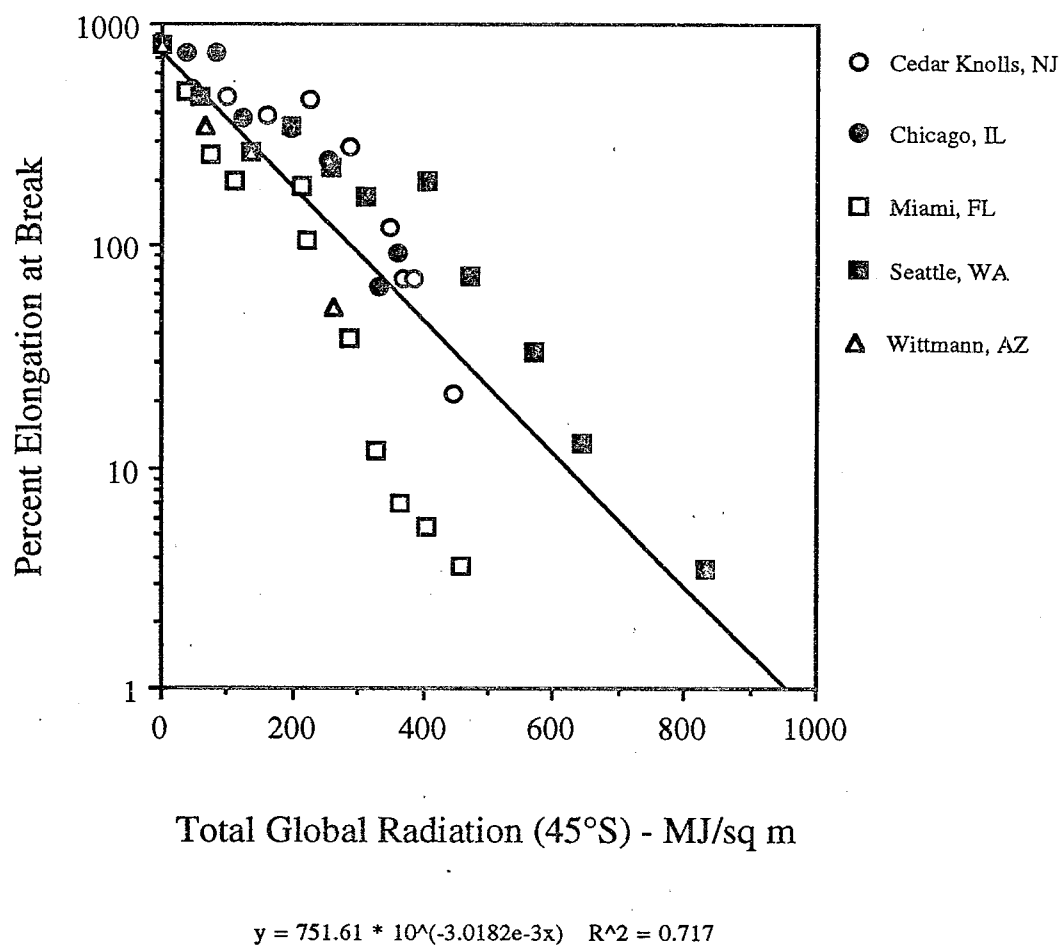
Figure 4.1.18 (b)   Semi-logarithmic plot of elongation at break versus the total radiation at exposure site: composite data for all outdoor locations (Plastigone [LDPE/MX] film).

Legend:
- ○ Cedar Knolls, NJ
- ◉ Chicago, IL
- □ Miami, FL
- ▣ Seattle, WA
- △ Wittmann, AZ

Total Global Radiation (45°S) - MJ/sq m

$y = 42.464 * 10^{(-6.6797e-3x)}$ $R^2 = 0.693$
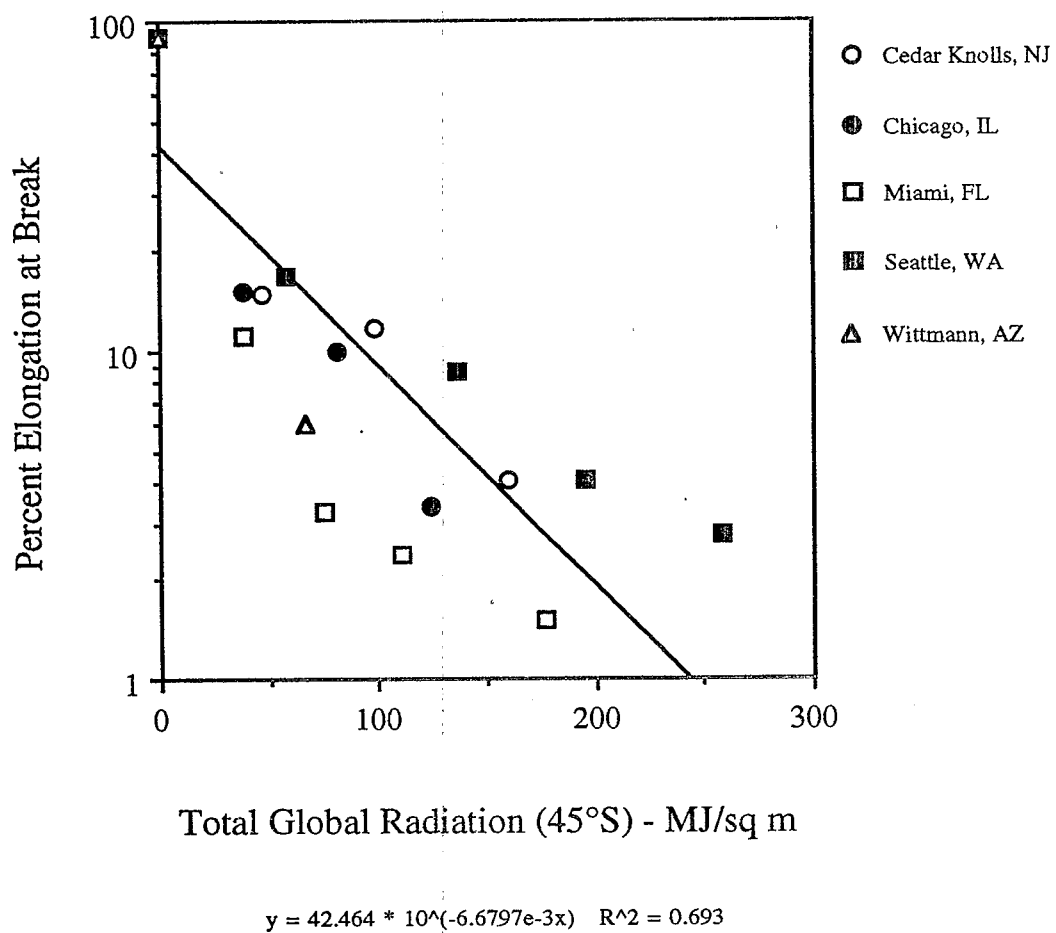
Figure 4.1.18 (c)   Semi-logarithmic plot of elongation at break versus the total radiation at exposure site: composite data for all outdoor locations (ADM [LDPE/starch/MX] film).
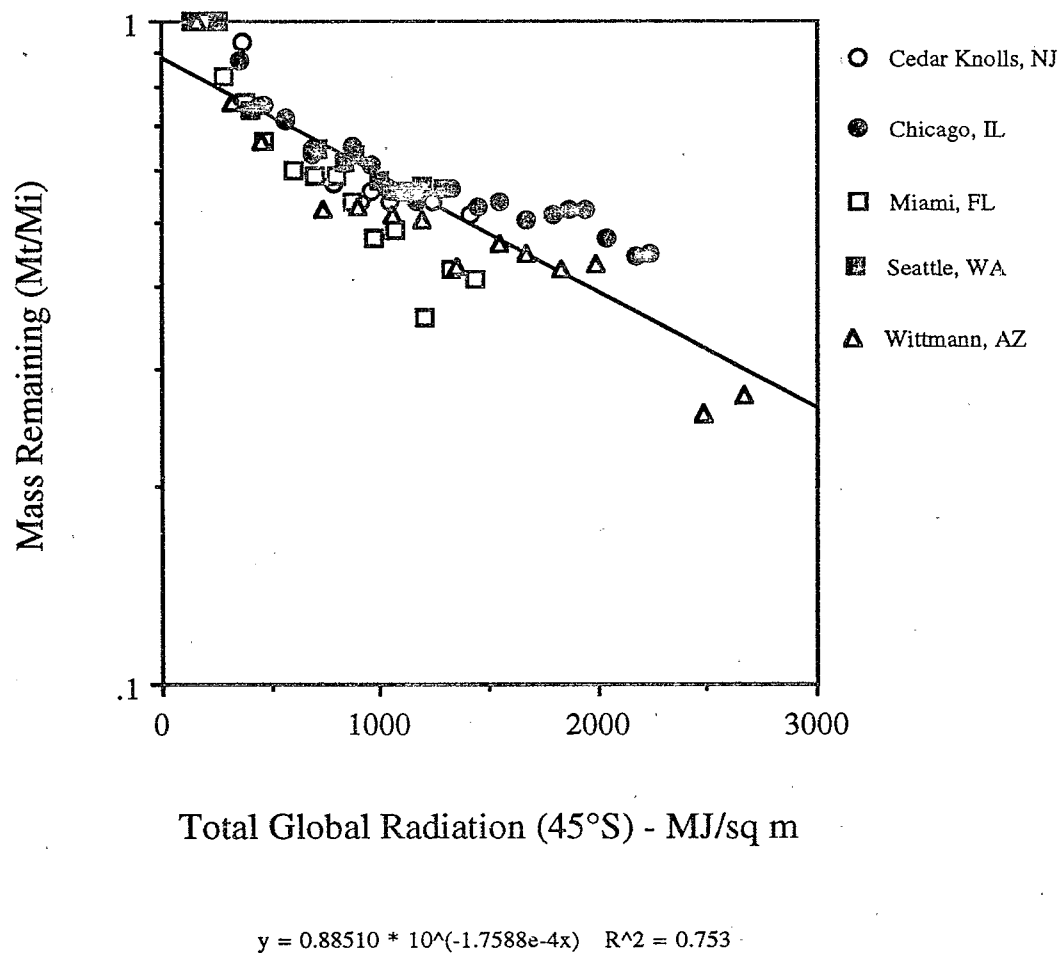
Figure 4.1.18 (d)   Semi-logarithmic plot of elongation at break versus the total radiation at exposure site: composite data for all outdoor locations (Expanded polystyrene foam [Polysar material]).
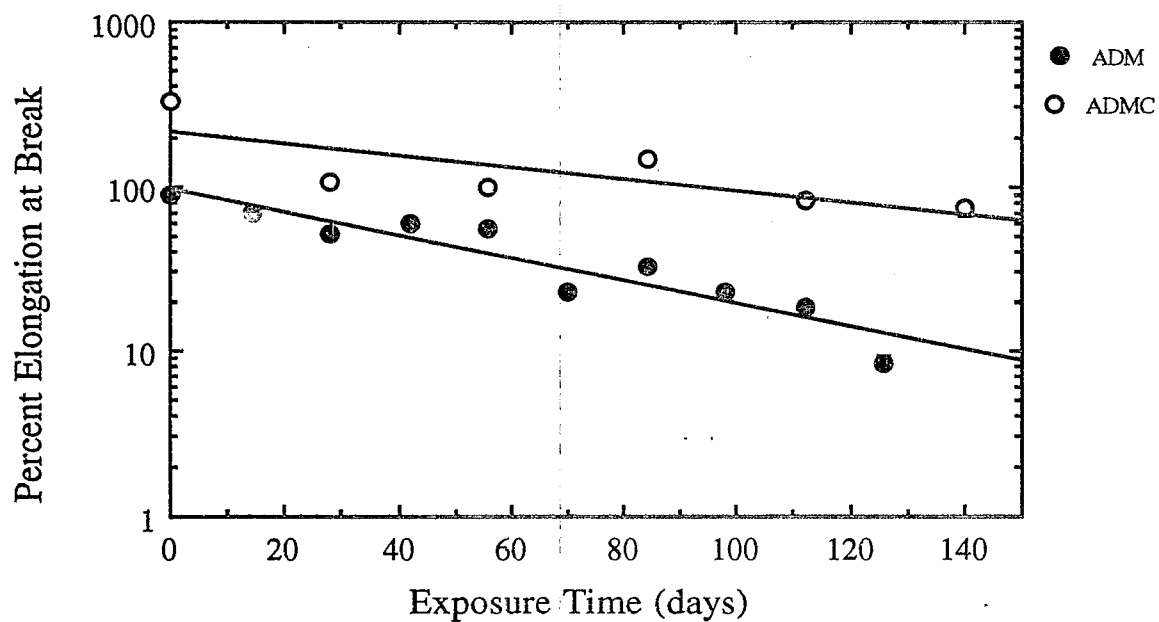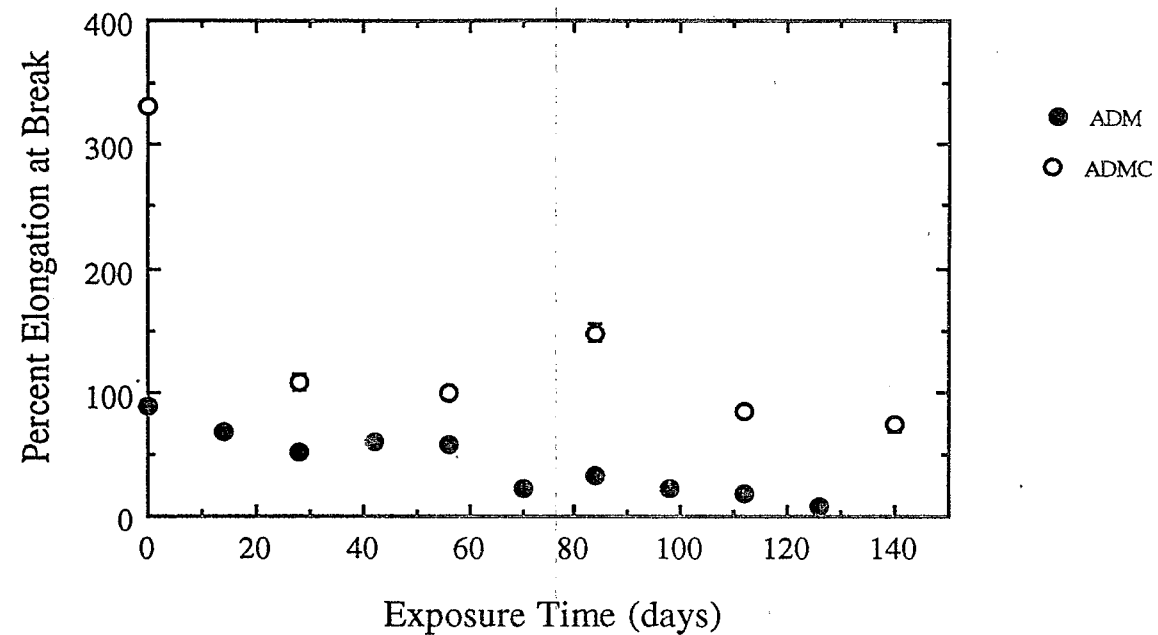
ADM: y = 98.041 * 10^(-7.0416e-3x)   R^2 = 0.880

ADMC: y = 213.17 * 10^(-3.4784e-3x)   R^2 = 0.593

Figure 4.1.19 (a)   Elongation at break versus duration of exposure for outdoor soil burial at Research Triangle Park, NC - (ADM/ADMC materials).

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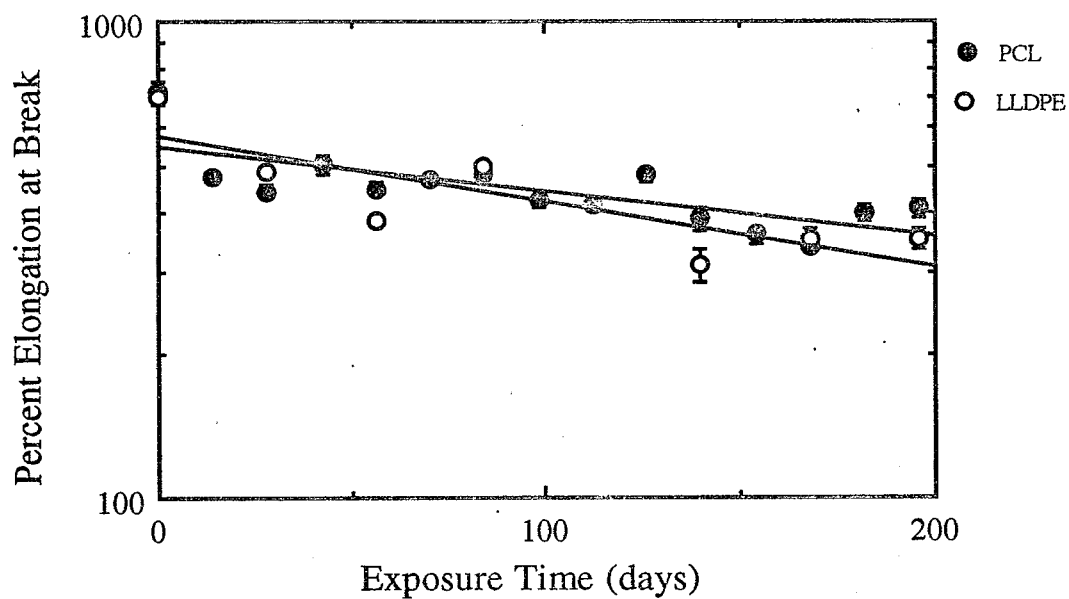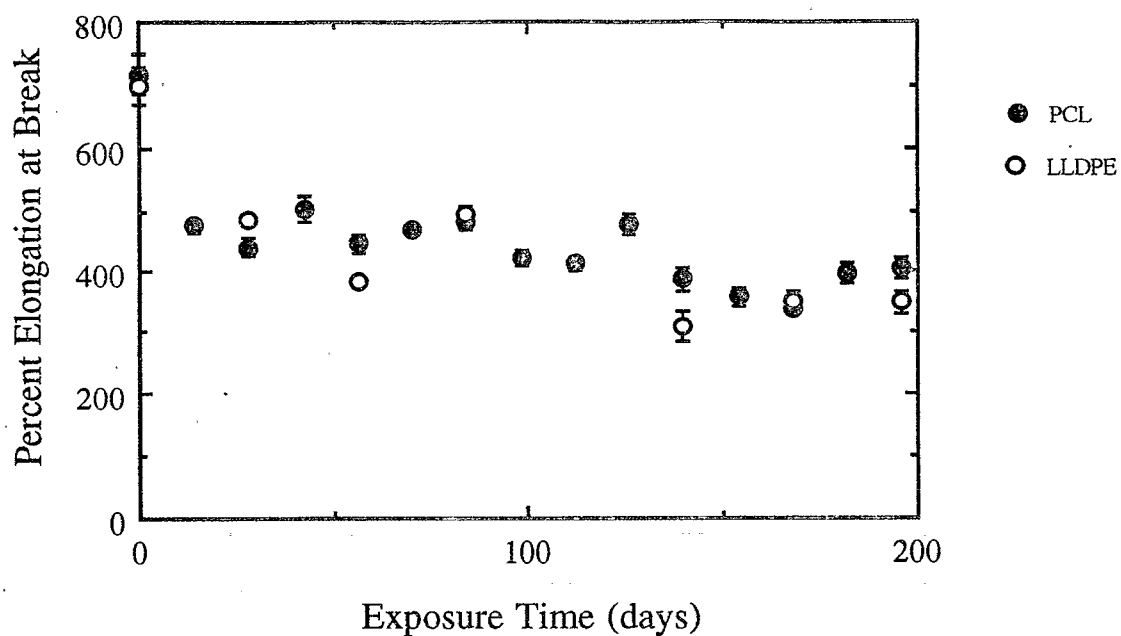
Figure 4.1.19 (b)   Elongation at break versus duration of exposure for outdoor soil burial at Research Triangle Park, NC - (PCL/LLDPE materials).

$$y = 40.999 * 10^{\wedge}(-3.8311e\text{-}2x) \quad R^{\wedge}2 = 0.933$$
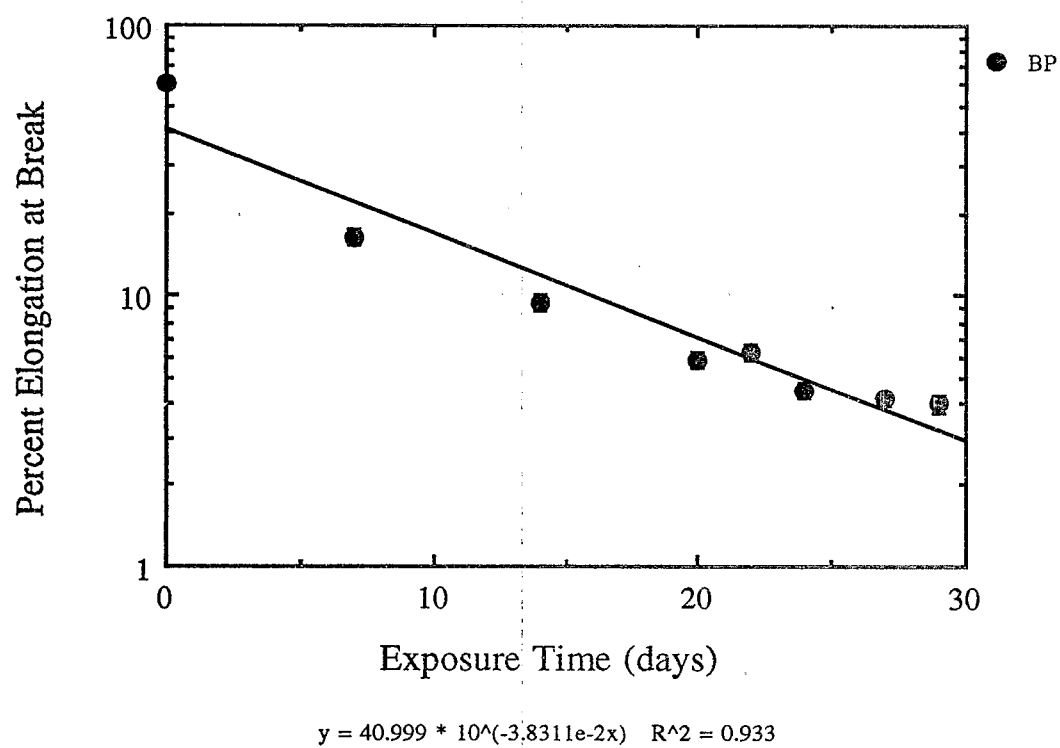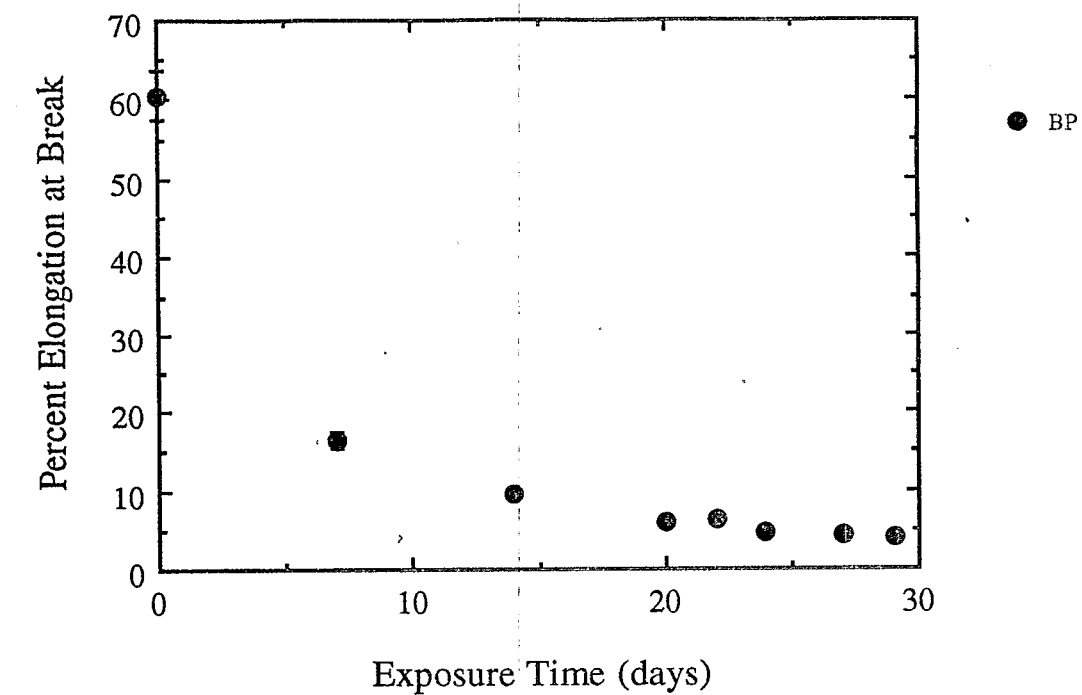
Figure 4.1.19 (c) Elongation at break versus duration of exposure for outdoor soil burial at Research Triangle Park, NC - (BP materials).

BIOPOL
SOIL BURIAL - RTI
BLOCK 2 - #64
24 DAYS: 3/27/90-4/20/90
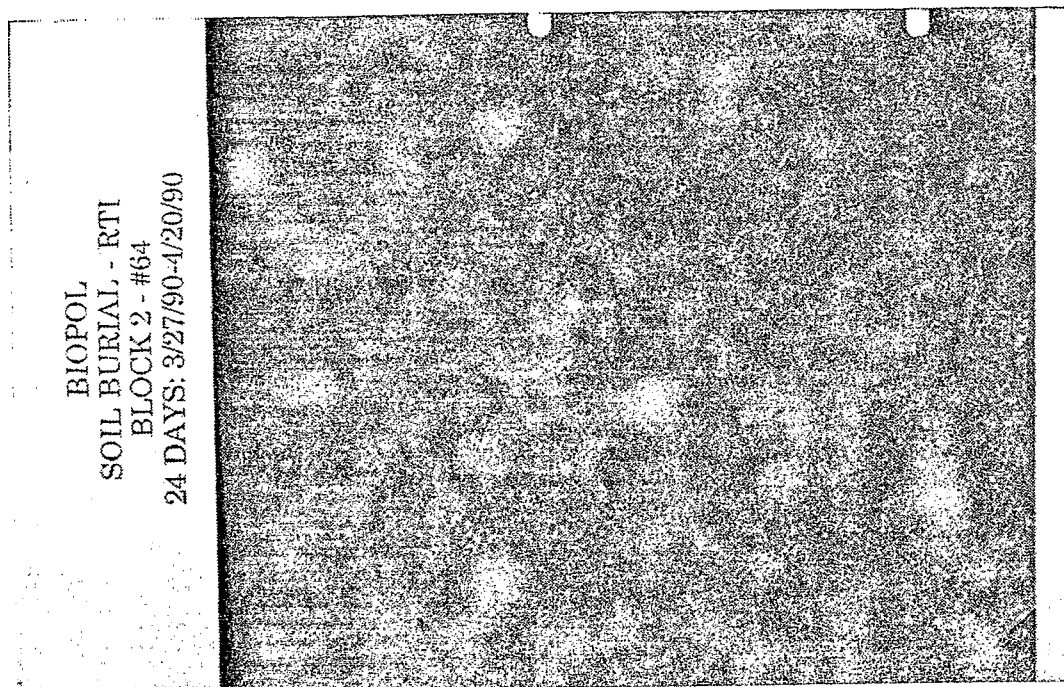
Figure 4.1.20 (b)   Outdoor soil burial of BP at Research
Triangle Park, NC - (24 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 3 - #72
22 DAYS: 3/27/90-4/18/90
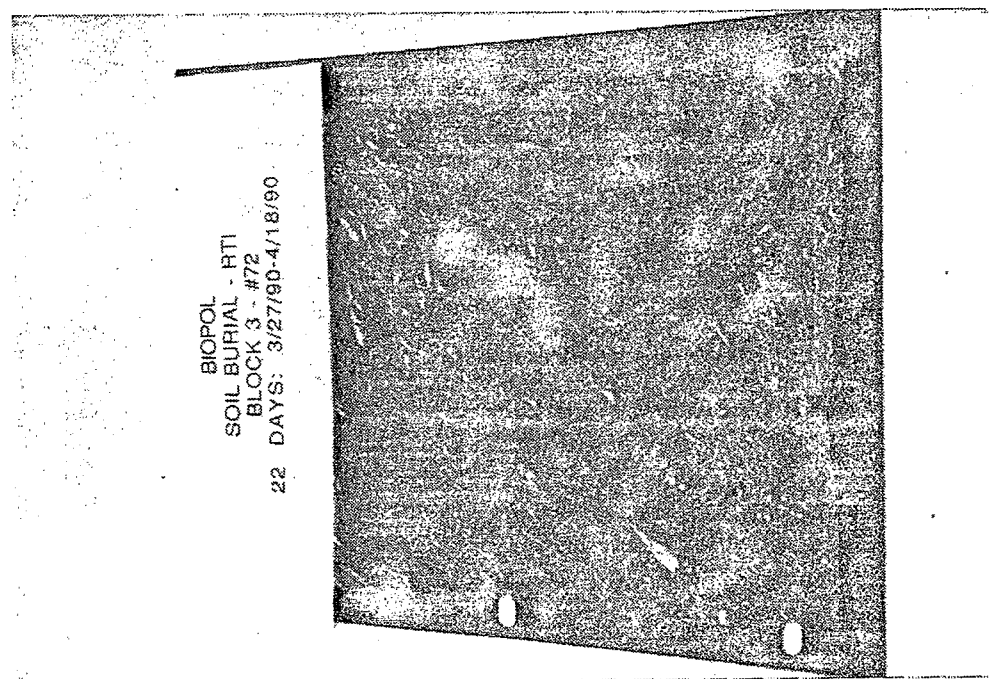
Figure 4.1.20 (a)   Outdoor soil burial of BP at Research
Triangle Park, NC - (22 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 1 - #53
36 DAYS: 3/27/90-5/2/90
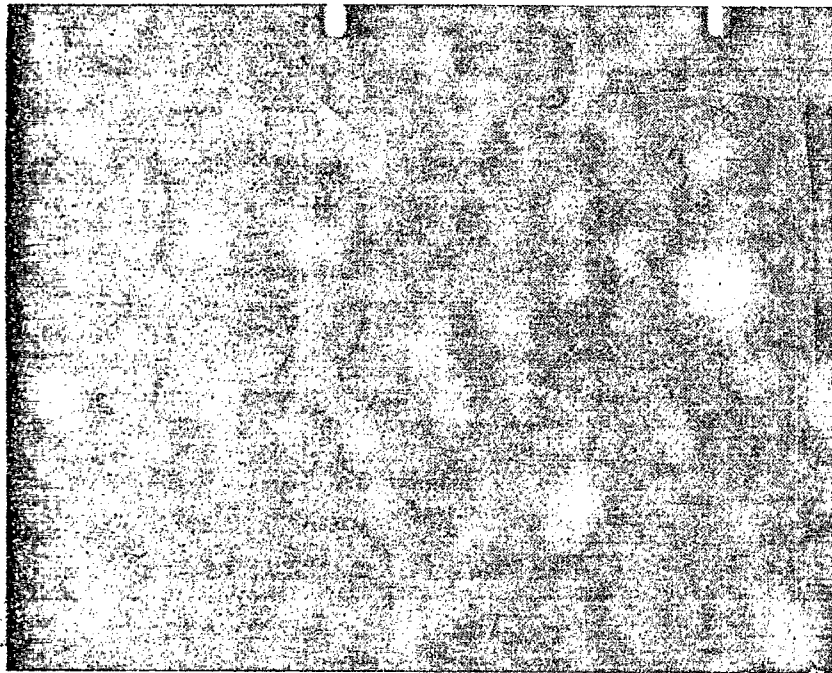
Figure 4.1.20 (d)   Outdoor soil burial of BP at Research
Triangle Park, NC - (36 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 2 - #85
27 DAYS: 3/27/90-4/23/90

Figure 4.1.20 (c)   Outdoor soil burial of BP at Research
Triangle Park, NC - (27 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK1 - #54
41 DAYS: 3/27/90-5/7/90

Figure 4.1.20 (f)   Outdoor soil burial of BP at Research Triangle Park, NC - (41 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 2 - #32
38 DAYS: 3/27/90-5/4/90

Figure 4.1.20 (e)   Outdoor soil burial of BP at Research Triangle Park, NC - (38 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 2 - #15
45 DAYS: 3/27/90-5/11/90

Figure 4.1.20 (h) Outdoor soil burial of BP at Research
Triangle Park, NC - (45 days).

BIOPOL
SOIL BURIAL - RTI
BLOCK 1 - #24
43 DAYS: 3/27/90-5/9/90

Figure 4.1.20 (g) Outdoor soil burial of BP at Research
Triangle Park, NC - (43 days).

BIOPOL
.SOIL BURIAL - RTI
BLOCK 1 - #67
48 DAYS: 3/27/90-5/14/90

Figure 4.1.20 (i)   Outdoor soil burial of BP at Research Triangle Park, NC - (48 days).

6P: y = 234.80 * 10^(-8.7401e-3x)   R^2 = 0.852

6PC: y = 903.41 * 10^(-1.6727e-3x)   R^2 = 0.958
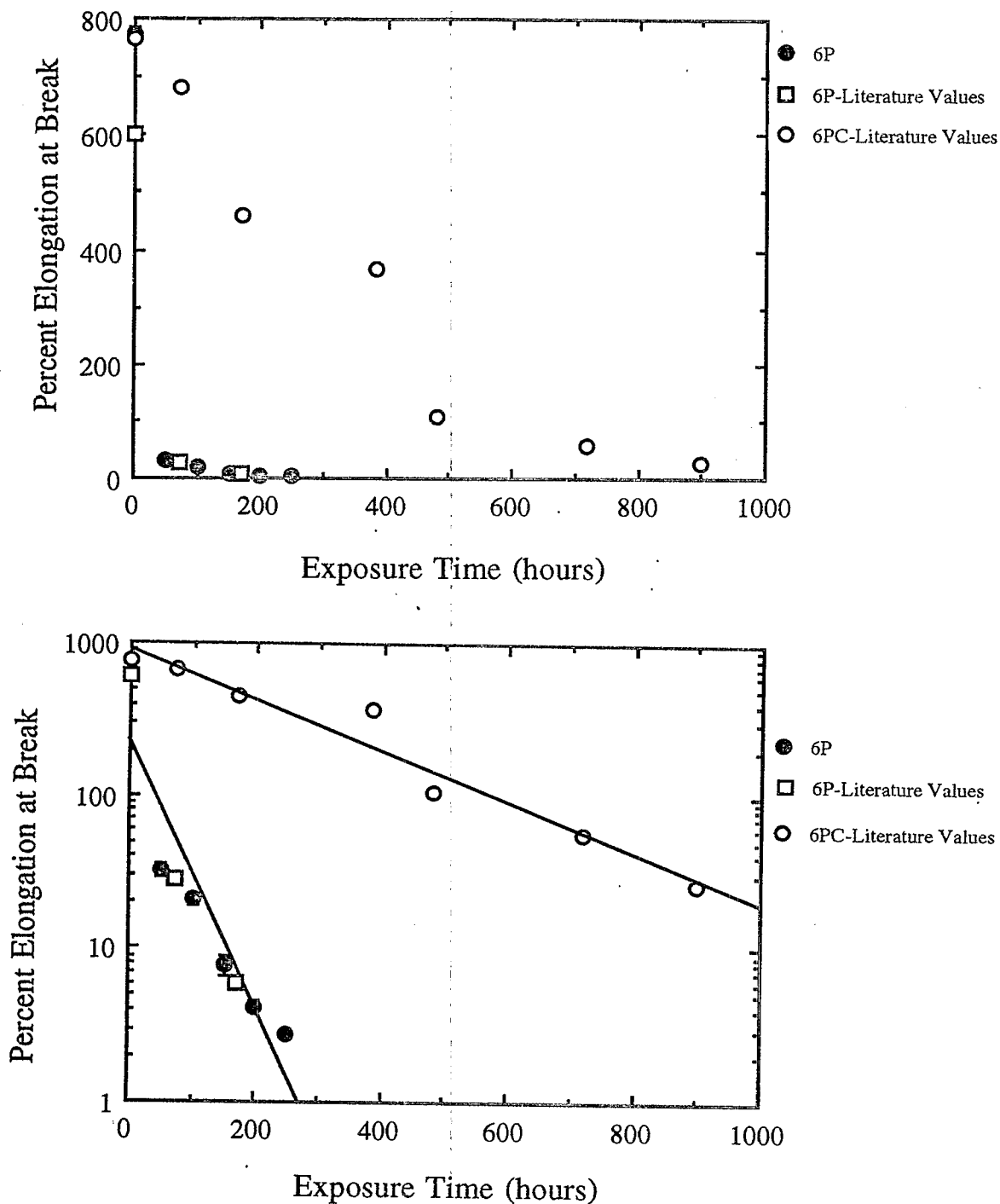
Figure 4.2.1 (a)   Elongation at break versus the duration of exposure for Weather-Ometer®
exposure - (6P/6PC).
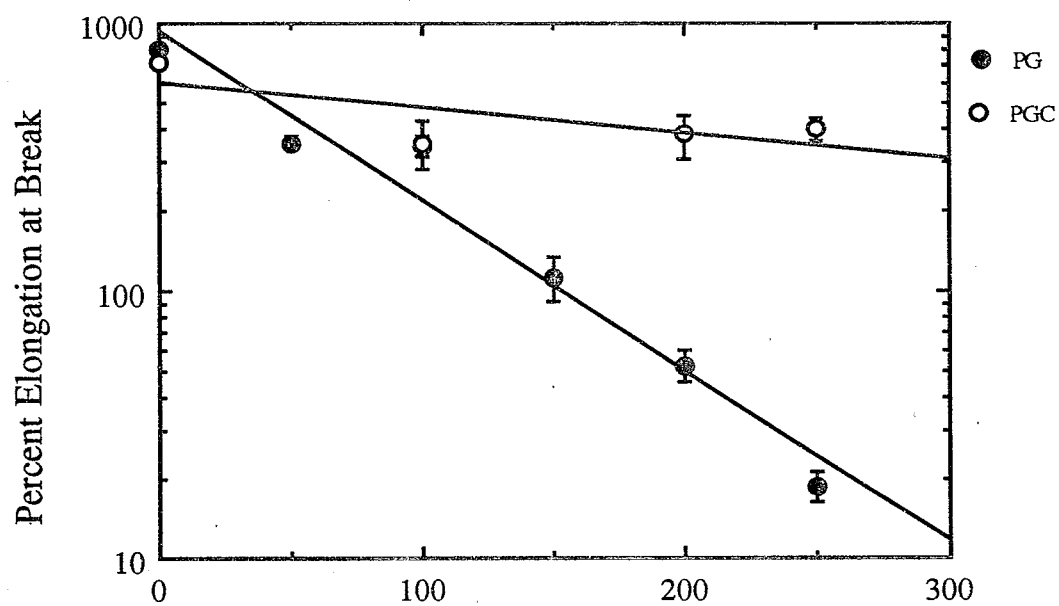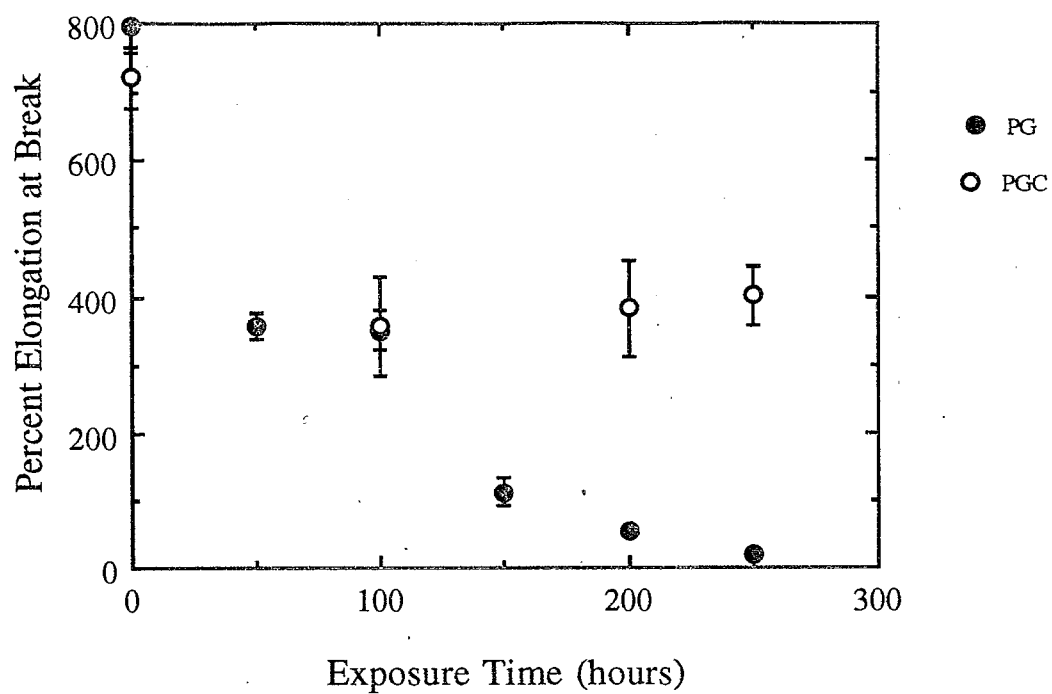
PG: y = 927.44 * 10^(-6.3486e-3x)   R^2 = 0.961

PGC: y = 598.72 * 10^(-9.3713e-4x)   R^2 = 0.534

Figure 4.2.1 (b)   Elongation at break versus the duration of exposure for Weather-Ometer®
exposure - (PG/PGC).
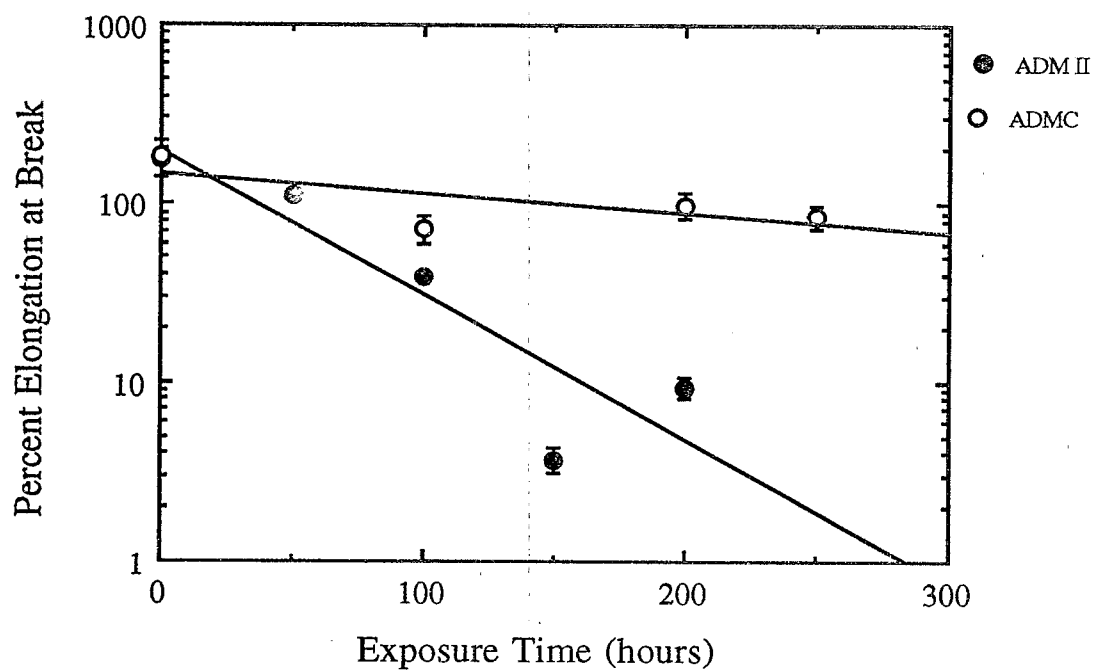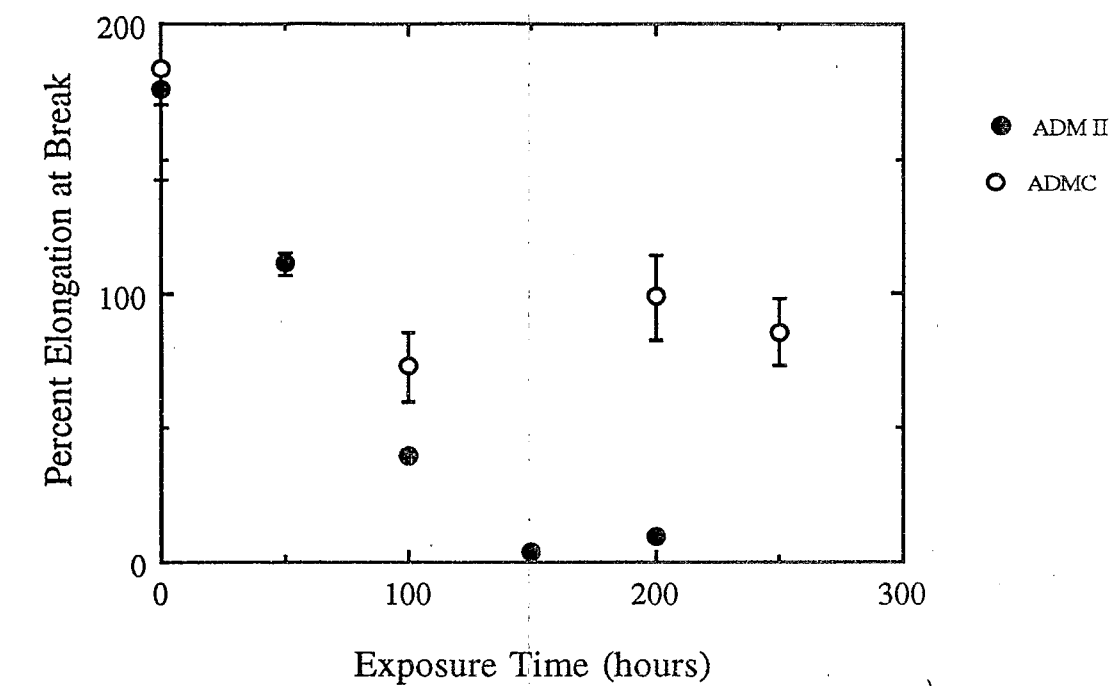
ADM II: y = 195.02 * 10^(-8.0638e-3x)   R^2 = 0.808

ADMC: y = 144.00 * 10^(-1.0682e-3x)   R^2 = 0.450

Figure 4.2.1 (c)   Elongation at break versus the duration of exposure for Weather-Ometer®
exposure - (ADM/ADMC).
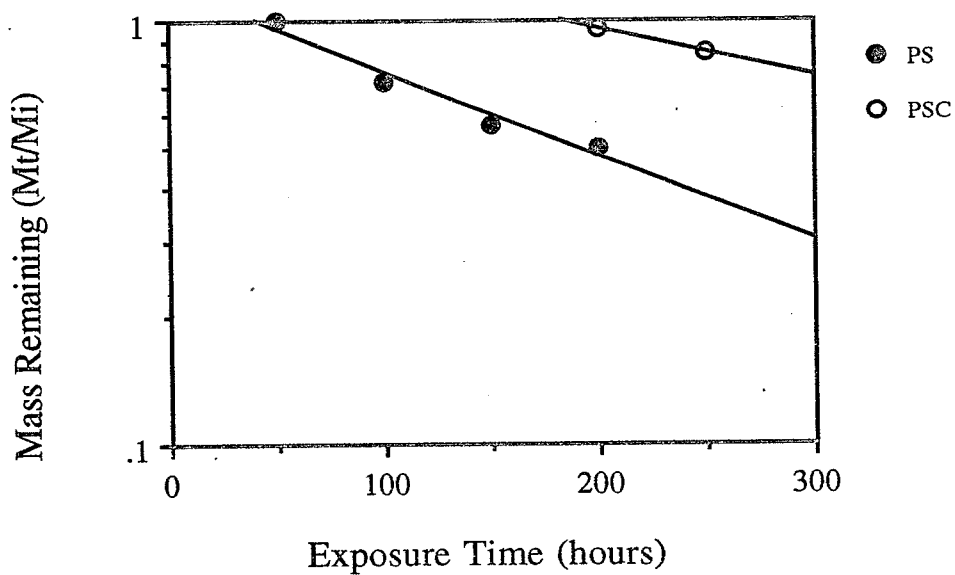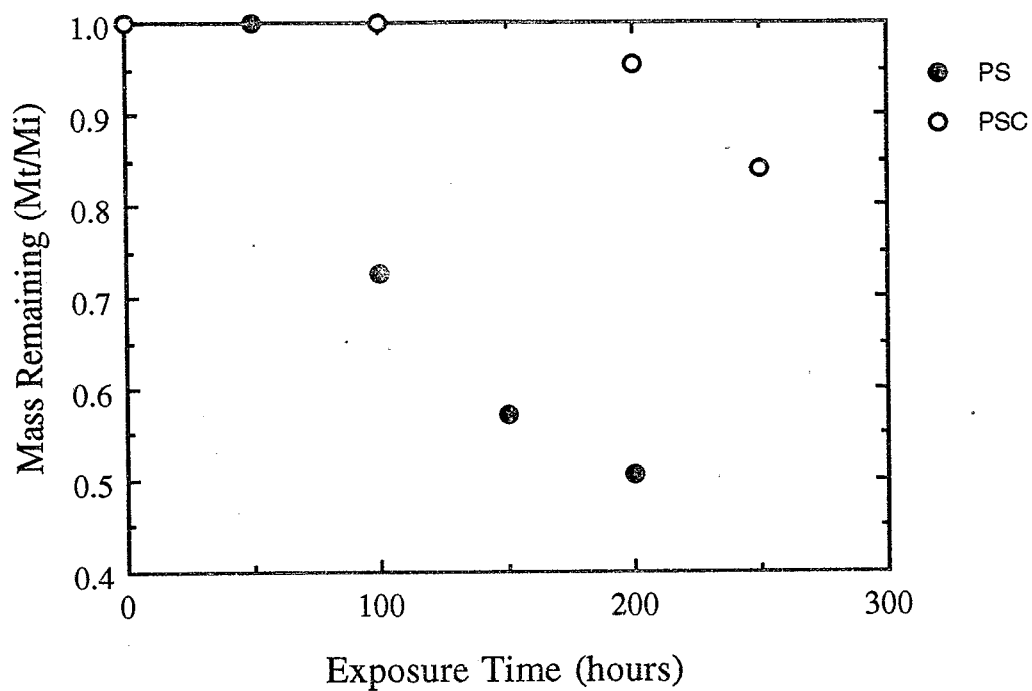
PS: y = 1.2002 * 10^(-1.9955e-3x)   R^2 = 0.964

PSC: y = 1.5985 * 10^(-1.1165e-3x)   R^2 = 1.000

Figure 4.2.2   Change in mass (as measured by tumbling friability) versus the duration of exposure for Weather-Ometer® exposure of photodegradable polystyrene foam .

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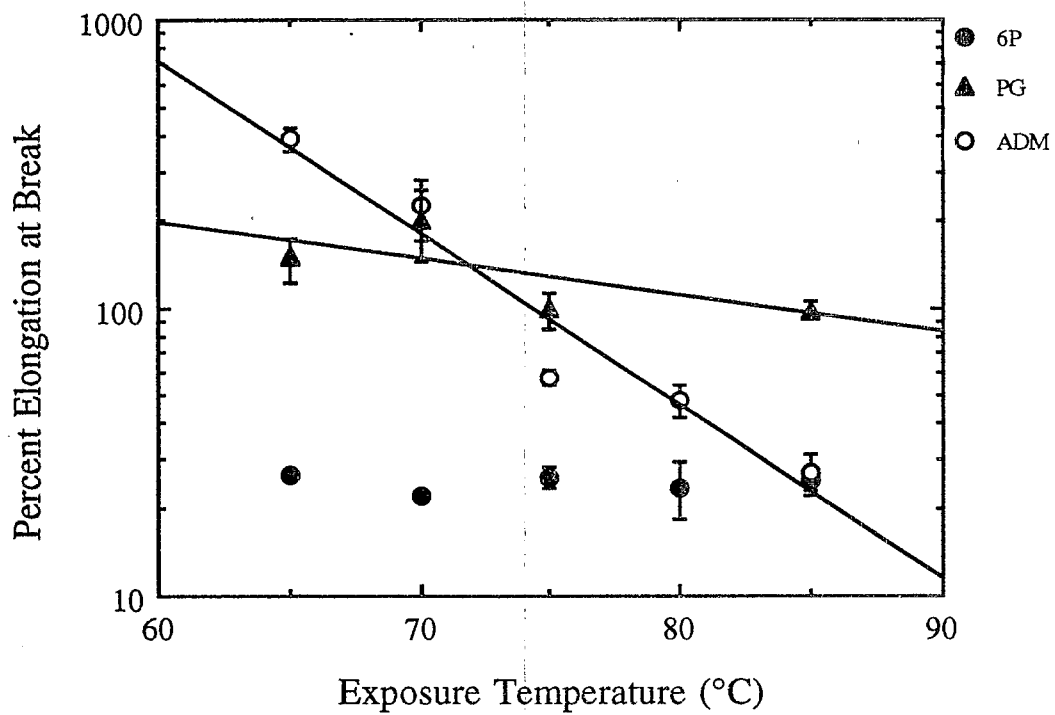
PG: y = 1105.6 * 10^(-1.2556e-2x)   R^2 = 0.513

ADM: y = 2.8544e+6 * 10^(-5.9924e-2x)   R^2 = 0.943

Figure 4.2.3   Elongation at break versus the exposure temperature for Weather-Ometer®
exposure (50 hours) for 6P, PG, and ADM samples.
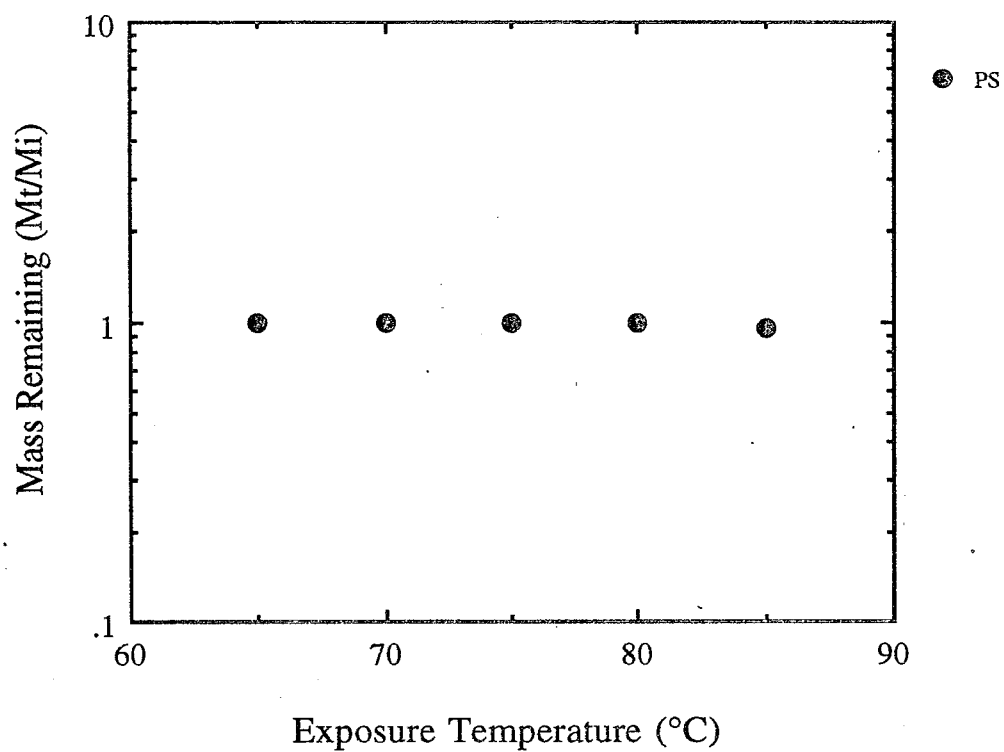
Figure 4.2.4   Change in mass (as measured by tumbling friability) versus exposure temperature for Weather-Ometer® exposure (50 hours) of photodegradable polystyrene foam .
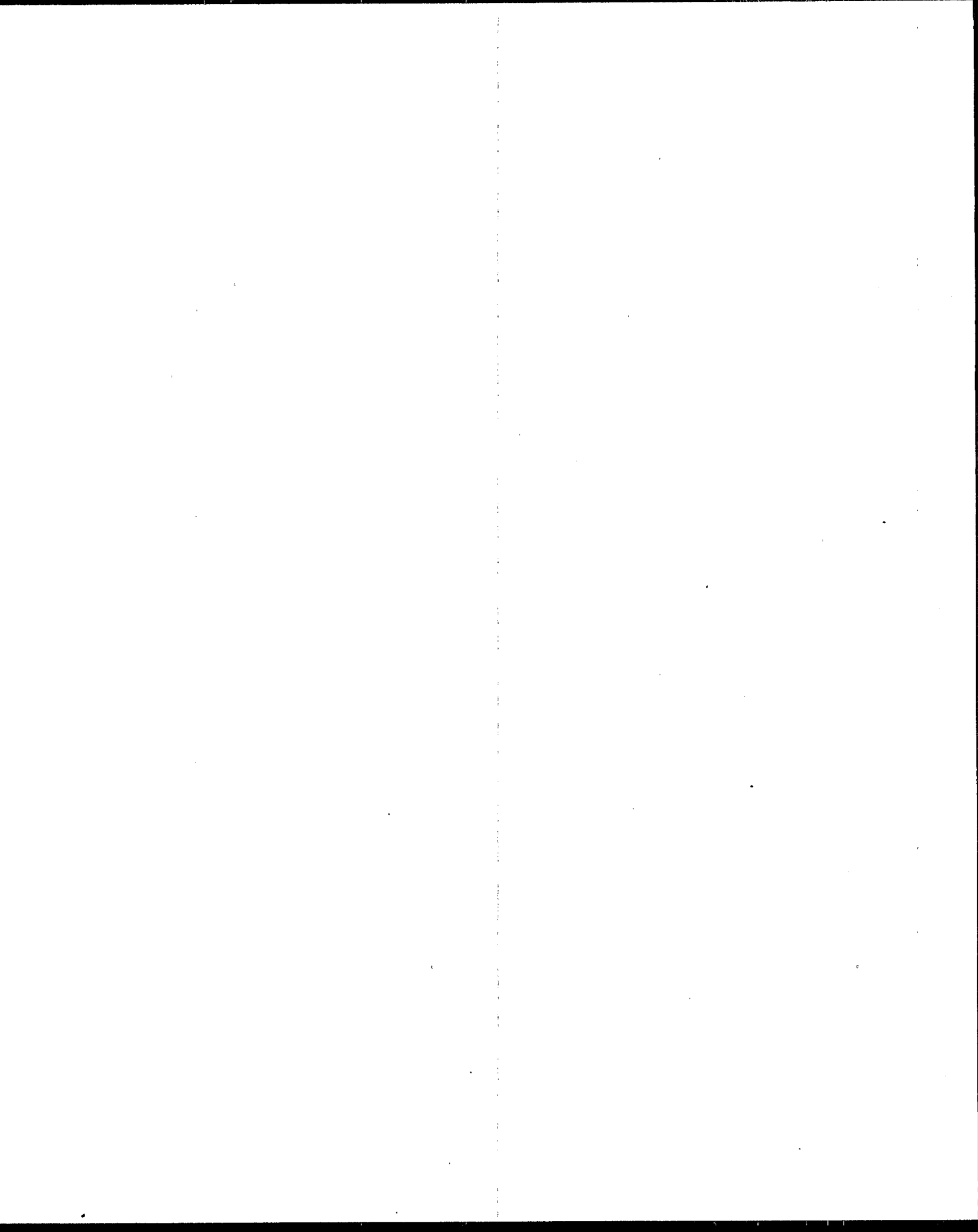
SECTION 5.0

OTHER EFFECTS OF WEATHERING

A convenient means of establishing the rates of disintegration is by monitoring the changes in mechanical properties of a plastic film undergoing environmental exposure. However, the mechanical properties of the material are not the only material properties affected by the weathering process. Changes in color, density, molecular weight, solution properties, transport properties, and electrical properties of the polymer can also change with degradation.

This chapter summarizes experiments pursued to study changes in selected physical properties of the disintegrating enhanced degradable plastic materials. Transport properties, thermal properties, and molecular weight changes, in particular, will be examined.

5.1 CHANGES IN MOLECULAR WEIGHT

The number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight distribution of partially degraded polymers were obtained from gel permeation chromatography (GPC) data. When chain scission is the predominant degradation mechanism, average molecular weight decreases with duration of exposure. However, some crosslinking may also take place concurrently. Molecular weight distribution (or polydispersity) is the ratio of weight average molecular weight to number average molecular weight and would be expected generally to increase with increased extent of polymer degradation. M_w is more sensitive to the presence of higher molecular weight species, whereas M_n is influenced more by the presence of low molecular weight species.

5.1.1 Polystyrene Foam

Previous studies [George and Hodgeman, 1976; Rabek and Ranby, 1974] on the mechanism of polystyrene degradation have shown it to occur due to photo-initiation by impurities. This leads to the formation of oxidation products which in turn absorb solar radiation and react to cause main-chain scission in the polymer, thereby reducing molecular weight. The enhanced photodegradable polystyrene is a blend of regular polystyrene resin with about 20% of a copolymer of styrene/vinyl ketone. This copolymer contains pendant ketone groups which are efficient chromophores able to absorb UV radiation and initiate degradation reactions.

Table 5.1.1 shows average values of molecular weight as determined by GPC for PS and PSC samples for selected exposure sites. For outdoor exposure in both Miami, FL

Table 5.1.1. Gel Permeation Chromatography Results for Polystyrene Foam.

Location	Exposure Type	Exposure Duration (days)	Photodegradable PS Foam			Control PS Foam		
			M_n (x 10⁻⁴)	M_w (x 10⁻⁴)	M_w/M_n	M_n (x 10⁻⁴)	M_w (x 10⁻⁴)	M_w/M_n
Unexposed		0	12.6	26.5	2.11	14.4	26.8	1.85
Chicago	Outdoor	7	5.1	17.3	3.38			
		14	4.6	13.5	2.93	10.2	22.6	2.22
		22	4.4	12.7	2.91			
		29	3.5	12.3	3.49	7.2	19.7	2.74
		36	3.3	12.8	3.95			
		43	2.9	11.5	3.93	6.3	18.7	2.97
		50	2.9	11.5	3.92			
		57	3.1	10.5	3.39	5.2	18.3	3.48
		64	2.8	11.0	3.96			
Miami	Outdoor	7	6.6	17.0	2.54			
		14	4.6	14.3	3.15	9.5	22.9	2.40
		21	4.6	13.0	2.86			
		28	4.0	13.2	3.28	8.2	20.4	2.49
		35	3.8	12.3	3.21			
		42	4.5	14.4	3.18	6.0	19.5	3.27
		49	3.4	11.6	3.36			
		56	4.0	12.1	3.03	7.4	19.7	2.64
		63	3.6	11.9	3.26			
		70	3.2	12.1	3.77			

- continued -

Table 5.1.1. (continued).

Location	Exposure Type	Exposure Duration (days)	Photodegradable PS Foam			Control PS Foam		
			M_n (x 10^{-4})	M_w (x 10^{-4})	M_w/M_n	M_n (x 10^{-4})	M_w (x 10^{-4})	M_w/M_n
Miami	Marine Floating	7	6.4	16.3	2.54	-	-	-
		29	3.6	11.1	3.13	-	-	-
		35	3.4	8.9	2.63	-	-	-
		43	-			7.2	19.0	2.64
		58	-			6.9	20.3	2.94
Seattle	Marine Floating	7	7.1	18.4	2.60	12.6	26.6	2.11
		14	7.1	17.7	2.48	12.0	26.6	2.22
		21	5.2	15.8	3.05	10.3	25.2	2.45
		28	5.0	15.0	2.99	9.6	24.5	2.56
		Exposure Duration (hours)						
-	Weather-Ometer®	50	4.4	15.3	3.47			
		100	3.5	12.6	3.64			
		150	2.3	10.9	4.83			
		200	3.0	11.2	3.61			
		250	2.4	11.1	4.56			

M_n = number average molecular weight

M_w = weight average molecular weight

M_w/M_n = polydispersity

and Chicago, IL, the degradation (based on decrease in the number average molecular weight) occurred more rapidly in the enhanced degradable material than in the control. After only 14 days of exposure in both locations, M_n of the enhanced degradable polystyrene had decreased by about 60%, while that of the control polystyrene had decreased only by about 30%. After 57 days of exposure in Chicago, IL, M_n for PS samples had decreased by 75% and for PSC by 64%. The degradation reactions in turn generate new light-absorbing functional groups. The control material, PSC, might be expected to eventually degrade to the same extent as the enhanced degradable material given a long enough exposure duration.

Studies of degradation in expanded polystyrene foam (as opposed to films) are complicated by the formation of a yellow, embrittled surface layer which absorbs UV radiation and, upon build-up, effectively screens the underlying polymer. In comparing polystyrene foam exposed on land and floating in sea water, Andrady and Pegram (1991) have shown that the degradation rate is initially faster in air, but for longer exposure durations, degradation in sea water is faster and occurs to a greater extent. This observation was attributed to gradual removal by the water of the outer protective yellow layer. For the present work, GPC data for marine floating exposures at longer durations could not be obtained due to excessive fouling, but the Miami, FL outdoor and marine floating exposure results showed similar extents of degradation for the exposure durations which could be directly compared.

Comparison of enhanced degradable polystyrene foam, PS material, to control material, PSC, for marine floating exposure shows that for both locations (Miami, FL and Seattle, WA), the enhanced degradable material showed much higher extents of degradation for comparable exposure durations. For example, in Seattle, WA, M_n for PS had decreased by 59% after 21 days, whereas M_n for PSC control samples had decreased only by 29% for the same exposure duration. The observation is consistent with that for regular polystyrene foam reported previously by Andrady and Pegram (1991).

Accelerated weathering (Weather-Ometer®) of the enhanced degradable material resulted in a large reduction (65%) in the average molecular weight after only 50 hours of exposure. This corresponded to about 14 days of outdoor exposure in Miami, FL or Chicago, IL. The extent of degradation (as measured by reduction in the molecular weight reduction) leveled off at about 80% after 150 hours of exposure. Longer exposure times did not further reduce molecular weight significantly. This might be due to the development of the yellow protective layer which, unlike the cases of outdoor and marine exposures, is left undisturbed and remains intact.

Figures 5.1.1.a through 5.1.1.i show molecular weight distributions for the PS and PSC samples obtained by GPC. The graphs show the fraction of each molecular weight species (M_i) plotted against GPC retention volume. The width of each peak relates to the molecular weight distribution, while the retention volume at the peak maximum is proportional to the number average molecular weight. These graphs illustrate the more rapid loss in molecular weight in the enhanced photodegradable polystyrene compared to the regular polystyrene control. The peaks (particularly for the PS samples) also tend to broaden with increased exposure duration, indicating higher values of molecular weight distribution at greater extents of degradation.

5.1.2 Polycaprolactone/Polyethylene Blend

Table 5.1.2 shows molecular weight values obtained from GPC on the extracted polycaprolactone fraction of PCL samples exposed to outdoor soil burial at RTI and to marine sediment conditions in Miami, FL. One month of exposure in both biotic environments had little or no effect on the average molecular weight at all, and only a slight decrease was noted for the longer exposure times (up to 6 months). Evidently, much longer exposure durations are required before the polycaprolactone begins to break down on a molecular level. The slow breakdown of the polycaprolactone (reported to be biodegradable) may be in part due to the fact that it is contained within the polyethylene matrix, which restricts its exposure to the microorganisms and/or extra-cellular enzymes which cause degradation. However, the test procedure employed does not take into account the oligomeric species which could have leached out of the plastic blend during exposure.

5.2 CHANGES IN TRANSPORT PROPERTIES

The transport properties of polymers to gases, vapors, and liquids are of great importance in applications such as packaging for food and other items, corrosion resistant coatings, electrical application of plastics, materials for biomedical applications, etc. In the packaging field, for example, the resistance of flexible films to moisture and oxygen is essential for the preservation of packaged goods. Polymer degradation (biodegradation, photodegradation, and thermal degradation) can potentially lead to changes in the permeability of such plastic materials. In this section, water vapor transmission rates (WVTR) of three kinds of plastic films, i.e., photodegradable plastic (PG), biodeteriorable plastic blends (PCL), and photodegradable-biodeteriorable plastic (ADM), were measured for samples exposed to several different environments, and the results were compared with that of unexposed film. Additionally, the gas (carbon dioxide) permeabilities of two types

Table 5.1.2.   Gel Permeation Chromatography Results for Polycaprolactone Fraction of
PCL/LLDPE Blend.

Location	Exposure Type	Exposure Duration (days)	M_n (x 10^{-4})	M_w (x 10^{-4})	M_w/M_n
Unexposed		0	3.7	5.6	1.53
RTI	Outdoor Soil Burial	28	3.6	5.4	1.49
		56	3.3	5.3	1.60
		84	3.0	5.0	1.65
		140	3.4	5.2	1.54
		168	3.1	5.0	1.59
Miami	Marine Sediment	29	3.6	5.5	1.54
		43	2.9	5.0	1.71

M_n = number average molecular weight

M_w = weight average molecular weight

M_w/M_n = molecular weight distribution

of photodegradable films (PG and 6P) exposed to Weather-Ometer® conditions were measured using a gravimetric technique. The relationships between the permeabilities and exposure time for different samples were determined.

5.2.1 Water Vapor Transmission Rate (WVTR)

Figure 5.2.1 shows the typical permeation results for PG samples which were exposed under outdoor conditions at Miami, FL for various durations. For both unexposed and exposed film samples, the amounts of water vapor which permeated through the films were proportional to the permeation time (correlation coefficient ≥ 0.97), and the longer the exposure, the larger the amount of water permeated. The intercept of the linear portion of the curve, the so-called "lag time", τ, allows the calculation of the diffusion coefficient D of the film, as follows:

$$D = \ell^2 / 6\tau \tag{5-1}$$

where ℓ is the film thickness. As the weight increase was not continuously recorded in the present experiments, lag time could not be accurately determined and are not reported here. The slope of the weight gain versus time curves, on the other hand, gave the water vapor transmission rate (WVTR). The plots of the WVTR as a function of exposure time are shown in Figure 5.2.2 where the WVTR of the PG films increased linearly with the exposure time. In outdoor weathering of PG material, the polymer (polyethylene) undergoes light-initiated thermo-oxidative degradation in a free-radical reaction, leading to scission of polymer chains. The shorter average chain length of degraded molecules may "plasticize" the film and render it more permeable to water vapor. Small molecules such as water and CO_2 tend to diffuse relatively easily through a plasticized polymer matrix. The linear relationship between WVTR and the time of weathering of the film, shown in Figure 5.2.2, suggests the meal-catalyzed chain scission process (which generates the oligomeric sol fraction of polyethylenes responsible for plasticization) to increase with duration of exposure. Table 5.2.1 summarizes WVTR data for PG.

Figure 5.2.3 and Table 5.2.2 show the WVTR data for a PCL film (blends of LLDPE and polycaprolactone) exposed in an aerobic soil slurry for 40 days in comparison with that of unexposed PCL. As can be seen in the figure, the WVTR of the exposed and unexposed film are about the same. This suggests that attempted biodegradation of the PCL sample by aerobic exposure was not successful in this short time-scale of exposure to an extent to alter the experimental WVTR values. This is consistent with the other data (GPC, mechanical strength) reported these blends.

Table 5.2.1. Water Vapor Transmission Test Data (LDPE/MX Samples).

Duration of Exposure* (days)	Water Vapor Transmission			Average of W/A (mg/cm^2)
	Time (day)	W** (g)	W/A (mg/cm^2)	
0	0	0	0.00	0.00
	3	0.088	4.54	
	3	0.093	4.79	4.59
	3	0.090	4.64	
	3	0.085	4.38	
	6	0.185	9.54	
	6	0.192	9.90	9.45
	6	0.176	9.07	
	6	0.180	9.28	
	8	0.269	13.87	
	8	0.279	14.38	13.94
	8	0.267	13.76	
	8	0.267	13.76	
	10	0.346	17.84	
	10	0.358	18.45	18.32
	10	0.358	18.45	
	10	0.360	18.56	
4	0	0	0.00	0.00
	3	0.164	8.45	7.63
	3	0.132	6.80	
	6	0.322	16.60	15.98
	6	0.298	15.36	
	9	0.471	24.28	23.48
	9	0.440	22.68	
7	0	0	0	0.00
	1	0.048	2.47	2.47
	1	0.048	2.47	
	3	0.132	6.80	6.96
	3	0.138	7.11	
	5	0.233	12.01	12.16
	5	0.239	12.32	
	8	0.382	19.69	20.10
	8	0.398	20.52	
11	0	0	0.00	0.00
	3	0.209	10.77	10.62
	3	0.203	10.46	
	6	0.377	19.43	19.54
	6	0.381	19.64	
	9	0.576	29.69	28.58
	9	0.533	27.47	

- continued -

Table 5.2.1. (continued).

Duration of Exposure* (days)	Water Vapor Transmission			Average of W/A (mg/cm²)
	Time (day)	W** (g)	W/A (mg/cm²)	
15	0	0	0	0.00
	3	0.187	9.64	10.21
	3	0.209	10.77	
	6	0.350	18.04	19.15
	6	0.393	20.26	
	9	0.593	30.57	29.23
	9	0.541	27.89	
19	0	0	0	0.00
	1	0.073	3.76	
	3	0.218	11.24	
	5	0.369	19.02	
	8	0.582	30.00	
22	0	0	0.00	0.00
	3	0.040	12.12	
	3	0.036	10.91	11.41
	3	0.037	11.21	
	6	0.074	22.42	
	6	0.064	19.39	21.72
	6	0.077	23.33	
	9.5	0.119	36.06	
	9.5	0.104	31.52	35.05
	9.5	0.124	37.58	
25	0	0	0	0.00
	3	0.042	12.73	
	3	0.050	15.15	13.64
	3	0.043	13.03	
	6	0.083	25.15	
	6	0.095	28.79	26.57
	6	0.085	25.76	
	9.5	0.128	38.79	
	9.5	0.138	41.82	40.30
	9.5	0.133	40.30	

* Exposure:Outdoor exposure at Miami

** W = mass of water uptake

Permeation Area: A = 19.4 cm² for 0 to 20 days exposure
Permeation Area: A = 3.3 cm² for 22 and 25 days exposure.

Table 5.2.2. Water Vapor Transmission Test Data (LLDPE/PCL Blend Samples).

Unexposed Samples				Samples Exposed Under Aerobic Conditions*			
Time (day)	W** (g)	W/A (mg/cm^2)	Average of W/A (mg/cm^2)	Time (day)	W (g)	W/A (mg/cm^2)	Average of W/A (mg/cm^2)
0	0	0	0.00	0	0	0.00	0.00
3	0.197	10.15		3	0.169	8.71	
3	0.181	9.33	9.10	3	0.177	9.12	8.78
3	0.151	7.78		3	0.160	8.25	
3	0.177	9.12		3	0.175	9.02	
				5	0.295	15.21	
				5	0.298	15.36	15.35
				5	0.293	15.10	
				5	0.305	15.72	
7	0.417	21.49					
7	0.420	21.65	20.89				
7	0.368	18.97					
7	0.416	21.44					
				9	0.512	26.39	
				9	0.522	26.91	26.61
				9	0.495	25.52	
				9	0.536	27.63	
10.5	0.660	34.02					
10.5	0.652	33.61	31.93				
10.5	0.558	28.76					
10.5	0.608	31.34					

*   Exposure was in a solution of mineral salts innoculated with garden soil
**   W = mass of water uptake

Permeation Area: A = 19.4 cm^2

Effects of the degradation of ADM samples (LDPE/starch/MX) on the WVTR are shown in Figure 5.2.4. The samples of ADM films were exposed outdoors for 10 days at Miami, FL (Table 5.2.3) and also immersed in enzyme (α-amylase) solutions for 40 days (Table 5.2.4). The WVTR of the outdoor-weathered film was apparently larger compared to the unexposed film because the chain scission (resulting from photooxidation) during weathering tends to make the film more permeable. The WVTR measurements of the film exposed in the enzyme solution, however, showed no difference in rate between the exposed film and unexposed one. In order to avoid the effect of thermal degradation of the ADM sample in the solution at 37°C, ADM films compounded solely for biodeteriorability only (no pro-oxidant metal compound additive) were used for the enzyme exposure experiment. According to thermogravimetric analysis (TGA) of the enzyme-exposed ADM, less than 10 percent of the starch content of the film was hydrolyzed by the enzyme after the exposure. Such a small decrease in the starch content may not significantly increase the WVTR of the sample. In conclusion, the photodegradation (or photooxidation) of the polyethylene films (PG and ADM) increased their WVTR in proportion to the exposure time. The biodeterioration of both PCL and ADM samples in the present study was too limited to make the change in the WVTR in the time scale of exposure used.

5.2.2 Gas Permeability

In order to investigate the effect of photodegradation of PG and 6P samples on gas permeability, measurements of CO_2 permeability were carried out with plastic films exposed for various durations in a Weather-Ometer®. Several techniques are available for the experimental determination of the diffusion coefficient (D), solubility (S), and the permeability (P) of a film to a gas or a vapor. These can be classified into four groups, i.e. (i) constant volume method, (ii) gravimetric method, (iii) volume loss method, and (iv) continuous flow method. The technique used in the present study was a gravimetric method where the gain in mass of a gas dissolving in a polymer was continuously measured as a function of time, using an electric microbalance.

Figures 5.2.5 and 5.2.6 show the time-dependent mass gain due to CO_2 absorbed in PG films and 6P films, respectively. In both figures, the results for the exposed (and therefore, weathered) samples with different exposure times of up to 250 hours are shown. All curves show a rapid increase in the amount of gas absorbed during the initial period and limiting values at steady state. The amount of CO_2 absorbed in PG film at any given time increased with the duration of Weather-Ometer® exposure (or the extent of photodegradation), while that in 6P material decreased. To obtain the diffusion coefficient D and the permeability P, the data from the sorption experiments are usually plotted as the relative

Table 5.2.3. Water Vapor Transmission Test Data (ADM Samples).

Unexposed Samples				Samples Exposed Ten Days (Outdoor)			
Time (day)	W* (g)	W/A (mg/cm^2)	Average of W/A (mg/cm^2)	Time (day)	W (g)	W/A (mg/cm^2)	Average of W/A (mg/cm^2)
0	0	0	0.00	0	0	0.00	0.00
2	0.169	8.71	8.61				
2	0.165	8.51	9.10				
4	0.323	16.65	16.62	4	0.069	20.91	23.03
4	0.322	16.60		4	0.083	25.15	
				6	0.106	32.12	35.45
				6	0.128	38.79	
7	0.560	28.87	28.71				
7	0.554	28.56					
				8	0.150	45.45	49.09
				8	0.174	52.73	
10	0.869	44.79	42.99				
10	0.799	41.19					

* W = mass of water uptake

Permeation Area: A = 19.4 cm^2 for unexposure
Permeation Area: A = 3.3 cm^2 for Outdoor Exposure

Table 5.2.4. Water Vapor Transmission Test Data (LDPE/Starch/MX Samples).

Unexposed Samples				Samples Exposed to Enzyme*			
Time (day)	W (g)	W/A (mg/cm²)	Average of W/A (mg/cm²)	Time (day)	W (g)	W/A (mg/cm²)	Average of W/A (mg/cm²)
0	0	0	0.00	0	0	0.00	0.00
2	0.175	9.02					
2	0.173	8.92	8.89				
2	0.173	8.92					
2	0.169	8.71					
				3	0.169	8.71	
				3	0.191	9.85	9.94
				3	0.226	11.65	
				3	0.185	9.54	
4	0.345	17.78					
4	0.346	17.84	17.85				
4	0.338	17.42					
4	0.356	18.35					
				6	0.398	20.52	
				6	0.402	20.72	21.64
				6	0.475	24.48	
				6	0.404	20.82	
7	0.583	30.05					
7	0.577	29.74	30.72				
7	0.615	31.70					
7	0.609	31.39					
9	0.765	39.43		9	0.622	32.06	
9	0.759	39.12	39.82	9	0.652	33.61	34.16
9	0.790	40.72		9	0.716	36.91	
9	0.776	40.00		9	0.661	34.07	
11	0.947	48.81	48.43				
11	0.932	48.04					
				13	0.925	47.68	
				13	0.997	51.39	51.91
				13	1.150	59.28	
				13	0.956	49.28	

*   α- Amylase

Permeation Area: A = 19.4 cm²

mass gain, M_t/M_{eq}, versus square root of time. The typical plots for both PG and 6P samples are shown in Figures 5.2.7 and 5.2.8, respectively. Here M_t and M_{eq} are the cumulative amount of CO_2 in the polymer at time t and at equilibrium respectively. All curves in the films were linear in the initial stage with a correlation coefficient ≥ 0.93. From the slope (k) of the initial linear portion, the diffusion coefficient D can be calculated as follows:

$$D = \frac{\pi}{16} (k \ell)^2 \tag{5-2}$$

The permeability P is obtained by

$$P = D \cdot S \tag{5-3}$$

where S is the solubility which can be determined from the equilibrium mass gain, M_{eq} (as described in the Section 2.5.7). The values of D, S, and P for CO_2 sorption to PG and 6P samples at various exposure times are listed in Table 5.2.5. In Figures 5.2.9 and 5.2.10, the permeabilities for both films are plotted as a function of the duration of Weather-Ometer® exposure. As seen in the figures, the relationships between the permeabilities and duration of exposure showed quite different trends for the two samples, although both films are made up of similar materials, i.e. low density polyethylene. The permeability for PG film increased linearly with the duration of exposure which is consistent with the result of the linear relationship between the WVTR and the outdoor exposure time as shown in Figure 5.2.2. The data for the (ethylene-carbon monoxide) copolymer (6P) samples, however, showed decreasing curvature with a sharp decline in permeability during the first 50 hours of ̣osure.

Inc̣ ̣e in permeability in the PG films made of LDPE/MX can be explained in terms of plasticization by the sol fraction generated during oxidation. Generation of sol molecules during catalyzed autoxidation of polyethylene is well established. Early decrease in tensile modulus on exposure(see Table 5.2.6) is also consistent with the generation of sol molecules. At longer durations of exposure, however, the modulus increases, indicating crosslinking of the matrix. Apparently the plasticizing effect of the sol fraction more than offsets any reduction in diffusion brought about by the crosslinking, yielding a net increase in permeability and water vapor transport rate (WVTR) with duration of exposure. Table 5.2.6 compares transport parameters and tensile moduli for PG and 6P.

In the case of (ethylene-carbon monoxide) copolymer (6P), ph ̣ ̣odegradation is predominantly a Norrish II type reaction which does not result in free-ṛ ̣ ̣al formation. However, the terminal unsaturation and methyl ketones resulting from the Norrish II process are readily autoxidizable. These would promote free radical processes within the matrix. These secondary oxidation reactions may involve radical-radical interactions

Table 5.2.5. Carbon Dioxide Permeation Data for 6P and PG Films.

Material: PG (Plastigone) (LDPE/MX)
Exposure Type: Weather-Ometer®
Film Thickness: 0.034 mm

Material Code	Exposure Time (hr)	Sample Weight (mg)	CO_2 Uptake at Equilibrium (μg)	Initial Slope of M/Mo vs. SQRT (time) (1/sec$^{0.5}$)	Diffusion Coefficient (x10^{-8} cm^2/s)	Solubility (x 10^{-3})	Permeability [x10^{-10} cc/(cm.s.cmHg)]
PG0	0	98.6	70.9	0.0860	1.68	4.53	0.761
PG50	50	96.3	73.9	0.0899	1.83	4.83	0.884
PG100	100	97.1	87.0	0.1046	2.48	5.64	1.399
PG150	150	96.5	98.1	0.1011	2.32	6.40	1.485
PG200	200	9?.8	99.5	0.1109	2.79	6.47	1.805
PG250	250	95.3	108.6	0.1136	2.93	7.18	2.104

Material: 6P (Ethylene-carbon Monoxide) Copolymer
Exposure Type: Weather-Ometer®
Film Thickness: 0.42 mm

Material Code	Exposure Time (hr)	Film Thickness (mm)	Sample Weight (mg)	CO_2 Uptake at Equilibrium (μg)	Initial Slope of M/Mo vs. SQRT (time) (1/sec$^{0.5}$)	Diffusion Coefficient (x10^{-7} cm^2/s)	Solubility (x 10^{-3})	Permeability [x10^{-10} cc/(cm.s.cmHg)]
6P0	0	0.424	170.40	59.2	0.0365	4.70	2.16	10.2
6P50	50	0.419	170.18	58.0	0.0310	3.31	2.12	7.02
6P100	100	0.423	171.88	57.1	0.0302	3.20	2.07	6.62
6P200	200	0.416	169.82	56.7	0.0300	3.06	2.08	6.36
6P250	250	0.417	169.34	55.8	0.0297	3.01	2.05	6.17

Table 5.2.6. Comparison of Transport Parameters and Tensile Modulus of Photodegradable
Films Weathered in Weather-Ometer®.

Type	Exposure Time (hr)	Diffusion Coefficient ($\times 10^{-8}$ cm^2/s)	Solubility ($\times 10^{-3}$)	Permeability [$\times 10^{-10}$ cc/ (cm.s.cmHg)]	Modulus (kg/mm^2)
Plastigone	0	1.68	4.53	0.761	15.1
PG	50	1.83	4.83	0.884	12.6
(0.034 mm)	100	2.48	5.64	1.399	16.0
	150	2.32	6.40	1.485	20.8
	200	2.79	6.47	1.805	23.1
	250	2.93	7.18	2.104	26.6
HiCone	0	47.0	2.16	10.2	16.8
6P	50	33.1	2.12	7.02	30.3
(0.42 mm)	100	32.0	2.07	6.62	36.5
	200	30.6	2.08	6.36	37.2
	250	30.1	2.05	6.17	37.4

leading to crosslinking. Such crosslinking is extensive and has been reported to render a fraction as high as 30 percent of polymer insoluble [Cornell et al, 1984]. The tensile modulus of (6P) films exposed in a Weather-Ometer® does show an increase consistent with crosslinking. Such increased moduli cannot be explained solely in terms of the Norrish II process. However, the free-radical processes in the 6P material do not lead to plasticization via sol formation. The permeability therefore decreases with the duration of exposure, as the effect of crosslinking and consequent decrease in diffusivity override the effects of any minor amounts of sol generated.

It is not unreasonable to expect crosslinking in both processes but sol formation in the case of PG material only. PG is a metal pro-oxidant catalyzed polyethylene (LDPE) system where the chain scission reaction is accelerated relative to that in regular LDPE. Multiple scission events on the same macromolecular chain are more likely to occur in such a catalyzed system. In the 6P material, the free-radical process is a secondary phenomenon, occurring at a slow rate. In a thick sample ($\ell \sim 0.42$ mm), the oxidation is likely to be diffusion-controlled with the radicals undergoing combination leading to crosslinking. Multiple scissions on the same macromolecular chain leading to sol formation are likely to be very limited.

5.3 DEVELOPMENT OF METHODOLOGY TO DETERMINE CHANGES IN STARCH CONTENT IN LDPE/STARCH BLENDS

5.3.1 TGA of Unweathered Samples

To determine the starch content of ADM (LDPE/starch) samples, thermogravimetric analysis (TGA) was used. Upon heating the ADM film samples to 450°C at a heating rate of 10°C/min. in He, a rapid step decrease in weight was seen in the temperature range of 270°C to 350°C, followed by a second large decline in weight at temperatures above 380°C. Figure 5.3.1 shows a typical TGA tracing for unexposed ADM film containing 6% starch. The initial weight loss is apparently due to pyrolysis of starch within the LDPE matrix, while LDPE itself pyrolyzes from about 380°C. A TGA tracing for regular LDPE film is shown in Figure 5.3.2. For LDPE/starch films, weight loss at the lower temperature range should be proportional to starch content. Percent weight losses in the temperature range of 250 to 350°C are listed in Table 5.3.1 for unexposed ADM(2) samples containing various weight percents of starch. The starch contents listed in column 2 of the table are the values provided by the manufacturer. A good linear relationship between the weight loss (TGA) and the known starch content of the film was obtained with a correlation coefficient of 0.98 as shown in Figure 5.3.3.

Table 5.3.1 TGA Data for ADM (LDPE/Starch), LDPE Mixes, and ADM(2) Films with Different Starch Contents.

Type	Weight Fraction*	Percent Decrease in Weight at $\Delta t \neq$
ADM Film Samples	0	0.35
ADM(2)	0.02	1.92
	0.04	2.17
	0.06	5.40
	0.08	6.46
	0.10	7.66
	0.12	8.75
ADM/LDPE Mixes	0	0.44
ADM(1)	0.197	1.73
	0.333	2.72
	0.501	3.79
	0.675	4.73
	0.803	5.59
	1.00	6.84

* For ADM(1) series, weight fractions are accurately known and indicate the amount of ADM material containing 6% starch blended with LDPE. For ADM(2) series, weight fractions of starch are approximate and were provided by manufacturer.

$\neq$ For ADM(1) series, $\Delta t = 194\text{-}350°C$.
For ADM(2) series, $\Delta t = 250\text{-}350°C$

To further validate the method, a second series of samples was prepared by mixing ADM film samples containing 6% starch with regular LDPE film of the same thickness. The LDPE compound used was the same used in ADM (LDPE/MX). The minced shreds of film samples were placed in the same sample pan and subjected to TGA analysis. In Figure 5.3.4 the percent weight losses in the temperature range 194 to 350°C are plotted against the weight fraction of ADM in the mixture of the ADM and LDPE. The data are listed in Table 5.3.1. As expected, the weight loss obtained by TGA increased linearly (correlation ~1.0) with the weight fraction of ADM (or the fraction of starch in mixture). It is apparent from Figures 5.3.3 and 5.3.4 that TGA can form the basis of an accurate test method to rapidly determine the starch content in LDPE.

5.3.2   Effect of Biodeterioration of ADM Samples on TGA

(a)   *Outdoor Soil Burial*

TGA measurements were carrried out on ADM(1) films exposed outdoors in a soil environment, and the results were compared with those for unexposed samples. Table 5.3.2 shows the percent weight decrease in the temperature range 250 to 350°C, W_D, for the samples exposed to different durations. The W_D values for 6 to 12 weeks exposure were smaller than W_D for unexposed samples, as might be expected. However, the values for samples with 16 and 20 weeks exposure were larger compared to the control. Assuming the weight decrease, W_D, is totally due to pyrolysis of the starch, percent of residual starch content after exposure (presumably due to biodegradation of starch) is expressed as the following:

$$\text{\% residual starch content after exposure} = \frac{W_D \text{ of exposed ADM} - W_D \text{ of unexposed LDPE}}{W_D \text{ of unexposed ADM} - W_D \text{ of unexposed LDPE}} \times 100$$

The calculated values of W_D are shown in Table 5.3.2.

The average value of weight loss obtained for unexposed LDPE samples was 0.35% (Figure 5.3.2), possibly due to losses in low molecular weight additives. The starch contents of ADM samples after exposure for 6 to 12 weeks outdoors were almost constant and were generally about 10 percent lower than that of the unexposed sample. This suggests that the 10 percent of starch in LDPE/starch blends can be consumed in relatively short exposure times, but little change in starch content occurs thereafter, even for fairly long exposure times. Surprisingly, the determined starch contents for 16 and 20 weeks exposure were observed to be larger than that for unexposed samples of ADM films. This was probably due to limitations of this technique in determining starch content of extensively deteriorated samples. Heavily deteriorated films often contain fungi and other organisms

Table 5.3.2. Effect of Environmental Exposure on Starch Content of ADM Film Samples.

Exposure	Duration (week)	Initial Starch Content (%)	% Weight Change at 250° - 350°C	% of Residual Starch Content
1. Outdoor soil burial	0	~6	5.20	-
	6		4.59	87
	10		4.98	95
	12		4.58	87
	16		5.85	>100
	20		6.19	>100
2. Laboratory soil burial at 37°C	0	~2	1.92	-
	16		1.73	88
	0	~6	5.40	-
	16		5.03	93
	0	~12	8.75	-
	16		7.69	87
3. α-amylase at 37°C	0	~6	5.61	-
	6		5.20	92
4. Soil innoculum at 37°C in mineral salt medium	0	~6	5.61	-
	6		4.96	88

Note:

(a) No shredding, cutting, or grinding was used to increase the surface area of film samples exposed to microbes

(b) Total weight change was assumed to be due to complete pyrolysis of starch

(c) % residual starch content after exposure $= \dfrac{\text{% wt. decrease of exposed ADM - % wt. decrease of LDPE [ADMC]}}{\text{% wt. decrease of unexposed ADM - % wt. decrease of LDPE [ADMC]}} \times 100$

growing within the plastic matrix. These, especially the cellulosic material, would probably pyrolyze at about the same temperature as starch and therefore interfere with the determination of weight loss. A second possibility was interference due to photothermal oxidation of the polyethylene due to exposure. In a metal compound catalyzed system, oxidation can yield low molecular weight oligomers and reaction products. Volatilization of these compounds also interferes with the determination.

Figure 5.3.5 is a TGA tracing for an ADM sample exposed 20 weeks outdoors showing weight losses at temperatures as low as 180°C. Accurate determination of weight loss by TGA requires a tracing which is essentially flat at lower temperatures.

(b) *Effect of Starch Content on W_D*

ADM(2) film samples specially prepared by the manufacturer with various starch contents (2, 6, and 12%) were exposed in the laboratory (accelerated soil under aerobic conditions) for up to 114 days. The percent weight decrease and the percent change in starch content for these exposed and unexposed ADM(2) samples are listed in Table 5.3.2. As can be seen from the table, the higher the percentage of starch contained in the sample, the larger is the percent residual starch as obtained by TGA of unexposed material. This high degree of correlation obtained suggests the technique to be a sensitive one. The percent change in starch content after exposure, however, was generally independent of initial starch content of the sample and was about 10 percent lower for all three starch contents.

(c) *Tests on Other Samples*

Both enzymatic and aerobic exposures were attempted to enhance the biological deterioration of ADM(3) film samples. An amount of enzyme (α-amylase) derived from *Bacillus sp.* (type X1-B having an activity of 575 units/mg protein) sufficient to hydrolyze the starch in the sample was placed in contact with the sample film in buffer solution (pH 6.9) at 37°C for 46 days. Enzyme solution was replaced twice during this period of exposure.

Samples were also placed in a soil environment with added urea and phosphate under aerobic conditions at 37°C in the dark. As shown in Table 5.3.2, only a 10% decrease in starch content after exposure was again observed for both types of samples.

From the above results, it appears that in soil burial exposure of a film sample of ADM, the starch content of the sample decreases by about 10% within a relatively short exposure time ($\leq$ 6 weeks), but this decrease in starch content does not continue for longer exposure times. In the presence of light or heat (such as in composting), additional chemical mechanisms are available for disintegration of material, and the rate of starch loss might be higher.

During exposure, only those starch particles near the surface of the film are likely to be decomposed rapidly by means of enzyme action. Assuming the starch particles to be uniform and to be distributed homogeneously throughout the whole LDPE matrix, the starch decomposed would then be that which exists in 5% of the total film thickness, approximately 3 μm from each side of the film. The thickness of this thin layer at the surface corresponds approximately to the average particle size of the starches blended in LDPE, suggesting that the layer of starch granules exposed or contacted to the surface would be readily decomposed in aerobic soil-burial exposure.

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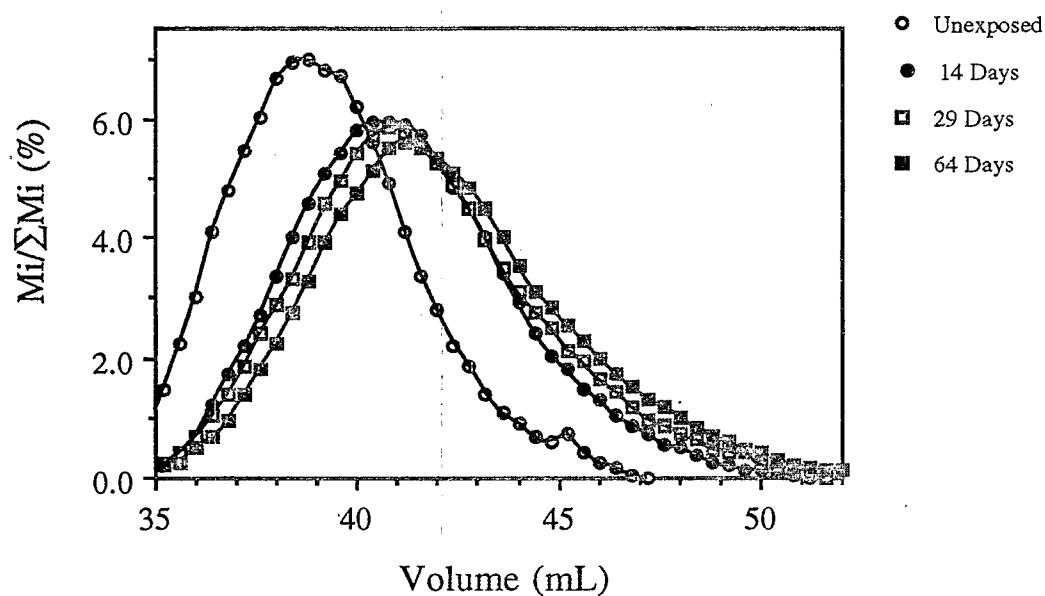
Figure 5.1.1 (a) Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PS - Outdoor - Chicago, IL).
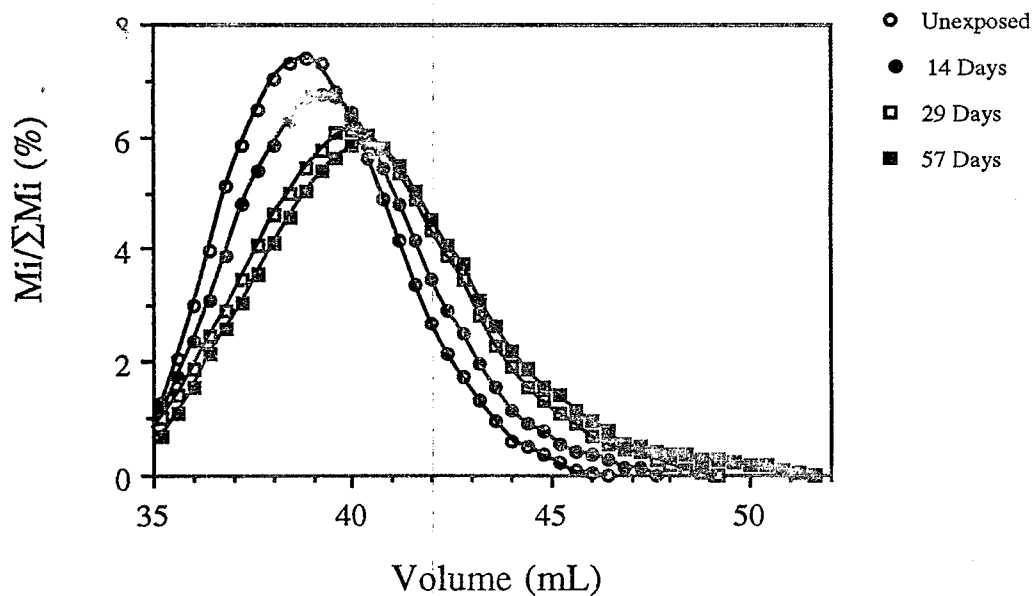

Figure 5.1.1 (b) Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PSC - Outdoor - Chicago, IL).
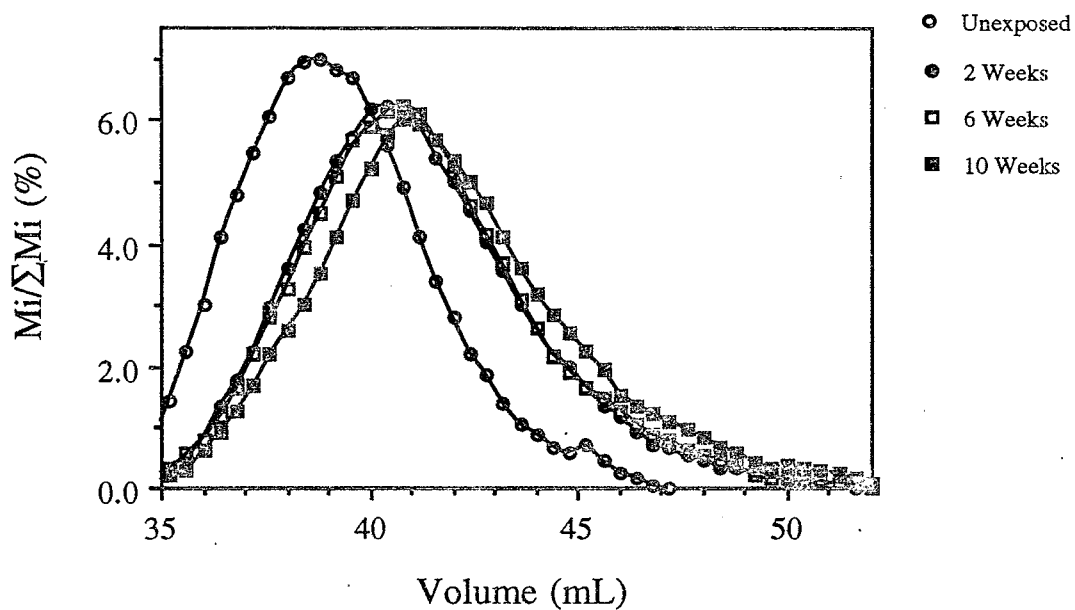
Figure 5.1.1 (c) Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PS - Outdoor - Miami, FL).
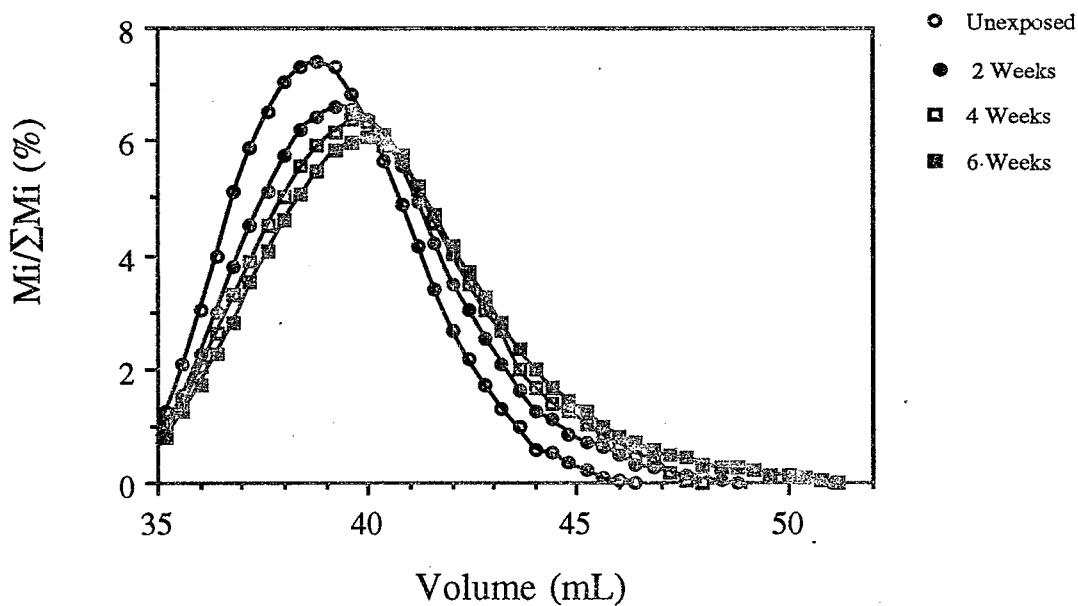

Figure 5.1.1 (d) Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PSC - Outdoor - Miami, FL).
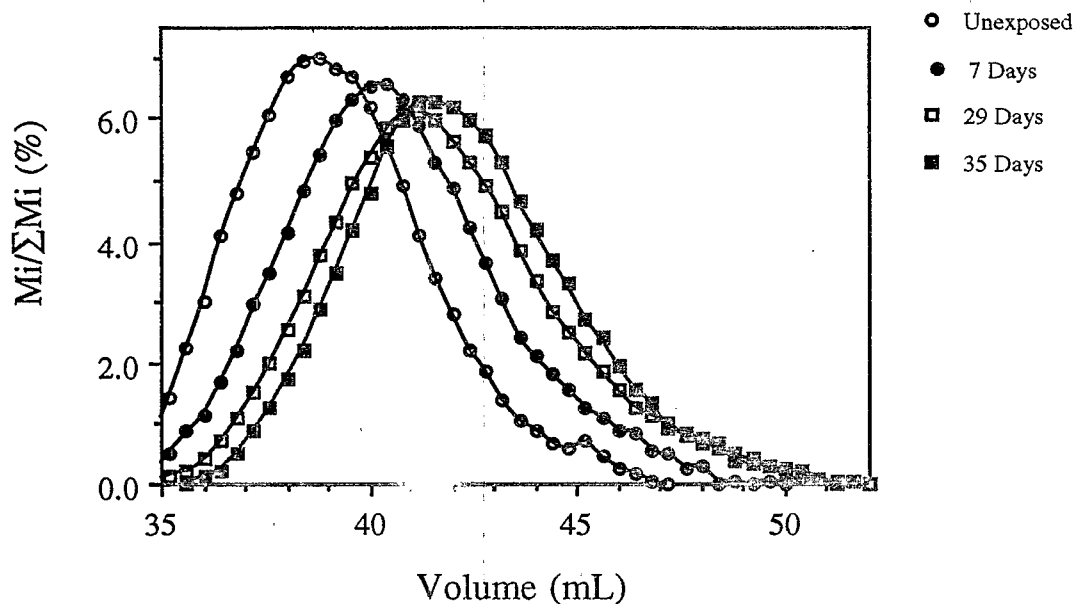
Figure 5.1.1 (e)   Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PS - Marine floating - Miami, FL).
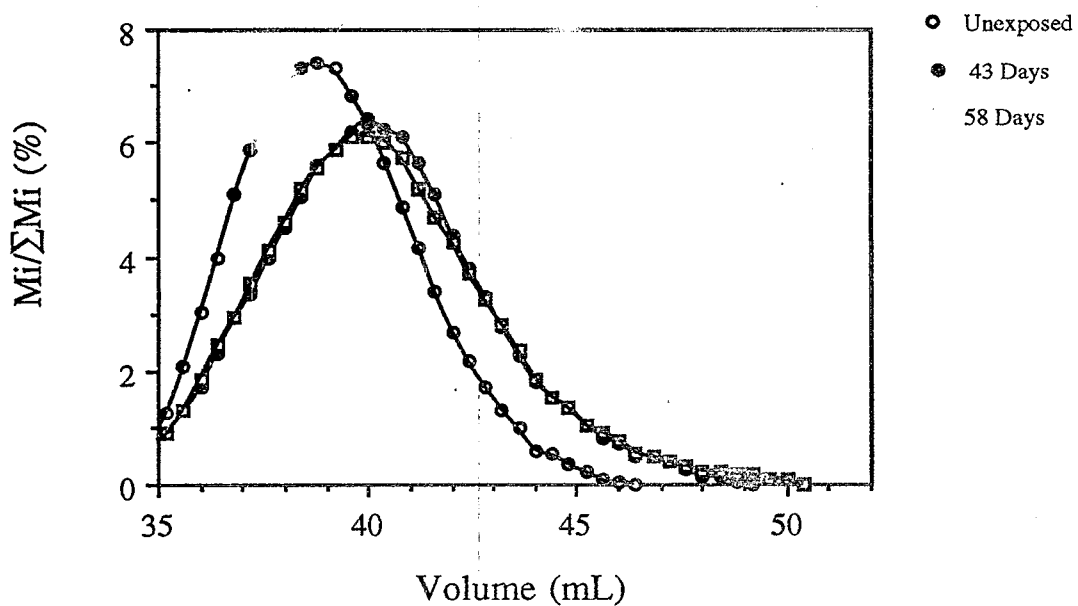

Figure 5.1.1 (f)   Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PSC - Marine floating - Miami, FL).

Figure 5.1.1 (g)   Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PS - Marine floating - Seattle, WA).
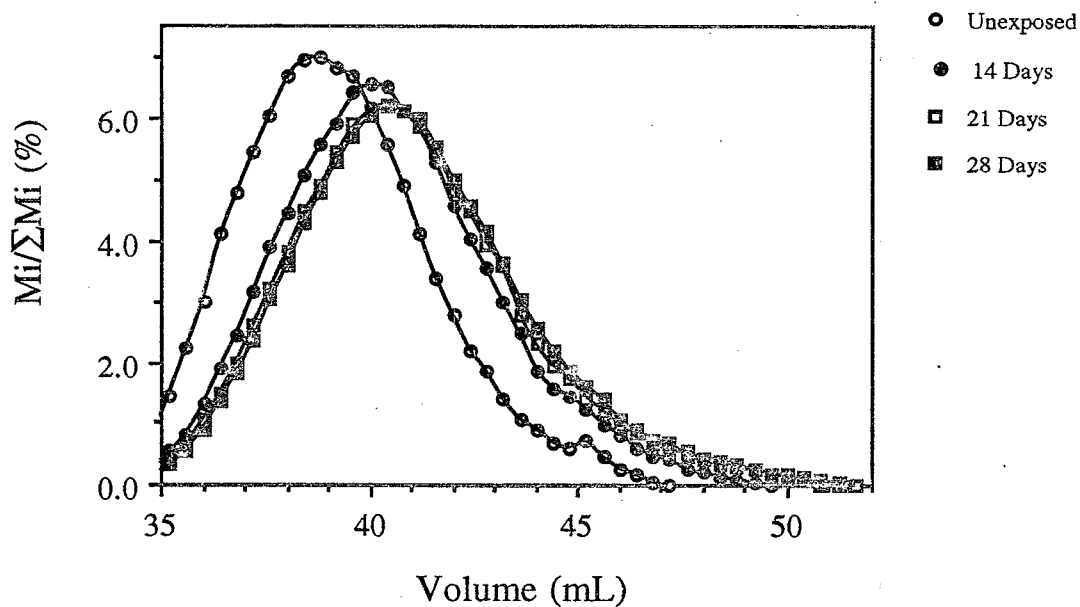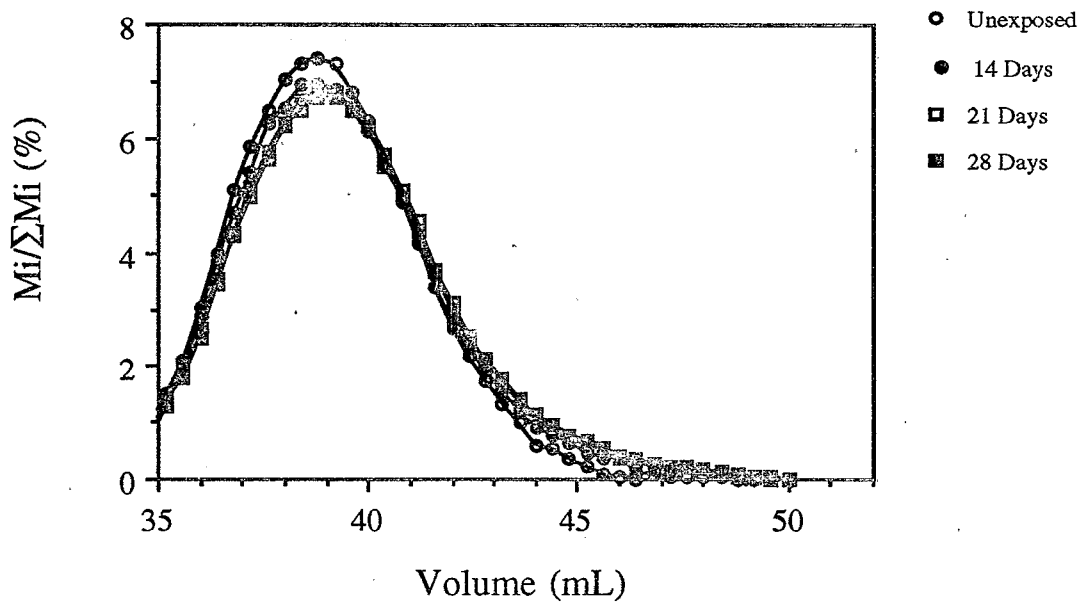

Figure 5.1.1 (h)   Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PSC - Marine floating - Seattle, WA).
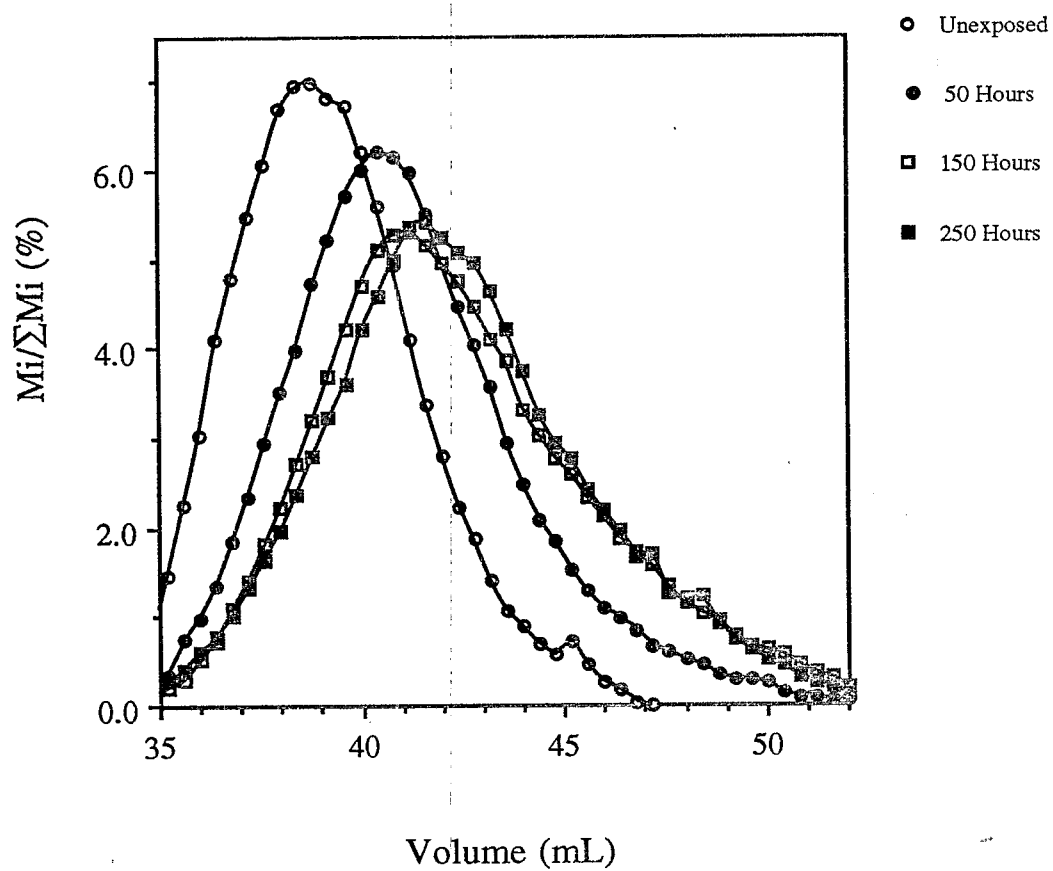
Figure 5.1.1 (i)   Molecular weight distribution (as measured by GPC) of exposed polystyrene foam - (PS - Weather-Ometer®).
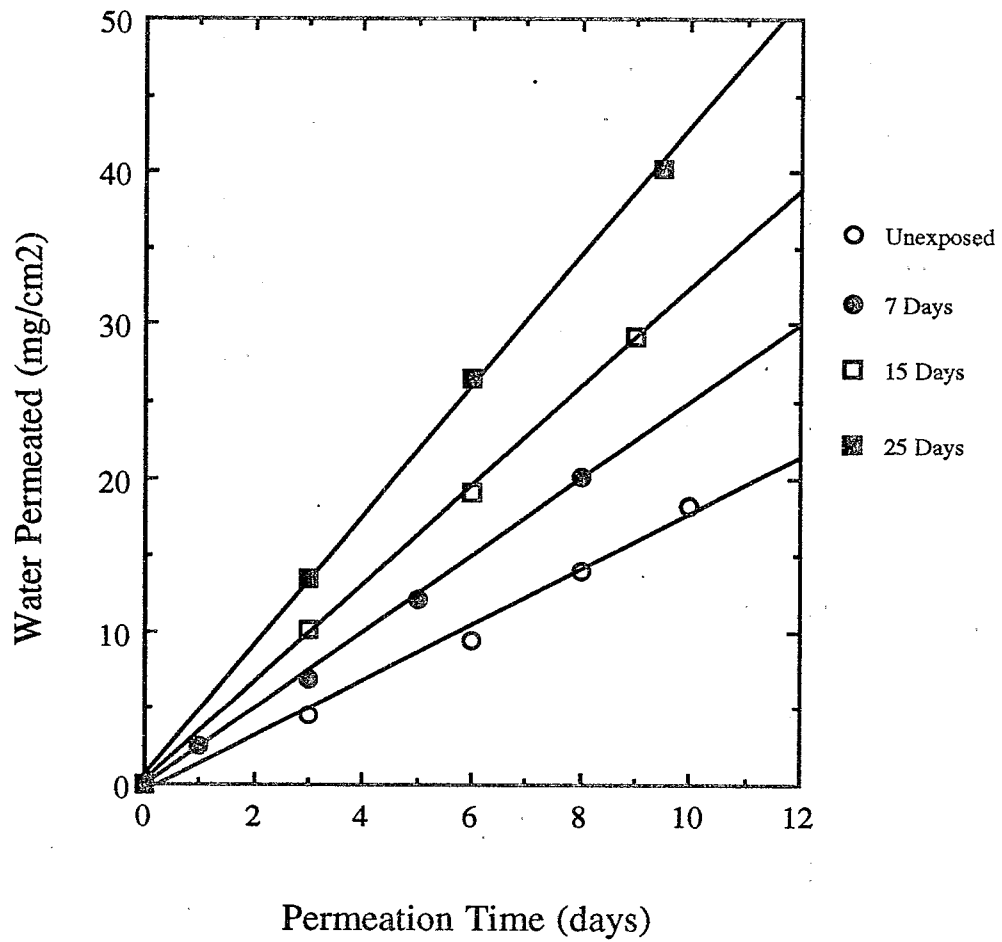
Figure 5.2.1   Water vapor transmission data for LDPE/MX samples weathered in Miami, FL.

$y = 8.4501e\text{-}2 + 3.5412e\text{-}3x \quad R^2 = 0.943$
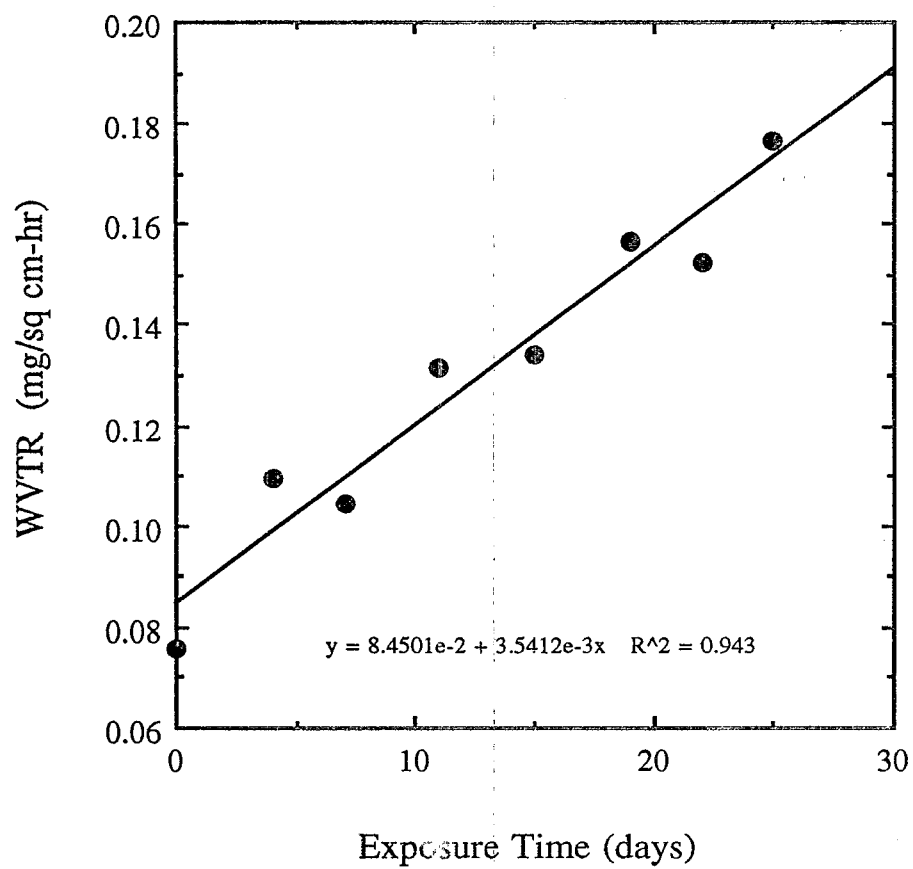
Figure 5.2.2   Change in WVTR with weathering time for PG (LDPE/MX) samples.
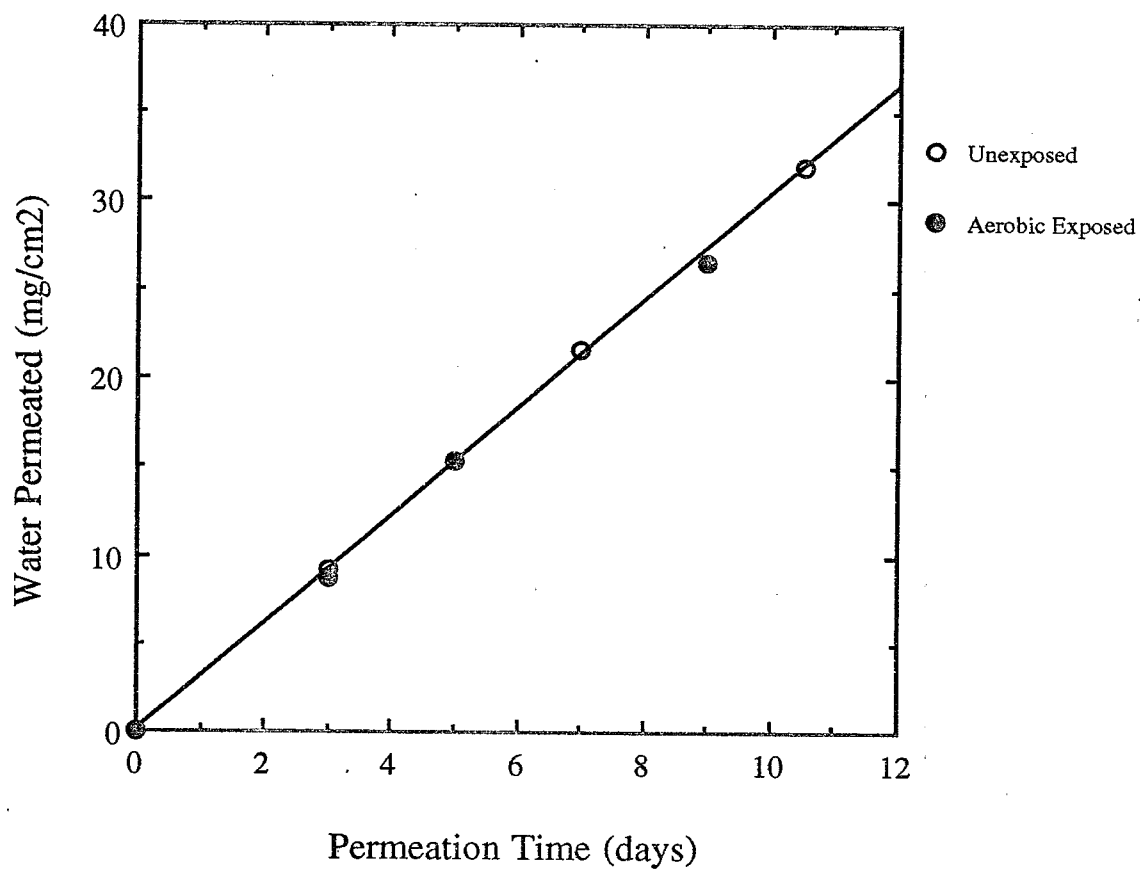
Figure 5.2.3   Water vapor transmission data for PCL (LLDPE/PCL blend) unaged film
and a film exposed to an aerobic biotic environment (40 days).
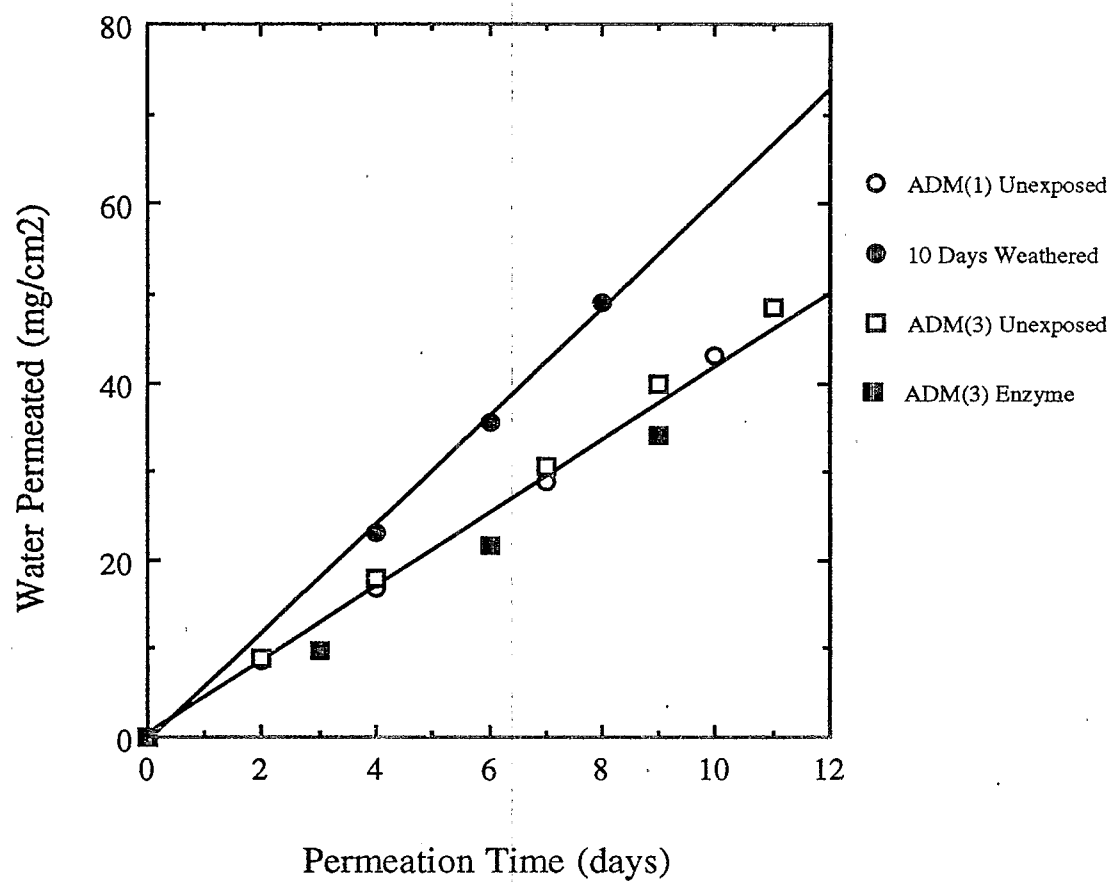
Figure 5.2.4   Water vapor transmission data for unexposed and weathered ADM (LDPE/starch/MX) films.
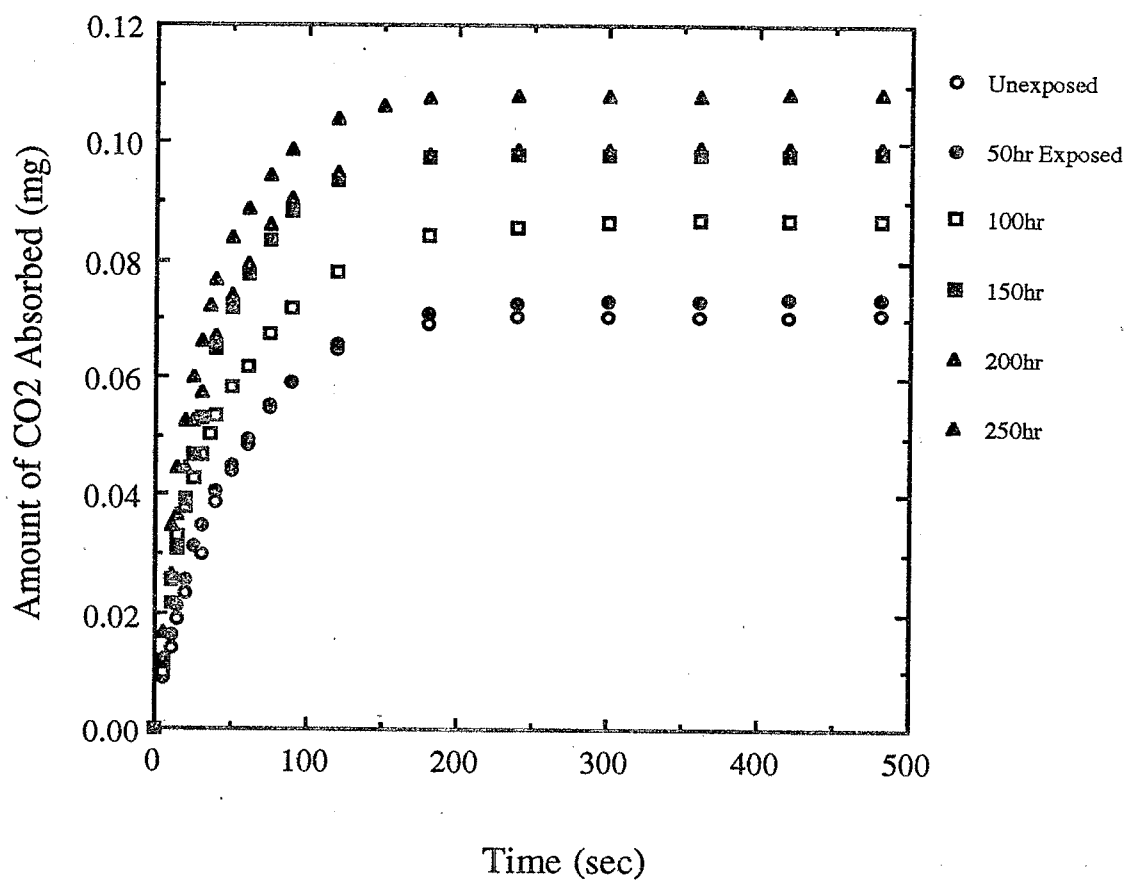
Figure 5.2.5   Gas (CO_2) sorption curves for weathered PG (LDPE/MX) films exposed in Weather-Ometer®.
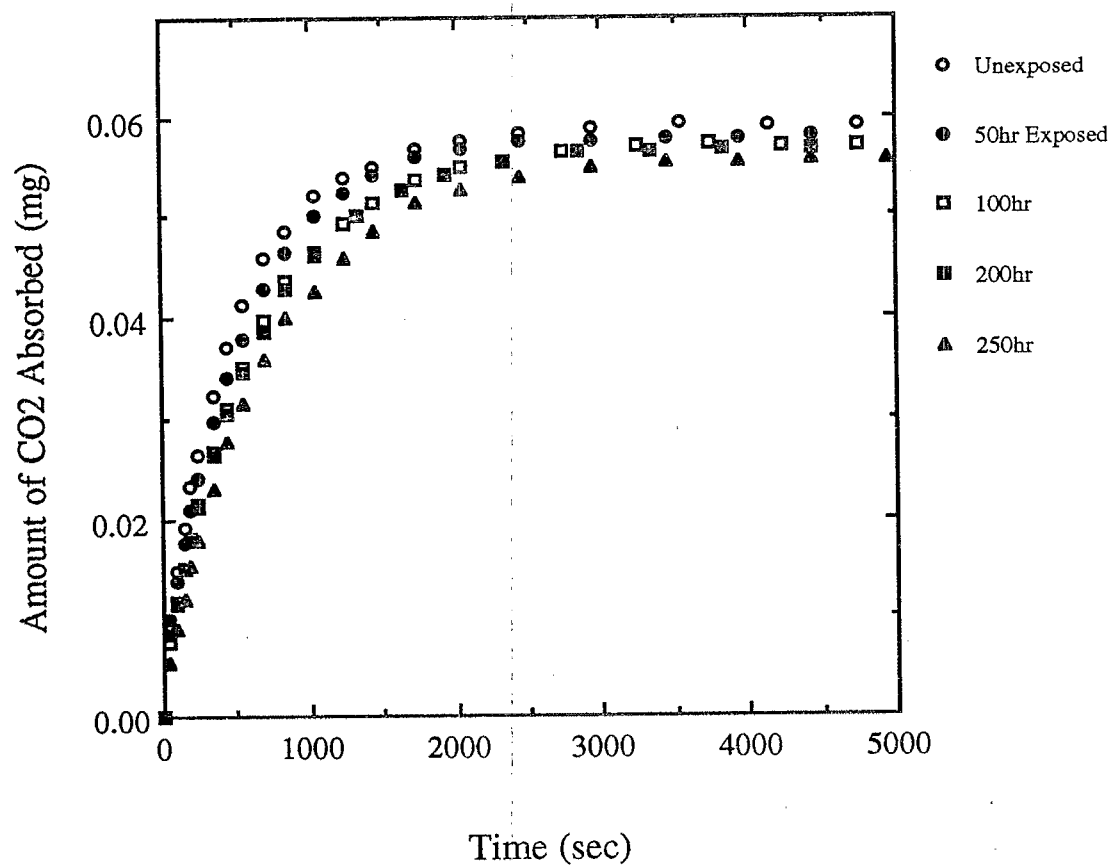
Figure 5.2.6   Gas (CO_2) sorption curves for weathered 6P (ethylene-carbon monoxide) copolymer films exposed in a Weather-Ometer® .
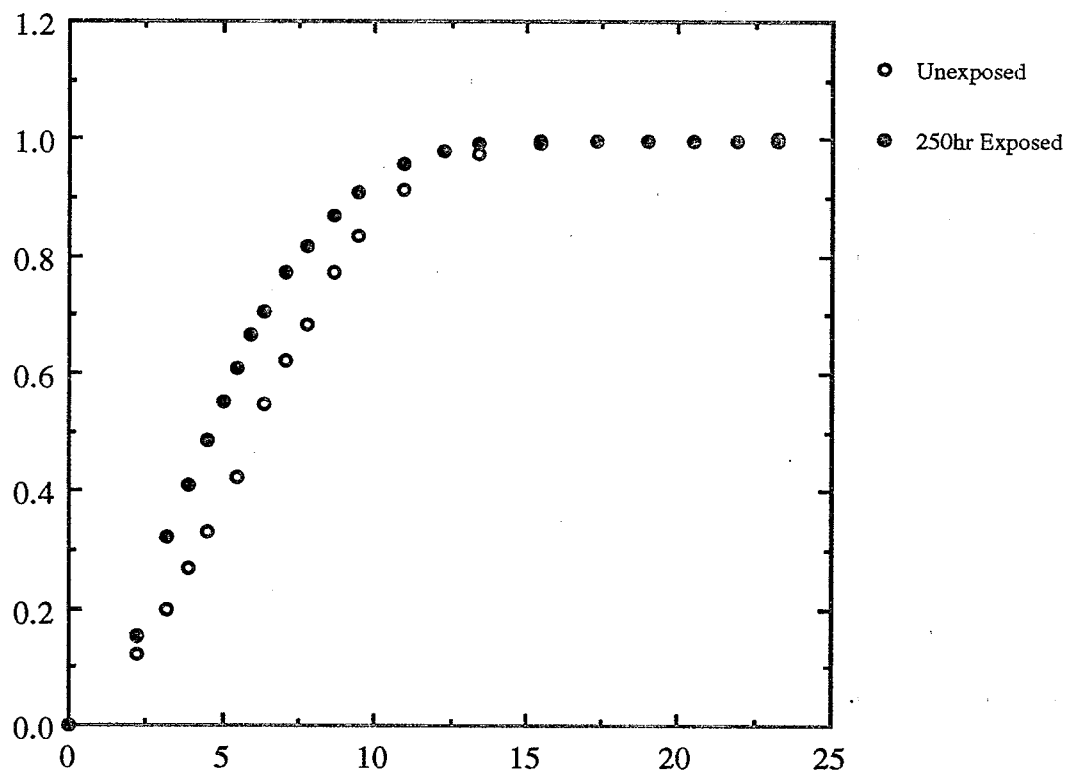
Figure 5.2.7   Difference in short-time gradient in sorption curves for aged and unaged PG samples.
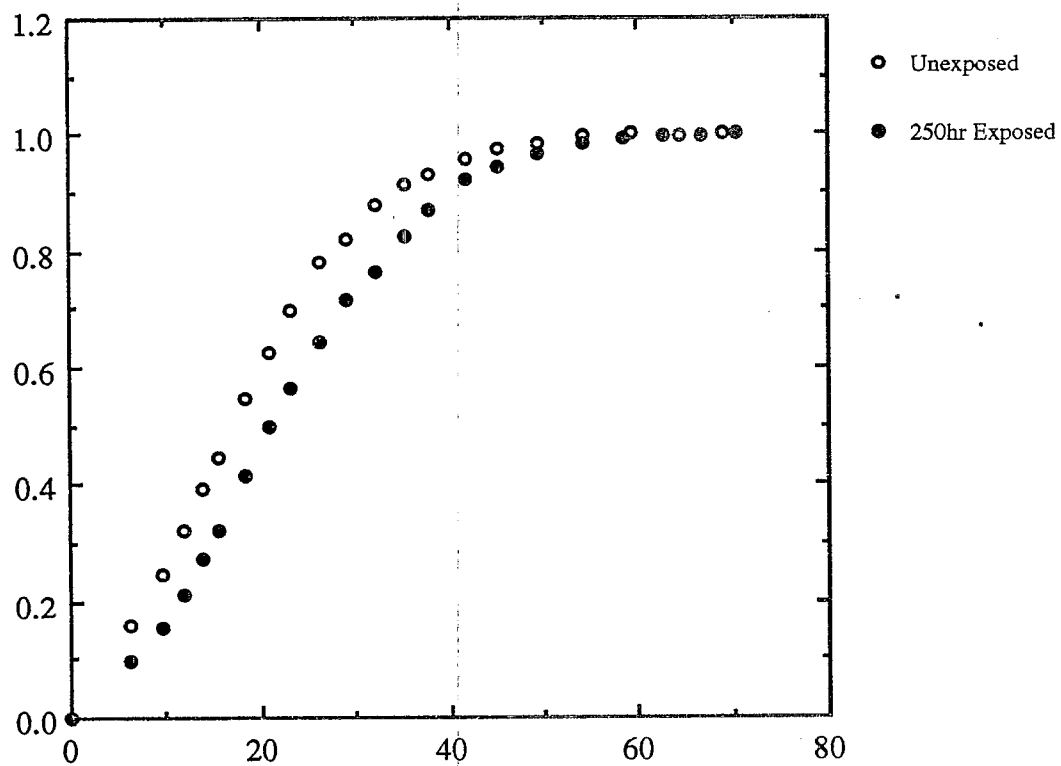
Figure 5.2.8   Difference in short-time gradient in sorption curves for aged and unaged 6P samples.
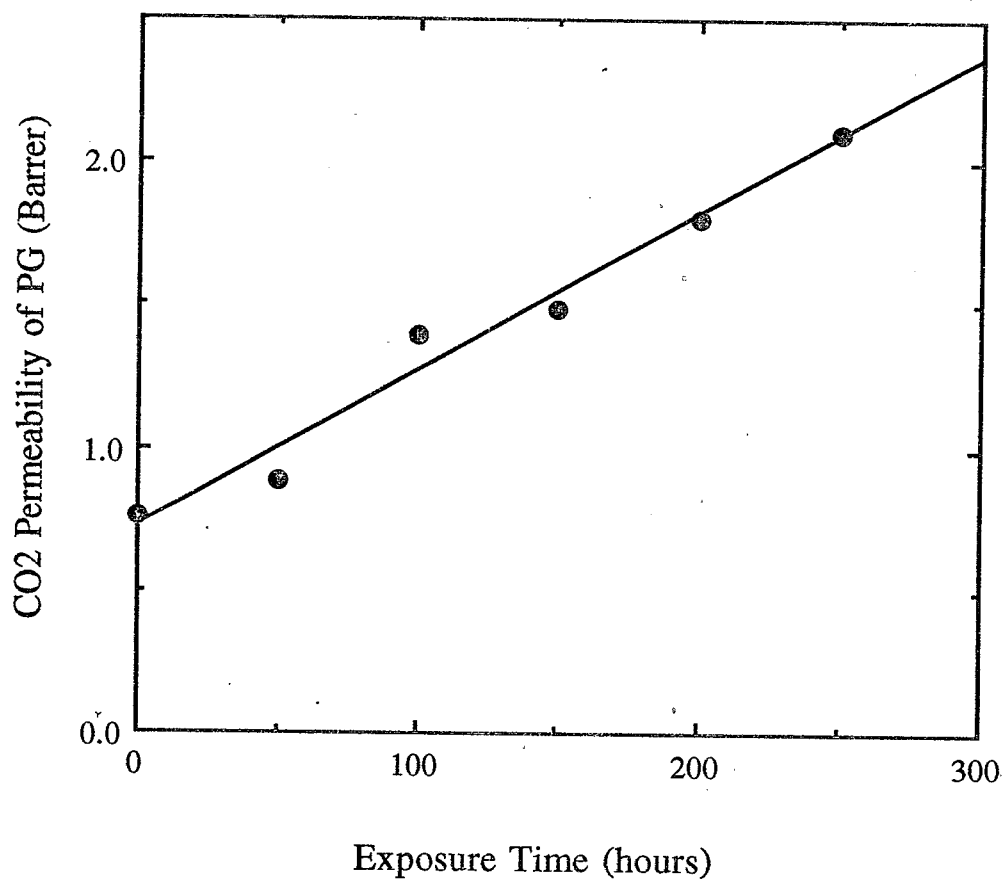
Figure 5.2.9   Effect of Weather-Ometer® exposure upon the CO_2 permeability for PG material.
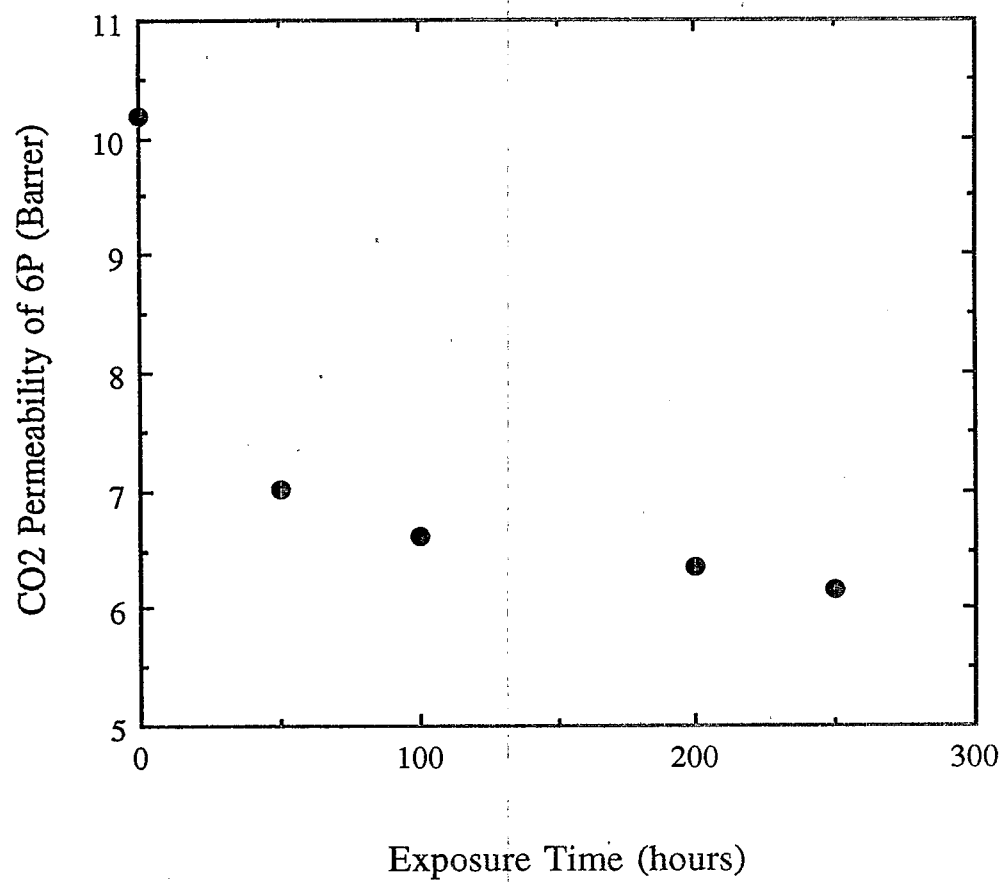
Figure 5.2.10   Effect of Weather-Ometer® exposure upon the CO_2 permeability for 6P material.
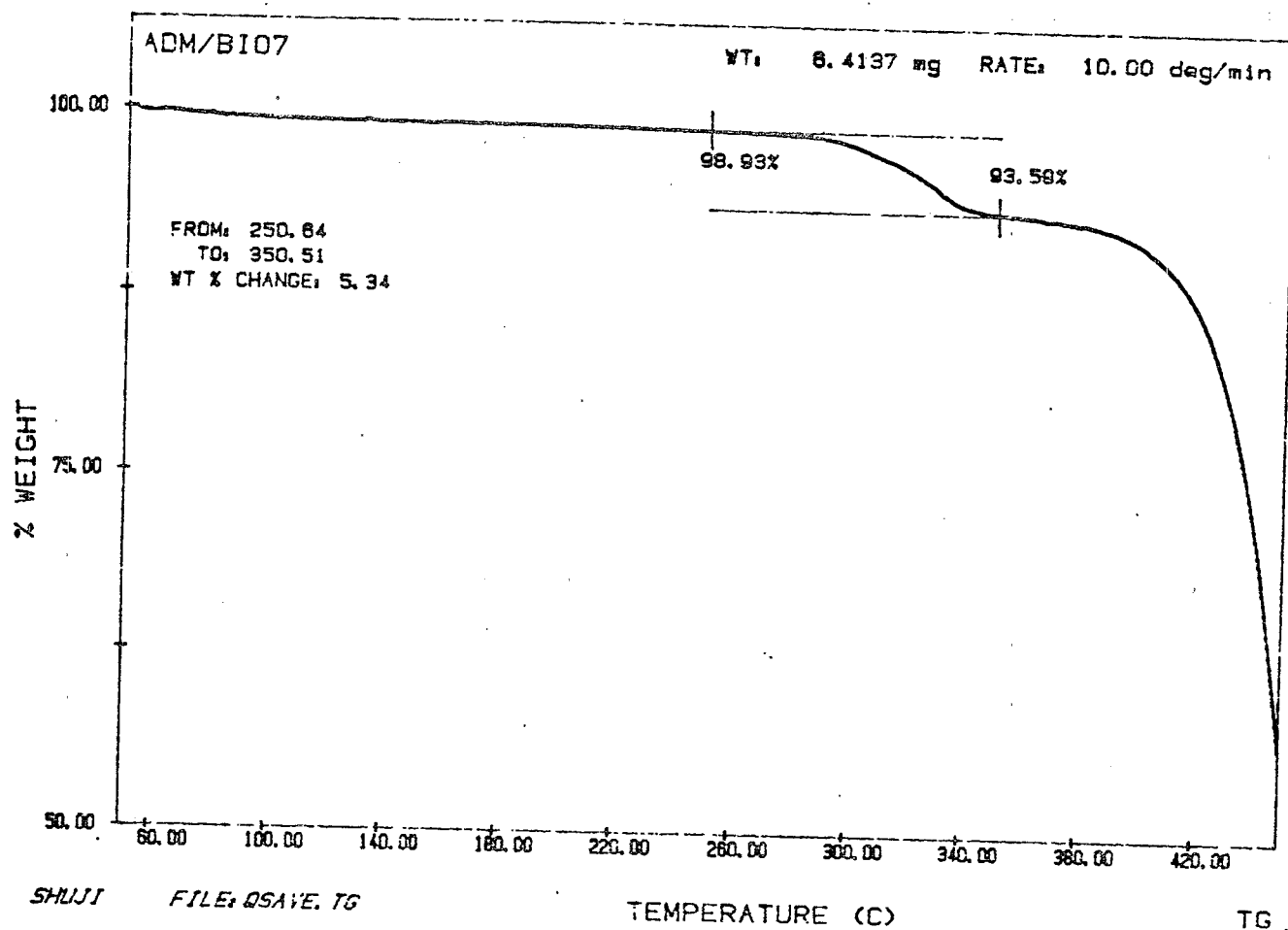
Figure 5.3.1   A TGA tracing of LDPE/starch/MX film containing ~6% starch.
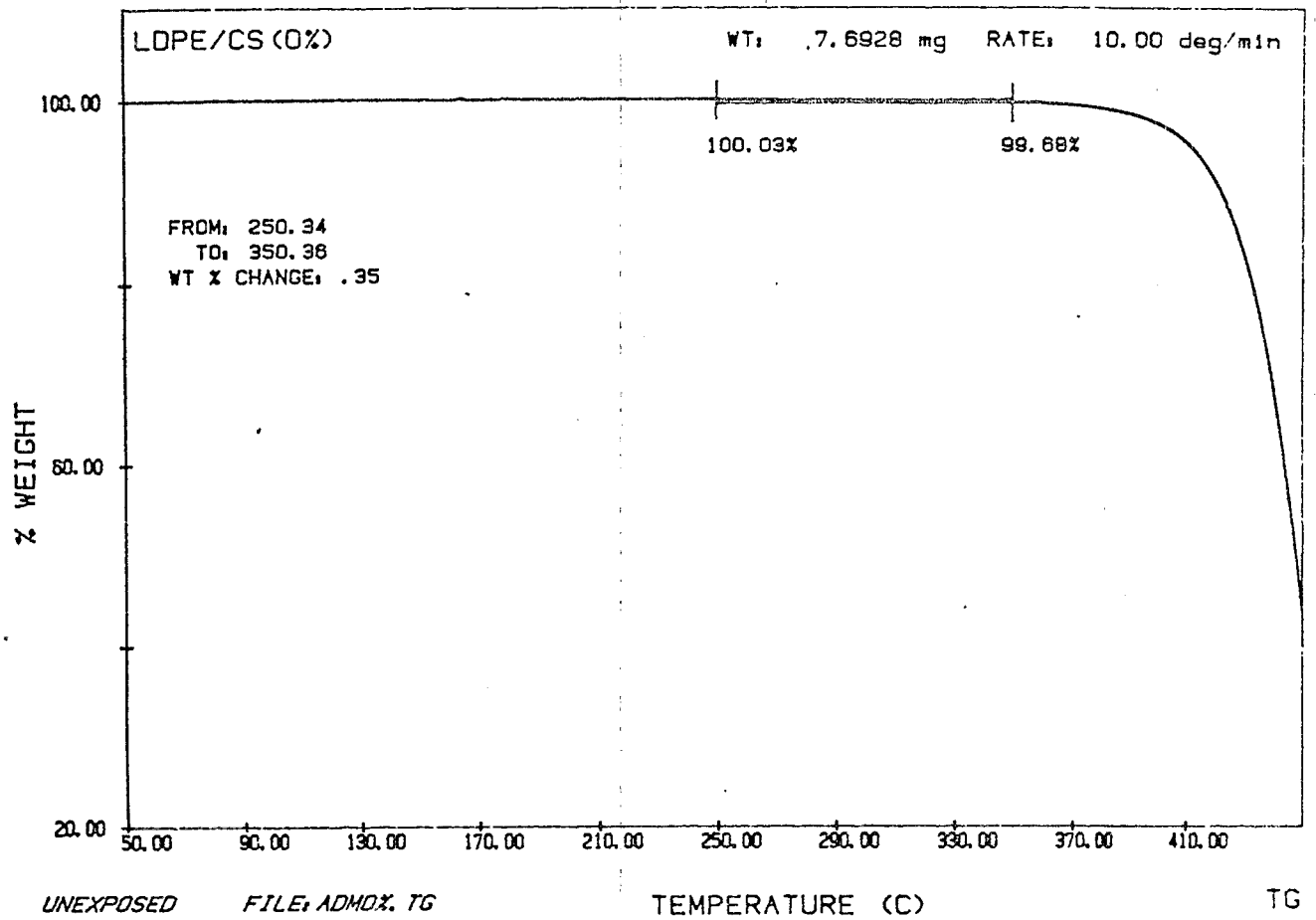
Figure 5.3.2   A TGA tracing of an LDPE control film.
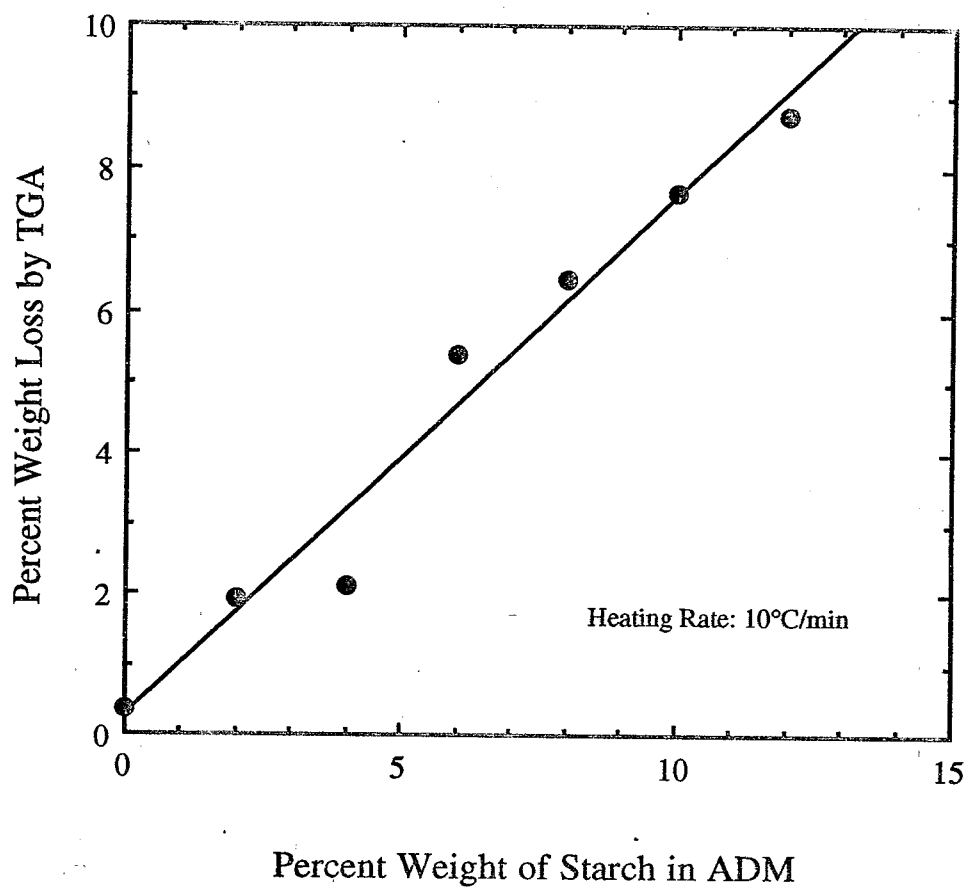
Figure 5.3.3   Percent weight loss versus known starch content of ADM
(LDPE/starch/MX) films in TGA experiments .
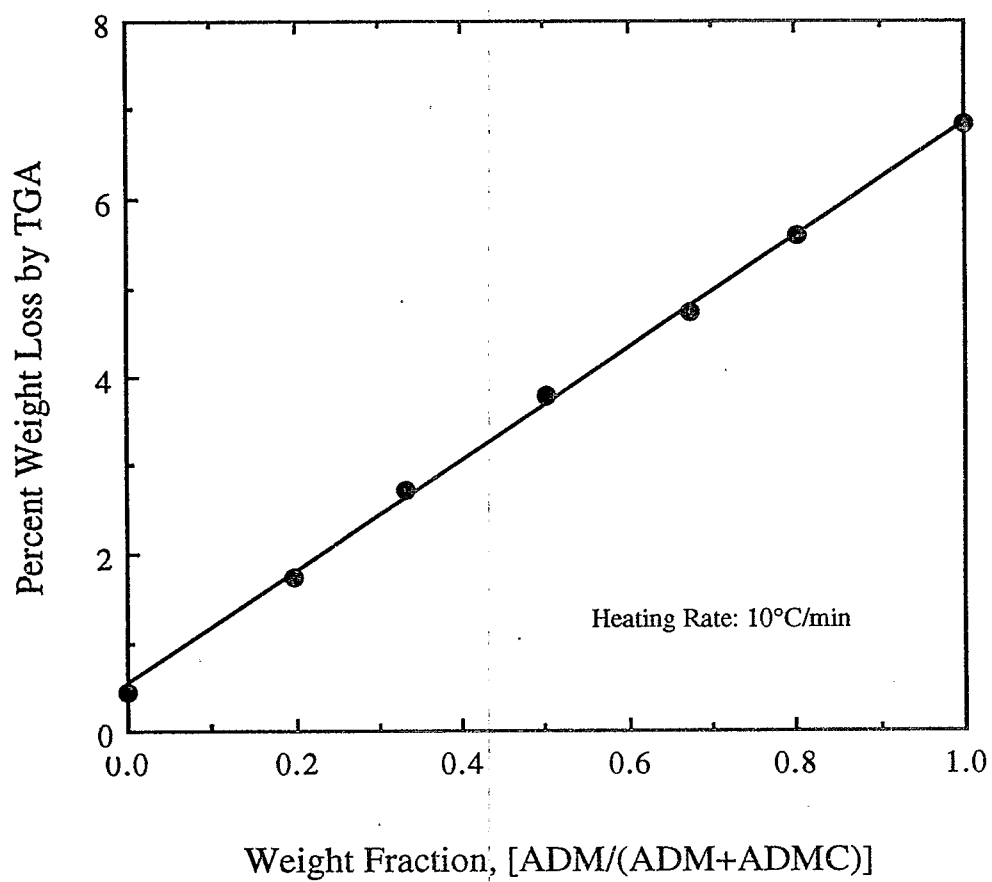
Figure 5.3.4   Percent weight loss versus weight fraction of ADM (LDPE/starch/MX) film in mixtures of ADM and control LDP.
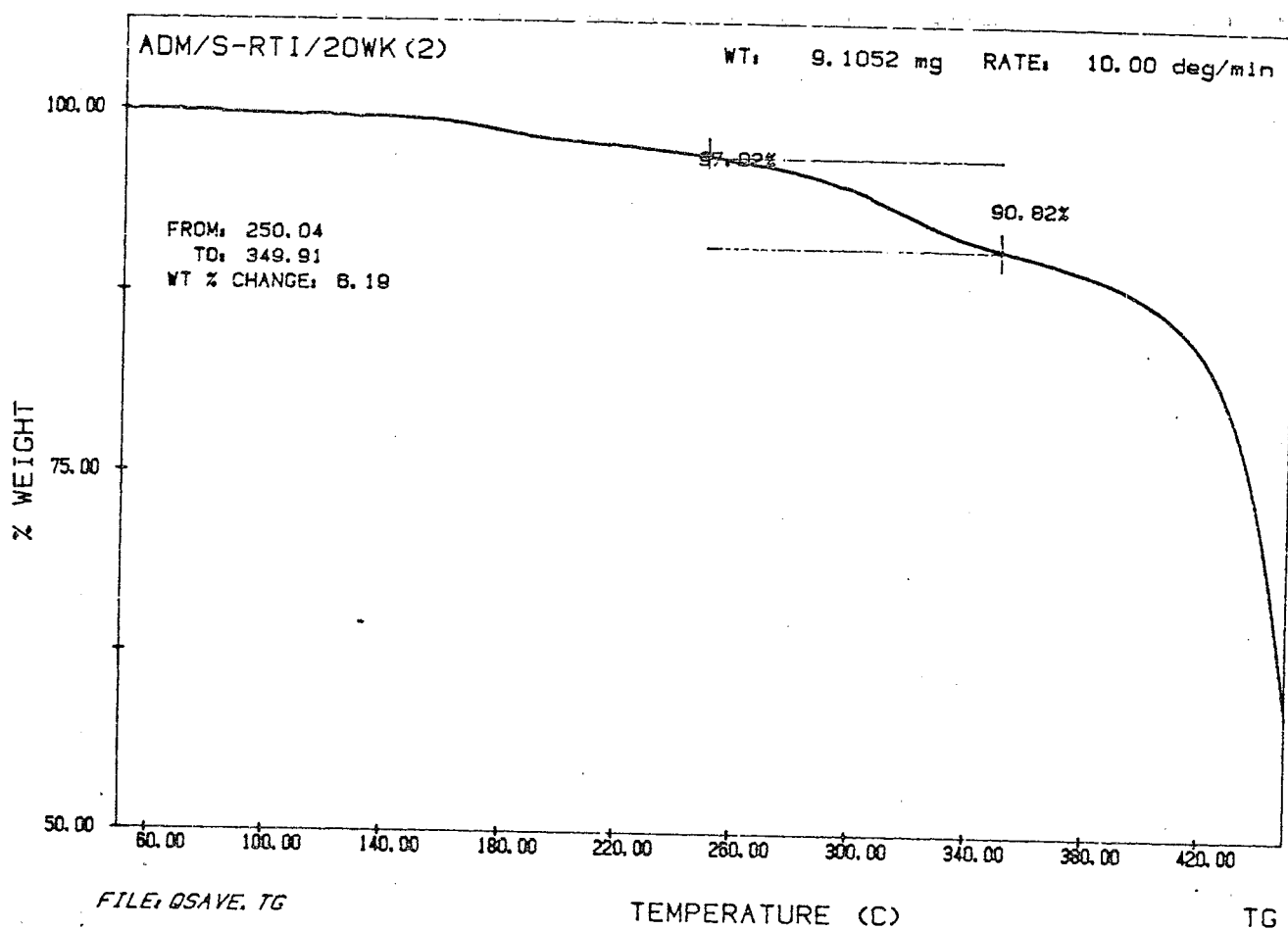
Figure 5.3.5   A TGA tracing of an ADM (LDPE/starch/MX) film exposed outdoors for 20
                 weeks showing variability in 140°C-260°C range.

SECTION 6.0

PRELIMINARY TOXICITY STUDIES

The toxicity of the degradation products generated from enhanced degradable plastics has always been a popular concern. For the most part, however, the products formed would qualitatively be little different from those formed during the photodegradation of the base plastic material. Both metal-catalyzed and uncatalyzed photooxidation of polyethylene will essentially result in similar products.

However, the rate of generation of these products is much higher in the case of enhanced degradable plastic materials. Since the rate of leaching (or diffusing out) of these from the plastic matrix will consequently be faster, higher local concentrations of products are likely to occur in the micro-environment about the degrading plastic film. As the toxicity is determined by the concentration to which the organism is exposed, both the identity and the kinetics of generation of the products of degradation needs to be addressed. The main issue is then to determine if any of the compounds accumulate at a rate high enough to allow the build up of unacceptably high local concentrations.

The comprehensive toxicity studies needed to address these concerns were outside the scope of this study. Such an exercise should ideally involve a study of rates of generation of compounds, soil microbial toxicity assessments as well as standardized toxicity studies (such as the EPA-accepted acute and chronic tests). It was, however, felt that some exploratory testing was needed to establish the toxicity of extracts from partially degraded photodegradable plastics to form the basis for a detailed study in the future.

Three factors determine the outcome of the toxicity studies:

(a)   Test organisms used.

(b)   Extent of degradation of the test plastic material prior to extraction.

(c)   Protocol for preparation of test solution ("effluent").

The use of a standard test organism was considered advantageous for the purpose of this exploratory experiment. EPA has a large database of information on tests carried out on two species [USEPA, 1989], *Ceriodaphnea dubia* (water flea) and *Pimiphales promelas* (fathead minnow). These indicator organisms are well suited for a test of this nature because of their importance in the food chain and also because of their cosmopolitan distribution. A second consideration is the extent to which the plastic material is degraded prior to testing. An undegraded enhanced-degradable plastic film is not likely to be associated with any toxicity, there being little or no organic materials which are water extractable. Manufacturers of the enhanced photodegradable plastics have sufficient test data to support

such a claim. Once exposed outdoors, the plastic material will contain extractives, the amount of which will depend on the duration and location of exposure. In the case of accelerated laboratory exposure, it will depend upon the spectral qualities of the source in the equipment as well as the duration of exposure. The other key issue is the extraction procedure to be used to prepare the "effluent" on which the tests are to be carried out. This is a critical consideration, as even relatively innocuous organic compounds in sufficiently high concentrations may show biological and toxicological effects. Florida protocol for toxicity testing, for instance, proposed the use of one percent by weight (undegraded) of the plastic in water and a 24 hr 20 - 25°C extraction procedure, to prepare the extract. Testing was then carried out on a diluted extract equivalent to a concentration of 1 g plastic in 2400 g of water. The methods under development at the ASTM (subcommittee D20.96) suggest the use of 2-4 g of degraded plastic material in 1-2 liters of water and extraction under similar conditions. The latter concentrations were based on considerations of levels of rainfall to be expected and the incidence of degraded litter under field conditions and are "worst case" concentrations. Testing in the presence of plastic fragments is acceptable, and complete filtration is not necessary in the case of this latter approach.

The intent of the testing carried out in this study was not to provide independent unbiased test data on commercially available enhanced degradable plastic materials. Results should not therefore be construed as being "acceptable" or otherwise under any specific set of requirements. The aim was more to obtain exploratory data to determine the concentration of extractives which may show biological effects for the two species in question. As such, the present work used the following basic experimental conditions.

(a) Test organisms: *Ceriodaphnea dubia* (water flea) and *Pimiphales promelas* (fathead minnow)

(b) Test method: A modified standard test method (given in Chapter 2).

(c) Duration of outdoor exposure: 15 days in Miami, FL under summer conditions. 190 MJ/sq.m total radiation.

(d) Extraction: 20 g (weight after degradation) per liter in distilled water. 24 hours. 20-25°C with moderate stirring. Plastic film cut into 1 cm squares for extraction. Polystyrene foam ground in blender with water prior to extraction.

(e) Test solutions : A series of solutions ranging from 3-100 percent of the above stock "effluent" solution. Figure 6.1 illustrates the concentrations in g/l for some of these solutions.

All testing was done by a subcontractor specializing in toxicity measurement and biological monitoring studies.

CONCENTRATIONS OF EXTRACTS USED IN TOXICITY TESTS
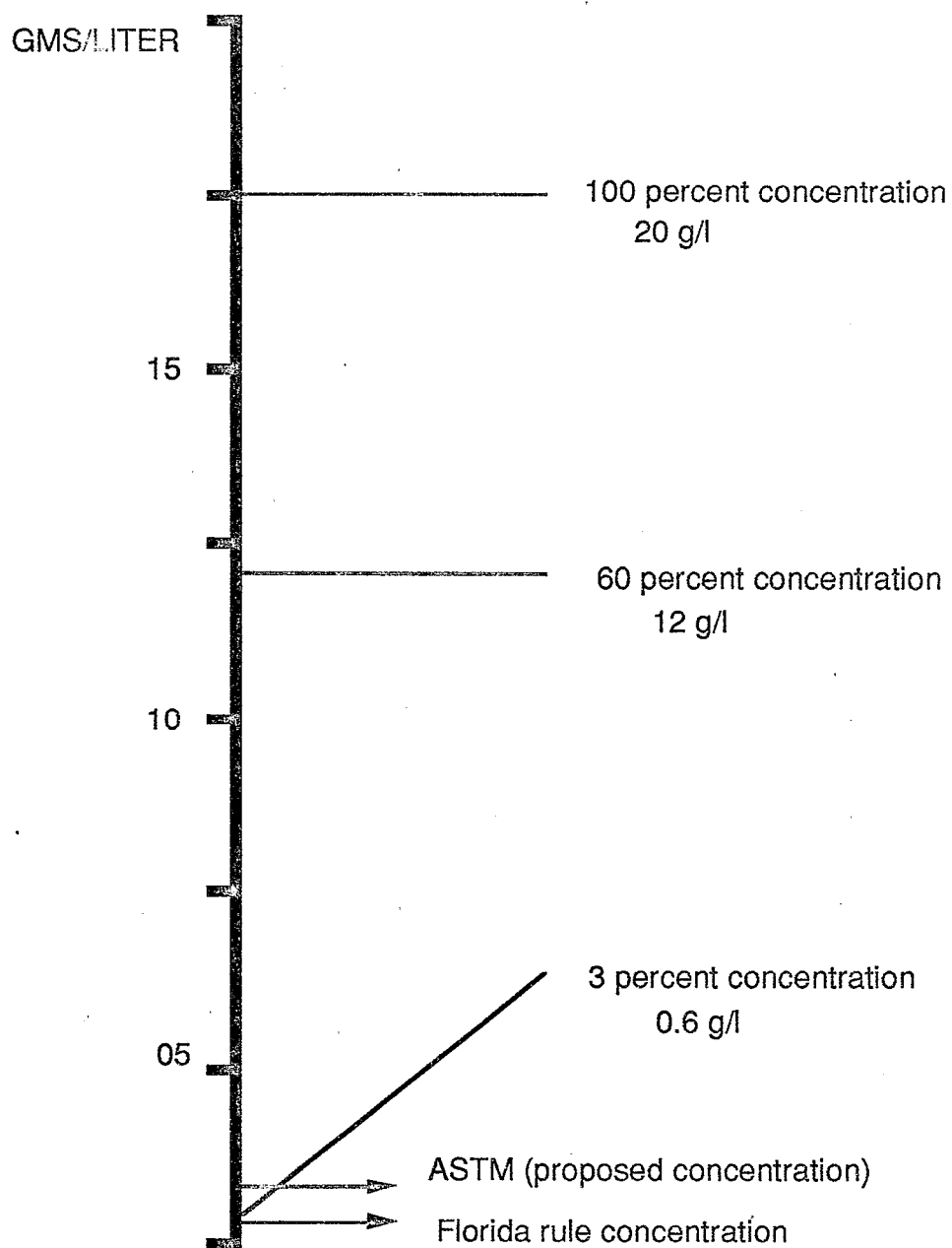
Figure 6.1 Concentrations of test solutions used in toxicity experiments.

6. (ETHYLENE-CARBON MONOXIDE) COPOLYMER

Table 6.1.1 shows the data from chronic toxicity tests using Ceriodaphnea species. While the data is of a preliminary nature, it suggests the extractives, even at the unrealistically high concentrations tested, to be without observable toxicity in this test procedure. All data passes the Chi Square test for normality. The detailed test data was statistically analyzed both for the control [6PC] and the test plastic [6P]. Fishers Exact test yielded NOEC values of 100 percent for survival and 60 percent for reproduction. LOEC value for reproduction calculated using Dunnett's test was 100 percent. NOEC is the concentration at which no effect is observed, and LOEC is the concentration at which the least effect is observed.

Table 6.1.2 shows acute toxicity test data using *Pimiphales promelas* species. Again the test data show high levels of survival except at the very high concentrations. The LC(50%) value is 91 percent for the enhanced degradable material and 100 percent for the control polymer. Since these concentrations are higher than those commonly employed, it is not surprising that the manufacturers claim the copolymer to pass the various state and EPA toxicity tests.

Special attention was paid to this particular enhanced degradable material in view of its use in six-pack rings. While the testing reported is not expected to be a pass/fail type test employed to qualify this plastic material, the test results are encouraging, and virtually no toxicity might be expected under field conditions. The conclusion applies to two species only and unfortunately cannot be necessarily extended to soil microorganisms and marine planktons. Further work involving a wider cross-section of organisms is needed for a complete assessment.

6.2 POLYSTYRENE BLENDED WITH (STYRENE - VINYL KETONE) COPOLYMER [PS]

The available resources did not allow the testing of a control sample of polystyrene foam for this study. Only a single set of test data is therefore available. In the case of polystyrene foam the possibility of the embrittled, yellow surface layer abrading off the foam during exposure complicates the interpretation of data. A significant removal of this layer, particularly rich in water-soluble degradation products, will result in the underestimation of any toxicity. With the 15 day exposures used, it is unlikely that significant amounts of the surface layer were lost during exposure and sample collection.

Table 6.1.1 Chronic Toxicity Test Data Summary for (ethylene-carbon monoxide) Copolymer Material (6P and 6PC). Test Organism: *Ceriodaphnea dubia*.

Concentration[1] (%)	Dissolved[2] oxygen (mg)	Control Polymer		Enhanced Degradable Polymer	
		Survival[3] (%)	Offspring (Number)	Survival[3] (%)	Offspring (Number)
0	7.1-7.4	100/100	247	100/100	245
3	7.0-7.6	100/100	273	100/100	276
10	-	100/100	288	100/100	338
30	7.0-7.7	100/90	293	100/100	385
60	-	100/100	331	100/100	394
100	7.0-8.5	100/100	139	100/90	11c

[1] 100 Percent concentration equals 20 gms degraded polymer/liter

[2] Range of pH values from start and end measurements for control and test samples.

[3] Survival at 48 hours/7 days are reported.

NOTE:

Test solution renewal: 2 times
Replicates of 1 organism per concentration: 10
Organism age at start of test: 16-24 hours
Test duration: 7 days

6-5

Table 6.1.2 Acute Toxicity Test Data Summary for (ethylene-carbon monoxide) Copolymer Material (6P and 6PC). Test Organism: *Pimephales promelas*.

Concentration[1] (%)	Dissolved oxygen (mg)	Control Polymer	Enhanced Degradable Polymer
		Percent Survival	Percent Survival
0	8.1-8.4	100	100
3	-	100	100
10	-	100	100
30	8.1-8.4	100	100
60	-	100	100
00	8.0-9.4	65	35

[1] 100 Percent concentration equals 20 gms degraded polymer/liter

NOTE:

Number of organisms per concentration: 20
Replicates per concentration: 2
Organism age at start of test: 8 days
Test duration: 96 hours

Table 6.2.1 shows the data from chronic toxicity tests using Ceriodaphnea species. Biological effects begin to be noticed only at the 60 percent concentration. All detailed test data was tested for homogeneity (Bartlett's test) and for normality (Chi Square test). Fishers Exact test yielded NOEC values of 60 percent for survival and 30 percent for reproduction. LOEC value for reproduction calculated using Dunnett's test was 60 percent. Due to non-availability of test data for control samples, it is not clear if the biological effects at very high concentrations are solely associated with enhanced degradable polymer or are generally common to all polystyrene.

Table 6.2.2 shows acute toxicity test data using *Pimiphales promelas* species. The data shows some toxicity to this species at very high concentrations. LC 50% value based on the data is about 25 percent, with 95% confidence limits of 18.7 to 32.5 percent.

It should be appreciated that the concentration of test solution (the 100 percent solution) was very high, nearly 25-50 times that used in the various test protocols discussed in Section 6.0. The 3 percent concentration is close to the concentrations generally employed in pass/fail type tests proposed by state authorities and the ASTM. This material does not show any significant toxicity at these lower concentrations typical of what might be expected under field exposure conditions. The comments on the need for more complete testing given in section 6.1 apply to this material as well.

6.3   LDPE/STARCH/MX MATERIAL [ADM FILMS]

In this instance as well, resource limitations did not allow the inclusion of a control sample in the experiment. The manufacturer (Archer Daniels Midland Company) provided resources to test a control sample to allow more complete interpretation of data. The extract from the ADM material stored in a refrigerator for a few days before testing developed growth (possibly fungal) which was filtered out before testing. As the effect of this growth on the test result cannot be determined, the data presented must be regarded as preliminary.

Table 6.3.1 shows the data from chronic toxicity tests using Ceriodaphnea species for the ADM material. Biological effects become apparent at the 30 percent level of concentration. However, Fishers Exact test shows NOEC for survival and for reproductive effects at 3 percent level of concentration. This concentration is close to that used in the pass/fail tests. Therefore, the enhanced degradable ADM material might be expected to be acceptable under the state and ASTM type toxicity test requirements.

Table 6.3.2 shows acute toxicity test data using *Pimiphales promelas* species. The data shows no measurable toxicity to this species and the LC (50%) concentration is greater than 100 percent. Interestingly, the control plastic material with no starch/MX does show

Table 6.2.1 Chronic Toxicity Test Data Summary for Polystyrene [(styrene-vinyl ketone) copolymer blends] Copolymer Material (PS).
Test Organism: *Ceriodaphnea dubia*.

Concentration[1] (%)	Dissolved[2] oxygen (mg)	Enhanced Degradable Polymer	
		Survival[3] (%)	Offspring (Number)
0	7.5-7.6	100/100	263
3	7.6-7.6	100/100	291
10	-	100/100	231
30	7.5-7.8	100/100	237
60	-	90/80	117
100	7.5-8.4	0/0	-

[1] 100 Percent concentration equals 20 gms degraded polymer/liter

[2] Range of pH values from start and end measurements for control and test samples.

[3] Survival at 48 hours/7 days are reported.

NOTE:

Test solution renewal: 2 times
Replicates of 1 organism per concentration: 10
Organism age at start of test: 16-24 hours
Test duration: 7 days

Table 6.2.2 Acute Toxicity Test Data Summary for (polystyrene/(styrene-vinyl ketone) blends) Copolymer Material (PS). Test Organism: *Pimephales promelas*.

Concentration[1] (%)	Dissolved oxygen (mg)	Enhanced Degradable Polymer
		Percent Survival
0	7.6-8.0	90
3	-	95
10	-	85
30	7.4-8.2	70
60	-	10
100	6.2-6.7	0

[1] 100 Percent concentration equals 20 gms degraded polymer/liter

NOTE:

Number of organisms per concentration: 20
Replicates per concentration: 2
Organism age at start of test: 8 days
Test duration: 96 hours

Table 6.3.1 Chronic Toxicity Test Data Summary for LDPE/starch/MX (ADM film) Material (ADM). Test Organism: *Ceriodaphnea dubia*.

Concentration[1] (%)	Dissolved[2] oxygen (mg)	Control Polymer		Enhanced Degradable Polymer	
		Survival[3] (%)	Offspring (Number)	Survival[3] (%)	Offspring (Number)
0	7.7-8.0			100/90	222
3	7.7-8.1			100/50	119
10	-			80/0	112
30	7.8-8.1			0	0

[1] 100 Percent concentration equals 20 gms degraded polymer/liter

[2] Range of pH values from start and end measurements for control and test samples.

[3] Survival at 48 hours/7 days are reported.

NOTE:

Test solution renewal: 2 times
Replicates of 1 organism per concentration: 10
Organism age at start of test: 16-24 hours
Test duration: 7 days

Table 6.3.2   Acute Toxicity Test Data Summary for LDPE/Starch/MX (ADM) Material.
Test Organism: *Pimephales promelas.*

Concentration[1] (%)	Dissolved oxygen (mg)	Control Polymer	Enhanced Degradable Polymer
		Percent Survival	Percent Survival
0	7.9-7.9		100
3	-		100
10	-		100
30	7.8-7.9		100
60	-		100
100	7.6-8.4		100

[1]   100 Percent concentration equals 20 gms degraded polymer/liter

NOTE:

Number of organisms per concentration: 20
Replicates per concentration: 2
Organism age at start of test: 8 days
Test duration: 96 hours

toxicity at 100 percent concentration. This reflects the experimental variability that might be associated with a test of this nature. There is no reason to expect the control sample to generate an extract more toxic than the test sample. However, since different populations or organisms were used in the two tests, some degree of variability was unavoidable.

6.4 CONCLUSIONS

An assessment of the impact of using enhanced-degradable plastics as a solid-waste management strategy must take into account the possible toxicity of degradation products. While the nature of the breakdown products is likely to be the same with enhanced-degradable polymers as well as regular polymers, the former allows these products to be accumulated faster in the environment.

A comprehensive approach to studying toxicity of leachate from degrading polymers to soil biota demands a broad study. In addition to standard test species, a wide selection of soil microbes, marine microorganisms, phytoplanktons, algae, and at least the key members of the primary food chain should be included in such a study.

The study reported in this chapter was not undertaken to generate such information because such a task would be outside the scope of this effort. The goal in this project was to conduct selected standard toxicity screening tests and to determine if the leachate showed marked toxicity. The data from the two tests did not show any toxicity at realistic levels of leachate concentrations.

REFERENCE

USEPA 1989. "Short term methods for estimating chronic toxicity of effluents and receiving waters to freshwater organisms. EPA/600/4-89/001 Method #1002.0

SECTION 7.0

PRELIMINARY RECYCLING STUDY

7.1 SAMPLE COMPOSITION

The compositions of films for the preliminary recycling study were identified in Table 2.7.2. The enhanced degradable plastics selected for the preliminary study were the enhanced photodegradable types: 6P and PS materials contain main-chain functional groups which absorb solar radiation to cause direct bond scission; PG and ADM contain metal complexes which use light to catalyze their oxidative reactions. All these materials demonstrated (see Section 4.1.3) significant changes in physical properties after relatively short durations of outdoor weathering. Exposure durations of approximately 5, 10, and 15 days in Miami, FL were chosen for the recycling study. During this interval, degradation appeared to be the most time-dependent, e.g., a plot of the physical property used to measure degradation versus exposure time showed the greatest change in slope for this time interval for all samples except PS. The levels arbitrarily selected for percent of exposed degradable material in the extruded films were 5, 10, and 20%.

7.2 TENSILE PROPERTIES OF RECYCLED MATERIALS

The polyethylene-based extruded films containing exposed degradable plastics were tested on an Instron Model 1122 according to the procedure described in section 2.5.1, using a gauge length of 5.0 cm and a crosshead speed of 500 mm/min. The polystyrene films were too brittle and thin to be tested. Future, more detailed recycling studies will require an alternate method such as gel permeation chromatography for testing the properties of polystyrene films.

Only unexposed films were tested for this preliminary study; this data can be used to study the effects of introducing small amounts of degradable plastic into the recycling stream and the resulting quality of the extruded plastic. Further studies will be needed to study the effects of the presence of enhanced degradable material on the weatherability of the recycled plastic.

Table 7.2.1 shows the tensile properties of the extruded films identified in Table 2.7.2. Inclusion of low levels of 6P and PG material with the virgin resin did not seem to have any detrimental effects on the properties of the extruded film; in fact, both strength and flexibility were enhanced by low concentrations of the degradable material, probably due to a plasticizing effect. For a given duration of exposure of the degradable material,

however, both strength and elongation tended to decrease as the percent of degradable material increased from 5 to 20%.

Extrusion of films containing ADM material was complicated by the presence of starch. The presence of unexposed ADM in virgin LDPE did not adversely affect the tensile properties of the extruded film, but with the extrusion conditions used for this preliminary study, the presence of ADM exposed for as little as 5 days resulted in films which were striated and very uneven in thickness. Additional studies are needed to optimize the extrusion parameters for films containing pre-exposed (partially degraded/deteriorated) ADM material.

It must be pointed out that the base resin used for this experiment was a medium-density polyethylene. The polyethylene-based enhanced degradable plastics used in the study were low-density polyethylenes. The blending of polyethylenes of different densities may also lead to variations in physical and mechanical properties. Of particular interest is the effect of including partially degraded enhanced-degradable polymers in a recycling stream on the weatherability of the recycled material. This aspect of the problem, however, was beyond the scope of the present investigation.

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions, based on the findings given in this Final Report, are summarized below along with recommendations based on the findings.

NOTE:

6P: Ethylene-carbon monoxide (~1%) copolymer used in six-pack ring applications.

PG: Metal compound/low-density polyethylene used in mulch and packaging applications

ADM: Low density polyethylene/6% starch/metal compound system. Used in mulch and packaging applications.

PS: Expanded, extruded polystyrene containing carbonyl groups to render it enhanced-photodegradable. Used in packaging applications.

8.1 CONCLUSIONS

(a) General Findings

1. Studies on the activation spectra for loss in tensile elongation at break of the enhanced photodegradable polyethylene materials studied (6P, PG) show the region of the sunlight spectrum most likely to cause the degradation to be ≤ 340 nm. Window glass (float glass) does transmit some of these wavelengths; the performance of enhanced photodegradable plastics behind window glass must therefore be experimentally established and not assumed.

2. A rapid thermogravimetric method suitable for reliable determination of starch content in polyethylene/starch blends was developed in the study. This method was found to be suited to study partially degraded films during early stages of degradation as well and will result in considerable savings in time and effort in determining residual starch contents in starch/polymer systems.

3. Data on the temperature dependence of the light-induced degradation in enhanced photodegradable plastic products films are not readily available in the literature. Studies carried out in the present research effort show that (a) the rate of photodegradation of six-pack ring material (ethylene-carbon monoxide copolymer containing ~1% CO) is not affected significantly by temperature (65°C - 85°C); (b) both PG and ADM systems show temperature dependence of degradation in the same temperature range, with the latter being more sensitive to temperature.

4. Gas permeability of plas.. films, an important cl acteristic to be considered in packaging applications, changes on photodegradation. In PG and 6P materials, where the photodegradation occurred at an accelerated rate, carbon dioxide transport rates were found to change markedly with duration of exposure.

   In 6P samples, permeability decreased with extent of photodegradation by 40 percent in 250 hours of Weather-Ometer® exposure. This decrease was due mainly to decreasing diffusion coefficient.

   In PG samples, the permeability increased by about 275 percent during the same exposure, with increases in both the diffusion coefficient and the solubility contributing to the increase. The finding is explained in terms of incr- ased crosslinking as well as generation of sol material in the case of PG material du g oxidation. The 6P material apparently undergoes crosslinking and/or crystallinity ing oxidation.

5. Water vapor transmission rate (WVTR) of films was also affected by enhanced photooxidative degradation. A 10 day weathered sample of the ADM material, for instance, showed a 30 percent increase in WVTR. In the case of PG samples, the increase in WVTR was measured as a function of the exposure time. With PCL films, however, 40 days of aerobic soil exposure in the lab did not result in any measurable change in the WVTR.

(b) Outdoor Exposure

6. Variations of several different tensile test properties with the duration of exposure for two enhanced photodegradable plastics at two exposure locations were studied to determine the tensile test property most sensitive to weathering-related changes. The results showed the elongation at break (or extensibility) and the ener_ to break to be the test parameters most sensitive to weathering-induced changes. The former is more convenient to measure and was adopted for monitoring disintegration for the purpose of this study.

7. Four types of enhanced photodegradable plastics studied showed marked increases in the rate of breakdown compared to control materials, as indicated by loss in extensibility (or tumbling friability data in the case of polystyrene) on exposure to outdoor conditions. The increase could be conveniently quantified using the ratio of empirical rate constants for enhanced degradable and control materials, and this ratio is called "enhancement factor" in this study.

   Average values of enhancement factors obtained for the different samples were as follows:

PG (0.03 mm film) = 4

ADM (0.05 mm) film = 15

6P (0.42 mm film) = 7

PS (1.96 mm foam sheet) = 1-2

These numbers are average values and should not be compared to each other due to different thicknesses of films used. They do, however, indicate the degree of enhancement associated with film thicknesses typically used in applications such as six-pack rings and mulch films. Note that the factor for polystyrene foam was based on tumbling friability measurements. Films exposed outdoors generally embrittled during the period of observation.

8. The effectiveness of the photodegradable plastic materials, as indicated by the value obtained for enhancement factor, depended on the geographic location of exposure. This was anticipated on account of different levels of sunlight and ambient temperatures at each location. A knowledge of location-dependent variability is of interest in formulating guidelines for standardizing and for legislative purposes.

9. In the case of enhanced photodegradable plastics, where light expected to be the predominant factor responsible for degradation, good correlation between loss in extensibility and the amount of light received by the sample is expected. However, the data for three types of photodegradable plastics showed only moderate levels of correlation with light levels. Other factors such as temperature possibly influence the rates of breakdowns of these plastic materials.

10. The order of exposure sites ranked in terms of degradation rate varied for the different types of enhanced degradable plastics, although the Wittmann, AZ location was generally the harshest. This lack of agreement suggests that while light might be the primary factor determining the rate, other factors such as temperature and even rainfall might be significant.

11. Photodegradable polystyrene foam degradation was predominantly a surface phenomenon with surface yellowing and development of an embrittled layer with the duration of exposure. Yellowness Index of samples increased with duration of exposure.

    The average enhancement factor of 1.5 obtained on the basis of tumbling friability measurements was verified using Gel Permeation Chromatography studies of changes in number average molecular weight. The average result from the latter experiment for Miami, FL and Seattle, WA locations was 1.8, a value which agreed well with that based on the mechanical property measurement.

12. In Weather-Ometer® studies, not surprisingly, nearly all enhanced photodegradable plastics tested showed faster rates of degradation. However, the acceleration factor (how much faster the degradation proceeded as compared to outdoor exposure) was not the same for each material. PS foam material showed the highest acceleration of 12-20 times the outdoor rate depending on the location being compared. ADM, PG, and 6P samples showed accelerations of only 1-5. Comparisons of the accelerated rate of degradation with that obtained in Wittmann, AZ generally yielded the smallest factors.

(c) Marine/Fresh Water Exposure

13. The fo␣␣ ␣es of enhanced photodegradable plastics underwent enhanced breakdown when exposed outdoors while floating in coastal marine environments (Florida and Washington) and in a freshwater lake (Virginia).
The rate of degradation in samples exposed floating at sea as indicated by loss in extensibility (or based on tumbling friability data for PS samples), was lower than that obtained for terrestrial exposure at the same location for both enhanced degradable and the control plastic samples.
This is possibly due to lower temperatures attained by floating samples as opposed to those exposed on land and also due to shielding of light by foulants.

14. While the rate of photodegradation of plastic films was slower under marine floating exposure compared to that on land, the breakdown of the control samples was retarded to a much greater extent than that of the enhanced degradable materials. In some instances the changes in extensibility in the control sample were b␣ ␣␣ measurable in the same time scale of exposure which resulted in marked loss in ␣␣tensibility of enhanced degradable film samples.
As a result, the enhancement factors for marine floating exposure of the enhanced photodegradable films are likely to be much higher than those obtained for exposure on land at the same location. Accurate values of enhancement factors, however, are not available for the marine exposures.

15. In general, the Miami, FL location yielded faster degradation rates as well as faster enhancement factors than Seattle, WA for the photodegradable materials tested. In the case of PG sam␣ ␣s, however, the rates were about th␣ ␣␣me for both locations and samples embr␣␣␣ ␣ during the period of observation.
Freshwater expos␣␣ also resulted in enhancement of de␣ ␣ation but t␣ ␣tes were generally lower th␣␣␣ those obtained for either of the mari␣␣ test locatior␣␣. Only a

minimal number of freshwater (lake) exposures were carried out, and the data was not sufficient to obtain reliable enhancement factors.

16. Enhanced degradable polystyrene foam materials exposed in Miami, FL, exhibited much faster degradation rates (as measured by GPC) for marine exposures than for outdoor exposure. The rate of breakdown at sea was found to be 2.5 times that for land exposure, a reverse of the trend obtained with other types of enhanced degradable samples. Degradation rates for the control polystyrene material were about the same for marine and outdoor exposure in Miami, FL.

17. Marine sediment exposures were carried out for those enhanced degradable plastics where the breakdown was biologically mediated. The BP samples readily biodegraded under sediment at a rate more than 30 times that obtained when the film was exposed to sunlight under land conditions. BP films also degraded in a freshwater lake sediment environment, but the rate was only about 85 percent of that at sea. All samples were embrittled within 2-4 weeks of exposure.

18. PCL samples designed to biodeteriorate in biotic environments were also subjected to marine sediment and freshwater lake sediment conditions. The project schedule did not allow exposure durations in excess of 21 weeks under these conditions. During this period under marine sediment exposure, the material lost about 50 percent of its extensibility; the time scale of observation was not sufficient to fully document the disintegration process, which was expected to take a longer time under these exposure conditions. Analysis of the polycaprolactone fraction of the blend showed an 18 percent decrease in the number average molecular weight during a six week period of exposure.

Freshwater lake sediment exposure was carried out for a period of 8 weeks and also resulted in a 50 percent decrease in extensibility. However, the rate of disintegration in freshwater was 4-6 times faster than in marine sediment.

Initial exposure in the biotic environment apparently does lead to significant chain scission in the biodegradable component of the blend, but more extensive degradation is required before changes in extensibility become apparent.

(d) Soil Exposure

19. Enhanced degradable plastic materials designed for biologically mediated breakdown were exposed under outdoor aerobic soil burial conditions. The project schedule did not allow exposure durations in excess of 29 weeks under these conditions. The maximum duration of exposure was too short to observe the disintegration of the PCL and ADM materials to a significant extent. The extensibilities at the end of 28

weeks were 406% for PCL films (initial extensibility 717%) and 9% for ADM films (initial extensibility 90%). In the case of PCL samples, about a 15 percent decrease in number average molecular weight (GPC) was obtained during this period of exposure.

20. Under exposure conditions similar to those discussed above, the BP films rapidly degraded to give an extensibility of 4% (initial extensibility 61%) at the end of 29 days of exposure. These films seem to biodegrade rapidly under both soil and marine exposure conditions. BP samples were embrittled by 29 days.

21. In addition to outdoor soil burial exposure, laboratory-accelerated soil burial studies were carried out. The duration of observation, up to 10 weeks, was insufficient to show any marked deterioration of the PCL and ADM films under these conditions; longer exposures were not possible because of the project schedule.
The scatter associated with the data was high in comparison to data from outdoor exposure. It was not clear if the elongation at break was, in fact, a sensitive measure for study of composite samples such as polyethylene/starch materials.

(e) Other

22. Preliminary toxicity studies were carried out using water extracts of partially photodegraded materials.

23. A preliminary blending study was carried out to identify the optimum blend compositions for studying the recyclability of enhanced degradable plastics. The data allowed the identification of a ratio of virgin/recycled plastics that might be used in a future recycling study. Establishing the levels of partially degraded post-consumer degradable plastics that might be added to a recycling stream without adversely affecting the quality of recycled materials is important.

8.2 RECOMMENDATIONS FOR FURTHER RESEARCH

1. The findings relating to rates of breakdown of photodegradable plastics, enhancement factors, and geographic variability, are based on five exposure locations. Additional data for alternate locations and exposures carried out in different seasons of the year will help to complete the documentation of the performance of photodegradable plastics.

2. The above considerations are even more important for the case of marine exposure, where only two exposure sites were used. While the data show the photodegradable plastics, and some biodegradable plastics, to perform adequately under these conditions, a study involving more exposure sites is needed before the observations can be unequivocally accepted.

3. A major limitation of this study was the relatively short duration of exposure used, which did not allow the performance of the biodegradable and biodeteriorable films to be properly studied. Specifically, the polyethylene/starch system needs to be studied to establish the limits of its performance. Research on enhanced biodegradable plastics to supplement this research effort is strongly recommended.

4. Further toxicity studies should be carried out to establish the full environmental impacts of the faster production of breakdown products in the case of enhanced degradable plastics.

5. A full-scale recycling study is needed to unambiguously establish if the inclusion of small amounts of degraded post-consumer enhanced degradable plastics in a recycling stream has any impact on the quality of recyc l product. The research should at least investigate 2-3 types each of enhanced photodegradable and biodegradable materials.

6. New generation starch/PE film.