DEGRADATION OF STARCH-BASED PLASTICS IN THE ENVIRONMENT

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Degradation of Starch-Based Plastics in a Municipal Solid Waste Landfill

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ABSTRACT

The rate and extent of deterioration of starch-based polyethylene and polypropylene plastic composites were determined over a two-year period for samples buried in a municipal solid waste landfill. The deterioration of the starch-based plastics following exposure was determined by measuring changes in tensile properties, weight loss, starch content, and morphology of samples retrieved from the landfill. Moisture content, temperature, and the presence and the extent of degradation of organics in the landfilled garbage indicated that conditions within the landfill burial site were favorable for biological activity. Results of physical testing showed that starch-based plastics weakened at an accelerated rate compared to corresponding control plastics following two-years exposure. Starch loss was measured for starch-based polyethylene films, however, the starch-based plastics did not fragment or lose mass during the two-year landfill burial. Limitations in the extent of degradation observed for the starch-based plastics are attributed to the ineffectiveness of the prooxidant additive to catalyze the thermal oxidation of the polyethylene or polypropylene component of the starch-based plastics under the environmental conditions present within the landfill.

INTRODUCTION

Landfilling continues to be the most common method for the disposal of municipal solid waste (MSW) generated in the United States. Over 80% of the estimated 160 million tons of MSW generated in the U.S. in 1986 was landfilled.[1] Plastics were estimated to comprise 8% by weight of the municipal solid waste stream in the U.S. in 1988.[2] Plastics however, are estimated to comprise up to 18% of the volume of MSW disposed in landfills.[3] Plastics are typically lightweight and chemically inert and may be manufactured to be rigid, flexible, and impermeable. As a result, plastics have replaced paper, glass and metal in many applications. In addition, plastics are typically long-lived and resistant to degradation in the natural environment. As such, landfilled post-consumer waste plastic may be entombed within the landfill occupying valuable landfill space.

Recently, starch-based plastic composites have been developed in an effort to make the materials more susceptable to biological degradation.[4,5] These starch-based plastics are designed to increase the rate of degradation of the product and lessen impacts associated with discarded plastic wastes. These composites are a mixture of a readily degradable starch component within a plastic matrix and they may possess starch contents of up to 50% by weight.[5] In addition to starch, these composites may also contain catalysts to oxidize the polymer to lower molecular weight

by-products which may then be metabolized by microorganisms. A reduction in the volume of the plastic component of MSW may occur providing additional landfill capacity if the incorporation of additives such as starch in plastic increases the susceptability of the product to biological degradation.

The overall rate of degradation of organic materials occuring in municipal solid waste sanitary landfills is slow. Recent studies have shown that food waste and newspapers excavated from landfills are readily identifiable following 20 years of burial. [3,6] Although the overall rate of degradation of organic materials in landfills is slow, high rates of degradation within landfills may exist if favorable environmental conditions are present. The rate at which degradation proceeds is a function of many environmental variables including moisture content, pH, temperature, number and types of organisms present, and garbage composition.[6]

The degradation processes for starch-based plastics following burial in modern sanitary landfills is not well known. The objective of this study is to measure the rate and extent of deterioration of starch-based and control plastics in a municipal solid waste landfill. The composition of the MSW buried at the landfill was determined and environmental conditions at the burial site were measured to determine if favorable conditions existed for

degradation to proceed. Both physical and chemical tests were conducted to measure the extent of deterioration of starch-based and control plastics during the 24 months burial in a municipal solid waste landfill.

EXPERIMENTAL

Starch-Based and Control Plastic Sample Descriptions

All starch-based and control plastic samples were supplied by the Archer Daniels Midland Company, Decatur, Illinois (Table I). Starch-based and control low density (LDPE) and linear low density (LLDPE) polyethylene films were provided. Starch-based LDPE and LLDPE films were manufactured using the Griffin process.[4] The starch-based films contain approximately 5.5% "masterbatch" which contains both starch and and a transition metal prooxidant additive.

High density polyethylene (HDPE) oil bottles containing 0%, 5% and 15% starch masterbatch were provided for placement in the landfill. Injection molded polypropylene (PP) parts containing 0%, 10%, and 35% starch masterbatch were also buried in the landfill. The injection molded parts were in the form of bars measuring 0.32 cm x 11.75 cm x 1.27 cm.

In addition to the starch-based and control plastic samples, untreated cellophane sheet samples were also

provided for placement in the landfill.

Sample Preparation for Landfill Placement

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

Polypropylene injection molded parts were mounted into 15.24 cm x 60.96 cm rectangular plexiglass frames designed to contain 6 injection molded parts. Duplicates of each of the three polypropylene sample types were mounted into each frame. The samples were secured to the frame between two 2.54 cm x 0.64 cm x 60.96 cm strips of plexiglass at each end of the injection molded part using nylon bolt assemblies. The sample type and the replicate number were then melted into the plexiglass frame using a soldering pen.

The HDPE oil bottles were labeled prior to placement in

two ways. Orange cubes of plexiglass, numbering 1-3 corresponding to samples 2A-2C, were put into ziplock plastic bags and inserted into the oil bottles prior to burial. Each bottle was also uniquely labeled with a marker pen on the exterior of the bottle.

Landfill Exposure Site

Starch-based and control plastic samples were buried in the Brookhaven Town Landfill, Yaphank, New York (Figure 1). The site is an 80 acre double-lined landfill which accepts all non-hazardous solid wastes except leaves and brush. During 1989, 492,680 tons of solid waste were buried in the landfill exclusive of yard wastes which are collected seperately and composted at Town facilities.

A fenced 30 x 46 meter area was established at the summit of the landfill (Figure 1). Within the landfill exposure site, seven 1.8 m x 1.8 m x 1.2 m areas were excavated on May 31, 1989 using a backhoe. Workers using pitchforks then leveled off the base of each of the excavated sites to a depth of 1.2 m below the landfill surface. A complete set of samples was then carefully placed within each of the excavated areas. Garbage was then carefully replaced by hand, covering the samples to a depth of 0.3 m. A fence post was then placed in the corner of each of the seven burial sites to identify each site location. The remaining garbage was then backfilled into

the excavated site using a backhoe, burying the samples to a depth of 1.2 m. The overlying garbage was not compacted following the burial of the samples in the landfill.

Local daily temperature and precipitation readings were obtained from the weather station at the Brookhaven National Laboratory, Upton, New York. Samples were removed from the landfill on a predetermined basis and returned to the laboratory for physical and chemical testing (Table II).

METHODS

Landfill Sampling

During each sampling event, a backhoe was used to excavate the first 0.5-1.0 m of garbage from the exposure site. Next, the remaining refuse was carefully removed using pitchforks and shovels until an identifiable sample was uncovered. The remaining refuse was then removed by hand until all samples were identified and removed. Paint brushes were used to remove dirt and particles adhering to the samples. Films were removed from the plexiglass frames at the site and placed in labeled ziplock plastic storage bags. Injection molded polypropylene parts remained in the exposure racks for transport to the laboratory. The HDPE bottles were identified, labelled, and placed together in large plastic bags for transport to the laboratory.

With the exception of the four month film sample 1A, all samples buried in the landfill were recovered for laboratory testing during the two-year study.

Cleaning and Storage of Samples

In the laboratory, the samples were rinsed in tap water, and sonicated in distilled-deionized water for 15 minutes. The samples were then towel dried, placed in labeled zip lock bags, evacuated with argon, and stored in the dark at 20°C.

Tensile Testing

An Instron Model 1011 Universal Testing Machine was used to determine the tensile properties of the starch-based and control plastic samples. Tensile properties of the polyethylene films were determined following ASTM method D882.[7] A gauge length of 5.08 cm and a crosshead speed of 50.8 cm/min was used. Six 1.27 cm x 15.24 cm specimens were prepared for testing from each sample sheet retrieved from the landfill. Tensile strength at break and percent elongation at break were determined for each sample.

The polypropylene injection molded parts were tested in the form provided following ASTM method D 638-87b.[8] A gauge length of 5.08 cm and a crosshead speed of 2.54 cm/min was used. Two 1.27 cm x 11.75 cm specimens were tested during each sampling event. Tensile strength at break and percent

elongation at break were determined for each sample.

The tensile properties of the high density polyethylene bottles were determined following ASTM method D638-87b. A gauge length of 5.08 cm and a crosshead speed of 50.8 cm/min was used. Six 1.27 cm x 15.24 cm specimens were prepared for testing from each bottle retrieved from the landfill. Tensile strength at break and percent elongation at break were determined for each sample.

Sample Weight

Starch-based and control polyethylene thin films and polypropylene injection molded parts were weighed prior to and following landfill burial. Sample weights (±0.001 gram) were obtained using a Sartorius Model 2462 HW analytical balance. Samples were conditioned at 50% humidity and 23°C for 48 hours prior to weighing.

Moisture Content of Landfill Garbage

Following each sampling event a minimum of 200 grams of garbage was carefully weighed on a top loading balance and oven dried at 110°C for 24 hours. The sample and pan were then reweighed and the percent moisture was calculated.

Scanning Transmission Electron Microscopy

A JEOL Model 1200 EX scanning transmission electron microscope (STEM) was used to obtain surface and cross-

sectional images of the starch-based films. Computer enhanced images were photographed off the CRT screen of a NORAN Series 2 computer.

Starch-based polyethylene films were frozen in liquid nitrogen and cut with scissors while frozen to obtain cross sections. After thawing, the films were mounted on edge using silver paint on carbon studs. The films were coated with gold using a Hummer VIA sputter coater.

Chemical Method for Starch Determination

Quantitative starch determinations of preplacement and weathered starch-based polyethylene films were conducted using a previously developed method.[9] The method consists of dissolving the polyethylene component followed by the solubilization and partial hydrolysis of the starch component. The solubilized starch is then isolated for carbohydrate analysis using the phenol-sulfuric acid method.

RESULTS

Analysis of Garbage at the Landfill Exposure Site

A waste composition analysis was conducted on the landfilled solid waste within the burial site on April 19, 1990. To recover garbage from the burial site, a backhoe initially removed the overlying soil cover and then proceeded to excavate the exposed garbage to a depth of 1.2

meters. The excavated garbage was placed by the backhoe on a primary sorting tarp, where the garbage was hand sorted and weighed. Paper, plastics, organics, and metal items were once again sorted into subcategories on a secondary sorting tarp and reweighed.

Air temperature at the time of sampling was 11.5°C while soil and water temperatures in the vicinity of the garbage were 10°C. Water pooled at the base of the excavated pit had a pH of 5.8. Soil and garbage moisture contents ranged from 30-35%. The total weight of the sorted garbage was 205.6 kg. Observed dates on newspapers and correspondence excavated from the site ranged from September through the last week of October 1989.

Paper accounted for almost 60% of the excavated refuse (Table III). Nearly all paper products were intact. Newspaper colors were fast and newspaper print was entirely legible. Most paper materials were wet, and appeared to be midway between "damp" and "soaked". Newspaper was weak but did not fall apart due to its own weight when picked up. Several telephone books were included as newsprint. Paper items were weighed wet; however excess water was allowed to drain from paper items before weighing.

Plastics comprised almost 8% of the garbage excavated with almost 70% of the plastic in the form of film or bags (Table III). Lesser amounts of styrofoam and bottles were observed. Diapers were disposable plastic. The diapers,

including fill, were intact.

Organics included only materials that were recognizably of organic origin and comprised 12.4% of the garbage excavated (Table III). Organic materials that were in a state of disintegration or degradation so advanced as to be indistinguishable from general slime and muck were not included in this category. Identifiable food items included crab claws, carrots, and pumpkin pieces.

Glass items included some bottles, broken flat glass, and a piece of dense fiberglass. Aluminum and ferrous materials consisted largely of cans. Both natural and synthetic textiles were identified and grouped under the textiles category. Textiles were damp to fairly soggy, but generally far from being completely water-logged. Only small quantities of water exuded when the textiles were squeezed.

The matrix category includes soil, sludge, small pebbles, and fines. Significant concentrations of mud or slime were shaken or scraped from objects before weighing. This mud or slime was also weighed and included in the matrix category.

While MSW compositions are known to be subject to great variations, the composition of the sampled MSW corresponds well to typical compositions reported in other major studies of landfills.[1,3,6] For example, the Office of Technology Assessment compares the percentages of different MSW

components reported as the mean percentage over nine studies in addition to the mean percentage over 40 studies (Table IV). While the definitions of components vary among studies, the percentages of various waste components found in the Brookhaven Town Landfill sampling are similar to those shown in Table IV. Yard waste is not a major component of Brookhaven Town's landfill because the Town collects these materials separately for composting. More paper and less glass was found in the Brookhaven sample than in the national figures.

The garbage excavated at the burial site had been buried for approximately 1.5 years. The observed condition of potentially degradable materials found within the MSW sample including paper, organics, and textiles suggest that rapid degradation of those materials is not occurring in the landfill at the depth from which the materials were recovered.

Weight Loss

The weight of both starch-based and control LDPE and LLDPE films increased slightly when compared to preplacement values during landfill burial (Figure 2). However, the measured weight increases were generally less than 5% of the preplacement weight for each respective sample.

Increases in sample weight were also measured for both the control and starch-based polypropylene injection molded

parts (Figure 3). Weight increases were proportional to the initial starch content of the sample. Following 24 months burial, increases in weight ranged from 0.91% to 6.88% for control sample 3A and starch-based sample 3C, respectively.

Weight increases may be due to water absorption by the starch and/or polyethylene in addition to material remaining on the samples following cleaning. Both the control and starch-based films and injection molded parts excavated from the landfill remained stained following cleaning.

Untreated cellophane sheets originally placed within the sample rack were only retrieved during the 2 month and 9 month sampling events. Weight losses of 6.3% and 13.1% were measured for the cellophane sheets recovered at 2 months and 9 months, respectively. Missing cellophane sheets may have been lost during the sample recovery and/or metabolized by microorganisms in the landfill.

Tensile Testing of Polyethylene Thin Plastic Sheets

Gradual decreases were measured in the tensile strengths of the LLDPE films retrieved from the landfill during 24 months burial. Starch-based LLDPE film 1D and control LLDPE film 1C lost 34% and 40%, respectively, of their initial tensile strength (Figure 4). Decreases in tensile strength of LDPE films were only measured in the control sample 1A, where a 35% decrease in tensile strength was measured following 24 months burial.

Decreases in the % elongation were measured for both starch-based and control films buried in the landfill (Figure 5). Decreases in the % elongation of LLDPE film 1C and starch-based film 1D were gradual during the 24 month exposure period. The % elongation for starch-based LLDPE film 1D decreased 44% from the preplacement value while the % elongation of the corresponding control LLDPE film 1C only decreased 21% from the preplacement value. In contrast, decreases in the % elongation of the LDPE films was variable. Decreases in the % elongation of control film 1A ranged from 49% at 2 months to only 13% at nine months. Control film 1A retained 80% of its initial % elongation after 18 months burial in the landfill. Large decreases in the % elongation were also observed for starch-based film 1B following 2 months burial. However, the % elongation for film 1B remained low, gradually decreasing to less than 8% of its initial % elongation following 24 months burial.

Tensile Testing of High Density Polyethylene Bottles

Tensile strengths of both control and starch-based high density polyethylene bottles buried in the landfill remained similar to preplacement values (Figure 6). Tensile strengths were within 12% of their preplacement values following 24 months landfill burial.

Decreases in the % elongation of high density polyethylene bottle control sample 2A and starch-based

sample 2B were measured during 24 months of landfill burial (Figure 7). The % elongation for both the starch-based sample 2B and control sample 2A decreased 55% from the preplacement value. In contrast, no trend was observed in the % elongation for starch-based sample 2C. The change in the % elongation for sample 2C was variable throughout the 24 month sampling period.

Tensile Testing of Polypropylene Injection Molded Parts

Tensile strengths of both control and starch-based polypropylene injection molded parts buried in the landfill remained similar to preplacement values (Figure 8). Although slight increases in tensile strength were measured for starch-based samples 3B and 3C, the tensile strengths were within 15% of their preplacement values.

Decreases in the % elongation of the control and starch-based polypropylene injection molded parts were measured during 24 months of landfill burial (Figure 9). Decreases in % elongation were greatest in samples containing the highest starch content. The % elongation for sample 3C decreased in excess of 92% from the preplacement value while the % elongation of the corresponding control sample 3A decreased 46% from the preplacement value.

Starch Content

The initial starch contents of starch-based

polyethylene films 1B and 1D were 6.6% ± 0.2%. Starch loss was continuous from both LDPE and LLDPE film samples during the 24 months burial period (Table V). Following 24 months landfill burial, LDPE film samples 1B and 1D lost 33% and 26% of their initial starch contents, respectively.

DISCUSSION

Landfill Environmental Conditions

Environmental conditions within the landfill which would affect the rate and extent of degradation of the starch-based plastics include garbage moisture content, temperature, and biological activity within the landfill burial site.

Moisture Content

Moisture is essential for the biological or chemical degradation of organic material in a landfill. Biological activity within a landfill may be retarded if the moisture content drops below 40% and decomposition essentially ceases when the moisture content drops below 20%.[10] Measured moisture contents of the garbage at the landfill burial site ranged from 20.0-56.0% (Table VI). These values fall within the range of moisture contents for garbage measured at other landfills.[6]

Landfill moisture content is a function of the initial

moisture content of the garbage, amount of rainfall, and the ability of landfill cover to retard rainfall infiltration. A total of 160 cm of precipitation was measured in Brookhaven town during the initial nine months of burial (Figure 10). The Spring and Summer months of 1989 were unusually wet and characterized by heavy rainfall events. Heavy rainfalls and the disturbance of the compacted daily cover during sample burial contributed to the observed high measured moisture contents of the garbage during the first year at the burial site.

Temperature

Temperatures within landfills vary depending on geographical location, depth of garbage, thickness of cover, season, and garbage composition.[10] Internal landfill temperatures as high as 35-60°C have been measured while temperatures within the upper two meters of the landfill may range from 6-32°C.[11] Landfill temperatures within the upper meter are influenced by changes in seasonal air temperatures.

Temperatures within the Brookhaven landfill at the depth of sample placement were not routinely measured. However, local air temperatures were monitored daily and are shown to vary seasonally (Figure 11). The temperature of the surrounding garbage was measured during the landfill composition study and showed that the garbage temperature at

depth on a sunny April day was 1.5°C cooler than the ambient air temperature. Burial of the garbage in the landfill at a depth of 1.2 meters may insulate the samples from the air temperature extremes. For example, during the six month sampling event when severe cold air temperatures were recorded, the garbage surrounding the buried samples was not frozen.

Biological Degradation

Biological degradation at the landfill was inferred on the basis of the following criteria: the disappearance of untreated cellophane sheets originally placed in the exposure racks, starch loss from starch-based plastic films, and the presence and extent of degradation of organic matter recovered during the landfill characterization study.

Organic materials comprised 12.4% of the landfilled garbage in the Brookhaven landfill (Table III). Organic materials in the garbage included primarily wood with lesser amounts of food waste. Although some food items were identifiable, other organic material had degraded to where it was not not distinguishable from the surrounding slime and muck. Results show that the starch component of the films was degraded following burial in the landfill. Starch-based films showed a continuous decrease in the starch content of the film samples during the second year of landfill burial (Table V). Untreated cellophane sheets were

only recovered from the landfill following the two month and nine month sampling events. If the disappearance of the cellophane sheets is primarily through biological processes, biological degradation within the landfill may be highly localized.

Sufficient organic content of the garbage, the disappearance of the cellophane sheets, and starch loss from the plastic films indicates biological degradation was occurring within the landfill burial site. However, the presence of recognizable organic materials within the garbage at the burial site along with the presence of the untreated cellophane sheets following nine months burial indicates that although biodegradation of organic materials is occurring, the rate of biodegradation in the landfill was slow.

Factors Affecting Degradation of Starch-Based Plastics in the Landfill

Environmental conditions monitored within the landfill during the two-year burial period indicated that conditions were favorable for microbial growth, therefore allowing the potential for biodegradation to occur. Several factors including the environmental conditions within the landfill, the morphology of starch-based plastics, and the ability of microorganisms to biodegrade the plastics affected the rate and the extent of degradation observed for the starch-based

plastics buried in the landfill.

Physical Stress

The samples placed in the landfill were subject to physical stresses including compaction and abrasion due to the placement, exposure, and sampling events. The physical stresses certanly contributed to some extent to the measured loss in tensile properties of the control and starch-based plastics.

Starch-based and control films retrieved from the landfill were typically discolored, crumpled, and some contained small holes or tears. Similar changes were observed in the physical appearance of the polypropylene injection molded parts and the HDPE bottles. Both the starch-based and control HDPE bottles collapsed under the weight of the overlying garbage. Many injection molded polypropylene parts were also discolored and slightly bent due to the weight of the overlying garbage. These physical processes may have resulted in some of the observed fluctuations in the tensile strengths and % elongations measured for both the starch-based and control plastic samples. Although varying degrees of physical damage was observed for the plastics retrieved from the landfill, both the control and starch-based plastics remained intact throughout the two-year landfill burial.

Morphology of Starch-Based Plastics

The surface of the starch-based film prior to burial shows starch grains both exposed on the surface and embedded within the polyethylene matrix (Figure 12a). The cross sectional view shows a starch grain readily accessible to the surface of the film while a second starch grain is deeply embedded within the polyethylene.

The surface of a starch-based film following 18 months burial in the landfill shows that some of the embedded starch grains remain intact, become exposed to the surface, or are missing (Figure 12b). The cross sectional view of the sample also shows the presence of starch grains deeply embedded in the polyethylene which were not accessible to the surface of the film and remained intact following 18 months burial in the landfill.

Both the SEM images and the starch content of films buried in the landfill indicate that much of the starch is not readily available for microorganisms to utilize. Following two years landfill burial starch loss ranged from 26% to 33% for film samples LLDPE 1D and LDPE sample 1B, respectively (Table V). The encapsulation of starch granules within the polyethylene matrix prevents easy access to the starch and requires that the polyethylene deteriorates prior to total starch loss for these composites.

Ability of Microorganisms to Degrade Starch-Based Plastics in Landfills

Results of previous studies have shown that the starch component of the starch-based plastics can be metabolized by microorganisms.[12,13] However, biodegradation of starch-based plastic materials occurs primarily by enzyme diffusion into the material, a process which is severely limited if a discontinuous matrix of starch is present.[14] SEM analysis of the starch-based films clearly shows isolated starch granules embedded within the polyethylene (Figure 12). Microorganisms are only able to assimilate low molecular weight fractions of ~(0Xpolyethylene which may have to be formed previously by chemical or physical processes.[15] Therefore, biological processes alone are not sufficient to rapidly degrade the starch-based composites.

A transition metal prooxidant is contained in the masterbatch additive which is capable of initiating the thermal oxidation of the polymer at elevated temperature.[4] Prooxidant activity on the polymer appears to be an essential requirement for microbial degradation of both the starch component isolated within the polymer matrix and the polymer matrix itself. Elevated temperatures may result in an increase in the rate of thermal oxidation of the polyethylene cataylized by the presence of the transition metal prooxidant additive.[16] Studies have shown that heating the starch-based plastics with the prooxidant

additive, thereby initiating oxidative degradation, increases the susceptability of starch to microbial degradation.[17] Elevated temperatures alone, however, may not be sufficient to induce rapid thermal oxidation of the polymer. Results of oven aging of thermal prooxidant containing starch-based plastics in the presence of oxygen at 50°C showed that air flow over the surface of the polymer significantly increased the rate of polymer degradation compared to films aged in sealed containers indicating that the removal of oxidation reaction by-products as they are formed facilitates degradation.[18] If thermal oxidation of the polymer does not occur in the landfill, the polymer and starch contained therein, may remain intact and unavailable for rapid degradation by microorganisms. In the absence of conditions allowing for the rapid oxidation of the polymer, increased physical forces including stretching, tearing, compaction, and puncturing of the plastic may assist in rendering encapsulated starch grains available for biodegradation.

CONCLUSIONS

Results of physical testing showed that starch-based plastics weakened at an accelerated rate compared to corresponding control plastics following two years exposure in a municipal solid waste landfill. Moisture content, pH, temperature, and the presence of organics in the landfilled

garbage indicated that conditions within the landfill burial site were favorable for biological activity. In addition, starch loss was measured for starch-based polyethylene films buried in the landfill. However, the starch-based plastics did not fragment or lose mass during the two year landfill burial. In the absence of significant polymer degradation via thermal oxidation catalyzed by prooxidant additives, the starch component of the starch-based plastics remains isolated within the polymer matrix and unavailable for biological degradation. As a result, it is not likely that a conversion to starch-based plastic materials would provide immediate additional landfill space through volume reduction.

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Table I. Starch-based degradable and control plastic samples.

Sample ID	Sample Description
	Sheet Plastic Samples
1A	Low density polyethylene (LDPE)
1B	LDPE + 5.5% cornstarch masterbatch
1C	Linear low density polyethylene (LLDPE)
1D	LLDPE + 5.5 % cornstarch masterbatch
	Oil Bottles
2A	High density polyethylene (HDPE)
2B	HDPE + 5.5% cornstarch masterbatch
2C	HDPE + 15% cornstarch masterbatch
	Injection Molded Parts
3A	Polypropylene (PP)
3B	PP + 10% cornstarch masterbatch
3C	PP + 35% cornstarch masterbatch
4A	Cellophane sheets

Table IV. Previously reported MSW landfill compositions.*

Material	9 Studies		40 Studies	
	Mean (%)	Range (%)	Mean (%)	Range (%)
Total Paper	38.8	29.9-45.9	46.7	36.5-54.7
Newspaper	6.3	4.3-8.1		
Corrugated	7.9	4.7-13.1		
Mixed	21.9	19.6-25.2		
Magazines	0.7	0.7		
Total Metal	4.9	1.5-9.4	8.5	4.0-14.7
Aluminum Cans	0.9	0.8-1.0		
Other aluminum	0.7	0.2-1.6		
Non-ferrous	1.0	0.0-3.4		
Total Glass	7.8	3.6-12.9	8.4	6.0-13.7
Glass containers	6.4	6.1-6.6		
Total Plastic	8.8	5.3-12.6	5.3	2.0-9.0
Plastic film	3.1	3.1		
Plastic containers	0.9	0.7-1.0		
Yard Waste	18.2	0.0-39.7	9.5	0.4-25.0
Food Waste	14.7	1.3-28.8	7.8	0.9-18.2
Wood	2.6	0.7-8.2	2.6	0.5-7.0
Textiles	3.4	1.1-6.2	3.3	0.7-5.0
Rubber	0.4	0.0-1.0		
Diapers	0.0		1.5	0.5-2.9
Unclassified	9.2	3.8-16.6		0.5-10.0

* Office of Technology Assessment, 1989.[1]

Table V. Percent starch remaining for starch-based polyethylene films following landfill burial.

Sample	Exposure Time			
	0 months	13 months	18 months	24 months
LDPE Sample 1B	100 (3.0)	84 (2.8)	79 (2.3)	67 (5.7)
LLDPE Sample 1D	100 (3.0)	90 (3.1)	88 (2.1)	75 (2.8)

Table VI. Garbage moisture content.

Sampling Date	Garbage Moisture Content (%)
May, 31, 1989	36.7
August 8, 1989	56.0
October 3, 1989	42.0
December 4, 1989	36.1
March 19, 1990	36.4
September 25, 1990	35.8
December 12, 1990	20.0
May 8, 1991	29.2

FIGURE LEGENDS

Figure 1. Location of the landfill burial site at the Brookhaven Town Landfill, Yaphank, New York.

Figure 2. Weight change for starch-based and control LDPE and LLDPE polyethylene films buried in the landfill.

Figure 3. Weight change for starch-based and control injection molded polypropylene parts buried in the landfill.

Figure 4. Variation in the tensile strength at break for LDPE and LLDPE polyethylene films during 24 months of landfill burial.

Figure 5. Variation in the % elongation at break for LDPE and LLDPE polyethylene films during 24 months of landfill burial.

Figure 6. Variation in the tensile strength at break for HDPE bottles during 24 months of landfill burial.

Figure 7. Variation in the % elongation at break for HDPE bottles during 24 months of landfill burial.

Figure 8. Variation in the tensile strength at break for polypropylene injection molded parts during 24 months of landfill burial.

Figure 9. Variation in the % elongation at break for polypropylene injection molded parts during 24 months of landfill burial.

Figure 10. Average weekly precipitation for Brookhaven Town during the 24 month burial period.

Figure 11. Average weekly maximum and minimum daily temperature for Brookhaven Town during the 24 month burial period.

Figure 12. Scanning electron micrograph of starch-based sample 1B; (a) 2000 x manification of a cross section of the film prior to placement in the landfill; (b) 2000 x manification of a cross section of the film following 18 months burial in the landfill.

Figure 1

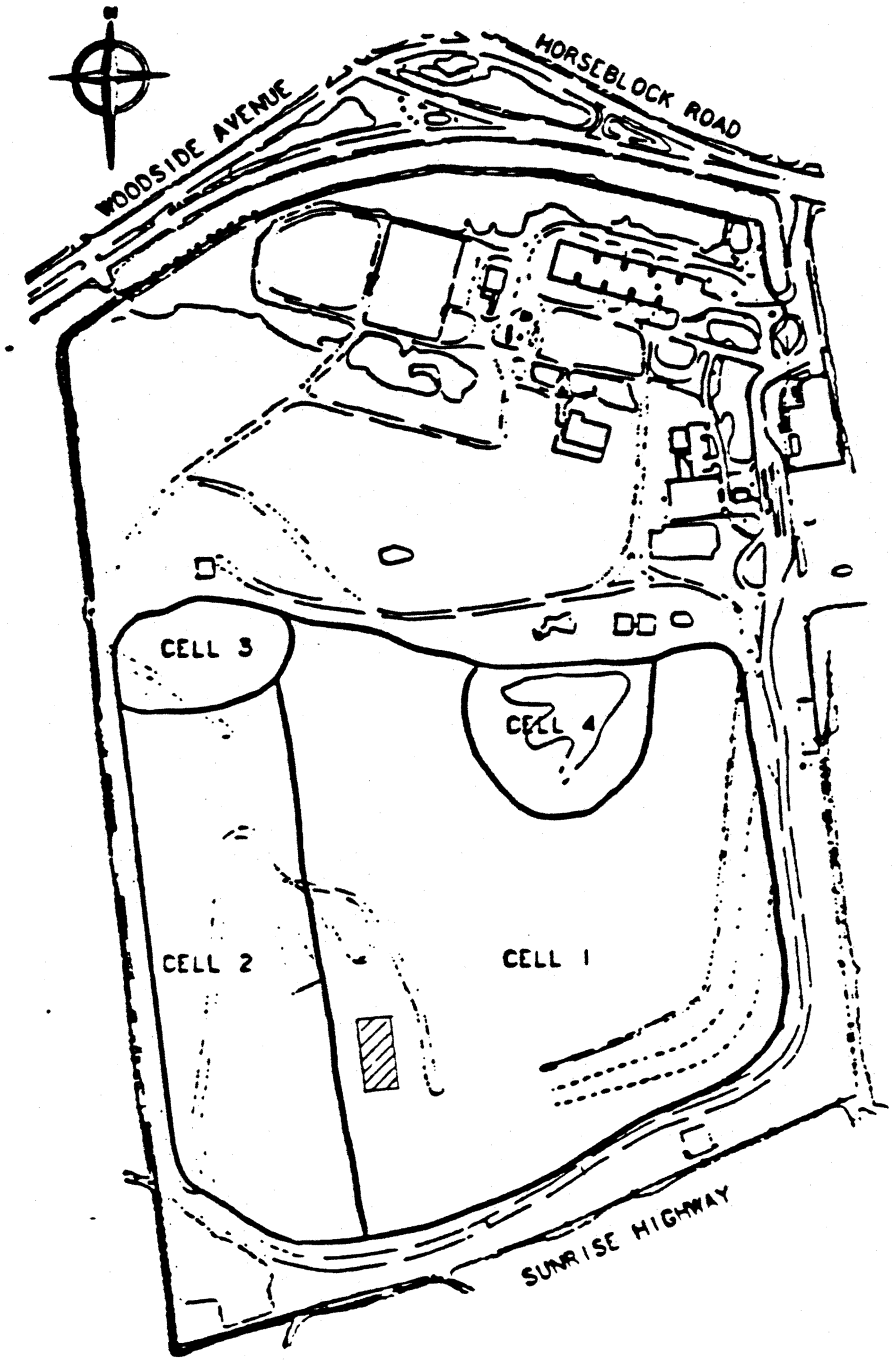

WOODSIDE AVENUE
HORSEBLOCK ROAD
CELL 3
CELL 4
CELL 2
CELL 1
SUNRISE HIGHWAY

Figure 2

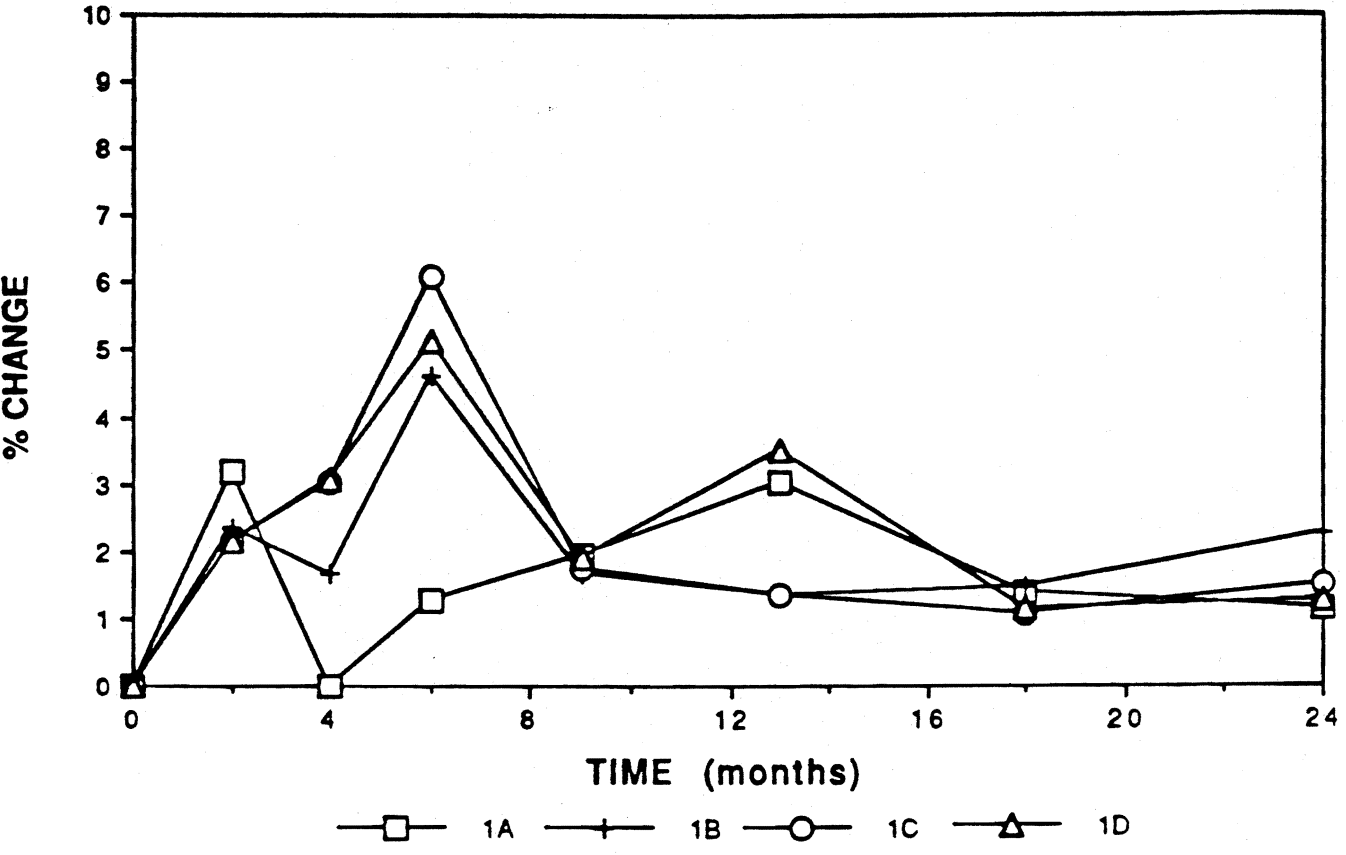


Figure 3

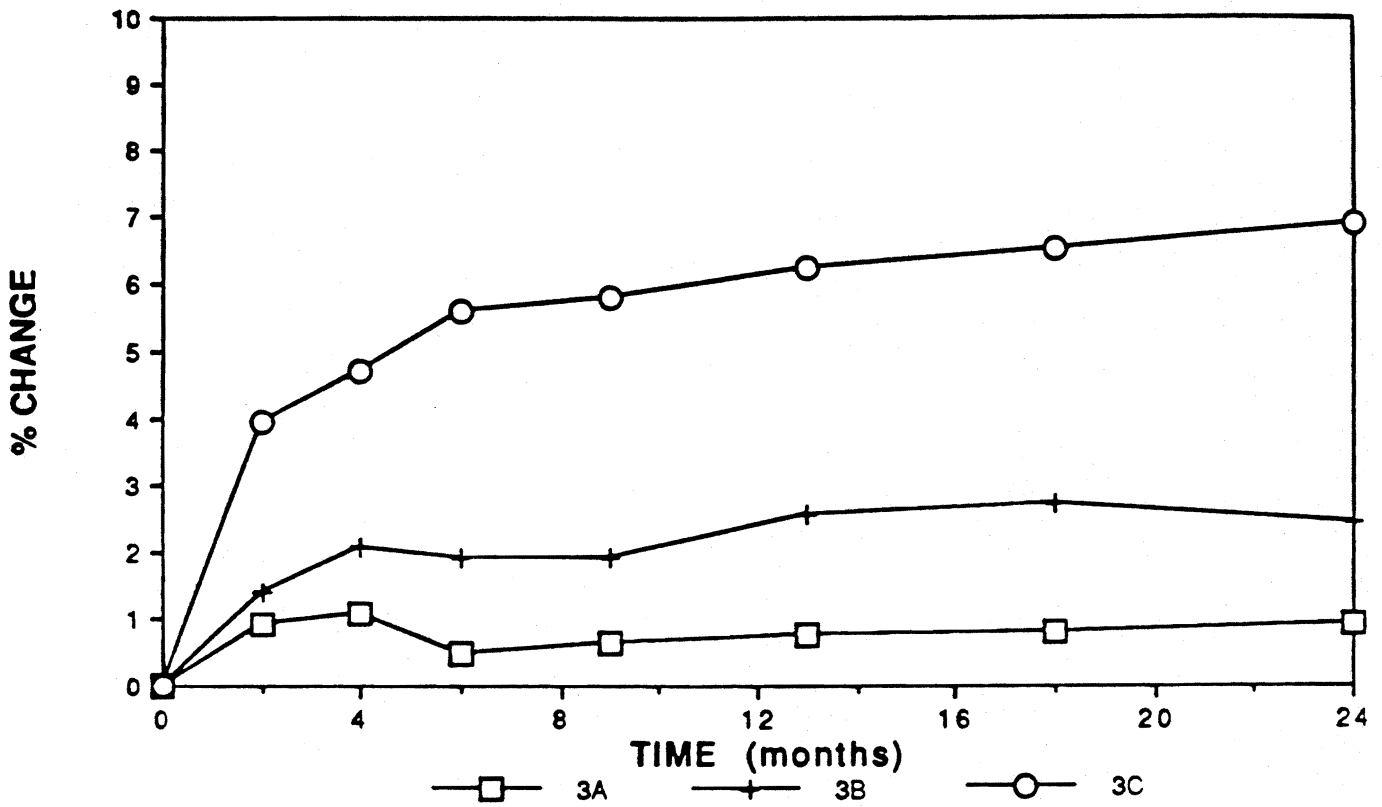


Figure 4

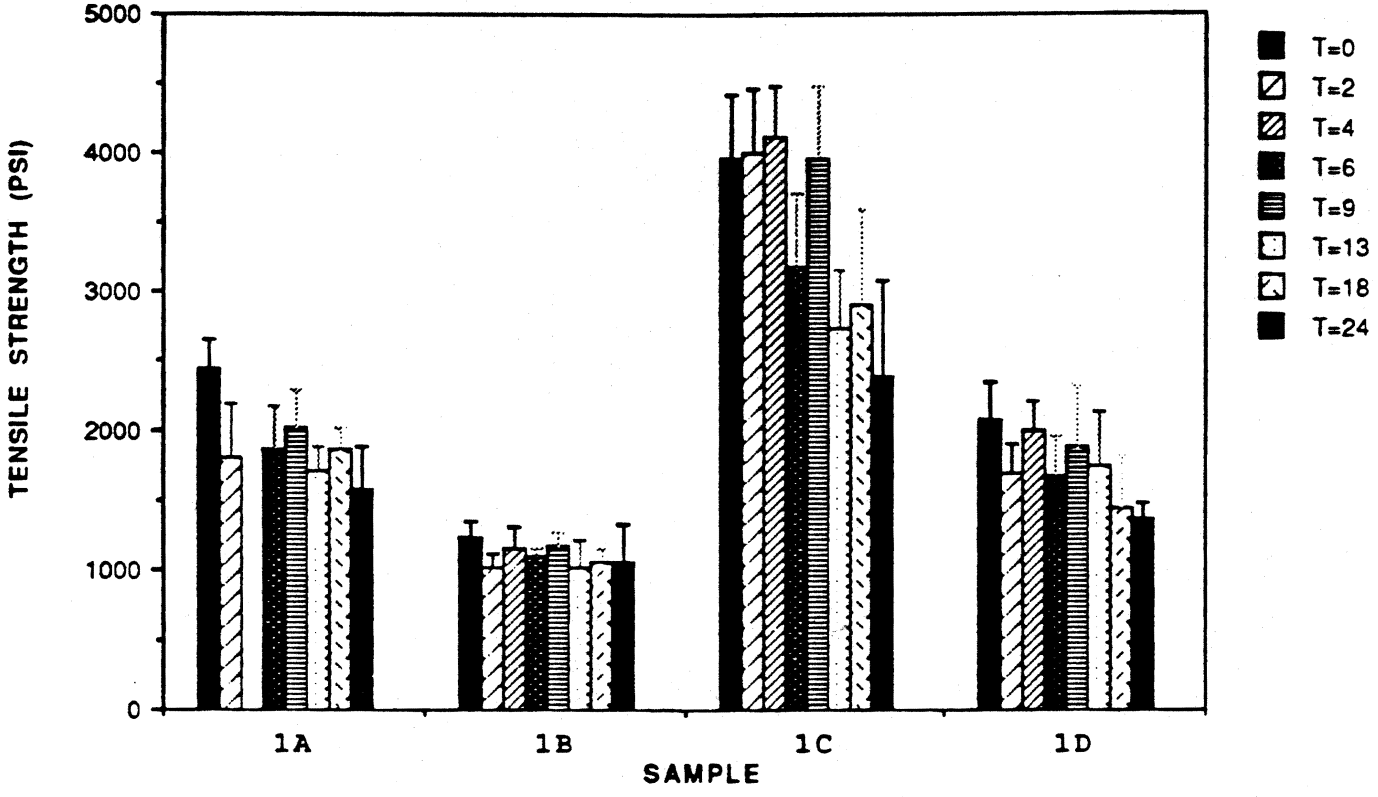

TENSILE STRENGTH (PSI)
5000
4000
3000
2000
1000
0
1A
1B
1C
1D
SAMPLE
T=0
T=2
T=4
T=6
T=9
T=13
T=18
T=24

Figure 5

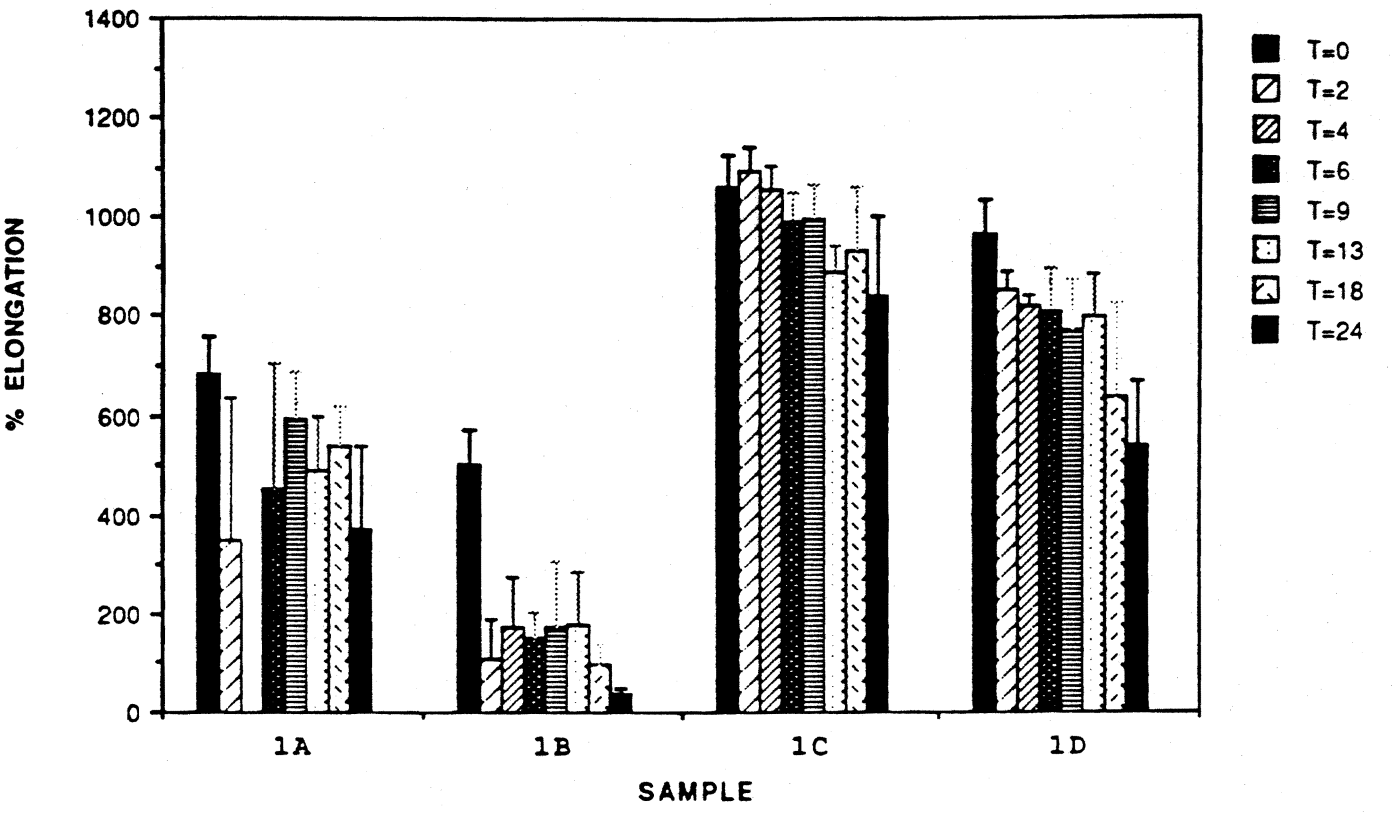

% ELONGATION
1400
1200
1000
800
600
400
200
0
1A
1B
1C
1D
SAMPLE
T=0
T=2
T=4
T=6
T=9
T=13
T=18
T=24

Figure 6

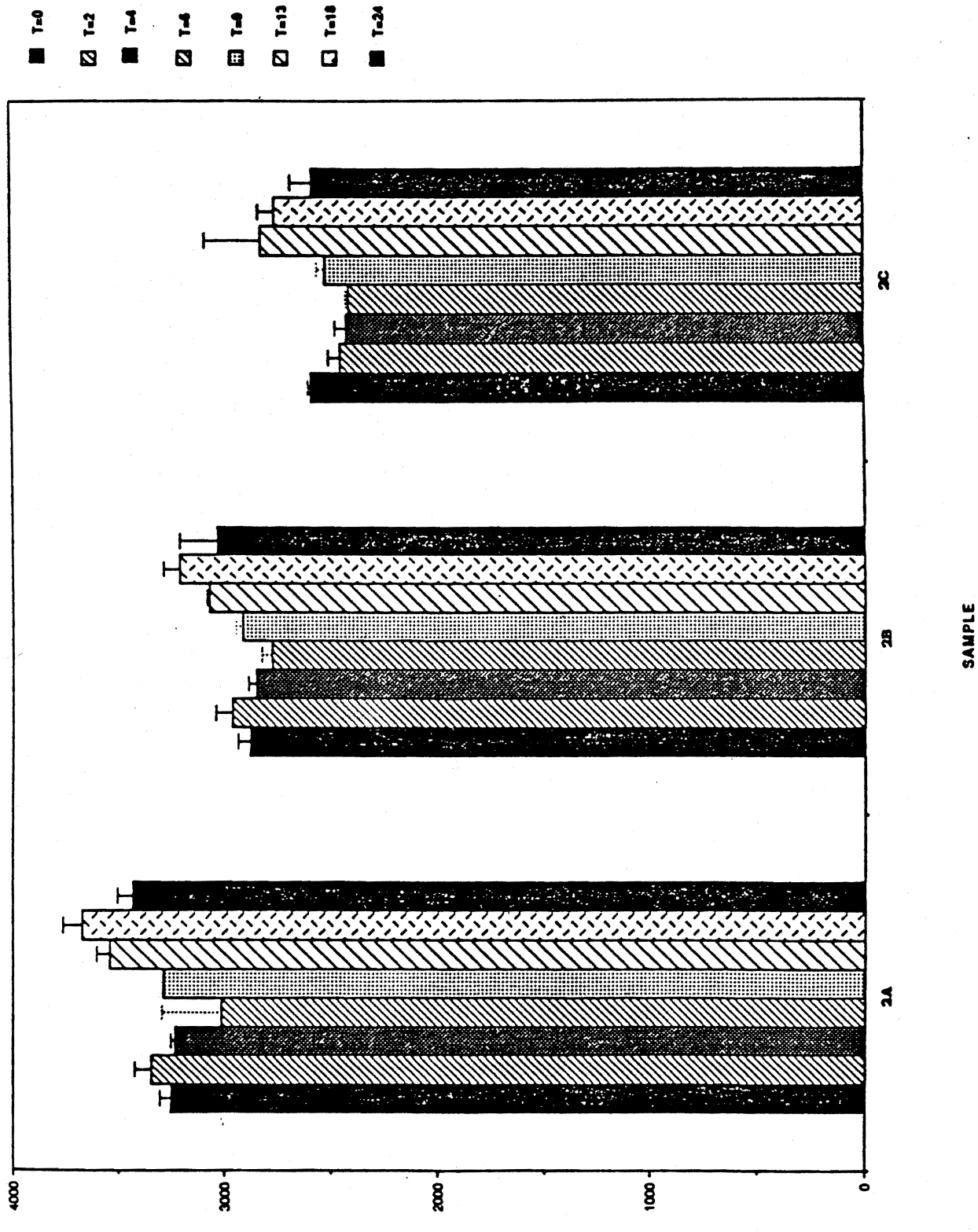

T=0
T=2
T=4
T=6
T=8
T=13
T=18
T=24
4000
3000
2000
1000
0
TENSILE STRENGTH (psi)
2A
2B
2C
SAMPLE

Figure 7

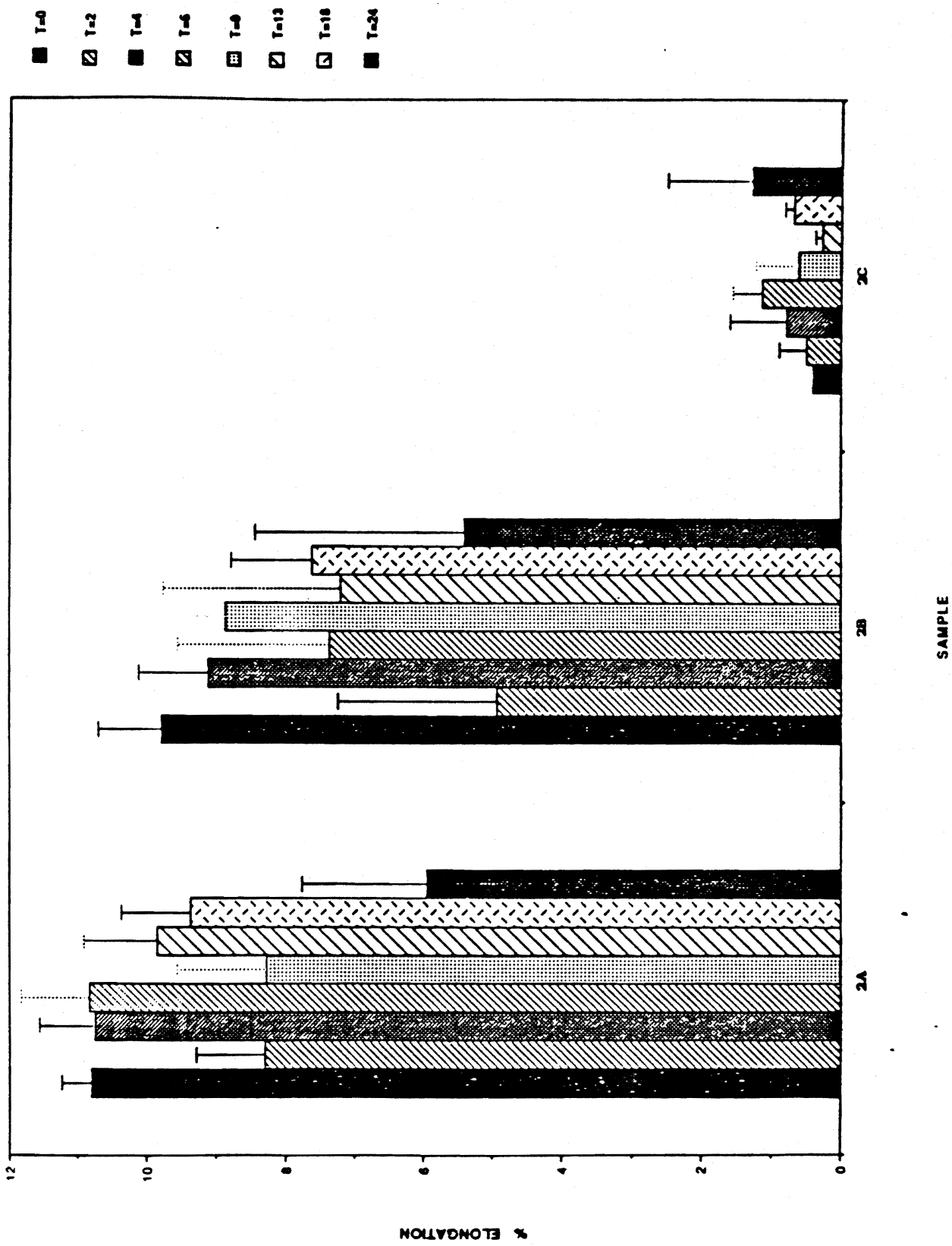

T=0
T=2
T=4
T=6
T=9
T=13
T=16
T=24
12
10
8
6
4
2
0
% ELONGATION
2A
2B
2C
SAMPLE

Figure 8

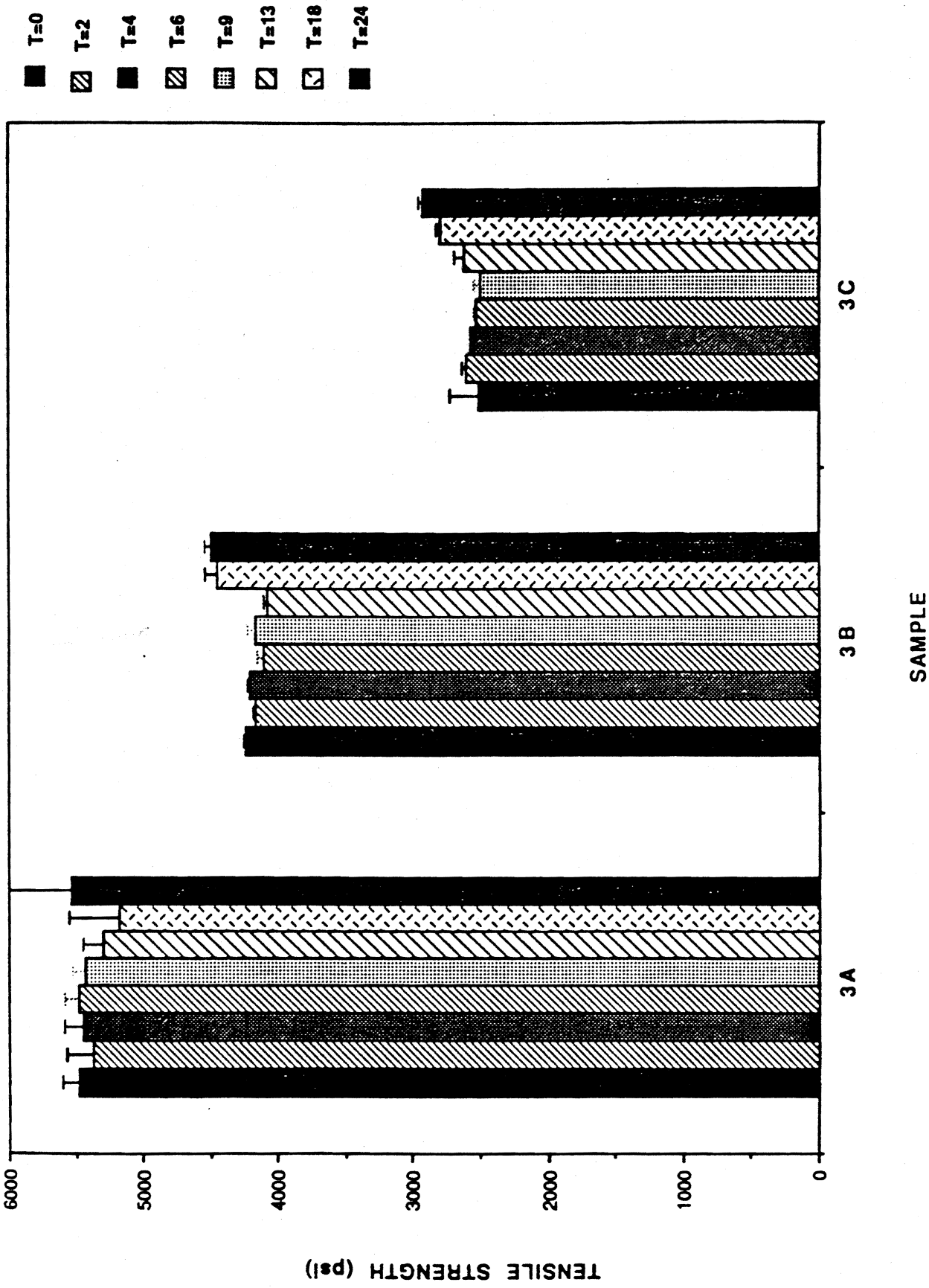

T=0
T=2
T=4
T=6
T=9
T=13
T=18
T=24
6000
5000
4000
3000
2000
1000
0
TENSILE STRENGTH (psi)
3A
3B
3C
SAMPLE

Figure 9

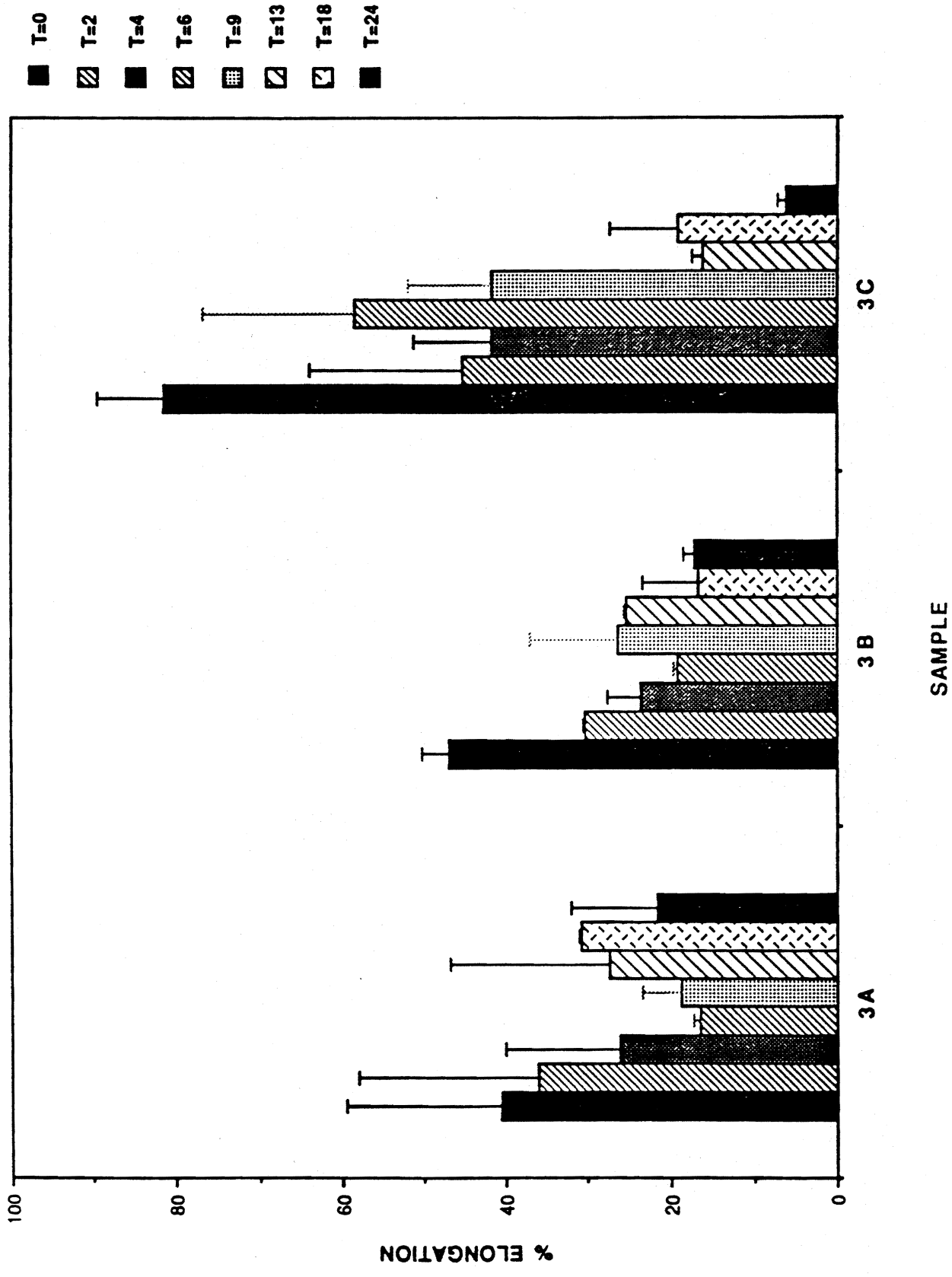

T=0
T=2
T=4
T=6
T=9
T=13
T=18
T=24
100
80
60
40
20
0
% ELONGATION
3A
3B
3C
SAMPLE

Figure 10

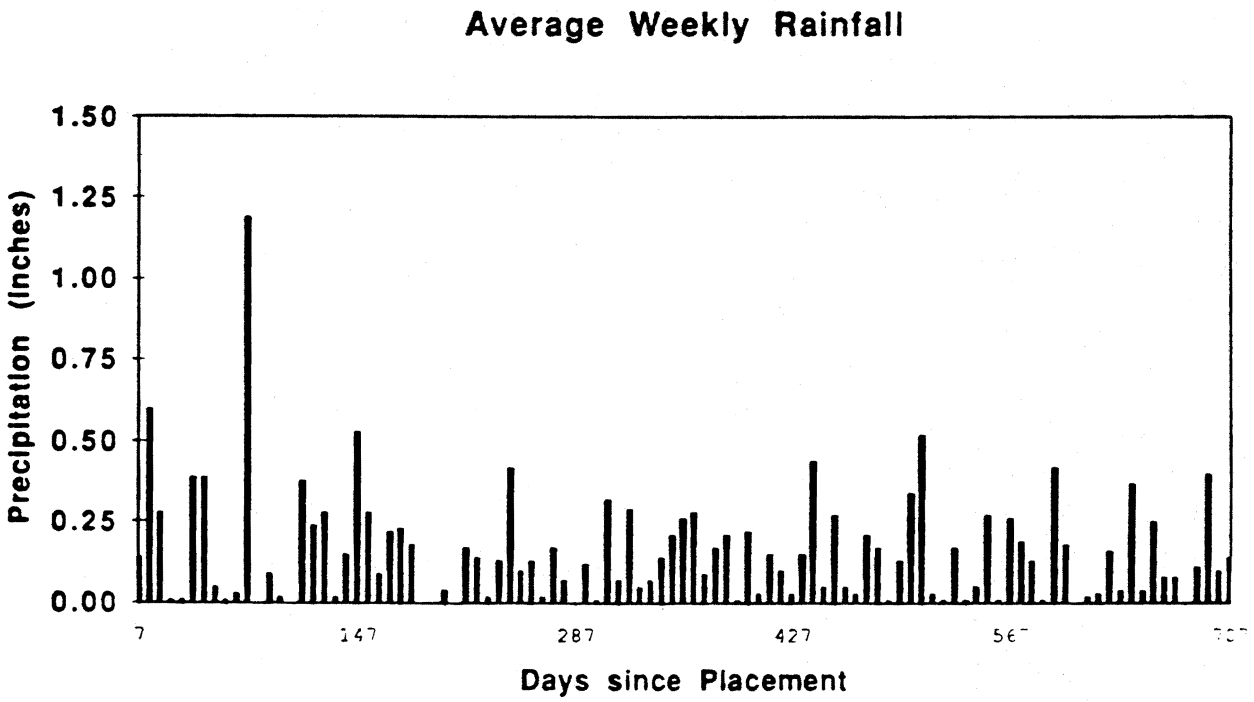

Average Weekly Rainfall
Precipitation (Inches)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
7
147
287
427
Days since Placement

Figure 11

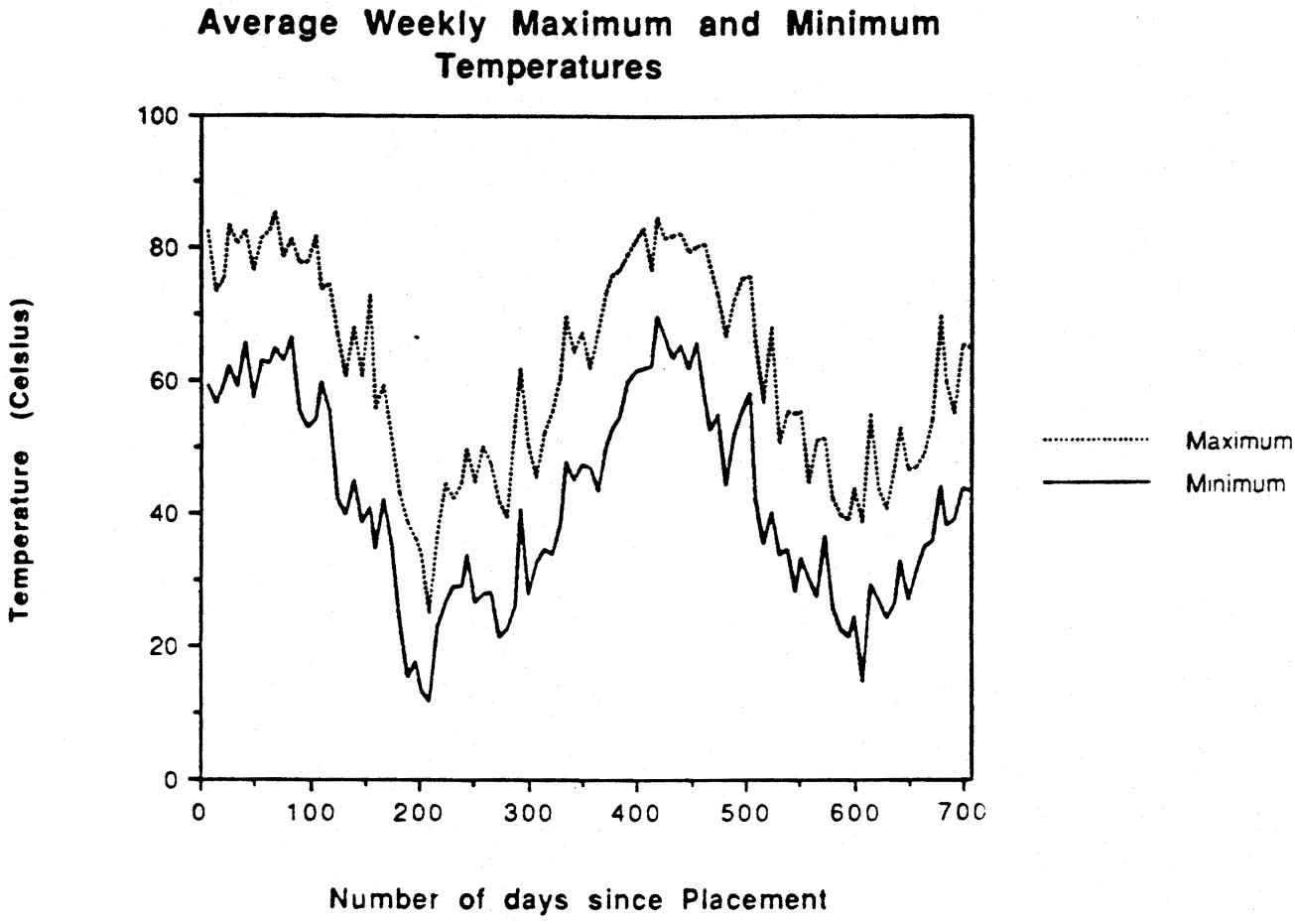
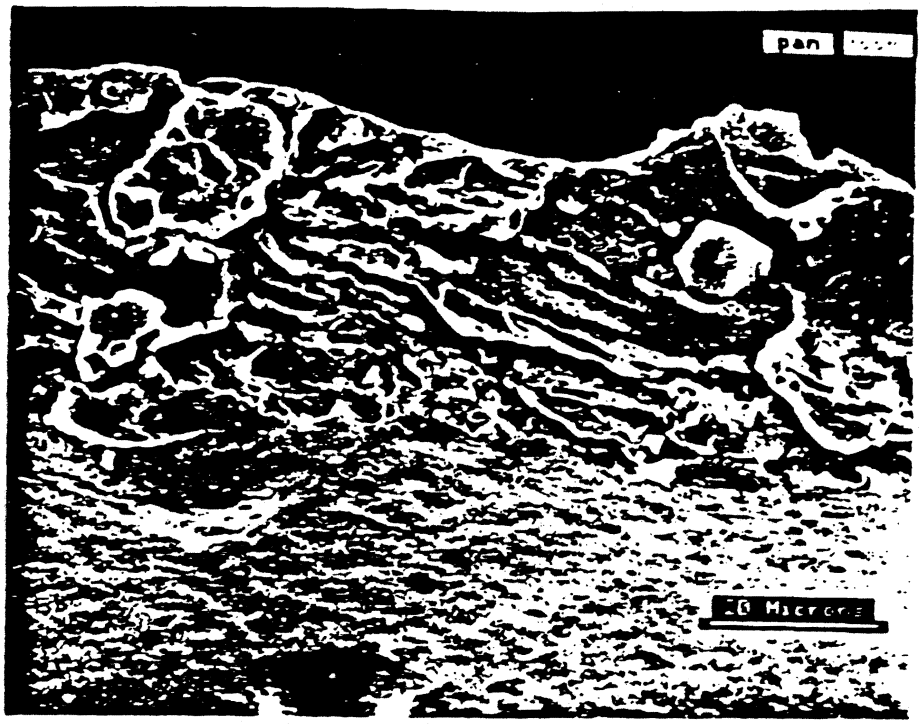
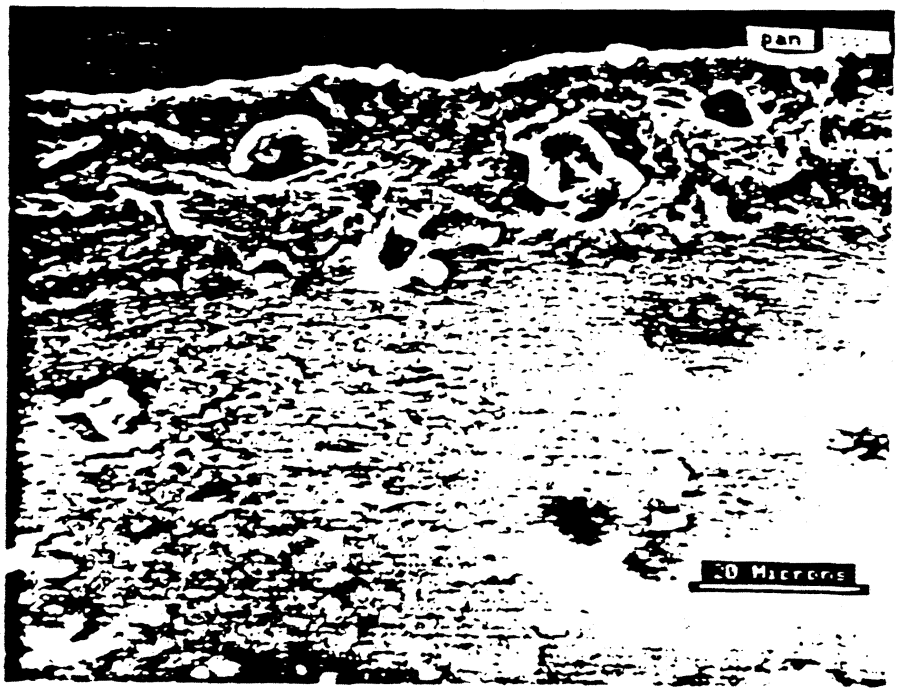

Average Weekly Maximum and Minimum Temperatures
Temperature (Celsius)
100
80
60
40
20
0
0
100
200
300
400
500
600
700
Number of days since Placement
Maximum
Minimum

Figure 12





Weathering of Starch-Based Polyethylene Films in the Marine Environment

A Technical Paper Prepared by:

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SYNOPSIS

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

KEY WORDS: polyethylene; starch-based plastics; photodegradation;seawater; strawline; degradable plastics.

INTRODUCTION

Plastics were estimated to comprise some 8% by weight of the municipal solid waste stream in 1988.[1] Many of the physical and chemical properties of plastics make them ideal materials for a variety of products and applications. Plastics can be manufactured to be durable, lightweight, flexible, impermeable, transparent or opaque. However, plastics are typically very resistant to degradation in the natural environment. As such, they are often considered to be environmental contaminants due to their widespread distribution and longevity. Recent studies have shown that plastic debris is widespread in the world's oceans.[2]

Plastic waste, along with other floatable debris, enters the marine environment via several pathways including litter, combined sewer overflows, solid waste handling, and recreational and fishing boats.[2,3] The plastic component of floatable debris may be in the form of large and small plastic pieces including plastic beads, packaging, diaper liners, tampon applicators, discarded fishing gear, and medically-related waste. Aside from being an asthetic problem, floatable plastic debris has been identified as a hazard to a variety of marine organisms. At sea and on beaches plastic debris is a threat to a variety of marine organisms including mammals, turtles, and birds.[4,5,6] The wash-up of floatable wastes along beaches has also closed beaches resulting in economic losses to coastal

communities.[7]

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

The degradation processes for starch-based plastics when they enter the marine environment are not well known. The objective of this study is to measure the rate and extent of deterioration of starch-based and control polyethylene films in seawater and the strawline of a marsh. Physical and chemical tests were conducted to determine the extent of deterioration of starch-based films during 13 months exposure in the marine environment.

EXPERIMENTAL

Sample Descriptions

All starch-based and control polyethylene films were supplied by the Archer Daniels Midland Company, Decatur, Illinois (Table 1). Low density (LDPE) and linear low density (LLDPE) polyethylene films were used as controls. Starch-based LDPE and LLDPE films were manufactured using the Griffin process.[8] The starch-based films contain approximately 5.5% "masterbatch" which contains both starch and proxident additives.

Sample Preparation for Exposure Site Placement

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

Seawater Exposure Site

Samples were placed on flow-through seatables at the Flax Pond Marine Laboratory, Old Field, New York. Seawater was pumped from the marsh into the laboratory through PVC pipes. The seawater PVC intake pipe lies within the entrance channel of the marsh 91.4 cm above the bottom. The intake pipe is equipped with a 0.32 cm screen to prevent large particles from entering the pumping system. Although large particles are removed at the intake pipe, the screen allows the passage of biologically active seawater.

The fiberglass seatable (224 cm x 91.4 cm x 15.2 cm) is equipped with an adjustable overflow drain set to allow a seawater depth of 10.2 cm on the table. Seawater flows from the laboratory plumbing into a multi-chambered sediment settling tank prior to discharge onto the table. Seawater flows onto the table at a rate of 2 liters per minute replacing the water on the seatable every 1.5 hours.

On May 5, 1989, starch-based and control polyethylene films were submerged to a depth of 5.1 cm in the seawater on the seatable. A plexiglass railing was constructed and held in place with C-clamps to keep the plexiglass exposure frames and samples submerged in seawater. Temperature and salinity of the seawater were recorded weekly. Samples were removed from the seatable on a predetermined basis and returned to the laboratory for physical and chemical testing (Table 2).

Strawline Exposure Site

Starch-based and control polyethylene films were placed in the strawline of a marsh on June 9, 1989. The exposure area was located in the marsh at the Flax Pond marine laboratory (Figure 1). Flax Pond is a 0.5 km^2 estuarine marsh on the north shore of Long Island with a single channel connection to Long Island Sound. During high tide the surface area of water is 574,000 m^2 with a volume of approximately 880,000 m^3.[10]

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

Daily temperature and solar radiation readings were obtained from the weather station at the Brookhaven National Laboratory, Upton, New York. Samples were removed from the strawline on a predetermined basis and returned to the

laboratory for physical and chemical testing (Table 2).

TESTING METHODS

Cleaning and Storage of Samples

In the laboratory, the samples were rinsed in tap water and sonicated in distilled-deionized water for 15 minutes. The samples were then towel dried, placed in labeled zip lock bags, evacuated with argon, and stored in the dark at 20°C.

Tensile Testing

An Instron Model 1011 Universal Testing Machine was used to determine the tensile properties of the starch-based and control polyethylene films following ASTM method D882.[11] A guage length of 5.08 cm and a crosshead speed of 50.8 cm/min was used. Six specimens were prepared for testing from each sample sheet retrieved from the exposure sites. Tensile strength at break and percent elongation at break were determined for each sample.

Sample Weight

Sample weights (±0.001 gram) were obtained using a Sartorius Model 2462 HW analytical balance. Samples were conditioned at 50% humidity and 23°C for 48 hours prior to weighing.

FTIR Testing

Difference fourier transform infrared (FTIR) spectroscopy was carried out on control and starch-based polyethylene films using a Perkin-Elmer model 1600 Spectrophotometer collecting 16 scans with a resolution of 4.0 cm^{-1} between 4400 to 450 cm^{-1}. Four replicates of each sample were analyzed. Each spectrum was recorded and stored on a floppy disc, and printed out with transmittance wave numbers for analysis.

Chemical Method for Starch Determination

Quantitative starch determinations of preplacement and weathered starch-based polyethylene films were conducted using a previously developed method.[12] The method consists of dissolving the polyethylene component followed by the solubilization and partial hydrolysis of the starch component. The solubilized starch component is then isolated for carbohydrate analysis using the phenol-sulfuric acid method.

RESULTS

Air Temperature and Solar Radiation

Weekly average high temperatures are shown in Figure 2 for the thirteen month exposure period. The highest recorded temperature was observed to be 34°C on July 23, 1989 while the lowest recorded temperature was observed to be -15°C on December 19, 1989.

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

Seatable Temperature and Salinity

Seawater salinity remained relatively constant throughout the thirteen month exposure period (Figure 3). Salinity varied from 24.5 ppt to 30.7 ppt with a mean of 27.4 ppt.

Temperature of the seawater varied seasonally (Figure 3). Water temperature was warmest during the summer months reaching a high of 24.0°C during August of 1989. The lowest temperature of 3.0°C was measured during February of 1990.

Tensile Properties

Seatable Exposure

Tensile strengths of both the control and starch-based polyethylene films remained similar to their preplacement values over the entire thirteen month exposure period, retaining greater than 86% of their initial tensile strength (Figure 4).

LLDPE control sample 1C and LLDPE starch-based sample 1D retained greater than 87% of their initial % elongation during the thirteen month exposure period (Figure 5). In contrast, the % elongation for LDPE starch-based sample 1B decreased by 70% of the preplacement value while the % elongation of the corresponding control LDPE sample 1A only decreased 13% from the preplacement value.

Strawline Exposure

Decreases in the tensile strengths of starch-based and control samples LDPE 1A, LLDPE 1C, and LLDPE 1D are observed over the six month sampling period while the tensile strength of starch-based LDPE sample 1B remained similar to preplacement values (Figure 6).

The % elongation of both starch-based and control films rapidly decreased following exposure (Figure 7). Following two months exposure, the % elongation for starch-based samples LDPE 1B and LLDPE 1D decreased by 98% and 29%

respectively of their preplacement values while the % elongation of their corresponding control samples decreased by 92% and 12% of their preplacement values. After 6 months, the % elongation for both control and starch-based plastic samples decreased to less than 5% of their preplacement values and further testing was discontinued.

Weight Loss

Seatable Exposure

The weight of both starch-based and control LDPE and LLDPE films increased slightly when compared to preplacement values during the thirteen month exposure period (Figure 8). Weight increases may be due to water absorption by the starch and/or polyethylene in addition to biological material remaining on the samples following cleaning. Both the LDPE and LLDPE control and starch-based films removed from the seatable retained dark green and brown pigments following cleaning.

Strawline Exposure

The weight of both starch-based and control LDPE and LLDPE films decreased as time progressed (Figure 9). Weight loss was most pronounced for the LDPE and LLDPE starch-based films. Following 13 months exposure, weight losses of 38% and 17% were observed for starch-based samples LDPE 1B and

LLDPE 1D, respectively. Both starch-based and control polyethylene films began tearing and fragmenting into smaller pieces following 4 months exposure.

FTIR Analysis of Starch-Based and Control Polyethylene Films

The FTIR spectra of LDPE and LLDPE films show characteristic C-H stretching bands within the 3000-2840 cm^{-1} region, weaker C-H bending bands within the 1465-1450 cm^{-1} and 1375-1365 cm^{-1} regions, and C-H out of plane bending within the 740-719 cm^{-1} region (Figure 10; Table 3). In addition to the functional groups common to LDPE and LLDPE, the starch-based films showed a broad O-H stretching absorbance in the 3600-3200 cm^{-1} region and a strong set of C-O stretching bands in the 1090-980 cm^{-1} region (Figure 11; Table 3).

Determination of Starch Loss From Starch-Based Polyethylene Films

A decrease in the area of the C-O absorption region of 1090-980 cm^{-1} was observed in samples retrieved from the strawline site (Figure 12). The observed decrease in this absorbance region has served as the basis for the determination of starch loss from starch-based films by previous investigators.[13] For this investigation, the change in the starch content of the films was estimated based on the decrease in the area of this absorbance region

relative to the total absorbance of absorbance regions common to LDPE and LLDPE films. Changes in the absorbance regions common to LDPE and LLDPE were not observed following weathering. FTIR estimates of the relative starch content (RSC) of the starch-based polyethylene films for this investigation was determined as follows:

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

A = Integrated absorbance within the region specified in Table 3.

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

% Starch Remaining =

[RSC at Time = T (%) / RSC at Time = 0 (%)] x 100

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

Continuous decreases in the starch content of both LDPE and LLDPE starch-based films was observed for samples placed in the strawline exposure site (Figure 13). Starch-based LDPE showed a decrease of 34% in the starch content while starch-based LLDPE showed a 32% decrease in the starch content after thirteen months exposure at the strawline

exposure site. The starch content of the thirteen month LDPE and LLDPE starch-based samples as determined using the chemical dissolution method were similar to the starch contents as determined by FTIR (Table 4).

FTIR analysis of the starch content of starch-based LDPE and LLDPE seatable samples was not possible due to the discoloration of weathered samples. However, starch contents of the weathered samples were determined using the chemical dissolution method.[12] The initial starch content of starch-based LDPE and LLDPE samples was 6.6 ± 0.2%. Results show that following thirteen months seawater submersion starch losses of 15% and 8% were measured for starch-based LDPE and LLDPE samples, respectively (Table 4).

Carbonyl Formation in Starch-Based and Control Polyethylene Films

In addition to an observed decrease in the intensity of the starch peak, FTIR analysis of weathered LDPE and LLDPE starch-based and control films retrieved from the strawline site showed the presence of a new absorbance band centered at 1712 cm^{-1}, representing the carbonyl functional group (Figure 12). FTIR determination of the carbonyl index of starch-based and control polyethylene films was calculated as follows:[14]

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

A = Integrated absorbance within the region specified in Table 3.

The carbonyl index of the starch-based and control LDPE and LLDPE films increased following exposure to increasing amounts of solar radiation. In general, the carbonyl index of the starch-based films was greater than the carbonyl index of the corresponding control film. The carbonyl index of starch-based films LDPE 1B and LLDPE 1D increased to 0.35 and 0.55, respectively, following exposure to 20.1 kLy after thirteen months in the strawline (Figure 14). Since these samples were placed on the ground within the marsh grasses, shading may have reduced the total radiation recieved by the samples.

DISCUSSION

Seatable Exposure Site

Low rates of deterioration were measured for both starch-based and control LDPE and LLDPE films weathered for thirteen months in seawater. Only starch-based LDPE sample 1B showed a significant reduction in % elongation when compared to the corresponding control sample after thirteen

months seatable exposure (Figure 5). In addition, high starch contents were measured for the starch-based films following thirteen months weathering on the seatable (Table 4). The starch-based and control LDPE and LLDPE films, although discolored, remained intact throughout the thirteen month exposure period. Several factors may act to influence the extent of degradation of the starch-based and control LDPE and LLDPE films weathered on the seatable (Table 5).

Previous research has identified cool seawater temperatures as a factor in retarding the rate of deterioration of plastics in seawater.[15] Seatable seawater temperatures varied from a low of 4.5°C to a high of 24°C during the thirteen month exposure period (Figure 3). Seawater temperatures were warm during the first four months of exposure. The average seawater temperature exceeded 20°C only during the first four months of exposure. During this exposure period decreases in the % elongation of starch-based LDPE sample 1B were observed. Following the initial four months, significant differences in the % elongation of starch-based samples were not observed. Seawater temperatures following the initial four month exposure period averaged only 12°C. Low water temperatures would also limit the effectiveness of the transition metal prooxidant additive in the starch-based films in initiating the thermal oxidative degradation of the polymer.

The effect of solar radiation on the starch-based and

control LDPE and LLDPE samples was limited. The seatable was located within the Flax Pond laboratory building. Although the seatable was located adjacent to a window and exposed to direct sunlight for several hours each day, most of the damaging wavelengths of solar radiation are filtered out as it passes through glass. In addition, the surfaces of the films exposed to seawater were rapidly fouled by a variety of marine organisms. The growth of organisms completely covered the surfaces of the sheet plastic samples further reducing the influence of solar radiation.

Biological activity on the seatable, as measured by the disappearance of cellophane sheets, was moderate. The cellophane sheets began to fragment following two months seawater exposure but did not completely disappear until the four month sampling event. Many of the marine organisms which fouled the surfaces of the samples used the samples as substrate and do not actively metabolize starch.

Measured starch contents of weathered films showed that only 8-15% of the starch content of the samples was lost. Previous research has demonstrated that the starch within starch-based films is susceptable to biodegradation.[13,16] However, recent research suggests that only a small fraction of the starch within the polyethylene matrix is available for biodegradation.[17] In the absence of conditions causing further physical deterioration of the sample, i.e. photodegradation, thermal degradation, or physical abrasion,

starch located within the polyethylene matrix will remain unavailable for biodegradation. As these additional physical and chemical forces were limited on the seatable, the deterioration of the starch-based samples during the thirteen month exposure period was most likely confined to the biodegradation of the surface available starch.

Strawline Exposure Site

Deterioration of the starch-based and control LDPE and LLDPE films placed in the strawline site occurred rapidly. Within four to six months of strawline exposure, the % elongation of control and starch-based polyethylene films was less that 2% of their preplacement values. The starch-based LDPE and LLDPE films were found to deteriorate more rapidly than their respective control films (Figure 7). In addition, starch-based LDPE and LLDPE films were brittle following four months weathering and began to fragment following six months weathering ~(0Xin the strawline. Factors affecting the deterioration of the films placed in the strawline include solar radiation, temperature, biological activity and starch loss (Table 5).

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

resulting in the formation of carbonyl groups. FTIR analysis of samples retrieved from the strawline exposure site showed an increase in the carbonyl index of the samples as weathering progressed (Figure 13). Initial increases in the carbonyl index of the samples correlated with the high intensity of the solar radiation during the first four months of sample weathering (Figure 2). Prolonged weathering of the samples however, did not result in continuous increases in the carbonyl index of the starch-based and control films.

The decrease in the % elongation of the film samples has been shown to be affected by the increase in the carbonyl index of the weathered plastic.[18] UV degradation also results in increasing in the amount of low molecular weight material by breaking bonds and increasing the surface area of the film through embrittlement.[14]

Other factors listed in Table 5 influence the rate of deterioration of starch-based and control LDPE and LLDPE films to a lesser degree. Biological activity at the strawline site did not appear to be an important factor since the cellophane sheets were present throughout the thirteen months of weathering. Record rainfall and high seasonal temperatures occurred during the first two to four months when the majority of the sample deterioration occurred (Figure 2). Average daily high temperatures exceeded 26°C while a total of 64.5 cm of precipitation fell

during the first four months of weathering in the strawline. Normal rainfall for this period is about 36 cm. High temperatures contribute to the heat buildup which may accelerate the deterioration of films weathered outdoors.[15] The heat buildup in the starch-based films may result in an increase in the rate of thermal oxidation of the polyethylene cataylized by the presence of the transition metal prooxidant additive.[19]

Starch loss was higher for the samples weathered in the strawline as compared to samples weathered in seawater (Table 4). Although starch loss was observed throughout the exposure period, the rate of starch loss was highest initially with greater than 72% of starch loss occuring within the first six months of weathering (Figure 13). The decrease in the rate of starch loss may be due to the lack of access to starch granules located within the polyethylene matrix. The initial high rate of starch loss seemingly conflicts with the low biological activity as indicated by the presence of the cellophane sheets throughout thirteen months exposure. Starch loss however, may not be due to biological processes alone. The physical deterioration of the polyethylene caused by photodegradation may render the starch more accessible for removal by a combination of biological, chemical and physical processes leading to lower starch contents of weathered samples.

CONCLUSIONS

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

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

physical processes.

ACKNOWLEDGEMENTS

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Table 1. Starch-based and control polyethylene films.

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

Table 2. Exposure site sampling activities.

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

Table 3. FTIR analysis of starch-based and control polyethylene films.

Characteristic Group	Position or Region (cm^{-1})
O-H Broad	3600-3200
C-H Stretching	3000-2840
C=O Carbonyl	1720-1710
C-H Bend (Asymmetrical)	1465-1450
C-H Bend (Symmetrical)	1375-1365
C-O (Starch Region)	1090-980
C-H Rock (Out of Plane Bend)	740-719

Table 4. Comparison of % starch remaining as determined by FTIR and the chemical method for the analysis of starch in polyethylene following 13 months exposure.

	% Starch Remaining LDPE Sample 1B		% Starch Remaining LLDPE Sample 1D	
	FTIR	Chemical[1] Method	FTIR	Chemical Method
Seawater	NA[2]	85 (1.8)	NA	92 (5.6)
Strawline	66 (0.06)	68 (3.5)	68 (0.07)	71 (4.3)

[1] Nikolov, 1990.[12]

[2] FTIR analysis for starch content was not conducted due to discoloration of the seawater samples.

Table 5. Factors affecting starch-based polyethylene film degradation

Factor	Seatable	Strawline
Temperature	Seasonal Figure 3	Seasonal Figure 2
Solar Radiation	Limited	Seasonal Figure 2
Moisture	Seawater Submersion	Rainfall Tidal Flooding
Biological Activity[a]	Medium	Low
Starch loss[b]	8-15% Table 4	29-34% Table 4
Extent of Degradation[c]	Low Figure 5	High Figure 7

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

[b] Starch loss for starch-based films LDPE 1B and LLDPE 1D as measured by FTIR and/or Nikolov, (1990)[12] following thirteen months exposure.

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

FIGURE LEGENDS

Figure 1. Strawline exposure site location, Old Field, New York.

Figure 2. Average weekly solar radiation and average weekly maximum daily temperature during thirteen month exposure period.

Figure 3. Seatable seawater temperature and salinity during the thirteen month exposure period.

Figure 4. Variation in the tensile strength at break for samples 1A, 1B, 1C, and 1D during thirteen months seawater exposure.

Figure 5. Variation in the ultimate % elongation for samples 1A, 1B, 1C, and 1D during thirteen months seawater exposure.

Figure 6. Variation in the tensile strength at break for samples 1A, 1B, 1C, and 1D during thirteen months strawline exposure.

Figure 7. Variation in the ultimate % elongation for samples 1A, 1B, 1C, and 1D during thirteen months strawline exposure.

Figure 8. Weight loss for samples 1A, 1B, 1C, and 1D during thirteen months seawater exposure.

Figure 9. Weight loss for samples 1A, 1B, 1C, and 1D during thirteen months strawline exposure.

Figure 10. FTIR spectra for LDPE (a) and LLDPE (b) control films.

Figure 11. FTIR spectra for starch-based LDPE (a) and LLDPE (b) films.

Figure 12. FTIR spectra of starch-based LDPE (a) and LLDPE (b) films following 13 months exposure in the strawline of a marsh.

Figure 13. FTIR determination of starch loss for starch-based LDPE and LLDPE films retrieved during exposure in the strawline site.

Figure 14. Carbonyl index of starch-based and control LDPE and LLDPE films during exposure in the strawline of a marsh.

Figure 1

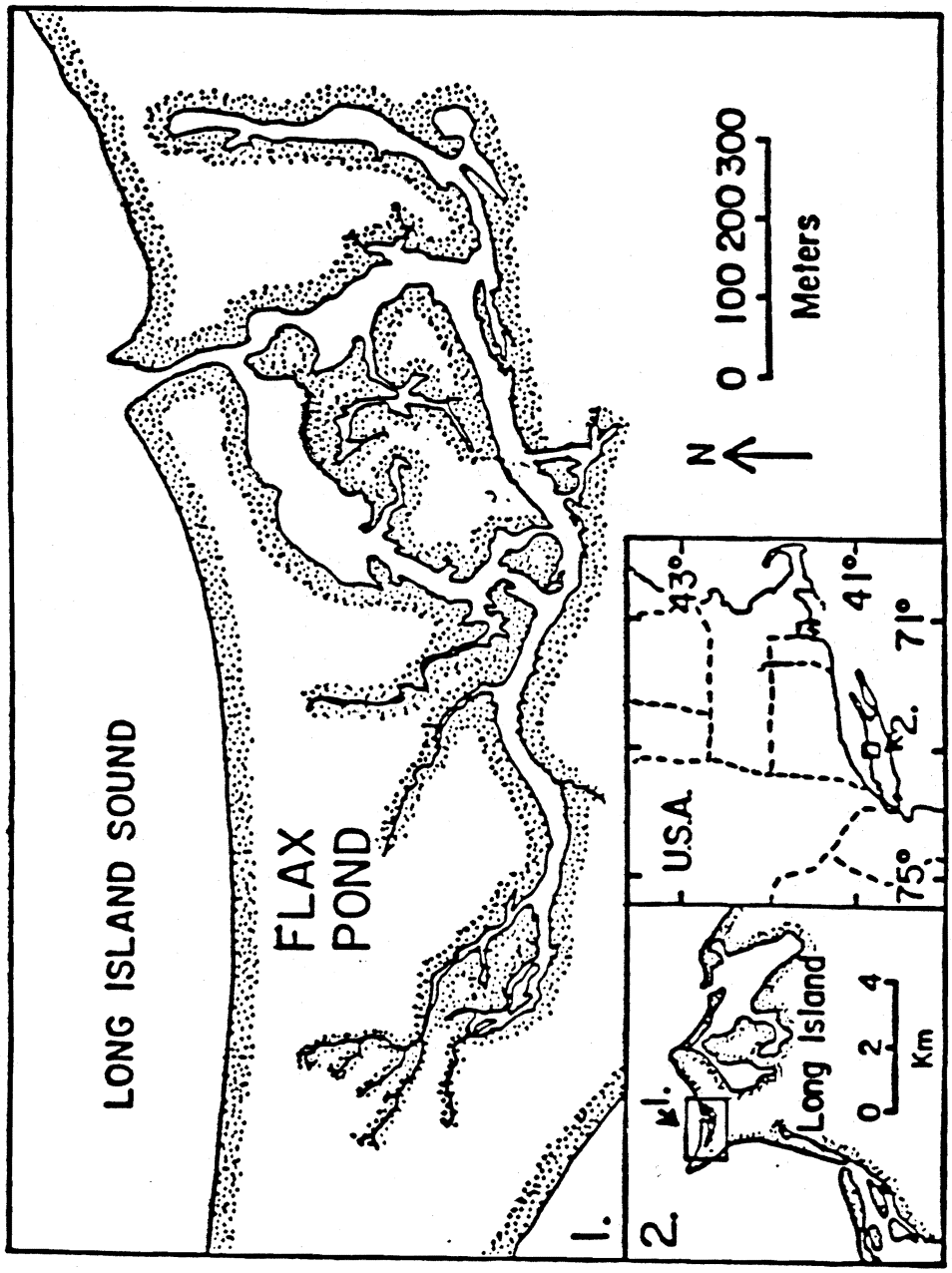

LONG ISLAND SOUND
FLAX
POND
1.
2.
N
0 100 200 300
Meters
USA
43°
41°
71°
75°
Long Island
0 2 4
Km

Figure 2

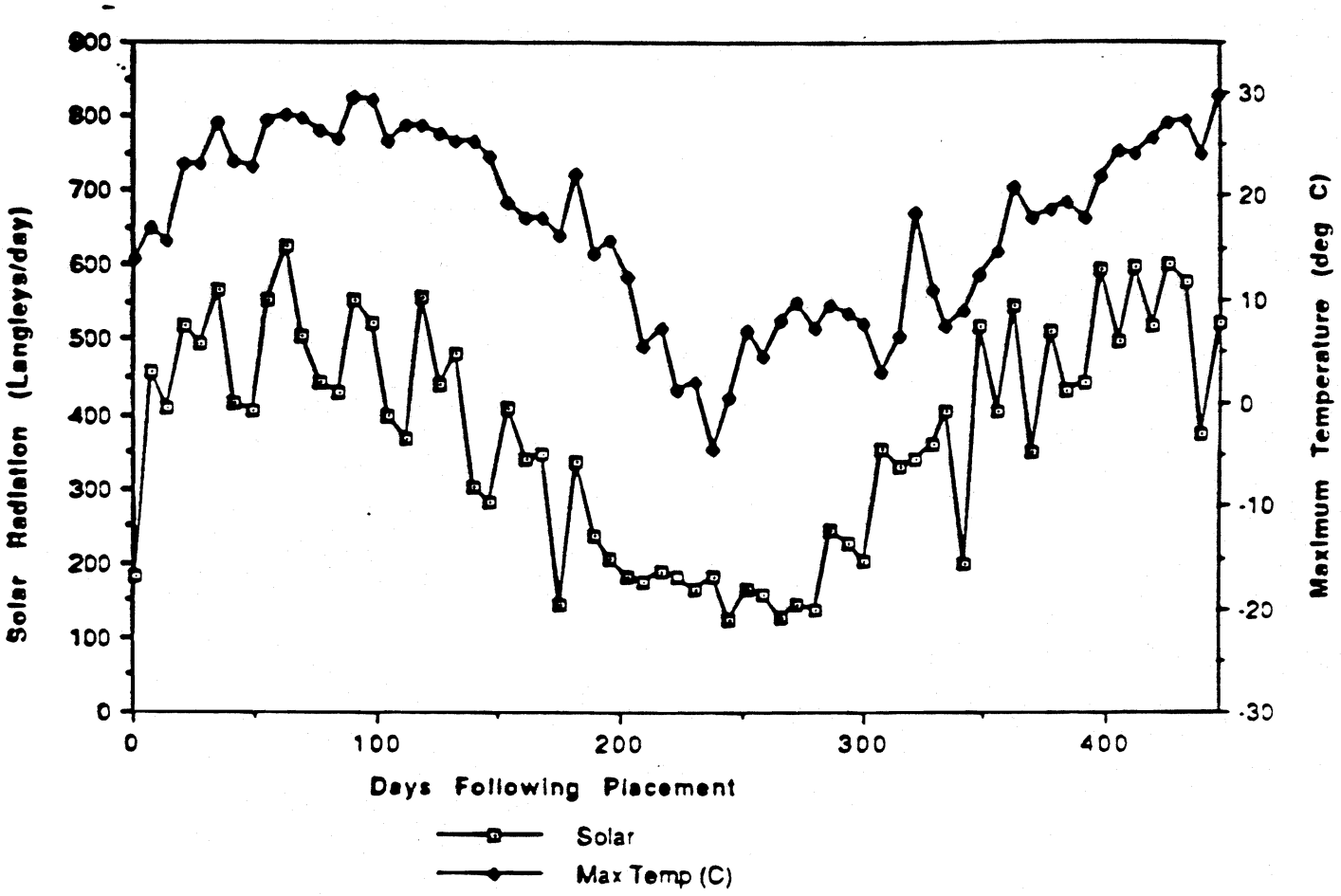

Solar Radiation (Langleys/day)
900
800
700
600
500
400
300
200
100
0
Maximum Temperature (deg C)
30
20
10
0
-10
-20
-30
0
100
200
300
400
Days Following Placement
Solar
Max Temp (C)

Figure 3

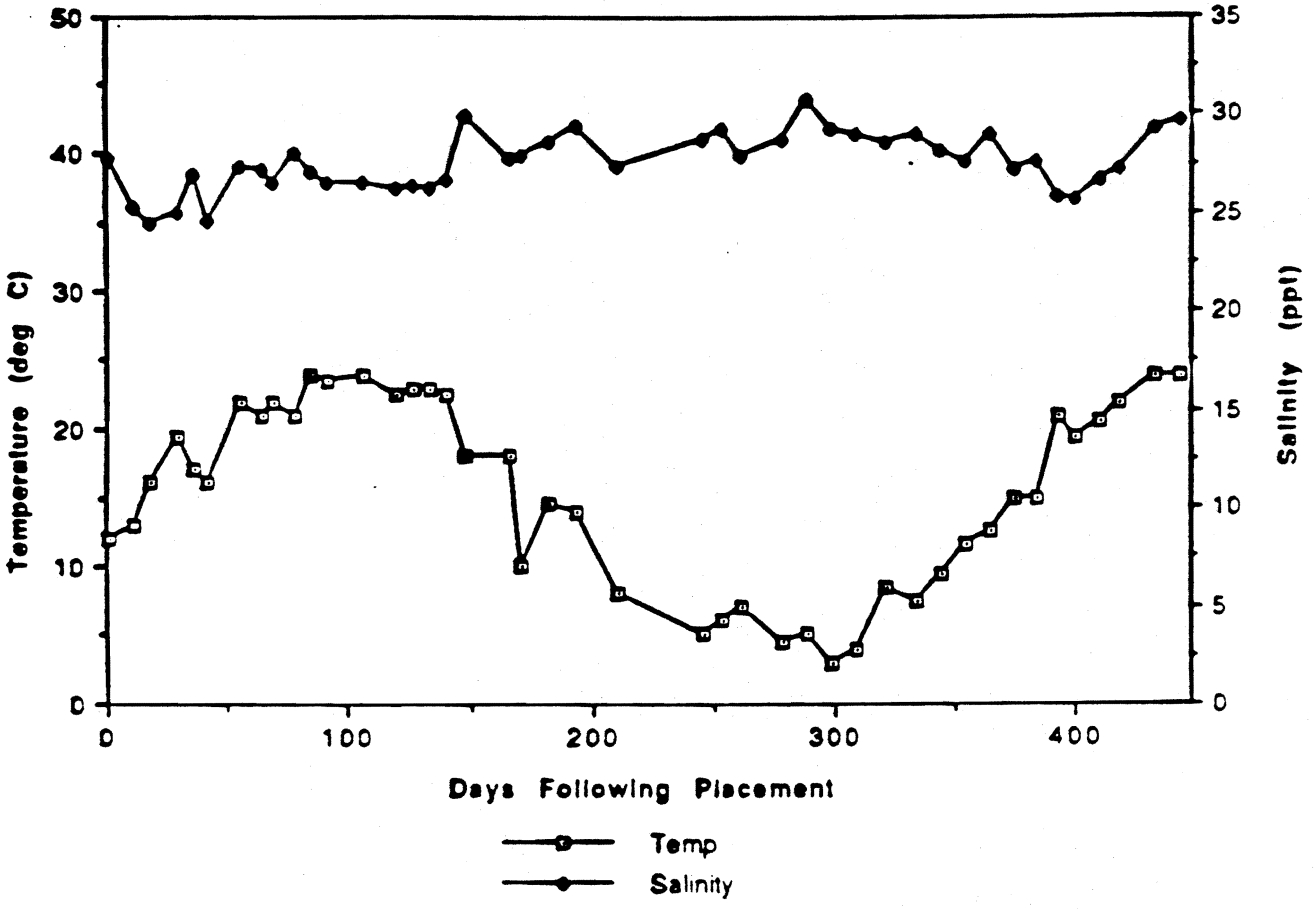

Temperature (deg C)
Salinity (ppt)
Days Following Placement
0
100
200
300
400
0
10
20
30
40
50
0
5
10
15
20
25
30
35
Temp
Salinity

Figure 4

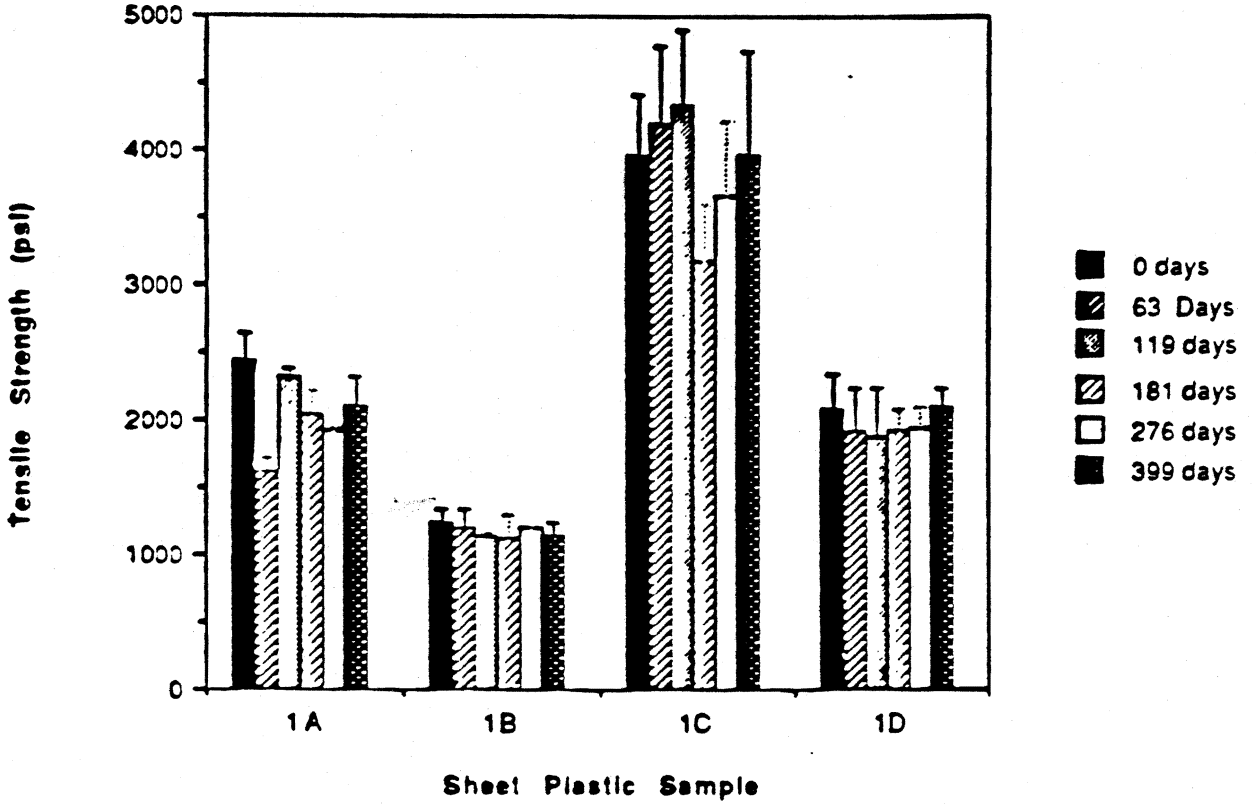

5000
4000
3000
2000
1000
0
Tensile Strength (psi)
1A
1B
1C
1D
Sheet Plastic Sample
0 days
63 Days
119 days
181 days
276 days
399 days

Figure 5

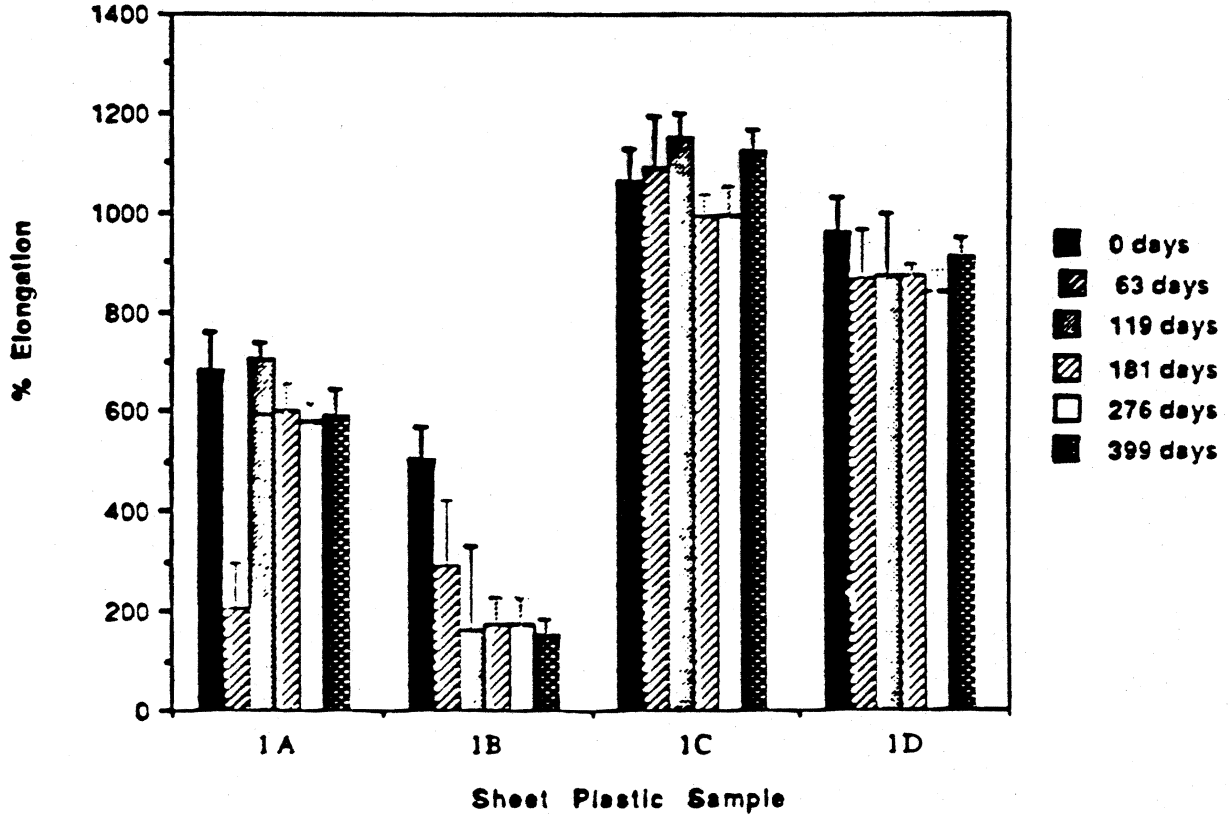

1400
1200
1000
800
600
400
200
0
% Elongation
1A
1B
1C
1D
Sheet Plastic Sample
0 days
63 days
119 days
181 days
276 days
399 days

Figure 6

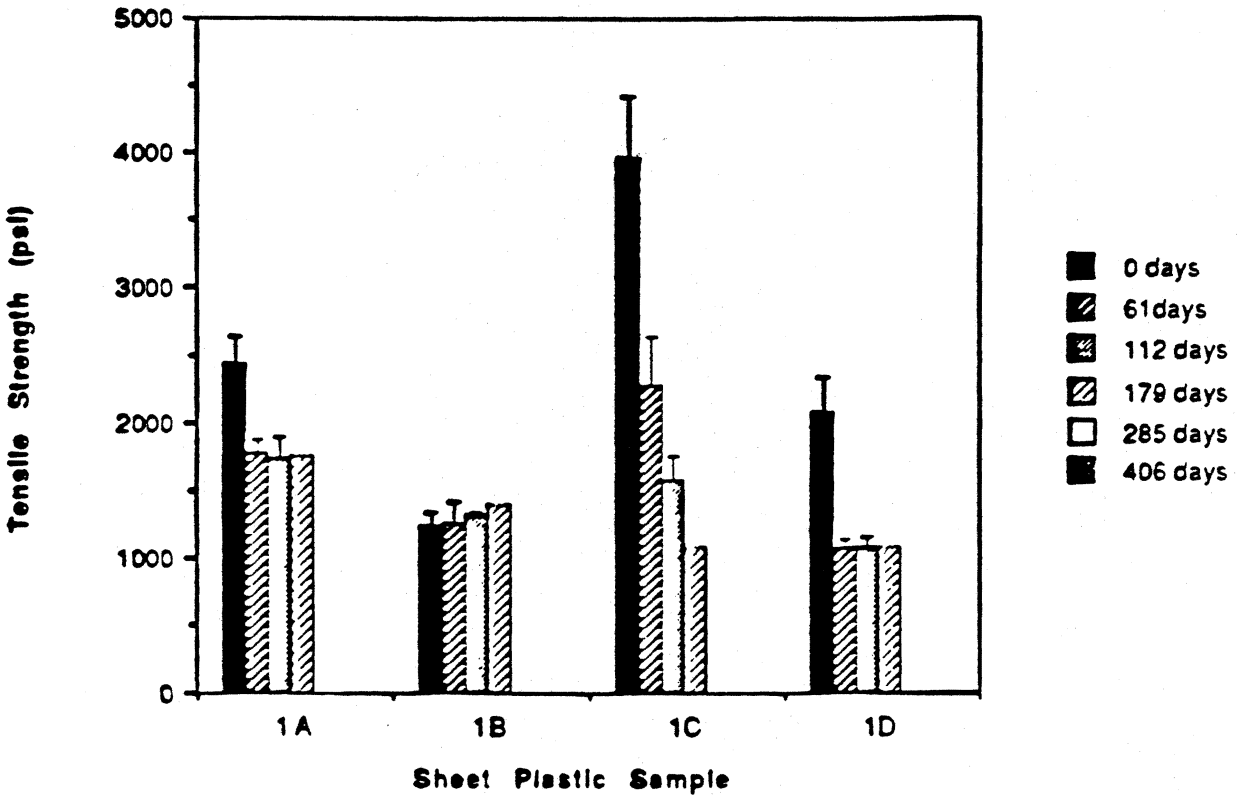

5000
4000
3000
2000
1000
0
Tensile Strength (psi)
1A
1B
1C
1D
Sheet Plastic Sample
0 days
61days
112 days
179 days
285 days
406 days

Figure 7

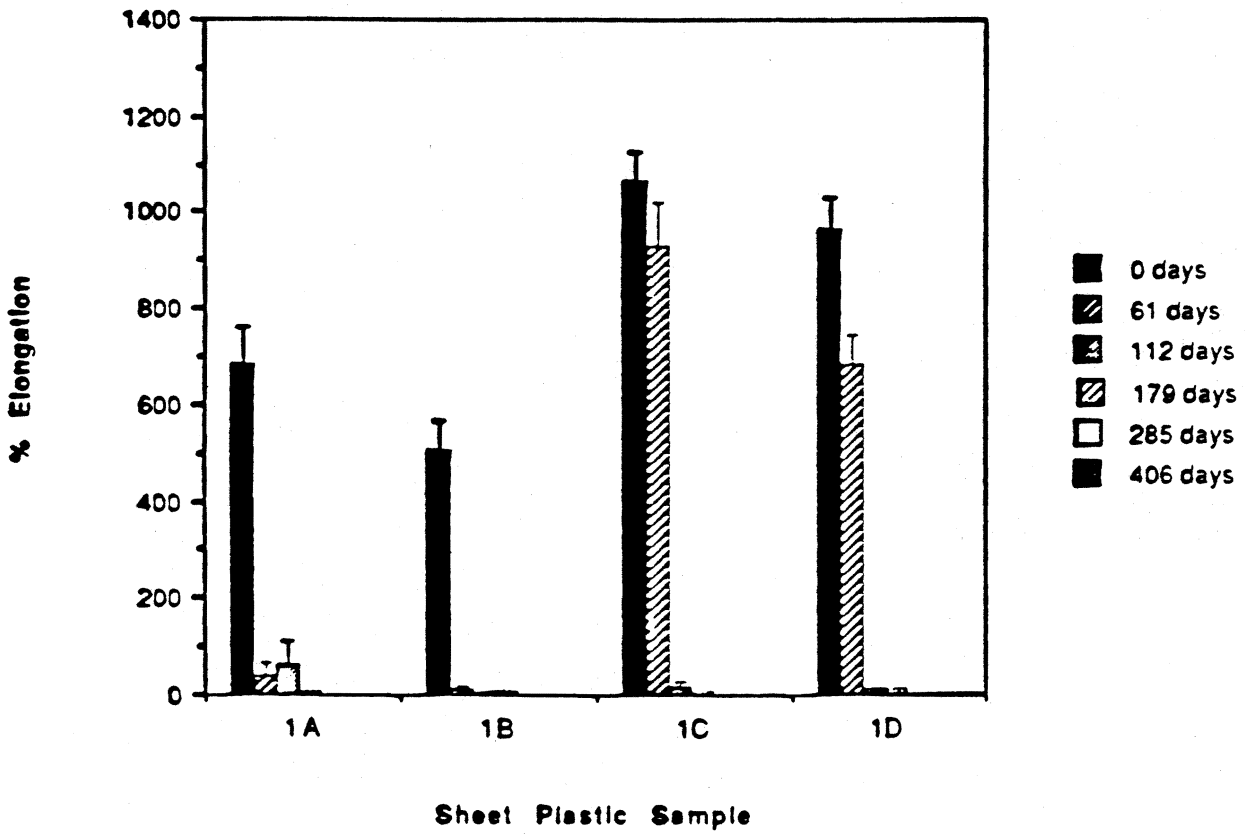

1400
1200
1000
800
600
400
200
0
% Elongation
1A
1B
1C
1D
Sheet Plastic Sample
0 days
61 days
112 days
179 days
285 days
406 days

Figure 8

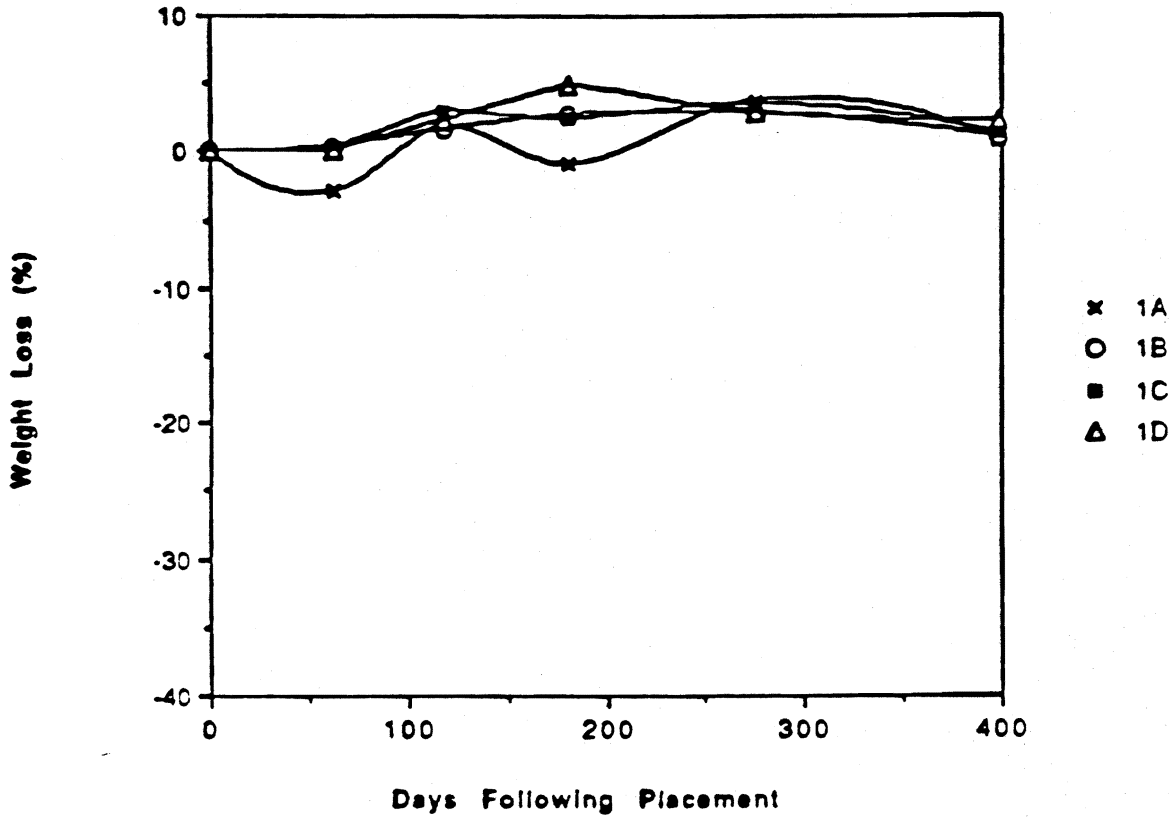

10
0
-10
-20
-30
-40
0
100
200
300
400
Weight Loss (%)
Days Following Placement
1A
1B
1C
1D

Figure 9

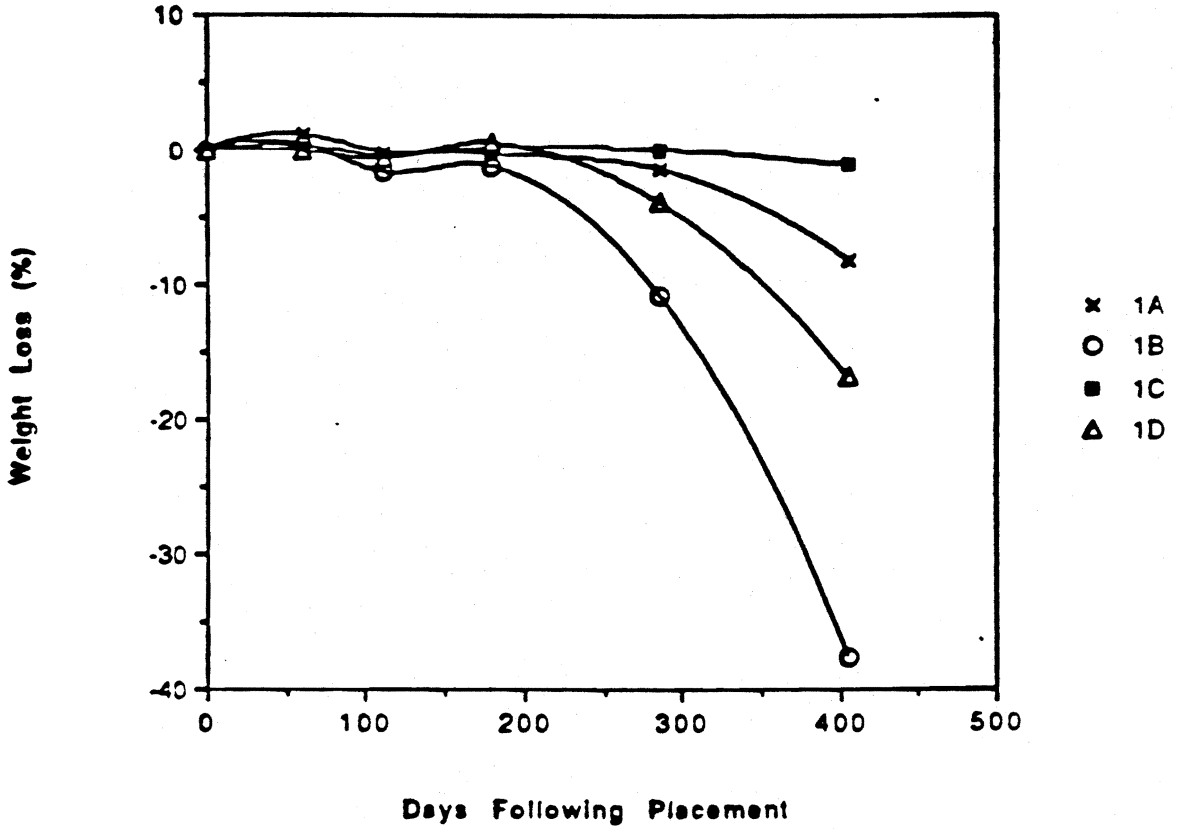
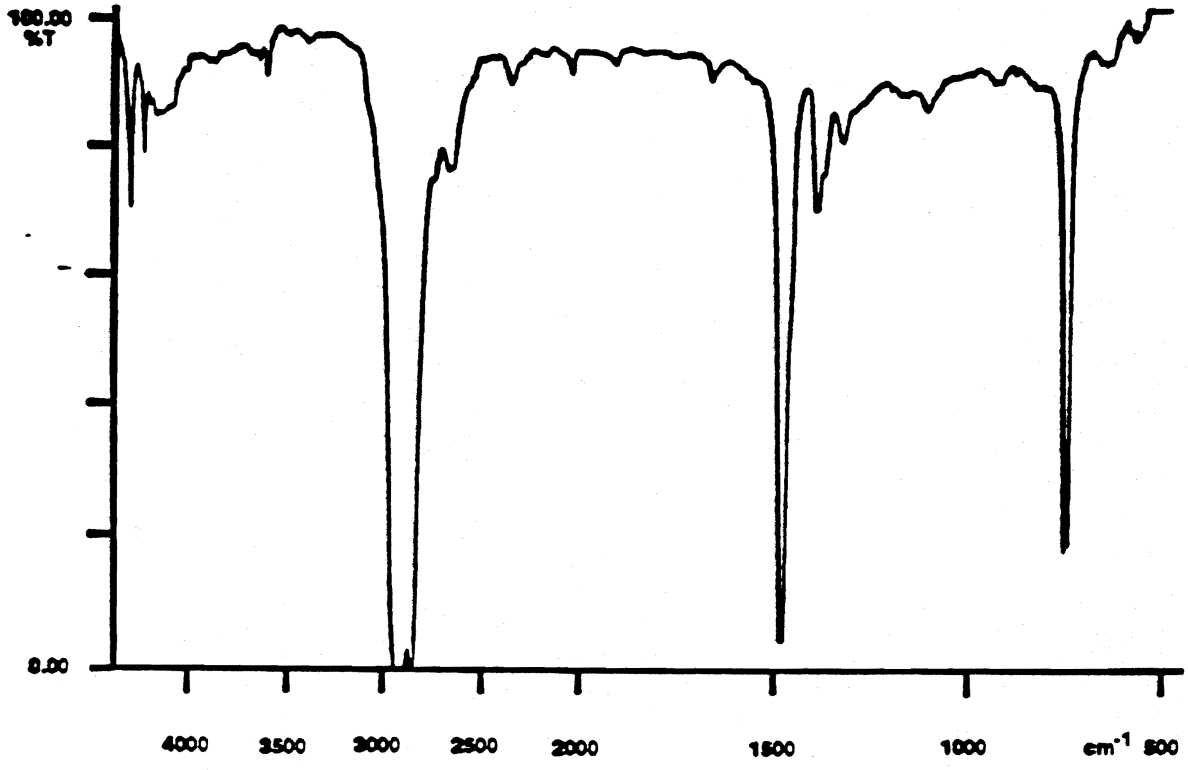
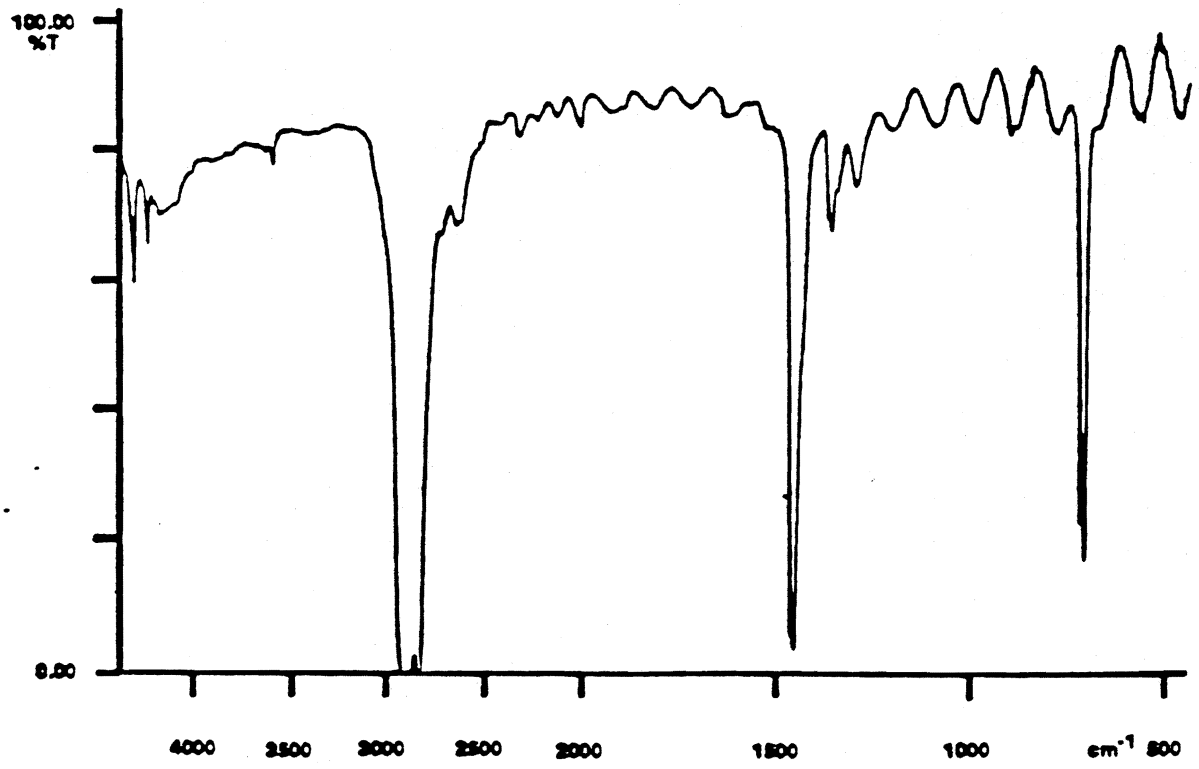

10
0
-10
-20
-30
-40
0
100
200
300
400
500
Weight Loss (%)
Days Following Placement
1A
1B
1C
1D

Figure 10

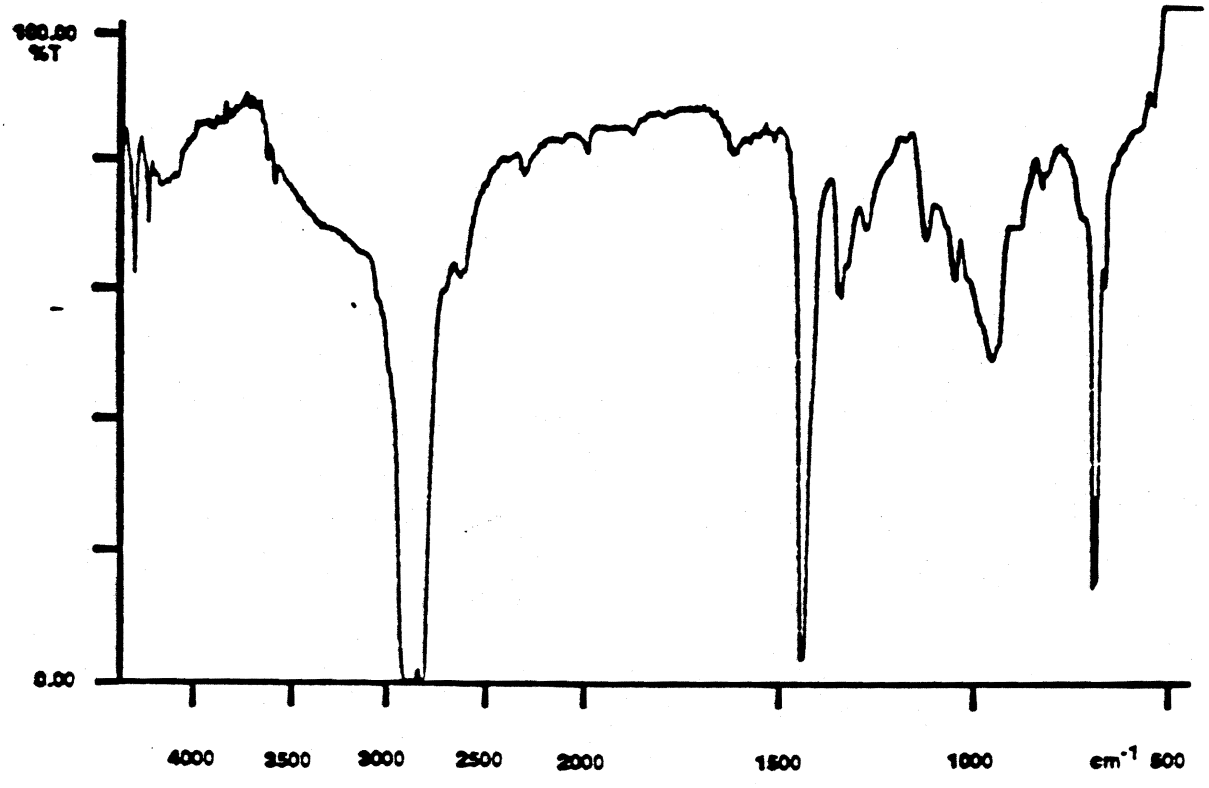

100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(a)


100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(b)

Figure 11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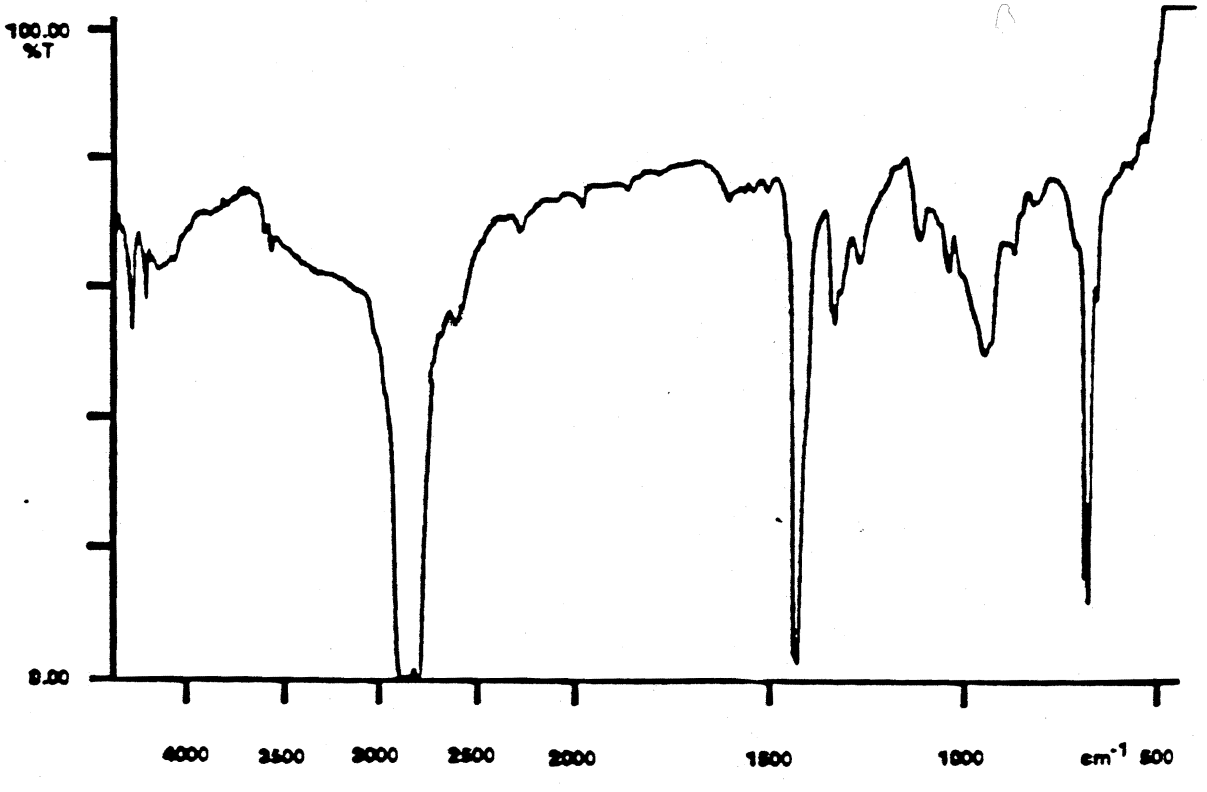
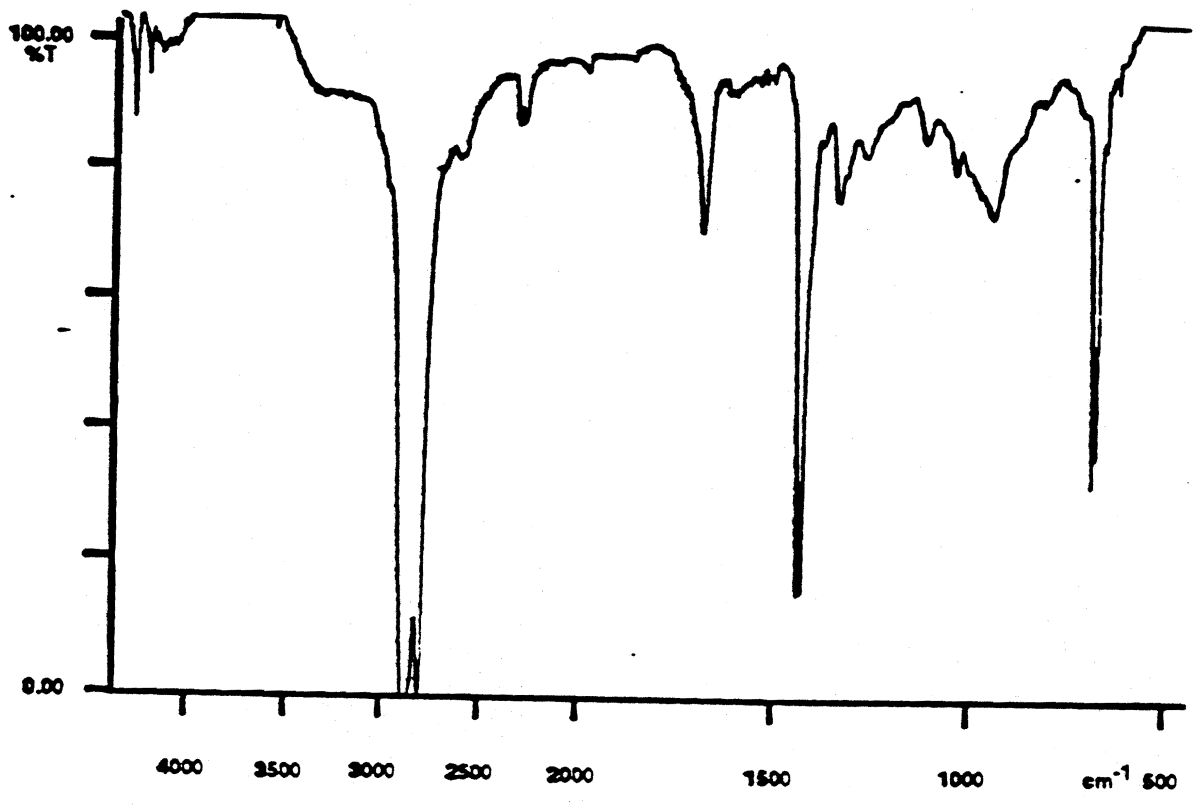
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(a)

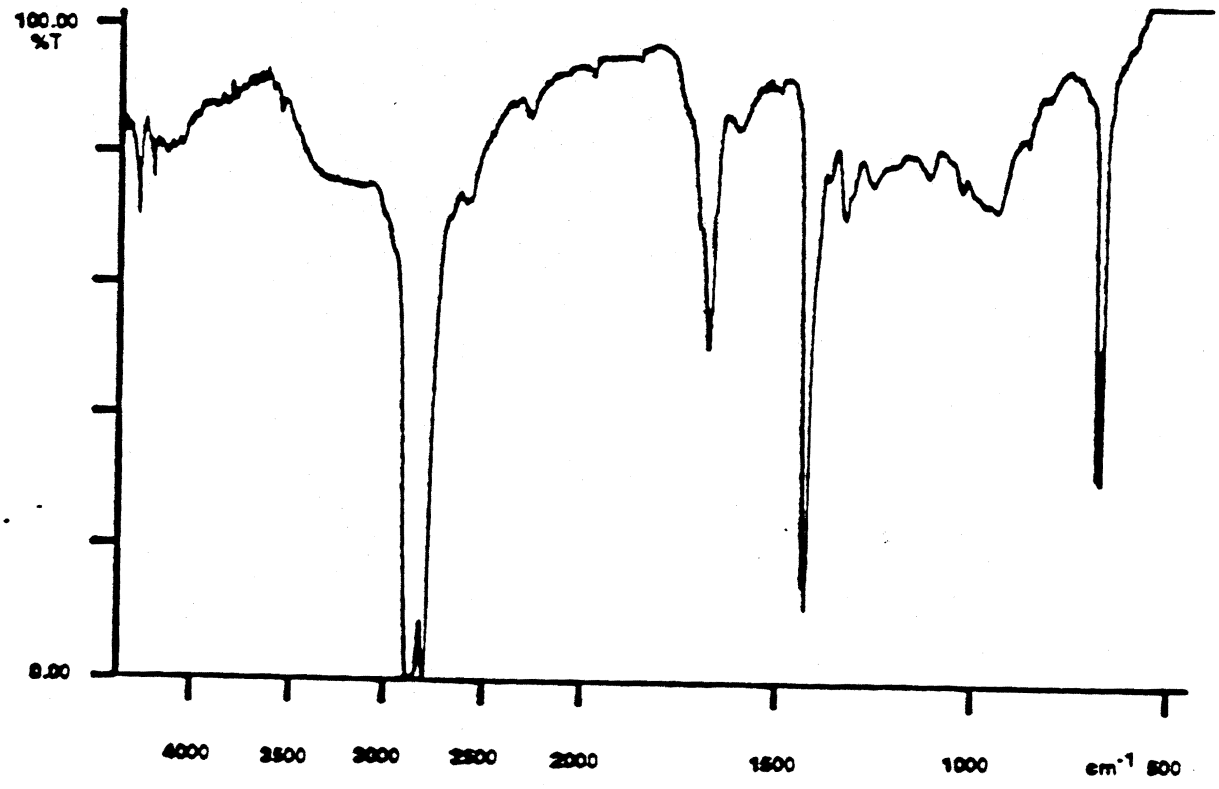

100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(b)

Figure 12


100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(a)


100.00
%T
0.00
4000
3500
3000
2500
2000
1500
1000
cm-1
500

(b)

Figure 13

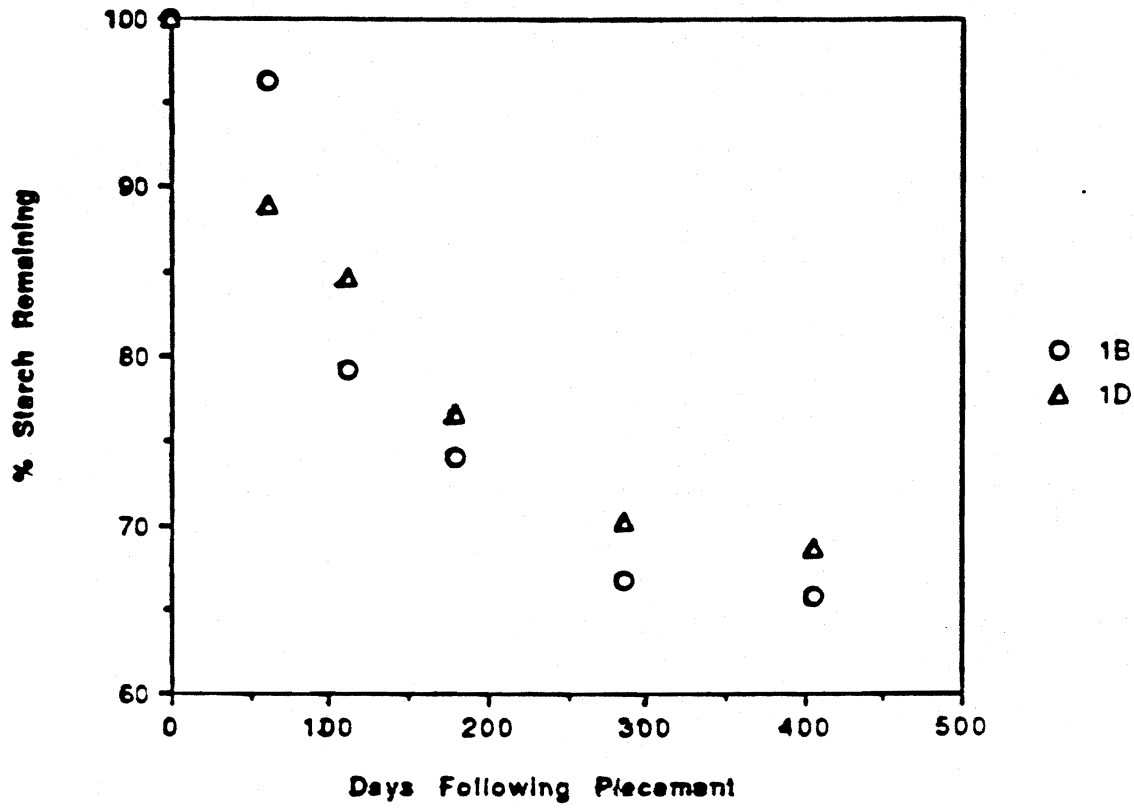
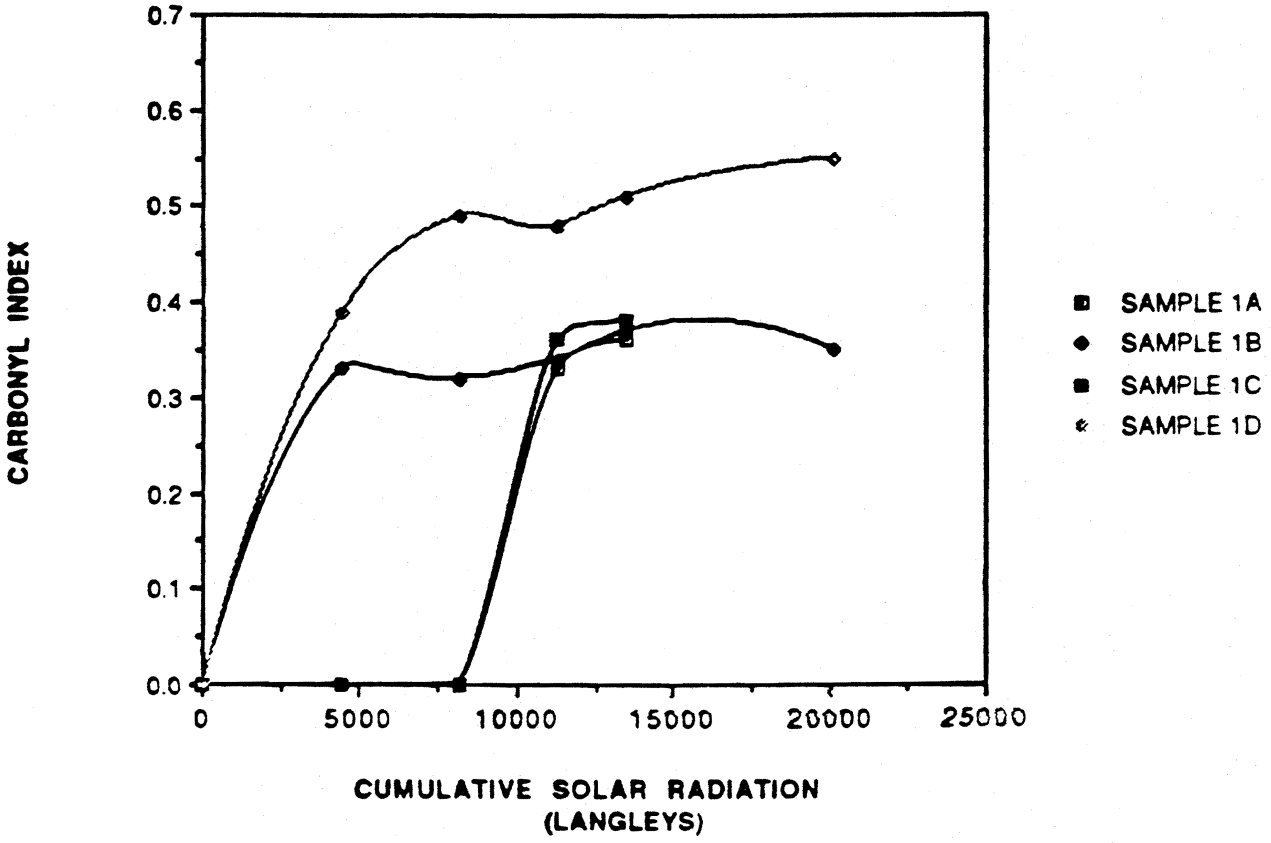

100
90
80
70
60
0
100
200
300
400
500
% Starch Remaining
Days Following Placement
1B
1D

Figure 14


CARBONYL INDEX
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5000
10000
15000
20000
25000
CUMULATIVE SOLAR RADIATION
(LANGLEYS)
SAMPLE 1A
SAMPLE 1B
SAMPLE 1C
SAMPLE 1D

3 1794 02299143 5