Testing Protocols for Oxidation and Hydrolysis of Geosynthetics

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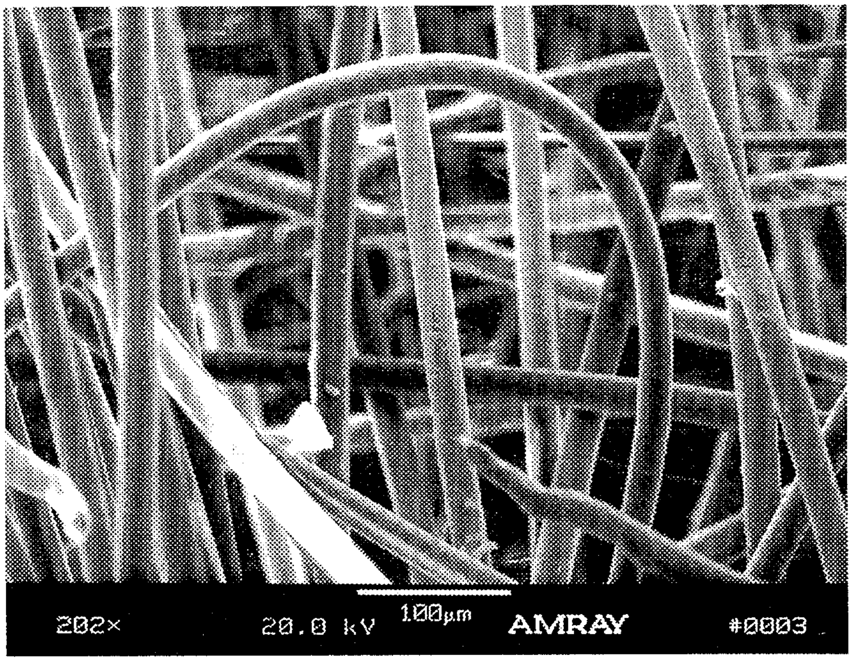

U.S. Department of Transportation
Federal Highway Administration

Research, Development, and Technology
Turner-Fairbank Highway Research Center
6300 Georgetown Pike
McLean, VA 22101-2296

FOREWORD

Geosynthetics as a soil reinforcement material have been used in retaining wall applications since the early 1970's, and more recently in reinforced slope and embankment applications. Because of the cost effectiveness, there is a strong desire to increase the use of geosynthetics in these applications because of the lack of information and defined test protocols regarding their long-term durability. In 1991, a pooled fund study was initiated through the FHWA to study geosynthetic durability and to develop test protocols to address the long-term durability issue. This report presents the development and verification of testing protocols and interpretations necessary to determine the oxidative durability of polyolefin geosynthetics and hydrolysis durability of polyester geosynthetic products. This report should be of interest to geotechnical and bridge engineers who are concerned with the durability of geosynthetic reinforced soil structures.

T. Paul Teng, P.E.
Director, Office of Infrastructure
Research and Development

NOTICE

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Author(s)
V. Elias, A. Salman, I. Juran, E. Pearce, S. Lu

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Earth Engineering and Sciences, Inc.
3401 Carlins Park Drive
Baltimore, MD 21215

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16. Abstract

This report presents the development and verification of testing protocols and interpretations necessary to determine the oxidative durability of polyolefm geosynthetics and hydrolysis durability of polyester geosynthetic products.

For polyolefm geosynthetics, the research findings indicate that the amount and type of antioxidant added determines the useful life’ in civil works. Oxidative degradation is further dependent on type of fiber, manufacturing process, and oxygen concentration of the in-use environment.

For polyester geosynthetics, the hydrolytic degradation rate is a function of the molecular weight of the polymer and the pH of the m-use environment.

This report is part of a comprehensive study on the “Durability of Geosynthetic Materials for Highway Applications.”

COVER PHOTO: Scanning electron micrograph of nonwoven polyester geosynthetic.

17. Key Words

Geosynthetics, Durability, Oxidation, Hydrolysis Testing Protocols for Durability., Durability Predictions

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.81	kilometers	km
		AREA		
in^2	square inches	845.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.838	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.785	cubic meters	m^3

NOTE: Volumes greater than 1000 l shall be shown in m^3.

Symbol	When You Know	Multiply By	To Find	Symbol
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or 'metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.78	lux	lx
fl	foot-Lamberts	3.428	candela/m*	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	8.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.821	miles	mi
		AREA		
mm^2	square millimeters	0.0018	square inches	in^2
m^2	square meters	10.784	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.388	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.284	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or 'metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m*	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

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CHAPTER 1

INTRODUCTION

This report presents the development and verification of testing protocols and interpretative procedures to determine the oxidative and hydrolysis resistance of geosynthetic commercial products used in civil works for in-ground applications.

The report summarizes the results of research performed under Tasks D and E of the research program titled "*Durability of Geosynthetics for Highway Applications.*"

The research program was primarily conducted by Polytechnic University Department of Civil Engineering and the Polymer Research Institute at Polytechnic University.

1.1 RESEARCH OBJECTIVES

The use of geosynthetic products has been steadily increasing in construction of reinforced fills as retaining walls and steepened slopes and for landfills in containment of hazardous waste. Responding to this market demand, the geosynthetic industry has developed new and more sophisticated materials at an increasing rate. As a consequence, new compositions of geosynthetics with specific additives are being introduced in the market. However, even small changes in composition can lead to considerable changes in the aging behavior of the materials. Therefore, to assess the durability of existing and improved geosynthetics, it becomes mandatory to assess their durability within a very short time with respect to environmental parameters to which they will likely be subjected. This requires the development of accelerated tests permitting prediction of the behavior of the geosynthetics in actual use.

The scope of the research developed is limited to the laboratory investigation of thermo-oxidative and hydrolytic degradation in a few typical commercial product samples selected to represent geosynthetic materials of importance as reinforcements in highway applications. The experimental program is intended as an empirical investigation of effects of specific variables of material composition and of environment on the degradation of geosynthetics representing classes of polymeric materials currently in use. The reliability of some widely used accelerated test methods is examined with respect to their correlation with test methods more closely reflecting in-service conditions.

The overall objectives of this study are:

- to assess the rate of chemical and mechanical degradation of selected commercial geosynthetic products with potential estimate of their service life, defined primarily as time to 50-percent strength loss;
- to investigate effects of specific variables of material composition and environment on the degradation behavior of selected commercial geosynthetics;
- to develop testing protocols for accelerated degradation for polyolefin and polyester commercial geosynthetic products as well as techniques to monitor chemical changes due to degradation; and

- to evaluate the reliability of some widely used test methods with respect to predictions of in-service conditions.

The scope of this study is, by necessity, limited in that:

- a relatively small number of commercial geosynthetic products (and polymers) are considered;
- commercial geosynthetic products are not well characterized or "pure" chemical species, and generally include residues, additives, etc. that can react and/or affect the chemical degradation of a polymer, adding to the complexity of the process by causing secondary reactions to occur; and
- only "severe" conditions of treatment, as compared to the in-service conditions, are used to accelerate degradation to achieve measurable chemical and mechanical changes during the 2 to 3 years available laboratory time.

Because of the limitations outlined above, the work was carried out in phases with the initial phases (Phases 1 and 2) intended to provide baseline chemical and physical characteristics for commercial geosynthetic products as well as to scope an experimental plan for the long-term degradation study of selected materials.

The preliminary phase of work (Phase 1) included analytical studies on polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET) base polymers used in commercial geosynthetic products as well as typical commercial products. The studies included:

- thermoanalytical studies of the base polymers and commercial polyolefins by Thermal Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC);
- assessment of antioxidant identification and antioxidant depletion by Oxygen Induction Time (OIT) measurements carried out by the DSC as well as by High-Performance Liquid Chromatography (HPLC);
- molecular weight determination by viscosity measurements and Carboxyl End Group (CEG) Analysis for PET commercial polymers; and
- adjustment and modification of the above methods to the particular properties of selected commercial geosynthetic products.

The second phase of work (Phase 2) included:

- physical and chemical characterization of commercial geosynthetic materials "as received" to develop a reference of their basic properties to be monitored during the degradation;
- development and modification of existing procedures, protocols, and techniques for thermo-oxidation (PP and PE) and hydrolytic (PET) degradation of commercial geosynthetics;
- limited preliminary experiments on accelerated degradation of selected commercial products at severe exposure conditions to assess the potential degradation rate of

those materials at the moderate conditions of exposure to be used in long-term experiments for Phase 3; and

- definition of the testing conditions and testing methods to be implemented for long-term degradation study of selected commercial geosynthetic products.

The initial work (Phases 1 and 2) resulted in the modification and development of testing methods to monitor chemical changes due to the thermo-oxidative and/or hydrolytic degradation. These methods were used with the standard mechanical tests to form a data base on certain key chemical and mechanical properties for the selected commercial products.

These initial assessments of degradation rates under severe exposure conditions provided the necessary data to refine the scope of work and exposure conditions.

The third phase (Phase 3) consisted of implementing a long-term systematic experimental program with sufficient exposure variables to permit lifetime estimates in conditions consistent with the end-use environments.

All studies were subdivided into two tasks, based on the type of base polymer in the commercial geosynthetic product. Task D is focused on the polyolefin-based commercial products, and Task E is focused on the polyester-based geosynthetics.

1.2 ORGANIZATION OF REPORT

This report summarizes data on chemical and mechanical degradation for selected commercial geosynthetic materials treated under different environmental conditions. The analysis of experimental data is presented with life estimates for geosynthetics in potential end-use environments.

The report contains:

1. Results of chemical and mechanical characterization for selected commercial geosynthetic materials;
2. A summary description of testing procedures and environmental conditions for oven aging and hydrolysis;
3. Summary of experimental data for all aging conditions;
4. Analysis of the experimental data on thermo-oxidative and hydrolytic degradation of selected geosynthetic products; and
5. Conclusions and recommendations.

1.3 REVIEWS

The research tasks reported have been initially developed by a project Interdisciplinary Advisor Team and formalized in a Task A Final Report that formed the basis of the research program.

The Task A Final Report was then reviewed by a project Peer Advisory Group whose valuable suggestions have been incorporated whenever possible prior to the commencement of the research. The Peer Advisory Group consisted of:

1. Dr. Robert Koerner - Geosynthetic Research Institute
2. Dr. Robert Holtz - University of Washington
3. Dr. Robert Duvall - Engineering Systems Inc.

During the course of the research, progress reviews were held with FHWA personnel and Mr. Tony Allen, Washington DOT, to monitor progress, review interim draft reports, and suggest modifications to the research.

Prior to finalizing the results of the research, a draft report was further reviewed by Dr. Koerner who made a number of suggestions to clarify some issues and improve the final product. These suggestions have been incorporated whenever possible in this final report.

CHAPTER 2

CHARACTERIZATION OF GEOSYNTHETIC MATERIALS "AS RECEIVED"

2.1 GEOSYNTHETIC MATERIALS TESTED

Polymers and commercial geosynthetic products used in the experimental program are listed in table 2.1 and table 2.2, with source information details (as available), and with the code designations used throughout this report. The selection of these materials as representative products available in the market was developed in the Task A Final Report dated November 1992.

Table 2.1. Polyolefin-based selected products.

Product	Type	Unit weight (oz/yd^2)	Tensile strength (lb/in)	Antioxidants
P-1	HDPE Uniaxially drawn geogrid	13	339	Carbon black, Hindered Phenol (Irganox 1010)
P-2	PP woven Fibrilated yarn	14	482	Unknown
P-3	PP nonwoven Needlepunched-continuous filament	8	83	Hindered Amine (HALS), trace carbon black additive
P-3a	PP nonwoven textile Needlepunched-continuous filament	6	24	Specially manufactured with minimum amount of additives
P-4	PP nonwoven textile Needlepunched staple	8	99	Unknown
P-4a	PP nonwoven textile Needlepunched staple	8	67	Specially manufactured with minimum amount of additives
P-9	PP woven Slit film	6	232	Unknown
S-1	HDPE Powder Reference material *Polymer products*	N/A	N/A	Unknown
S-2	PP Powder Reference material *Polymer products*	N/A	N/A	Unknown

N/A – not applicable

$1\ oz/yd^2 = 33.9\ g/m^2$, 1 lb/in = 0.018 kg/mm

Table 2.2. Polyester-based selected products.

Material	Type	Tenacity	Unit weight (oz/yd^2)	Tensile strength (lb/in)
P-5	Nonwoven, continuous filament spunbonded needlepunched	Low	16	205
P-6	Grid, PVC dipped - PET filament	High	11	1040
P-7	Woven	High	11	500
P-10	PET filament corresponding to P-6	High	N/A	N/A
S-3	PET powder, reference material	N/A	N/A	N/A

N/A - not applicable $1\ oz/yd^2 = 33.9\ g/m^2$, 1 lb/in = 0.018 kg/mm

Complex antioxidant mixtures are commonly used to reduce the rate of oxidation for commercial polyolefin products during processing and in end-use. Therefore, the amount and composition of additives are important factors which affect the degradation performance of commercial products; however, the type and amounts are often considered proprietary.

Common antioxidants used in geosynthetic applications are shown in table 2.3. Their molecular structure and typical use are available from the manufacturer's technical literature.

Table 2.3. Stabilizers and antioxidants.

Stabilizer	Type
Irganox 1010	Phenolic stabilizer
Irganox 1076	Phenolic stabilizer
Irgafos 168	Phosphate processing stabilizer
Tinuvin 622LD	Hindered amine (HALS)
Chimassorb 944FL	Hindered amine (HALS)
Ultranox 626	Phosphate

2.2 CHEMICAL CHARACTERIZATION OF POLYOLEFIN-BASED GEOSYNTHETICS "AS RECEIVED"

Methods of chemical characterization for polyolefin geosynthetics have been generally summarized by Cassidy et al. (1990) and Koerner et al. (1992). It has been suggested in the literature that chemical aspects of thermo-oxidation of polyolefins could be studied by thermoanalytical techniques such as TGA, DSC, and OIT and/or by chromatography. However, each of the suggested analytical techniques requires an adjustment to the particular commercial polymeric product tested. It appears that some of the potentially useful techniques for chemical monitoring of model (laboratory grade) polymers in degradation studies have significant limitations when applied to commercial products.

2.2.1 Thermal response.

An initial scan of thermal response for the materials received was carried out by TGA and DSC to provide a basis for the future study of thermoanalytical techniques as potential indicators of chemical change and degradation. Results are shown in table 2.4.

Table 2.4. Thermoanalysis by TGA and DSC.

Material	T_d^*, °C (TGA, 20°C/min)		T_m^{**}, °C (DSC, 20°C/min)
	Nitrogen	Air	Nitrogen
S-1, reference HDPE	465	406	129.6
S-2, reference PP	426	315	160.7
S-3, reference PET	433	431	251.4
P-1, HDPE grid	461	416	134.2
P-2, fibrilated PP	458	345	159.9
P-3, nonwoven PP	443	305	161.4
P-4, nonwoven PP	443	316	158.2
P-5, nonwoven PET	442	327	257.0 (T_g=80.8)***
P-6, PVC coating for PET grid	280 (PVC) 422	276 (PVC) 420	245.9

* T_d - Decomposition temperature

** T_m - Melting peak temperature

***T_g - Glass transition temperature

Only minor differences were noted in the onset of decomposition temperatures in nitrogen for all polyolefin samples. In air, decomposition temperatures were generally lower for PP than for HDPE samples. The thermal response (TGA) of the geosynthetic was similar to that of the reference polymers in all instances. Even in air, there was no significant weight loss up to temperatures of about 250°C.

The thermal response of the materials was also initially evaluated by oxygen induction time (OIT) tests at 200°C according to the procedure documented in the literature (ASTM D-3895; Gray, 1990). Results indicated only minor differences between materials. Reference polymers reported to be free of antioxidant additives actually contained antioxidants and, therefore, may be considered as additional types of polyolefin products. Studies of antioxidants' depletion as a function of a degradation of polyolefins at elevated temperatures are an important element of the proposed research, and OIT was reported to be the preferred method for evaluation of antioxidant concentration and effectiveness (Howard and Gilroy, 1975; Wisse, 1982; 1988; 1990; Kramer and Koppelmann, 1986; 1987; Wyzgoski, 1981). For these reasons, the optimum conditions for OIT measurements, and various aspects of antioxidant effects in polyolefins were investigated in depth, with results discussed in some detail.

2.2.2 Oxidation Induction Time (OIT).

Thermal and photo-oxidative degradation of polyolefins are the primary source causes of discoloration, crack formation, brittleness, and ultimately tensile failure. Chemical additives, such as antioxidants and/or light stabilizers are used in commercial polyolefins to protect against thermal and photo-oxidation during processing as well as during service life. Therefore, quantification of antioxidants and light stabilizers present in the polymeric system is of a prime importance when long-term stability of commercial products is considered.

The antioxidant and light stabilizer additives are usually incorporated in the polymer matrix at a very low level, typically less than 0.5 percent for geotextiles and geogrids. The type and amount of antioxidants and their combination in the polymeric system, determine retention of mechanical properties over the service life of a commercial polymeric product.

Oxidation induction time at 200°C by Differential Scanning Calorimetry (DSC) was reported to be a method for monitoring degradation in oven-aged polyolefins (ASTM D-3895; Gray, 1990). The method is widely cited, and correlations are frequently attempted or presented between "OIT time" and "strength loss," or other mechanical parameter changes. In fact, OIT is seemingly employed as the first criterion of degradation in most investigations of geosynthetic aging. Therefore, a widely recommended procedure for OIT measurement (1993-1994), ASTM D-3895, was used on commercial products and reference polymers that contained unknown antioxidants. The results of OIT measurements in accordance with this procedure are presented in table 2.5.

Table 2.5. OIT values measured for polyolefin products in accordance with ASTM D-3895.

Product	S-1	S-2	P-1	P-2	P-3	P-4
OIT, min	5.26	6.46	5.12	9.75	6.11	5.82

The results indicated that there are only minor differences between products, including the reference polymers apparently containing antioxidants. For this reason, OIT measurements were studied by scanning the effect of selected variables in the test method. Initially the influence of heating and oxygen flow as variables in OIT was studied for the HDPE commercial sample P-1 and reference commercial polymer S-1 and results are summarized in table 2.6.

Table 2.6. OIT values measured under different test conditions.

Test conditions	OIT, min	
	S-1	P-1
Isothermal 200°C, Oxygen 100 cc/min (Gray, 1990)	5.26	5.12
Isothermal 180°C, Oxygen 150 cc/min	3.13	3.13
Isothermal 180°C, Oxygen 100 cc/min	5.43	5.56
Heating rate 10°C/min. Oxygen 100 cc/min	Exotherm start 248°C	Exotherm start 244°C

These results indicated that there is no differences in OIT for the compared materials, and the variables evaluated are not the cause of the apparent lack of differentiation by OIT for the materials tested.

Based on these initial studies, an improved OIT testing procedure was developed as Method "A". The developed procedure for OIT differs from the standard ASTM method as follows:

- Use a two-step heating program and variable heating rate to avoid overheating during the test.
- Lower nitrogen and oxygen flow rates to increase time required for oxidation and, therefore, obtain better differentiation of OIT between materials.
- Decrease time to shift from nitrogen to oxygen to increase accuracy of OIT measurements.
- Use aluminum (instead of copper) material for the sample pan to avoid induced oxidation caused by copper.

OIT results on commercial products using procedure "A" are shown in table 2.7.

Table 2.7. OIT values at 200°C measured with testing Method "A".

Material →	S-1	S-2	S-2*	P-1	P-2	P-3
OIT (min)	68.4	2.5	4.1	48.6	3.1	2.5

* - 0.1% Irganox 1010 and 0.1% Irgafos 168

These results for the products or polymers are significantly different from those obtained by the earlier ASTM procedure and are more consistent with current ASTM (D-3895-95) procedures and provide a better differentiation. Therefore, it has been used for further evaluation of other testing variables, primarily temperature.

Temperatures lower than 200°C have been used for the determination of OIT in the literature. For example, Wisse (1990) reported OIT values at 150°C requiring 2 to 8 hours for each measurement. Considering the time requirements at the lower temperatures, as well as the small differences noted in the OIT times of all materials measured at 200°C, a preliminary study of OIT (by DSC) versus temperature was carried out for polypropylenes. Typical results are shown in table 2.8.

Note that the OIT value for the commercial reference polymer S-1 is greater than the OIT value for the P-1 material containing antioxidants. Therefore, it is suspected that reference polymer S-1 contains unknown stabilizers.

Table 2.8. OIT measured at various temperatures, Method "A".

Material	OIT (min)			
Temp. °C →	200	180	170	160
S – 1	68.4			
S – 2	2.5	3.5	5.6	6.0
S - 2/0.1% Irganox 1010	4.9	8.8	25	50
P – 1	48.6			
P – 2	3.1	8.9	17	49
P – 3	2.5	6.4	16	22
P – 4	3.3	9.5	17	173
P – 9	5.5	15	45	369

It should be noted that a High-Pressure OIT (HP-OIT) method has been recently developed and adopted as ASTM D-5885-95. It uses high pressure and a temperature of 150°C for HDPE and 170°C for PP materials and is reported to provide better differentiation of OIT times for HDPE geomembranes (Hsuan, Guam, 1997). Similar studies on PP geotextile products have not been published to date.

The complexity of additive formulations (including carbon black) in the commercial products is such that quantitative correlation of OIT values with temperature measurements is not possible. However, the above data suggests that for polypropylene, the optimum temperature for OIT determination is 175°C, yielding reasonable differences between materials. Additionally, 175°C is above the melt temperature for polypropylene and, therefore, full diffusion of oxygen in the sample should occur and provide identical conditions of OIT measurements for both PP and HDPE materials. Below the melt temperature, the diffusion process is different because the polymer is in a solid phase. Therefore, 175°C is the lowest temperature yielding some differentiation of OIT values for products tested just above the melting point. For polyethylene, OIT's are much longer and a temperature of 200°C can conveniently be used.

The developed method of OIT measurements at temperatures lower than 200°C and designated as "Method A" appeared to provide a reasonable difference between the commercial reference polymer S-1 and the commercial product P-1 reported to contain an antioxidant. However, the only minor difference between OIT values was obtained for P-2, P-

3, and P-4 samples. Therefore, the next step in improving the OIT testing procedure has been undertaken with a focus on such variables as nitrogen and oxygen flow rates. Technical details of the procedure, designated as "Method B," are reported in Appendix A.

The results of OIT (at 200°C for HDPE and at 175°C for PP) measurements (table 2.9) using test "Method B" indicated a greater difference between OIT values for P-2, P-3, P-4, and P-9 samples, as compared to those obtained from "Method A." With respect to repeatability, the difference between two measured values of OIT for the HDPE P-1 sample appeared to be significantly less than the 5.9 minutes which is suggested by ASTM D-3895 as a critical difference between paired OIT values for polyethylene products. The OIT values for polypropylene products obtained at 175°C indicate that the difference in OIT values measured for P-2 and P-9 samples meets the accuracy suggested by ASTM D-3895 for polypropylene products.

The results from initial OIT measurements using "Method B" provided a notable difference in OIT values for polyethylene products as well as for polypropylene products. The deviation of experimental results (2 to 4 specimens tested) appeared to be within the range of allowable variation suggested by ASTM D-3895.

Table 2.9. OIT values at 175°C for PP and at 200°C for HDPE products, "Method B."

Material	OIT (min)		Number of samples	Range of OIT values (min)
Temperature, °C →	200	175		
P – 1	63		2	62.2 - 63.6
P – 2		22	4	20 - 25
P – 3		12		
P – 4		15		
P – 9		97	4	92 - 103

Based on the results of this study, the improved testing procedure ("Method B") for OIT measurements is presently recommended as a "standard" procedure when OIT values are used to characterize geosynthetic products and to index their antioxidant consumption rate.

These procedures were used on a model system to obtain calibration curves with respect to varying concentrations of antioxidants. The effect of antioxidants in DSC determinations of OIT is illustrated by the calibration curves obtained at 200°C and at 175°C for model systems consisting of polypropylene powder standard (S-2) containing varying concentrations of antioxidant Irganox 1010. These are shown in figures 2.1 (200°C) and 2.2 (175°C).

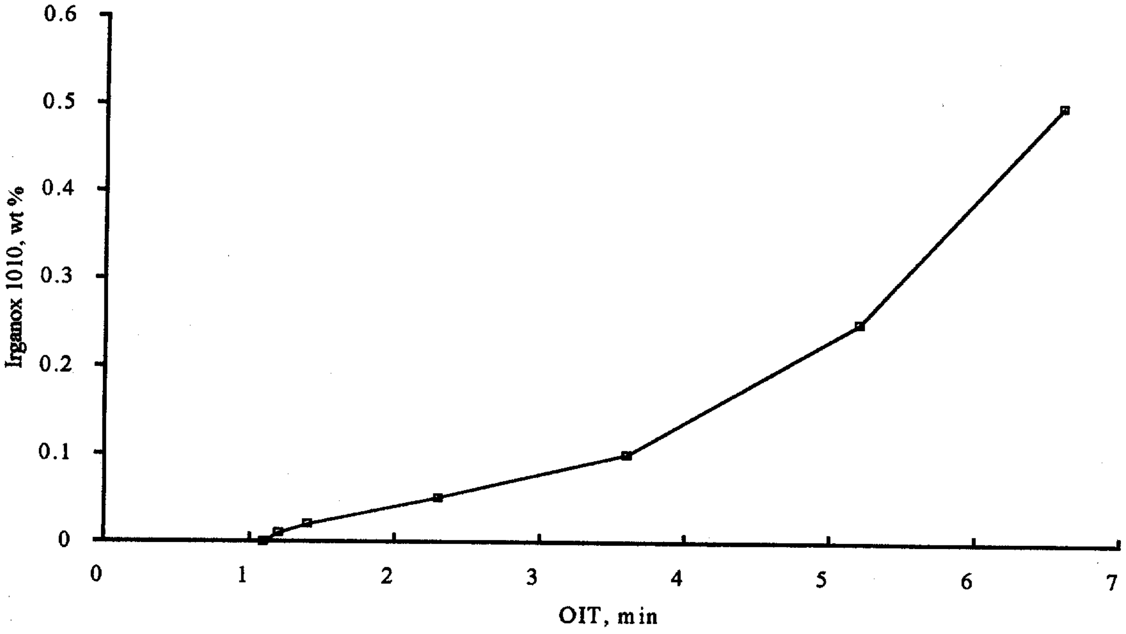


Figure 2.1. OIT calibration curve at 200°C for S-2/Irganox 1010 system.

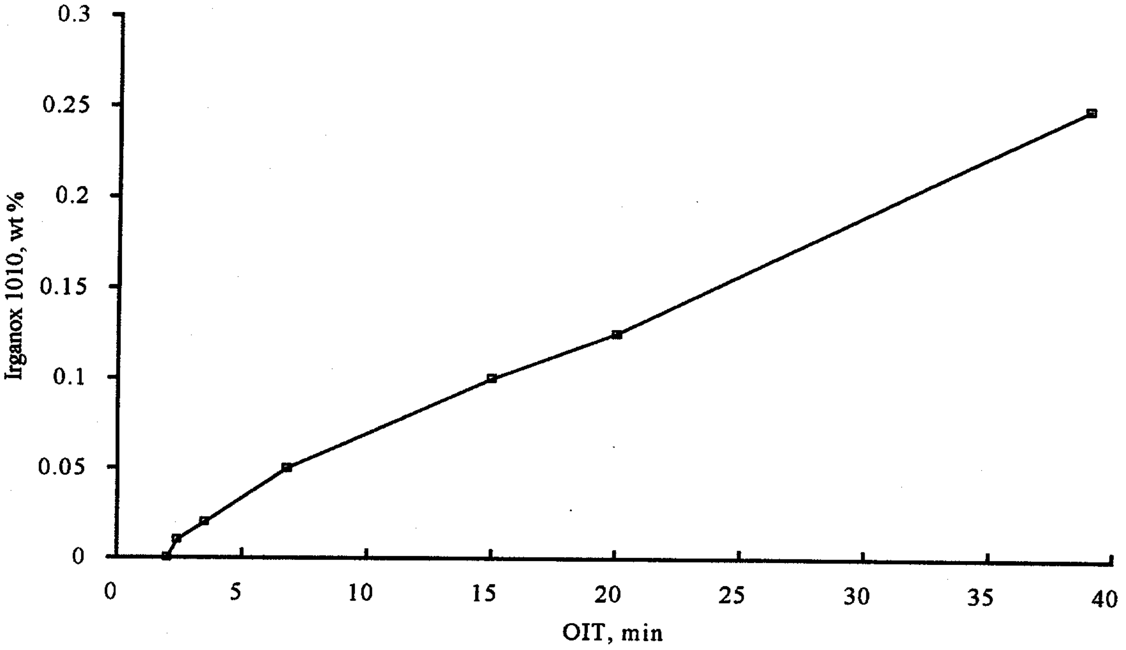


Figure 2.2. OIT calibration curve at 175°C for S-2/Irganox 1010 system.

The calibration curves indicate that OIT potentially could be a useful index for monitoring antioxidant content in a polymeric mixture. However, in commercial products, antioxidant formulations are seldom single components and vary greatly, and OIT thus cannot be the sole criterion by which degradation is evaluated.

It therefore appeared that OIT may serve only as a measure for oxidative stability (resistance to oxidation measured by the time required to full oxidation in a flow of oxygen at a given temperature) of polyolefins. The oxidative stability of polyolefins is controlled by the base polymer along with the antioxidant additives. Therefore, monitoring of antioxidant additive concentrations during degradation becomes of prime interest to characterize chemical degradation. However, the potential of using OIT measurements to monitor antioxidant concentration in a complex polymer system is limited generally by the following:

- Hindered amines type of antioxidants (HALS) are effective over temperature ranges below 135°C (Fay, King, 1994). However, all OIT measurements are conducted above the melting point of a polymer, which is for most commercially produced polyolefins well above 135°C. Therefore, OIT values obtained at temperatures above 135°C will not reflect the presence and effectiveness of HALS antioxidant additives in the polymer system.
- OIT is a measure of oxidative stability, but does not provide quantitative estimates of the concentration of multicomponent antioxidant additives.

Geotextile P-3 reportedly contains a HALS antioxidant package and, therefore, OIT measurements would be ineffective in monitoring antioxidant depletion during thermo-oxidative degradation. P-3a and P-4a are products that were specially manufactured with a minimum amount of antioxidant additives and, therefore, again would be ineffectively monitored using the OIT technique. Therefore, the prime focus of OIT measurements in monitoring antioxidant depletion during aging will be on commercial products P-1 (geogrid), P-4 (nonwoven polypropylene geotextile), and P-9 (woven polypropylene geotextile).

The first step in establishing reference values of OIT for these geosynthetics is to assess the repeatability of results obtained with the developed technique. Table 2.10 presents results of multiple OIT measurements on commercial products P-1, P-4, and P-9 made by a single operator using the same equipment. These values are used as baseline values for Phase 3 testing.

Table 2.10. OIT values at 175°C for PP and at 200°C for HDPE.

Material	OIT (min)		Number of samples	Range of values (min)	Coefficient of variation, %
Temperature, °C	200	175			
P – 1	61		17	37-78	15
P – 4		11	4	9-15	23
P – 9		77	16	32-113	32

The high variation of OIT values for the materials tested by a single operator suggests that there potentially is a problem with uniformity of antioxidant distribution in these commercial products. During the thermo-oxidative process, the antioxidant additives undergo significant physical and chemical transformations, adding to the complexity. It was therefore anticipated that OIT values measured on aged specimens would exhibit a higher or the same degree of variation and may not provide sufficient information to quantitatively trace antioxidant consumption.

These potential limitations to the use of OIT as a technique to identify and quantitatively monitor antioxidant depletion during thermo-oxidative degradation suggested that alternate techniques be examined. High-Performance Liquid Chromatography (HPLC) was selected and tested as an alternative method in an attempt to quantify antioxidant concentrations during the degradation period.

2.2.3 Conclusions, OIT measurements.

- Chemical degradation or antioxidant depletion of commercial geosynthetic products containing HALS-type antioxidant additives cannot be monitored by measuring standard OIT values.
- For polypropylenes, OIT measurements should be conducted at 175°C in accordance with Method B for best results. For high-density polyethelene, OIT measurements may be conducted at 200°C.

2.2.4 Antioxidants identification by HPLC.

The information source for the HPLC testing is analytical procedures suggested in "In Polymer Analysis Method/ADD-298," Ciba-Geigy Additives Division, and by Solvay Chemical Company. The details of equipment, sample preparation, and procedure are outlined in Procedures and Test Standards for Evaluating the Properties of Geosynthetics, developed in cooperation with Industrial Fabrics Association International (IFAI).

The method is essentially based upon chromatographic analysis. The additives are identified based upon retention time and are quantified by integrating the area of the additive peak and multiplying by a response factor derived from known standards. The concentration of the extract solution is used to calculate the quantity of additives in the polymer by assuming 100-percent extraction efficiency from the matrix.

The polymer extract taken from several specimens (representing retrieval in oven aging testing) is injected into a liquid chromatograph equipped with an ultraviolet detector and a chromatogram is obtained. The areas of individual peaks are integrated and the concentrations of the species of interest are determined using an external standard calculation based on predetermined response.

A limited experimental study of the HPLC performance has been conducted on a model mixtures of the reference commercial polymer S-1 with different antioxidants (Irganox 1010, Irganox 1076, Irgafos 168, Chimassorb 944) in order to determine sensitivity of the method to the presence of different antioxidants. Calibration curves for varying concentrations of additives have been established.

Examples of a typical chromatogram for analysis of Irganox 1010 and 1076, Irgafos 168, and Chimassorb 944 are shown in figure 2.3. The results indicated that antioxidants such as Irganox 1010 and 1076, Irgafos 168, and Chimassorb 944 can be identified in a simple mixture (reference commercial polymer + antioxidant) by retention time as follows:

Irganox 1010	2.17 min
Chimassorb 944	2.32 min
Irganox 1076	2.65 min
Irgafos 168	3.00 min

Results obtained on the selected column (C8, 10 μm irregular particle, Alltech Associates, Inc.) indicated lower sensitivity of analysis for Chimassorb 944 as compared to the sensitivity of Irganox 1010, Irganox 1076, and Irgafos 168. However, antioxidants such as Irganox 1010 and 1076, and Irgafos 168 can be separated and identified in the mixture by using the selected column, but Irganox 1010 may overlap with Chimassorb 944. Therefore, a combination of antioxidants, including Irganox 1010 and Chimassorb 944, may not be separated by employing this column. This can, of course, be true for other mixtures of antioxidants.

In order to measure the antioxidant content in the multicomponent mixture of several different additives within a polymer, the calibration curve for each of the antioxidants presented in the mixture has to be obtained. The model mixtures of solvent with different amounts of Irganox 1010 were used to obtain the calibration curve for Irganox 1010. The areas of spectral peaks were plotted versus weight content of Irganox 1010 in the model mixture. The results (figure 2.4) indicated linear dependency of the spectral peak area on the weight content of the Irganox 1010 in the model mixture.

Preliminary evaluation of the content of Irganox 1010 in the P-1 and S-1 samples are based on the calibration curve and chromatogram for P-1 and S-1 materials (figure 2.5). The content of Irganox 1010 in the samples tested is as follows:

P-1	0.26%
S-1	0.54%

It indicated that the Irganox 1010 content in the S-1 sample is much higher than in the P-1 sample. This may explain why the OIT value (at 200°C) for S-1 (68.4 min) using Method A was significantly higher than for P-1 (48.6 min). However, it should be noted that carbon black was present in P-1 and not in the S-1 sample, and without knowledge of the particular type and amount of carbon black used in the P-1 sample, the role of this factor cannot be defined in OIT results.

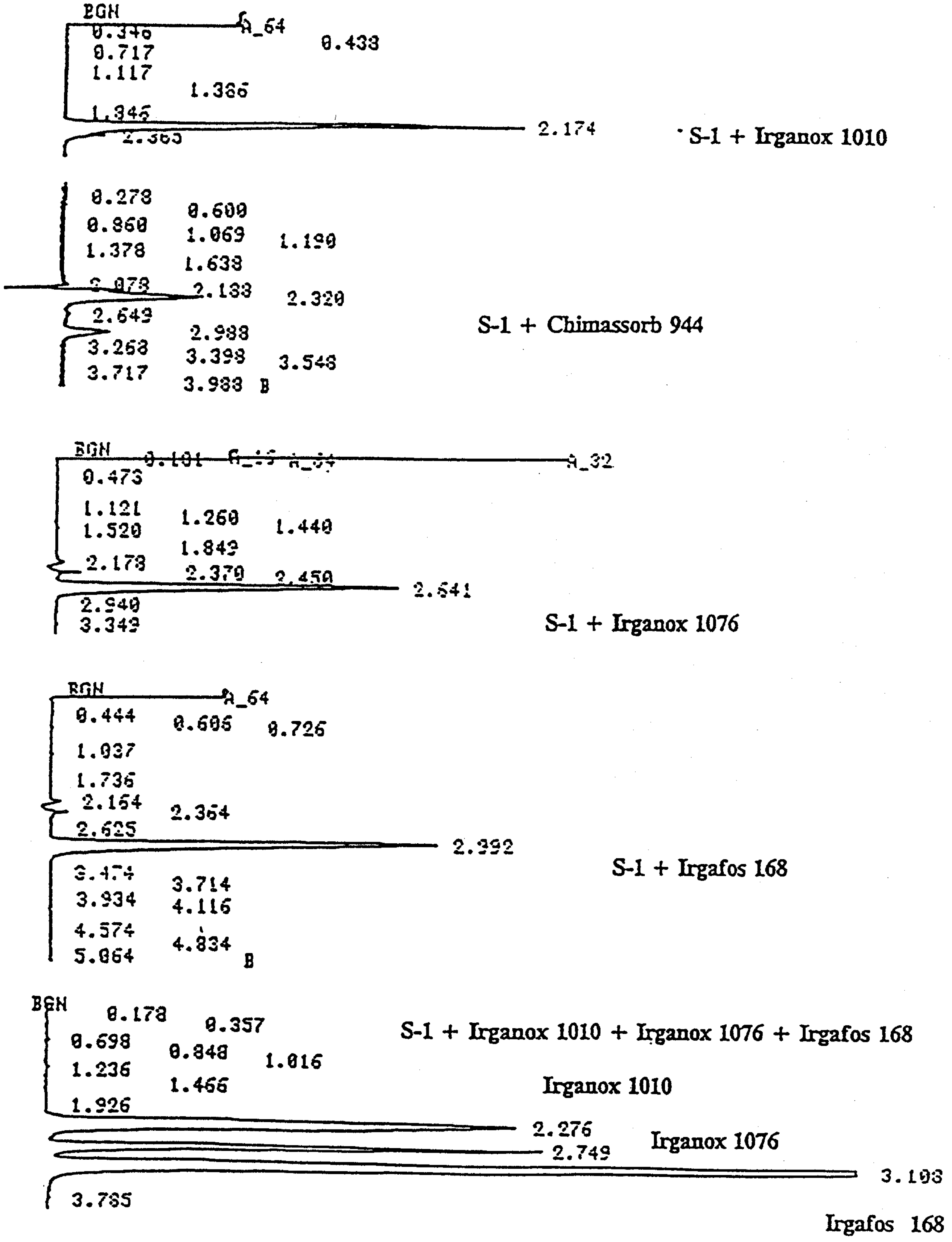


Figure 2.3. HPLC chromatogram for model mixtures of the reference polymer S-1 with different antioxidants.

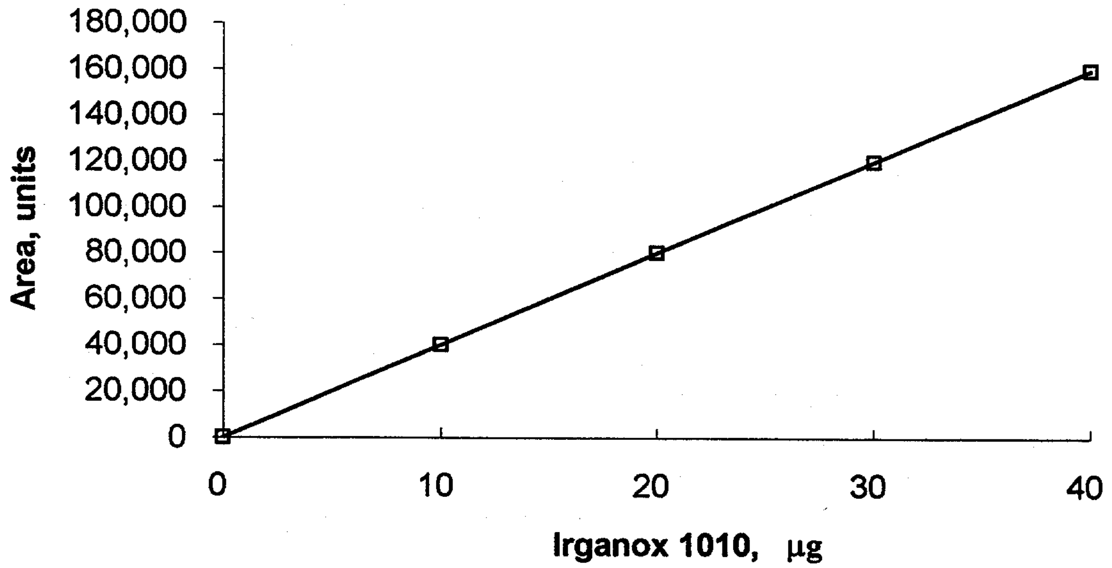


Figure 2.4. HPLC calibration curve, Irganox 1010.

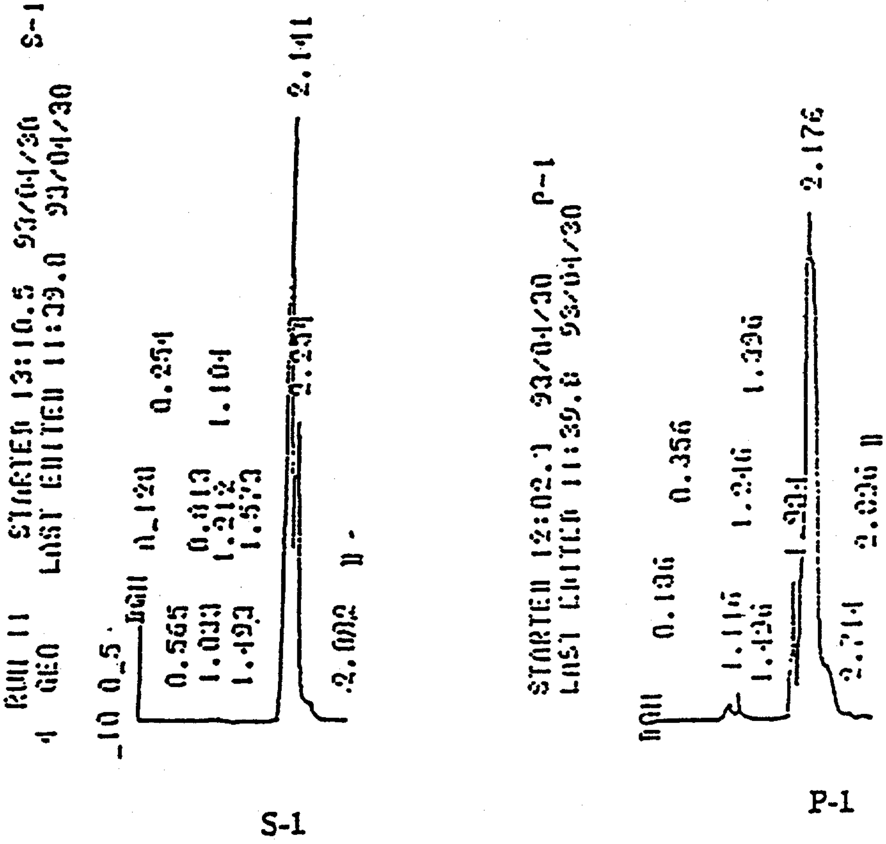


Figure 2.5. HPLC spectra of reference samples S-1 and P-1.

There are four types of geosynthetic polyolefins under investigation. P-1 was reported to contain Irganox 1010, a hindered phenol antioxidant; P-3 was reported to contain a hindered amine light stabilizer (HALS); information on the types of antioxidants in P-4 and P-9 was lacking and considered proprietary by the manufacturers. Therefore, repeatability studies have been conducted on P-1.

Results of HPLC analysis for extracted P-1 samples are listed in table 2.11. As indicated, there is a ± 12-percent variation of Irganox 1010 antioxidant content among each of the extracted samples for the P-1 "as received" product.

Table 2.11. HPLC results for Irganox 1010 antioxidant content in P-1.

No.	Irganox 1010 content, (wt.%)	Average content (variation, %)
1	0.142	0.143 ± 0.0165 (11.5%)
2	0.127	
3	0.160	

To obtain a better understanding of the range of variations in antioxidant content for each extracted sample, the following experiment was performed: 10 strips of P-1 for a total weight of 8 g (cut from two separated positions) were chopped and mixed, then three separate samples of 1.000 ± 0.0005 g were weighed and the antioxidant extracted using the described procedure. These measures did not improve the repeatability of HPLC results with the coefficient of variation still remaining as high as 18 percent. The results are listed in table 2.12.

Table 2.12. HPLC results obtained for 10 mixed strips of HDPE commercial product P-1 "as received."

No.	Number of specimens	Irganox 1010 (wt.%)
1	10	0.095
2	10	0.105
3	10	0.074
Average value		0.091 ± 0.016
Variation, %		± 17.6%

HPLC study of P-3 samples indicated that there are no distinctive features of a HALS antioxidant identifiable on chromatograms. Therefore, HPLC could not be used for identification and monitoring of antioxidant consumption during oven aging for this geotextile.

Considering that the procedure used for the extraction of antioxidant is the same for each run and that the observed variations of antioxidant content among samples are high, the following conclusions with respect to the variations of antioxidant content are suggested:

- When carbon black is incorporated into the polymer, the extraction and quantification become even more complicated. Carbon black is known to adsorb stabilizers, and any non-uniformity in the surface of and dispersion of carbon black in the polymer matrix will also result in poor distribution of the stabilizers and difficulties in extraction.

- The first step for the analysis of the stabilizers in polyolefins is extraction. Stabilizers are normally present in polymers at low concentration, less than 0.5 percent, and any loss of the stabilizers in handling is significant. Antioxidants and light stabilizers may suffer decomposition during extraction, and the presence of very small amounts of metal and even trace catalyst residues in polyolefins may catalyze the auto-oxidation process during extraction.

- HALS-type antioxidants are the source of nitroxyl radicals (formed during high-temperature processing or photooxidation from the parent HALS) which are known to be the main antioxidants. HALS is consumed/transformed rapidly at the early stage of thermo-oxidation (Fay 1995).

- Antioxidants, such as hindered phenols and aromatic amines, are converted to higher molecular weight products during their function as antioxidants. These oxidative transformation products increase the oven-aging stability of the polymer. These transformation products may not be monitored simply by HPLC.

In light of the difficulties encountered with HPLC analysis, Professor Eli M. Pearce and Dr. Shaoxiang Lu of Polytechnic University Research Team visited Dr. Joseph J. Fay at Ciba-Geigy at Ardsley, NY, a leading manufacturer of all types of antioxidants for the geotextile industry. During this visit, the results of HPLC analysis of antioxidants and antioxidants in general used for geosynthetic applications, were discussed.

Based on our request, Ciba Analytical Department conducted analysis of antioxidant content in selected geosynthetic materials by HPLC. Their results indicated that the variation of the antioxidant content in non-aged polyolefins (without carbon black) is about ± 10 percent.

The results of HPLC testing for the P-1 geogrid "as received" appeared to be consistent with those reported by Ciba-Geigy. However, the variation of results obtained for oven-aged polymers is significant. Dr. Fay was not surprised by the observed results. He agreed that recovery of antioxidants during extraction in the presence of carbon black which adsorbs antioxidants prior to or during extraction is difficult to improbable. He pointed out in addition that the transformation of antioxidants for oven-aged polymers at high temperature will make quantitative analysis of the antioxidants impossible. Figure 2.6 was developed by Fay (1995) and schematically illustrates that there is no direct connection between the antioxidant content and mechanical properties of oven-aged polymers as a function of time, while there is available antioxidant.

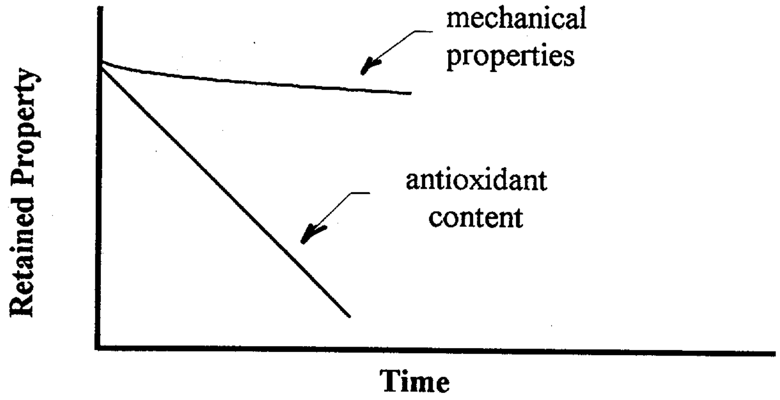


Figure 2.6. Anticipated behavior of mechanical properties and antioxidant content for commercial geosynthetic products during oven aging.

2.2.5 Conclusions, HPLC.

- The extraction results on Irganox 1010 content by HPLC for the non-aged P-1 geogrid appeared to be within the range of accuracy expected from the HPLC technique.
- Experimental results, a literature review, and discussions with industry experts suggest the extreme complexity and uncertainty of antioxidant loss monitoring for oven-aged geosynthetic polyolefins by HPLC.
- It appears that HPLC is an ineffective technique to conduct routine monitoring of antioxidant losses in commercial geosynthetic products.

2.2.6 Fourier Transformation Infrared (FTIR) analysis.

FTIR was not considered for monitoring polyolefin aging for the following reasons:

1. Transmission FTIR is not sensitive, because oxidation occurs predominantly on the surface.
2. Surface-reflection FTIR will improve the sensitivity, but there are several difficulties:
    - The sample is not consistent from point to point.
    - The oxidized products consist of carbonyl-containing functional groups (aldehydes, ketone acids, esters, even peroxidized acids and esters, etc.) and the ratios of each will change upon aging conditions, time, and environmental factors (including the presence of contaminants - trace of iron etc.). The IR peaks will overlap each other (at least partially), and will be extremely difficult to interpret.
    - The geosynthetic polyolefins chosen contain mostly Irganox 1010 and 1076, which will provide esters IR carboxyl peaks overlapping with C=0 peak of oxidized products.
    - Aging is a dynamic process, therefore, during aging, the geosynthetic materials will gradually lose antioxidants (a decrease of the C=0 peak), while the oxidized

products will gradually increase (an increase of the C=0 peak), further complicating interpretation.

Use of FTIR to detect, correlate, and define the oxidized products of polyolefin is too complex a problem. The effect of carbon black, type, amount, dispersion, etc., further complicates the ability to use FTIR. Therefore, it is not viable for routine monitoring of polyolefin aging.

2.2.7 Antioxidants' leachability.

Preliminary studies of antioxidant leachability were made using water extraction to provide a ranking order with respect to leachability for polypropylene product samples to be used in Phase 3 and as a possible method to obtain antioxidant-free samples. Water leaching of antioxidant for selected products has been examined by immersing samples in water at 70°C with stirring for up to 18 days. OIT at 175°C was determined at intervals. Results are shown in table 2.13 and presented in figure 2.6.

Table 2.13. OIT (at 175°C) after 70°C water leaching, Method "B".

Material	OIT (min)				
days →	0	2	4	7	18
P-3	12	3.3	2.2	1.8	1.0
P-4	15	6.0	5.1	4.9	2.2
P-9	97	71	64	51	27

There are significant differences for the products tested, probably because of differences in antioxidant formulations, antioxidant molecular weight, and in the texture of materials. Rapid loss in 2 to 5 days followed by slow change, likely reflects essentially removal of stabilizers in a short time under the conditions used.

These preliminary severe leaching tests suggest that geotextiles used within flowing water or potentially below the water table may be subject to antioxidant depletion by leaching in a relatively short time. This is evident by comparison of OIT measurements on P-9 during Phase 3 oven aging at 70° C (figure 4-18), which produced the same decrease of OIT after 250 days.

These findings are consistent with Wisse (1990) and suggest an antioxidant depletion mechanism in addition to oxidation.

Leaching by this method appears to be temperature, product, and antioxidant-related and, therefore, not an appropriate method to obtain antioxidant-free specimens for Phase 3 testing. However, the use of specially manufactured textiles P-3a and P-4a with minimal amount of antioxidant additives makes possible the qualitative assessment of the influence of stabilizers on the rate of thermo-oxidation for selected commercial products.

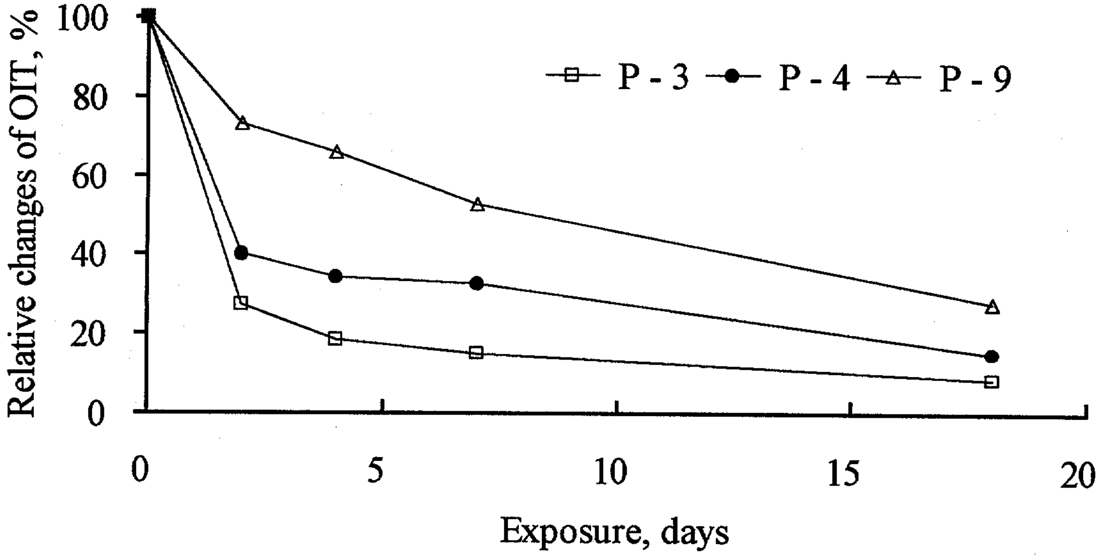


Figure 2.7. OIT in water leached at 70°C.

2.2.8 Metal salt contamination.

The literature has indicated the potentially accelerating influence of the most widespread transition metal, iron, on oxidative degradation (Kelen, 1982). Therefore, model experiments on the effect of iron on reference polymers were carried out. The procedure of salt contamination is described in a forthcoming companion Volume II, Summary of Research Methods and Data for model plaques and commercial geotextile products. For this preliminary study, sample plaques have been molded in which the polymer was mixed with $FeCl_3$ at known quantities and characterized by OIT measurements only. Results of OIT at 175°C are shown in figure 2.7 for polypropylene (S-2) containing 0.10-percent Irganox 1010 and varying concentration of $FeCl_3$. As expected, low concentrations of iron cause major changes in OIT. Results on reference polymers without antioxidant are shown in table 2.14.

Table 2.14. Effect of the presence of $FeCl_3$ on reference PP and HDPE (without antioxidant).

Material	OIT (min)			
$FeCl_3$ Wt.%→	0	0.2	0.5	1.6
S-2*	1.4	0.4	-	-
S-1**	68.4	-	24	17

* OIT at 175°C
** OIT at 200°C

Increasing concentrations of $FeCl_3$ decrease OIT. Therefore, the anticipated time to 50-percent strength loss for polyolefins' products contaminated by $FeCl_3$ is expected to be less as compared with "pure" samples at the same exposure conditions.

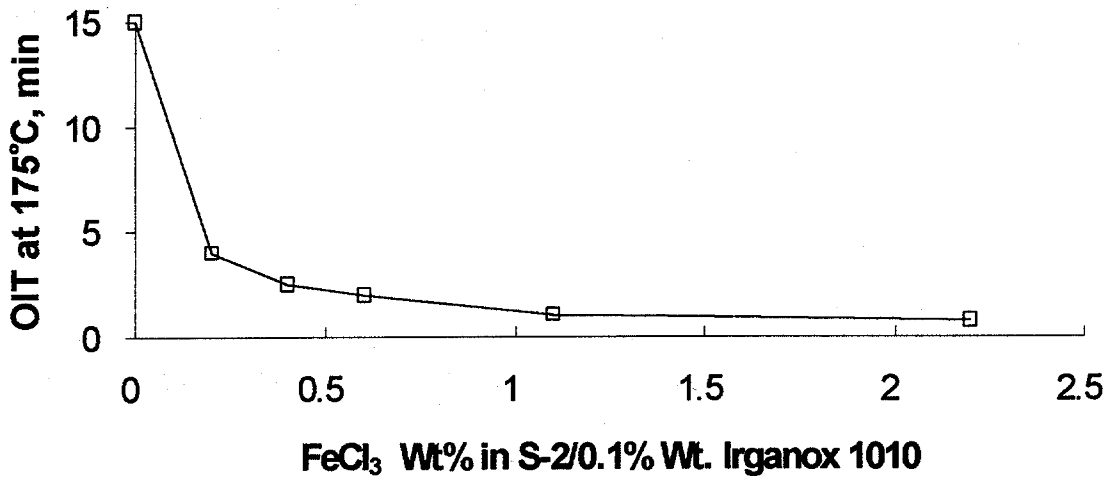


Figure 2.8. Effect of $FeCl_3$ contamination on OIT, S-2/Irganox 1010 system.

From the results, it appeared that the $FeCl_3$ content amounted up to 1.1% w/w in the model PP, and HDPE samples significantly decreased OIT values as compared with OIT values for "pure" reference polymers.

The procedure for salt contamination by hot pressing is not feasible to produce films with dimensions for wide-strip testing. Therefore, metal salt contamination of polyolefin products, similar to the procedure suggested by Wisse (1990), has been used for the sample preparation of commercial products. The specimens have been prepared by soaking for different periods in aqueous $FeCl_3$ solutions of various strength, and subsequently drying. In this way, a defined amount of iron salt is deposited on the specimens. The contamination by soaking could result in nonuniform salt distribution along the specimens tested and, therefore, the results of testing may not have a direct quantitative relation to in-situ regimes, where variables such as geosynthetic structure, solubility, permeability, etc. at each location will play a major role. However, salt contamination of geotextiles by soaking in aqueous salt solution may simulate natural conditions in use and, therefore, would provide an estimate of an order of magnitude for long-term degradation when contaminated by metal salts.

2.2.9 Conclusions.

Comprehensive study of analytical techniques for chemical characterization of degradation behavior for commercial polyolefin geosynthetics suggests that:

- OIT by DSC, widely recommended in the literature, cannot be used for products containing HALS-type antioxidant additives.

- The use of thermoanalytical methods such as TGA, DSC, and OIT is limited by the complexity of antioxidant mixtures as well as by the complexity of thermodegradation itself and can provide only a qualitative index of antioxidant depletion.
- HPLC, initially sought as a supplementary method or substitution to OIT, is an ineffective test for routine monitoring of antioxidant losses in commercial geosynthetic products.

2.3 CHEMICAL CHARACTERIZATION OF POLYESTER-BASED GEOSYNTHETICS "AS RECEIVED"

2.3.1 Intrinsic viscosity and Carboxyl End Group (CEG).

The literature has established that all important mechanical properties, particularly tensile strength, elongation to break, impact strength, and reversible elasticity depend on molecular weight (Mark and Pearce, 1976). Therefore, molecular weight is the major chemical index in the context of the overall objectives of the project regarding the effects of chemical change on mechanical properties and durability of geosynthetic products.

For a given polymer plus solvent system at a specified temperature, viscosity $[\eta]$ can be related to the molecular weight $\bar{M}$ through the Mark-Houwink equation

$$[\eta] = K\,\bar{M}^{\alpha} \tag{2-1}$$

and K (dl/g) and α can be established, by calibrating with polymer fractions of known molar mass. Once this has been established for a system, $[\eta]$ alone will give $\bar{M}$ for an unknown fraction (Hergenrother and Nelson, 1974).

Several polymer plus solvent systems were tested at different temperatures to define conditions for viscosity measurement. The results of viscosity measurements for different conditions and related calculations of the molecular weight for P-10 PET yarn samples are shown in table 2.15.

The results indicated that the viscosity of the polymer tested depends on the condition of the test, e.g., temperature and solvent system. Therefore, a sole condition must be chosen to be used for characterization of the polyester products under Phase 3. Moreover, results on viscosity measurements can be compared to those obtained only under the same experimental conditions such as solvent system and temperature. The Phenol/TCE=6/4 (w/w) mixed solvents system at 30°C [ASTM D-4603] was chosen as a sole condition for viscosity measurements, and those conditions are used during Phase 3.

End-group analysis (CEG) and viscosity-determined molecular weight are among the simplest and most rapid ways of determining molecular weight change. Therefore, the polyester materials "as received" were characterized by molecular weight (intrinsic viscosity) under the conditions specified above and by the number of CEG. Results are shown in table 2.16.

For PET geogrids coated with PVC (P-6), the experimental approach to the study of hydrolytic degradation of fibers in the grid requires consideration of the role of the PVC coating, which is to protect PET reinforcing fibers from damage during construction and to provide dimensional stability during manufacture. Furthermore, degradation of the PVC coating itself can yield significant concentrations of hydrochloric acid and other gaseous products that diffuse into the PET, and possibly accelerate hydrolysis in the presence of moisture. Therefore, the PVC-coated PET geogrid (P-6) "as received" was characterized by weight content of PVC in the geogrid. PVC content of 34 percent, by weight, in PVC-coated PET geogrid P-6 was obtained by soaking the specimen of the geogrid in tetrahydrofuran (THF) overnight, washing, and decanting with THF several times, and then by weighing.

Table 2.15. Viscosity and molecular weight under different experimental conditions, P-10 PET yarn.

	Solvents System Phenol/TCE (w/w)					
	5/5		4/6	6/4	3/5	
Temp. (°C)	20	25	25	30	30	
Viscometer	150/79					No. 1/B443
$[\eta]$	0.9523	0.9251	0.9651		0.9691	0.9583
$[\eta]_{corr.}$		0.9361	0.9789		0.9641	
$K \times 10^4$	7.55	2.1	14	21	2.29	
α	0.685	0.82	0.64	0.58	0.73	
$\bar{M}_n \times 10^{-3}$ *	33.6 ($\bar{M}_n$)	28.2 ($\bar{M}_{n\,corr.}$)	27.9 ($\bar{M}_{n\ corr.}$)	30.2 ($\bar{M}_n$)	92.2 ($\bar{M}_{w\,corr.}$)	91.5 ($\bar{M}_w$)
Method for obtaining K, α	End Group			Tritium Exchange	Light Scattering	
Reference	Handbook of Fiber Science & Technology, Vol. IV, Ed. By M. Lewin, E. Pearce, 1985	Andre Conix, Makromo l. Chem. 1958, Vol. 26, p. 226	Scientific Polymer Products Inc., personal report, 1992	Journal of Polymer Science (1974) Vol. 12, p. 2905	M.L. Wallach, Makromol. Chem., 1967, Vol. 103, p. 19	

* Using the chemical convention.

Table 2.16. Molecular weight (intrinsic viscosity) and CEG of polyesters "as received."

Material	$[\eta]^{(2)}$	$\bar{M}_n{}^{(3)} \times 10^{-3}$	CEG$^{(4)}$, meq/Kg (reported value)
P-5, Nonwoven fabric	0.62	18.2	47 (45-49)
P-6, PVC-coated geogrid$^{(1)}$	0.83	30.2	19 (17)
P-7, Woven fabric	0.84	30.6	18
P-10 PET fiber (same as P-6)	0.83	30.2	19 (17)

(1) After stripping off PVC coating.
(2) Intrinsic viscosity is measured at 30°C in Phenol/TCE=6/4 (w/w) mixed solvents system.
(3) $\bar{M}_n$ is calculated by using Mark-Houwink equation in which $K = 2.1 \times 10^{-3}$ and $\alpha = 0.58$.
(4) For CEG, see Appendix B.

The values of intrinsic viscosity were calculated from a single-point measurement of relative viscosity using Billmeyer relationship instead of an extrapolation method:

$$[\eta] = \frac{0.25(\eta_r - 1 + 3 \ln \eta_r)}{C} \tag{2-2}$$

The specimen tested by the technique of viscosity measurements actually consists of material taken from several specimens (each specimen in a retrieval). Therefore, the viscosity measurement will be actually an average test result for the entire retrieval.

2.3.2 Conclusions and recommendations.

- Molecular weight (intrinsic viscosity) and CEG number of polymer products are factors of prime importance that govern tensile strength. Therefore, molecular weight (intrinsic viscosity) and CEG are recommended as indexes to monitor chemical degradation of polyester products during Phase 3.
- The intrinsic viscosity depends on the conditions of measurements such as solvents and temperature. Therefore, a sole condition of viscosity measurements must be chosen for viscosity degradation monitoring. Phenol/TCE=4/6 (w/w) mixed solvent systems at 30°C have been chosen to be used for characterization of the polyester products under Phase 3.

2.4 PHYSICAL AND MECHANICAL CHARACTERIZATION OF GEOSYNTHETIC MATERIALS "AS RECEIVED"

In the context of the overall objectives of the project, one key element of the Phase 1 and Phase 2 studies was the development of a data base of physical (weight and thickness) and mechanical properties (tensile strength) of geosynthetic materials tested, from which selections for Phase 3 are made. The data are used in Phase 3 of the project as a baseline reference for modeling and estimates of anticipated time to 50-percent strength loss for commercial geosynthetic products tested.

2.4.1 Weight of geosynthetic materials.

The weighing of geosynthetic materials was performed in accordance with ASTM D-3776, "Standard Test Method for Weight (Mass per Unit Area) of Woven Fabric," Option C - Small Swatch of Fabric.

Ten samples (8 inches (203 mm) wide and 8 inches (203 mm) long) of each material were tested at normal laboratory conditions at 21°C and 64% r.h. The results are presented in table 2.17.

2.4.2 Thickness of geosynthetic materials.

The measurement of the thickness of geosynthetic materials was conducted in accordance with ASTM D-1777, "Standard Method for Measuring Thickness of Textile Materials." The parameters of the test were as follows:

(1) applied pressure: 0.1 psi (0.69 kPa);

(2) time interval after loading: 5 sec;

(3) accuracy of thickness measurement: 0.0005 in (0.013 mm);

(4) number of samples tested: 10; and

(5) laboratory conditions: 21°C and 64% r.h.

The results are presented in table 2.17.

2.4.3 Tensile strength by Wide-Width Strip Method.

Tensile strength at failure and corresponding strain were measured to characterize mechanical properties of geosynthetic materials. These measurements were conducted on dry samples in a machine direction only. The specimens to be tested were taken at random from the laboratory sample and from different positions across geotextile roll width. For the laboratory sample, a full-width swatch about 4 to 5 feet (1.2 to 1.5 m) long in the machine direction was taken from a roll. The samples excluded fabric from both sides of a roll. Woven and nonwoven geotextiles were tested in accordance with ASTM D-4595.

All tests were conducted at normal laboratory conditions of 21°C and 64% r.h.

The measured values of tensile force and corresponding strain at failure are presented in table 2.17.

Table 2.17. Physical and mechanical properties for selected commercial geosynthetic materials "as received."

Material	weight/area oz/sq.yd.	thickness inches	tensile strength lb/in	strain %	number of samples	standard deviation	variation %	MIN	MAX
HDPE geogrid P-1	12.66				9	0.26	9.65	12.43	13.21
		0.07			9	0.002	4.03	0.0068	0.0077
			339		8	16	4.86	308	365
				37.8	8	5.8	15.3	27.9	49.9
PP Woven geotextile P-2	13.92				10	0.23	1.7	13.61	14.45
		0.06			10	0.0006	0.97	0.058	0.0605
			482		17	46	13.15	407	546
				20.6	17	3.2	20.95	12.5	31.1
PP Nonwoven geotextile P-3	10.01				9	0.123	1.2	9.79	10.15
		0.074			9	0.001	1.3	0.072	0.075
			83		7	4	4.7	90	77
				117	7	15	13.1	97	137
PP Nonwoven geotextile P-3a (minimum antioxidants)	8.51								
			24		10	2.3	11	20	27
				114	10	11	10	96	132
PP Nonwoven geotextile P-4	11.09				10	0.05	4.52	10.17	11.95
		0.1			10	0.004	4.79	0.095	0.111
			99		10	3	3.08	95	104
				83.5	10	7.5	9.02	69	96
PP Nonwoven geotextile P-4a (minimum antioxidants)	6.15								
			67		10	8.4	12	55	79
				158	10	22	14	125	180

Table 2.17 (cont.).

Material	weight/area oz/sq.yd.	thickness inches	tensile strength lb/in	strain %	number of samples	Standard Deviation	variation %	MIN	MAX
PP Woven geotextile P-9	7.23	0.026	232	21.1	10 10 10 10	0.089 0.0009 6 0.8	1.24 3.35 2.51 3.88	7.08 0.025 219 19.8	7.41 0.0275 241 22.6
PET Nonwoven geotextile P-5	16.44	0.177	204	75.3	9 9 9 9	0.37 0.004 9 1.5	2.26 2.34 4.59 2.1	1594 0.172 191 0.73	17.04 0.184 224 0.784
PET Geogrid P-6	10.83 (oz/yd)	0.05	1037 (lb/rib)	17	9 9 9 9	0.54 0.003 107 3	5 5.1 10.3 15.4	10.11 0.045 916 13.79	11.87 0.056 1212 20.36
PET Woven geotextile, P-7	10.64	0.031	544	18.8	9 9 8 8	0.33 0.001 23 1.4	3.1 3.8 4.3 7.4	9.98 0.029 505 16	11.01 0.033 580 21

1 oz/yd^2 = 33.9 g/m^2, 1 in = 25.4 mm, 1 lb/in = 0.018 kg/mm

There is no present ASTM method for tensile testing of geogrids, although it is common industry practice to test one or a few longitudinal ribs for tensile properties. Therefore, the effect of the specimen's geometry on the measured tensile properties required assessment in order to determine the effect of sample size on strength. Specimens of the HDPE geogrid were tested with different numbers of longitudinal ribs. The test conditions were as follows:

(1) 8 ribs. Transverse ribs are held in the jaws. The gauge length is 5.7 in (145 mm).

(2) 1 rib. Transverse ribs are held in the jaws. The gauge length is 5.7 in (145 mm).

The results of the tests are in table 2.18.

Table 2.18. Tensile test results on HDPE geogrid, 1 and 8 ribs.

Number of ribs	Number of samples	Tensile force, lb/rib	Coefficient of variation, %	Strain, %	Coefficient of variation, %
8	9	275	4.9	25.2	15.3
1	9	278	4.6	21.0	2.0

1 lb = 0.454 kg

The tests indicated that there is no statistically significant difference between the tensile force at failure as measured on 1-rib and 8-rib samples. Therefore, one longitudinal rib sample has been used in Phase 3 testing.

2.4.4 Statistical analysis of mechanical properties materials tested "as received."

The data base of "as received" mechanical properties of geosynthetic materials has been created to provide guidelines to the number of samples for degradation studies and as reference values of tensile force at failure and corresponding strain. A statistical analysis is required by ASTM D-4595, "Standard Test Method for Tensile Properties of Geotextiles by the Wide-Width Strip Method" to determine the number of samples to be tested, such that one may expect at 95-percent probability level that any test result is not more than 5.0 percent above or below the true average value.

The number of samples tested to satisfy the above conditions is calculated as follows:

$$n = (tv/A)^2 \qquad (2\text{-}3)$$

where:

n = number of specimens (rounded upward to a whole number);

v = reliable estimate of the coefficient of variation of individual observations on similar materials in the user's laboratory under conditions of single-operator precision, %;

t = the value of Student's t for one-side limits, a 95-percent probability level, and the degrees of freedom associated with the estimate of v;

A = 5.0%, the allowable variation from the true average value.

When there is no reliable estimate of ν, equation 2-3 is not used directly. Instead, the fixed number of six is specified. The number of specimens is calculated using ν = 7.4 percent of the average. Therefore, at least 10 specimens of each material have been tested by the Wide-Width Strip Method to estimate a coefficient of variation of individual observation under conditions of single-operator precision.

The results are summarized in table 2.19 as coefficients of variation for each material and corresponding minimum proposed specimens for wide-width testing.

Table 2.19. Number of specimens to be tested by wide-width test per one retrieval.

Material	Total number of specimens tested	Number of valid tests	Tensile strength, lb/in (manufacturer's values)	Coefficient of variation, %, (manufacturer's values)	Number of specimens, ASTM D-4595	Number of specimens to be tested per one retrieval
P-1	10	8	339 (308)	4.86	4	5
P-2(1)	20	17	482 (556)	13.5 (7.8)	21	21
P-3	10	7	83 (87)	4.7 (5.5)	4	5
P-3a	12	12	24	11	16	5(2)
P-4	10	10	99 (N/A)	3.08	3	5
P-4a	10	10	67	12	18	5(2)
P-5	10	9	204 (205)	4.59	3	5
P-6 (one rib)	22	18	1037 (lb/rib) (N/A)	10.3	15	15
P-7	10	8	544 (648)	4.3 (3.1)	3	5
P-9	10	9	232 (N/A)	2.51	3	5

(1) to be excluded from testing matrix

(2) specially manufactured materials with minimum amount of antioxidants tested as reference polymers for the assessment of the effectiveness of antioxidant additives.

1 lb/in = 0.018 kg/mm

These results indicated that the coefficient of variation, ν, for materials P-1, P-3, P-4, P-7, and P-9 was less than 7.4 percent. The value of ν = 7.4 percent has been used by the ASTM to specify minimum required number of specimens to be tested when there is no reliable estimates of n. Moreover, for materials P-3 and P-7, the coefficient of variation appeared to be close to the values provided by manufacturer's laboratories. Therefore, five specimens are to be tested for each of the following materials: P-1, P-3, P-4, P-5, P-7, and P-9. The minimum required number of specimens for materials P-2, P-3a, P-4a, and P-6 with ν greater than 7.4 percent has been estimated in accordance with equation 2-3.

The minimum required number of samples to be tested by the Wide-Width Strip Method in accordance with ASTM D-4595 and based on the results of the testing materials "as received" is shown in table 2.19. However, it is recommended to increase the minimum required number of samples to be tested by Wide-Width Tensile Test from 3-4 to 5 to account for a potential deviation contributed by the nonuniformity of the degradation process (nonuniformity of the degradation itself and nonuniformity of the treatment). Furthermore, this increase in the number of samples to be tested would be in conformance with the proposed European Standards.

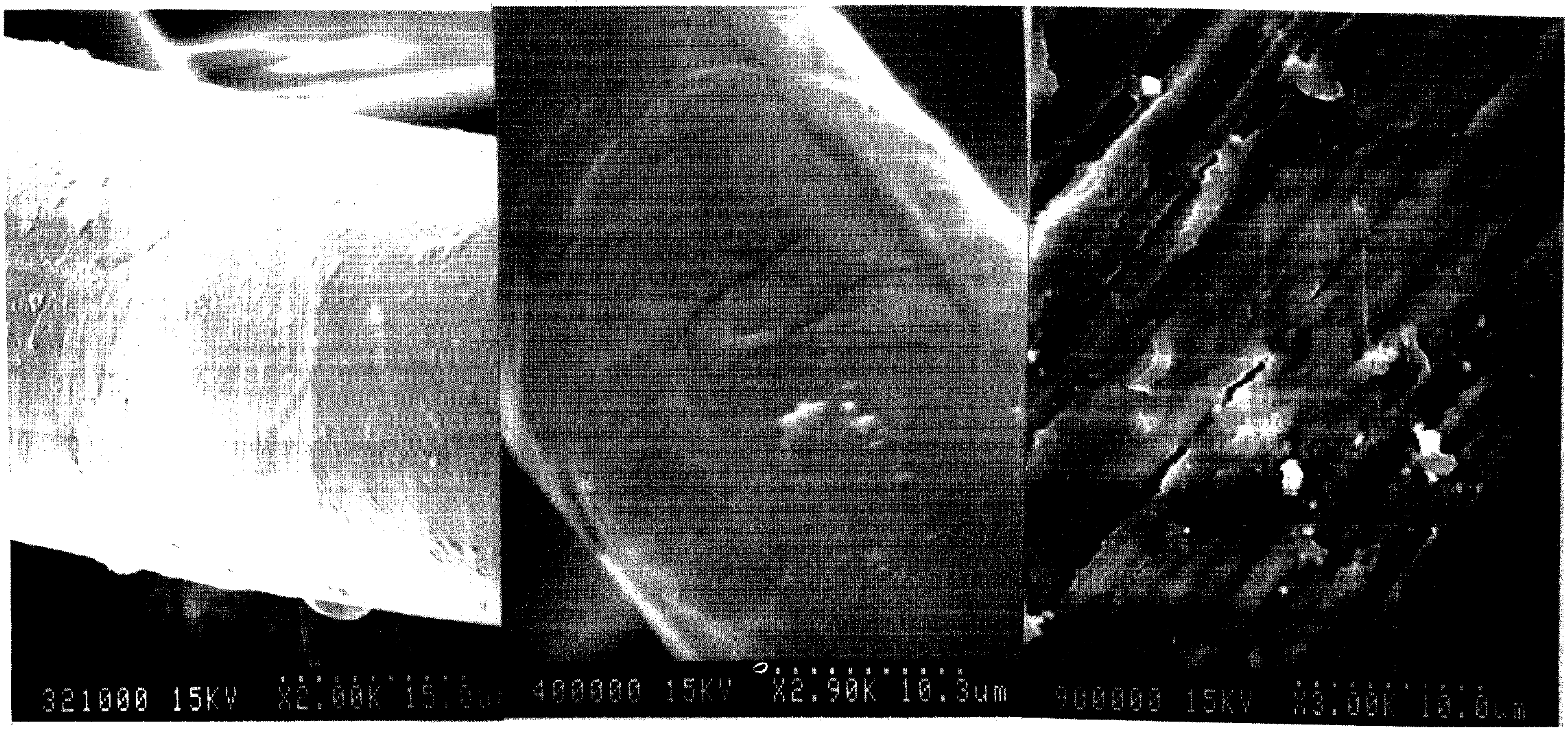
The minimum required number of samples to be tested for the P-3a and P-4a, the specially manufactured products, is 15 and 18, respectively. Compliance with ASTM requirements for these particular materials would significantly increase total number of specimens treated under the same condition resulting in a substantial increase of the volume of testing chambers. However, accelerated degradation of these materials was planned for qualitative study of effectiveness of antioxidant additives. Therefore, the anticipated results will serve more as a qualitative reference frame for comparison, than as a quantitative one. Given these considerations, only five specimens of each material are to be tested per retrieval.

2.4.5 Fiber surface morphology by scanning electron microscopy (SEM).

Fiber surface morphology as well as fiber diameter may be important factors which affect the rate of degradation for polymeric products. Initial cracks and/or crazes, caused by the manufacturing process or from construction damage, on the surface of virgin fibers may provide reaction sites for either oxidation or hydrolysis. Fiber diameter may affect the rate of aggressive media penetration into the fiber, affecting the overall degradation performance for the product studied.

The scanning electron microscope has been used for studies of fiber surface morphology for the selected commercial geosynthetic products. SEM microphotographs with magnification of 3000x indicate a significant difference in surface morphology for fibers of virgin polyolefin-based geotextiles. Figure 2.8 shows that the surface of virgin fibers for the P-3 product, which is continuous filament textile, is smooth and that there is no apparent cracks or crazes. Surface of virgin fibers for the staple product P-4 and for slit film product P-9 appeared to be covered with crazes and cracks (figure 2.8). Fiber surfaces of PET products are smooth when examined at a magnification of 3000x. The average diameter of virgin fibers varies for PET products as follows: 27 μm for P-5, 21 μm for P-6, and 17 μm for P-7.

Results of SEM studies indicate that scanning electron microscopy may be a useful tool to characterize fiber surface morphology for virgin commercial products and, therefore, may be used to establish for each products fiber integrity.



(a) P-3 “As received” (b) P-4 “As received” (c) P-9 “As received”

Figure 2.9. SEM microphotographs at magnifications of 1500x (P-3), 2900x (P-4), and 1500x (P-9).

CHAPTER 3

TESTING CONDITIONS AND TESTING PROCEDURES FOR LONG-TERM DEGRADATION BY OXIDATION

3.1 LONG-TERM DEGRADATION OF POLYOLEFIN-BASED COMMERCIAL GEOSYNTHETICS

Polyolefin geosynthetic materials are widely used in highway construction. The combination of strength, light weight, and resistance to severe environmental conditions make them suitable for use as reinforcement for reinforced soil structures and slopes.

It is known that polyolefin material may oxidize, resulting in polymeric molecular chain breaks. The reduction of the polymer chain length directly results in strength loss of a material. The available studies on polyolefin oxidation indicate that rates of oxidation are very low at ambient temperatures; however, in the context of the lifetime of civil engineering applications, the amount may not be negligible. Therefore, the assessment of the degradation rates in different environmental conditions become of prime importance in the evaluation of commercial polyolefin geosynthetic products.

Comprehensive studies of polyolefin oxidation (Chien and Boss, 1967; Zolotova and Denisov, 1971) indicated that the rate of reaction depends on the oxygen partial pressure in the system as well as on the temperature. It is further indicated in the literature (Reich and Stivala, 1971; Kelen, 1982), that the presence of transition metals or their salts in the system will accelerate the oxidation of polyolefins.

3.1.1 Conditions and variables for thermo-oxidative degradation, matrix of testing conditions.

The basic principles of thermo-oxidative degradation of polyolefin polymers indicate that environmental conditions such as oxygen partial pressure and presence of transition metals or their salts have a significant impact on the rate of degradation. Therefore, in order to assess the influence of these environmental conditions on the rate of mechanical degradation for commercial polyolefin geosynthetics, the following conditions have been selected for accelerated laboratory testing:

- Oven aging in circulating air (21% O_2).
- Oven aging in stagnant air (21% O_2).
- Oven aging in a stagnant atmosphere containing 8% O_2 balanced by N_2.
- Oven aging of geosynthetic samples contaminated in 0.2% and 2% aqueous solutions of $FeCl_3$.

The overall effect of antioxidant additives is assessed by testing specially manufactured polyolefin textiles P-3a and P-4a. These materials are reportedly identical to the commercial products P-3 and P-4 in terms of polymeric composition and manufacturing, except that they are manufactured with a minimum amount of additives required for production purposes.

The planned temperature of exposure varies from 50 to 110°C. However, the unique performance of each of the selected commercial products determines the temperature range for a particular product and will be discussed along with experimental results. At least five consecutive retrievals are scheduled over the period of aging at each specific condition for each selected geosynthetic product.

Exposure Times

In order to estimate anticipated time to 50-percent strength loss at different elevated temperatures required for long-term aging, accelerated degradation under a severe exposure temperature of 110°C in circulating air has been performed during Phases 1 and 2 for the selected commercial geosynthetics. Summarized results of these highly accelerated tests are presented in table 3.1.

Table 3.1. Tensile strength loss for selected commercial geosynthetic products aged in circulating air at 110°C.

Exposure (days)	P-1, lb/rib (range)	P-2, lb/in (range)	P-3, lb/in (range)	P-4, lb/in (range)	P-9, lb/in (range)
"as received"	275 (246-292)	482 (407-546)	83 (90-77)	99 (95-104)	233 (219-241)
20	250 (231-262)	356 (312-442)	81 (81-82)	36 (11-20)	226 (209-230)
40	273 (231-276)	74 (56-103)	68 (66-75)	embrittlement	204 (201-206)
80	250 (243-258)	10 (7.7-11.6)	36 (24-44)	embrittlement	88 (78-101)

1 lb/in = 0.0179 kg/mm

The results of these accelerated tests, along with the results reported in the literature, permitted rough estimates of anticipated time to 50-percent strength loss at different temperatures of exposure for these products. The Arrhenius-type modeling has been used as an initial approximation to estimate the anticipated time to 50-percent strength loss for geosynthetics. Arrhenius-type kinetics yields the following:

$$ln(t/t_0) = U/R \times (1/T - 1/T_0) \qquad (3\text{-}1)$$

where t is time to 50-percent strength loss at temperature T; t_0 is time to 50-percent strength loss at temperature T_0; U is effective or apparent activation energy; and R is a universal gas constant.

The published value of effective activation energy for polypropylenes (Wisse, 1982, 1990) of 65 kJ/mol obtained in a temperature range from 70 to 140°C and time to 50-percent strength loss at 110°C obtained from the test results has been used to estimate anticipated time to 50-percent strength loss at temperatures varying from 50 to 110°C. The results are presented in table 3.2 and are shown in figure 3.1.

Table 3.2. Estimates of anticipated time (days) to 50-percent strength loss for polyolefin geosynthetics tested.

Temperature		Products				
°C	°K	P-2	P-4	P-9	P-3	P-1
110	383	33	21	72	75	516
100	373	58	37	125	130	892
90	363	103	65	222	232	1589
80	353	189	120	409	427	2926
70	343	360	229	780	815	5582
60	333	714	455	1547	1616	11072
50	323	1478	941	3200	3343	22911

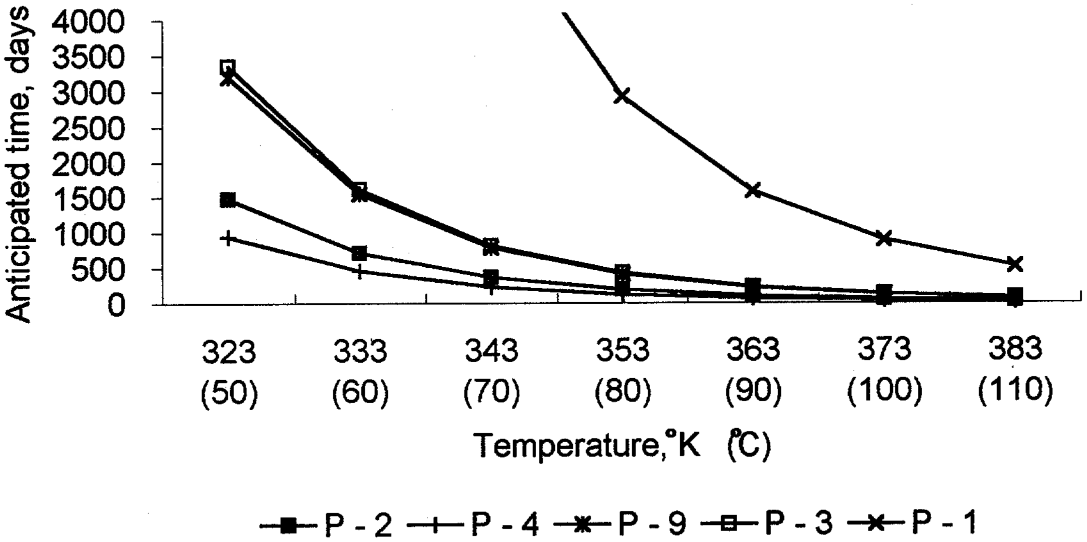


Figure 3.1. Anticipated time to 50-percent strength loss for selected geosynthetics tested under a severe exposure condition of 110°C in circulating air.

Based on the above, the implemented testing matrix for long-term aging of polyolefin-based commercial geosynthetics was developed and is shown in table 3.3. Actual laboratory incubation times differed somewhat based on obtained results.

Table 3.3. Task D, Testing matrix implemented for Phase 3.

Geosynthetic Designation code	Environment			Salt contamination $FeCl_3$ w/w %(1)	Temperature of aging, °C	Anticipated duration of aging(2) (days)
	Circulating air, 21% O_2	Stagnant diluted air, 8% O_2	Stagnant air, 21% O_2			
P-1	X				80	1100
					90	800
					100	600
					110	200
		X			90	1000
					100	700
					110	150
P-3	X				50	1000
					60	800
					70	550
					80	280
					90	171
		X			70	750
					80	500
					90	250
	X			X	60	300
					70	300
					80	150
P-3a	X				50	440
					60	360
					70	200
					80	100
		X			70	380
					80	300
					90	250
P-4	X				50	275
					60	210
					70	200
					80	100
		X			70	475
					80	300
					90	250
			X		60	150
					70	150
	X			X	60	80
					70	60
P-4a	X				50	260
					60	200
					70	75
					80	55
		X			70	475
					80	300
					90	250

Table 3.3 (cont.).

Geosynthetic Designation code	Environment			Salt contamination $FeCl_3$ w/w %[1]	Temperature of aging, °C	Anticipated duration of aging[2] (days)
	Circulating air, 21% O_2	Stagnant diluted air, 8% O_2	Stagnant air, 21% O_2			
P-9	X				60	400
					70	600
					80	210
					90	110
		X			70	475
					80	200
					90	250

[1] Contamination of samples conducted in 0.2% and 2% solutions of $FeCl_3$.

[2] Actual exposure time to be adjusted to the observed rate of mechanical degradation for specific materials.

OIT and Weight Loss

The preliminary testing of incubated samples (table 3.1) included OIT and weight loss measurements. Weight loss at 80 days ranged from approximately 1 percent for P-1, P-3, and P-9 to 4.5 percent for P-2 and 6.5 percent for P-4. The results of OIT measurements are shown in table 3.4.

Table 3.4. OIT (at 175°C) after 110°C oven aging.

Material (number of samples)	OIT (min), Method "B" (range of values)				
Days →	0	20	40	60	80
P-2 (4)	22 (20-25)	5.2 (4.5-5.3)	3.1 (2.7-3.6)	2.7 (2.4-3.0)	2.4 (2.1-2.6)
P-3	12	10	9.6	8.1	7.2
P-4	15	3.2	2.2	1.8	1.5
P-9 (4)	97 (92-103)	24	11 (10.7-11.1)	7.8 (7.5-8.1)	4.7 (4.4-4.9)
P-1* (2)	63	35	10.7	5.3 (5.2-5.4)	3.3

*For P-1 (HDPE), OIT is tested at 200°C.

This preliminary assessment indicated a general correlation between weight and strength loss at this incubation temperature.

No apparent correlation between OIT values for materials "as received" and strength degradation at 110°C is indicated. However, retained OIT values as function of incubation time appear to indicate the current state of oxidative stability and/or antioxidant depletion for some of the geosynthetics tested.

The results of this preliminary testing suggest:

- OIT as a measure of oxidative stability or antioxidant depletion should be monitored in Phase 3 for P-1, P-4, and P-9.
- Initial OIT values (as received) do not provide a relevant index for ranking materials with regard to strength loss or antioxidant depletion.

Shrinkage

A study was undertaken to evaluate the possible effect of shrinkage due to temperature exposure. The specimens of selected materials (P-2, P-3, P-4, and P-9) were exposed to elevated temperature of 90°C±3°C in a force-draft oven (Isotemp 655F). All samples were measured before and after treatment at standard laboratory conditions of 22°C and 65% r.h. The results indicated no apparent shrinkage over the period of aging for tested geosynthetics.

By contrast, the literature reports (Tisinger et al., 1993) that PP geotextile yarns exposed to an elevated temperature exhibited shrinkage observed by optical microscopy. Tisinger et al. (1993) attempted an evaluation of the shrinkage effect on degradation. One sample was restrained when oven-aged, the other sample was not restrained. The results indicated that holes developed randomly in the unrestrained geotextile in the same manner as they had developed in the field-exposed sample. In addition, the unrestrained sample shrunk. The restrained sample did not develop holes. It can be concluded that unrestrained conditions for oven aging provide results similar to those obtained in field exposure testing.

Horrocks and D'Souza (1990, 1992) have undertaken a comprehensive study of experimental and actual oriented polypropylene tapes subjected to accelerated elevated temperature aging under varying levels of stress. Their results indicated that applied stress increased the degradation rate of the polymers tested.

If the sample is restrained by a frame, stress will develop due to shrinkage and a change in the degradation rate would be anticipated. In this case, the degradation rate of the polymer could depend on the temperature of exposure and on the stress as follows (Bartenev, Zuyev, 1968; Hertzberg, Manson, 1980):

$$\ln (t/t_0) = \{[U - g(s)]/R\} \times (1/T - 1/T_0) \qquad (3\text{-}2)$$

where t is time to 50-percent strength loss at any given temperature $T(^\circ K)$; t_0 is time to 50-percent strength loss at temperature T_0; U is effective activation energy; R is universal gas constant; s is stress developed in the restrained sample due to the shrinkage.

As indicated in this relationship, the restraining of samples will have a synergistic effect on the degradation rate. The decoupling of the "pure" temperature degradation from the degradation caused by thermoelastic stress is an independent research task which is beyond the scope of this work.

The results of experimental work and the literature survey on shrinkage response indicated:

- No apparent shrinkage of tested polyolefins after 40 days of exposure at 90°C. Therefore, no restraint was used in Phase 3 testing.
- When shrinkage occurs, the degradation behavior of unrestrained samples of polypropylene geotextile is similar to the degradation under the field conditions.
- Oven aging of restrained materials may degrade at a different rate than unrestrained samples.
- The synergism of temperature and thermoelastic stresses (when shrinkage occurs on restrained samples) on the degradation rate complicates the use of kinetic modeling in estimating the anticipated time to 50-percent strength loss at different temperatures.

3.1.2 Testing procedures and equipment.

The accelerated thermo-oxidative degradation test procedure developed involves: (i) sample preparation; (ii) oven aging of prepared samples at different levels of oxygen concentration; (iii) mechanical testing to determine tensile strength using the Wide-Width Strip Test; (iv) chemical testing to determine Oxygen Induction Time (OIT) by Differential Scanning Calorimetry (DSC) and antioxidant concentration by High-Performance Liquid Chromatography (HPLC); and (v) analysis of surface morphology by SEM and/or optical microscopy. The major features of the testing procedure are outlined below.

To perform accelerated thermodegradation of polyolefin geosynthetics in circulating air (21% O_2), forced-draft ovens (figure 3.2) with a temperature uniformity of ±1 percent and substantial fresh air intake were used, in compliance with ASTM D-3045, "Heat Aging of Plastics Without Load." To conduct aging in the stagnant atmosphere containing 8% O_2, a special chamber was designed and manufactured. This apparatus, whose schematic and photograph are shown in figure 3.3, provides temperature uniformity of ±1°C, and allows the control of oxygen concentration in the chamber. The specimens are suspended in the oven or in the chamber without pretension and without touching each other. To perform accelerated degradation of polyolefin geosynthetics in stagnant air (21% O_2), a gravity convection oven with a temperature uniformity ±3 percent and minimal air circulation was used.

Geosynthetic specimens are retrieved at five consecutive time intervals. The duration of the time interval is defined for each specific condition of thermo-oxidation. If the obtained data are insufficient for further interpretation, additional retrievals are scheduled. Retrieved specimens are tested for mechanical properties using the Wide-Width Strip Test Method [ASTM D-4595]. All specimens are weighed before and after treatment. OIT determination and HPLC analysis are conducted, where applicable, for the same samples. The study of surface morphology is conducted by SEM for selected samples of aged geosynthetics where significant degradation is observed.

Each retrieval for all conditions of thermo-oxidative degradation (temperature, O_2 concentration, salt contamination, presence of antioxidants) is represented by five specimens retrieved at appropriated time intervals. The number of specimens per retrieval was determined and shown in table 2.18. Specimens of P-3, P-4, and P-9 geotextiles are of full "wide width" dimensions (8 x 8 in [203 x 203 mm]), while the P-1 specimen consists of one rib 6 to 8 in (152 to 203 mm) long.

The OIT for products P-4 and P-9 was measured by DSC at 175°C. OIT for HDPE product P-1 is measured by DSC at 200°C.

The method of determining antioxidant concentration by HPLC is essentially based upon chromatographic analysis. The additives are identified based upon retention time and are quantified by integrating the area of the additive peak and multiplying by a response factor derived from known standards. The concentration of the extract solution is used to calculate the quantity of additives in the polymer by assuming 100-percent extraction efficiency from the matrix.

3.2 LONG-TERM DEGRADATION OF POLYESTER-BASED COMMERCIAL GEOSYNTHETICS

Polyester geosynthetic materials are widely used in highway construction for a variety of purposes. The combination of strength and low creep makes them cost-effective for a number of applications compared to other geosynthetic materials.

It is known that polyester fibers will hydrolyze, with H^+ ions attacking the ester linkage and breaking the chain. This reduces the polymer chain length, with a direct impact on the strength of the fiber. The comprehensive studies in the literature for polyester hydrolysis indicated that rates of hydrolysis are low, but in the context of the lifetime of civil engineering applications, they were not negligible. Therefore, the assessment of the degradation rates for different environmental conditions becomes of prime importance for polyester commercial geosynthetic products.

3.2.1 Commercial geosynthetic products tested.

Three commercial geosynthetic PET materials were selected to represent a wide variety of the products available in the market. As limited by their number, however, these materials represent major types of commercial products: (i) low-tenacity nonwoven PET geotextile; (ii) high-tenacity woven geotextile; and (iii) high-tenacity PVC-coated geogrid. The main properties of these products are presented in table 3.5.

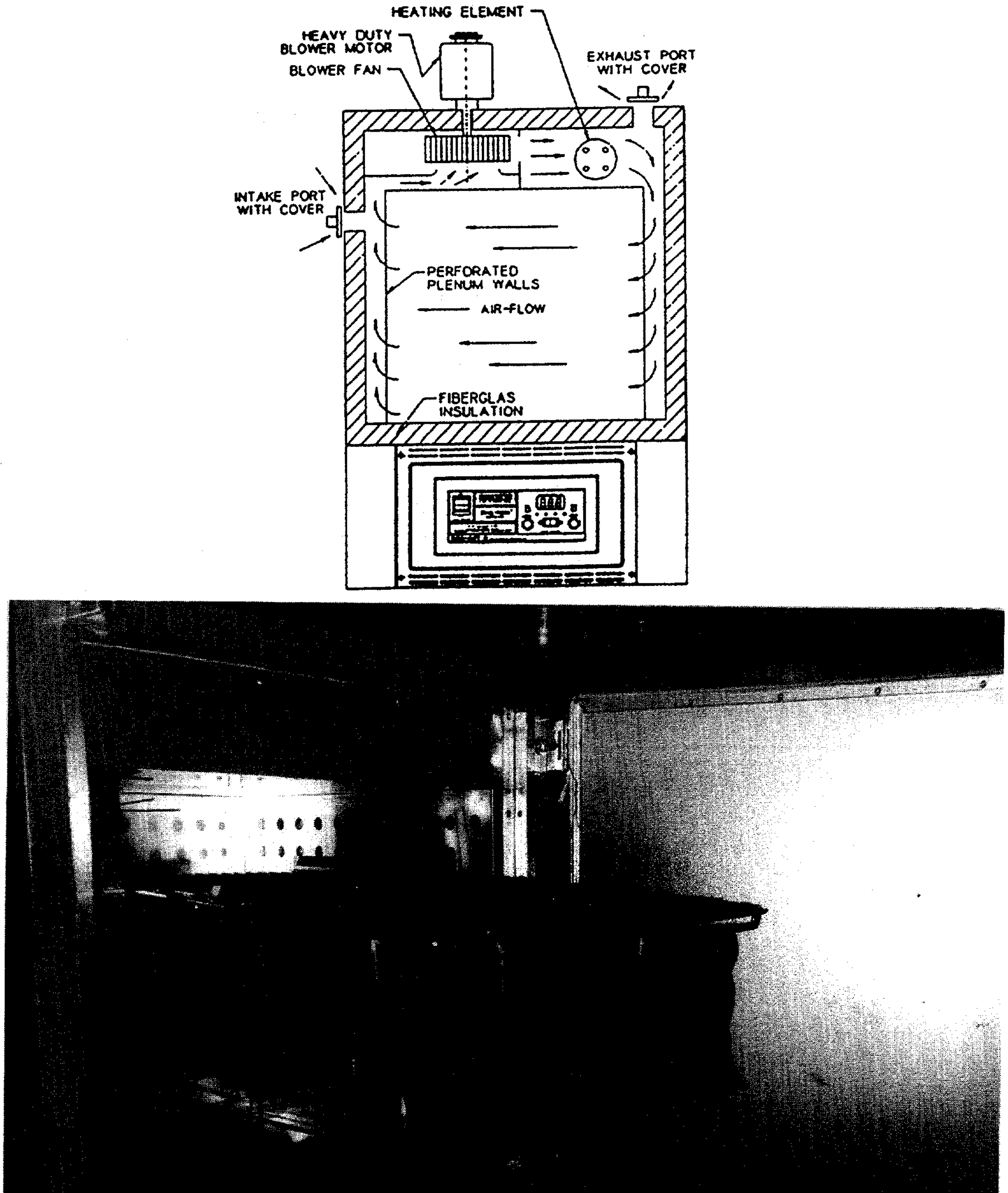


Figure 3.2. Schematic of air flow pattern in force draft oven and photograph of a set-up used for oven aging in circulating air (21% O_2).

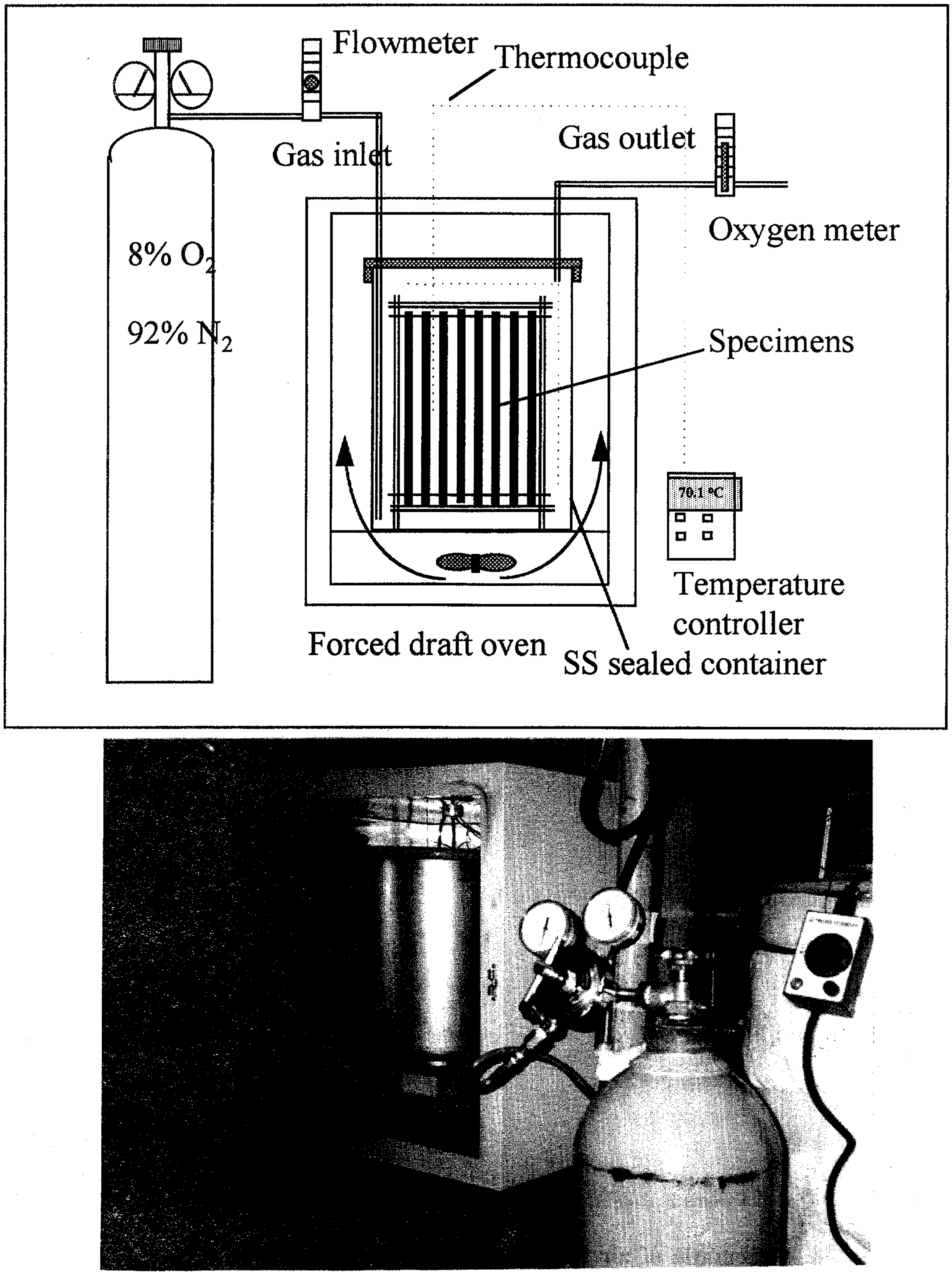


Figure 3.3. Schematic and a photograph of a set-up for oven aging of polyolefin commercial products in stagnant diluted air (8% O_2).

Table 3.5. Physical and chemical properties of selected commercial PET products.

Material	Type	Unit weight (oz/yd^2)	Molecular weight, $\bar{M}_n \times 10^{-3}$	CEG, meq/kg	Tensile strength (lb/in)	Fiber diameter, µm
P-5	Nonwoven, continuous filament spunbonded needlepunched.	16	18.2	44.7	205	27
P-6	Grid, PVC-dipped - PET filament T-811	10.8	30.2	26.7	1040	21
P-7	Woven, from PET filament T-250	10.6	30.6	18.4	544	17

1 oz/yd^2 = 33.9 g/m^2, 1 lb/in = 0.0179 kg/mm

3.2.2 Conditions and variables for hydrolytic degradation, matrix of testing conditions.

The basic principles of hydrolysis indicate that environmental conditions have a strong impact on the hydrolytic degradation of PET materials leading to two different mechanisms of tensile strength deterioration. In order to assess the influence of pH of the environment on the rate of mechanical degradation due to hydrolysis, the following conditions have been selected:

- Neutral environment of distilled water with pH=7.
- Acidic environment of aqueous solution of H_2SO_4 at pH=1.
- Alkaline media at pH=10 and pH=12 by aqueous solutions of NaOH and $Ca(OH)_2$.

In order to achieve measurable changes of tensile strength and molecular weight for the selected commercial geotextiles within the laboratory time limited to 3.5 years, samples of materials are aged at elevated temperatures ranging from 40 to 90°C. At least five consecutive retrievals over the period of exposure were planned for each condition.

Preliminary tests were conducted under severe conditions for the selected PET products to obtain rough estimates of anticipated time to 50-percent strength loss under different pH conditions. Hydrolysis of the P-7 and P-5 products has been performed in 0.1N sodium hydroxide solution at 90°C. The PVC-coated PET geogrid P-6 has been treated separately at the same conditions. The results shown in table 3.6 were used for preliminary estimates of anticipated time to 50-percent strength loss in highly alkaline media.

Table 3.6. Strength loss due to hydrolysis at 90°C in 0.1N (pH=12) sodium hydroxide solution (NaOH).

Period of exposure (days)	P-6, PVC-coated PET geogrid	P-5, PET nonwoven geotextile	P-7, PET woven geotextile
"as received"	1037 lb/in	204 lb/in	550 lb/in
5	-	122 lb/in	-
9	707 lb/in	24 lb/in	337 lb/in
16	-	dissolved	217 lb/in
21	-	-	210 lb/in

1 lb/in = 0.0179 kg/mm

Additional insight has been obtained from data reported by AKZO (1993) on hydrolysis of high-tenacity PET yarn that provided guidelines for the estimates of anticipated time to 50-percent strength loss for hydrolysis in distilled water at pH 7 and in alkaline solution at pH 10. According to these results, the degradation of PET yarn in a distilled water appears slower than the degradation in alkaline solution at elevated temperatures. The anticipated time to 50-percent strength loss in an alkaline solution at pH 10 at 70°C is approximately 500 days. Therefore, it may be assumed that the time to 50-percent strength loss of PET yarn (P-6) at 70°C in distilled water is longer than 500 to 700 days.

Degradation rates of products P-5 and P-7 determined by strength loss are greater than the degradation rate of P-6 . Therefore, it is assumed that the required time of exposure to 50-percent strength loss for these materials is less than for the P-6 product.

Based on limited results of hydrolytic degradation of the P-6 material with and without PVC coating (P-10) presented in table 3.6, it appears that the PVC coating is initially a barrier to viscosity degradation in the 0.1N NaOH solution. However, longer exposure in Phase 3 to assess the effect of the PVC coating on the degradation rate of polyester fibers was undertaken.

Table 3.7. Viscosity degradation of PVC-coated PET product P-6 and PET fibers P-10 in 0.1N (pH=12) solution of NaOH at 90°C.

Material	Viscosity , dl/g			
Days⇒	0	9	11	23
P-6	0.98		0.90	0.83
P-10	0.98	0.85		0.74

Based on the results of hydrolysis under severe exposure conditions as well as on data reported in the literature, the testing matrix for long-term hydrolytic degradation of polyester-based geosynthetics developed is shown in table 3.8.

Table 3.8. Task E, Testing matrix implemented for Phase 3.

Material	Environment							Temper. °C	Anticipated duration of aging (days)
	pH→	1	7	10	10	12	10		
	Solution	H_2SO_4	H_2O	NaOH	$Ca(OH)_2$	NaOH	Sand (NaOH)		
P-5			X					50	1000
								60	700
								70	480
								80	200
P-5		X						50	700
								60	450
								70	250
P-5						X		40	75
								50	60
								60	40
P-5				X				50	800
								60	400
								70	225
P-5							X	70	250
P-5					X			50	620
								60	275
								70	80
P-6			X					50	1000
								60	900
								70	700
								80	250
								90	130
P-6		X						50	700
								60	750
								70	250
P-6						X		40	400
								50	135
								60	60
P-6				X				50	850
								60	365
								70	300
P-10						X		60	60
P-7 P-7		X X						50	700
								60	600
								70	500
								80	250
								90	160

Table 3.8 (cont.)

Material		Environment						Temper.	Anticipated duration of aging
	pH→	1	7	10	10	12	10	°C	(days)
	Solution	H_2SO_4	H_2O	NaOH	$Ca(OH)_2$	NaOH	Sand (NaOH)		
P-7		X						50	750
								60	575
								70	250
P-7						X		40	300
								50	110
								60	75
P-7				X				50	410
								60	365
								70	300
P-7					X			50	1000
								60	450
								70	200
								80	125

3.2.3 Testing procedures.

The accelerated hydrolytic degradation test procedure involves: (i) sample preparation; (ii) treatment of prepared samples in aqueous solutions of different pH; (iii) mechanical testing to determine tensile strength; (iv) chemical testing to determine average molecular weight $\bar{M}_n$ by intrinsic viscosity (η), and CEG measurements; and (v) analysis of surface morphology by SEM and/or optical microscopy. The technical details of those procedures and methods are described in chapter 9 of this report. However, the major features of the testing procedure are outlined below.

Each of the five retrievals for particular conditions of hydrolytic degradation (temperature, pH) is represented by 5 specimens for geotextiles P-5 and P-7, and by 15 specimens for PVC-coated geogrid P-6. The number of specimens was determined from "as received" testing to comply with minimum required number of specimens to be tested by "Standard Test Method for Tensile Properties of Geotextiles" [ASTM D-4595]. The specimens of the P-5 and P-7 geotextiles are of full "wide width" dimensions (8 x 8 in [203 x 203 mm]), while the P-6 specimen consists of one strip 8 to 10 in (203 to 254 mm) long with open cut ends.

The average molecular weight $\bar{M}_n$ for PET materials is a function of intrinsic viscosity $[\eta]$ defined as:

$$\bar{M}_n = \{[\eta]/K\}^{1/\alpha} \qquad (3\text{-}3)$$

where K and α are constants for a particular method of viscosity measurement.

The specimens for the selected commercial geosynthetic products are suspended on a frame without pretension and then submerged into the hydrolytic solution. The specially designed and manufactured reactor (figure 3.4) allows the placement of up to 40 specimens in the heated hydrolytic environment. Intensive stirring of the hydrolytic media is deployed to maintain temperature uniformity of a solution at the level of ±1°C.

Consideration of mechanisms for hydrolytic degradation suggests that in an alkaline environment, the surface erosion of polymeric fibers and yarns may occur due to hydrolysis. Therefore, to assess the rate of hydrolysis in stagnant alkaline media that more closely simulates potential end-use conditions, specimens of the P-5 geotextile were also buried into sand saturated with aqueous solution of NaOH of pH=10 and then hydrolyzed at 70°C. A schematic of a specially developed chamber is presented in figure 3.5.

For each hydrolytic environment and temperature of exposure, the specimens are retrieved at least at five consecutive time intervals and their tensile strength is measured by the Wide-Width Strip Test Method. Intrinsic viscosity measurements along with CEG analysis are conducted for the same specimens. All specimens are weighed before and after the treatment. The study of surface morphology is conducted by SEM for samples of aged geosynthetics where significant degradation is observed.

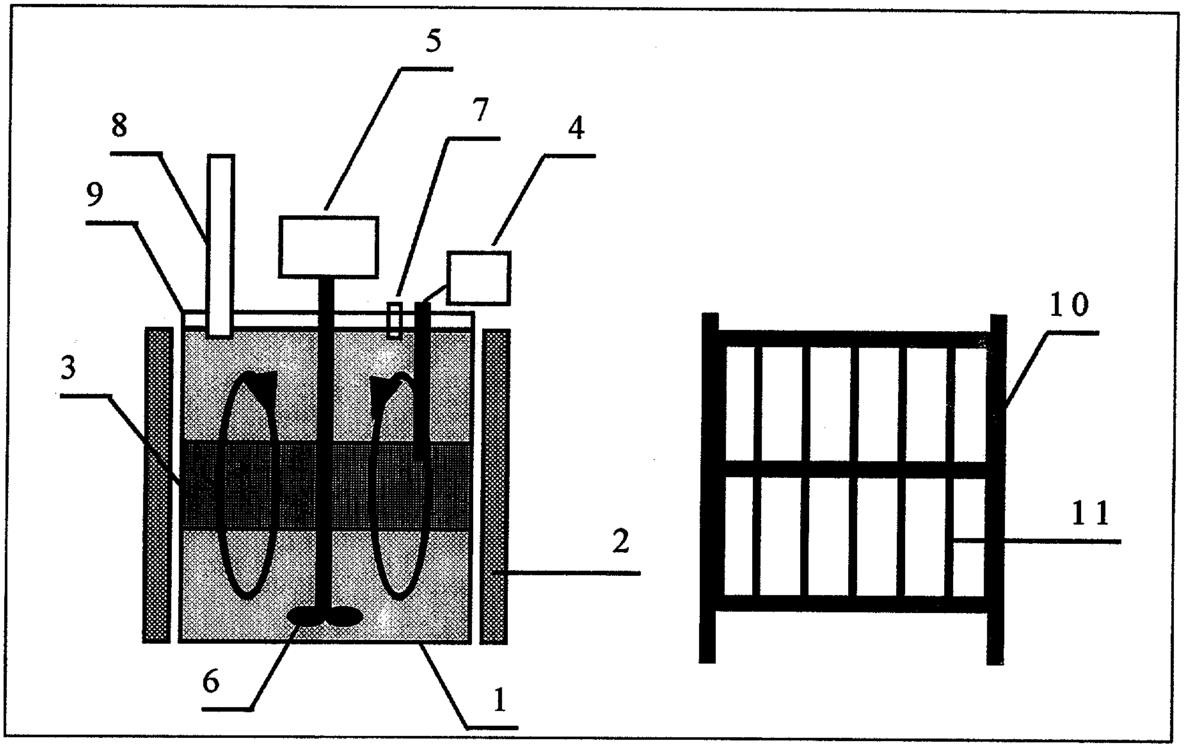


Figure 3.4. **Schematic of temperature-controlled reactor for hydrolytic degradation: 1 - Pyrex glass or SS container, 2 - insulation, 3 - heating tape, 4 - temperature controller, 5 - stirrer, 6 - agitator, 7 - nitrogen inlet port, 8 - condenser, 9 - teflon or SS head, 10 - teflon or SS frame, and 11 - specimens.**

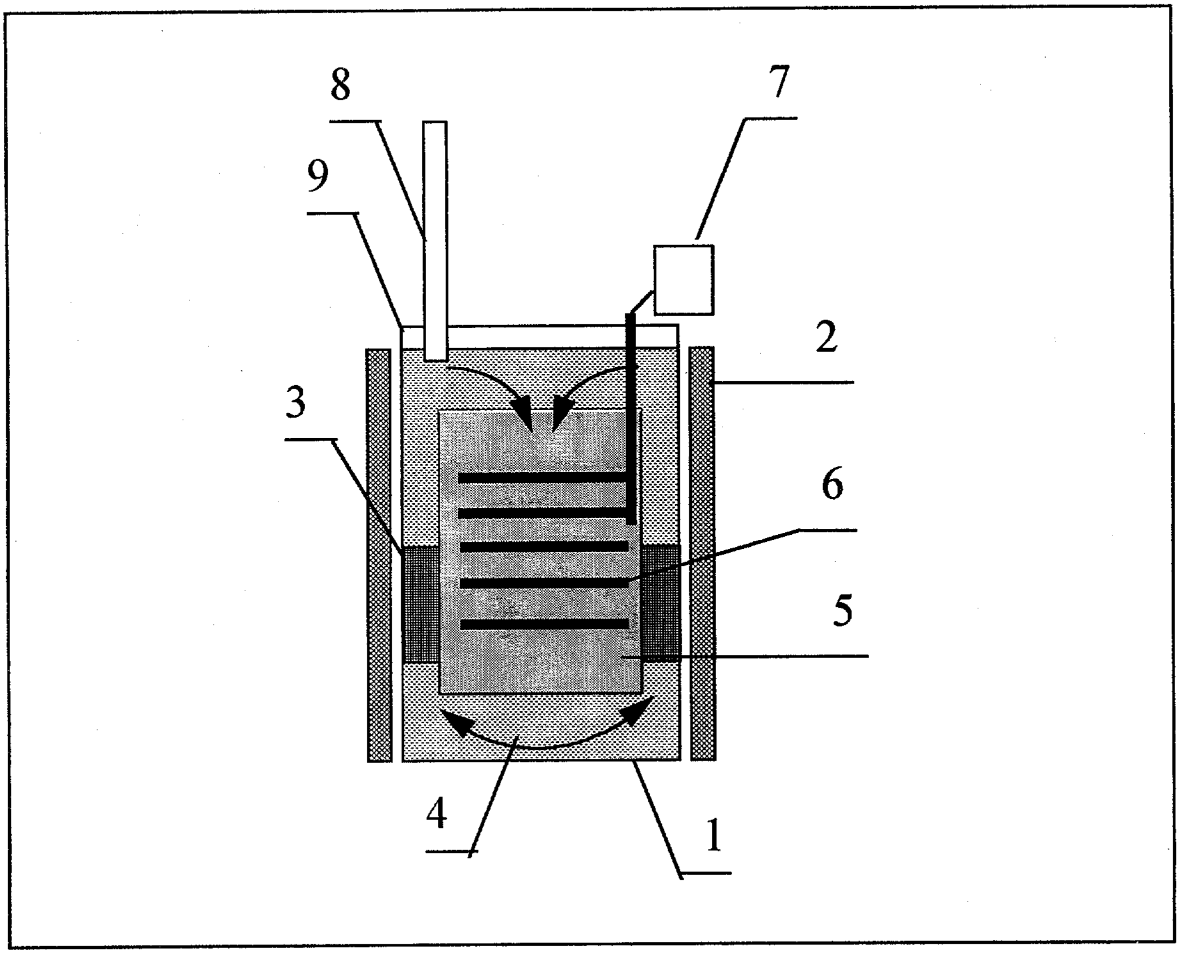


Figure 3.5. **Schematic of temperature-controlled reactor for "in-soil" hydrolytic degradation: 1 - stainless steel container, 2 - insulation, 3 - heating tape, 4 - hydrolytic media (NaOH at pH=10 or pH=12), 5 - inner stainless steel container filled with sand and open to hydrolytic media, 6 - samples of geosynthetic embedded in sand, 7 - temperature controller, 8 - condenser, and 9 - stainless steel head.**

CHAPTER 4

OVEN AGING OF SELECTED COMMERCIAL POLYOLEFIN GEOSYNTHETIC PRODUCTS

4.1 EXPERIMENTAL RESULTS FOR MECHANICAL DEGRADATION OF SELECTED COMMERCIAL POLYOLEFIN GEOSYNTHETIC PRODUCTS

This chapter summarizes the results of mechanical testing for the completed series of tests performed under different environmental conditions (temperature, O_2 pressure, type of air circulation, and salt contamination). Surface morphology studies are discussed only when significant deterioration of mechanical properties is observed for aged geosynthetics.

It appears that each of the selected geosynthetic products tested exhibits a unique pattern of degradation. Therefore, the presentation of experimental results will be on a material-to-material basis.

4.1.1 P-1, HDPE geogrid.

Appearance

The longitudinal rib of the P-1 geogrid appeared to be twisted at the joints of the thicker transverse reinforcement node. The transverse node portion reveals no apparent changes in shape. A similar curling of the HDPE ribs has been observed on samples aged in an atmosphere of diluted air (8% O_2, 92% N_2). The specimens of the P-1 HDPE geogrid aged in air and in diluted air indicated no discoloration of the polymer at any temperature. The SEM study for P-1 indicated that there are no apparent changes in the surface morphology over the period of exposure to elevated temperature ranging from 80 to 110°C, in any environment.

Weight Loss

All the observed weight changes do not exceed 2 percent of initial weight, regardless of temperature or environment.

Mechanical Properties

Table 4.1 summarizes the results for the P-1 geogrid aged in air and in a stagnant atmosphere containing 8 percent O_2 balanced by N_2.

Results indicate that strain at peak strength increases over the period of exposure to elevated temperature. It appears that relative changes of strain at peak strength (ratio of measured values for aged specimens to values obtained for material "as received") are greater than relative changes of tensile strength. For instance, the strain at failure increased by a factor of 3 for specimens aged at 110°C for 150 days, while the observed strength loss for the same specimens is about 11 percent. Figure 4.1 summarized results of determination of the tensile strength and strain at failure for the P-1 geogrid, aged at different temperatures.

Table 4.1. Summary of test results for P-1 HDPE geogrid oxidized in different environments.

Temperature °C	Exposure, days	Retained strength ratio(1)				Retained strain ratio at peak strength(2)	
		Circulating air, 21% O_2		Stagnant diluted air, 8% O_2		Circulating air, 21% O_2	Stagnant diluted air, 8% O_2
		Strength	Variation Coefficien	Strength	Variation Coefficient	Strain at peak strength	Strain at peak strength
80	0	1	0.05	N/A	N/A	1	N/A
	100	0.90	0.05	N/A	N/A	2.4	N/A
	200	0.79	0.05	N/A	N/A	4.5	N/A
	300	0.68	0.05	N/A	N/A	4.9	N/A
	400	0.63	0.05	N/A	N/A	5.8	N/A
	500	0.68	0.06	N/A	N/A	7.1	N/A
	700	0.80	0.07	N/A	N/A	3.9	N/A
	1100	0.42	0.04	N/A	N/A	2.5	N/A
90	0	1	0.05	1	0.05	1	1
	100	0.98	0.03	0.91	0.05	1.6	1.6
	200	0.90	0.04	0.71	0.03	1.35	1.9
	300	0.82	0.07	0.86	0.03	1.22	2.2
	475	0.70	0.10	0.94	0.03	1.05	2.5
	700	0.98	0.10	0.96	0.20	1.06	1.9
	900	0.89	0.08	N/A	N/A	1.06	N/A
	1100	N/A	N/A	0.70	0.8	N/A	1.5
100	0	1	0.05	1	0.05	1	1
	80	0.95	0.05	0.99	0.04	1.8	1.8
	160	0.93	0.03	0.96	0.03	1.65	2.15
	240	0.89	0.04	0.91	0.04	1.95	1.8
	415	0.80	0.06	0.92	0.09	1.4	1.5
	600	0.96	0.03	N/A	N/A	2.0	N/A
	880	N/A		0.81	0.13	N/A	1.9
110	0	1	0.05	1	0.05	1	1
	50	0.87	0.05	0.87	0.06	1.6	2.5
	100	0.91	0.05	0.87	0.09	1.6	2.7
	150	0.81	0.03	0.89	0.11	2.1	3.0
	200	0.79	0.05	N/A	N/A	N/A	N/A

(1) Ratio between remaining and "as received" values of peak tensile strength;

(2) Ratio between remaining and "as received" values of strain at peak strength

N/A - Not available, testing was not performed under this condition.

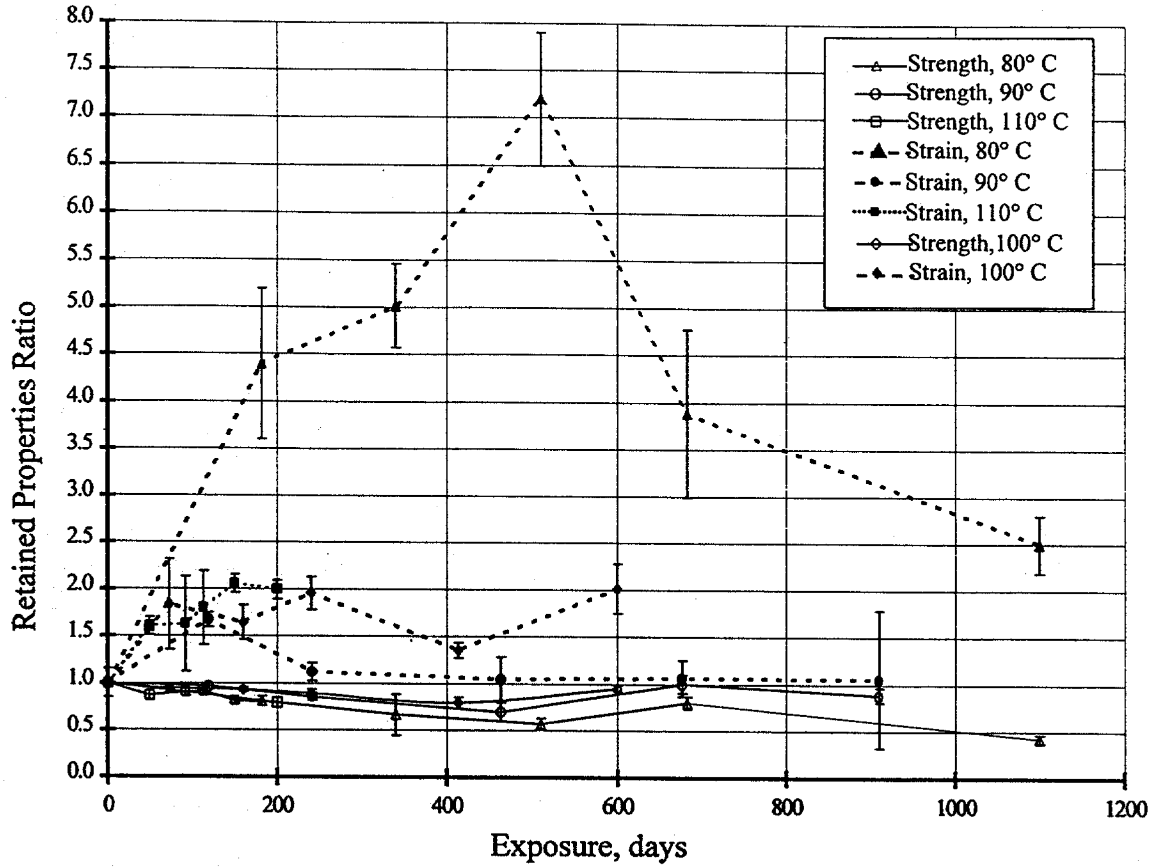
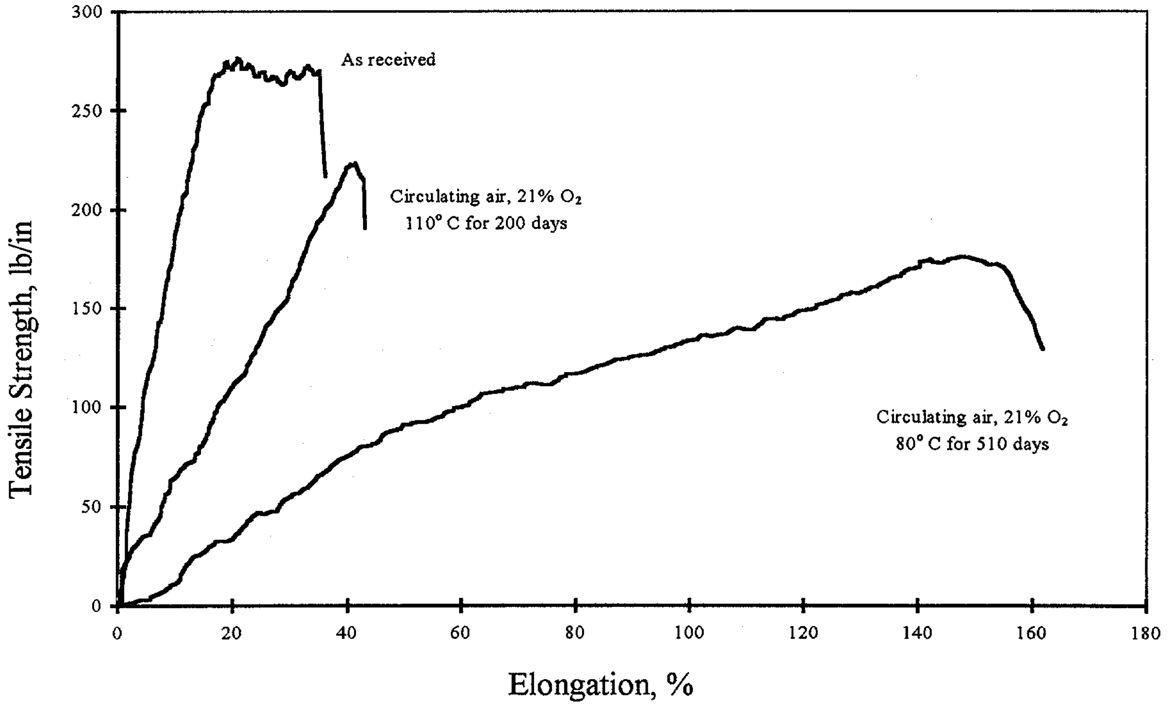


Figure 4.1. Change of mechanical properties for P-1 geogrid during oven aging in circulating air at 21% O_2.

Load-Strain Relationships for P-1 Aged in Circulating Air

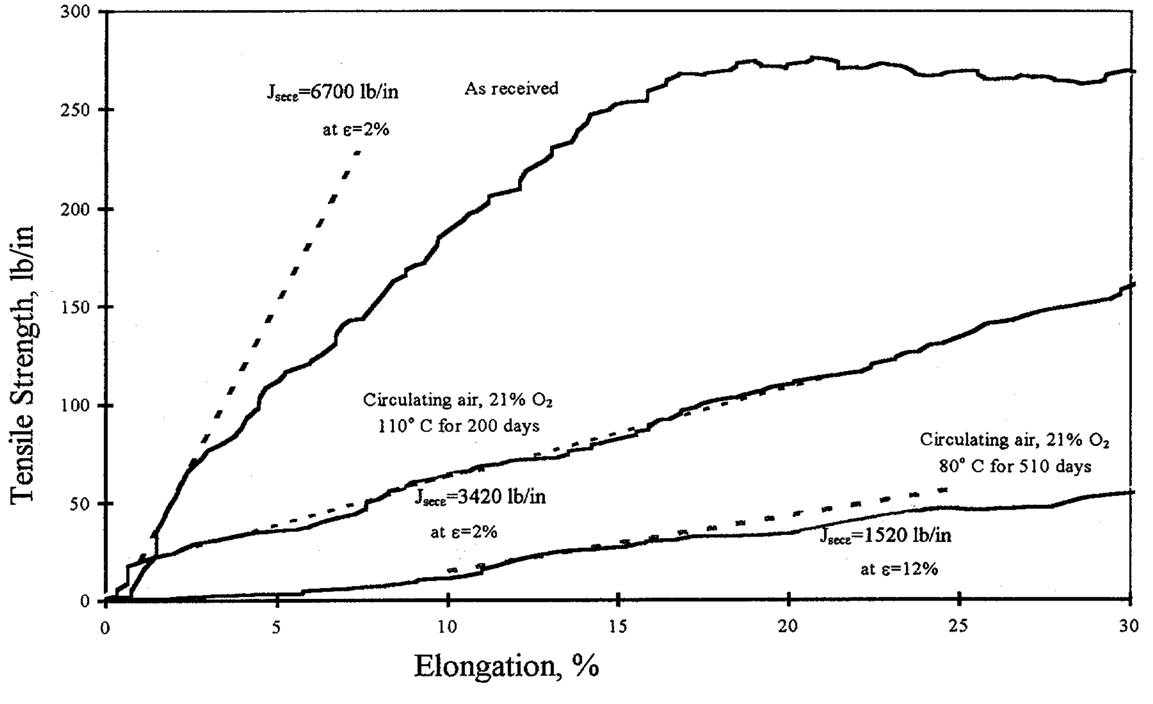
The load-strain relationship may be described by three parameters that can be used to assess the effect of oven aging on mechanical performance of geosynthetic materials. In this study, the change in peak tensile strength and corresponding strain are characterized by a ratio of aged parameters to parameters obtained on virgin samples, as discussed in previous sections. In engineering applications, initial modulus is of importance and this parameter, a fundamental characterization of a material, depends primarily on chemical composition and structural features of a polymer. Results reported in the literature [Allen and Bathurst, 1994; 1996], indicated high variability of initial modulus determined for industrial geosynthetics and, therefore, the offset secant modulus at low strain was suggested as an index parameter to minimize the variability of measured characteristics. This approach is utilized in this study to characterize mechanical behavior at low strain for the products tested. Alternately, retained yield strain tabulated in table 4.1 may be compared.

Figure 4.2 illustrates typical load-strain curves for the P-1 product, virgin and aged in circulating air at 80°C and 110°C.



1 lb/in = 0.0179 kg/mm

Figure 4.2. Typical load-strain curves for virgin and oven-aged P-1 product.



1 lb/in = 0.0179 kg/mm

Figure 4.3. Change in index load-strain behavior due to oven aging in circulating air for P-1 product.

Figure 4.3 shows that there is a significant change in index properties due to oven aging for the P-1 product.

Estimates of the offset secant modulus are shown in table 4.2. In this study, confidence limits on values of the offset modulus have not been developed. The obtained results only indicate trends in the data.

Table 4.2. Offset modulus for oven-aged P-1 product.

Condition	Virgin	Circulating air, 21% O_2, 80°C, 510 days	Circulating air, 21% O_2, 110°C, 200 days
Offset modulus $J_{sec\varepsilon}$, lb/in	6700	1520	3420
Strain, % @ $J_{sec\varepsilon}$	2	12	2
Tensile strength loss, %	0	42	20

1 lb/in = 0.0179 kg/mm

The developed relationships (offset modulus or retained strain) suggest that the physical nature of P-1 has been changed by the oven-aging process at temperatures of 80°C and greater. Therefore, interpretation and extrapolation of this strength data are fraught with uncertainties.

4.1.2 P-3, nonwoven continuous filament geotextile.

Appearance

Geosynthetic product P-3 exhibits discoloration over the period of oven aging in circulating air. Salt-contaminated specimens exhibit yellow-brownish spots on the surface over the period of oven aging. The degree of the discoloration increases as time of exposure increases. The phenomenon of discoloration has not been observed on samples of the P-3 geotextile treated in a diluted air atmosphere. The P-3a textile, which is the base material for the commercial product P-3, contains no color additives and, therefore, no change in initial color (off-white) has been observed. Neither shrinkage nor swelling have been observed for P-3 and P-3a materials over the period of exposure.

SEM study of the fiber surface morphology indicated that there are no apparent changes on the fiber surface on a microlevel at a magnification of 3000x, for the P-3 and P-3a geotextiles, aged in different atmospheric environments and at temperatures varying from 50 to 90°C.

Weight Loss

The monitoring of weight changes during exposure to elevated temperatures in different atmospheres indicated that there are no statistically significant variations of weight for the P-3 and P-3a geotextiles.

Mechanical Properties

The samples of the nonwoven commercial geotextile P-3 were exposed to five temperatures of 50, 60, 70, 80, and 90°C, in circulating air. The progressive strength loss versus time curves for the P-3 geotextile, shown in figure 4.4, indicate a nonlinear strength loss and the presence of an induction period. The induction period is defined as the initial period of oven aging, when no statistically significant changes of tensile strength are observed and can be considered as the time required for significant antioxidant depletion (Griveson et al. 1961). It appeared that the induction period increases as the temperature of the exposure decreases. The highest temperature of exposure of 90°C appeared to be extremely severe for this product, which almost lost its total strength by the end of the 170-day exposure. At lower temperatures, the strength loss versus time curves display a non-linear behavior after the induction period. There is an indication that the retained strength tends to decrease at a slower rate of about 40 to 50 percent of initial values.

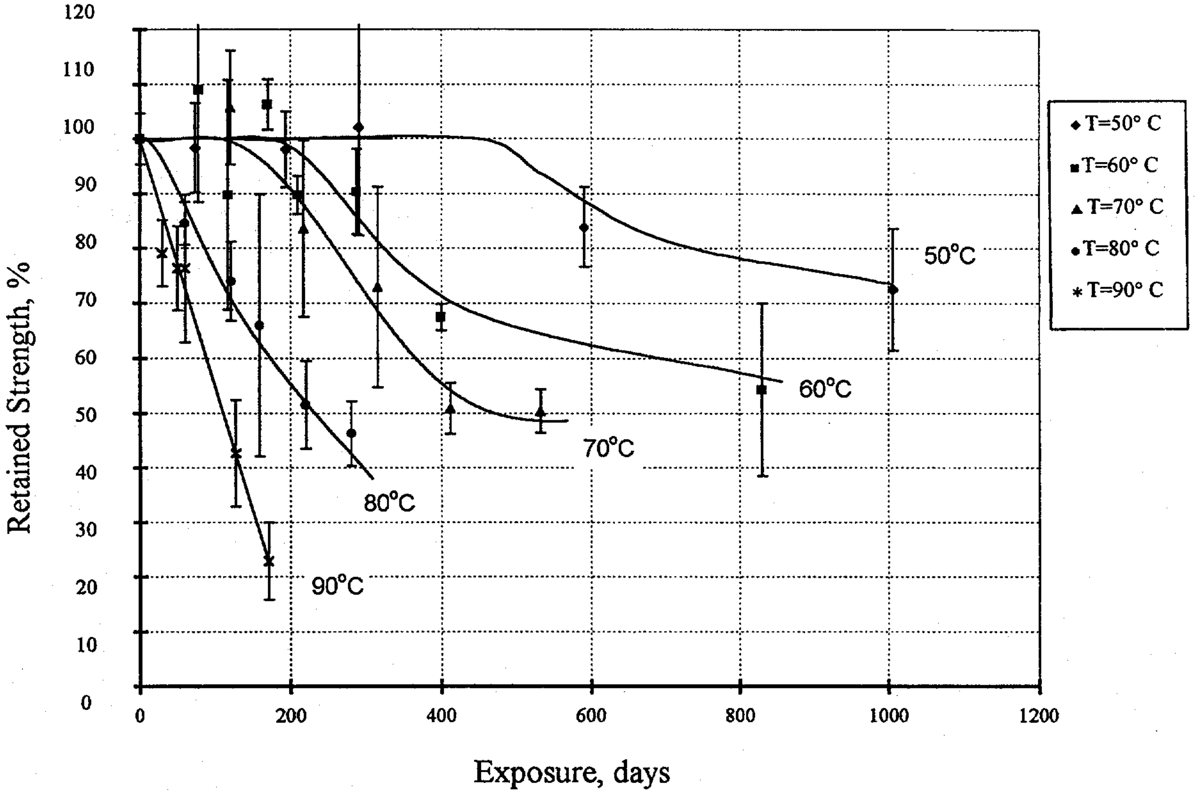


Figure 4.4. Tensile strength loss for P-3 geotextile due to aging in circulating air at 21% O_2.

The summary of the results for mechanical testing for P-3, aged at elevated temperatures in circulating air at 21 percent O_2, is shown in table 4.3.

Table 4.3. Tensile strength loss for P-3 commercial geotextile in circulating air at 21% O_2.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
50	0	1.00	0.05	1.00	0.13	1.00
	74	0.98	0.08	0.91	0.10	1.08
	194	0.98	0.07	0.82	0.07	1.20
	290	1.02	0.20	0.92	0.09	1.11
	591	0.84	0.07	0.61	0.08	1.37
	1070	0.73	0.11	0.49	0.13	1.49
60	0	1	0.05	1.00	0.13	1.00
	78	1.09	0.20	1.13	0.17	0.97
	117	0.90	0.21	0.94	0.16	0.96
	170	1.06	0.05	0.89	0.15	1.20
	209	0.90	0.03	0.84	0.10	1.07
	287	0.90	0.08	0.89	0.10	1.02
	400	0.67	0.02	0.65	0.12	1.04
	830	0.54	0.16	0.64	0.20	0.85
70	0	1.00	0.05	1.00	0.13	1.00
	120	1.06	0.10	0.54	0.29	1.96
	217	0.84	0.16	0.68	0.15	1.24
	315	0.73	0.18	0.60	0.07	1.22
	412	0.51	0.05	0.74	0.22	0.68
	532	0.50	0.04	0.59	0.23	0.86
80	0	1.00	0.05	1.00	0.13	1.00
	60	0.85	0.04	1.01	0.11	0.83
	121	0.74	0.07	0.67	0.05	1.11
	159	0.66	0.24	0.51	0.09	1.29
	220	0.52	0.08	0.35	0.10	1.48
	280	0.46	0.06	0.34	0.03	1.36
90	0	1.00	0.05	1.00	0.13	1.00
	30	0.79	0.06	0.63	0.14	1.26
	50	0.76	0.08	0.70	0.07	1.09
	60	0.76	0.14	0.91	0.11	0.84
	127	0.43	0.10	0.49	0.15	0.88
	171	0.23	0.07	0.37	0.27	0.62

Results indicate (table 4.4) that the rate of mechanical degradation in a circulating oven is at least two times slower for the P-3 commercial product than the rate of mechanical degradation of the P-3a research-grade textile containing a minimum amount of antioxidant additive (figure 4.5).

Table 4.4. Tensile strength loss for P-3a research-grade geotextile in circulating air at 21% O_2.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
50	0	1.00	0.11	1.00	0.08	1.00
	124	0.90	0.03	0.58	0.17	1.54
	236	0.80	0.20	0.62	0.03	1.29
	200	0.72	0.12	0.64	0.25	1.13
	312	0.67	0.17	0.44	0.20	1.50
	436	0.63	0.21	0.85	0.60	0.75
60	0	1.00	0.11	1.00	0.08	1.00
	82	0.79	0.16	0.63	0.03	1.26
	162	0.70	0.13	0.78	0.15	0.90
	201	0.69	0.12	0.71	0.33	1.18
	281	0.58	0.25	0.64	0.09	0.89
	363	0.54	0.20	0.74	0.21	0.73
70	0	1.00	0.11	1.00	0.08	1.00
	42	0.78	0.15	0.83	0.11	0.94
	80	0.71	0.19	0.62	0.10	1.14
	122	0.75	0.21	0.69	0.25	1.09
	160	0.47	0.19	0.56	0.21	0.84
	202	0.27	0.05	0.41	0.11	0.64
80	0	1.00	0.11	1.00	0.08	1.00
	20	0.99	0.18	0.94	0.09	1.05
	40	0.74	0.21	0.69	0.12	1.07
	63	0.51	0.18	0.67	0.07	0.76
	83	0.48	0.06	0.64	0.15	0.75
	103	0.35	0.12	0.44	0.09	0.79

Results indicate that the research-grade textile P-3a exhibits high variations of measured values for tensile strength at failure over the period of exposure to elevated temperatures. This phenomenon may be attributed to the lack of antioxidant additives, resulting in the nonuniform oxidation of a base polymer. It could also be a result of higher variability in the "as received" specimens as shown in table 2.18.

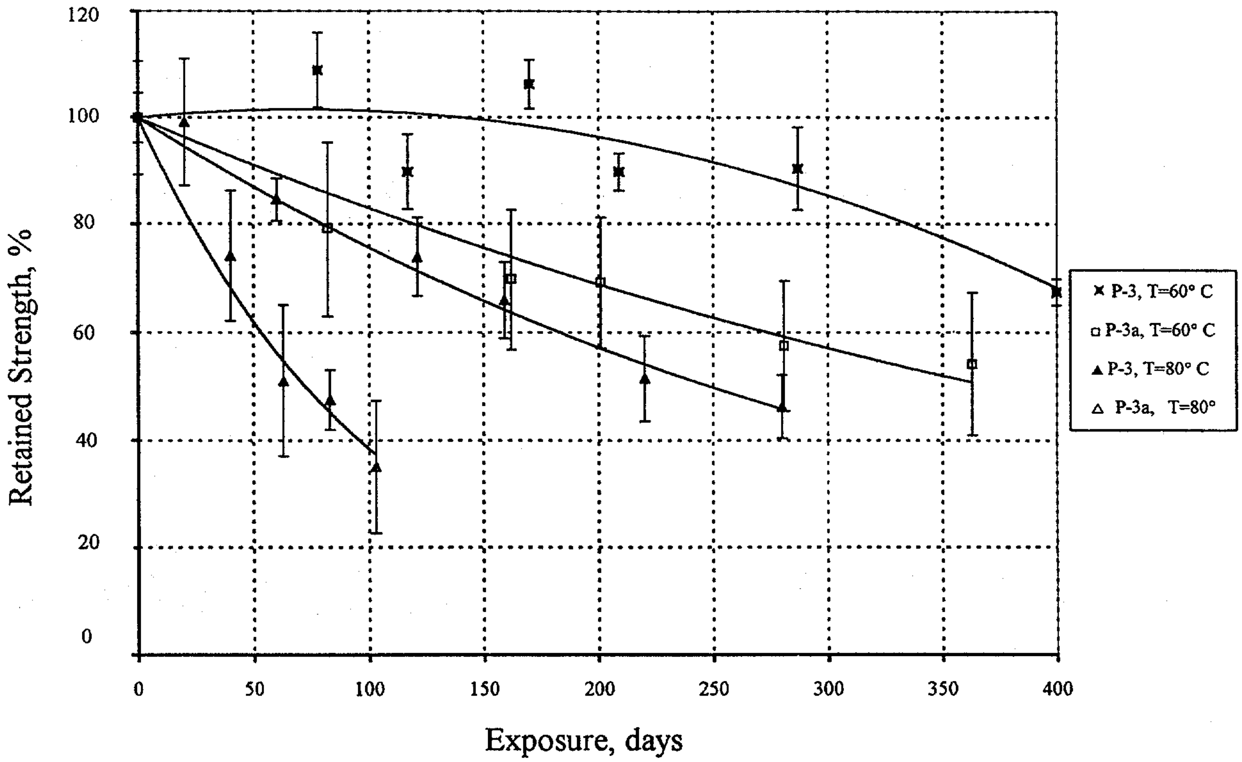


Figure 4.5. Effect of antioxidant additives on the rate of thermo-oxidation for the P-3 commercial product and P-3a research-grade textile.

Samples of P-3 commercial product as well as samples of P-3a research-grade textile were exposed to elevated temperatures of 70, 80, and 90°C in a stagnant atmosphere of 8-percent oxygen balanced by nitrogen. The summary of the results for mechanical testing for specimens of P-3 commercial product, aged in circulating air and in stagnant diluted air, is shown in table 4.5.

Table 4.5. Tensile strength loss for P-3 commercial geotextile in circulating air and stagnant diluted air ovens.

Temperature, °C	Exposure, days	Circulating air, 21% O_2		Stagnant diluted air, 8% O_2	
		Retained peak tensile strength[1]	Coefficient of variation	Retained peak tensile strength	Coefficient of variation
70	0	1	0.05	1	0.05
	100	1	0.10	N/A	
	200	0.83	0.05	1.30	0.10
	300	0.73	0.07	1.20	0.16
	400	0.50	0.05	1.10	0.16
	500	0.50	0.04	1.08	0.04
	800	N/A	N/A	0.83	0.14
80	0	1	0.05	1	0.05
	50	0.89	0.04	N/A	N/A
	100	0.78	0.07	0.74	0.16
	150	0.67	0.12	N/A	N/A
	200	0.56	0.08	0.82	0.09
	250	0.49	0.06	N/A	N/A
	300	0.45	0.06	1.01	0.05
	400	N/A	N/A	1.08	0.05
90	0	1	0.05	1	0.05
	50	0.76	0.07	1.00	0.09
	100	0.55	0.09	0.88	0.12
	150	0.32	0.07	0.99	0.17
	200	N/A	N/A	0.66	0.05
	250	N/A	N/A	0.63	0.05
	300	N/A	N/A	0.59	0.05

(1) The data for circulating air has been interpolated to match retrievals for diluted air.
N/A - not available

The variability of measured values of the tensile strength for each retrieval of the P-3 geotextile appears to be higher than variability obtained for the same material "as received." For some samples, the coefficient of variation for measured tensile strength is about 10 percent. However, it appears that the increase in the variability does not have any pattern with regard to either testing temperature or duration of aging.

Results indicate that for P-3 there is no statistically significant change for the secant modulus at failure, defined as a modulus corresponding to peak tensile strength.

Results for product P-3 indicate that the rate of mechanical degradation in stagnant diluted air is much slower than the rate of degradation in circulating air ovens. It is observed that in stagnant diluted air (8 percent O_2), product P-3 exhibits an initial tensile strength increase when tested at 70°C. However, tensile strength decreases with an increase in exposure time. The rate of mechanical strength loss in a stagnant diluted air oven appears to be slower that the rate of degradation in a circulating air oven.

Additional specimens of P-3 were contaminated in $FeCl_3$ solution at two concentrations, 0.2 percent and 2 percent. Immersion in a 0.2-percent solution resulted in a 0.8-percent weight-to-weight contamination of the specimens. Comparison between table 4.3 and table 4.6 indicates that the observed rate of mechanical degradation for the P-3 specimens contaminated at the level of 0.8-percent w/w, appears to be within the range of the observed degradation rate for non-contaminated specimens.

Table 4.6. Results for P-3 geotextile contaminated by $FeCl_3$ at 0.8% w/w and aged in circulating air at 21% O_2.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
60	0	1.00	0.05	1.00	0.13	1.00
	20	1.00	0.04	0.47	0.03	2.13
	80	1.08	0.06	0.48	0.12	2.23
	140	0.99	0.09	0.39	0.04	2.51
	220	0.94	0.10	0.38	0.11	2.44
	300	0.85	0.06	0.90	0.01	0.94
70	0	1.00	0.05	1.00	0.13	1.00
	63	0.88	0.02	0.68	0.05	1.29
	120	0.83	0.12	0.73	0.20	1.14
	180	0.77	0.05	0.61	0.01	1.27
	240	0.81	0.04	0.74	0.07	1.10
	300	0.72	0.09	0.69	0.08	1.05
80	0	1.00	0.05	1.00	0.13	1.00
	25	0.86	0.01	0.65	0.10	1.33
	50	0.81	0.07	0.89	0.11	0.91
	88	0.78	0.21	0.46	0.12	1.67
	120	0.70	0.16	0.48	0.13	1.47
	150	0.73	0.19	0.52	0.22	1.41

Results for the P-3 contaminated by $FeCl_3$ less than 1-percent w/w indicate that this geotextile becomes more brittle over the period of exposure to the elevated temperature. The most pronounced change is observed when aged at 60°C.

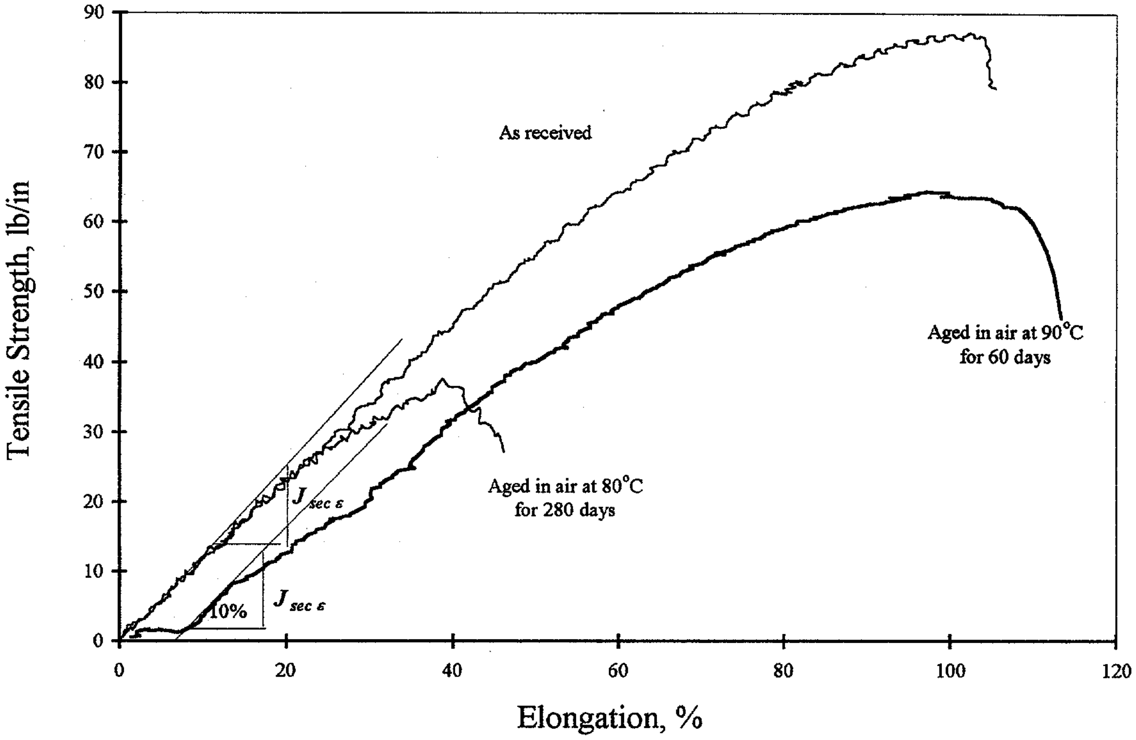
The specimens of the P-3 product immersed in the 2-percent solution of $FeCl_3$ resulted in levels of 8 to 10 percent weight to weight, and appeared to be more susceptible to oxidation. Table 4.7 indicates a significant increase in degradation rate for the more heavily contaminated specimens of the P-3.

Table 4.7. Results for P-3 geotextile contaminated by $FeCl_3$ at 8% to 10% w/w and aged in circulating air at 21% O_2.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
60	0	1.00	0.05	1.00	0.13	1.00
	25	0.95	0.09	1.06	0.21	0.89
	60	0.90	0.11	0.96	0.13	0.94
	90	0.89	0.15	N/A	N/A	N/A
	120	0.89	0.18	0.89	0.05	1.00
	150	0.90	0.04	N/A	N/A	N/A
70	0	1.00	0.05	1.00	0.13	1.00
	25	0.85	0.04	1.08	0.28	0.78
	52	0.84	0.05	0.91	0.20	0.92
	70	0.96	0.05	0.86	0.12	1.11
	101	0.75	0.11	0.80	0.06	0.94
	112	0.62	0.15	0.77	0.16	0.80
80	0	1.00	0.05	1.00	0.13	1.00
	25	0.75	0.02	1.04	0.15	0.72
	40	0.74	0.04	0.29	0.16	2.58
	52	0.71	0.09	0.27	0.06	2.66
	60	0.71	0.07	0.33	0.02	2.12
	70	0.59	0.12	0.31	0.18	1.91

Load-Strain Relationships for Oven Aged P-3 Product

Figure 4.6 shows typical load-strain curves for P-3 product, including: (i) “as received”, (ii) aged in circulating air at 80°C for 280 days with more than 50-percent strength loss, and (iii) aged in circulating air at 90°C for 60 days with 34-percent strength loss. The initial part of the load-strain curves appears to be identical for virgin specimens and specimens aged at 80°C exhibiting almost no curvature at low strain values. However, some specimens did exhibit pronounced curvature on the load-strain curve at low strain as shown on figure 4.6 for samples aged at 90°C. Comparison of the initial secant modulus for virgin and aged materials exhibiting this behavior is difficult due to the uncertainty in determining the slope of the load-strain curve at low strain value although tabulated ratios are shown in table 4.3. Therefore, the values of the offset modulus $J_{sec\varepsilon}$ [Allen and Bathurst, 1994; 1996] were calculated in addition at 10-percent strain for different load-strain curves with the results presented in table 4.8.



1 lb/in = 0.0179 kg/mm

Figure 4.6. Load-strain curves for virgin and aged samples of P-3.

Table 4.8. Offset modulus for virgin and aged P-3 geosynthetic.

Condition	Virgin	Circulating air, 21% O_2, 80°C, 280 days	Circulating air, 21% O_2, 90°C, 60 days
Offset modulus $J_{sec\varepsilon}$ lb/in	116	115	112
Tensile strength loss, %	0	53	34

1 lb/in = 0.0179 kg/mm

The results indicate that there is no significant difference in the offset secant modulus for virgin and aged specimens of the P-3 product, suggesting that oven aging did not fundamentally alter this material. Secant modulus data suggest greater variations, but do not alter the conclusion.

4.1.3 P-4, nonwoven staple geotextile.

Appearance

Commercial polypropylene product P-4 does not exhibit any apparent changes in color over the period of oven aging. The P-4a textile, which is the base material for the commercial product P-4, contains no color additives and, therefore, no change in initial color has been observed. Neither shrinkage nor swelling have been observed for P-4 and P-4a materials over the period of aging in circulating air and stagnant diluted air ovens.

Preliminary analysis of the microscopic changes on the fiber surface morphology has been conducted by SEM. The microphotographs of the fibers "as received" and fibers taken from the specimens aged in a circulating air oven at 50°C and 70°C are shown in figure 4.7. The surface of the virgin fibers appears to be smooth and clean. However, there are traces of initial cracks on the surface of virgin fibers transverse to the fiber length. The SEM study strongly indicates progressive development of circumferential cracks on the fiber surface during exposure to the elevated temperatures in circulating air.

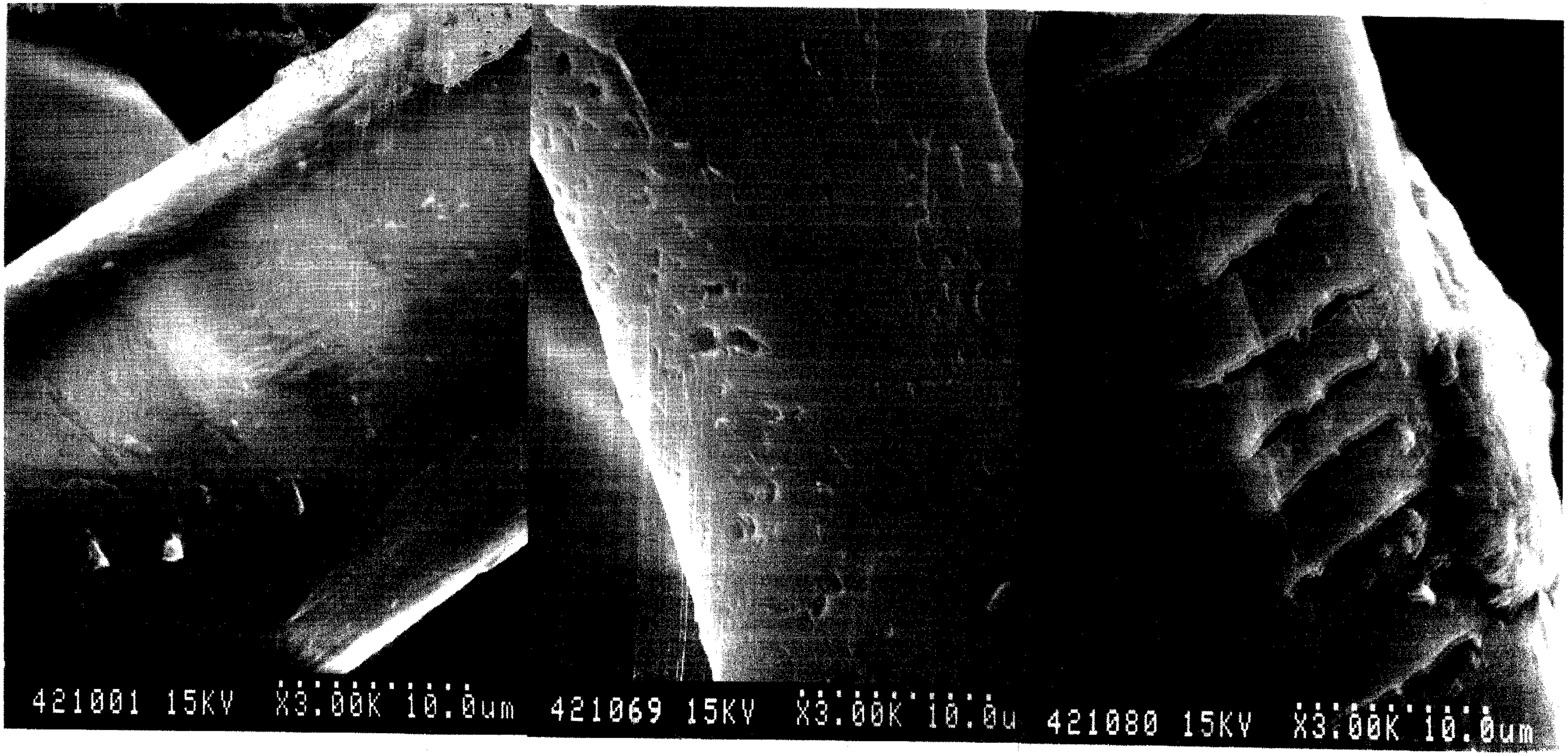
The SEM study of the fiber surface morphology for the P-4 geotextile aged in stagnant diluted air (8% O_2) at 70°C indicated that there is no apparent circumferential cracks on the surface of fibers after the 473-day thermal treatment. No changes of the fiber diameters have been observed.

Weight Loss

Changes of weight of P-4 and P-4a measured over the period of exposure in air to different temperatures are minimal. The weight changes measured for both P-4 and P-4a products vary within the range of 0 to 2 percent. In a diluted air atmosphere (8% oxygen, 92% nitrogen), no statistically significant variations of weight have been observed for either P-4 or P-4a geotextiles.

Mechanical properties

Specimens of P-4 geotextile were exposed to four elevated temperatures of 50, 60, 70, and 80°C in circulating air ovens. The observed development of fiber cracking explains the rapid loss of tensile strength during the thermo-oxidation in intense circulating air. It appears that the material loses 50-percent or more of its initial strength during the first 50 days of exposure in temperatures varying from 50 to 80°C as shown in table 4.9. The summarized results of tensile strength loss are presented in figure 4.8 for P-4. Mechanical degradation of the P-4a geotextile (see table 4.10), which is reported to contain minimum amounts of antioxidant additives, appears to be similar to the degradation behavior of the commercial P-4 geotextile.



(a) P-4 “As received”

(b) P-4, Forced Air, 50°C
69 Days

(c) P-4, Forced Air, 70°C
80 Days

Figure 4.7. SEM microphotographs at a magnification of 3000x for P-4 fibers: (a) "as received", (b) 50°C for 69 days, (c) 70°C for 80 days, aged in circulating air at 21% O_2.

Table 4.9. Tensile strength loss for P-4 commercial geotextile aged in intense circulating air.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
50	0	1.00	0.03	1.00	0.08	1.00
	10	0.81	0.04	1.09	0.11	0.75
	14	0.78	0.05	0.65	0.08	1.20
	69	0.46	0.13	0.40	0.09	1.16
	112	0.44	0.03	0.54	0.18	0.83
	160	0.40	0.02	0.48	0.04	0.83
	258	0.35	0.01	0.42	0.03	0.84
	272	0.35	0.02	0.46	0.04	0.76
60	0	1.00	0.03	1.00	0.08	1.00
	10	0.66	0.01	0.89	0.14	0.74
	26	0.57	0.04	0.70	0.18	0.81
	46	0.44	0.03	0.45	0.08	0.97
	82	0.41	0.01	0.42	0.04	0.96
	126	0.35	0.03	0.39	0.10	0.90
	162	0.37	0.02	0.37	0.02	0.99
	208	0.36	0.02	0.40	0.02	0.88
70	0	1.00	0.03	1.00	0.08	1.00
	17	0.47	0.04	0.39	0.01	1.21
	31	0.40	0.04	0.44	0.03	0.89
	42	0.32	0.01	0.54	0.02	0.59
	80	0.33	0.01	0.47	0.04	0.69
	160	0.28	0.03	0.34	0.04	0.84
	202	0.26	0.01	0.40	0.06	0.66
80	0	1.00	0.03	1.00	0.08	1.00
	7	0.93	0.05	0.78	0.10	1.20
	9	0.45	0.09	0.53	0.16	0.85
	12	0.38	0.03	0.57	0.05	0.67

Table 4.9 (cont.)

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
80	20	0.37	0.01	0.44	0.05	0.83
	83	0.29	0.02	0.30	0.04	0.99
	103	0.29	0.01	0.28	0.03	1.02

Table 4.10. Tensile strength loss for P-4a research-grade geotextile aged in intense circulating air.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
50	0	1.00	0.13	1.00	0.14	1.00
	50	0.58	0.02	0.52	0.11	1.12
	83	0.47	0.06	0.52	0.06	0.90
	104	0.59	0.06	0.43	0.16	1.39
	160	0.51	0.02	0.52	0.06	0.99
	181	0.50	0.05	0.38	0.22	1.30
	264	0.49	0.05	0.39	0.23	1.25
60	0	1.00	0.13	1.00	0.14	1.00
	25	0.65	0.20	0.71	0.34	0.92
	40	0.52	0.04	0.59	0.05	0.87
	82	0.47	0.03	0.54	0.05	0.86
	119	0.49	0.05	0.48	0.03	1.03
	161	0.59	0.14	0.45	0.05	1.30
	201	0.50	0.11	0.57	0.18	0.87
70	0	1.00	0.13	1.00	0.14	1.00
	13	1.04	0.27	0.79	0.16	1.31
	27	0.53	0.08	0.56	0.14	0.96
	42	0.47	0.04	0.62	0.11	0.75
	58	0.41	0.06	0.55	0.19	0.74

Table 4.10 (cont.)

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
	73	0.37	0.05	0.48	0.02	0.77
80	0	1.00	0.13	1.00	0.14	1.00
	12	0.81	0.08	1.09	0.07	0.74
	20	0.96	0.24	0.62	0.40	1.54
	27	0.51	0.09	0.55	0.08	0.94
	42	0.39	0.01	0.51	0.04	0.75
	54	0.40	0.03	0.51	0.09	0.79

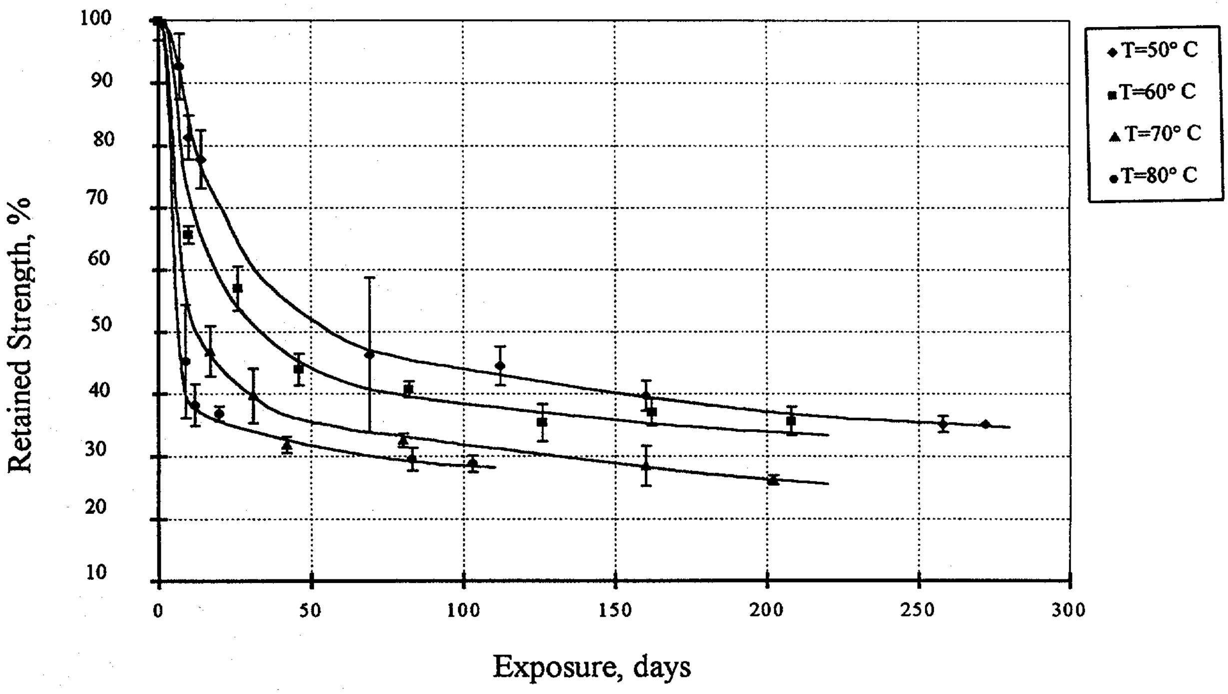


Figure 4.8. Tensile strength loss for geotextile P-4, aged in circulating air at 21% O_2.

The results of mechanical testing for P-4 and P-4a geotextiles aged in a stagnant atmosphere of diluted air (8% O_2, 92% N_2) are at first quite unexpected and are shown in table 4.11 and table 4.12. The specimens of the P-4 commercial geotextile aged at 70°C in diluted air with stagnant circulation exhibit a strength increase by a factor of 1.8 after the first 80 days of exposure, followed by statistically insignificant changes of tensile strength. The summarized experimental results on mechanical degradation in stagnant diluted air for the commercial product P-4 are shown in figure 4.9.

Table 4.11. Tensile strength loss for P-4 geotextile in stagnant diluted air at 8% oxygen.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation	Secant modulus ratio at peak strength
70	0	1.00	0.03	1.00	0.08	1.00
	10	0.84	0.09	0.81	0.10	1.04
	80	1.88	0.03	0.88	0.09	2.13
	136	1.71	0.09	1.04	0.14	1.65
	219	1.63	0.11	1.31	0.28	1.25
	342	1.59	0.24	1.09	0.08	1.46
	473	1.81	0.16	1.08	0.26	1.68
80	0	1.00	0.03	1.00	0.08	1.00
	62	1.76	0.06	1.01	0.14	1.74
	125	1.74	0.06	0.93	0.12	1.86
	179	1.65	0.01	0.86	0.18	1.91
	242	1.58	0.07	1.02	0.27	1.54
	304	1.56	0.10	1.13	0.06	1.38
90	0	1.00	0.03	1.00	0.08	1.00
	50	0.75	0.13	1.02	0.01	0.73
	102	0.80	0.14	0.87	0.09	0.93
	150	0.82	0.04	0.93	0.15	0.89
	200	0.88	0.01	1.07	0.09	0.82
	314	0.70	0.12	0.93	0.10	0.76

Table 4.12. Tensile strength loss for P-4a research-grade geotextile in stagnant diluted air at 8% oxygen.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation
70	0	1.00	0.13	1.00	0.14
	80	1.00	0.04	0.95	0.02
	136	1.01	0.15	0.71	0.21
	219	0.99	0.16	0.77	0.12
	299	1.01	0.07	0.84	0.10
	379	0.97	0.10	0.70	0.08
80	0	1.00	0.13	1.00	0.14
	45	1.04	0.07	0.83	0.12
	80	0.98	0.06	0.94	0.15
	120	1.19	0.15	1.10	0.24
	155	1.21	0.15	0.78	0.11
	200	1.07	0.14	0.60	0.15
90	0	1.00	0.13	1.00	0.14
	50	1.07	0.13	0.76	0.10
	102	0.99	0.10	0.81	0.10
	150	0.94	0.07	0.80	0.30
	200	1.16	0.12	0.97	0.15
	314	0.81	0.31	0.70	0.18

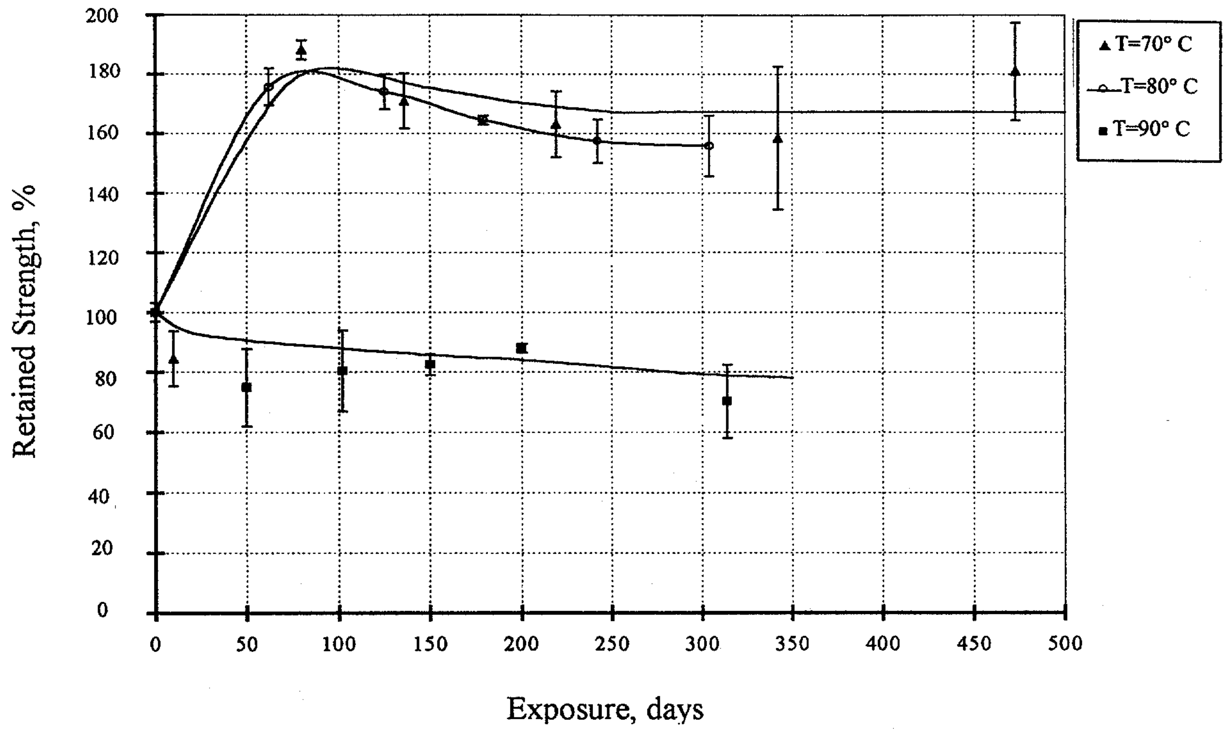


Figure 4.9. Tensile strength loss for commercial geotextile P-4, aged in a stagnant atmosphere of diluted air at 8% O_2.

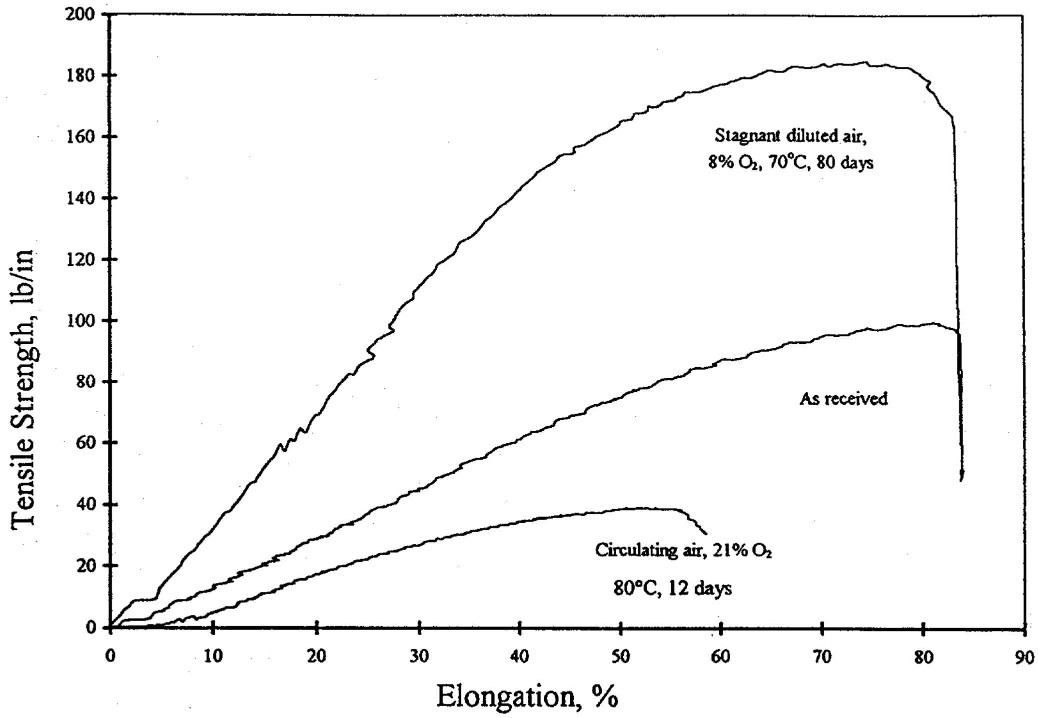
Load-Strain Relationships for P-4 Product

Figure 4.10 and figure 4.11 illustrate a significant difference in load-strain curves and index properties at low strain for virgin and oven-aged samples of P-4 product. The differences of the offset modulus are believed to be due to the decrease in fiber diameter caused by cracking rather than fundamental changes in the geosynthetic. Estimates of the offset modulus are shown in table 4.13.

Table 4.13. Offset secant modulus for P-4, virgin and oven-aged in different environmental conditions.

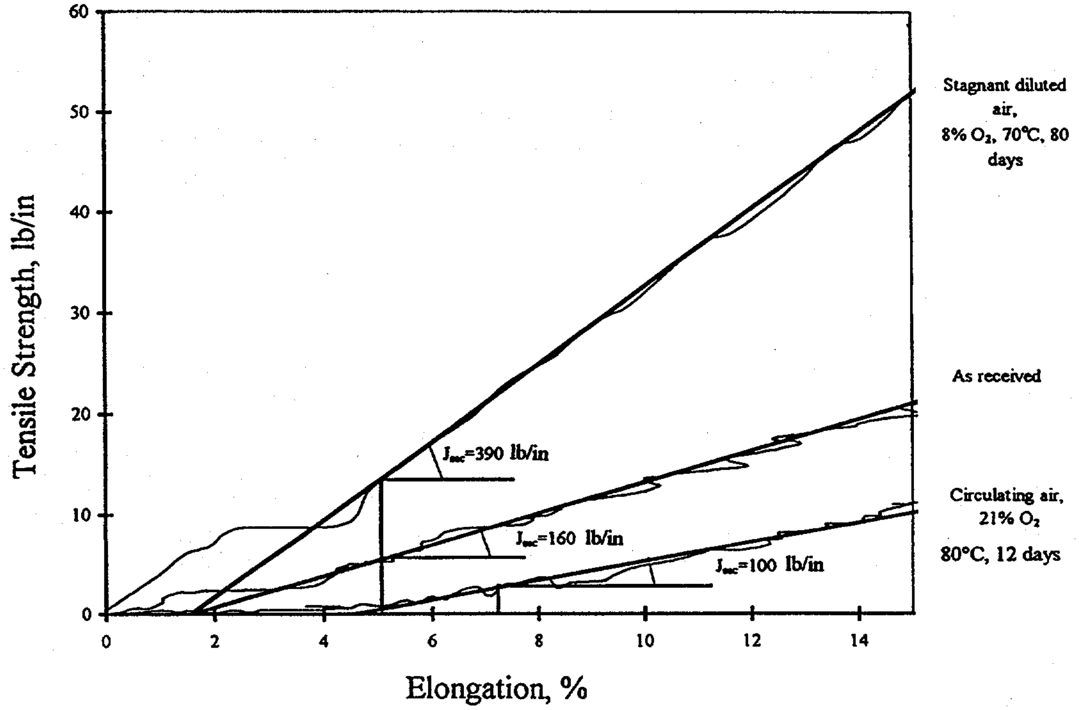
Condition	Virgin	Circulating air, 21% O_2, 80°C, 12 days	Stagnant diluted air, 8% O_2, 70°C, 80 days
Offset modulus $J_{sec\varepsilon}$, lb/in	160	100	390
Strain, % @ $J_{sec\varepsilon}$	5	7.5	5
Retained strength, %	100	40	190
Fiber surface integrity	Initial cracks and crazes	Intensive cracking	Crack healing

1 lb/in = 0.0179 kg/mm



1 lb/in = 0.0179 kg/mm

Figure 4.10. Typical load-strain curves for P-4 as received and oven-aged in different conditions.



1 lb/in = 0.0179 kg/mm

Figure 4.11. Determination of offset secant modulus for P-4 product as received and aged in different conditions.

4.1.4 P-9, slit-film woven geotextile

Appearance

The SEM study of surface morphology for the P-9 split-film yarns "as received" indicates that film surface is covered with micro-cracks that are transverse and parallel to the length of the film. Over the period of exposure to elevated temperatures, initial micro-cracks transform into a perpendicular system of deep developed cracks. Microphotographs of a P-9 slit film "as received" and aged at 80°C for 209 days are shown in figure 4.12. SEM analysis of a P-9 split film aged in stagnant diluted air (8% O_2) indicates no apparent healing of initial cracks over a period of exposure to elevated temperatures ranging from 70 to 90°C.

Weight Loss

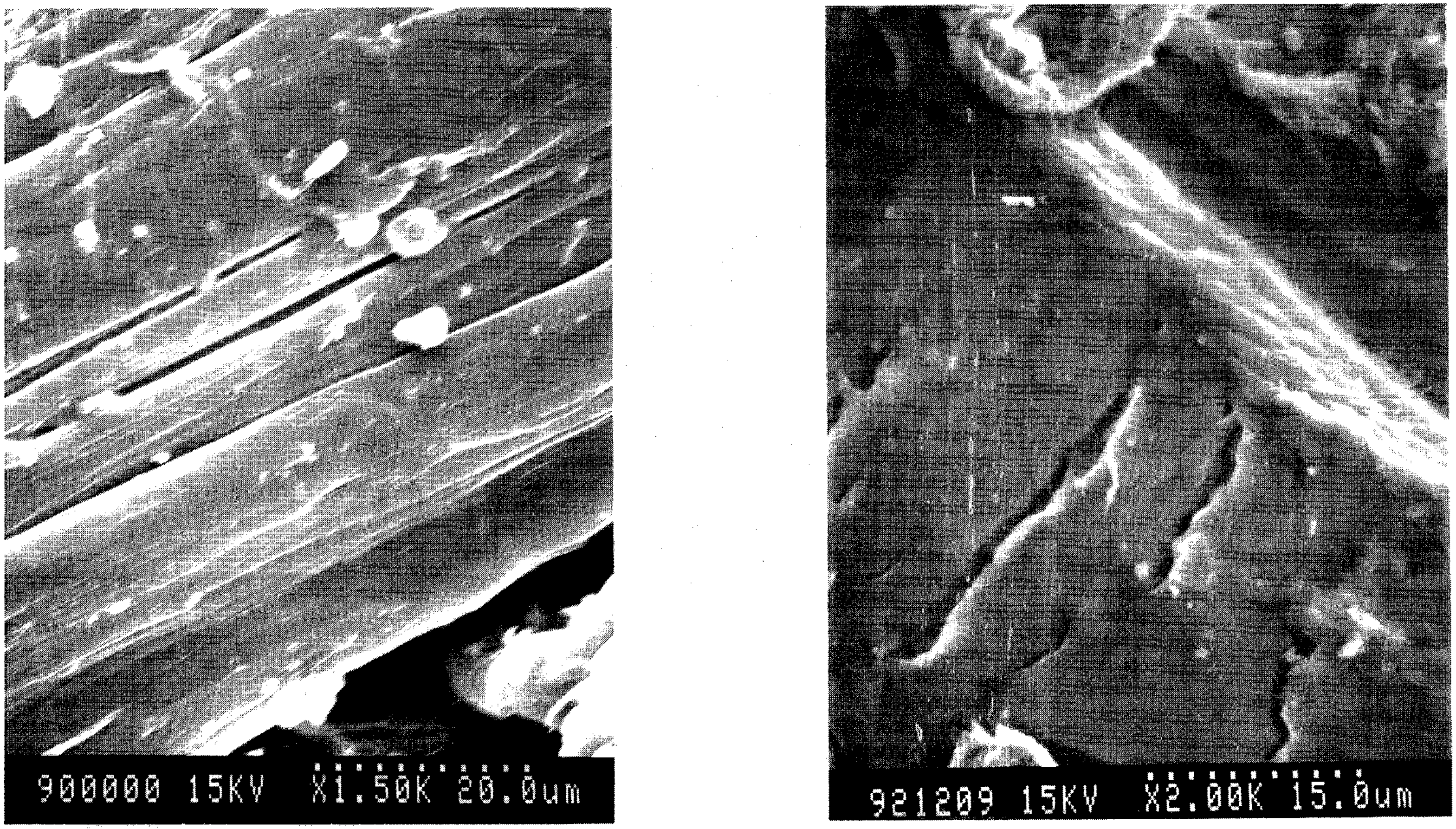
Weight loss for the P-9 geotextile over the period of exposure to elevated temperatures in circulating air and in the atmosphere containing 8-percent oxygen indicated no evidence of weight changes.

Mechanical Properties

The results of Wide-Strip Tensile Tests conducted on aged specimens are summarized in table 4.14 and table 4.15 and are shown in figure 4.13 and figure 4.14. Experimental data on tensile strength loss monitoring during thermo-oxidation in circulating air (21% O_2) as well as in stagnant diluted air (8% O_2) indicate no apparent pattern, except a general tendency to decrease. The remaining values of tensile strength vary from 25 percent to 90 percent of the initial value during the period of oven aging. Results suggest that the rate of degradation is slower in stagnant diluted air as compared to the degradation in circulating air for the P-9 product.

Strain at failure was examined in an attempt to discern a pattern for the degradation process. Again, no apparent pattern is indicated by examination and analysis of strain at failure data as shown in tables 4.14 and 4.15. The scatter is on the same order.

It should be further noted that the variation coefficient for retained strength on aged samples tested is somewhat higher than that for the virgin samples, but not sufficient to explain the noted scatter of results.



(a) P-9 “As received

(b) P-9 Forced air, 80 °C
209 Days

Figure 4.12. SEM microphotographs for P-9 films: (a) “as received” (1500x) and (b) aged in intense circulation air at 80°C for 209 days (2000x).

Table 4.14. Tensile strength loss for P-9 geotextile in circulating air at 21% oxygen.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation
60	0	1.00	0.03	1.00	0.04
	93	0.30	0.06	1.02	0.26
	170	0.71	0.06	0.96	0.08
	217	0.38	0.07	0.95	0.19
	287	0.30	0.04	1.02	0.15
	387	0.31	0.06	0.98	0.33
70	0	1.00	0.03	1.00	0.04
	120	0.93	0.09	0.80	0.02
	241	0.72	0.11	0.70	0.05
	360	0.52	0.11	0.87	0.14
	481	0.48	0.04	1.26	0.50
	601	0.40	0.10	0.61	0.15
80	0	1.00	0.03	1.00	0.04
	20	0.27	0.04	0.56	0.18
	40	0.29	0.02	0.71	0.13
	60	0.70	0.03	0.99	0.10
	88	0.50	0.03	0.95	0.07
	120	0.63	0.14	0.61	0.13
	121	0.73	0.02	0.94	0.04
	149	0.54	0.04	0.95	0.11
	209	0.67	0.03	0.86	0.06
90	0	1.00	0.03	1.00	0.04
	30	0.32	0.01	1.10	0.20
	60	0.28	0.04	0.96	0.11
	50	0.52	0.04	0.92	0.06
	80	0.51	0.04	0.88	0.07
	110	0.45	0.07	0.76	0.10

Table 4.15. Tensile strength loss for P-9 geotextile in stagnant diluted air at 8% oxygen.

Temperature, °C	Exposure, days	Retained peak tensile strength ratio	Coefficient of variation	Retained strain ratio at peak strength	Coefficient of variation
70	0	1.00	0.13	1.00	0.06
	130	0.82	0.20	1.42	0.92
	200	0.65	0.09	0.89	0.11
	273	0.86	0.09	0.61	0.24
	309	0.99	0.15	0.60	0.03
	473	0.71	0.03	0.69	0.32
80	0	1.00	0.13	1.00	0.06
	39	0.59	0.13	0.70	0.14
	83	0.52	0.04	1.07	0.32
	102	0.57	0.10	0.77	0.46
	146	0.62	0.36	0.80	0.20
	185	0.55	0.12	1.05	0.17
90	0	1.00	0.13	1.00	0.06
	50	0.76	0.01	1.02	0.35
	102	0.73	0.04	1.22	0.40
	150	0.83	0.15	1.17	0.19
	200	1.19	0.06	0.48	0.07
	314	0.73	0.12	0.83	0.14

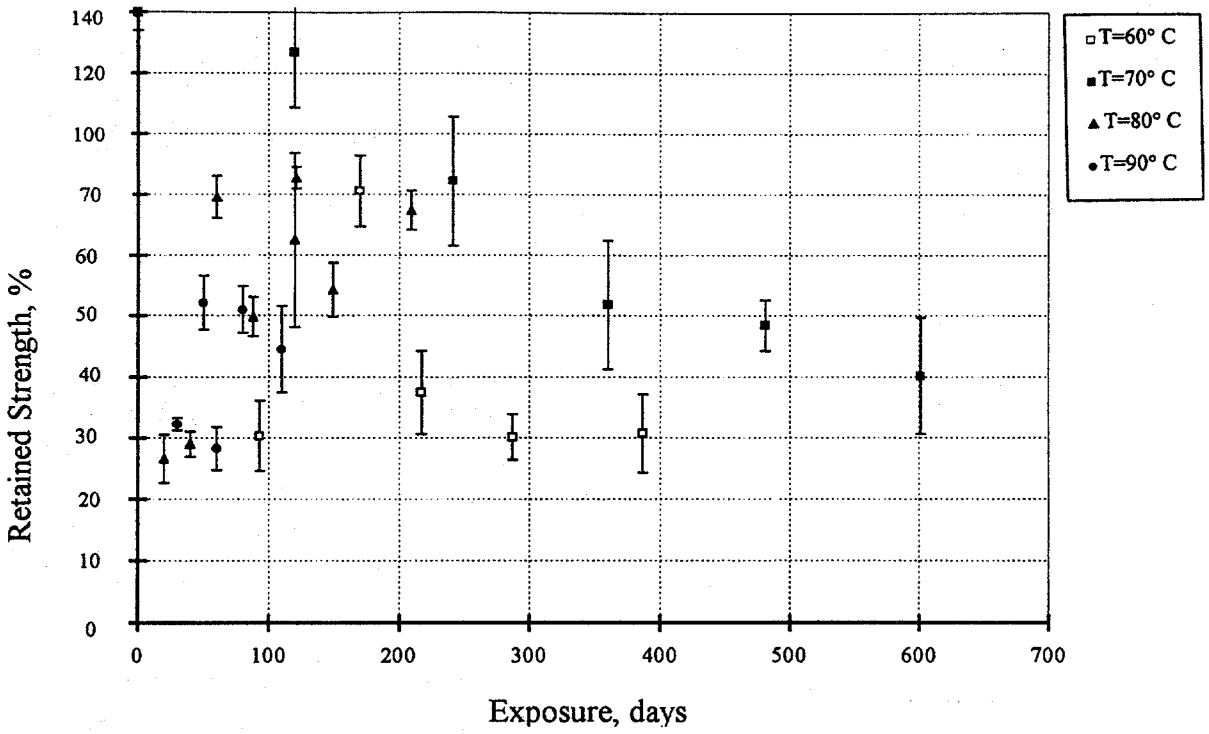


Figure 4.13. Tensile strength loss for geotextile P-9 aged in circulating air (21% O_2).

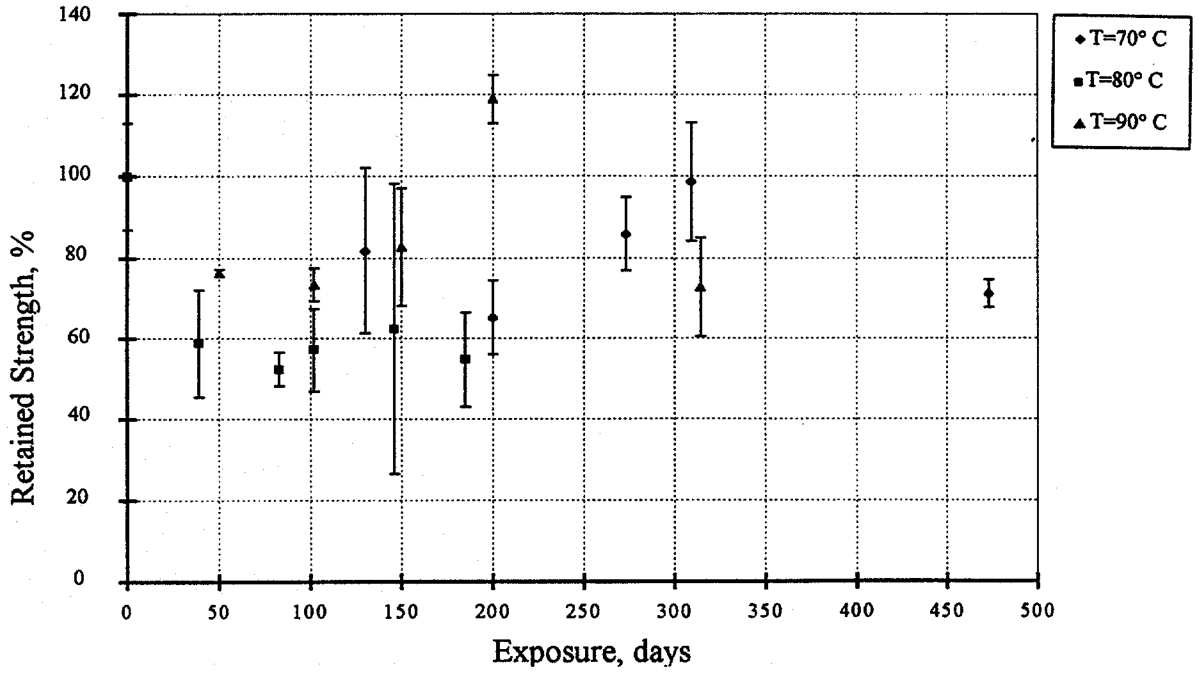


Figure 4.14. Tensile strength loss for geotextile P-9 aged in stagnant diluted air at 8% O_2.

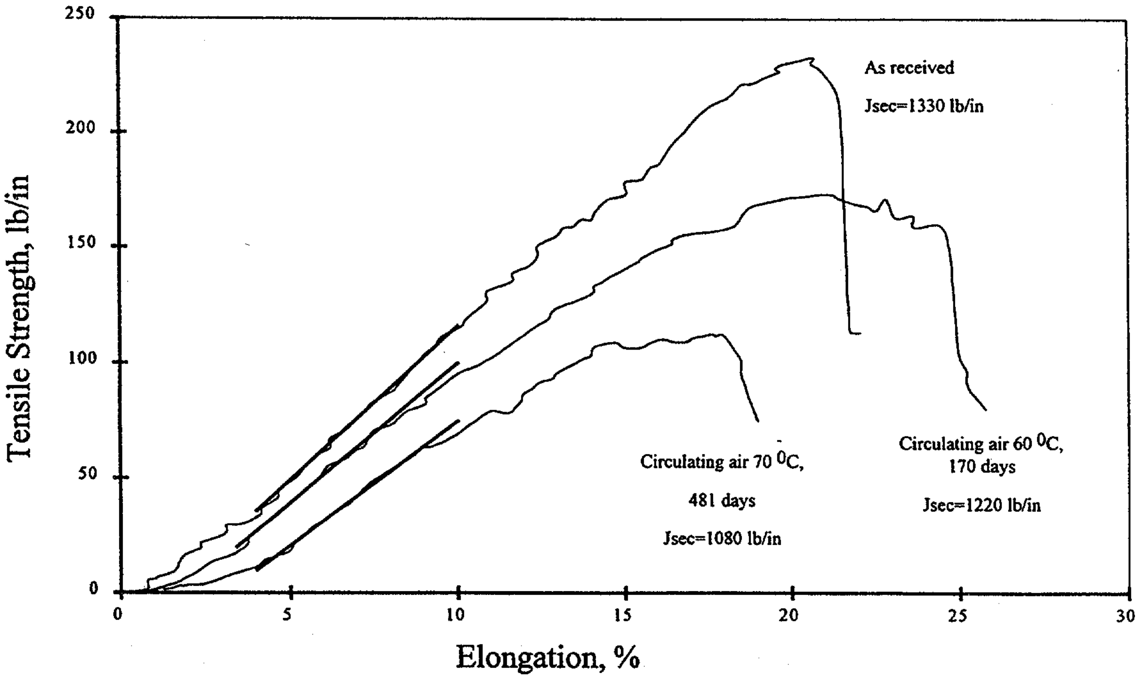
Load-Strain Relationships for P-9 Product

Figure 4.15 shows typical load strain curves for the P-9 product, including: (i) virgin, (ii) aged in circulating air at 70°C for 481 days with about 50-percent strength loss, and (iii) aged in circulating air at 60°C for 170 days with 30-percent strength loss. The initial part of the load-strain curves appears to be identical for these conditions. The values of the offset modulus were calculated at 5-percent strain for different load-strain curves with the results presented in table 4.16.

Table 4.16. Offset secant modulus for P-9, virgin and oven aged in different temperatures.

Condition	Virgin	Circulating air, 21% O_2, 60°C, 170 days	Circulating air, 21% O_2, 70°C, 481 days
Offset modulus $J_{sec\varepsilon}$ lb/in	1330	1220	1080
Tensile strength loss, %	0	30	50
Fiber surface integrity	Initial cracks and crazes mostly parallel to the length of fiber	Development of orthogonal system of deep cracks	Development of orthogonal system of deep cracks

1 lb/in = 0.0179 kg/mm



1 lb/in = 0.0179 kg/mm

Figure 4.15. Load-strain curves for virgin and aged samples of P-9.

4.2 ASSESSMENT OF CHEMICAL PROPERTIES DURING DEGRADATION

Thermal and photo-oxidative degradation of polyolefins are the primary source causes of discoloration, crack formation, brittleness, and ultimately tensile failure. Chemical additives, such as antioxidants and light stabilizers are used in commercial polyolefins to protect them against thermal and photo-oxidation during processing as well as during service life. Therefore, analysis of antioxidants and light stabilizers present in the polymeric system is of prime importance when long-term stability of commercial products is considered. The antioxidant and light stabilizer additives are usually incorporated in the polymer matrix at a very low level, typically less than 0.5 percent. The type of antioxidants and their combination in the polymeric system along with the amount determine the behavior of mechanical properties over the service life of a commercial polymeric product. Comprehensive study of chemical techniques for monitoring antioxidant depletion due to oven aging for commercial geosynthetic products (Chapter 2) indicates that OIT by DSC method could by used only as a qualitative measure of oxidative stability for products containing no HALS-type additives. This disqualifies the P-3 commercial geotextile from being monitored by OIT.

High-Performance Liquid Chromatography (HPLC) was used in an attempt to quantify antioxidant presence in polyolefin products as measured by OIT during the degradation period. It appeared, due to the complexity of the thermodegradation process in the presence of antioxidant additives, that only products with simple and well-identified antioxidant ingredients could be characterized by means of HPLC. Only the P-1 product appears to meet these criteria. However, the interpretation of the HPLC results may be complicated by processes other than degradation developed in aged P-1 samples.

4.2.1 Chemical degradation monitoring by OIT for P-1, P-4, and P-9 products.

The prime focus of OIT measurements in monitoring antioxidant depletion during aging is on commercial products P-1 (geogrid), P-4 (nonwoven polypropylene geotextile), and P-9 (polypropylene woven geotextile). Progressive loss of OIT values for the P-1 geogrid, aged at elevated temperatures in circulating air and in 8-percent oxygen, is shown in figure 4.16. It appears that the rate of "chemical degradation" measured by OIT is slower in the stagnant atmosphere containing 8-percent oxygen than in circulating air (21% O_2) at the same temperature. The pattern of OIT decrease does not correlate with the pattern of tensile strength losses, neither in the condition of circulating air nor in the stagnant diluted air for any of the temperatures tested. It does qualitatively suggest that antioxidants should be significantly depleted before significant strength loss will be observed. Karlsson (1992) indicates that a depletion level of about 10-percent for polyethylenes signals the onset of oxidative degradation.

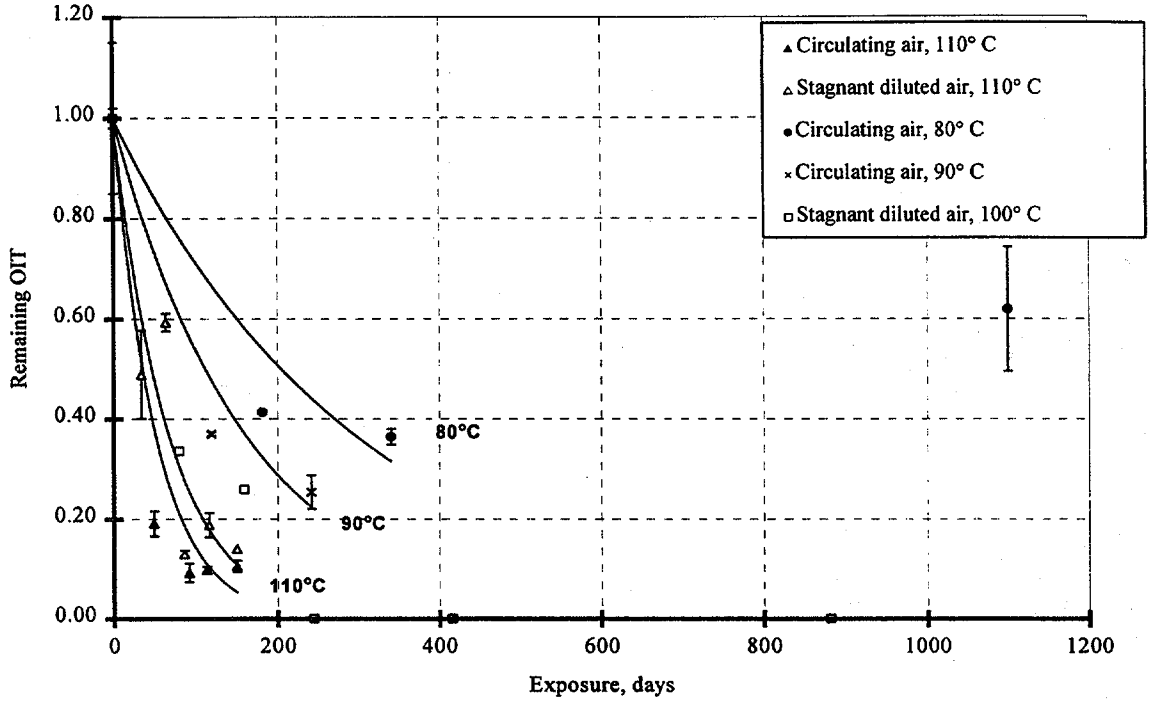


Figure 4.16. OIT changes for P-1 product aged in circulating air (21% O_2) and in stagnant diluted air (8% O_2).

The initial value of OIT for the P-4 geotextile is low, compared to the values for P-1 and P-9 materials (see table 2.10). The initial low average value of 11 minutes with a variation of 23 percent is such that decreases cannot be measured accurately and they appear random. Furthermore, there is no correlation with tensile strength losses. Figure 4.17 illustrates the scatter of OIT measured for aged specimens of the P-4 geotextile.

The OIT for the P-9 geotextile "as received" (see table 2.10) indicates a high variability, which may indicate nonuniformity of antioxidant distribution in the product "as received". Results of OIT monitoring for the P-9 geotextile are shown in figure 4.18. It appears that the rate of OIT loss in stagnant diluted air (8% O_2) is slower than in circulating air (21% O_2) at the same temperature. Furthermore, there is no apparent correlation with tensile strength losses at 60 and 90°C, and there is a weak correlation at 70 and 80°C.

The same level of scatter is evident if strain at failure is used as a correlation criterion.

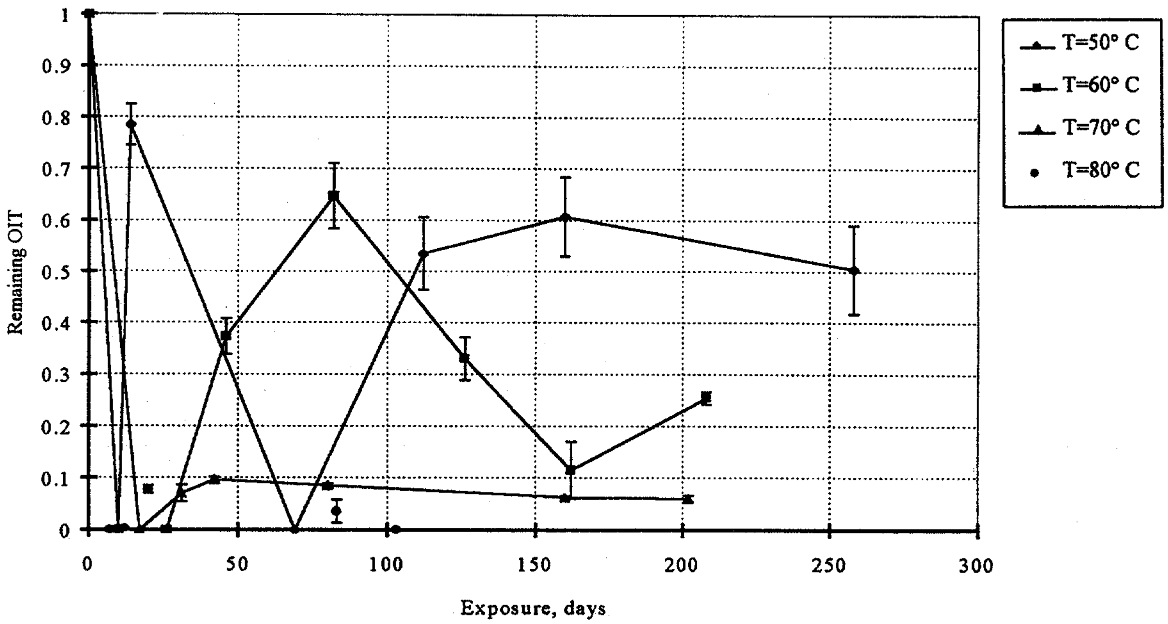


Figure 4.17. Results of OIT measurements for P-4 geotextile aged in intense circulating air at 21% O_2.

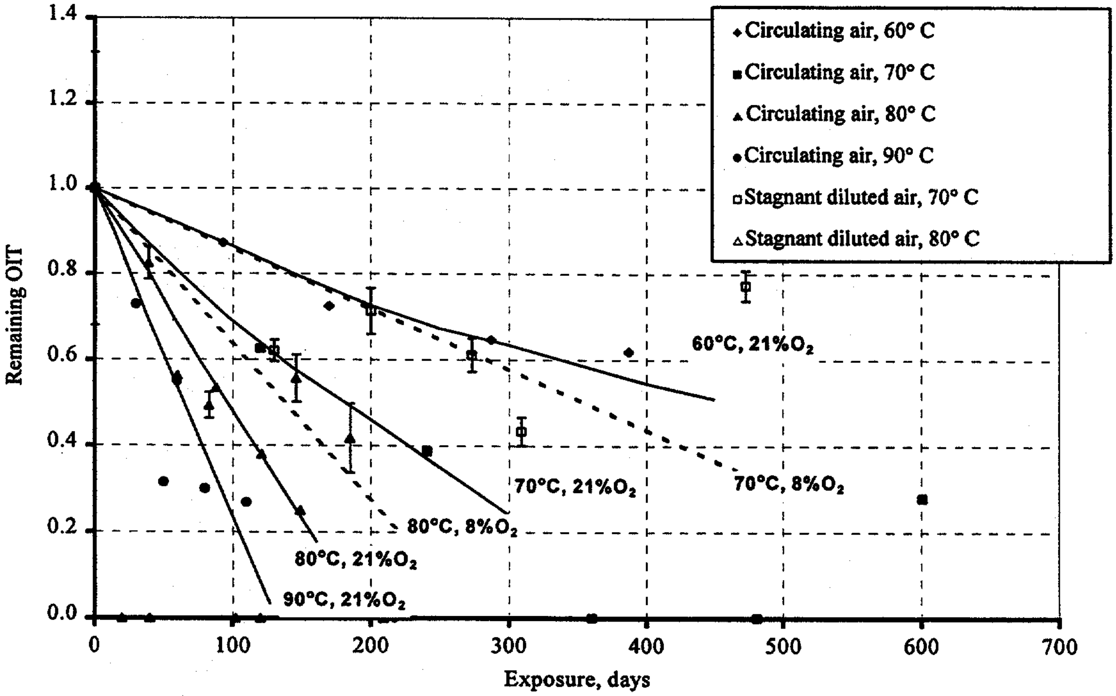


Figure 4.18. OIT changes for P-9 product aged in circulating air (21% O_2) and in stagnant diluted air (8% O_2).

4.2.2 High-Performance Liquid Chromatography (HPLC) for P-1.

Results of HPLC analysis for P-1 samples are listed in table 4.17. Note that there is a ±12-percent variation in Irganox 1010 content for non-aged P-1. Greater variations of Irganox 1010 content were observed for oven-aged P-1 samples, although a general pattern of decreasing antioxidant concentration as a function of exposure time is apparent.

Table 4.17. HPLC results for Irganox 1010 antioxidant content in P-1 aged in intense circulating air (21% O_2) at 110°C.

Exposure, days	Average content of Irganox 1010 (wt. %)	Maximum measured value (wt. %)	Minimum measured value (wt .%)	Coefficient of variation, %
0	0.143	0.160	0.127	11.5
49	0.033	0.067	0.007	94
92	0.013	0.020	0.006	77
113	0.021	0.027	0.015	40

Comparison of retained antioxidant content and retained OIT values (figure 4.16) for this aging condition suggests a very similar pattern of rapid depletion in the initial stages of aging. This confirms that OIT can track antioxidant depletion for HDPE products. Therefore, OIT measurements, where applicable, should be considered as the preferred method for tracking antioxidant depletion.

Considering that the procedure used for extraction of antioxidant from P-1 is the same for each retrieval and that the observed variation of concentration increases with exposure, the following reasons for this variation of the antioxidant content are suggested:

- The antioxidants and light-stabilizers have to be uniformly distributed in the polymer matrix. However, the concentration of stabilizers in the polymer may vary from batch to batch and even within the same batch for commercial materials. This leads to some of the variations developed in testing.
- When carbon black is incorporated into the polymer, the extraction and quantification become even more complicated. Carbon black is known to adsorb stabilizers, and any non-uniformity in the surface of and dispersion of carbon black in the polymer matrix will also result in poor distribution of the stabilizers and difficulties in extraction.
- The first step for the analysis of the stabilizers in polyolefins is extraction. Stabilizers are normally present in manufactured geosynthetics at low concentration, (e.g., 0.15 for P-1) and any loss of the stabilizers in handling is significant. Antioxidants and light-stabilizers may suffer decomposition during extraction, and the presence of very small amounts of metal and even trace catalyst residues in polyolefins may catalyze the auto-oxidation process during extraction.

4.3 SUMMARY

4.3.1 Mechanical strength.

Results of tensile strength monitoring for polyolefin-based geosynthetics indicate that each of the products studied exhibits a unique pattern of tensile strength changes during exposure to elevated temperatures in different environmental conditions (oxygen partial pressure). However, the common features are as follows:

- The rate of mechanical degradation for polyolefin-based products tested is dependent on aging conditions. Oven aging in stagnant diluted air (8% O_2) results in the decrease of the rate of tensile strength loss as compared to the rate observed in circulating air (21% O_2) at the same temperature.
- The higher temperature of oven aging results in the increase of the rate of tensile strength loss.

The surface morphology of fibers, analyzed with SEM, appeared to be different for all products tested. SEM microphotographs at a magnification of 3000x reveal the presence of initial crazes/cracks on the surface of virgin fibers for nonwoven staple geotextile P-4 and on the surface of virgin films for the P-9 product. There is no indication of surface cracks for virgin fibers of nonwoven continuous filament product P-3 and HDPE geogrid P-1. This difference in surface morphology may explain the differences in the mechanical degradation pattern for products tested, which are as follows:

- Oven aging in circulating air (21% O_2) causes further development of cracks, resulting in rapid tensile strength loss for product P-4, and in high variation of tensile strength values over the period of oven aging for product P-9.
- Continuous filament product P-3 and HDPE geogrid P-1 exhibit no surface crack development during the oxidation in circulating air (21% O_2), and a much lower rate of mechanical deterioration with a significant period of no tensile strength loss (induction period).
- Aging in stagnant diluted air (8% O_2) results in the healing of the initial crazes on the fiber surface of the P-4 product. This may explain a tensile strength increase by a factor of about 1.5 to1.6, observed for the P-4 product in stagnant diluted air (8% O_2).
- Products P-1 and P-3, aged in stagnant diluted air (8% O_2), exhibit statistically insignificant changes of tensile strength within the time and temperature range studied.
- Continuous filament product P-3 and staple film product P-9 exhibit no changes in initial modulus during the course of oven aging, whereas the initial modulus of staple product P-4 and HDPE geogrid P-1 appears to be sensitive to the incubation at elevated temperatures.

Commercial polyolefin products tested differ in the composition of the basic polymer and antioxidant additives.

- HDPE geogrid P-1 exhibits a much slower rate of tensile strength loss due to oven aging than the polypropylene products tested. Experimental data indicate a significant increase in extensibility (strain at break) and a decrease in modulus for HDPE product due to oven aging.

- Product P-3, containing effective antioxidant additives, has a much lower degradation rate than the research-grade material P-3a, containing a minimum amount of antioxidants. The beneficial effect of antioxidants is clearly demonstrated under all test conditions.

Experimental data on mechanical degradation of polyolefin-based geosynthetics suggest that oven aging in circulating air (21% O_2) is the most severe condition for the products tested, and is probably not indicative of "end use" conditions.

Experimental data on fiber surface morphology and on initial modulus indicate that incubation at elevated temperatures may result in the development of processes other than thermo-oxidation for P-1, P-4, and P-9 products.

4.3.2 Chemical properties.

Assessment of chemical changes in oven-aged polyolefin-based geosynthetics by OIT monitoring suggests the following:

- A general pattern of decreasing OIT values as a function of oven-aging time is apparent for the P-1 and P-9 products. Test data indicate that OIT changes are slower in stagnant diluted air (8% O_2) than in circulating air (21% O_2), the same general pattern obtained from strength testing.
- For products with low initial OIT values, decreases cannot be measured accurately and they appear random.
- There is no apparent correlation between OIT changes and tensile strength loss for the geosynthetic products tested.

In light of the lack of correlation between antioxidant consumption measured by OIT and loss of tensile strength, this methodology does not appear reasonable to track the oxidation process for geosynthetic materials. However, OIT appears to track antioxidant depletion for materials not containing HALS.

High-Performance Liquid Chromatography can quantify antioxidant consumption for polyolefin-based geosynthetics. However, experimental results, literature review, and discussions with experts from the industry suggest the extreme complexity and uncertainty of HPLC. Therefore, this method is an ineffective technique to conduct routine monitoring of antioxidant losses in commercial geosynthetic products.

CHAPTER 5

ANALYSIS OF EXPERIMENTAL RESULTS FOR POLYOLEFIN-BASED SELECTED COMMERCIAL PRODUCTS

5.1 STATE-OF-THE-PRACTICE FOR DURABILITY TESTING FOR COMMERCIAL GEOSYNTHETIC PRODUCTS

The investigation of chemical and mechanical durability of polyolefin commercial geosynthetics was developed for potential analysis using an "Arrhenius type" modeling (Koerner, Lord and Hsuan, 1992; Wisse and Birkenfeld, 1982; Wisse et al., 1990; Wisse, 1988; Allen, 1991). The concept of "Arrhenius modeling" in accelerated degradation studies of geosynthetic materials is based on the well-established concept that chemical reactions of all types proceed more rapidly at higher temperatures than at lower temperatures. It is assumed that laboratory experimental results on mechanical properties of polymeric materials exposed to elevated temperatures could be used within the framework of an Arrhenius model to evaluate the life cycle of commercial materials at ambient temperatures. The Arrhenius equation widely used in the geosynthetic industry to predict a given strength loss, typically 50 percent, for geosynthetic reinforcement, is as follows:

$$R_r = Ae^{-(U_{act}/RT)} \tag{5-1}$$

where:

R_r -the reaction rate constant;

A - the pre-exponential factor, usually considered as a constant that is independent of temperature;

U_{act} - the activation energy, which is also treated as a constant for each particular material and is independent of temperature;

R - the ideal gas constant; and
T - the temperature in °K.

Taking the natural logarithm of both sides of equation (5-1) results in:

$$\ln R_r = \ln A - \frac{U_{act}}{RT} \tag{5-2}$$

Arrhenius equations in this form are used to determine accelerated degradation from laboratory testing and are currently used in durability evaluation of commercial geosynthetic products. There are two unknown variables in equation (5-2), A and U_{act}, where the R_r reaction rate or rate of mechanical degradation is being determined experimentally. If the log reaction rate is plotted against reciprocal temperature, the slope of the line will be - U_{act}/R and the intercept on the vertical axis will be the constant ln A. It follows from (5-2) that ln R_r is a linear function of inverse temperature $1/T$. Therefore, at least two experimental values of a degradation rate (for example, time required to 50-percent tensile strength loss) obtained at two different elevated temperatures will be sufficient to determine, at least theoretically, the degradation rate at any temperature of interest (see figure 5.1).

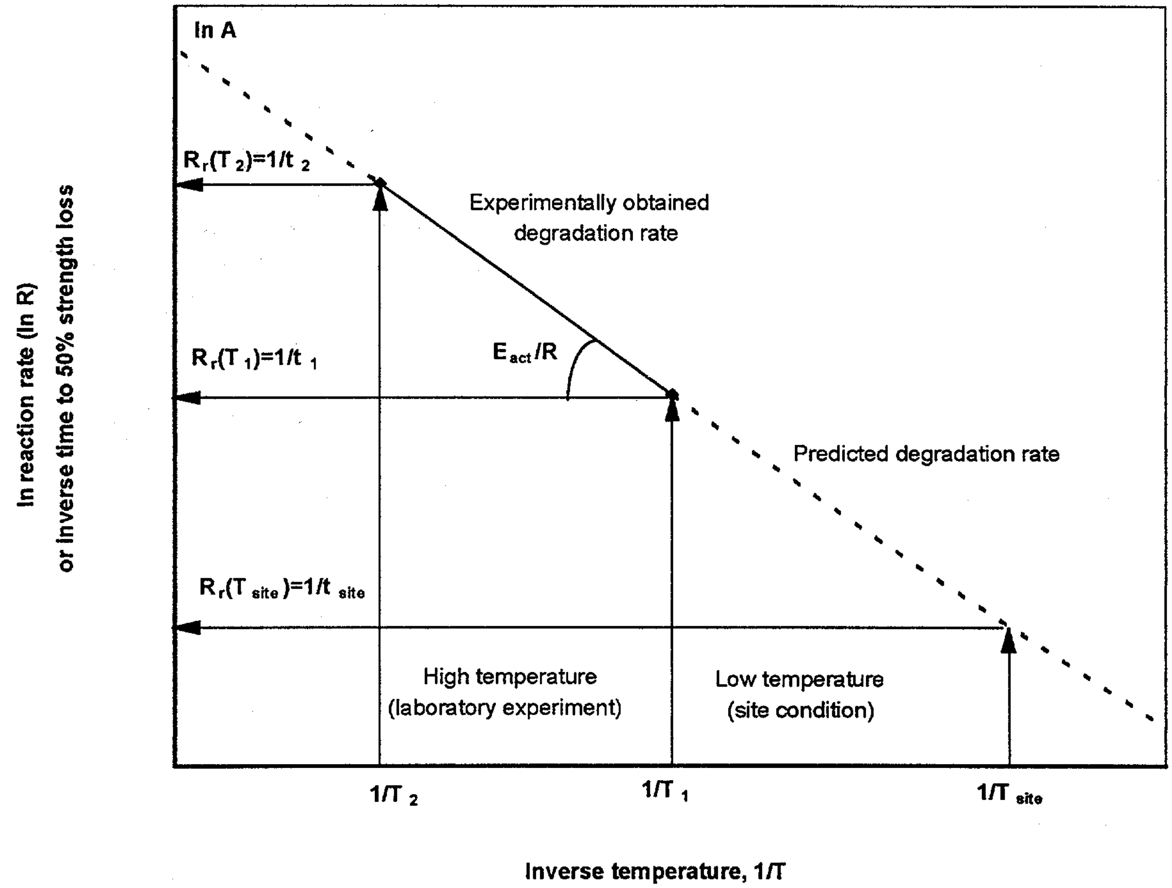


Figure 5.1. Generalized Arrhenius plot used for low-temperature predictions from high-temperature experimental data from laboratory tests.

5.1.1 Previous experimental results for thermo-oxidative degradation of commercial polyolefin geosynthetics.

The degradation of polyolefin geosynthetics is a complex process and there are many factors affecting the degradation behavior of polymeric materials. Some of those factors, such as presence and formulation of antioxidant additives, are inherent properties of the material. Other factors, such as induced stress, chemical environment, humidity, etc., are external factors and can be controlled during the experiment. Most of the experiments reported in the literature were conducted with polypropylene geotextiles of woven and nonwoven types. Published results indicate that the degradation rate increases with an increase in the temperature of exposure as indicated by the Arrhenius model. Typical published experimental plots of the log oven-life time against inverse temperature for polypropylene geosynthetics are shown in figure 5.2.

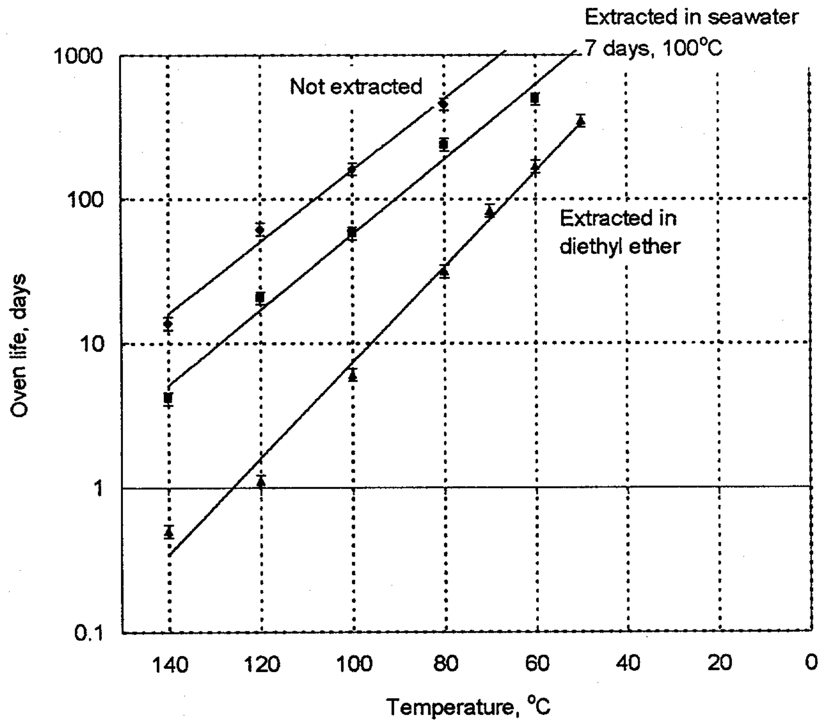


Figure 5.2. Experimental results for time to mechanical failure of a nonwoven spunbonded polypropylene sheet, by heat aging as a function of temperature (Wisse and Birkenfeld, 1982).

Moreover, Wisse and Birkenfeld (1982) suggest that the values of activation energy derived from experimental results by using an Arrhenius model are not constant for the same material within the range of applied temperatures. Wisse and Birkenfeld (1982) report an E_{act} value of 93 kJ/mol for temperatures above 80°C and a value of 65 kJ/mol for temperatures below 70°C. This appears to be inconsistent as the activation energy of any polymeric material is a fundamental constant that does not depend on the temperature, suggesting that the degradation process is more complex than assumed by a simple Arrhenius model.

The presently obtained results of progressive tensile strength losses during oven aging in circulating air (ASTM 3045) indicate that a simplified Arrhenius approximation could not be used to describe the observed experimental results for product P-3 or for P-4 (figures 4.2 and 4.4). Geotextile P-3 at elevated temperatures up to 70°C exhibits a substantial period of time with no changes in mechanical strength. Geotextile P-4 (figure 4.5) demonstrates an exponential decay of its mechanical strength from the early stages of exposure to elevated temperature. Data in the literature and as obtained in this study suggest that the Arrhenius type of modeling may be too simplistic to describe degradation behavior of commercial geosynthetic products. Therefore, the basic principles of kinetics of chemical reactions in general, and kinetics of thermo-oxidation in particular, must be considered in formulating an appropriate numerical model.

5.2 BASIC PRINCIPLES OF KINETICS OF CHEMICAL REACTIONS

In chemical kinetics (Adamson, 1973), the rate R of a reaction $A+B+C+\ldots \rightarrow \mathit{Products}$ at constant temperature and pressure is expressed as a function of composition of the system

$$R=-\frac{d[P]}{dt}=f([A],[B],[C],\ldots) \qquad (5\text{-}3)$$

The complete function expressed by (5-3) may be complicated, but it is often of the form

$$R=k[A]^x[B]^y[C]^z \qquad (5\text{-}4)$$

where $[A]$, $[B]$, and $[C]$ are the concentrations of reactants, and k is the rate constant, being independent of the concentration of the reactants, but dependent on the temperature and pressure.

A major category of rate laws is that for which R is given by an expression of the form of equation (5-4). The order of the rate law is the sum of the exponents ($x+y+z+\ldots$). The important cases are zero-, first-, and second-order reactions. However, the rate law has no relationship to the chemical equation for the overall reaction and should be determined experimentally (Atkins, 1986).

The rates of most reactions increase as the temperature is raised. An empirical observation is that many reactions have rate constants k that follow the Arrhenius equation:

$$k=Ae^{-E_a/RT} \qquad (5\text{-}5)$$

> A - the pre-exponential factor, usually considered as a constant that is independent of temperature; E_a - the activation energy; R - the ideal gas constant; and T - the temperature in °K.

This simplified approach in considering the kinetics of chemical reactions permits presentation of the rate laws for reactions of different orders in integrated forms as shown in table 5.1.

Table 5.1. Integrated rate laws (after Adamson, 1973; Atkins, 1986).

Order of reaction $A \rightarrow P$	Kinetics law, $x=f(t)$ ($x=[A]/[A]_0$)	Rate law, dx/dt	Half-life $t_{1/2}$ of the reaction when $[A]/[A]_0=1/2$
0	$x=1-kt$	$dx/dt=-k$	$[A]_0/2k$
1	$x=e^{-kt}$	$dx/dt=-k[A]$	$(\ln 2)/k$
2	$x=\frac{1}{1+[A]_0 kt}$	$dx/dt=-k[A]^2$	$1/k[A]_0$
$n \geq 2$	$x=\{kt(n-1)[A]_0^{n-1}+1\}^{-\frac{1}{n-1}}$	$dx/dt=-k[A]^n$	

5.3 BASIC AUTO-OXIDATION SCHEME

Oxidation of polyolefins is a well-known and well-studied process. The reaction of organic compounds initiated by the attack of molecular oxygen is called auto-oxidation. The effect of auto-acceleration in the degradation of organic compounds caused by a reaction with oxygen had been well recognized in the literature. Studies on this phenomenon led to the development of a basic auto-oxidation scheme (BAS) (Bolland, 1948; Kelen, 1982). This scheme includes all the important steps in oxidation and explains many features of the process. Recent theories of polymer oxidation are based on BAS, with minor modifications and extensions (Reich and Stivala, 1971; Kelen, 1982).

The oxidative degradation of polymers is a free-radical reaction and may be described by the following steps:

I. *Initiation.* Formation of free-radicals initiated by polymerization catalyst residues, heat or shear which initiate chain scission in the polymer generating free-radicals:

$$polymer \xrightarrow{k_i,\ Energy, shear, heat} R^\bullet \qquad (5\text{-}6)$$

II. *Radical conversion.* The conversion of the hydrocarbon radical is an important step in which the majority of oxygen is absorbed by the polymer:

$$R^\bullet + O_2 \xrightarrow{k_i} ROO^\bullet \qquad (5\text{-}7)$$

III. *Chain propagation.* At this stage, oxygen-centered radical species absorbs a hydrogen atom from the surrounding polymer to form hydroperoxide and create yet another free-radical:

$$ROO^\bullet + polymer \xrightarrow{k_i} R^\bullet + ROOH \qquad (5\text{-}8)$$

IV. *Degenerate chain branching.* That is the decomposition of hydroperoxides to radicals. This step is similar to the initiation step and therefore leads to auto-acceleration of the oxidation, producing new portions of free-radicals that can react with oxygen to continue the cycle:

$$ROOH \xrightarrow{k_i} RO^{\bullet} + {}^{\bullet}OH \qquad (5\text{-}9)$$

V. *Termination*. Under most conditions, termination of free-radicals in polymer oxidation occurs almost exclusively by participation of peroxy radicals:

$$ROO^{\bullet} + ROO^{\bullet} = products \qquad (5\text{-}10)$$

5.4 SIMPLIFIED KINETICS OF AUTO-OXIDATION OF POLYOLEFINS

The general scheme of polymer oxidation presented is a simplified description of auto-oxidation of polyolefins and can be used for a kinetic description of the main characteristics of the process. Such characteristics are time dependence of oxygen absorption, temperature, pressure, and concentration dependence on oxidation rate. There are many other important parameters of polymer oxidation, such as the change in molecular weight distribution, the formation of volatile products, and the change in polymer composition. A scheme that would allow the kinetic treatment of all processes would include many more steps than outlined below, and the reactions would be chemically much more specific. Such an approach and the potential additional accuracy are not warranted.

The usual and justified assumption of kinetics for a chain reaction is that the concentration of *RH*, i.e., the *C-H* bonds participating in oxidation, is constant, and that a steady state is reached very soon after the onset of the reaction. The following expression for time dependence of hydroperoxide concentration could be obtained by solving the system of differential equations describing the BAS as shown in equations 5-6 through 5-10:

$$[ROOH] = a(1 - e^{-bt}) \qquad (5\text{-}11)$$

where *a* and *b* are complex constants.

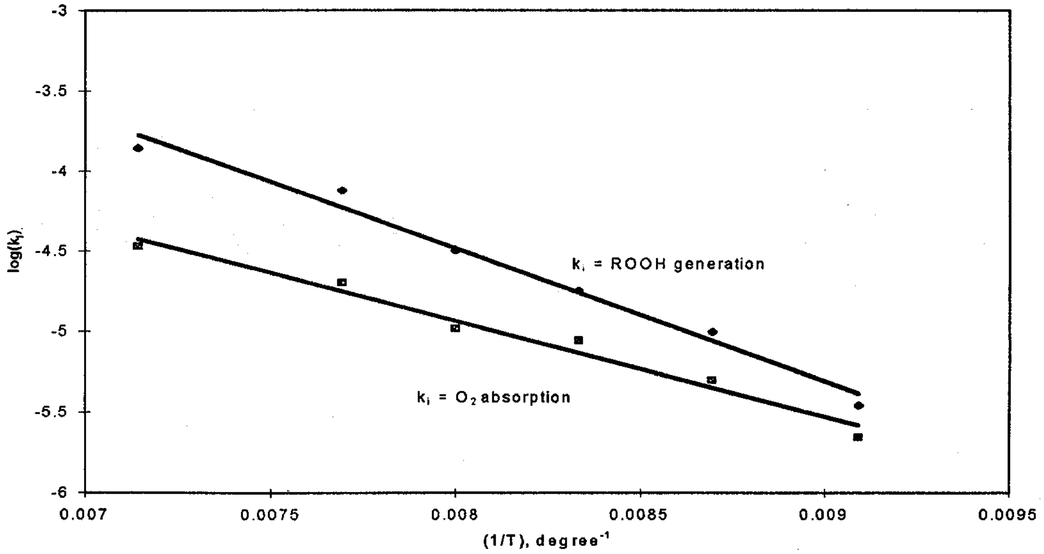


Figure 5.3. Temperature dependence of the rate constant of ROOH generation and oxygen absorption (Zolotova and Denisov, 1971).

Equation (5-11) indicates that the reaction of thermo-oxidation, described in BAS, is a first-order reaction where the complex constant b is treated as the apparent rate constant. Figure 5.3 clearly indicates the linear dependency of log kinetic constants plotted against the inverse of temperature, suggesting an Arrhenius-type dependency for the rate constant b in equation (5-11) (Zolotova and Denisov, 1971).

According to BAS, thermo-oxidation results in polymer chain breaks and in the decrease of polymer molecular weight. The concentration of hydroperoxide, as a product of chain breaks, is proportional to the number of main chain breaks. The decrease in molecular weight, in turn, results in the decrease of tensile strength of the original polymer. Therefore, as a first approach, it can be assumed that the degree of mechanical degradation defined as mechanical strength loss of a polymer due to thermo-oxidation is proportional to the hydroperoxide concentration in a polymer mixture at any given time of oven aging. Considering that thermo-oxidation is a first-order reaction equation (5-11) with an Arrhenius-type rate constant, the normalized retained tensile strength F of a polymer can be expressed as:

$$F(t)= e^{-\bar{k}\, t}\text{; where } \bar{k} = A_1 e^{-U/RT} \text{ is an apparent rate constant} \qquad (5\text{-}12)$$

This chain of assumptions is illustrated in figure 5.4.

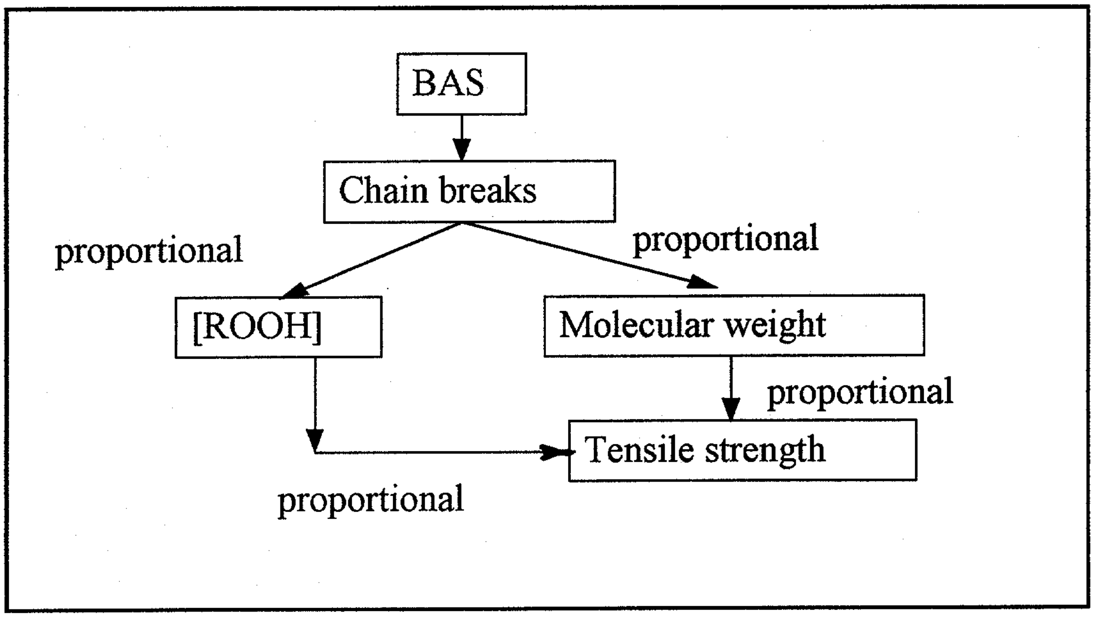


Figure 5.4. Assumptions on the kinetics for deterioration of tensile strength of a polymer, caused by the thermodegradation.

5.5 MODEL PARAMETERS

Equation (5-12) contains two independent unknown parameters A_1 and U, and it has two laboratory-controlled variables, temperature T, and time of exposure t at constant pressure. The parameter A_1 is a pre-exponential factor that is usually independent of temperature. The parameter U is an apparent activation energy of thermo-oxidation.

Note that in equation (5-4) one of the reactants is oxygen, whose concentration in the system is directly proportional to its partial pressure. This fact has a direct impact on the laboratory protocol for accelerated degradation testing of geosynthetic products. Current methods of accelerated degradation (ASTM 3045) require the exposure of tested materials to an elevated temperature in air with a normal oxygen concentration of 21-percent. However, for in-situ regimes for buried geosynthetics, the concentration of oxygen could be less, maybe about 8 to10 percent or less (Yanful, 1993). Moreover, the current method (ASTM 3045) of oven aging recommends the use of forced-draft ovens with intensive air circulation. The oxygen partial pressure considered in BAS is the pressure at the surface of the polymer, and if oxidation occurs in stagnant conditions, the concentration of oxygen in boundary layers decreases due to the resulting consumption, thereby resulting in a decrease of the degradation rate. With an intense supply of fresh oxygen to the surface of a polymer from intensive circulation, for example, the oxygen pressure remains constant. Thus, the oxidation rate becomes dependent on the surface condition of a polymer as well as on the intensity of air circulation in the reaction chamber. By contrast, for field conditions, geosynthetics are exposed to low oxygen concentration and a stagnant atmosphere, which creates a different effective oxygen pressure ***resulting in a different, lower oxidation rate.***

5.6 EFFECT OF ANTIOXIDANT ADDITIVES ON THE KINETICS OF AUTO-OXIDATION

Antioxidants used in polymer products are generally classified by the mechanism in which they act as stabilizers during oxidation. Primary antioxidants provide stabilization by trapping or deactivating free-radicals after they are formed. Secondary antioxidants decompose hydroperoxides, which may otherwise be transformed into free-radicals, into non-radical species, thereby slowing the formation of free-radicals. For each of these two categories, there are kinetic equations describing the consumption of antioxidants.

The most advanced mixtures of antioxidants provide almost complete protection against oxidation, while their concentration in the polymer mixture is insignificant. After antioxidant consumption, the degradation of the polymer occurs in a manner similar to the process described by BAS. The rate of consumption of antioxidants depends on the temperature in the reaction as well as on the oxygen partial pressure in the system.

The data reported in the literature (Karlsson, Smith, and Gedde, 1992) indicate that there is an induction period with no degradation for medium-density polyethylene (MDPE) oxidized at elevated temperatures. The summarized results are shown in figure 5.5, which indicate that the logarithm of the rate of consumption of antioxidant k_{ind} is a linear function of the reciprocal temperature, suggesting that the reaction constant for antioxidant consumption may follow the Arrhenius equation.

Similar results were reported earlier (Griveson et al., 1961) for polyethylene, further indicating that the length of the induction period (time) is directly proportional to the amount of antioxidant added to the polymer.

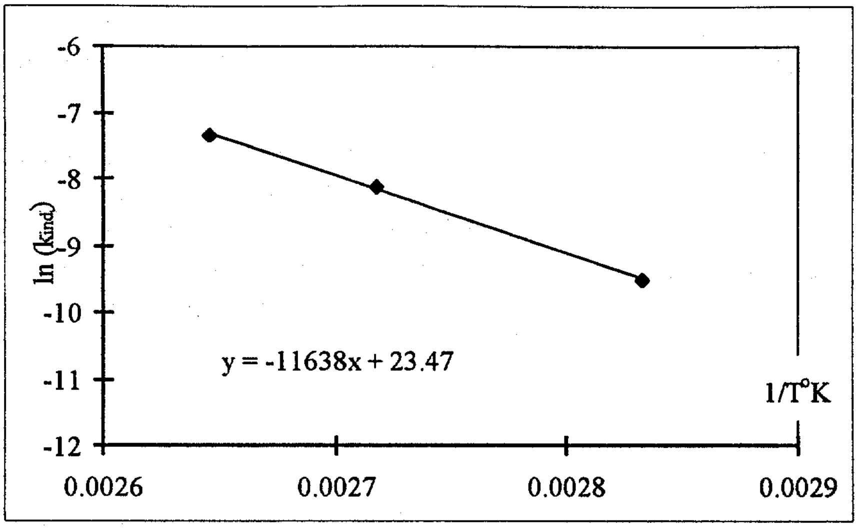


Figure 5.5. Arrhenius plot for the rate of induction observed for thermo-oxidative degradation of MDPE commercial products (Karlsson, Smith, and Gedde, 1992).

5.7 ASSESSMENT OF THE EFFECT OF MATERIAL PROPERTIES ON THE DEGRADATION BEHAVIOR

5.7.1 Effect of antioxidant additives.

One of the properties that affect the rate of thermo-oxidation processes is the composition and concentration of antioxidant additives in the commercial products. The effect of antioxidant additives on the rate of mechanical degradation of the polyolefin geosynthetic products is clearly illustrated by the performance of two products, P-3 and P-3a. The P-3 product contains HALS-type antioxidant additives, and P-3a is a specially manufactured textile with only a minimum amount of antioxidants required for production purposes. The summarized comparisons between degradation rates for these two products are shown in figure 4.5, indicating essentially no induction time for the P-3a textile.

5.7.2 Physical properties of commercial geosynthetics.

Physical properties of a geotextile, such as integrity and homogeneity of fibers, also play an important role in determining the rate of thermodegradation. SEM studies indicate that there are initial cracks on the surface of fibers for geotextile P-4, which is a needlepunched nonwoven staple type. These initial cracks, apparently induced during manufacturing, are additional locations for free-radical reactions during auto-oxidation, which accelerate the degradation of the polymer as well as create an additional surface for oxygen penetration into the polymer. The strength loss is not only a function of increased oxidation rate, but is also due to the crack propagation phenomenon itself. For the same level of oxidative degradation and the same level of free-radicals, strength loss will be more severe when failure is by crack propagation than when failure is by ductile mechanisms. It takes less energy to fail by crack propagation than to fail by ductile mechanism. As shown in figure

4.7, thermo-oxidation of the P-4 product results in intensive cracking of polymeric fibers with drastic tensile strength loss during exposure to elevated temperature in intense circulating air.

SEM analysis indicates (figure 4.12) that there are cracks on the fiber surface of the P-9 "as received" product, which is a slit-film woven geotextile. The cracks are distributed in a parallel direction to the length of fiber with variable density. The density of transverse cracks distribution is also variable along the fiber length. These initial cracks are again additional locations for free-radical reaction, and result in the observed variations of strength losses during aging in circulating air.

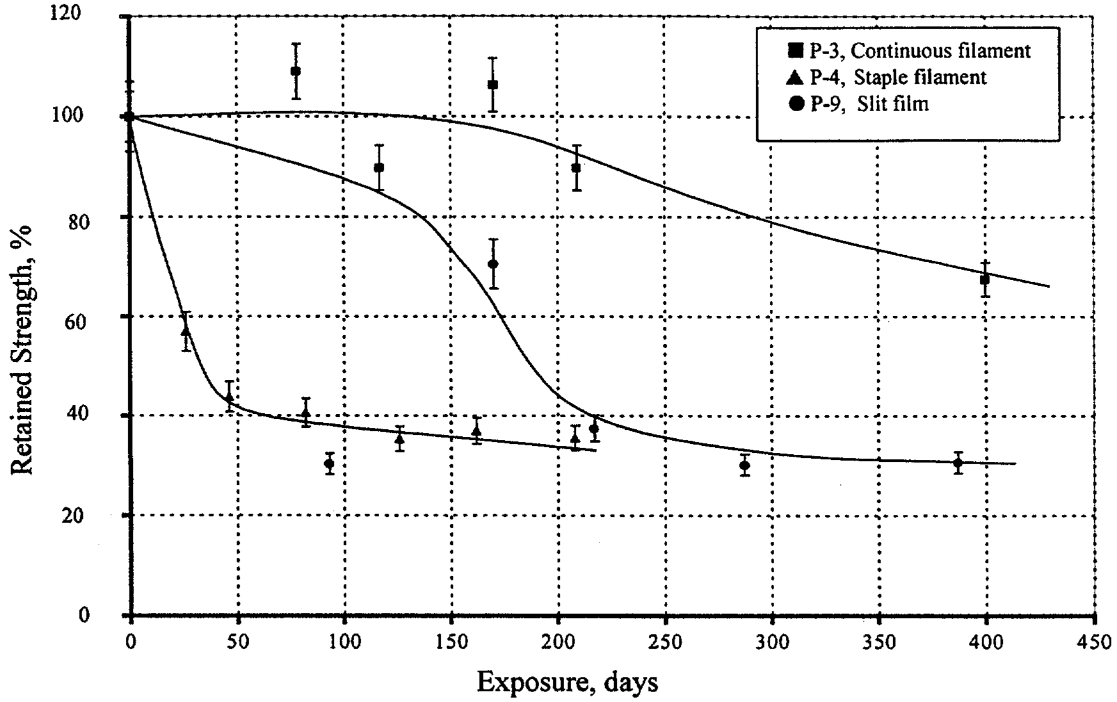


Figure 5.6. Degradation rate for selected commercial geosynthetics, oven aged in circulating air at 60°C.

Morphology analysis of the fiber surface for the P-3 product, which is a continuous filament nonwoven geotextile, indicates that there are no apparent cracks on the fibers "as received." Fibers of highly degraded specimens with a strength loss of more than 50 percent exhibit no surface cracks either.

It appears that degradation of commercial geotextiles in circulating air depends on the specifics of the manufacturing process. Materials made of staple-type filaments or films (P-4, P-9) exhibit cracks on the surface of virgin fibers or films. These initial cracks, which provide reaction sites for thermo-oxidation, result in significant cracking and rapid strength loss during exposure to elevated temperatures in circulating air. A continuous filament-type product (P-3) does not exhibit apparent cracks on the surface of virgin fibers. This results in a slower degradation compared to slit-film and staple-type geotextiles. The comparison of degradation rates in circulating air for the different types of geosynthetics is presented in figure 5.6.

5.8 ASSESSMENT OF THE EFFECT OF ENVIRONMENTAL CONDITIONS ON THE DEGRADATION RATE FOR COMMERCIAL POLYOLEFIN GEOSYNTHETIC PRODUCTS

5.8.1 Metal salt contamination.

The literature reports that the presence of metal salts in polymeric mixtures accelerates the thermo-oxidation process (Kelen, 1982). Metal salts and their products work as a catalyst for the formation of free-radicals in a polymer, resulting in the acceleration of oxidation. Another mechanism by which metal salts affects the degradation process is that the salts and their derivatives react with antioxidant additives, reducing their protective effect.

Samples of P-3 contaminated to a 0.8-percent and 10-percent weight-to-weight ratio (w/w) exhibit distinctive differences in their pattern of degradation in circulating air. A low level of contamination (0.8-percent w/w) results in a degradation rate that is similar to the degradation for non-contaminated samples. High levels of contamination by $FeCl_3$ (10% w/w) lead to the acceleration of degradation as compared with non-contaminated samples aged under the same oven condition. Summarized results for the P-3 commercial product contaminated by $FeCl_3$ to 0.8 percent and 10 percent w/w are shown in figure 5.7.

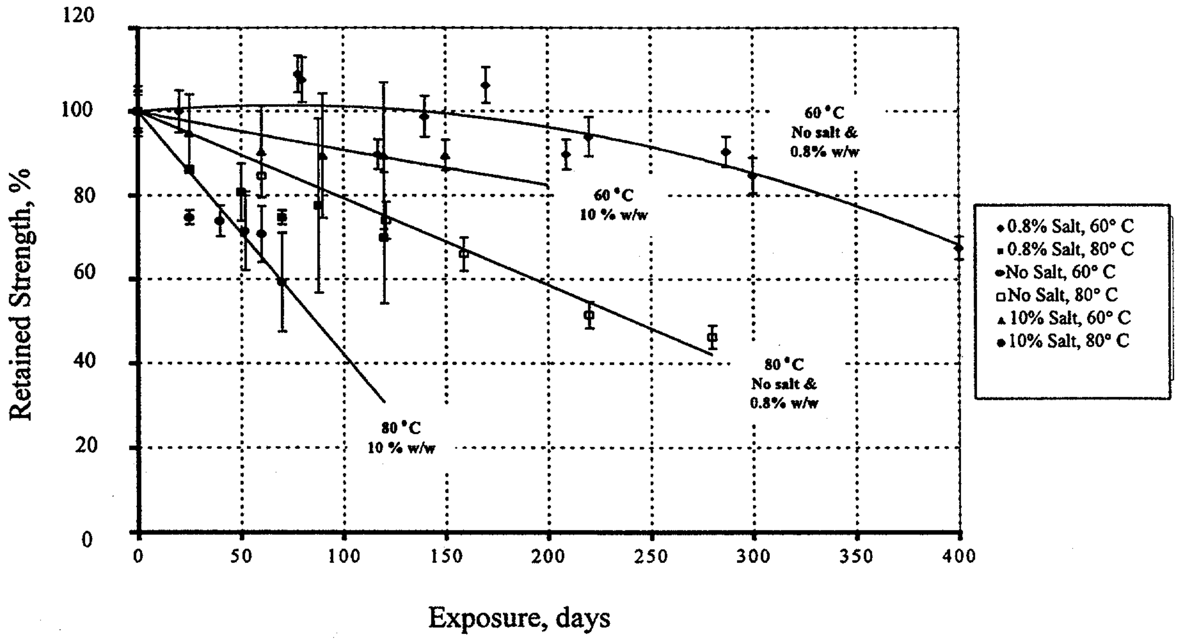


Figure 5.7. Effect of $FeCl_3$ salt contamination on the degradation rate of P-3, oven aged in circulating air at 21% O_2.

It should be noted that the contamination levels studied represent extreme levels of deposited salts in order to study behavior. Potential in-ground levels have not been determined.

5.8.2 Effect of oxygen partial pressure.

Consideration of the Basic Auto-Oxidation Scheme for polyolefins indicates that oxygen partial pressure (or concentration of oxygen) in the atmosphere is the most important variable with the temperature of reaction in controlling the rate of mechanical degradation caused by oxidation. The summarized results on mechanical degradation in circulating air (21% O_2) and in stagnant diluted air (8% O_2) at various temperatures for products P-4 and P-3 are shown in figure 5.8 and in figure 5.9, respectively.

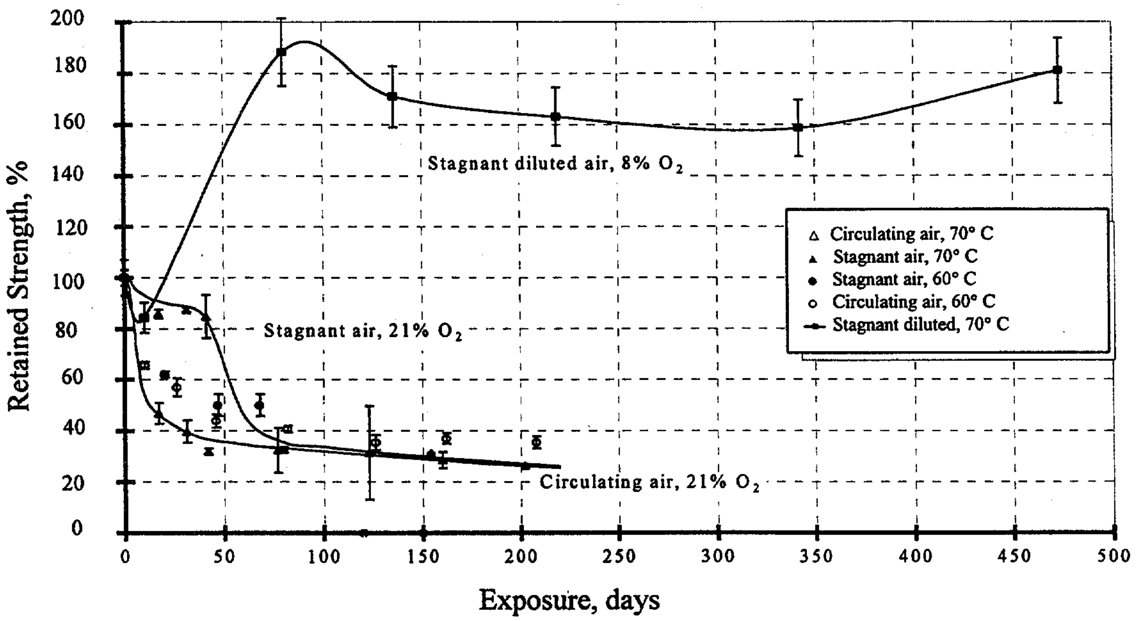


Figure 5.8. Effect of oxygen partial pressure and intensity of air circulation on the rate of mechanical degradation for geotextile P-4.

It appears that in a stagnant atmosphere of diluted air (8% O_2), geotextile P-4 gains tensile strength during exposure to elevated temperatures. The initial cracks observed on the P-4 fibers "as received" disappear with oven-aging time. The crack disappearance phenomenon may occur due to the increase of the rate of molecular diffusion in the polymer, leading to crack healing, analogous to the cold welding for metals. When the rate of diffusion and crack healing prevails over the rate of oxidation, a strength gain effect is observed.

Stagnant air circulation (21% O_2) in the oven results in an initial decrease of the degradation rate and toward the end of the exposure period, tensile strength values for P-4 almost reach the same values as when this geotextile is aged in intense circulating air. For both conditions, it is hypothesized that the rate of oxidation is greater than the rate of crack healing, due to the higher oxygen concentration in air than in the diluted air (8% O_2) condition.

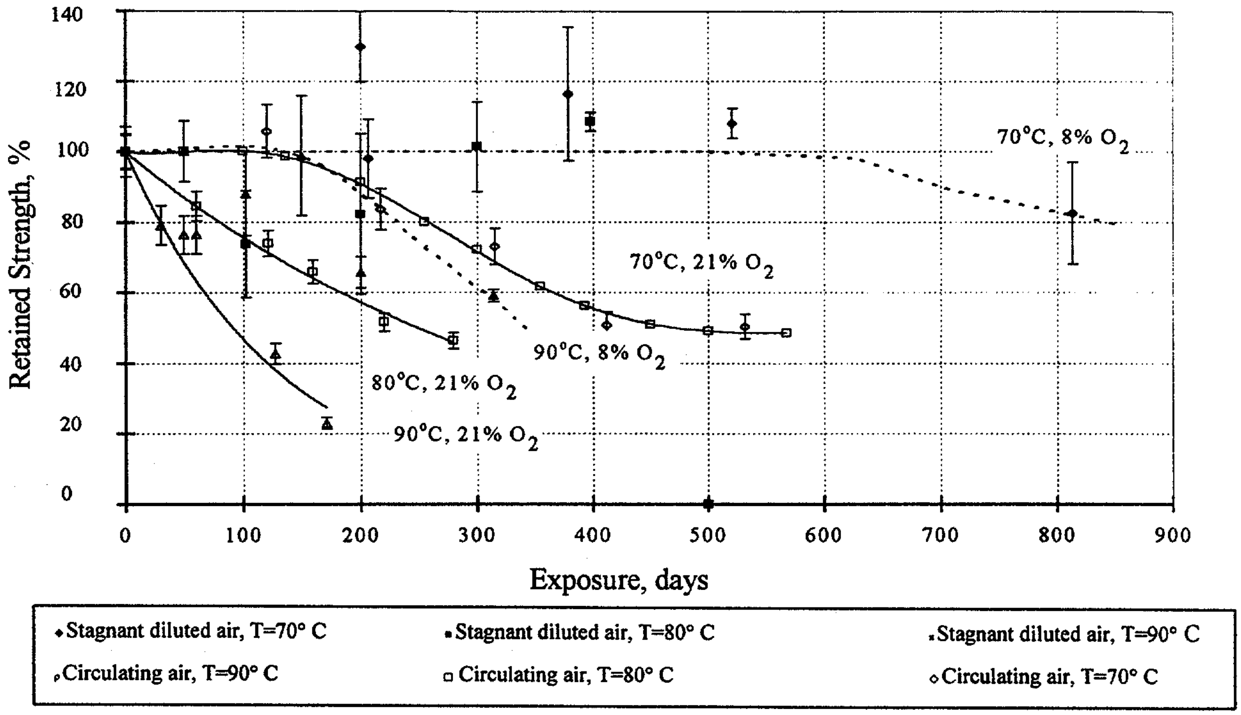


Figure 5.9. Tensile strength for continuous filament geotextile P-3 during oven aging in stagnant diluted air at 8% O_2 and in circulating air at 21% O_2.

The continuous filament P-3 geotextile does not exhibit a statistically significant strength increase or decrease when aged in stagnant diluted air (8% O_2) at 70°C and 80°C until approximately 600 days of exposure. Oven aging at 90°C results in a measurable strength loss over the period of exposure. However, degradation in diluted air (8% O_2) at 90°C is slower than degradation in circulating air (21% O_2) at the same temperature. The summarized comparisons between degradation rates in stagnant diluted air (8% O_2) and in circulating air (21% O_2) are shown in figure 5.9.

Additional studies have been made (funded by Polyfelt Inc.) to assess the effect of soil confinement on the rate of degradation in diluted air for the P-3 product. A special chamber has been developed, similar to the one described in figure 3.5, filled with diluted air (8% O_2) instead of a hydrolytic solution. The results of this limited study indicate that there is no difference between the rate of degradation in sand and in stagnant diluted air at 8% oxygen. It appears that the difference between degradation rate in circulating air (21% O_2) and in sand (8% O_2) is more pronounced at a lower temperature of incubation (90°C) than at 110°C. The highest incubation temperature of 110°C is close to the working limit temperature of 135°C for the HALS antioxidant, contained in P-3, which may explain the results. The summarized comparisons between degradation rates in stagnant diluted air (8% O_2), in circulating air (21% O_2), and in sand are shown in figure 5.10.

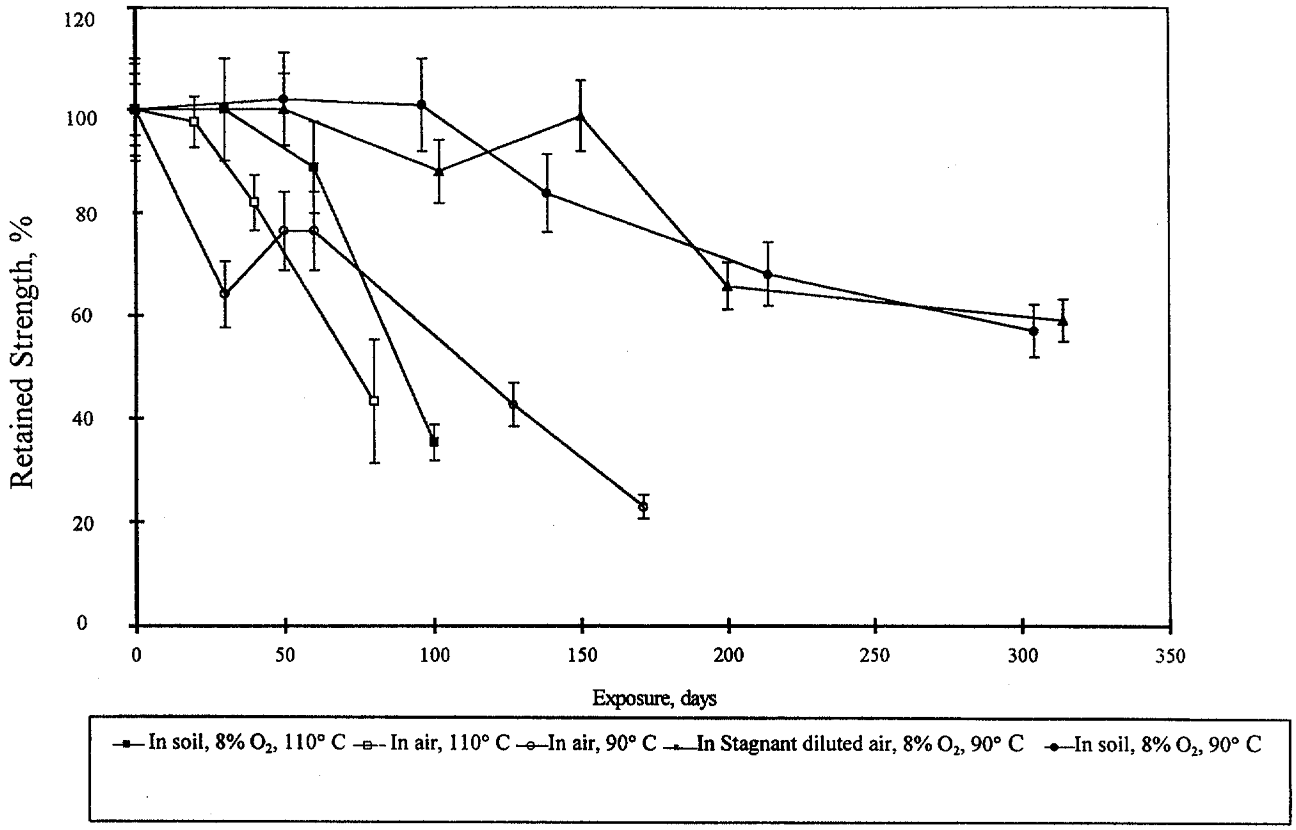


Figure 5.10. Tensile strength for P-3 product during oven aging in stagnant diluted air at 8% O_2, in circulating air at 21% O_2, and in sand at 8% O_2.

5.9 INTERPRETATION PROCEDURE

The kinetics of auto-oxidation for the general case of antioxidant presence consist of two phases. The first phase (induction period) describes the consumption of antioxidants, with the reaction constant for consumption defined by an Arrhenius-type dependency. During the second phase, oxidation and corresponding mechanical degradation is described by the kinetics of the BAS.

The assumptions for auto-oxidation and the corresponding kinetic equations at a constant oxygen concentration (pressure) suggest a first-order kinetics reaction for numerical modeling of laboratory aging data for mechanical degradation of polyolefin geosynthetic products. However, all the assumptions regarding the order of reaction must be verified by a regression analysis of experimental data.

The data usually obtained in the laboratory, does not provide sufficient information on the kinetics of antioxidant depletion during aging. Therefore, the order of the reaction for antioxidant consumption cannot be determined directly from experimental data. However, analysis of integrated rate laws presented in table 5.1 yields a general expression for induction time versus temperature at any chosen level of antioxidant depletion $[A]/[A]_0=c$. Assuming that the reaction constant for antioxidant consumption obeys the Arrhenius law, this relationship is as follows:

$$\ln \frac{1}{t_{ind}} = C_1 + C_2 \frac{E_a}{RT} \qquad (5\text{-}14)$$

where C_1 and C_2 are the constants for a particular antioxidant and a chosen level of depletion *c*.

Equation (5-14) suggests a procedure for estimating the induction time at a given temperature T_0°K:

1. The induction period t_{ind} is determined at each temperature of exposure. It is defined as the period of no statistically significant changes in mechanical strength. For a geosynthetic exhibiting a period of no strength loss prior to deterioration, a tangent is constructed to the maximum slope of the post-induction degradation curve. This is extended to intersect the no-strength loss line. The abscissa of this intersection point is the induction period t_{ind} (see figure 5.11).

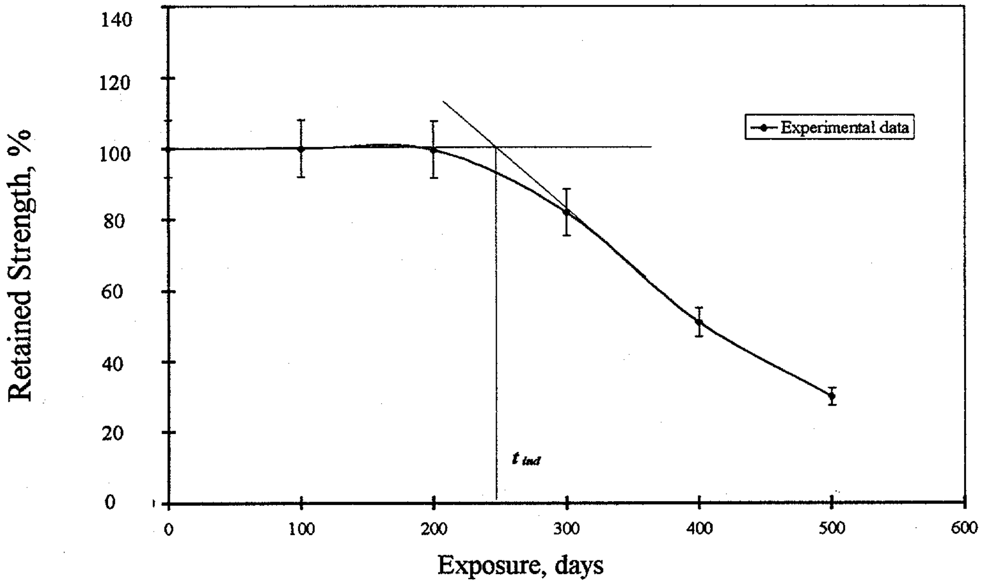


Figure 5.11. Determination of induction period from experimental data.

2. A linear regression analysis is conducted for the function $\ln(1/t_{ind})$ versus the reciprocal temperature ($1/T$°K). The obtained linear equation $\ln(1/t_{ind}) = a(1/T)+b$ is used to find the value of the induction period at any given temperature, T_0°K:

$$t_{ind} = 1/\{\exp[a(1/T_0)+b]\} \qquad (5\text{-}15)$$

Interpretation of data for mechanical degradation observed in the post-induction period requires the determination of the order of the degradation reaction for the particular product tested to be used in numerical estimates of the anticipated rate of degradation (strength loss per 100 years) and corresponding time to 50-percent strength loss at any given temperature. Consideration should be limited to reactions of the zero, first, and second order. The procedure for determining the order of reaction and the following estimates are as follows:

3. Functions representing the kinetics of the zero, first, and second order are used to fit experimental data for the observed progressive mechanical degradation after the induction period for each temperature of aging. These functions are (table 5.1):

   $x=1-kt$ - zero order; $x=e^{-kt}$ - first order; $x=\dfrac{1}{1+[A]_0 kt}$ - second order.

   - Zero-order approximation is required to plot the normalized retained strength $F(t)/F_0$ versus time for different temperatures. The slope of a linear regression line will correspond to the reaction constant k at the temperature of aging.
   - A semi-natural log chart may be used to plot $\ln[F(t)/F_0]$ versus time t for the first-order approximation. The slope of a linear regression line is the reaction constant k at a specific temperature of testing.
   - The kinetic equation for a second-order reaction may be transformed into the form $1/x = 1+k_1 t$, where $k_1=F_0 k$, which permits a linear regression analysis of $F_0/F(t)$ versus t curves with corresponding estimates of k_1.

   The square of the Pearson product moment correlation coefficient R^2 (Mood, Graybill, and Boes, 1974) is calculated for each of the regression lines. The highest values of R^2 indicate the order of reaction to be chosen.

4. The obtained values of the natural logarithm of reaction constant $ln(k)$ for the chosen type of kinetics are plotted versus the reciprocal temperature of aging (Arrhenius plot).
5. A linear regression analysis is used to find the equation for $ln(k)$ as a function of reciprocal temperature $1/T$, $ln(k) = a(1/T)+b$. This equation yields the value of k for the temperature of interest, T_0: $k(T_0)= exp[a(1/T_0)+b]$.
6. The obtained $k(T_0)$ value of the rate constant is used to calculate the normalized retained strength at a given time $x(t)=F(t)/F_0$ or to calculate time t_i to reach a certain level of retained strength $c= F_i/F_0$ at a given temperature T_0 °K for a specific reaction law:

   - $x(t)=1-k(T_0)t$; $t_i=\dfrac{1-c}{k(T_0)}$ - for zero-order reactions (5-16)
   - $x(t)= exp(-k(T_0)t)$; $t_i =[ln(1/ c)]/k(T_0)$ - for first-order reactions (5-17)
   - $x(t)=\dfrac{1}{1+k_1(T_0)t}$; $t_i=\dfrac{1-c}{k_1(T_0)c}$ - for the second-order reaction law (5-18)

5.10 KINETIC MODEL IMPLEMENTATION OF EXPERIMENTAL DATA FOR MECHANICAL DEGRADATION.

5.10.1 P-3, nonwoven needlepunched continuous filament geotextile.

Commercial geotextile P-3 containing antioxidant additives exhibits an induction period as shown in the degradation curves (figure 4.4) in circulating air at elevated temperatures. As discussed above, Arrhenius-type modeling is used to extrapolate values of an induction period obtained at elevated temperatures to predict values for an induction period at an ambient temperature (steps 1 and 2).

1. The summarized data on the induction period in circulating air at elevated temperatures for P-3 are shown in table 5.2 and in figure 5.12.

Table 5.2. Induction period for product P-3, aged in circulating air (21% O_2).

Material	Temperature, °C	Induction period, days
P-3	90	0
	80	20
	70	120
	60	200
	50	450

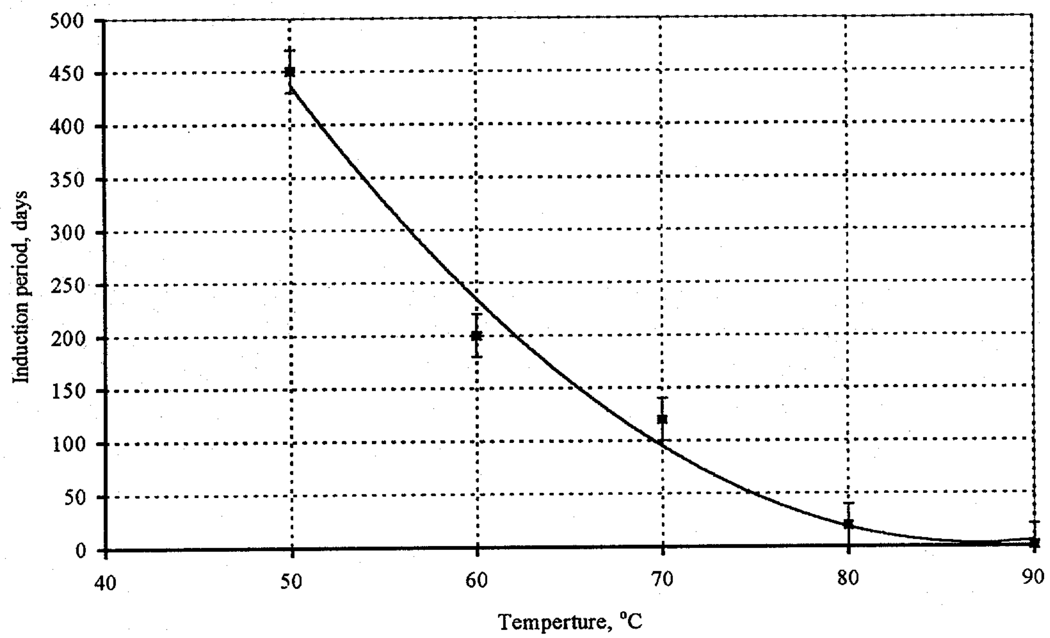


Figure 5.12. Induction period for P-3 geotextile oven aged in circulating air at 21% O_2.

2. The next step in the interpretation procedure is to plot $ln(1/t_{ind})$ versus reciprocal temperature $1/T$ (figure 5-13). It appears that a linear approximation satisfactorily fits experimental data for $ln(1/t_{ind})$ on an Arrhenius-type plot.

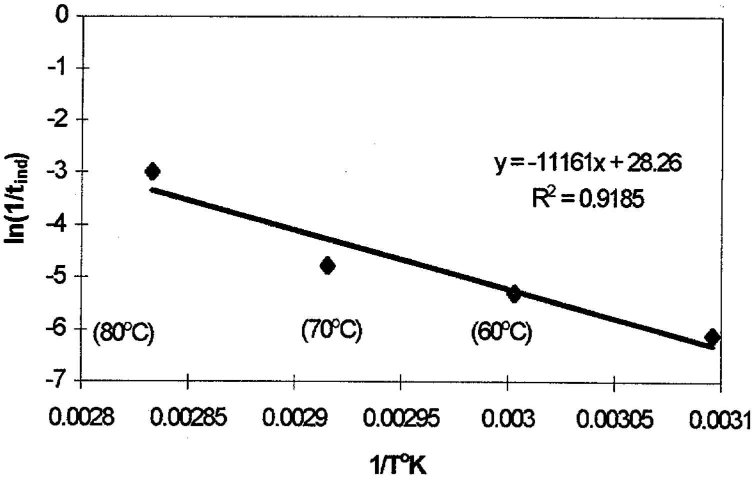


Figure 5.13. Arrhenius plot for the induction time t_{ind} for P-3 geotextile, oven aged in circulating air at 21% O_2.

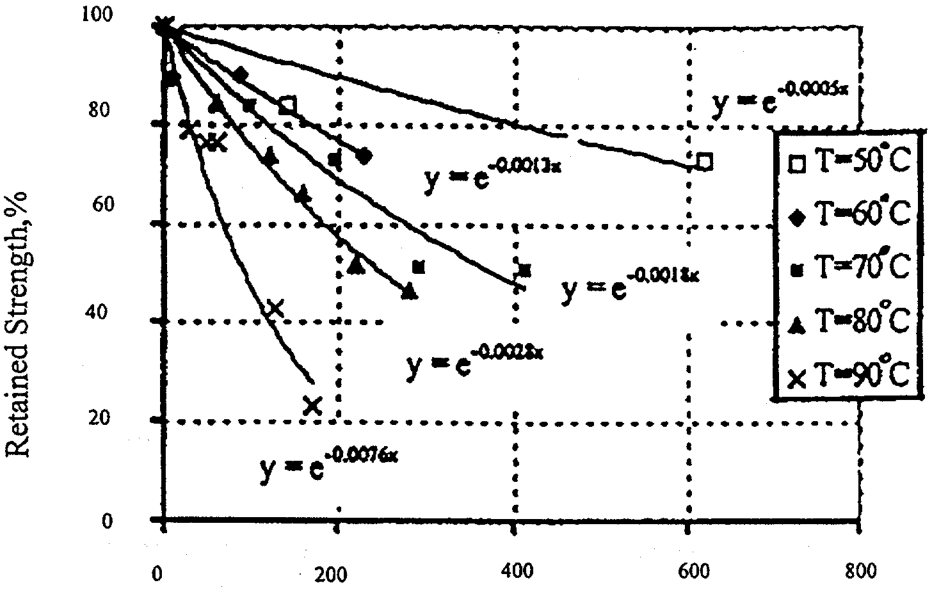
The solution of the equation for the linear regression of $ln(1/t_{ind})$ versus reciprocal temperature $1/T$, $ln(1/t_{ind})=-11161(1/T)+28.26$ at 20°C or T=293°K, yields a value of anticipated induction period t_{ind} = 51 years.

Interpretation of data for mechanical degradation observed after the induction period is conducted in accordance with the scheme for auto-oxidation previously described in steps 3 through 6.

3. Regression functions corresponding to zero-, first-, and second-order reaction laws are used for the curve fitting of experimental data. The result of the exponential curve fitting ($x=e^{-kt}$) corresponding to the first-order reaction is shown in figure 5.14. The square of the Pearson product moment correlation coefficient R^2 is calculated for the well-developed regression lines used in the approximation and the results are presented in table 5.3.

Table 5.3. Correlation by R^2 for reaction laws and experimental data on mechanical degradation of the P-3 product.

Reaction order, *n*	Kinetics law (approximation function)	R^2			$\bar{R}^2$
		T=70°C	T=80°C	T=90°C	
0	$x=1-kt$	0.92	0.98	0.98	0.96
1	$x=e^{-kt}$	0.93	0.99	0.94	0.95
2	$x=\frac{1}{1+k_1t}$	0.91	0.96	0.81	0.86



Time, days

Figure 5.14. Exponential curve fitting for tensile strength degradation after the induction period for the P-3 geotextile aged in circulating air at 21% O_2.

Results of a regression analysis indicate that zero- and first-order reactions are the most likely laws in describing the actual kinetics of mechanical degradation in circulating air at 21-percent oxygen for P-3 within the temperature range of testing. A first-order reaction is predicted by the BAS model for polyolefins without antioxidants at a constant oxygen pressure (equation 5-12). Therefore, the priority in the selection of the reaction order is given to the exponential law (first order).

4. The obtained values of the reaction constant *k* are used to plot *ln(k)* versus corresponding reciprocal temperature (Arrhenius plot) as shown in figure 5.15.
5. A linear regression analysis of the *ln(k)* versus $1/T$ curve yields an equation for the regression line as $ln[k(T)]=-7361.4(1/T)+15.218$ with $R^2=0.97$.
6. The solution of a linear regression line equation at $T_0=293°K$ (20°C) yields $k=5.5\times10^{-5}$. The substitution of the obtained value for the reaction constant *k* into equation (5-17) yields an estimate of time to 50% strength loss at 20°C after the induction period of 38 years.

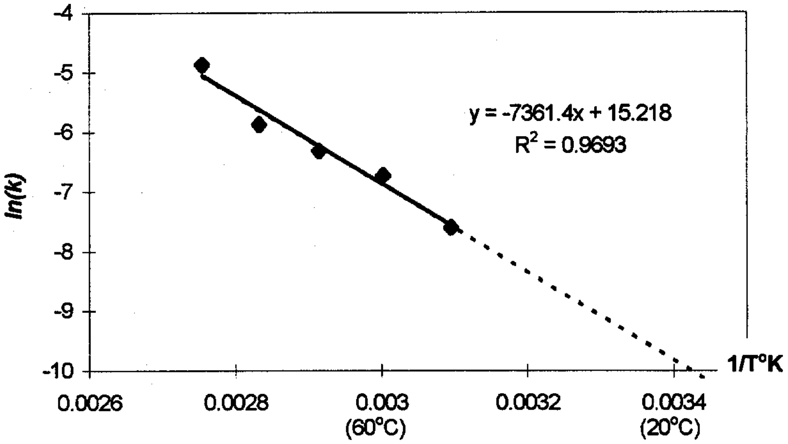


Figure 5.15. Linear regression analysis of the reaction constant for P-3 commercial geotextile, oven aged in circulating air at 21% O_2.

The overall anticipated time to 50-percent strength loss at a room temperature of 20°C in an atmosphere of circulating air is 89 years for commercial product P-3. It appears that the estimate for the induction period of 51 years with no strength loss suggests that the antioxidant consumption rate primarily determines the practical durability of this commercial product under the conditions of testing.

The obtained estimate of anticipated time to 50-percent strength loss for this geotextile is valid only for the conditions of testing, e.g., circulating air.

Assuming that the engineering life of a structure using geosynthetics is at least several decades, the degradation rate obtained in laboratory experiments may be expressed as a percentage of tensile strength loss per year (%/ yr). The laboratory data obtained for the P-3 product yields a degradation rate of 1.3 %/ yr *after the induction period of 51 years.*

The Arrhenius equation for the reaction rate constant could be rewritten as $ln(k) = C - U/RT$, where U is the apparent activation energy, and $R = 8.31$ J/mol. Solving this equation with respect to U, one obtains a value of $U = 61$ kJ/mol, which is in reasonable agreement with the value of 65 kJ/mol reported by Wisse and Birkenfeld (1982) for PP geosynthetic with extracted antioxidants.

Furthermore, the data indicates that lower oxygen concentration and a stagnant atmosphere will result in the decrease of this degradation rate. Therefore, the obtained estimates of time to 50-percent strength loss for the product tested are valid for severe environments that are not anticipated for in-ground use and may be considered only as very conservative estimates for the product performance in "in-service" conditions.

The data obtained in stagnant diluted air (8% O_2) provides a lower limit estimate of induction period for the P-3 geotextile as shown in table 5.4.

Table 5.4. Induction period for product P-3, aged in stagnant diluted air (8% O_2).

Material	Temperature, °C	Induction period, days
P-3	90	150
	80	450
	70	650

The lower limit estimates of induction period may be used in a numerical modeling of induction time at 20°C for P-3 in stagnant diluted air. The calculation yields an induction period at 20°C of 240 years.

For the research-grade textile P-3a, the interpretation of experimental data in circulating air at 21 percent O_2 yields an estimate of anticipated time to 50-percent strength loss at 20°C of 29 years. This result is in good agreement with the estimate of post-induction degradation to a 50-percent strength loss for geotextile P-3, which is manufactured from the same polymer mixture.

The interpretation of data in stagnant diluted air at 8 percent O_2 yields an estimate of anticipated time to 50-percent strength loss at 20°C as of 47 years for the P-3a textile, which is a decrease by a factor of 1.6 when compared to the degradation rate in air at 21 percent O_2. This result is in general agreement with an estimate of the reduction of the degradation rate in diluted air at 8 percent O_2 based on the integrated law of chemical kinetics (equation 5-4).

5.10.2 P-4, nonwoven needlepunched staple geotextile.

In order to apply the auto-oxidation model for mechanical degradation of geotextile P-4, it is assumed that the observed rate of mechanical degradation is proportional to the rate of oxidation that leads to the crack propagation. There is no observed induction period in the degradation curves for the P-4 product (see figure 4.8) aged in circulating air; therefore, only applicable portions of the step-by-step procedure (steps 3 through 6) are used to model the degradation of mechanical properties for this particular product.

The implementation of the step-by-step interpretation procedure for the P-4 product is as follows:

1. Regression functions corresponding to zero-, first-, and second-order reaction laws are used for the curve fitting of experimental data. Exponential curve fitting ($x=e^{-kt}$), corresponding to first-order kinetics, is shown in figure 5.16. The result of a hyperbolic curve fitting ($x=\frac{1}{1+k_1 t}$), corresponding to a second-order reaction, is shown in figure 5.17. The square of the Pearson product moment correlation coefficient R^2 is calculated for each of the regression lines used in the approximation and the results are presented in table 5.5.

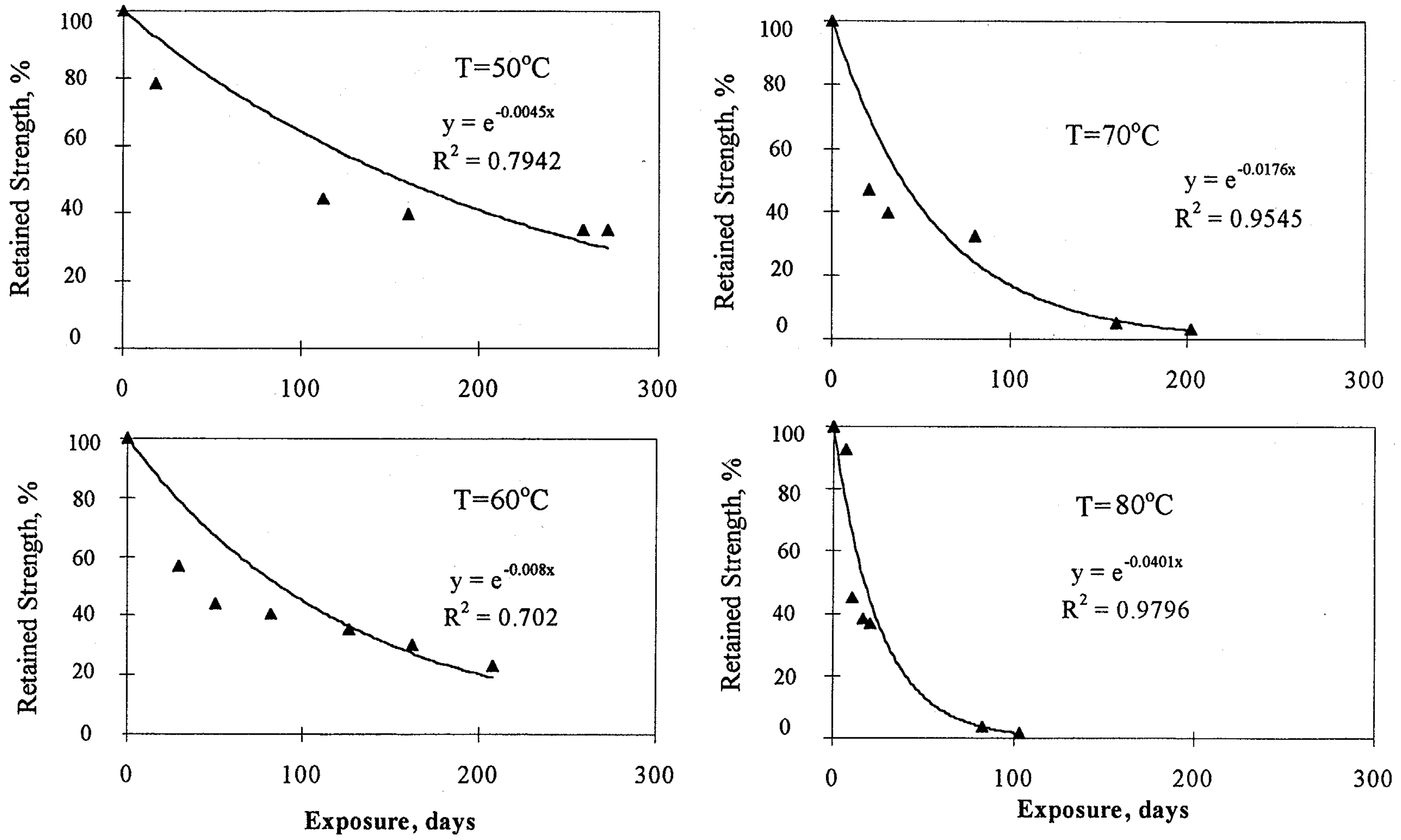


Figure 5.16. Exponential curve fitting, corresponding to a first-order reaction, of experimental data for tensile strength loss for P-4 commercial geotextile, oven aged in circulating air at 21% O_2.

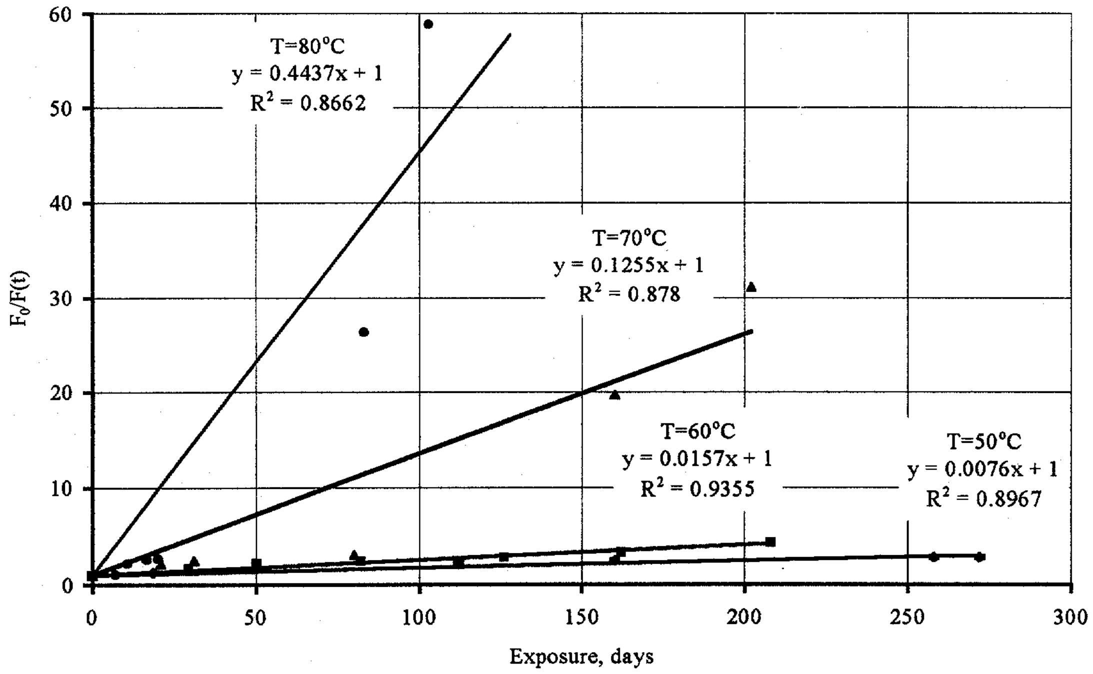


Figure 5.17. Hyperbolic curve fitting, corresponding to a second-order reaction law, for tensile strength degradation for P-4, aged in circulating air (21% O_2).

Table 5.5. Likelihood by R^2 of different reaction laws for an approximation of experimental data on mechanical degradation of the P-4 product.

Reaction order, *n*	Kinetics law (approximation function)	R^2				$\bar{R}^2$
		T=50°C	T=60°C	T=70°C	T=80°C	
0	$x=1-kt$	0.65	0.27	0.30	0.37	0.40
1	$x=e^{-kt}$	0.79	0.70	0.95	0.98	0.85
2	$x=\frac{1}{1+k_1t}$	0.89	0.93	0.87	0.86	0.89

The results of a regression analysis indicate that equations of first- and second-order reactions provide the best fit of experimental data on tensile strength loss in circulating air for the P-4 product. The equation of the first-order reaction provides a better fit at higher temperatures of 70 and 80°C than the hyperbolic function of a second-order reaction. A hyperbolic function of a second-order reaction satisfactorily fits experimental data at temperatures ranging from 50 to 80°C. There is no apparent reason at this point to prefer one kinetics reaction over another. Therefore, these two approximations are used in further interpretations.

2. The values of the reaction constant k, obtained for first- and second-order approximations, are used to plot $ln(k)$ versus corresponding reciprocal temperature (Arrhenius plot) as shown in figure 5.15 for the P-3 product.
3. A linear regression analysis of the $ln(k)$ versus $1/T$ curve yields equations for regression lines as:

   $ln[k(T)]=-8359.55(1/T)+20.387$ with $R^2=0.99$ for the first-order approximation; and

   $ln[k(T)]=-16235.41(1/T)+45.11$ with $R^2=0.96$ for the second-order approximation.

   The higher value of R^2, obtained in linear regression analysis, indicates that a first-order approximation provides a better fit to the Arrhenius equation for the reaction constant. Therefore, the first-order reaction law is used to calculate time to 50-percent strength loss at 20°C for the P-4 product.
4. The solution of a linear regression line equation $ln[k(T)]=-8359.55(1/T)+20.387$ at $T_0=293°K$ (20°C) yields $k=3.08\times10^{-4}$. The substitution of the obtained value for the reaction constant k into equation (5-17) yields an estimate of time to 50-percent strength loss at 20°C of 6.5 years, ***which is unrealistic in light of documented field performance***.

It should be understood that the model of auto-oxidation developed and applied to laboratory-obtained data for the P-4 product only illustrates the application of the BAS concept. The thermo-oxidation of the P-4 product in an atmosphere of circulating air at elevated temperatures results in the development of surface cracking, leading to the embrittlement of the polymer. The aging in intense circulating air appears to be an ineffective model of condition expected in the field, e.g., low oxygen concentration and stagnant atmosphere. By comparison, results in a stagnant atmosphere of diluted air indicate no crack development over the period of exposure to elevated temperatures.

Therefore, the obtained estimates for the anticipated time to 50-percent strength loss for the P-4 product, using this testing protocol, must not be used to evaluate in-field performance of this product.

Tests for P-4 in stagnant diluted air indicate that some process other than oxidation controls the behavior of this material at elevated temperatures. Therefore, the numerical model developed within the framework of BAS cannot be directly applied to laboratory data obtained under these conditions for the P-4 product.

5.10.3 P-9, slit-film woven geotextile.

Oven aging in circulating air (21% O_2) results in intensive surface crack development for this geotextile. Incubation in stagnant diluted air (8% O_2) at elevated temperatures indicates that there is no healing of initial cracks on the surface of the P-9 film. Experimental data on a tensile strength loss monitoring during the thermo-oxidation indicate no consistent degradation pattern, except a general tendency toward strength decrease (see figure 4.13). High variation of remaining strength values obtained over the period of exposure to elevated temperatures *does not permit application of the BAS numerical model to estimate anticipated rate of degradation at 20 °C for the P-9 product.* Therefore, an alternate procedure using OIT measurements has been implemented to estimate induction time, since it has been shown as a potentially viable method of tracking antioxidant depletion for geosynthetics containing no HALS.

Since it has been demonstrated for simple mixtures that the OIT value is proportional to the amount of antioxidants at any time, valid OIT data could be used to estimate the rate of antioxidant consumption at an ambient temperature. A procedure similar to those used to estimate the anticipated rate of mechanical degradation can be used to calculate the rate of antioxidant consumption at an ambient temperature for the P-9 product. The results of regression analyses indicate that an equation of the first order provides the best fit of experimental data for OIT loss in circulating air for this product. The values of reaction constant *k* are used to plot *ln(k)* versus $1/T$ (Arrhenius plot) as shown in figure 5.18 for P-9.

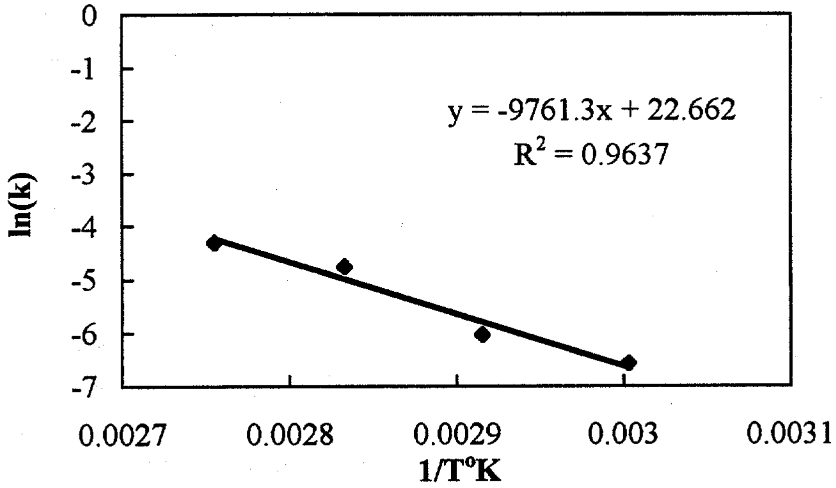


Figure 5.18. Arrhenius plot for OIT loss for P-9 geotextile aged in circulating air at 21% O_2.

The solution of the equation for linear regression of *ln(k)* versus reciprocal temperature $1/T$: $ln(k)=-9761.3(1/T)+22.662$ at 20°C or T=293°K, yields a value of anticipated time to a 70% OIT loss of 127 years. Time to 80% OIT loss is 160 years.

Assuming that a minimum effective amount of antioxidants is from 20 to 30 percent of the initial amount, the induction period based on OIT may be estimated as between 120 and 160 years for the P-9 product, which suggests that antioxidant consumption if correctly measured by OIT determines the durability of this product.

It must be noted that the results of this analysis are not supported by the oven-aging results, which indicate an inconsistent pattern of significant strength loss during the early stages of oven aging.

For this PP geosynthetic, OIT depletion to some baseline minimal level may not be a measure of induction time. Therefore, analyses using OIT depletion should not be considered as indicative of the potential durability of this project, but rather as an example of the use of this alternate analysis method.

It should be noted that induction time estimates based on OIT (Std. OIT or HP-OIT) are potentially less reliable for PP products than estimates obtained from strength-loss measurements, primarily because of the following:

1. The OIT sample is very small and may not reflect antioxidant distribution in the product, which may be non-uniform. It should be understood that the antioxidant in geotextiles is often less than 0.25 percent by weight.
2. Minimum intrinsic OIT values representing an essentially unstabilized product have not been established and may vary as a function of type of antioxidant product and testing method.
3. OIT measurements have been shown to be relatively reliable for HDPE stabilized with hindered phenols, phosphite, or thiosynergist antioxidants. They are less reliable when the antioxidant is a hindered amine (HALS) as the latter antioxidant effective temperature range is below the OIT test temperature range (150°C for HP-OIT and 200°C for Std. OIT). For polypropyelene (PP) products stabilized with HALS, they are even less reliable as the OIT test temperature is in the 170 to 175°C range for either test.

5.10.4 P-1, uniaxially drawn HDPE geogrid.

Results available for P-1 indicate a different degradation behavior as compared to that of PP geotextiles. A significant increase of ultimate elongation during oven aging indicates that some process other than oxidation may be responsible for the strength losses. Analysis of load-strain curves for virgin and oven-aged samples indicate that there is a significant decrease in initial modulus by a factor of 2 to 4 when aged at elevated temperatures. As discussed in chapter 4, this may indicate the development of processes other than oxidation in the polymer, suggesting that the protocol of oven aging implemented in this study may be invalid for the P-1 product at temperatures of incubation above 80°C. It is anticipated that lowering the incubation temperature to 50 to 60°C may reduce the temperature-induced changes in the P-1 product and permit measurement of an induction time reflecting the beneficial effects of the antioxidant used. However, lower incubation temperatures will result in the significant extension of the incubation time to 5 to 7 years, making this approach impractical. One additional test subsequently performed indicated no statistically significant changes of mechanical properties for the P-1 product incubated at 60°C for 250 days, compared to an approximate loss of 25 percent when incubated at 80°C. A crude approximation of the 60°C results would suggest an induction period in excess of 60 years.

The above strongly suggests the necessity of developing an alternate protocol for laboratory-accelerated testing for commercial geosynthetic products exhibiting abnormal behavior due to incubation at elevated temperatures as outlined below.

Notwithstanding the above, the alternate procedure using OIT measurements was used to predict the induction period. Assuming that the minimum effective amount of antioxidant is approximately 10 percent of the initial amount, an induction period of 55 to 60 years was estimated in circulating air. Insufficient credible data was developed to predict induction time in a reduced-oxygen atmosphere.

This estimate for HDPE is within the range of induction times determined by Hsuan and Guam (1998) for HDPE geomembranes that used hindered phenols and/or phosphites as antioxidants, although the amounts of antioxidant used in the reported geomembranes may not be consistent with the antioxidant in P-1.

5.11 FEASIBILITY ASSESSMENT OF HIGH OXYGEN PRESSURE AS AN ALTERNATE ACCELERATED DURABILITY TEST FOR POLYOLEFIN-BASED GEOSYNTHETICS

Data developed in these studies have indicated the complexity of the aging process at elevated temperatures performed in forced draft ovens in air (21% O_2) as recommended in ASTM D-3045, "Heat Aging of Plastics Without Load," and in stagnant diluted air at an 8-percent oxygen level.

These studies indicated that using temperature to accelerate oxidation requires long incubation times to achieve measurable degradation at moderate temperatures and that for some products, the high incubation temperature significantly changes the nature or morphology of the products tested, making the results invalid. Therefore, the feasibility of an alternate protocol using oxygen pressure at ambient temperature has been assessed on a preliminary and limited basis.

Numerical modeling of the degradation rate indicated that service life, i.e., anticipated time to 50-percent strength loss at an ambient temperature at 21-percent oxygen, is primarily determined by the induction period for the products tested. Evaluation of the data shown in figure 5.12 suggests an induction period of more than 50 years for the P-3 geosynthetic. To accurately determine the induction period requires lowering the temperature of exposure, possibly extending the incubation period to 2 to 4 years. An incubation period of 2 to 4 years to determine this key degradation characteristic for commercial geosynthetic products is somewhat impractical.

Experimental results for the nonwoven staple fiber P-4 geotextile (figure 4.7a) indicate that there is intensive fiber surface crack development (figure 4.7b and c) with a substantial tensile strength decrease during oven aging in circulating air. Evaluation of the data yields an unrealistically low lifetime estimate of 6.5 years to 50-percent strength loss for in-use conditions. However, geosynthetics of this type exhibit almost no tensile strength loss after being in service for more than 10 years.

By contrast, the same product exhibits a tensile strength increase up to two times when incubated at elevated temperatures in stagnant diluted air at 8-percent oxygen content (figure 4.9). Surface morphology analysis conducted with a scanning electron microscope (SEM) indicates that cracks and crazes, initially present on virgin staple fibers, tend to heal during exposure to elevated temperatures in stagnant diluted air (8% O_2).

These results indicate that oven aging of staple and tape products may trigger processes other than oxidation that would not have occurred or would have been negligible for in-service conditions when the ambient temperature is about 20°C and the oxygen level is 8 to 10 percent.

In light of the above, it is suggested that currently used oven-aging testing protocols based on ASTM D-3045 do not provide adequate estimates of a lifetime for staple and tape polypropylene geotextiles and possibly HDPE products. Therefore, it is necessary to develop an alternative protocol for accelerated durability testing for some polyolefin geosynthetics.

5.11.1 Theoretical model for high oxygen pressure accelerated degradation testing.

In chemical kinetics (Adamson, 1973), the rate R of a reaction $A+B+C+\ldots \rightarrow Products$ at constant temperature is expressed as a function of composition of the system according to a mass action law as:

$$-\frac{d[P]}{dt} = R = k[A]^x \times [B]^y \times \ldots \qquad (5\text{-}19)$$

where $[A]$ and $[B]$ are the concentrations of reactants, and k is the rate constant being independent of the concentration of the reactants, but dependent on temperature.

The order of the rate law is the sum of the exponents $(x+y+\ldots)$. The typical cases are zero-, first-, and second-order reactions. The rate should be determined experimentally (Atkins, 1986).

In a simplified process of polyolefin oxidation, it is assumed that the rate of reaction at constant temperature depends on the concentration of the original polymer $[A]$ and the concentration of oxygen $[B]$ in equation (5-19). Data reported in the literature (Zolotova and Denisov, 1971; Kelen, 1982) indicates that the rate of oxidation may be proportional to the concentration of oxygen in the system, which corresponds to a first-order reaction. Therefore, an increase in oxygen pressure should result in the proportional increase of the rate of mechanical degradation for polyolefins. For example, the exposure of polyolefin-based geosynthetics to an atmosphere of pure oxygen may result in the acceleration of the degradation rate by a factor of 5 as compared to the rate anticipated in air (21% oxygen) at ambient temperature. The increase of oxygen pressure to 50 atm should result in a total acceleration of reaction by a factor of 250, as compared to the rate of oxidation under ambient conditions. However, the external factors such as the thickness of the polymeric film may complicate this simplified model (Faulkner, 1983).

5.11.2 Testing conditions and experimental results.

An atmosphere of pure oxygen at a pressure of 50 and 100 atm has been selected for an initial feasibility assessment of high oxygen pressure accelerated degradation for polyolefin geosynthetics. It is anticipated that this condition may accelerate the degradation rate by a factor of 250 in 50 atm and by a factor of 500 in 100 atm as compared to the rate under ambient (1 atm, 21% O_2, 20°C) conditions. Strip-size specimens (38 mm wide, 102 mm long) of five geosynthetics previously tested (P-1, P-3, P-3a, P-4, and P-9) were placed in a high-pressure chamber filled with pure oxygen at 50 and 100 atm at 20 to 22°C. The chamber was ventilated and refilled with oxygen once a day.

Mechanical tensile strength tests were conducted on strip-size specimens for materials as received and after the incubation. Relative changes of tensile strength are presented in table 5.6.

Table 5.6. Tensile strength loss for geosynthetics aged in pure oxygen at 50 and 100 atm and 20°C.

Condition		Equivalent time in normal condition,* years	Strength loss, %				
Oxygen pressure, atm	Incubation time, days	Material ⇒	P-1	P-3	P-3a	P-4	P-9
50	60	40	0	0	42	10	N/A
100	30	40	0	0	N/A	N/A	26
100	90	120	9	16	N/A	N/A	N/A

* 21% O_2, 20-22°C

5.11.3 Interpretation of test results.

The simplified kinetics for oxidation under oxygen pressure yields an acceleration factor of 250 for an oxygen pressure of 50 atm and a factor of 500 for an oxygen pressure of 100 atm. Strength losses from oven aging in circulating air at 21% oxygen and under high-pressure oxygen incubation at ambient temperature were calculated within the framework of the Basic Auto-oxidation Scheme and are shown in table 5.7. The comparison is based on strength losses in equivalent periods of time.

The results of this limited study indicate that oxygen pressure can be used as an accelerator and that the acceleration factor can be predicted by the simplified kinetics of oxidation for polyolefins. The estimates of strength loss over 40 years based on data developed under high oxygen pressure conditions are in satisfactory agreement with estimates obtained from oven aging in circulating air for some products tested. As expected, the P-3 product, with an estimated 50-year induction period, exhibits no tensile strength loss over a period equivalent to 40 years. The P-1 product, with a strength-loss estimate of less than 10%, also exhibits no tensile strength loss over a period equivalent to 40 years. The research-grade textile P-3a yields a strength loss of 42% tested under a high oxygen pressure condition that is in reasonable agreement with the 63% strength loss over 40 years obtained for oven aging in circulating air. The difference may be attributed to the intrinsic variability of mechanical properties for the P-3a product nonuniformity of the degradation process at different temperatures and in high oxygen pressure, etc.

Table 5.7. Comparison between oven aging and high oxygen pressure strength-loss estimates.

Equivalent time in normal conditions, years	High-pressure oxygen strength loss, % / oven-aging strength loss estimate, %				
Material ⇒	P-1	P-3	P-3a	P-4	P-9
40	0/NA	0/0	42/63	10/100	26/NA
80	0/NA	NA/50	N/A	N/A	N/A
120	9/NA	16/100	N/A	N/A	N/A

NA= not available

Of significant importance is the preliminary finding that the estimated strength loss in 40 years measured for the P-4 nonwoven staple fiber geotextile is more consistent with the anticipated and reported performance for this geosynthetic. Interpretation of P-4 losses from oven-aging protocols suggests a 50% strength loss in 6.5 years, which is unreasonable in light of the actual performance of this material over 10 years as measured from retrieved sites. In addition, SEM examinations of samples incubated at elevated temperatures have shown significant alterations to the surface morphology (figure 3b). Examination of P-4 samples incubated under high oxygen pressure suggests no changes in surface morphology.

5.11.4 Conclusions.

The results of this limited feasibility assessment of high oxygen pressure accelerated degradation for polyolefin geosynthetics indicate that:

- High oxygen pressure appears to be a viable accelerator for oxidative strength-loss measurements.
- The acceleration factor in oxidative degradation in high-pressure pure oxygen can be reasonably predicted by the simplified kinetics of oxidation for polyolefins.
- Estimates of anticipated strength loss over 40-year and 120-year periods under ambient conditions based on high oxygen pressure degradation are in satisfactory agreement with estimates obtained in oven aging in circulating air for monofilament products.
- A high oxygen pressure testing protocol appears to be the only viable testing protocol for products where high temperature changes the surface morphology.
- Additional verification testing should be performed to completely validate this testing protocol.

5.12 CONCLUSIONS

Based on the data and the results of interpretation developed in these studies, the following conclusions could be drawn regarding the thermo-oxidative performance of the selected commercial polyolefin geosynthetic products:

- The degradation performance of the selected commercial polyolefin geosynthetic products is sensitive to the concentration of oxygen in the surrounding atmosphere. The reduction of oxygen concentration, together with almost complete elimination of circulation in the atmosphere, results in a substantial decrease of the rate of degradation and may even lead to the tensile strength gain over the period of aging.
- Commercial products containing effective and sufficient antioxidant additives have much longer useful lives than ones with minimum amounts of antioxidants, as evidenced by longer induction periods.
- The degradation performance of the selected commercial polyolefin products appears to be dependent on material properties such as type of base polymer and manufacturing process. Geosynthetics made from staple fibers appeared to have initial cracking on the surface of "virgin" fibers and films, resulting in rapid degradation in circulating air. HDPE geogrids exhibit significant changes in initial modulus and strain at break values when exposed to elevated temperatures, which could be attributed to other processes rather than oxidation. Oven-aging protocols for these materials appear inadequate.
- The degree of fiber surface integrity for materials "as received" (presence of initial face cracking) may be an index of susceptibility to oxidation for polyolefin commercial geosynthetics.
- A commercial product containing a HALS type of antioxidant exhibits a significant induction period during degradation.
- The degradation performance of selected commercial products is sensitive to the level of metal salt contamination. Low levels of metal salt contamination (less than 1 percent weight to weight) have a statistically insignificant impact on the rate of degradation. High levels of contamination (about 10 percent weight to weight) result in a significant impact and accelerate mechanical deterioration.
- Kinetic models developed within the framework of the Basic Auto-Oxidation Scheme appear to provide satisfactory analysis of the observed experimental data and permit conservative estimates of time against strength loss at ambient temperature for materials that exhibit no cracks in their virgin state.
- Oven-aging protocols used in this study do not model induction times developed as a result of antioxidant leaching that may result from engineering applications below the ground water or in marine applications.
- Scanning electron microscopy appears to be a useful tool to characterize and monitor the changes of fiber surface morphology during thermodegradation.

- OIT measurements appear to be effective in monitoring antioxidant depletion for some commercial polyolefin geosynthetic products not containing HALS antioxidants.
- Additional testing conditions, such as aging in an atmosphere containing 15 to16% O_2, would enhance understanding of the factors affecting the degradation of the commercial geosynthetic products, and would improve the reliability of estimates of anticipated time to 50-percent strength loss, based on the BAS model.

CHAPTER 6

HYDROLYTIC DEGRADATION OF SELECTED COMMERCIAL POLYESTER GEOSYNTHETIC PRODUCTS

This chapter summarizes the results of physical, mechanical, and chemical testing for hydrolysis testing performed under different environmental conditions (temperature, pH of the environment). Mechanical testing includes the determination of the peak value for tensile strength with the corresponding value of strain. Chemical characterization for aged samples of the selected commercial products consists of average molecular weight determination by intrinsic viscosity measurements as well as CEG analysis. The results of the surface morphology studies are discussed only when significant deterioration of physical and mechanical properties are observed for the aged geosynthetics.

The main objective of this study is to assess the rate of the degradation of physical and mechanical properties (tensile strength, weight, and fiber diameter) and chemical parameters (intrinsic viscosity or molecular weight, and CEG) for PET commercial geosynthetic products from hydrolysis in different environments. Therefore, all testing results are presented relative to values normalized to the initial value of a particular parameter.

The testing conditions, sample number, and size, as well as the description of the hydrolysis reactor used, have been discussed in chapter 3.

6.1 RESULTS OF HYDROLYSIS IN NEUTRAL MEDIA (DISTILLED WATER, pH=7)

Tables 6.1, 6.2, and 6.3 are the summaries of test results for the selected commercial geosynthetic products, hydrolyzed in distilled water at different temperatures.

Table 6.1. Summary of mechanical test results for P-5 PET geotextile, hydrolyzed in distilled water.

Temperature, °C	Exposure, days	Retained weight ratio	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	1.00	5	1.00	2	1.00	1.00
	180	1.00	1.02	4	0.96	6	0.89	1.07
	359	1.00	1.05	8	0.74	6	0.92	1.06
	617	1.00	0.86	8	0.71	10	0.86	1.08
	700	1.01	0.80	5	0.61	5	0.84	1.10
	1037	1.00	0.72	7	0.63	9	0.81	1.14
60	0	1.00	1.00	5	1.00	2	1.00	1.00
	147	1.00	1.04	4	1.01	4	0.84	1.12
	282	1.01	1.01	5	0.76	6	0.86	1.17
	416	1.00	0.81	5	0.90	3	0.86	1.17
	658	1.01	0.75	15	0.77	20	0.81	1.19

Table 6.1 (cont.)

Temperature, °C	Exposure, days	Retained weight ratio	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
	960	1.01	0.53	3	0.73	8	0.65	1.36
70	0	1.00	1.00	5	1.00	2	1.00	1.00
	72	1.00	0.98	4	0.86	9	0.73	1.12
	142	1.00	0.97	3	0.78	5	0.70	1.30
	215	1.00	0.93	2	0.77	7	0.60	1.64
	411	1.00	0.75	2	0.72	7	0.54	1.48
	483	1.01	0.58	3	0.58	3	0.56	1.58
80	0	1.00	1.00	5	1.00	2	1.00	1.00
	41	1.00	0.96	6	0.92	7	0.81	1.16
	95	1.00	0.90	1	0.81	4	0.68	1.39
	105	1.00	0.79	3	0.78	9	0.60	N/A
	159	1.00	0.57	4	0.61	6	0.51	2.49
	200	1.00	0.33	3	0.42	2	0.43	3.21

Table 6.2. Summary of mechanical test results for PVC-coated PET geogrid P-6, hydrolyzed in distilled water.

Temperature °C	Exposure, days	Retained weight	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity	Retained CEG
50	0	1.00	1.00	10	1.00	15	1.00	1.00
	133	0.99	1.05	8	1.49	11	0.89	N/A
	312	0.99	0.91	9	1.32	23	0.94	1.02
	684	0.95	0.93	10	1.18	18	0.94	1.02
	960	1.07	0.95	22	1.14	21	0.92	1.09
	1093	1.12	0.89	23	0.95	14	0.90	1.20
60	0	1.00	1.00	10	1.00	15	1.00	1.00
	203	0.98	1.00	25	1.45	36	0.96	1.17
	298	0.97	1.09	21	1.46	72	0.98	1.20
	400	0.98	0.89	15	1.29	42	0.95	1.13
	527	0.97	1.00	27	1.31	41	0.95	1.04
	837	0.96	0.82	18	0.93	12	0.90	1.32
70	0	1.00	1.00	10	1.0	15	1.00	1.00
	77	0.99	0.97	7	1.09	16	0.96	1.09
	142	1.02	0.95	13	1.00	16	0.86	1.16
	280	1.03	0.90	9	0.95	48	0.87	1.13
	458	0.99	0.73	13	0.97	24	0.76	1.37
	600	0.98	0.63	14	1.24	25	0.63	1.67
80	0	1.00	1.00	10	1.00	15	1.00	1.00
	41	0.99	0.94	20	1.19	20	1.00	1.03
	105	0.98	0.81	11	1.12	21	0.76	1.25
	145	0.99	0.72	22	1.06	23	0.75	1.55

Table 6.2 (cont.)

Temperature °C	Exposure, days	Retained weight	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity	Retained CEG
	209	0.97	0.66	18	1.07	28	0.59	1.86
	250	0.98	0.58	17	1.00	26	0.59	2.31
90	0	1.00	1.00	10	1.00	15	1.00	1.00
	20	0.99	1.07	17	1.17	20	0.92	1.30
	40	0.98	0.75	27	1.22	22	0.84	1.38
	93	0.98	0.41	9	0.95	18	0.61	2.11
	113	0.97	0.14	2	0.4	13	0.43	2.99
	133	1.06	0.00	0	0		0.46	2.22

Table 6.3. Summary of mechanical test results for PET woven geotextile P-7, hydrolyzed in distilled water.

Temperature °C	Exposure days	Retained weight	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity	Retained CEG
50	0	1.00	1.00	4	1.00	7	1.00	1.00
	93	0.99	1.00	7	1.09	9	0.99	1.01
	202	0.99	1.02	6	0.81	9	0.99	0.88
	300	0.99	0.98	4	0.80	23	0.98	0.89
	496	0.99	0.95	5	0.95	8	0.96	0.92
	630	0.98	0.91	4	1.05	23	0.94	1.30
60	0	1.00	1.00	4	1.00	7	1.00	1.00
	118	1.00	0.98	7	0.85	12	0.98	1.36
	160	1.00	0.99	6	0.91	22	N/A	N/A
	203	1.05	0.96	6	0.98	9	0.95	1.95
	282	0.97	0.96	4	1.26	13	0.85	1.34
	367	1.00	0.93	5	1.00	28	0.94	1.27
	601	1.00	0.87	7	1.13	16	0.90	1.28
	802	1.05	0.77	7	0.77	9	0.88	1.68
70	0	1.00	1.00	4	1.00	7	1.00	1.00
	77	1.00	0.99	6	0.63	5	0.79	1.33
	142	1.00	0.93	5	1.17	14	0.92	1.41
	280	1.00	0.86	6	0.60	6	0.77	1.97
	341	1.00	0.83	5	0.79	21	0.77	1.32
	512	1.00	0.67	6	0.98	22	0.73	1.46
80	0	1.00	1.00	4	1.00	7	1.00	1.00
	41	0.94	0.81	7	1.53	4	0.88	1.41
	105	1.04	0.74	7	1.11	4	0.82	1.79
	145	0.96	0.62	3	0.88	7	0.71	2.68
	209	1.04	0.63	4	0.88	14	0.70	2.23
	250	1.00	0.58	3	0.86	13	0.68	2.80
90	0	1.00	1.00	4	1.00	7	1.00	1.00

Table 6.3 (cont.)

Temperature °C	Exposure days	Retained weight	Retained peak tensile strength ratio	Coefficient of variation, %	Retained strain ratio at peak strength	Coefficient of variation, %	Retained viscosity	Retained CEG
	20	0.99	0.98	14	0.76	7	0.86	1.55
	40	0.99	0.92	5	0.68	19	0.80	1.80
	93	1.00	0.45	3	1.36	20	0.65	2.08
	141	0.99	0.38	5	0.63	19	0.43	3.39
	161	0.97	0.38	15	0.52	35	0.35	4.28

There were no apparent significant changes in the visual appearance of the P-5 and P-7 geotextiles over the duration of hydrolysis in distilled water at different temperatures. However, there are some indications that the PVC coating of PET geogrid P-6 deteriorated with hydrolysis time.

Monitoring of weight loss indicates no statistically significant changes in initial weight during hydrolysis in distilled water for the tested PET products. Corresponding to no weight loss, there are no observed changes in the fiber diameter for any of the PET products tested in distilled water. Therefore, results of the SEM study are not discussed further.

The mechanical property results indicate that there is a progressive tensile strength loss over the period of hydrolysis in distilled water for the tested PET products. The experimental data of tensile strength loss are shown graphically in figures 6.1, 6.2, and 6.3.

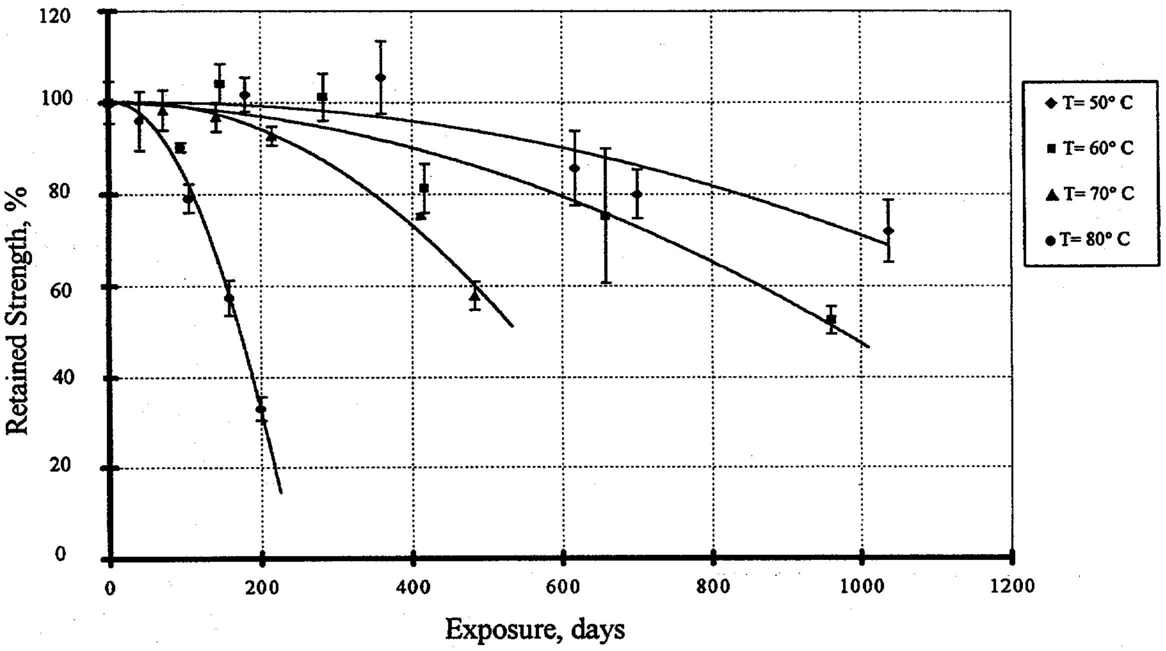


Figure 6.1. Tensile strength loss for P-5 geotextile, due to hydrolysis in distilled water.

Examination of strain data for P-5 indicates a decrease in strain at failure generally consistent with the decrease in strength. For P-6 and P-7, strain at failure generally increases in the earlier stages of hydrolysis and then decreases at a rate considerably slower than the decrease in strength.

The variability of measured values of the tensile strength for each retrieval of geotextiles P-5 and P-7 appears to be similar to the variability of tensile strength obtained for the specimens as received. The coefficient of variation of the measured tensile strength for the PVC-coated P-6 geogrid is higher when compared to the coefficient of variation obtained for the "as received" material. This could be attributed to the observed deterioration of the PVC coating due to hydrolysis in distilled water as well as to the intrinsic high variability of material properties for this product.

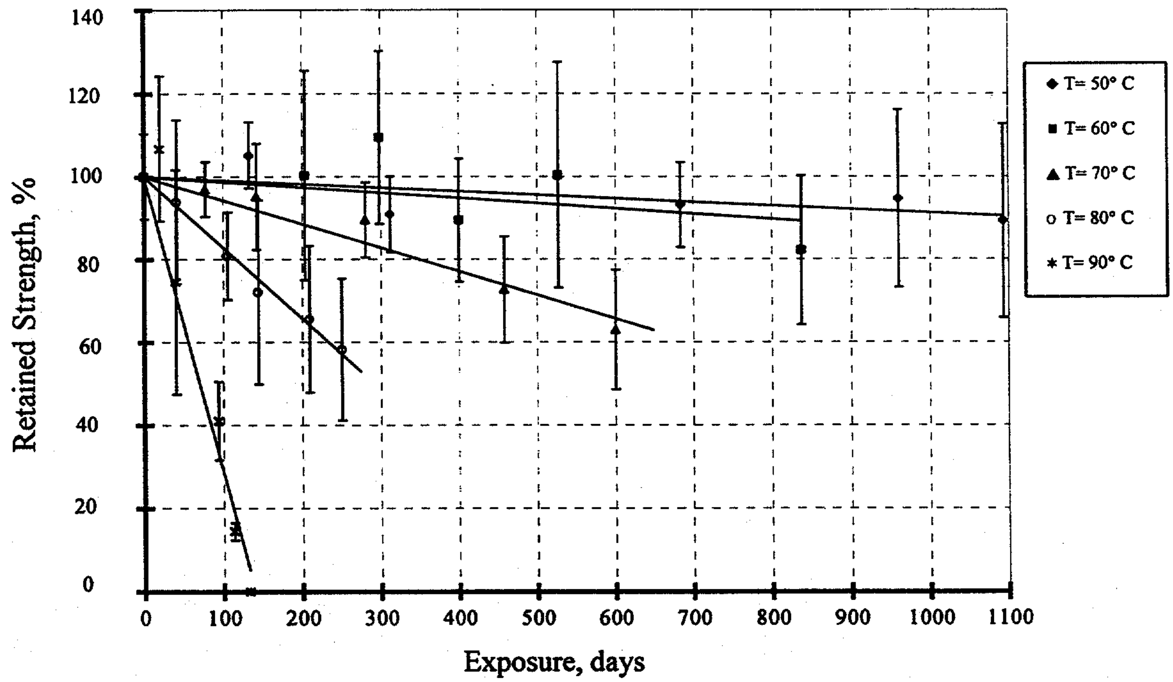


Figure 6.2. Tensile strength loss for P-6 PVC-covered geogrid, due to hydrolysis in distilled water.

Results for P-6, the PVC-coated geogrid, indicate no apparent mechanical deterioration at the beginning of hydrolysis at low temperatures similar to the induction period for polyolefin-based products. This observation could be explained by the protective effect of PVC coating, which initially prevents penetration of water to the PET fibers.

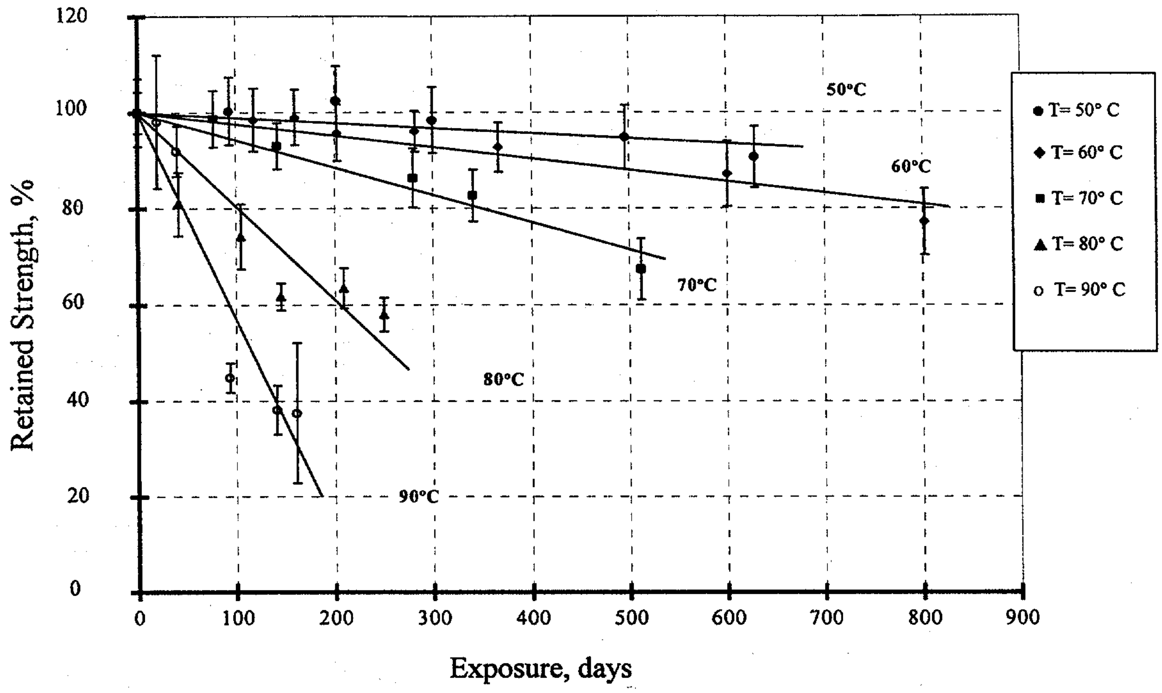


Figure 6.3. Tensile strength loss for P-7 geotextile, due to hydrolysis in distilled water.

6.2 RESULTS OF HYDROLYSIS IN ACIDIC MEDIA (H_2SO_4, pH=1)

The experimental data that characterize the degradation of the P-6 and P-7 PET products due to hydrolysis in aqueous solution of H_2SO_4 at a pH=1 appear to be similar to those obtained for the same geosynthetics hydrolyzed in distilled water at temperatures of 50, 60, and 70°C. A comparative summary plot at 50°C is shown as figure 6-4. However, there are some differences in the degradation behavior of PET products aged in acidic as compared to neutral solutions. It appears that the degradation in acidic media occurs faster than in distilled water and that strain at failure consistently decreases with strength. The summary of experimental results obtained for geosynthetics P-5, P-6, and P-7 aged in the aqueous solution of H_2SO_4 at pH=1 are shown in tables 6.4, 6.5, and 6.6.

Table 6.4. Summary of test results for the PET nonwoven geotextile P-5 hydrolyzed in an aqueous solution of H_2SO_4 at pH=1.

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength ratio	Variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0.0	1.00	5	1.00	1.00
	144	1.00	0.0	0.95	5	0.87	0.98
	280	1.01	0.3	0.97	3	0.89	1.08
	444	1.00	0.1	1.00	5	0.87	0.92
	556	0.99	1.0	0.88	11	0.81	1.07

Table 6.4 (cont.)

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength ratio	Variation, %	Retained viscosity ratio	Retained CEG ratio
	746	1.03	2.0	0.63	12	0.75	1.05
60	0	1.00	0.0	1.00	5	1.00	1.00
	89	1.00	0.1	0.92	4	0.90	N/A
	179	1.00	0.1	0.86	7	0.87	1.05
	270	1.00	0.1	0.89	7	0.81	N/A
	395	1.00	1.0	0.85	14	0.81	0.96
	575	1.01	0.1	0.65	8	0.76	1.02
70	0	1.00	0.0	1.00	5	1.00	1.00
	50	1.00	0.1	0.99	5	0.83	1.11
	104	0.99	0.5	0.82	3	0.79	1.33
	147	0.99	1.3	0.79	3	0.78	1.49
	201	1.00	2.3	0.78	3	0.75	1.33
	251	1.00	0.1	0.72	8	0.67	2.15

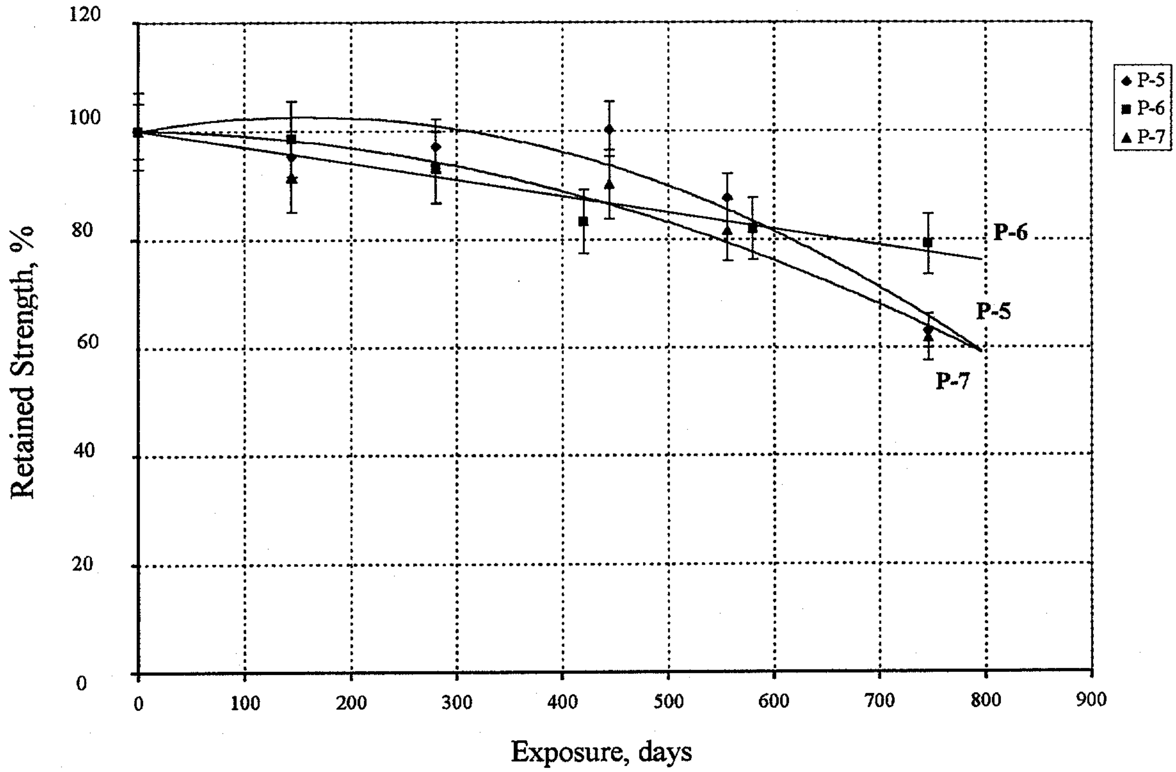


Figure 6.4. Tensile strength loss for selected products, hydrolyzed in H_2SO_4 at pH=1 at 50°C.

Table 6.5. Summary of test results for the PVC-coated PET geogrid P-6, hydrolyzed in an aqueous solution of H_2SO_4 at pH=1.

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength ratio	Variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0	1.00	10	1.00	1.00
	144	0.98	2	0.98	5	0.96	1.16
	280	0.98	10	0.93	8	0.96	1.09
	420	0.99	0	0.83	9	0.88	1.50
	580	0.99	0	0.82	10	0.80	2.15
	746	0.98	2	0.79	6	0.78	1.55
60	0	1.00	0	1.00	10	1.00	1.00
	89	1.00	0	0.94	13	0.96	1.37
	179	0.99	2	0.85	12	0.75	1.54
	270	0.97	1	0.83	7	0.78	2.72
	395	0.97	1	0.74	6	0.73	3.35
	575	0.96	1	0.72	3	0.72	3.37
	725	0.96	1	0.47	14	0.71	3.50
70	0	1.00	0	1.00	10	1.00	1.00
	50	0.99	1	0.94	7	0.92	1.15
	104	0.98	0	0.88	6	0.75	1.52
	147	0.99	1	0.78	7	0.61	1.84
	201	0.99	0	0.70	8	0.72	2.48
	251	0.98	0	0.68	9	0.82	2.27

Table 6.6. Summary of test results for the PET woven geotextile P-7 hydrolyzed in an aqueous solution of H_2SO_4 at pH=1.

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength ratio	Variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0	1.00	4	1.00	1.00
	144	0.99	0	0.92	6	0.96	1.11
	280	0.99	1	0.93	8	0.99	1.27
	444	1.00	2	0.90	9	0.99	1.89
	556	1.00	0	0.82	13	0.95	3.04
	746	1.00	0	0.62	7	0.75	5.47
60	0	1.00	0	1.00	4	1.00	1.00
	89	0.99	0	0.86	6	0.81	1.46
	179	0.99	0	0.86	4	0.96	1.39
	270	1.00	0	0.77	6	0.83	4.36
	395	1.00	0	0.74	7	0.89	1.29

Table 6.6 (cont.)

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength ratio	Variation, %	Retained viscosity ratio	Retained CEG ratio
	575	0.99	1	0.67	11	0.77	1.31
70	0	1.00	0	1.00	4	1.00	1.00
	50	0.99	0	0.75	7	0.96	1.93
	104	0.99	0	0.55	3	0.88	2.01
	147	1.00	0	0.50	5	0.87	1.45
	201	1.00	0	0.49	5	0.82	1.74
	251	0.99	0	0.46	5	0.79	3.22

6.3 RESULTS OF HYDROLYSIS IN ALKALINE MEDIA (NaOH, pH=10 and pH=12; $Ca(OH)_2$, pH=10)

Aqueous solutions of NaOH at pH=10 and pH=12, as well as a solution of $Ca(OH)_2$ at pH=10, were used to produce severe conditions of alkaline hydrolysis for the selected commercial geosynthetic products. It appeared during the experiment that significant precipitation of lime or lime derivative crystals occurs on the surface of submerged specimens. The degree of precipitation increases with an increase of temperature in $Ca(OH)_2$ solution. The crystals are seen only under the microscope on the surface of the P-5 and P-7 specimens aged at 50°C, whereas the surface of the geotextiles is completely covered with precipitation when treated in the solution at 80°C. This phenomenon creates difficulties with determining the actual pH on the fiber surface as compared with the pH of the bulk aqueous solution of $Ca(OH)_2$ and the actual weight loss. Therefore, the results of tensile strength monitoring as well as viscosity measurements may be used only as a qualitative illustration of the effect of high pH from $Ca(OH)_2$ media on the degradation performance. No precipitation has been observed on specimens of geosynthetics treated in aqueous solutions of NaOH at pH=10 and pH=12.

SEM studies of surface morphology for hydrolyzed specimens of the PET products indicate:

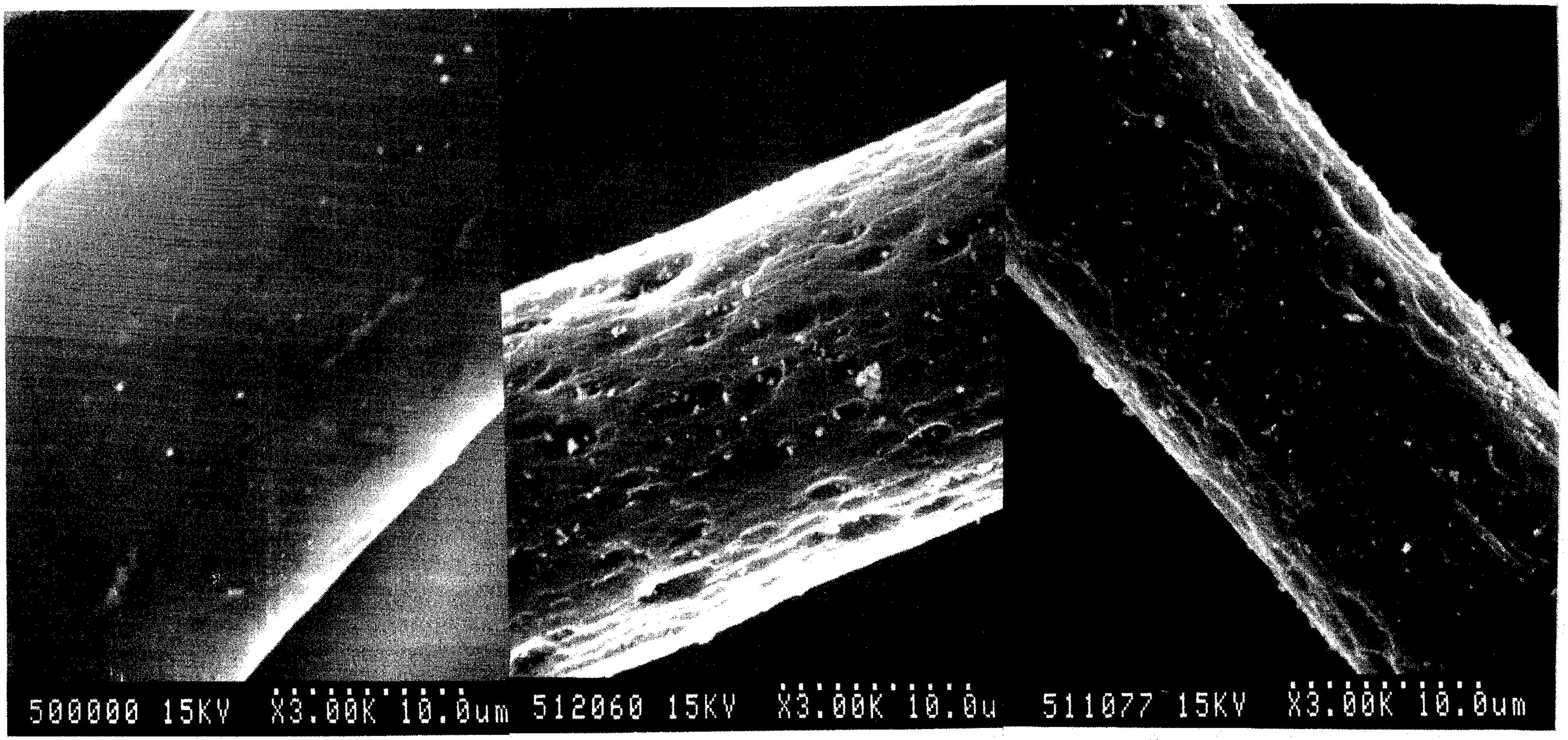
- Hydrolysis of the low-tenacity geotextile P-5 in an alkaline environment of NaOH at pH=12 and in $Ca(OH)_2$ at pH=10 results in progressive development of fiber surface erosion by pitting and significant reduction of fiber diameter as shown on figure 6.5.
- The PVC-covered P-6 fibers exhibit only isolated surface pitting that developed during the hydrolysis in alkaline media of high pH as shown on figure 6.6.
- The surface erosion of high-tenacity P-7 fibers hydrolyzed under the same conditions appears to be less developed as compared to the degree of erosion observed for the low-tenacity P-5 product as shown on figure 6.7.

The summary of experimental mechanical and chemical results for geosynthetics tested in alkaline solutions are tabulated in tables 6.7 through table 6.14. Figure 6.8 and figure 6.9

illustrate the pattern of the tensile strength deterioration in alkaline solutions of pH=10 and pH=12 for the P-5 and P-7 products.

Table 6.7. Summary of test results for the PET nonwoven geotextile P-5, hydrolyzed in an aqueous solution of NaOH at pH=10.

Temperature °C	Exposure, days	Retained weight ratio	Variation, %	Retained peak tensile strength	Variation, %	Retained viscosity ratio	Retained CEG ratio	Retained fiber diameter ratio
50	0	1.00	0.0	1.00	4.6	1.00	1.00	1
	133	1.00	0.2	1.03	3.5	0.86	0.98	
	261	1.01	0.4	0.92	5.5	0.90	1.04	
	489	1.00	0.1	0.93	3.3	0.89	0.93	1
	567	1.00	0.1	0.86	13	0.89	0.90	1
	800	0.99	3.7	0.76	3.0	0.86	0.89	
60	0	1.00	0.0	1.00	4.6	1.00	1.00	1
	25	1.00	0.1	0.86	5.4	0.90	1.14	
	50	1.01	0.2	0.96	4.7	0.83	0.94	
	62	1.00	0.1	0.82	7.9	0.92	1.03	1
	87	1.00	0.1	0.92	7.7	0.94	1.17	
	112	1.00	1.9	0.99	3.4	0.90	1.10	1
	200	1.00	0.1	0.84	4.5	0.90	1.13	
	279	0.98	1.0	0.79	1.0	0.83	0.85	1
	420	0.97	0.3	0.73	12	0.76	1.66	
70	0	1.00	0.0	1.00	4.6	1.00	1.00	
	28	0.97	5.4	0.88	6.6	0.93	1.11	1
	61	1.02	4.4	0.99	5.0	0.94	1.37	1
	152	0.97	2.3	0.84	4.2	0.75	1.20	
	151	0.97	7.1	0.83	7.8	0.79	1.43	1
	235	0.93	2.4	0.61	9.4	0.70	1.77	1

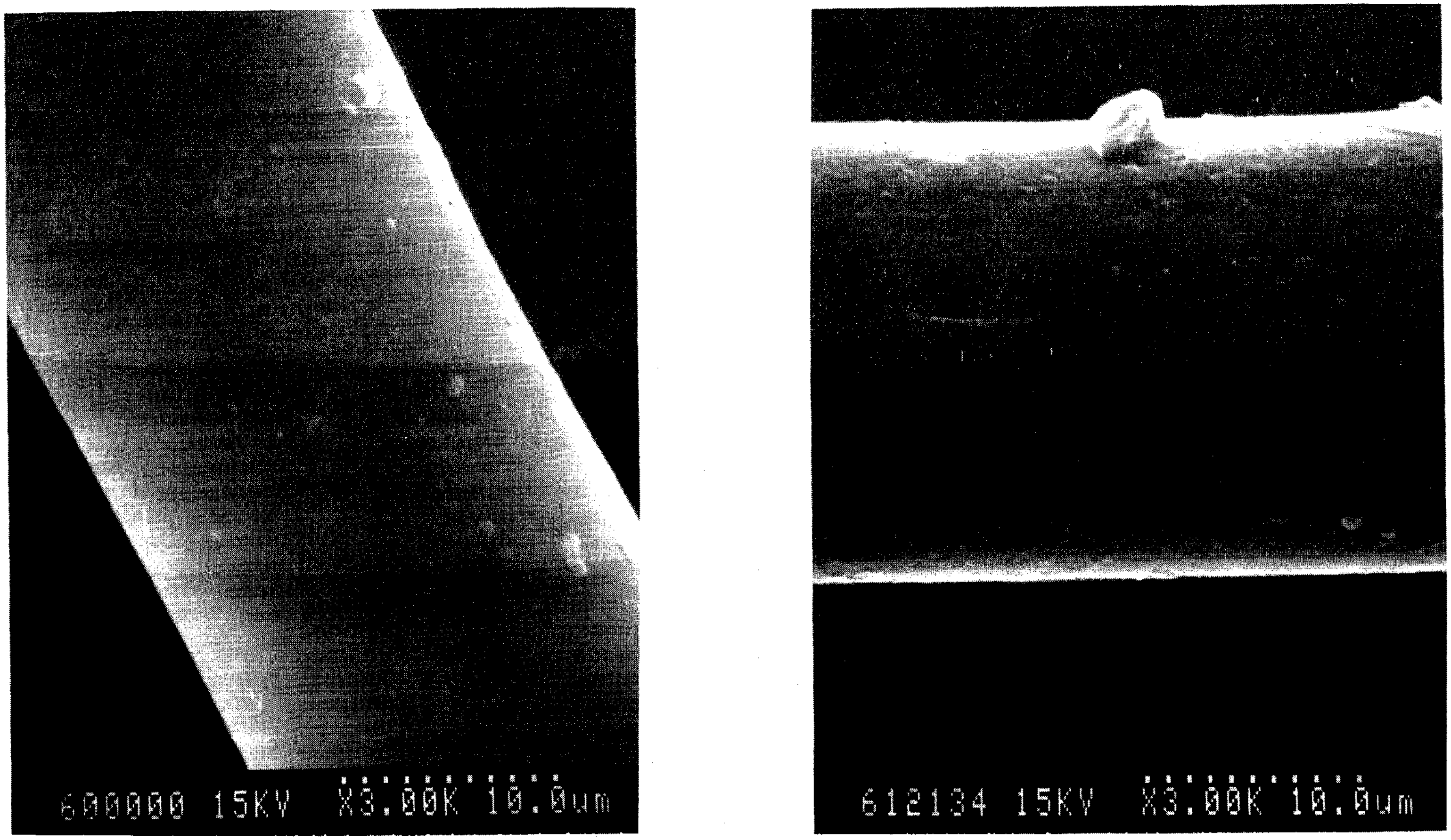


(a) P-5 “As received.”

(b) P-5, NaOH, pH=12, 50°C, 60 Days.

(c) P-5, $Ca(OH)_2$, pH=10, 70°C, 77 Days.

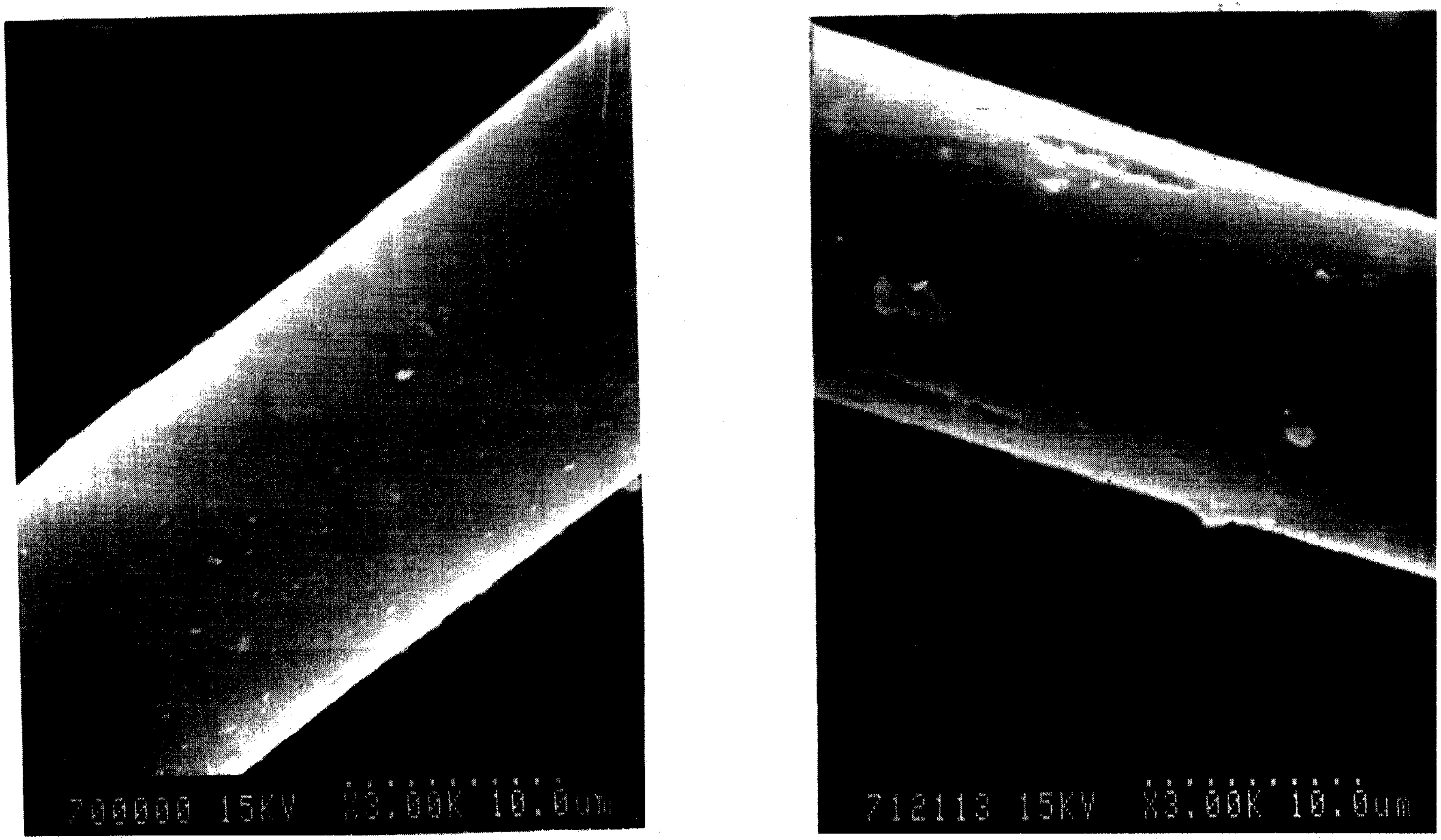
Figure 6.5. SEM microphotographs (3000x) for P-5 fibers: (a) "as received," and (b) hydrolyzed in NaOH, pH=12 at 50°C for 60 days, and (c) $Ca(OH)_2$, pH=10 at 70°C for 77 days.



(a) P-6, “As received.”

(b) P-6, NaOH, pH=12, 50°C, 134 days.

Figure 6.6. SEM microphotographs (3000x) for P-6 PET fibers: (a) "as received", and (b) hydrolyzed in NaOH, pH=12 at 50°C for 134 days.



(a) P-7, “As received.”

(b) P-7, NaOH, pH=12, 50°C, 113 days.

Figure 6.7. SEM microphotographs (3000x) for P-7 fibers: "as received", and (b) hydrolyzed in NaOH, pH=12 at 50°C for 113 days.

Table 6.8. Summary of test results for PVC-coated PET geogrid P-6, hydrolyzed in an aqueous solution of NaOH at pH=10.

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0	1.00	10	1.00	1.00
	170	0.99	0	1.00	8	0.99	0.88
	340	0.98	0	0.96	5	1.01	1.01
	517	0.89	9	0.91	21	0.98	0.99
	752	0.98	6	0.79	5	0.96	1.06
	1030	0.87	4	0.81	5	0.96	1.01
60	0	1.00	0	1.00	10	1.00	1.00
	41	0.00	0	0.98	8	0.89	0.87
	84	1.04	1	0.97	5	0.96	1.37
	112	1.01	0	0.97	8	0.96	0.93
	200	0.99	0	0.94	10	0.98	1.01
	354	1.00	0	0.90	5	0.90	1.07
	549	1.00	1	0.84	8	0.63	0.92
70	0	1.00	0	1.00	10	1.00	1.00
	60	0.99	0	0.95	6	1.01	1.14
	121	0.98	5	0.92	4	0.88	0.98
	182	0.98	0	0.85	12	0.88	1.22
	334	0.98	0	0.84	13	N/A	1.29
	426	0.97	0	0.71	10	0.69	1.51

Table 6.9. Summary of test results for PET woven geotextile P-7, hydrolyzed in an aqueous solution of NaOH at pH=10.

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0	1.00	0.04	1.00	1.00
	54	0.99	0	0.99	0.07	0.89	1.23
	103	0.99	0	0.95	0.05	0.96	N/A
	170	1.00	0	0.96	0.07	0.88	N/A
	219	0.99	5	0.98	0.05	0.94	1.22
	273	1.01	4	0.92	0.08	0.99	1.03
	361	0.99	0	0.87	0.06	1.00	1.30
	410	0.99	0	0.94	0.07	0.96	1.46
	734	0.97	1	0.83	0.05	0.94	1.52
60	0	1.00	0	1.00	0.04	1.00	1.00
	41	0.99	0	0.98	0.05	0.95	1.07
	84	0.99	0	0.96	0.09	1.01	1.44
	112	0.99	1	0.90	0.10	1.01	1.46
	200	0.99	0	0.83	0.08	0.96	1.41
	354	1.00	0	0.78	0.09	0.90	0.81

Table 6.9 (cont.)

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
	548	0.97	0	0.64	0.05	0.85	1.47
70	0	1.00	0	1.00	0.04	1.00	1.00
	59	0.99	0	0.86	0.05	0.88	1.16
	120	0.97	4	0.81	0.07	0.86	1.12
	205	0.98	0	0.72	0.10	0.79	0.83
	274	0.98	2	0.65	0.11	0.88	1.52
	425	0.97	0	0.53	0.05	0.82	1.74

Table 6.10. Summary of test results for PET nonwoven geotextile P-5, hydrolyzed in an aqueous solution of NaOH at pH=12.

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio	Retained fiber diameter ratio	Coefficient of variation, %
40	0	1.00	0.0	1.00	4.6	1.00	1.00	1	7
	15	0.99	2.6	0.92	6.6	0.92	0.98	N/A	N/A
	30	0.97	0.9	0.90	4.3	0.90	1.06	N/A	N/A
	43	0.97	0.2	0.76	2.4	0.86	1.15	1	7
	58	0.96	0.6	0.78	7.7	0.86	1.04	1	9
	73	0.93	0.4	0.86	4.7	0.86	1.01	1	8
	89	0.76	0.2	0.69	3.3	0.86	1.15	0.90	7
	123	0.65	0.6	0.57	3.6	0.89	1.09	0.85	5
50	0	1.00	0.0	1.00	4.6	1.00	1.00	1	7
	7	0.92	0.2	0.88	4.4	0.89	1.00	0.99	5
	10	0.85	0.2	0.78	4.8	0.86	1.03	0.98	7
	16	0.75	0.8	0.68	4.5	0.79	1.02	0.99	7
	26	0.71	0.3	0.61	2.7	0.79	0.98	0.90	7
	60	0.15	0.7	0.09	0.5	0.76	1.02	0.36	15
60	0	1.00	0.0	1.00	4.6	1.00	1.00	N/A	N/A
	8	0.87	0.2	0.75	7.7	0.97	0.99	N/A	N/A
	16	0.85	0.4	0.78	2.3	0.92	1.08	N/A	N/A
	21	0.77	0.5	0.58	6.8	0.97	1.23	N/A	N/A
	29	0.75	0.6	0.63	5.3	0.95	1.21	N/A	N/A
	37	0.62	0.2	0.53	3.8	0.87	1.08	N/A	N/A

Table 6.11. Summary of test results for PVC-coated PET geogrid P-6, hydrolyzed in an aqueous solution of NaOH at pH=12.

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
40	0	1.00	0.0	1.00	0.10	1.00	1.00
	62	0.99	0.0	1.04	0.19	1.02	0.95
	121	0.93	0.1	0.97	0.16	1.00	0.83
	199	1.05	0.1	0.98	0.20	0.99	0.86

Table 6.11 (cont.)

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
	292	0.97	0.0	0.81	0.15	0.95	0.84
	422	0.91	0.1	0.67	0.15	0.92	0.86
50	0	1.00	0.0	1.00	0.10	1.00	1.00
	21	0.99	0.0	0.99	0.06	1.00	N/A
	49	0.96	0.0	0.94	0.08	0.92	0.23
	64	0.97	0.0	0.89	0.10	0.99	0.88
	85	0.96	0.0	0.89	0.10	0.95	0.80
	134	0.92	0.0	0.79	0.07	1.01	N/A
	200	0.91	0.0	0.78	0.15	0.99	0.97
60	0	1.00	0.0	1.00	0.10	1.00	1.00
	15	1.02	0.0	0.86	0.07	0.95	0.67
	25	0.92	0.1	0.78	0.08	0.96	0.88
	31	0.96	0.0	0.77	0.12	1.00	1.27
	39	0.95	0.0	0.81	0.07	1.01	0.86
	59	0.94	0.0	0.76	0.16	0.98	0.84

Table 6.12. Summary of test results for PET woven geotextile P-7, hydrolyzed in an aqueous solution of NaOH at pH=12.

Temperature °C	Exposure, days	Retained weight ratio	Coefficient of variation, %	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
40	0	1.00	0.00	1.00	0.04	1.00	1.00
	62	0.98	0.00	0.90	0.24	N/A	0.94
	121	0.98	0.00	0.86	0.08	0.99	0.71
	180	0.98	0.01	0.76	0.11	0.99	0.82
	240	0.97	0.00	0.73	0.06	0.98	0.82
	303	0.93	0.00	0.62	0.14	0.96	0.92
50	0	1.00	0.00	1.00	0.04	1.00	1.00
	19	0.97	0.00	0.87	0.13	0.98	1.23
	32	0.94	0.02	0.90	0.02	0.97	1.17
	49	0.89	0.02	0.86	0.04	0.83	1.05
	87	0.90	0.01	0.81	0.03	0.86	N/A
	113	0.88	0.00	0.75	0.06	1.02	N/A
	150	0.87	0.00	0.68	0.05	0.99	1.21
	200	0.86	0.00	0.54	0.08	0.96	0.67
60	0	1.00	0.00	1.00	0.04	1.00	1.00
	31	0.89	0.00	0.75	0.08	1.00	1.19
	39	0.89	0.01	0.63	0.01	0.99	1.29
	55	0.84	0.00	0.53	0.04	0.96	1.11
	59	0.84	0.00	0.48	0.03	1.00	1.31
	73	0.82	0.00	0.38	0.15	0.96	0.89

Table 6.13. Summary of test results for PET nonwoven geotextile P-5, hydrolyzed in an aqueous solution of $Ca(OH)_2$ at pH=10.

Temperature °C	Exposure, days	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0.02	1.00	1.00
	115	0.75	0.03	0.81	0.94
	239	0.61	0.02	0.87	0.59
	363	0.78	0.06	0.84	0.81
	502	0.68	0.04	0.78	0.84
	617	0.00	0.00	0.75	0.87
60	0	1.00	0.02	1.00	1.00
	35	0.65	0.09	0.92	1.13
	120	0.00	0.00	0.83	0.90
	154	0.69	0.03	0.89	1.21
	239	0.57	0.04	0.54	1.24
	274	0.65	0.09	0.65	1.13
70	0	1.00	0.02	1.00	1.00
	11	0.73	0.08	1.00	1.12
	21	0.79	0.09	0.87	1.14
	39	0.76	0.09	0.76	1.28
	56	0.76	0.05	0.67	1.23
	77	0.66	0.05	0.73	1.25

Table 6.14. Summary results for PET woven geotextile P-7, hydrolyzed in an aqueous solution of $Ca(OH)_2$ at pH=10.

Temperature °C	Exposure, days	Retained peak tensile strength	Coefficient of variation, %	Retained viscosity ratio	Retained CEG ratio
50	0	1.00	0.04	1.00	1.00
	208	0.73	0.05	0.93	1.19
	400	0.60	0.07	0.88	0.81
60	0	1.00	0.04	1.00	1.00
	96	0.41	0.03	0.96	0.71
	170	0.72	0.12	0.92	1.33
	299	0.44	0.03	0.94	0.77
	340	0.48	0.08	0.93	1.29
	469	0.29	0.03	0.79	0.88
70	0	1.00	0.04	1.00	1.00
	39	0.71	0.04	0.94	0.71
	80	0.46	0.11	0.98	1.31
	120	0.32	0.05	0.95	0.89
	161	0.27	0.08	0.83	0.90
80	0	1.00	0.04	1.00	1.00
	25	0.55	0.22	0.88	1.55
	50	0.32	0.03	0.81	1.97
	75	0.17	0.02	0.86	1.78

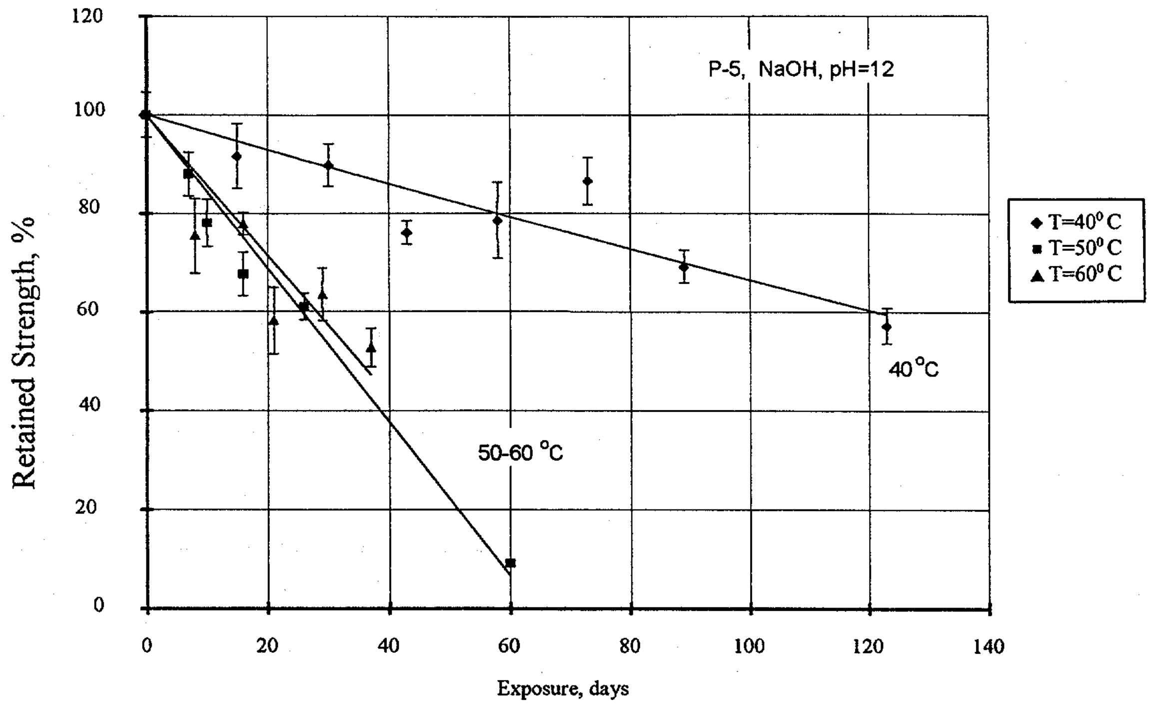


Figure 6.8. Tensile strength loss for P-5 geotextile, due to hydrolysis in NaOH at pH=12.

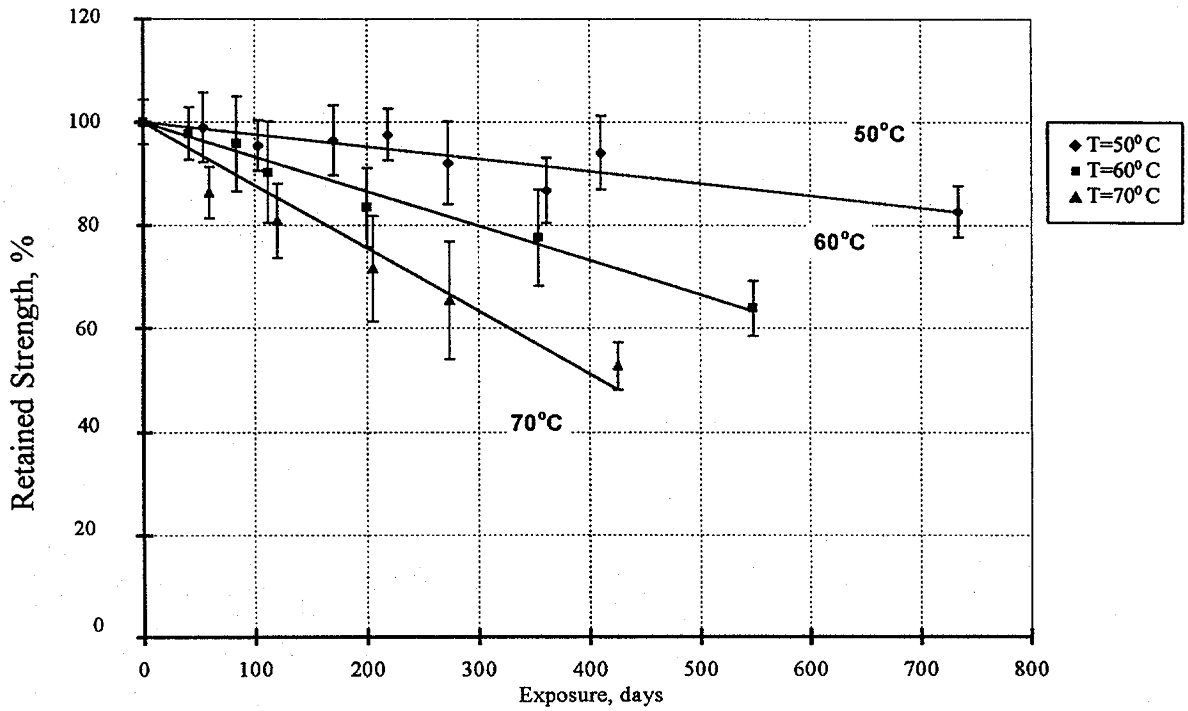


Figure 6.9. Tensile strength loss for P-7 geotextile, due to hydrolysis in NaOH at pH=10.

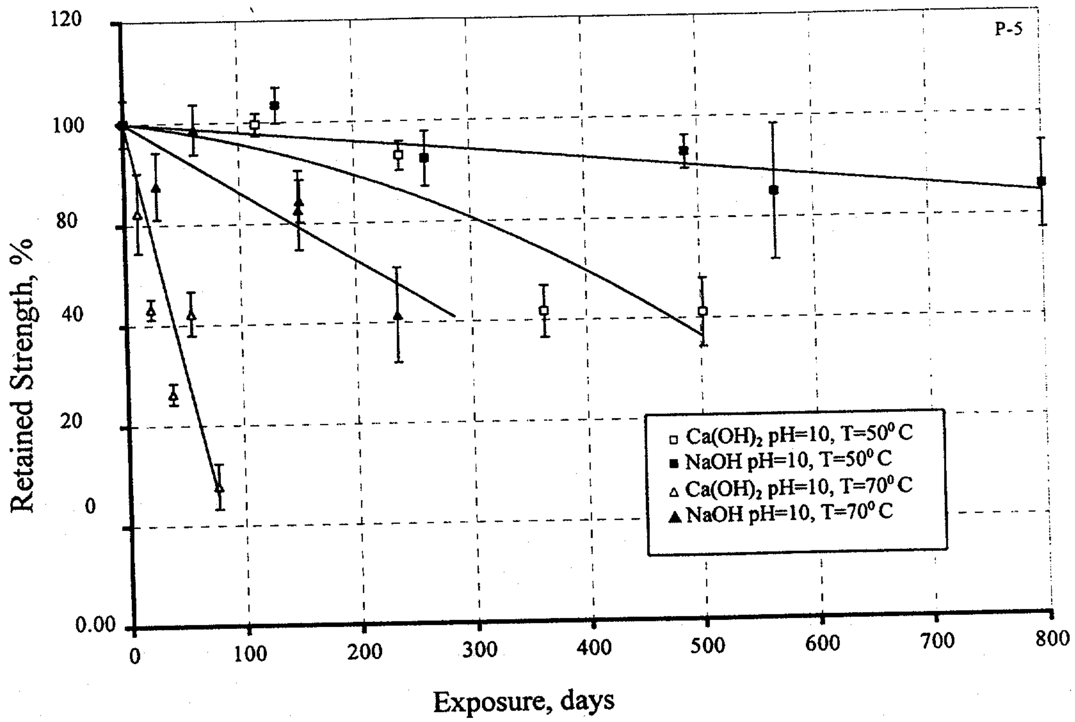


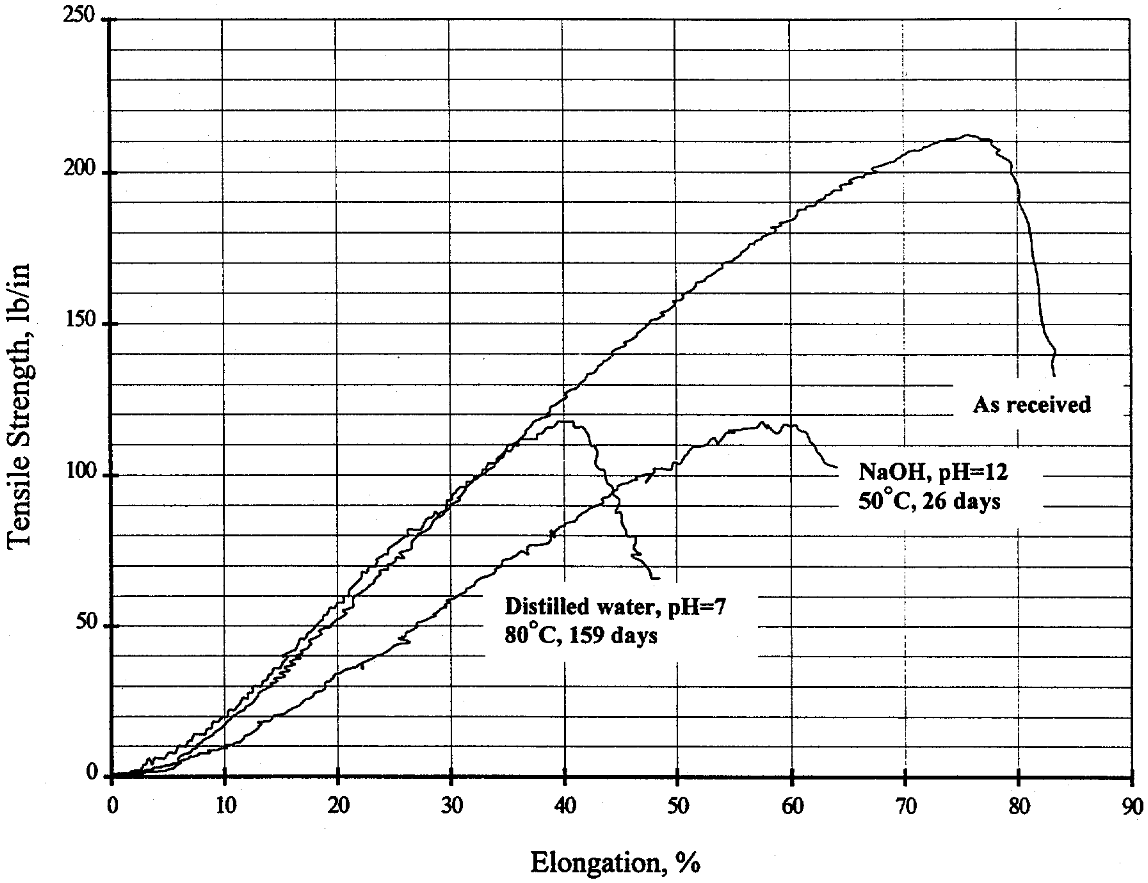
Figure 6.10. Tensile strength loss for P-5 product, hydrolyzed in $Ca(OH)_2$ and NaOH aqueous solutions of pH=10.

Figure 6.10 illustrates the accelerating effect of lime or lime derivatives on the rate of mechanical degradation in $Ca(OH)_2$ aqueous solution of pH=10, as compared to the rate of degradation in NaOH of pH=10 for P-5 product.

6.4 LOAD –STRAIN RELATIONSHIPS FOR PET PRODUCTS HYDROLYZED IN DIFFERENT ENVIRONMENTS

The primary objective of this section is to characterize the change in load-strain behavior for PET products from hydrolysis. Figure 6.11 illustrates typical load-strain curves for the P-5 product, including: (i) "as received", (ii) hydrolyzed in distilled water at 80°C for 159 days, and (iii) hydrolyzed at 50°C in an aqueous solution of NaOH at pH=12 for 26 days. Comparison of the load-strain curves of the virgin sample of P-5 and the sample aged in distilled water (60% of initial tensile strength) indicates similarity in the initial portions of the load-strain curves. By contrast, the slope of the initial portion of the load-strain curve is less steep for P-5 aged in NaOH at pH=12.

The values of the offset modulus (Allen and Bathurst, 1994; 1996) calculated at 10-percent strain for different load-strain curves are presented in table 6.15.



1 lb/in = 0.0179 kg/mm

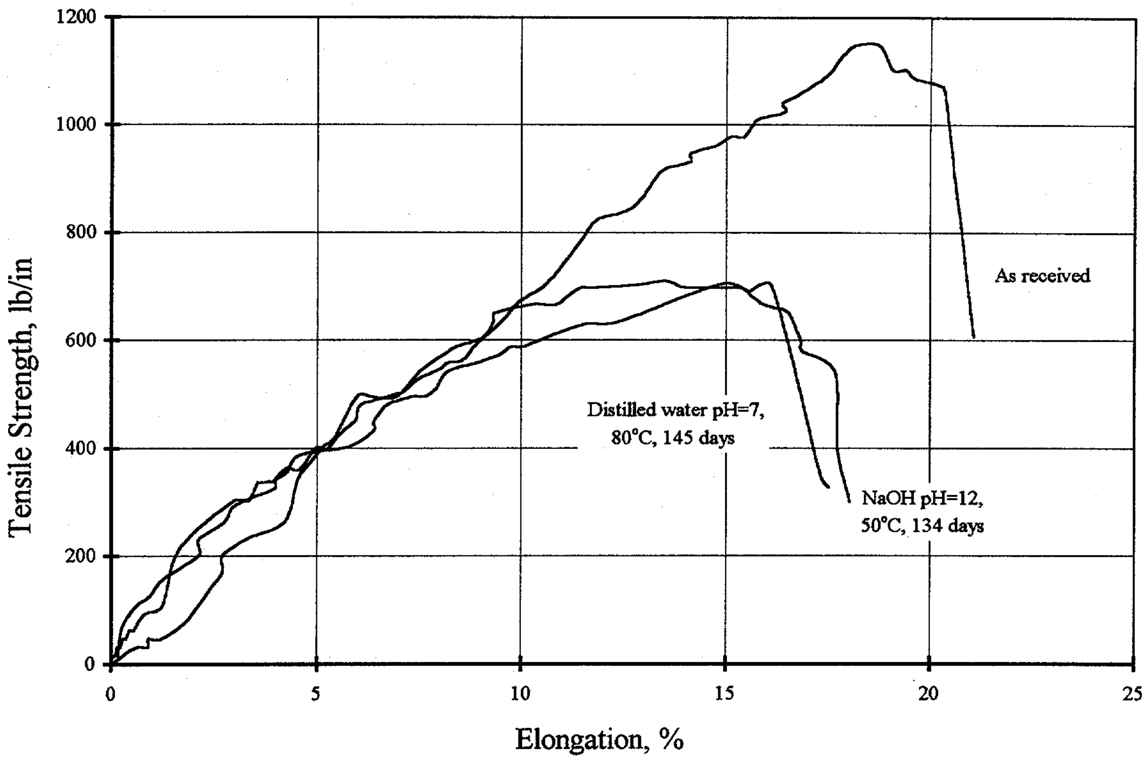
Figure 6.11. Load-strain curves for P-5 aged in varying pH.

Table 6.15. Offset modulus for P-5 aged in varying pH.

Condition	Virgin	Distilled water, 80°C, 159 days	NaOH at pH=12, 50°C, 26 days
Offset modulus $J_{sec\varepsilon}$, lb/in	360	380	240
Tensile strength loss, %	0	40	39
Weight loss, %	0	0	29
Fiber diameter loss, %	0	0	10

1 lb/in = 0.0179 kg/mm

The load-strain curves for the P-6 product indicate that there are no significant changes in the behavior of index properties at low-strain ($J_{sec\varepsilon}$ at ε=5%) hydrolyzed under the most severe conditions, i.e., high temperature of 80°C in distilled water for 145 days, and in an aqueous solution of NaOH at pH=12 and 50°C for 134 days resulting in 20- to 30-percent strength loss. Load-strain curves for P-6 aged in different environmental conditions are shown in figure 6-12. It appears that the PVC coating reduces the rate of surface erosion and corresponding weight loss during alkaline hydrolysis.



1 lb/in = 0.0179 kg/mm

Figure 6.12. Typical load-strain curves for PVC-coated PET geogrid P-6 hydrolyzed in different environmental conditions.

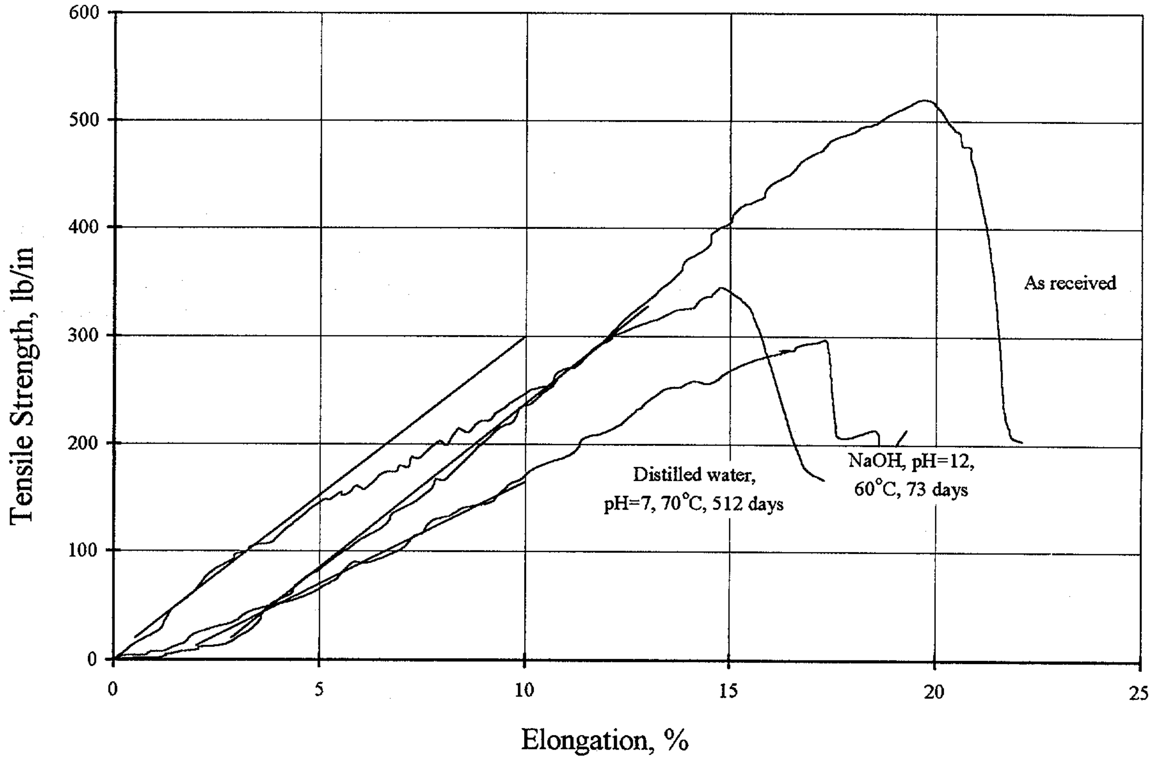
Figure 6.13 illustrates typical load-strain curves for the P-7 product, including: (i) "as received", (ii) hydrolyzed in distilled water at 70°C for 512 days, and (iii) hydrolyzed at 60°C in an aqueous solution of NaOH at pH=12 for 73 days. Comparison of the load-strain curves for the virgin sample of P-7 and the sample aged in distilled water (67% of initial tensile strength) indicates a similarity for the initial part of the load-strain curves. By contrast, the slope of the initial part of the load-strain curve is less steep for P-7 aged in NaOH at pH=12.

The values of the offset modulus calculated for different load-strain curves are presented in table 6.16.

Table 6.16. Offset modulus for P-7 aged in varying pH.

Condition	Virgin	Distilled water, 70°C, 512 days	NaOH of pH=12, 60°C, 73 days
Offset modulus J_{sec5}, lb/in	3040	2950	1900
Tensile strength loss, %	0	33	62
Weight loss, %	0	0	18

1 lb/in = 0.0179 kg/mm



1 lb/in = 0.0179 kg/mm

Figure 6.13. Typical load-strain curves for P-7 hydrolyzed in varying pH.

6.5 SUMMARY

6.5.1 Mechanical properties.

The results of laboratory tensile strength loss monitoring during hydrolysis for the PET products indicate that:

- The rate of mechanical degradation depends on the pH of the hydrolytic environment. The lowest rate of mechanical degradation is observed in a neutral media of distilled water at pH=7.
- Hydrolysis in acidic (H_2SO_4, pH=1) and alkaline media (NaOH, pH=10 and pH=12; $Ca(OH)_2$, pH=10) results in an increase of the degradation rate for the PET products studied. The most significant rate of mechanical degradation is observed in an aqueous solution of NaOH at pH=12.
- SEM studies as well as tensile strength loss and initial modulus data suggest that the PVC coating reduces the rate of mechanical degradation for the PET products tested.
- Hydrolysis in an aqueous solution of $Ca(OH)_2$ at pH=10 results in the acceleration of the mechanical degradation rate as compared to the rate observed in an aqueous

solution of NaOH at pH=10 for the PET products studied. This test condition is less controllable due to precipitation of lime derivatives on the fibers.

- Hydrolysis in an aqueous solution of NaOH at pH=12 results in a decrease of the offset modulus at 10-percent strain for the P-5 product.

6.5.2 Chemical changes.

Results of weight loss monitoring indicate that:

- There are no statistically significant changes of weight during hydrolysis in neutral (pH=7) and acidic (pH=1) environments over the period of laboratory testing.
- Hydrolysis in an alkaline environments of pH=10 and pH=12 results in measurable weight losses over the period of laboratory testing.
- SEM analysis of fiber surface morphology as well as weight loss data indicate that hydrolysis in an alkaline environment results in statistically significant weight loss and fiber erosion.

Intrinsic viscosity and CEG data suggest the following:

- Intrinsic viscosity decreases during hydrolysis. A higher temperature of immersion results in an increase of the viscosity degradation rate.
- The CEG number increases over the period of hydrolysis for the PET products studied.

CHAPTER 7

ANALYSIS OF EXPERIMENTAL RESULTS FOR HYDROLYTIC DEGRADATION OF POLYESTER-BASED COMMERCIAL GEOSYNTHETIC PRODUCTS

7.1 EFFECT OF HYDROLYTIC ENVIRONMENT

Environmental variables such as pH of the immersion media play a dominant role in determining the mechanism leading to mechanical strength degradation.

As indicated in section 3.2, there are two mechanisms responsible for the strength loss of PET that depend on the pH of the environment:

- Viscosity degradation in neutral and acidic environments ($pH \leq 7$).
- PET fiber surface erosion in alkaline media ($pH > 7$).

The experimental data developed has been analyzed for correlation between changes of tensile strength and viscosity, and between tensile strength and fiber diameter during the process of hydrolysis. The degree of fiber surface erosion is characterized by a reduction of the fiber diameter, where this information is available, or weight loss, assuming that the latter is proportional to the change of fiber diameter. Correlation coefficient $\rho_{x,y}$ is a measure of a linear relationship of X and Y, where X is tensile strength loss and Y is one of the following parameters: (i) viscosity, (ii) weight loss, and (iii) fiber diameter where applicable. The correlation coefficient is dimensionless and satisfies $-1 \leq \rho_{x,y} \leq 1$. The greater the value of the coefficient of correlation, the stronger the linear relationship of X and Y. It is assumed that the correlation between X and Y is significant when $\rho_{x,y} \geq 0.67$. Negative values of the correlation coefficient reflect the linear relationship of X and Y.

The equation for the correlation coefficient is:

$$\rho_{x,y} = \frac{Cov(XY)}{\sigma_x \sigma_y} \tag{7-1}$$

where:

$-1 \leq \rho_{xy} \leq 1$

and:

$$Cov(X,Y) = \frac{1}{n}\sum_{i=1}^{n}(x_i - \mu_x)(y_i - \mu_y) \tag{7-2}$$

where x_i and y_i are the current values of testing parameters X and Y, for example, tensile strength and intrinsic viscosity; μ_x and μ_y are the average values for the set of parameters X and Y; σ_x and σ_y are the values of the coefficient of deviation for parameters X and Y.

Using the developed test data, the correlation coefficients $\rho_{x,y}$ have been calculated and are shown in table 7.1 through table 7.6.

Table 7.1. Correlation coefficient of tensile strength and viscosity changes for PET product P-5, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.63
50		0.82	0.80	0.40	0.81
60		0.84	0.81	0.97	0.35
70		0.86	0.67	0.88	
80			0.89		

Table 7.2. Correlation coefficient of tensile strength and weight losses for PET product P-5, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.87
50		-0.85	-0.58	0.59	0.99
60		-0.86	-0.72	0.76	0.92
70		0.37	-0.53	0.96	
80			-0.60		

Table 7.3. Correlation coefficient of tensile strength and viscosity changes for PET product P-6, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.83
50		0.95	0.04	0.82	0.48
60		0.79	0.78	0.85	0.12
70		0.67	0.96	0.83	
80			0.97		
90			0.98		

Table 7.4. Correlation coefficient of tensile strength and weight losses for PET product P-6, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.50
50		0.37	-0.36	0.51	0.96
60		0.84	0.01	-0.30	0.67
70		0.76	0.47	0.84	
80			0.83		
90			-0.36		

Table 7.5. Correlation coefficient of tensile strength and viscosity changes for PET product P-7, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.93
50		0.86	0.93	-0.24	-0.05
60		0.79	0.44	0.87	0.64
70		0.71	0.71	0.75	
80			0.99		
90			0.93		

Table 7.6. Correlation coefficient of tensile strength and weight losses for PET product P-7, hydrolyzed in varying pH.

T°C	Solution	H_2SO_4	H_2O	NaOH	NaOH
	pH	1	7	10	12
40					0.85
50		0.09	0.44	0.59	0.85
60		0.24	-0.56	0.81	0.98
70		0.27	-0.08	0.80	
80			-0.11		
90			0.49		

Analysis of the developed correlation matrix coefficients strongly indicates that there is statistically significant correlation between tensile strength loss and changes of intrinsic viscosity for PET geosynthetic products hydrolyzed in acidic and neutral environments as shown on tables 7.1, 7.3, and 7.5. There is poor correlation between tensile strength losses and changes of weight for the P-5 and P-7 geotextiles in neutral and acidic conditions as shown on tables 7.2, 7.4, and 7.6. The significance of the correlation between strength loss and viscosity changes and the poor correlation between strength loss and weight changes strongly suggests that in neutral and acidic environments, the chemical mechanism leading to viscosity degradation is responsible for mechanical strength losses.

The pH level of the hydrolytic environment also affects the rate of mechanical degradation. Figure 7-1 shows that the rate of mechanical degradation in neutral (distilled water, pH=7) and acidic (H_2SO_4, pH=1) media is lower than the rate of degradation in alkaline media (NaOH, pH=10). It appears that in an aqueous solution of NaOH at pH=12 and 60°C, the degradation rate of the P-5 geotextile is much higher than in NaOH with a pH=10 at 60°C.

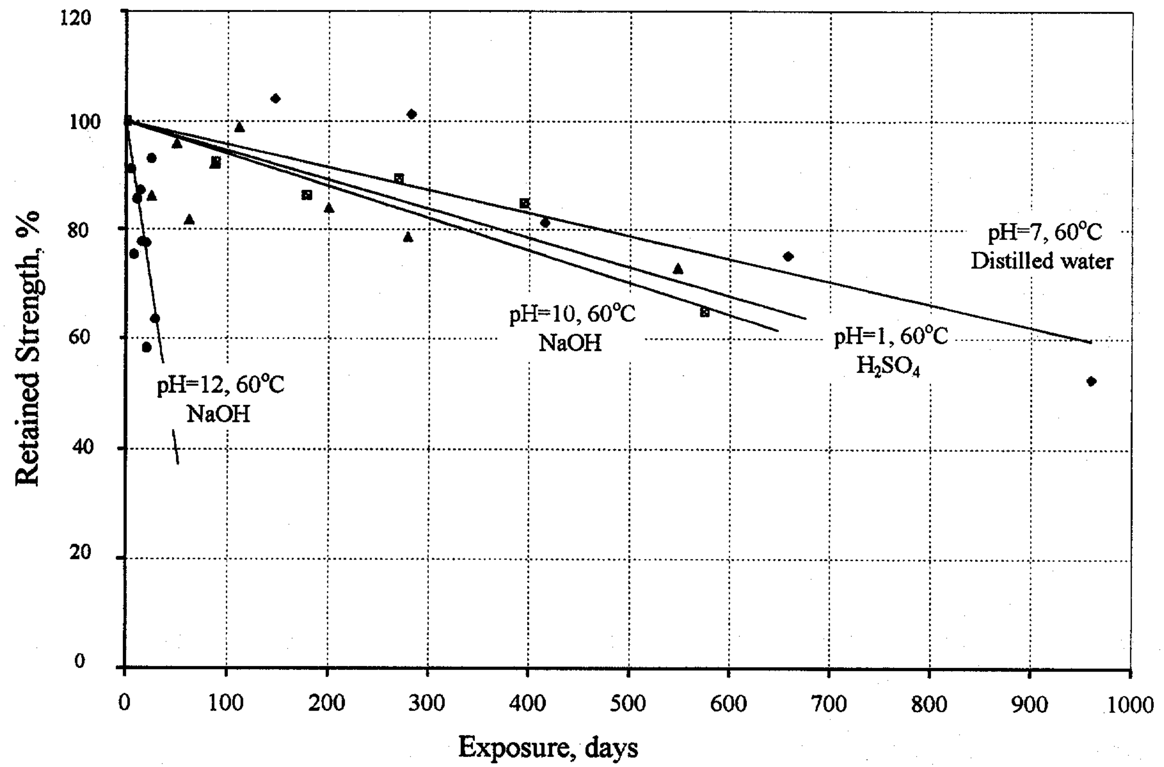


Figure 7.1. Effect of pH in a hydrolytic media on the rate of mechanical degradation for P-5 nonwoven PET geotextile at 60°C.

7.1.1 Neutral and acidic environment

Figure 7.2 shows retained tensile strength normalized to its initial value, for P-5, as a function of molecular weight normalized to the initial value. The molecular weight was calculated from viscosity measurements in accordance with the Mark-Howink equation (2-

1), where K =21 x 10^{-4} and α=0.58 consistent with the used solvent and temperature for the viscosity measurements.

It appears that the same reduction in molecular weight, due to hydrolysis in distilled water (pH=7), results in a smaller decrease in tensile strength than in acidic solution (pH=1, H_2SO_4). Results of CEG analysis indicate that in acidic environments the CEG number is higher than in distilled water for the same degree of average molecular weight degradation (figure 7.2).

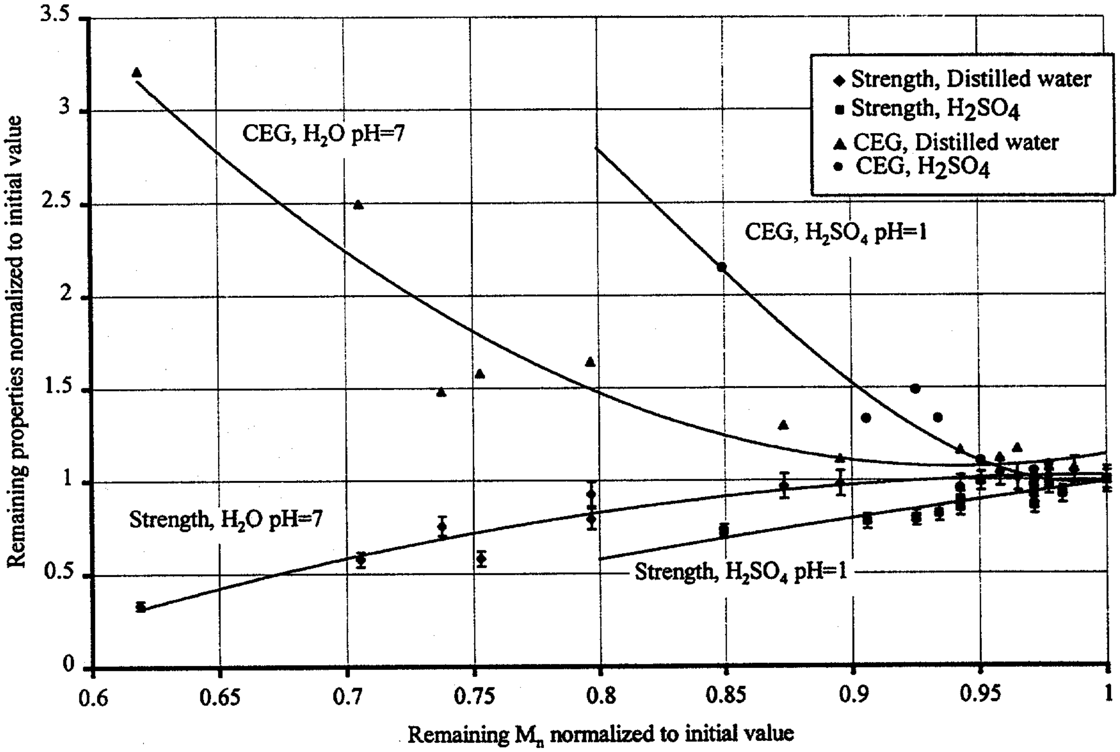


Figure 7.2. Remaining tensile strength and CEG number as a function of remaining average molecular weight ($\overline{M}_n$) for P-5 geotextile, hydrolyzed in distilled water and in H_2SO_4 solution.

7.1.2 Alkaline environment.

In alkaline media characterized by a pH=10, the correlation coefficients between strength loss and both weight loss and viscosity are statistically significant for the tested PET products. For the P-5 geotextile at pH=12, good correlation between strength loss and viscosity changes is observed only at 50°C. For P-6 and P-7, this occurs only at the lowest temperature of 40°C. Therefore, there is evidence that in an environment of moderate pH, hydrolysis of PET products results in both viscosity degradation and surface erosion manifested by weight loss. It appears that at higher values of pH, there may be only a surface erosion mechanism related to strength loss, as in the case of the P-7 geotextile, or both the P-6 and P-7 geotextile. Viscosity and surface erosion may be present simultaneously as indicated by the deterioration of the P-5 geotextile.

The surface erosion developed in alkaline media results in fiber thinning with consequent tensile strength loss. It can be assumed, as a first approximation, that the tensile strength of the geotextile is proportional to the strength of the constituting fibers. The strength of the fibers, in turn, is proportional to the cross-section area of a fiber or proportional to the diameter of a fiber, squared. Therefore, when the degradation of PET fibers occurs primarily due to the surface erosion in alkaline media, it is anticipated that the remaining tensile strength should follow a parabolic loss as a function of diameter dependency. Figure 7-3 qualitatively illustrates the parabolic dependency of the retained tensile strength as a function of fiber diameter for P-5, hydrolyzed in a highly aggressive alkaline media of pH=10 ($Ca(OH)_2$) and pH=12 (NaOH).

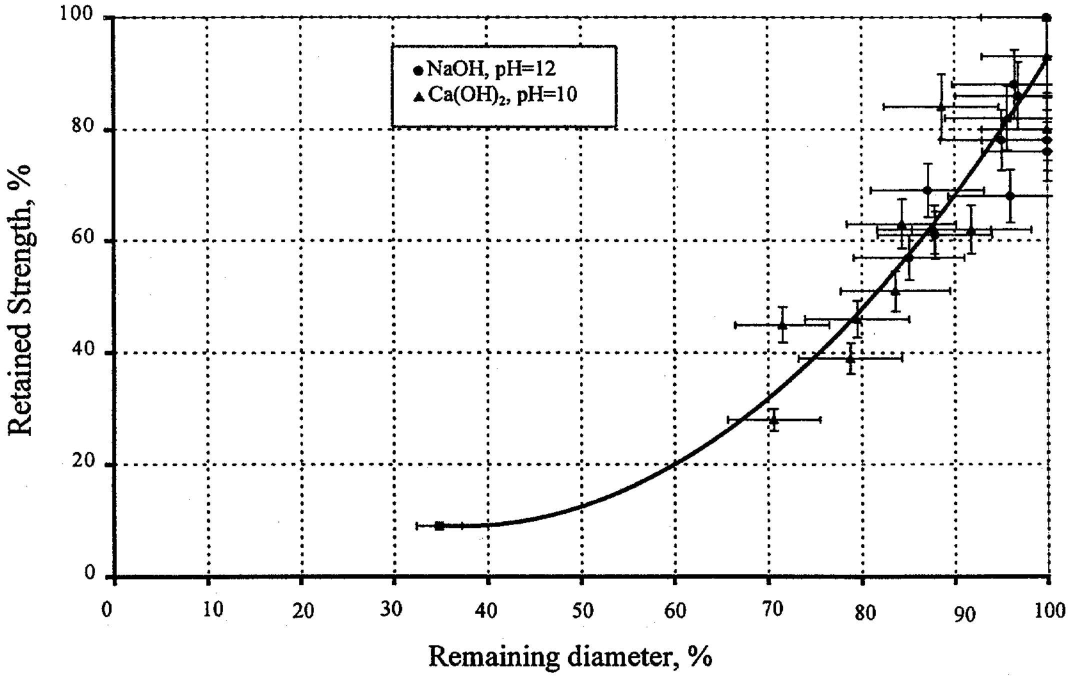


Figure 7.3. Tensile strength loss caused by fiber thinning, due to hydrolysis in highly alkaline media, for P-5 commercial product.

It can therefore be concluded that the type of environment (pH) is chiefly responsible for the mechanism leading to the degradation of mechanical strength of PET products. The type of mechanism, either viscosity degradation or surface erosion, is described by its own kinetics, which can be applied to any geosynthetics regardless of the environment in which hydrolysis takes place. Knowledge of the type of mechanism, therefore, is essential in the modeling of degradation behavior of PET geosynthetic products in different environments.

7.1.3 Conclusions.

- It appears that in neutral and acidic environments the chemical mechanism leading to viscosity degradation is responsible for the loss of mechanical strength of PET products.
- In alkaline media of moderate pH, both molecular weight degradation and surface erosion determine the degradation of mechanical properties of PET products.
- In a high alkaline environment of pH=12, the degradation of mechanical properties correlates either with surface erosion or with both molecular weight degradation and surface erosion.

7.2 MATERIAL PROPERTIES

7.2.1 Effect of tenacity and PVC coating on the rate of degradation.

Material properties such as an average number molecular weight $\overline{M}_n$ and morphology of a product (woven, nonwoven, PVC-coated, etc.) affect the rate of mechanical degradation caused by hydrolysis. The P-5 nonwoven geotextile is made of low-tenacity PET filaments; P-7 is a woven geotextile made of high-tenacity fibers; and P-6 is a PVC-coated product of high-tenacity PET fibers. The experimental data showing the effect of material properties are shown in figure 7.4 and figure 7.5.

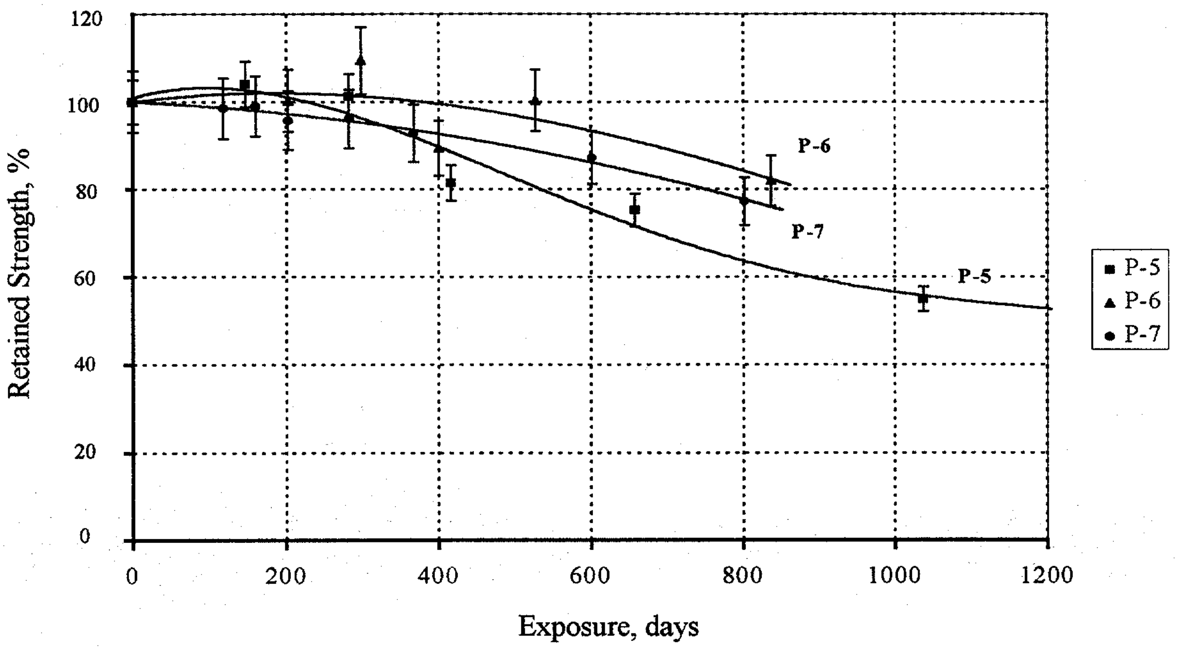


Figure 7.4. Assessment of the effect of material properties on mechanical degradation in distilled water at 60°C for low-tenacity PET product P-5, high-tenacity PVC-coated product P-6, and high-tenacity PET product P-7.

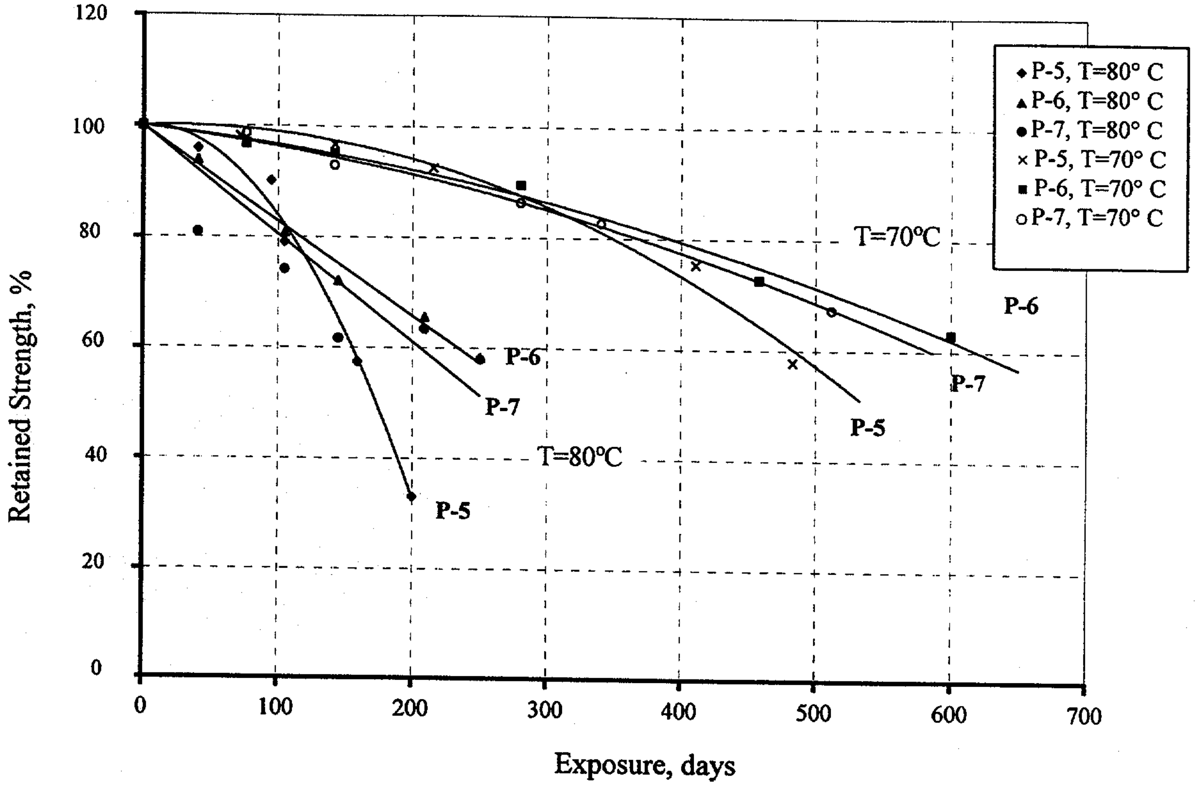


Figure 7.5. Assessment of the effect of material properties on mechanical degradation in distilled water for low-tenacity PET product P-5, high-tenacity PVC-coated product P-6, and high-tenacity PET product P-7, at 70°C and 80°C.

The PVC-coated high-tenacity P-6 fibers exhibit the lowest rate of mechanical degradation in distilled water, indicating some protective properties of the PVC coating against water penetration into the fibers.

At the initial stage of hydrolysis, nonwoven geotextile P-5 exhibits a rate of mechanical degradation that is comparable or even lower than the rate of deterioration observed for the high-tenacity products P-6 and P-7. However, the rate of mechanical degradation for P-5 increases as the time of hydrolysis progresses, exceeding the rate observed for the P-6 and P-7 products. The diameter of the low-tenacity P-5 fibers is about 27 μm, as compared to 21 μm for the P-6 fibers and 17 μm for the P-7 fibers (table 3.4). The larger the diameter of the fiber, the smaller the effective surface of the fiber involved in hydrolysis. This may explain the "delay" in hydrolysis observed for "thick" P-5 fibers compared to the hydrolysis of "thin" P-6 and P-7 fibers. This may indicate that the rate of tensile strength loss caused by hydrolysis may be a function of at least two material variables, such as the fiber diameter and tenacity or molecular weight for PET geosynthetics.

7.2.2 Conclusions.

- The rate of hydrolysis for low-tenacity PET products is higher than the rate for high-tenacity PET products.
- It appears that the PVC coating reduces the rate of mechanical degradation of the PET fibers used in geogrids.
- There is an indication that the initial fiber diameter is one of the factors determining the rate of hydrolysis for PET products.

7.3 MODELING OF THE DEGRADATION BEHAVIOR FOR PET PRODUCTS

The understanding of the chemical mechanisms leading to hydrolysis provides a means for numerical modeling of the degradation of the tensile strength for PET geosynthetics.

7.3.1 Hydrolysis mechanisms.

Hydrolysis in Neutral Environment (Distilled Water, pH=7)

Hydrolysis basically is a very slow inverse reaction of the synthesis of PET, i.e., a long chain linear molecule is split again by an H_2O molecule, resulting in a scission of an ester-bond and a consequent reduction in molecular weight:

$$\begin{gathered}\text{(PET) } [\text{-}\,\mathrm{OC}\,\text{-}\,\langle\circ\rangle - COOCH_2CH_2O -] + H_2O \xrightarrow{k_{neutral}} \\ -OC-\langle\circ\rangle - COOH + HOCH_2CH_2O \quad \textit{products of hydrolysis}\end{gathered} \tag{7-3}$$

Where $k_{neutral}$ is a reaction rate constant.

The strength of a polyester fiber depends on molecular orientation and chain length, with hydrolysis resulting in a reduction of the tensile properties. As more ester links are destroyed, the fiber disintegrates.

In neutral water, this reaction is catalyzed by COOH, the carboxyl end group of the macro-molecule itself. In this case, the rate of hydrolysis is proportional to the square root of the carboxyl end group concentration (Burgoyne and Meii, 1993). Therefore, this reaction should be considered as autocatalytic, because the product of hydrolysis carries a new carboxyl end group. If this is the case, the autocatalytic process should be accounted for in the consideration of kinetics of hydrolysis. However, it is assumed that the influence of the carboxyl end groups on the rate of hydrolysis is small (Risseeuw and Schmidt, 1992). Therefore, as a first approximation, the reaction of hydrolysis in neutral media will be treated as a simple chemical reaction without auto-acceleration.

Hydrolysis in Acidic Environment

The mechanism of acid hydrolysis is the same as neutral hydrolysis because in both cases the H^+ ions are involved. However, the acid attack should occur more rapidly, since the H^+ ions are present at higher concentrations.

Hydrolysis in Alkaline Environment

In an alkaline environment, the reaction mechanism is different. The ester-bond is split by an OH^- ion producing a new carboxyl end group and an $-O-CH_2CH_2-$ ion that reacts immediately with the carboxyl end group, giving a COO^- ion:

$$\left.\begin{array}{l}[\text{- OC - } \langle \circ \rangle - COOCH_2CH_2O -] + OH \Rightarrow \\ -OC - \langle \circ \rangle - COOH + -OCH_2CH_2O - \Rightarrow \end{array}\right\} k_{alkali} \qquad (7\text{-}4)$$

$$-OC - \langle \circ \rangle - COO- \; + HOCH_2CH_2O \quad product\ of\ hydrolysis$$

where k_{alkali} is a rate of hydrolysis in alkaline solution.

This molecule split results in the drop of molecular weight and eventually in the loss of tensile strength of the PET polymer. It was reported (Buxbaum, 1968) that dielectric properties of PET work as a barrier that reduces penetration of the hydroxyl ions through the fiber core. This results in an increase of hydrolysis intensity at the fiber surface. Shorter chains formed as a result of the reaction are removed and dissolved, leading to a weight loss and decrease of fiber diameter. In a moderate pH environment, the concentration of H^+ ions may be significant enough to cause molecular weight degradation. Therefore, it appears that the tensile strength of PET fibers may be affected by both the molecular weight reduction and surface erosion caused by hydrolysis in an alkaline media. The mechanism of hydrolysis strongly depends on the type of hydrolytic environment. In a neutral environment, hydrolysis basically is a very slow inverse reaction of the synthesis of PET, i.e., a long chain linear molecule is split again by an H_2O molecule, resulting in a scission of an ester-bond and as a consequence, a reduction in molecular weight and tensile strength occurs.

7.3.2 Kinetic model for hydrolysis in neutral and acidic environments.

The chemical reaction of hydrolysis is described by the equation (7-3) for hydrolysis in neutral or acidic environments. This process results in a molecular chain split that causes a decrease in molecular weight. The tensile strength of a polymer is proportional to its average molecular weight (Mark and Pearce, 1967); therefore, the rate of a tensile strength deterioration is directly proportional to the rate of a molecular weight decrease. As in many simple chemical reactions, temperature plays the dominant role in determining the rate of hydrolysis (Burgoyne and Merii, 1993). The rate of chemical reaction R can be expressed as:

$$R = k[A]^n ; \; k = Ae^{-(U_{act}/RT)} \qquad (7\text{-}5)$$

where k is a reaction constant (sec^{-1}); n is a reaction order; A is a constant for a particular process; U_{act} is an apparent activation energy for PET; R is the universal gas constant (8.3 $J/mol^{-1}\ K^{-1}$); and T is the absolute temperature (°K).

Kinetic equations describing zero-, first-, and second-order reactions are discussed in section 5.2 (table 5.1).

This system of kinetic equations describes the decrease in the retained tensile strength for PET geosynthetics hydrolyzed in neutral or acidic media. Equations for zero-, first-, and second-order reactions provide a key tool to the interpretation of the observed data on mechanical strength losses in neutral or acidic environments. The steps in the interpretation of experimental data are as described in section 5.9 in steps 3 through 6.

This step-by-step procedure is used to interpret the experimental results of hydrolytic degradation for geosynthetic products. Regression functions corresponding to zero-, first-, and second order reaction laws ($x=1-kt$ – zero order; $x=e^{-kt}$ – first order; $x=\frac{1}{1+[A]_0kt}$ - second order) are used for curve-fitting of experimental data. Analysis indicates that an equation corresponding to a zero-order reaction provides the best fit of the observed data for the P-5 product, hydrolyzed in distilled water as shown in table 7.7.

Table 7.7. Correlation by R^2 for reaction laws and experimental data on mechanical degradation of P-5 product in distilled water.

Reaction order, n	Kinetics law (approximation function)	R^2				$\overline{R}^2$
		T=50°C	T=60°C	T=70°C	T=80°C	
0	$x=1-kt$	0.72	0.83	0.86	0.84	0.81
1	$x=e^{-kt}$	0.74	0.69	0.81	0.75	0.75
2	$x=\frac{1}{1+k_1t}$	0.84	0.79	0.82	0.72	0.79

Figure 7.6 shows the results of a linear regression analysis for the degradation of the P-5 product in distilled water.

Values of the rate constant of mechanical degradation at different temperatures determined from linear regression analysis are summarized in table 7.8.

Table 7.8. Rate constant of mechanical degradation ($k_{neutral}$) for P-5 product, hydrolyzed in distilled water.

Material	Temperature, °C	$k_{neutral}$ (rate), 1/day
P-5	50	0.0002
	60	0.0004
	70	0.0007
	80	0.0027

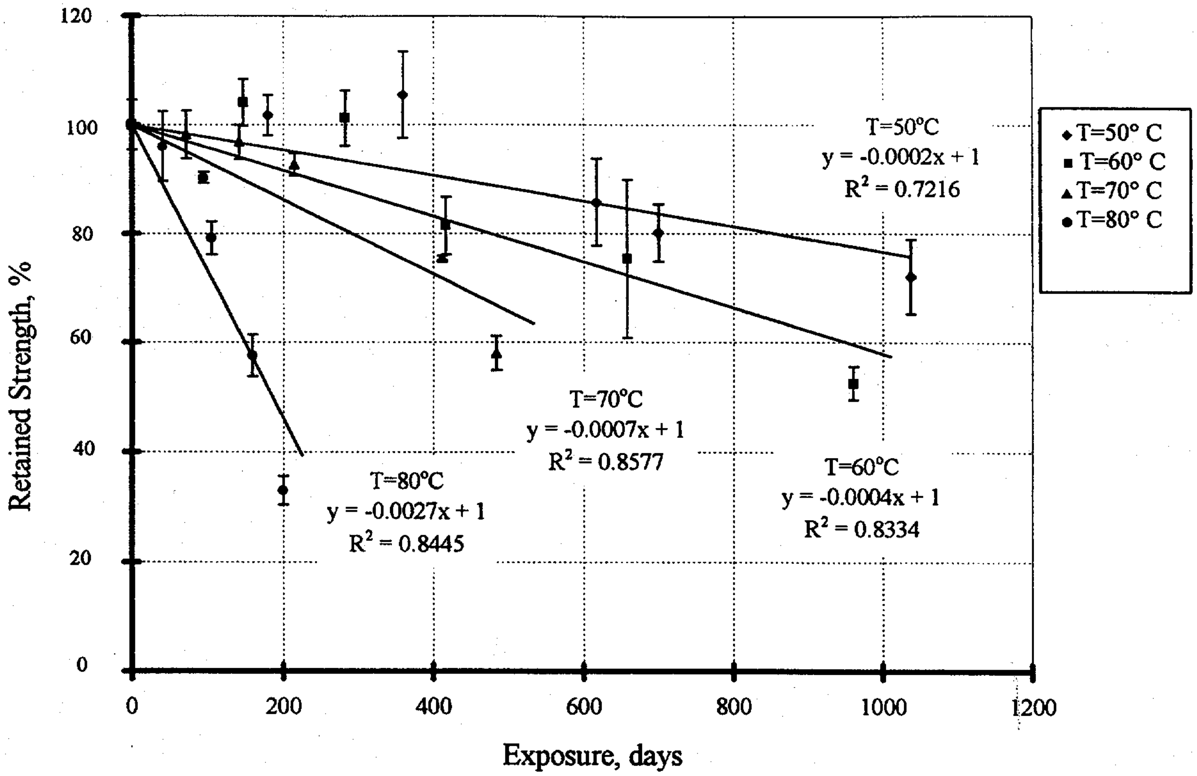


Figure 7.6. Linear regression analysis of experimental data for tensile strength loss in distilled water for PET product P-5.

The natural logarithm of the degradation rate ln(k) was plotted versus reciprocal values of temperature 1/T°K (figure 7.7) for the products studied. Linear regression analysis of ln(k) versus 1/T provides a relationship for k at any given temperature T°K for P-5 hydrolyzed in distilled water

$$ln(k_{neutral}) = -9492(1/T) + 20.734 \qquad (7\text{-}6)$$

This empirical relationship estimates the anticipated time to 50-percent strength loss due to hydrolysis in neutral media for P-5. At 20°C, equation (7-6) yields a value of $k_{neutral}$ = 8.6×10^{-6} 1/day. Using this rate constant, the anticipated strength loss over a 100 year-period (%/100 yr) was estimated from equation (5-16) where t=100 yr (365×10^{2} days) and k = 8.6×10^{-6} 1/day. The solution of equation (5-16) with these parameters yields F(100 yr)/F_0 = 31%/100 yr. Anticipated time to 50-percent strength loss is estimated as 159 years.

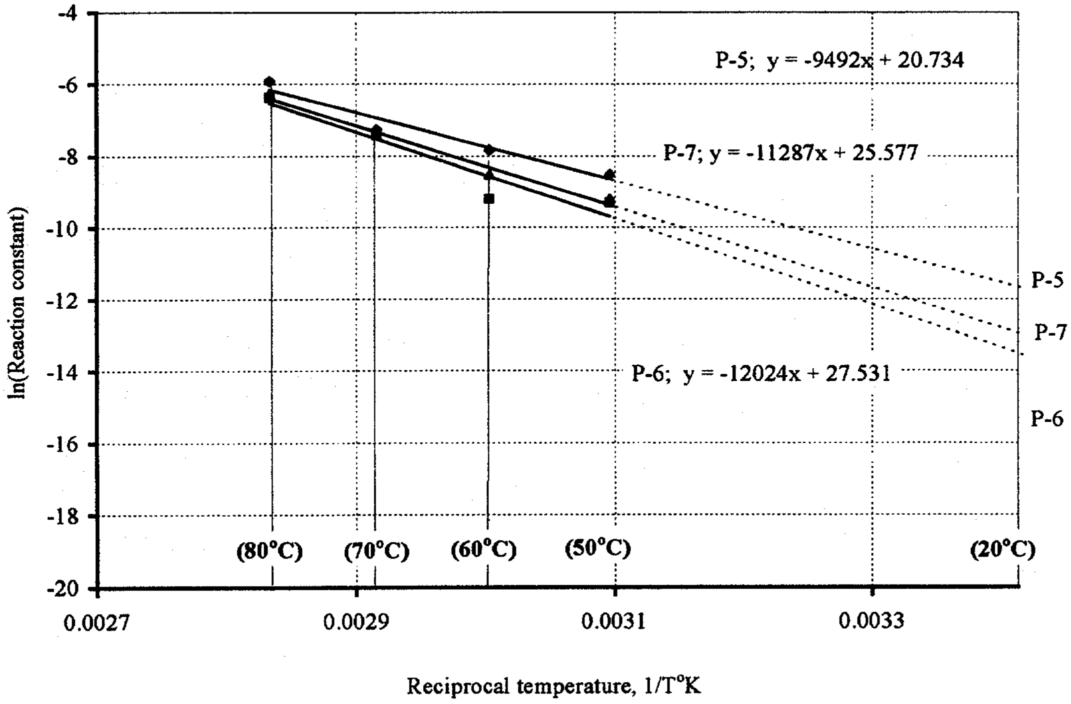


Figure 7.7. Arrhenius plot for the reaction constant in distilled water for PET products tested.

The Arrhenius equation for the reaction constant could be rewritten as:

$$ln(k_{neutral}) = C - U_{act}/RT \qquad (7\text{-}7)$$

where U_{act} is the activation energy and R is the universal gas constant, R= 8.31 J/mol K. Solving this equation with respect to U_{act}, one obtains a value of U_{act}=79 kJ/mol.

Similarly, a linear regression analysis of ln(k) versus 1/T°K provides a relationship for k at any given temperature T°K for PVC-coated product P-6, hydrolyzed in distilled water as follows:

$$ln(k_{neutral}) = -12024(1/T) + 27.531 \qquad (7\text{-}8)$$

The empirical relationship in equation (7-8) yields the estimate of the rate of tensile strength loss in distilled water at 20°C as 5%/100 yr for PVC-coated P-6 product.

A linear regression analysis of ln(k) versus 1/T°K provides the following relationship for k at any given temperature T°K for PET woven product P-7, hydrolyzed in distilled water

$$ln(k_{neutral}) = -11287(1/T) + 25.557 \qquad (7\text{-}9)$$

Equation (7-9) yields the estimate of the rate of tensile strength loss in distilled water at 20°C as 8%/100 yr for P-7 product. The obtained value of the degradation rate for high-tenacity P-7 product is comparable with the estimate of the degradation rate of about 5%/100 yr in distilled water at 20°C, reported in the literature by Schmidt et al. (1994) for high-tenacity PET yarns.

A rate constant regression equation yields estimates of activation energy of 100 kJ/mol and 94 kJ/mol for P-6 and P-7 products, respectively. The activation energy values can be compared with the value of 105 to 125 kJ/mol, reported in the literature by McMahon with co-authors (1959) for PET films, and with 112 kJ/mol reported by Burgoyne and Merii (1993) for a high-tenacity PET product.

7.3.3 Kinetic model for hydrolysis in an alkaline environment.

A hydrolytic reaction in alkaline media results in molecular weight degradation, which is similar to hydrolysis in neutral and acidic solutions, in addition to surface erosion of PET fibers. Both of these mechanisms cause tensile strength deterioration for PET products exposed to an alkaline environment. In this case, the tensile strength F is a complex function of two variables M (molecular weight) and S (polymeric fiber cross section). The rate of the tensile strength loss can be defined as a time derivative of a complex function:

$$\frac{\partial F}{\partial t} = \frac{\partial F}{\partial M}\frac{\partial M}{\partial t} + \frac{\partial F}{\partial S}\frac{\partial S}{\partial t} \qquad (7\text{-}10)$$

The following assumption may be made with regard to this process:

1. Molecular weight degradation and fiber surface erosion are independent processes.
2. The strength for a PET is proportional to both molecular weight M and fiber cross-section S, therefore $\partial F/\partial M = C_M$ and $\partial F/\partial S = C_S$, where C_M and C_S are constants for the particular product. Results of this program (figure 7-2) and Schmidt et al. (1994) demonstrated that the molecular weight/tensile strength relationship appears to be a second-degree polynomial that can be approximated within the range of measured values of molecular weight by a linear function, justifying the above assumption.
3. The rate of molecular weight degradation according to mass action law (Adamson, 1973) is $\frac{\partial M}{\partial t} = k_M = Ae^{-U_M/RT} \times [C]^n$, where U_M is the apparent activation energy of hydrolysis, $[C]$ is a concentration of reactant, n is the order of the rate law (n=0, 1, 2 ...). Similarly, the rate of the surface erosion is given as: $\frac{\partial S}{\partial t} = k_S = Ae^{-U_S/RT} \times [C]^m$, where U_S is the apparent activation energy of the surface erosion process.

   Equation (7-10) could be rewritten according to the above assumptions as:

$$R = C_M A e^{-(U_M/RT)} \times [C]^n + C_S A e^{-(U_S/RT)} \times [C]^m \qquad (7\text{-}11)$$

If the activation energy of surface erosion is much greater than the activation energy of chain scission resulting in molecular weight loss, the deterioration will occur primarily due to polymer chain scission. When activation energy of chain scission is greater, the degradation will be determined by the surface erosion process.

As discussed earlier, no surface erosion has been observed in distilled water and acidic solution of pH=1 for the PET tested. Therefore, only the first term in equation (7-11) should be used for numerical modeling. Experimental results of this program (table 7.7) as well as the results reported in the literature (Burgoyne and Merii, 1993; Schmidt et al., 1994), suggest that the kinetics of hydrolysis may be described by a zero-order reaction law (n=0 in equation 7-11), thereby transforming equation (7-11) into:

$$R = k = C_M \times Ae^{-(U_M/RT)} \qquad (7\text{-}12)$$

Hydrolytic reaction in alkaline media resulted in some molecular weight degradation, similar to hydrolysis in neutral and acidic solutions, in addition to surface erosion of PET fibers. Both of these mechanisms are the causes of tensile strength deterioration. However, the apparent rate of surface erosion observed in an aqueous solution of NaOH at pH=12 is much higher than the rate of molecular weight degradation, thereby suggesting that the first term in equation (7-11) may be neglected. Data developed in this program suggests that the zero-order rate law, similar to equation (7-12), could be used in numerical modeling of the apparent surface erosion rate for the PET product tested in NaOH at pH=12.

The results obtained in an aqueous solution of NaOH at pH=10 indicated that the apparent rate of molecular weight degradation was comparable with the apparent rate of surface erosion. This suggests that the apparent activation energies of both processes may have close values. Assuming that both reactions are of the zero order, equation (7-11) may be reduced to an expression similar to equation (7-12):

$$R = k = C \times e^{-(U/RT)} \qquad (7\text{-}13)$$

where C is a complex constant and U is an apparent activation energy.

In general, when the apparent activation energy of polymer chain scission is not equal to the apparent activation energy of the surface erosion process, the apparent rates of both processes should be measured and kinetic modeling developed for each.

It appears that equation (7-13) is the same type as the reaction rate for PET products hydrolyzed in neutral and acidic solutions. Therefore, the same step-by-step procedure could be used to analyze experimental data on the tensile strength loss caused by the hydrolysis in alkaline media for PET geosynthetics.

Regression analysis indicates that zero-order equations provide a satisfactory fit of experimental data on a viscosity degradation and fiber diameter loss in alkaline media for the P-5 product. This verifies an assumption that molecular weight degradation and surface erosion are reactions of the same order.

The results of a linear regression analysis of tensile strength loss data caused by hydrolysis in NaOH at pH=10 for product P-5 are shown in figure 7.8. The rate of mechanical degradation values determined at different temperatures for the P-5 PET geotextile are summarized in table 7.9.

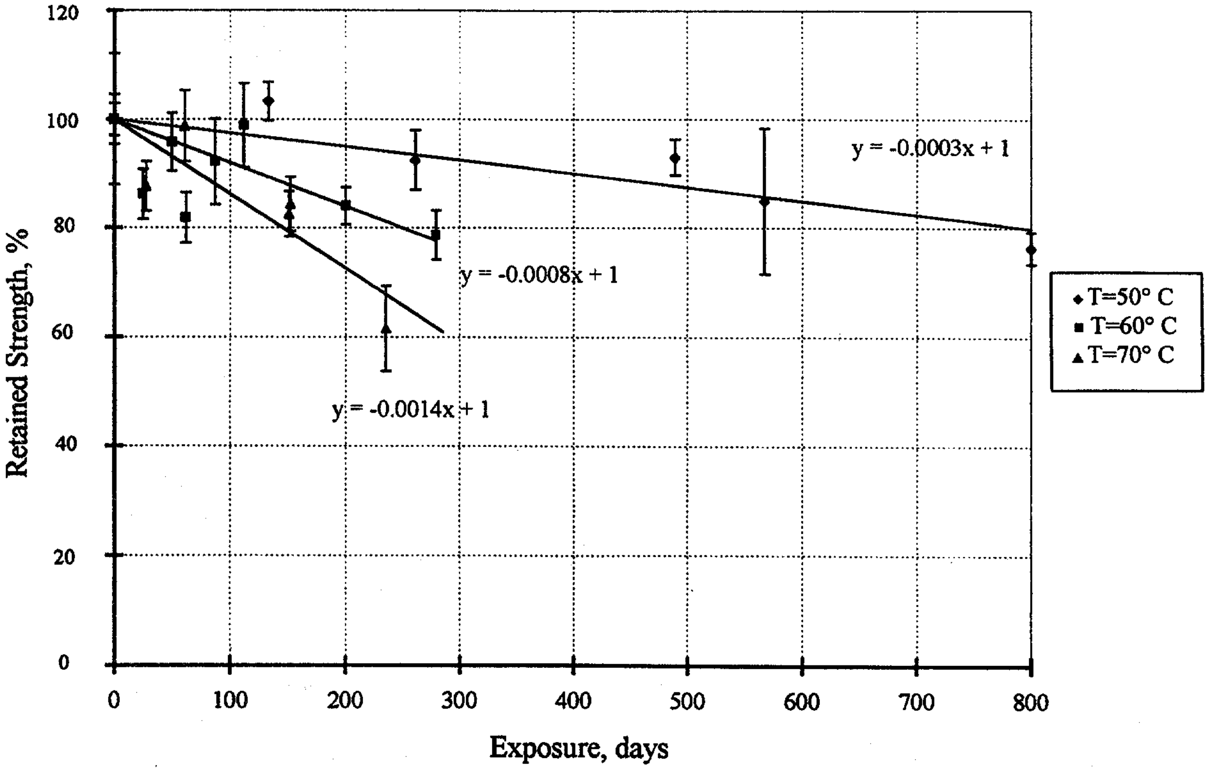


Figure 7.8. Linear regression analysis of experimental data for tensile strength loss in NaOH at pH=10 for PET product P-5.

Table 7.9. Rate constant of mechanical degradation for commercial PET product P-5 hydrolyzed in NaOH at pH=10.

Material	Temperature, °C	Rate, 1/day
P-5	50	0.0003
	60	0.0008
	70	0.0014

Arrhenius plots for reaction rate constant in NaOH at pH=10 for PET products studied are shown in figure 7.9. A linear regression analysis of *ln(k)* versus *1/T°K* yields an equation for *ln(k)* at any given temperature T°K for product P-5 as:

$$ln\,(k) = -8554(1/T) + 18.432 \qquad (7\text{-}14)$$

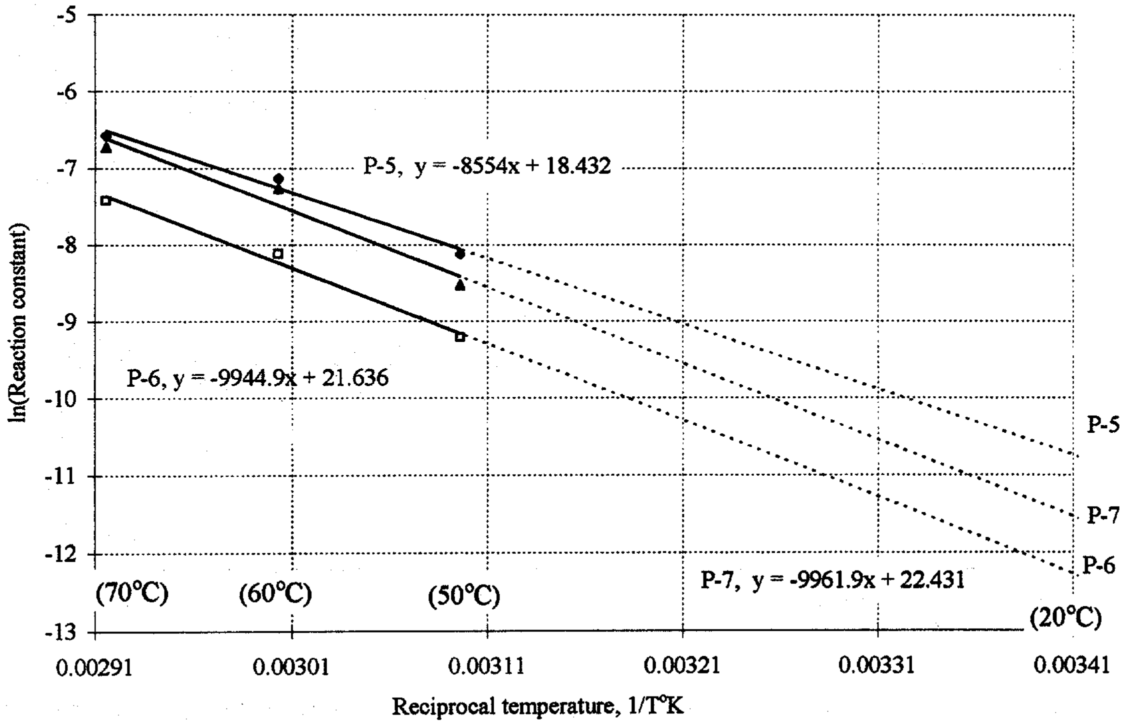


Figure 7.9. Arrhenius plot for reaction constant in NaOH at pH=10 for PET products tested.

The solution of equation (7-14) for k at T=293°K (20°C) yields $k = 2.04 \times 10^{-5}$ 1/day and permits an estimate for anticipated time to 50-percent strength loss as 67 years for hydrolysis in NaOH at pH=10, and the rate of tensile strength loss as 77%/100 yr.

A linear regression analysis of ln(k) versus 1/T°K provides a relationship for *k* at any given temperature T°K for PVC-coated P-6 product, hydrolyzed in NaOH at pH=10, as follows:

$$ln(k_{pH=10}) = -9944.9(1/T) + 21.636 \qquad (7\text{-}15)$$

Solution of equation (7-15) yields an estimate of the rate of tensile strength loss in an aqueous solution of NaOH at pH=10 as 17%/100 yr.

Experimental data yields an Arrhenius relationship for the P-7, hydrolyzed in this condition, as follows:

$$ln(k_{pH=10}) = -9961.9(1/T) + 22.431 \qquad (7\text{-}16)$$

Solution of equation (7-16) with respect to $k_{pH=10}$ at 20°C yields the rate of tensile strength loss as 35%/100 yr for the P-7, hydrolyzed in NaOH at pH=10.

The results of Arrhenius modeling for the geosynthetics tested in aqueous solutions of H_2SO_4 (pH=1) and NaOH (pH=12) are shown in figure 7.10 and figure 7.11.

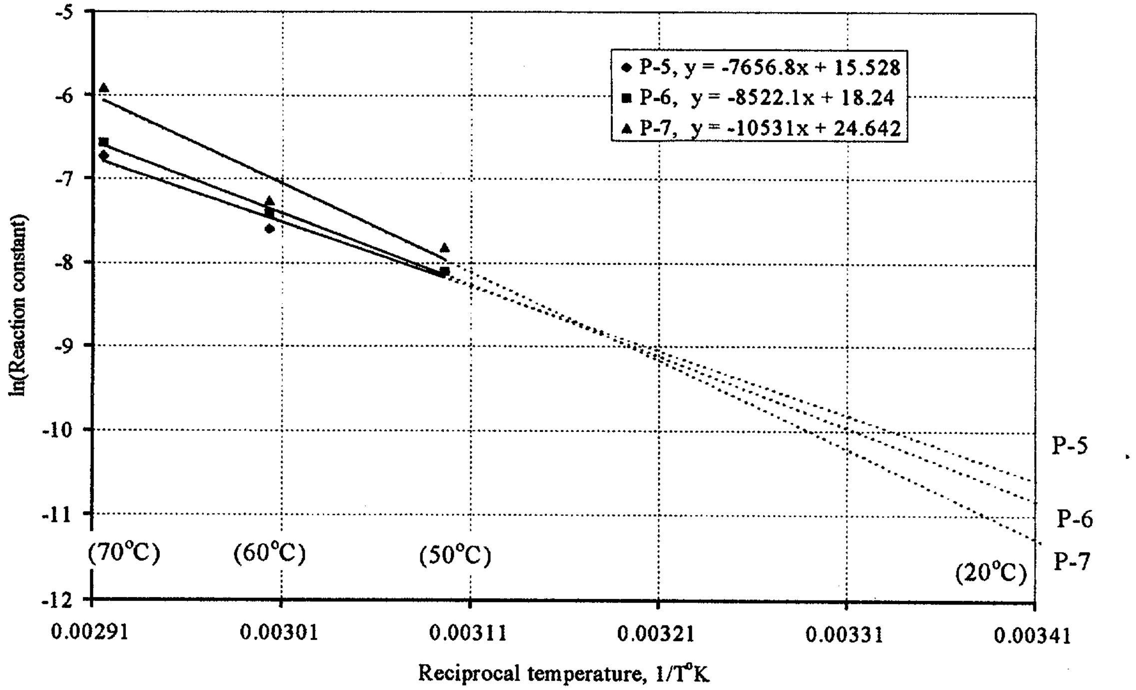


Figure 7.10. Arrhenius plot for reaction constant in H_2SO_4 at pH=1 for PET products tested.

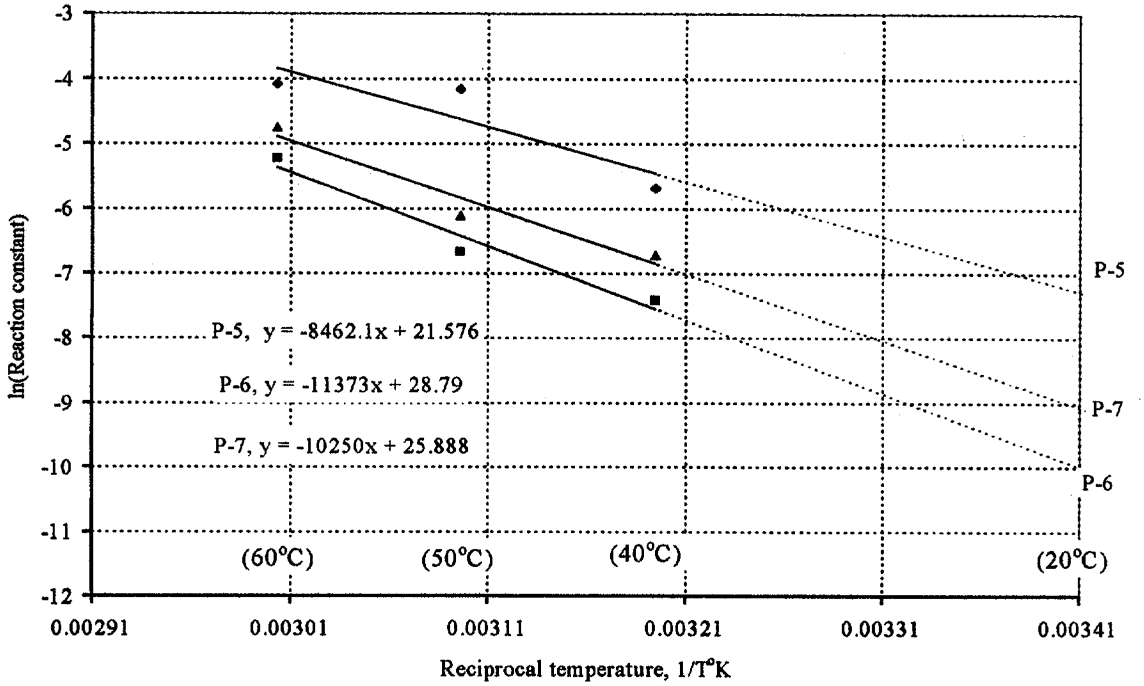


Figure 7.11. Arrhenius plot for the reaction constant in NaOH at pH=12 for PET products tested.

Arrhenius modeling of laboratory-obtained experimental data permits estimates of anticipated time to 50-percent strength loss at 20°C, and a corresponding rate of strength loss (%/yr) in environments of different pH for the products studied. The summarized results of the Arrhenius modeling of the rate of tensile strength loss at 20°C are presented in table 7.10 and in figure 7.12 for PET products tested.

Table 7.10. Estimates of the rate of tensile strength loss in %/ yr at 20°C in varying pH for PET products tested.

Condition Product	H_2SO_4 pH=1	H_2O pH=7	NaOH pH=10	NaOH pH=12
P-5	1.0	0.31	0.77	25
P-6	0.70	0.05	0.17	1.61
P-7	0.21	0.08	0.35	4.10

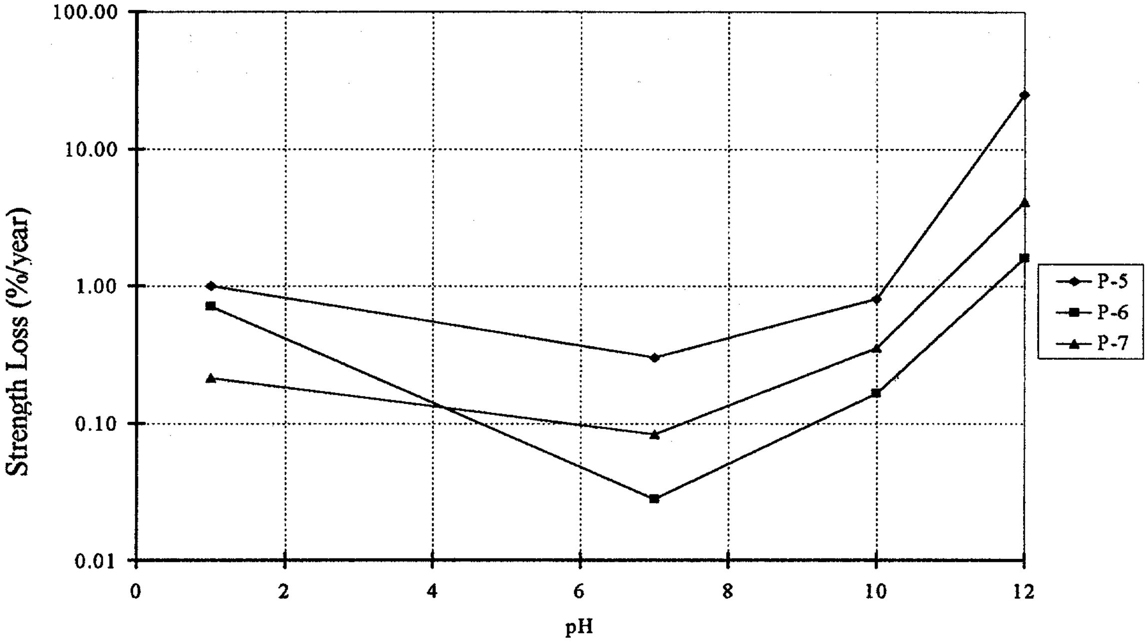


Figure 7.12. Estimates of the rate of tensile strength loss in %/ yr at 20°C in varying pH for PET products tested.

The obtained values of degradation rates are applicable only to the conditions of the testing protocol, which uses intensive stirring of the hydrolytic media. For in-service conditions, geosynthetics are exposed to a stagnant hydrolytic media, which should result in a lower rate of surface erosion and mechanical degradation. Therefore, the results obtained for the condition of intensive stirring should provide conservative estimates of anticipated time to 50-percent strength loss and a corresponding rate of tensile strength loss (%/yr) for PET geosynthetic products for in-service conditions.

In order to assess the effect of the intensity of stirring on the rate of mechanical degradation, additional limited testing has been conducted as outlined in 7.3.4.

7.3.4 Additional testing in "in-soil" condition for the P-5 product.

Consideration of the mechanism of hydrolysis and fiber erosion has suggested that the estimates of the rate of degradation may depend on the intensity of stirring in the testing reactor. The intensity of stirring is the least controllable parameter in the accelerated testing for commercial products. The wide range of surface types (roughness, density of material, etc.) makes this problem even more complex. Therefore, it is not feasible to reproduce the same intensity of stirring and, more importantly, the same conditions of heat and mass exchange of the surface of specimens of different commercial products.

The following conditions have been tested to assess the effect of stirring intensity on the rate of mechanical degradation, due to hydrolysis, for product P-5:

- Intensity of stirring – tested in stagnant conditions.
- Hydrolytic media – tested in Ottawa sand fully saturated with the solution of NaOH at pH=10 and 70°C temperature of hydrolysis.

This limited result indicates that the rate of mechanical strength loss is slower in sand as compared to the degradation rate in stirred solution in NaOH at pH=10, 70°C. Figure 7.13 illustrates this finding.

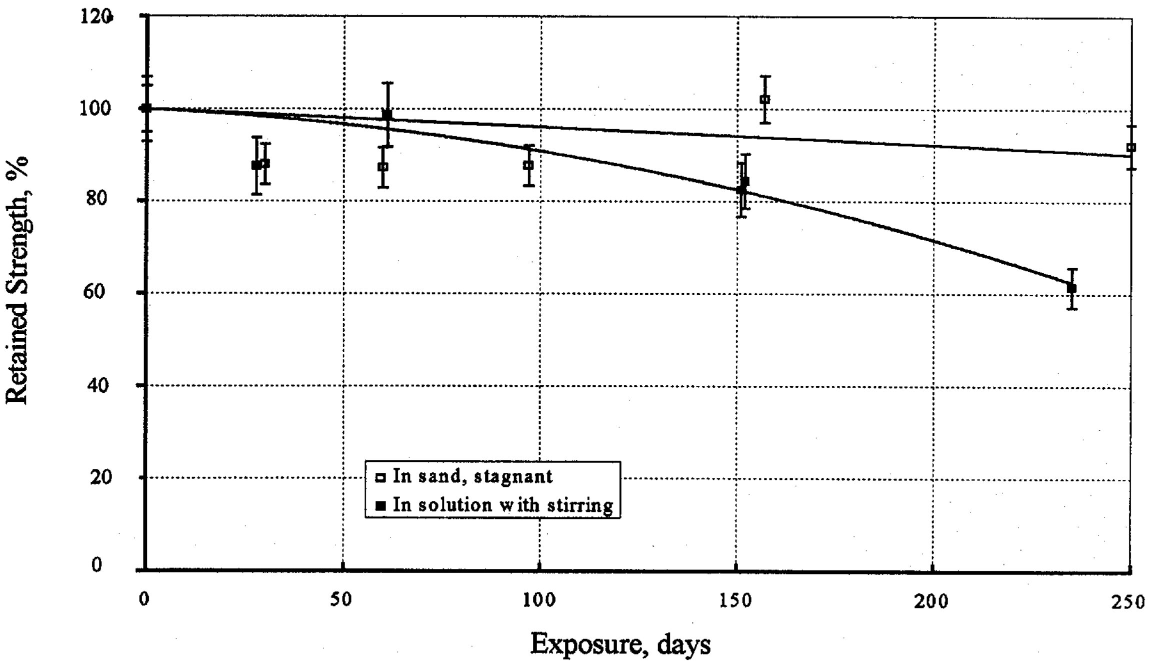


Figure 7.13. Tensile strength loss for P-5 product, hydrolyzed in NaOH at pH=10 at 70°C in sand and in solution with stirring.

This limited finding in an alkaline solution suggests that the protocol utilizing stirred solutions measures an upper degradation limit, especially in alkaline media.

7.4 Conclusions.

This analysis of experimental data on hydrolysis for the selected PET commercial geosynthetic products suggests the following conclusions:

- The dominant mechanism of hydrolytic reaction in neutral and acidic environments is molecular chain split, leading to molecular weight and tensile strength degradation.
- In alkaline media, molecular weight degradation and fiber surface erosion (weight loss) are the key factors in determining the loss of tensile strength.
- Low-tenacity PET commercial products are more susceptible to hydrolysis than high-tenacity PET products, due to their lower molecular weight and higher CEG.
- SEM studies indicate that in an alkaline environment, hydrolysis of PET geosynthetic products results in fiber surface erosion, where the PVC coating reduces the rate of this process.
- It appears that PVC coating reduces the rate of mechanical degradation as compared to the rate of degradation obtained for a similar PET fiber without PVC coating.
- Larger diameters of PET fibers may result in the "delay" of hydrolysis and mechanical deterioration, which may be caused by a diffusion process.
- Application of Arrhenius-type modeling permits estimates of anticipated time to a given strength loss and corresponding rate of degradation due to hydrolysis in media of varying pH at 20°C.
- Arrhenius model estimates presented are based on results obtained under conditions of intense stirring of a hydrolytic media that intensifies the hydrolytic reaction. Therefore, all calculations of tensile strength loss over a 100-year period should be considered as a conservative estimate for the degradation rate for "in-use" conditions.

CHAPTER 8

RECOMMENDED TESTING PROTOCOL FOR OVEN AGING OF POLYOLEFIN-BASED GEOSYNTHETICS

8.1 SCOPE

This testing protocol describes a procedure for determining tensile strength loss caused by thermo-oxidation for polyolefin-based geosynthetics exposed to elevated temperatures under controlled conditions of air circulation and oxygen concentration. Correlation between this accelerated test and in-ground aging has not been established, but may provide upper-bound values of strength losses due to thermo-oxidation.

8.2 REFERENCED DOCUMENTS

ASTM standards:

ASTM D-3045, "Standard Practice for Heat Aging of Plastics Without Load."

ASTM D-3776, "Standard Test Method for Weight (Mass per Unit Area) of Woven Fabric, Option C - Small Swatch of Fabric."

ASTM D-3895, "Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry."

ASTM D-4595, "Standard Test Method for Tensile Properties of Geotextiles by the Wide-Width Strip Method."

8.3 SUMMARY OF TEST METHOD

This method consists of subjecting test specimens with previously determined physical and chemical properties to controlled conditions for known periods, after which these properties are again measured and the changes are noted. The physical properties monitored are weight, tensile strength and strain at break, and the integrity of the fiber surface. This test method involves exposure of specimens to elevated temperatures in controlled conditions of air circulation and oxygen concentration.

Unless otherwise specified, the determination of tensile strength and strain at break should be carried out in accordance with ASTM D-4595. Weight is determined in accordance with ASTM D-3776. The changes in fiber surface morphology are monitored by Scanning Electron Microscopy (SEM) or optical microscopy.

The use of Differential Scanning Calorimetry (DSC) in determining Oxygen Induction Time (OIT) in accordance with ASTM D-3895 and modified as described in the appendix, and the use of High-Performance Liquid Chromatography (HPLC) may provide additional insight in monitoring chemical degradation.

8.4 SIGNIFICANCE AND USE

Polyolefin-based geosynthetics should be qualified for their resistance to deterioration of their physical properties with time caused by oxidative aging. This test method provides a method to assess the performance characteristics, such as the rate of tensile strength loss in %/100 yr and the corresponding time to 50-percent loss for polyolefin geosynthetics under specified conditions. At present, it only appears applicable to geosynthetics, which, as produced, do not exhibit initial cracking or crazes.

Effects of exposure to high temperature may be quite variable, resulting in the development of fiber cracking or in the change of physical properties, such as extensibility and modulus. Data obtained for certain materials at elevated temperatures may, therefore, be unreliable for engineering estimates. This test method does not predict degradation behavior of polyolefin geosynthetics other than under conditions of testing, e.g., oxygen concentration and intensity of air circulation.

8.5 OVEN APPARATUS

8.5.1 Oven apparatus for aging in circulating air at 21% oxygen.

The apparatus for heat aging in circulating air at 21% oxygen should be in accordance with ASTM D-3045. The size of the chamber is optional, but is such that the specimens may be suspended vertically in parallel to the air flow without crowding and without touching each other or the sides of the chamber. Automatic temperature control by means of thermostatic regulations shall be used. The regulation system shall be provided with power-failure protection and over-shoot protection to prevent accidental runaway temperature increases.

8.5.2 Controlled oxygen concentration chamber for heat aging.

The controlled oxygen concentration chamber should consist of a stainless steel container. The size of the chamber is optional, but is such that the specimens may be suspended therein vertically without crowding and without touching each other or the sides of the chamber. The source of heat is optional, but shall be located outside the chamber. The heating medium is optional. Positive, rapid, and complete circulation of the heating medium shall be maintained to ensure accurate uniform heating. Thermostatic regulation shall be employed to control exposure temperature. The chamber shall be equipped with the inlet ports to provide constant through flow for the gas mixture of a controlled oxygen concentration.

8.6 SAMPLING

Unless otherwise specified, sampling should be in accordance with ASTM D-4595 for the tensile properties to be determined.

8.7 TEST SPECIMENS

8.7.1 Specimen size.

Specimens prepared as described in ASTM D-4595 are preferable, but not mandatory. The specimens of the geogrid should be sufficient in size to permit the determination of the tensile properties. The number of ribs in a grid specimen should be determined experimentally and should depend on the structure of a particular product.

8.7.2 Number of test specimens.

The number of test specimens required should be in accordance with ASTM D-4595 for determining the tensile properties of geotextiles. This requirement should be met for each time retrieval and temperature selected. A minimum of five specimens shall be prepared per retrieval.

8.8 TEST CONDITIONS

8.8.1 Aging in circulating air at 21% oxygen.

This aging condition is recommended for polyolefin geosynthetics with monofilament fibers and tapes that are intact in their virgin state. Staple fiber and film products should be examined by SEM for surface cracks and crazes. The presence of cracks and crazes on virgin fibers and films disqualifies those products from oven aging under the present protocol.

Testing at a minimum of three exposure temperatures should be used in order to determine the relationship between a tensile strength loss and temperature. The unique performance of commercial products determines the temperature range for a particular product. In general, it is suggested that the temperature of exposure should range from 50°C to 90°C for polypropylene products (PP). At least five retrievals shall be scheduled at each incubation temperature. The lowest temperature of exposure should produce a measurable level of tensile strength change in approximately 18 to 24 months. The next higher temperature should produce the same level of strength loss in about 12 to 15 months. The highest temperature of exposure should be much less than the temperature of melting for the particular polymer and should not exceed the upper temperature of antioxidant effectiveness. For HDPE products, the aging temperature should be less than 80°C, resulting in a considerably longer testing duration.

8.9 PROCEDURE

In practice, it is often difficult to estimate the effect of heat aging on strength reduction. Therefore, it is suggested to start short-term heat aging at the highest temperature. The obtained data may be used as a basis for selecting the remainder of the aging temperatures, as well as for preliminary scheduling of the retrievals. At least five retrievals should be scheduled at each exposure temperature.

Geosynthetic specimens are retrieved at five consecutive time intervals. The duration of the aging intervals depends on the rate of deterioration of the particular geosynthetic being tested. If the obtained data are insufficient for further interpretation, additional retrievals should be scheduled.

The retrieved set of specimens is tested for the selected property (tensile strength, weight, fiber morphology, chemical degradation) in accordance with the appropriate test method specified in section 8.3.

8.9.1 Procedure of aging in circulating air.

A forced draft oven shall be used to perform aging in circulating air as described in section 8.5.1. Specimens are suspended parallel to the direction of air flow in the middle of the oven chamber with a 12.7-mm (0.5-in) distance between each other and without touching the sides of the chamber. Hangers for specimens shell be made of a non-corrosive material, such as stainless steel. Periodical observations of the chamber should be made once a week and precipitation cleaned, if there is any. The temperature should be checked on a daily basis.

8.9.2 Procedure of aging in stagnant diluted air.

Specimens shall be suspended parallel to the direction of the gas mixture flow in the chamber described in section 8.5.2, with a 12.7-mm (0.5-in) distance between each other and without touching the sides of the chamber. After the container with the specimens is sealed and placed into the oven, a vacuum is applied to the chamber for 10 to 15 minutes to evacuate air before filling with the gas mixture. The gas mixture consists of a specified concentration of oxygen balanced by nitrogen and industrially produced by a special gases manufacturer. The inlet gas flow shall be controlled by a two-stage gas regulator and a flow meter. It is maintained at the level of 10 to 20 mL/min throughout the total period of the experiment. The oxygen concentration should be periodically checked with an oxygen meter three times a day for the first 3 days, and then once every week if the concentration is stable within a range of ±1%. The precipitation is cleaned, if there is any, when the chamber is opened for retrieval.

8.10 CALCULATIONS

8.10.1 Estimates of induction period at a given temperature.

Results from the oven-aging tests are expressed as a ratio between aged values and initial values for measured properties. Degradation curves shall be prepared for each exposure temperature by plotting residual values of the measured properties as a function of aging time. Remaining tensile strength versus time curves shall be examined for the presence of an induction period. For a geosynthetic exhibiting a region of no strength loss prior to deterioration, a tangent shall be constructed to the maximum slope of the post-induction degradation curve, and extended to intersect the no-strength loss line. The abscissa of this intersection point is the induction period t_{ind}. The logarithm of the induction period versus the reciprocal temperature of aging (Arrhenius plot) shall be prepared. Regression analysis shall be used to determine the relationship between the reciprocal of the exposure temperature and the logarithm of the induction period. The linear regression equations shall be used to estimate the anticipated induction period at any given temperature.

8.10.2 Estimates of anticipated rate of thermal degradation without induction period.

Regression analysis shall be used to determine the relationship between the remaining properties and time for the post-induction period of aging. The regression equations selected provide the relationship between reaction constant and aging temperature. An Arrhenius plot shall be used for a linear regression analysis. The regression equation is used to calculate the anticipated value of a rate constant at a given temperature. The obtained value of a rate constant is used to calculate the rate of tensile strength loss in %/100 yr, utilizing the regression equation obtained previously for the remaining strength versus time relationship.

8.11 OIT AND SEM

If measured, OIT times shall be examined against tensile strength loss to determine if a correlation exists. Regression analysis shall be used to establish the relationship between strength loss and OIT times.

SEM microphotographs, if performed, should be examined for fiber cracking in the virgin and aged conditions.

8.12 REPORTING

The following information should be reported:

1. Exposure temperature, oxygen concentration and condition of circulation utilized, and times of exposure at each temperature.
2. Observation of any visible and microscopic changes in the test specimens.
3. Graphs derived in accordance with 8.10.1 and 8.10.2 for each material tested.
4. Regression equations for property change and regression equation for reaction constant.
5. Estimates of anticipated property change in %/100 yr and corresponding time to 50-percent property change.
6. Typical SEM microphotographs of virgin and aged conditions.

CHAPTER 9

RECOMMENDED TESTING PROTOCOL FOR HYDROLYTIC DEGRADATION OF POLYESTER-BASED GEOSYNTHETICS

9.1 SCOPE

This testing protocol describes a procedure for determining tensile strength loss caused by hydrolytic degradation of polyester-based geosynthetics, by exposure to aqueous solutions of controlled pH at elevated temperatures. Correlation between this accelerated test and in-ground aging has not been definitively established, but may provide upper-bound values of strength loss due to hydrolysis.

9.2 REFERENCED DOCUMENTS

ASTM standards:

ASTM D-3776, "Standard Test Method for Weight (Mass per Unit Area) of Woven Fabric, Option C - Small Swatch of Fabric."

ASTM D-4595, "Standard Test Method for Tensile Properties of Geotextiles by the Wide-Width Strip Method."

ASTM D-4603, "Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate)."

9.3 SUMMARY OF TEST METHOD

This method consists of subjecting test specimens with previously determined physical and chemical properties to controlled conditions for known periods, after which these properties are again measured and the changes are noted. The test involves exposure of specimens to aqueous solutions of controlled pH at elevated temperatures. Physical properties monitored are weight, tensile strength and strain at break, and fiber surface morphology. Chemical properties measured are intrinsic viscosity and Carboxyl End Group (CEG).

Unless otherwise specified, the determination of tensile strength and strain at break should be carried out in accordance with ASTM D-4595. Weight shall be determined in accordance with ASTM D-3776. The changes of fiber surface morphology should be monitored by Scanning Electron Microscopy (SEM) or optical microscopy. Intrinsic viscosity shall be measured in accordance with ASTM D-4603 and CEG shall be measured by the method outlined in the appendix.

9.4 SIGNIFICANCE AND USE

Polyester-based geosynthetics should be qualified for their resistance to deterioration of their physical properties with time, caused by hydrolysis. This test method provides a method to assess performance characteristics such as the rate of tensile strength loss in %/100 yr and corresponding time to 50-percent loss for polyester geosynthetics under specified conditions.

This test method does not predict degradation behavior of polyester geosynthetics in conditions other than the conditions of testing, including pH and intensity of stirring.

9.5 APPARATUS FOR HYDROLYTIC DEGRADATION

The reactor for hydrolytic degradation should consist of a Pyrex-type glass container to resist aggressive solution. Stainless steel containers may be used for hydrolysis in neutral and alkaline solutions. The size of the chamber is optional, but should be such that the specimens may be suspended vertically without crowding and without touching each other or the sides of the chamber, to allow free liquid flow. An elevated temperature shall be maintained with a stability of ±1°C by temperature-controlled heaters and outer thermal insulation of the reactor. Nitrogen is poured into the space between the reactors' head and the liquid to minimize the possibility of oxidation. Stirring is deployed to maintain uniform concentration and temperature in the hydrolytic solution. The liquid to solid ratio should be in the range of 40:1.

9.6 SAMPLING

Unless otherwise specified, sampling should be in accordance with ASTM D-4595 for the tensile properties to be determined.

9.7 TEST SPECIMENS

9.7.1 Specimen size.

Specimens prepared as described in ASTM D-4595 are preferable, but not mandatory. The specimens of the geogrid should be sufficient in size to permit the determination of the tensile properties. The number of ribs in a grid specimen should be determined experimentally and depend on the structure of a particular product. Fiber specimens may be used instead of full wide-width specimens for woven geotextiles and geogrids. Coated geogrid specimens shall have uncapped ends.

9.7.2 Number of test specimens.

The number of test specimens required is in accordance with ASTM D-4595 for the tensile properties of geotextiles. This requirement should be met at each time and temperature selected. A minimum of five specimens shall be prepared per retrieval. ASTM D-4595 guidance should be used in determining the minimum required number for fiber specimens tested.

9.8 TEST CONDITIONS

Testing at a minimum of three exposure temperatures should be used to determine the relationship between tensile strength loss and temperature. The unique performance of commercial products determines the temperature range for a particular product. In general, it is suggested that the temperature of exposure should vary from 40 to 80°C and should be lower than the rubber-glass transition temperature for a particular product. The lowest temperature of exposure should produce the measurable level of tensile strength change in approximately 18 to 24 months. The next higher temperature should produce the same level of strength loss in about 12 to 15 months.

The mechanism of hydrolysis depends on the type of the hydrolytic media. Exposure to acidic and neutral solutions results in molecular weight degradation. In alkaline media, there are two mechanisms leading to mechanical strength loss. They are molecular weight degradation and surface erosion. Therefore, accelerated hydrolytic degradation should be performed in solutions of different pH covering acidic, neutral, and alkaline environments. The suggested range of pH varies from pH=1 to pH=3 to 4 for acidic environments, pH=7 for neutral environments, and pH=9 to pH=12 for alkaline environments. The particular acid or alkali could be chosen to simulate the anticipated end-use environment for the product tested. If not specified, H_2SO_4 should be used to formulate acidic solutions and NaOH for alkaline solutions. If precipitation on the surface of specimens occurs during the hydrolysis, the actual pH at the fiber may not be the same as measured in the solution.

9.9 PROCEDURES

It is often difficult to estimate the effect of hydrolysis on strength reduction at elevated temperatures. Therefore, it is suggested to start with short-term hydrolytic aging at the highest temperature and in the most severe pH condition planned. The obtained data may be used as a basis for selecting the remainder of the aging temperatures and the range of pH, as well as for preliminary scheduling of the retrievals. At least five retrievals should be scheduled initially at each exposure temperature.

Geosynthetic specimens are retrieved at five consecutive time intervals. The duration of aging intervals depends on the rate of deterioration of the particular geosynthetic being tested. If obtained data are insufficient for further interpretation, additional retrievals should be scheduled.

The retrieved set of specimens shall be tested for the selected property (tensile strength, weight, fiber morphology, chemical degradation) in accordance with the appropriate test method specified in section 9.3.

Specimens are suspended on a teflon or stainless steel frame with a 12.7-mm (0.5-in) distance between each other and without touching the sides of the reactor. When all specimens are suspended, the frame is fully submerged into the solution and the pH is checked. The pH of the solution in the beginning and after each retrieval shall be adjusted to the required values as necessary.

The pH values are monitored and adjusted as needed on a daily basis for a week after the start of the hydrolytic reaction. Then, when the pH value is stabilized within the range desired ±0.1, readings are taken once a week and the pH is adjusted as necessary. The temperature is monitored every 3 hours after the start of the reaction, and when it stabilizes in approximately 20 to 24 hours, readings are taken at the same time as the pH measurements. The precipitation on the wall of the reactor above the liquid level and on the cover shall be cleaned as necessary.

9.10 CALCULATIONS

Results from hydrolysis tests are expressed as a ratio between aged values and initial values for measured properties. Degradation curves shall be prepared for each exposure temperature by plotting residual values of the measured properties as a function of aging time. Regression analysis shall be used to determine the relationship between the remaining properties and time as discussed in section 7.3. The regression equations selected provide the relationship between the reaction constant and aging temperature. The logarithm of the reaction constant versus the reciprocal of the temperature of aging (Arrhenius plot) shall be prepared. Regression analysis shall be used to determine the relationship between the reciprocal of the exposure temperature and the reaction constant. The linear regression equation shall be used to calculate the anticipated value of a rate constant at a given temperature. The obtained value of a rate constant shall be used to calculate the rate of tensile strength loss or any other measured property in %/100 yr, utilizing the regression equation obtained previously for the remaining strength versus time relationship as discussed in section 7.3.

9.11 SEM MICROPHOTOGRAPHS

SEM should be made of fibers aged in alkaline environments and used to measure fiber diameter in the virgin and aged conditions. Fiber diameters shall be examined against tensile strength loss to determine if a correlation exists. Regression analysis can be used to establish the relationship between strength loss and fiber diameter.

9.12 REPORTING

The following information should be reported:

1. Exposure temperature, type and pH of the solution and condition of circulation utilized, and times of exposure at each temperature.
2. Observation of any visible and microscopic changes in the test specimens.
3. Graphs derived in accordance with section 9.10 for each material tested.
4. Regression equations for property change and regression equation for reaction constant.
5. Estimates of anticipated property change in %/100 yr and corresponding time to 50-percent property change.
6. Typical SEM microphotographs of virgin and aged fibers.

CHAPTER 10

FURTHER RESEARCH NEEDS

Results of these studies have indicated the complexity of the aging processes at elevated temperatures for commercial geosynthetic products. Analysis of the developed data have suggested further research needs to fully understand the degradation process and develop more appropriate protocols.

10.1 POLYOLEFIN-BASED GEOSYNTHETICS

10.1.1 Development of alternative protocols to oven aging.

The present research has indicated that using temperature to accelerate oxidation requires long incubation times to achieve measurable degradation at moderate temperatures and that for some products, the high incubation temperature significantly changes the nature or morphology of the products tested, making the results invalid.

Numerical modeling of the degradation rate indicated that service life, i.e., anticipated time to 50-percent strength loss at ambient temperature, is primarily determined by the induction period for the products tested. For example, the data shown in figure 5.10 suggests that induction period of more than 50 years for the P-3 geosynthetic at 21% oxygen and more than 200 years in a reduced oxygen atmosphere at 8%. To more accurately determine the induction period requires lowering the temperature of exposure and extending the incubation period to 2 to 4 years. An incubation period of 2 to 4 years to determine this key degradation characteristic for commercial geosynthetic products is impractical. Therefore, the development of testing protocols within a laboratory time limited to 3 to 6 month becomes of prime importance for the routine durability assessment of commercial polyolefin products.

Furthermore, incubation of staple fiber and film products in circulating air at 21% oxygen at elevated temperatures in accordance with currently accepted practices for laboratory-accelerated testing of geosynthetics (ASTM D-3045) results in an intensive surface crack development followed by a significant change of initial modulus and tensile strength losses. Exposure of these materials to elevated temperatures in stagnant diluted air at 8% oxygen leads to surface cracks annealing followed by a tensile strength increase.

Incubation of the HDPE geogrid in circulating air at elevated temperatures (80°C) results in a significant decrease in initial modulus, strongly suggesting that processes other than thermo-oxidation are initiated during oven aging.

In light of the above, it is suggested that currently used oven-aging testing protocols based on ASTM D-3045 do not provide adequate estimates of degradation for staple and tape polypropylene geotextiles and probably HDPE products.

To overcome these obstacles, a limited study has been conducted to assess the feasibility of high oxygen pressure incubation at ambient temperature to accelerate degradation of commercial geosynthetics. Preliminary results indicated that incubation of polypropylene geosynthetics in pure oxygen at 50 atm and ambient temperature may accelerate the degradation process by a factor of 250. However, the data developed during this limited scope of work permits only qualitative estimate of the acceleration factor required for modeling the in-situ behavior for commercial products. A research program that considers various products, multiple pressures, and oxygen concentrations should be initiated to correlate oven-aging results and permit the development of more reliable estimates of the acceleration factor for products tested that might lead to a more inclusive test protocol better suited for short-term evaluations of degradation potential.

10.1.2 Assessment of antioxidant leachability.

The role of antioxidants in the improvement of durability performance is well understood for commercial geosynthetic products. However, data reported in the literature, as well as the limited results of these studies (section 2.2.7), strongly suggest that antioxidant leaching due to exposure of geosynthetics to moist or wet conditions can affect the induction period for underwater applications.

10.2 POLYESTER-BASED GEOSYNTHETICS

One of the mechanisms leading to tensile strength deterioration is surface erosion of fibers and films in alkaline media for polyester-based products. Environmental test conditions, such as intensity of stirring of the hydrolytic media, appear to be a factor in determining the rate of surface erosion for polyester fibers in an alkaline solution. Therefore, it is advisable to develop a practice of accelerated testing in conditions with minimal circulation of hydrolytic solutions for polyester materials. Data obtained in this condition should provide more realistic estimates of anticipated degradation rates in alkaline solutions. Further studies could be conducted to quantitatively identify lower-bound losses.

10.3 STRESS SYNERGY

The literature reports that tensile stress applied to a polymer results in the acceleration of the degradation process among other phenomena. Design with geosynthetics assumes that geosynthetics work under a specific level of tension. Laboratory estimates of the durability parameters are based on data obtained without mechanical stress and, therefore, these estimates may not accurately reflect end-use conditions where mechanical stress is present. Therefore, it becomes necessary to develop a laboratory-accelerated testing practice to assess the influence of mechanical stress on degradation performance for both polyolefin and polyester geosynthetic products under stress.

10.4 IN-SOIL OXYGEN CONTENT

The research studies have demonstrated that oxygen concentration is a key parameter in determining degradation rates for polyolefin products. The oxygen content in soil is largely unknown and, therefore, the laboratory protocols developed cannot be reliably indexed to in-situ regimes until this parameter is documented for fills by field or laboratory measurements.

10.5 TRANSITION METALS DEPOSITION

The research studies on the effect of metal salt contamination were performed by immersing the geosynthetic in aqueous metal salt solutions until a sufficient amount of metal salt was deposited as measured by w/w. The relationship between transition metals in nature, measured in (parts per million), needs to be related to potential deposition measured as w/w on geosynthetics in the laboratory.

APPENDIX A
OIT MEASUREMENT PROCEDURES

A.1 MODIFICATION OF ASTM-BASED OIT MEASUREMENT PROCEDURE – METHOD "A"

The procedure below is based on ASTM D-3895 with modifications for greater accuracy. OIT is determined by measuring the length of time between the introduction of oxygen to a DSC instrument and the onset of the exotherm resulting from the initiation of rapid thermo-oxidative degradation. A Perkin-Elmer DSC 7 Differential Scanning Calorimeter is used for this purpose. A special aluminum sample pan is used. After placing the sample (60±1 mg), the bottom is folded toward the center at three positions to hold the lid firmly.

Flow Rate. The DSC cell is purged with nitrogen at a flow rate of 200 mL/min before starting the heating program.

Heating Program. The heating program is designed as follows:

- From 30°C to 180°C at a heating rate of 50°C/min.
- From 180°C to 200°C at a heating rate of 20°C/min.
- Isothermal at 200°C under nitrogen for 1 minute.

At exactly 5 minutes from the start of the heating program, the purge gas is shifted to oxygen, and the oxidation induction process is started. The process is ended when a strong exothermic peak appears. Typical results of OIT measurements obtained by using the above procedure are shown in figure A.1.

A.2 MODIFICATION OF ASTM-BASED OIT MEASUREMENTS – METHOD "B"

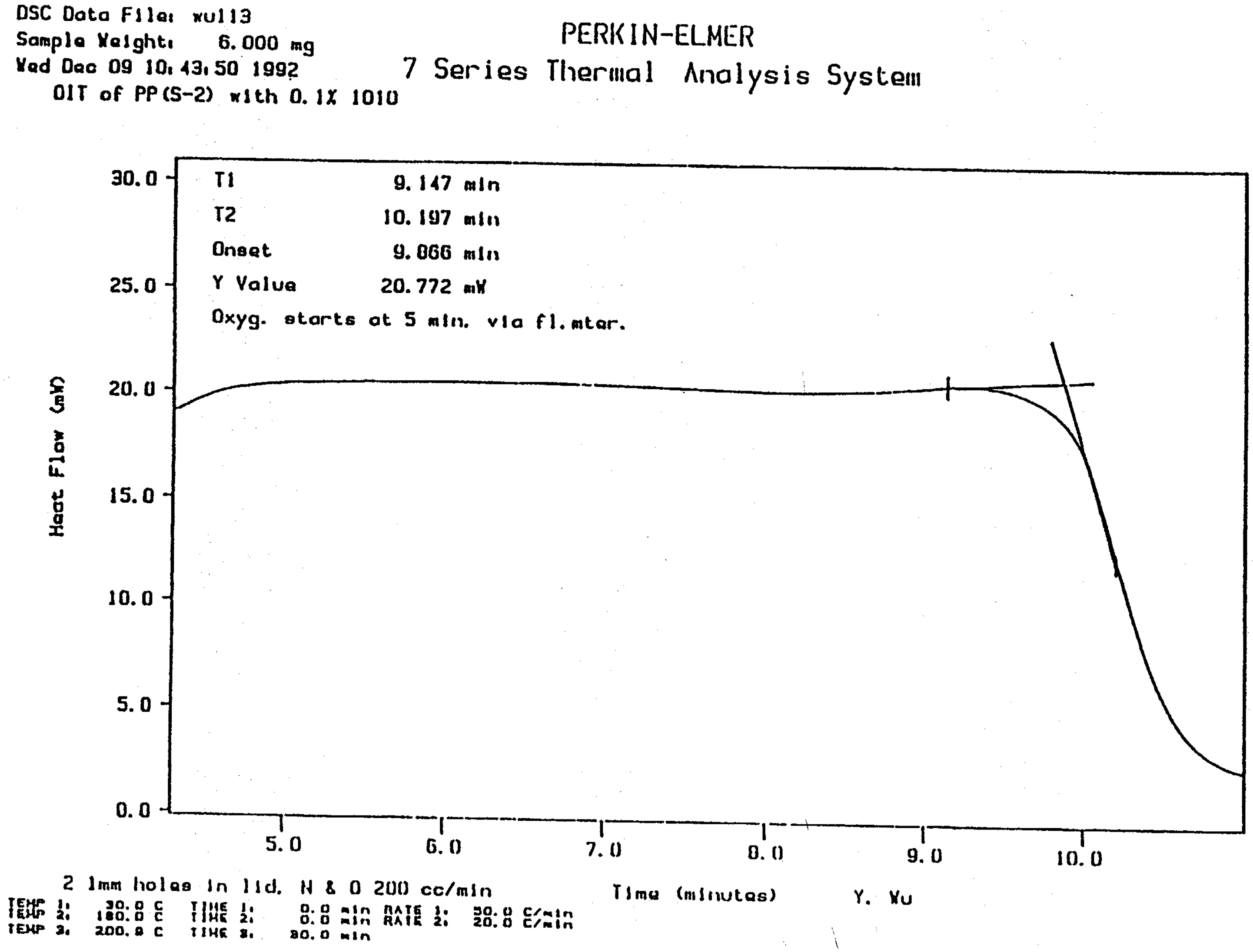
A.2.1 Equipment and sample preparation.

OIT is measured by using a Perkin-Elmer DSC 7 instrument. The polyolefin material is hot pressed to 0.2-mm-thick film and then punched to obtain a 0.64-mm-diameter disc. The disc is put into a flat-bottom aluminum sample pan and covered with an aluminum screen (also punched to 0.64 mm diameter from a 20-mesh screen). The edge of the sample pan is then crimped (folded toward the center) in four places. The schematic of the sample pan is shown in figure A.2.

A.2.2 Procedure.

Flow Rate. The DSC cell is purged with nitrogen at a flow rate of 50 mL/min before starting the heating program.

Heating Program. The heating program is designed as follows:



DSC Data File: wu113
Sample Weight: 6.000 mg
Wed Dec 09 10:43:50 1992
OIT of PP(S-2) with 0.1% 1010

PERKIN-ELMER
7 Series Thermal Analysis System

T1 9.147 min
T2 10.197 min
Onset 9.066 min
Y Value 20.772 mW
Oxyg. starts at 5 min. via fl.meter.

2 1mm holes in lid. N & O 200 cc/min

TEMP 1: 30.0 C TIME 1: 0.0 min RATE 1: 50.0 C/min
TEMP 2: 180.0 C TIME 2: 0.0 min RATE 2: 20.0 C/min
TEMP 3: 200.0 C TIME 3: 80.0 min

Figure A.1. DSC curve for S-2 sample (PP with 0.1% Irganox 1010) obtained under conditions specified in Method “A”.

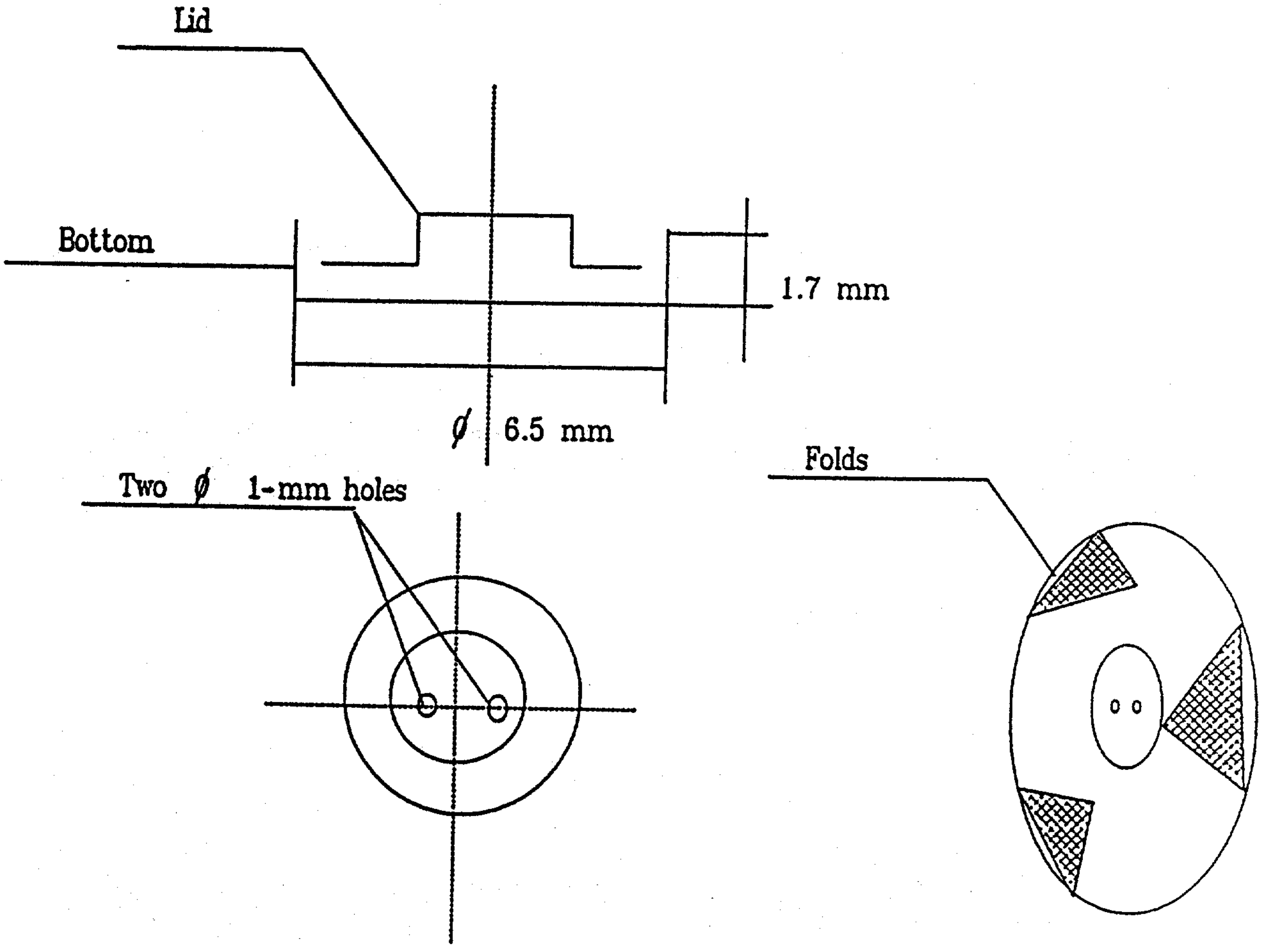


Figure A.2. Sample pan for DSC cell.

For HDPE:

- From 30°C to 180°C at a heating rate of 50°C/min.
- From 180°C to 200°C at a heating rate of 20°C/min.
- Isothermal at 200°C.

For Polypropylene:

- From 30°C to 175°C at a heating rate of 50°C/min.
- Isothermal at 175°C.

At exactly 5 minutes from the start of the heating program, the purge gas is shifted to oxygen. The oxygen induction reaction is then started. The process is ended when a strong exothermic peak appears. The real OIT is taken from the time of oxygen entering the DSC cell to the intersection of the base line and tangent inflection of the exothermic peak.

For better results, the DSC cell should be cleaned by burning at 500°C for 5 min after each run, especially after running HDPE samples at 200°C. The DSC instrument should be calibrated from time to time, at least each day. Indium (mp=156.6°C) and Tin (mp=231.7°C) can be used for calibration; three to five samples should be run to obtained an average value of OIT.

A.2.3 Sample preparation for OIT calibration.

Sample preparation for calibration curve was as follows:

- For reference polypropylene S-2, 0.2 g of powder were placed in a flask. 30 mL of octane were added. The mixture was heated to boiling under nitrogen, with stirring until the polymer dissolved.
- After cooling to about 80°C to 90°C, the calculated amount of Irganox 1010/ethyl acetate solution (0.05 g/100 mL) was added. Methanol was then added to the polymer.
- The suspension was concentrated under a vacuum with strong stirring to a paste and then dried in a vacuum at 50°C overnight.
- The product was wetted with cyclohexane and ground in a mortar to obtain a wet-sand-like powder and was dried again at 50°C in a vacuum for 2 hours.

APPENDIX B
CEG ANALYSIS

The procedure for the CEG analysis is described in the literature (Pohl H.A., *Anal. Chem.*, Vol. 26, No. 10, 1954).

B.1 MATERALS

(a) Benzyl alcohol (Aldrich) must be dried and distilled before use. The blank on a 10-mL sample of freshly purified material should not exceed 6 mL of 0.1N sodium hydroxide after the sample is heated at 203°C for 1.8 minutes.

(b) Chloroform. If the blank on a 10-mL sample exceeds 2.0 mL of 0.1N sodium hydroxide, it must be distilled.

(c) 0.1N sodium/ethanol solution.

(d) 0.1% (in ethanol) Phenol red = Bromothymol blue = 1:1 mixed indicator.

B.2 CEG MEASUREMENT

Measure 3 to 6 grams of PET and put into a 15- x 125-cm Pyrex test tube; 5 mL of purified benzyl alcohol and a small magnetic stir bar are added. The test tube is then immersed into a 203 ±1°C oil bath with strong stirring for 105 to 110 seconds (the PET will completely dissolve in benzyl alcohol), followed by quenching to 140°C in 20 to 30°C water bath for 6 to 7 seconds. The content is then poured into a 10-mL cold $CHCl_3$ solution with strong stirring in a 50-mL beaker to obtain fine emulsion. The test tube is rinsed well with 5 mL benzyl alcohol and heated in 203 ±1°C oil bath for 60 ±1 seconds and this is added to the $CHCl_3$ emulsion obtained above. Two drops of mixed indicator are added, and the sample is titrated with 0.1N NaOH/ethanol via micro burette or syringe to blue-violet end point. Blank of 10 mL benzyl alcohol should be run.

B.3 CALCULATIONS

CEG (meq/kg) = {(mL of titration for sample - mL of blank) x 10^{-6} x concentration of titration solution}/weight.

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