Lifetime Prediction of Polymers

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SYNOPSIS

Natural and artificially accelerated weathering trials were carried out on low-density polyethylene samples used for agricultural and disposable purposes. Modifications in polymer characteristics were studied using Fourier transform infrared (FTIR) spectroscopy, different scanning calorimetry (DSC), gel permeation chromatography (GPC), scanning electron microscopy (SEM), and mechanical properties testing. The natural exposure trials were conducted at five geographical locations representing varying ambient temperature and humidity conditions and receiving different doses of solar radiation. The artificially accelerated exposure trials were carried out in an Atlas weatherometer for 5,000 hours, whereas the natural exposure was for 24 months. Rates of photo-oxidative and thermal degradation have been determined by measuring the formation of non-volatile carbonyl oxidation products which absorb in the infrared region with a maximum absorbance level at 1710 cm^{-1}. Thermal characteristics were noticed to vary in terms of the shape and size of melting peak for both the natural and artificial weathering. This implies a change in crystallinity, which has indicated an increasing trend with exposure time. The crystalline melting temperature (T_m) remains almost steady for both exposure tests. The drop in mechanical properties and the modification in polymer chain length were also monitored. The GPC analysis indicated the change in molecular weight distribution (MWD), which shows the formation of lower molecular-weight species. Surface modifications were revealed in terms of abrasion effects apparent from SEM micrographs. A correlation between natural and artificial weathering was considered for lifetime prediction in a short exposure time. It was found that the confidence level of predicting lifetime on the basis of artificially accelerated exposure trials is dependent on many parameters, which include time, material, equipment, etc. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Natural weathering of plastic refers to the adverse response of plastic to climate. The factors that influence climate and therefore the degree of weathering include: solar radiation (primarily ultraviolet wavelengths), heat (the time-averaged plastic surface temperature), moisture (dew, rain, humidity), and pollutants (aerosols, acid rain, ozone). These climatic factors vary so widely over the earth's surface that the weathering of plastics is not always an exact science. Therefore, plastic performance varies with changes in climatic conditions and with the chemistry of the plastic product (formulation).

Information regarding the potential weathering behavior of polymeric materials can be obtained from laboratory devices which are referred to as "artificial" or "accelerated" weathering devices. These weatherometers provide information regarding material behavior in a short duration of artificial exposure trials, as compared to long-term exposure trials in a natural environment. Artificial weatherometers usually involve controlled conditions where exposure to various factors can be standardized and compared. In addition, it permits the isolation and control of particular environmental factors for detailed evaluation. The most important feature of artificial devices is that they can accelerate degradation of the materials under study. Accelerated weathering of material is achieved by continuous exposure to light, elevated temperature, and humidity. Furthermore, it can increase the intensity of ra-

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diation by exposure to high energy wavelengths, which accelerate the degradation process.[1] The information received from artificially accelerated weathering can be correlated with natural weathering by utilizing mathematical models and correlations.[2] The results obtained from artificially accelerated trials should correlate with results of natural weathering for the same polymer. This is only theoretically true, however, because the reproducibility of the results of natural weathering as well as artificial weathering of the same materials exposed at different times is poor. One of the major reasons for this inconsistency may be the small consideration given to geographic climatological data in the test criteria adopted in setting the artificially accelerated weatherometer and the variation in natural weather conditions with time. The variability of climatic conditions between various locations and at different times in the same location makes it difficult to extrapolate natural weathering results from one location or time to another.[3]

In an artificial weatherometer, it is possible to simulate and increase the intensity of some natural weather parameters. This leads to the faster degradation of the polymeric materials exposed to reasonably known conditions. The experimental results of this artificially accelerated weathering exposure can be analyzed by means of available mathematical models or statistical analysis.

In this work, natural and artificially accelerated weathering trials were carried out on low-density polyethylene samples. The changes in polymer characteristics were studied using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and mechanical properties testing. The natural exposure trials were carried out at five geographical locations, which are representative of different weather con-

ditions. The artificially accelerated weathering trials were conducted in a laboratory weatherometer for about 5,000 hours. A correlation between natural and artificial weathering was considered for lifetime prediction in a short exposure time.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin–Elmer FTIR spectrophotometer Model 1500 linked to a data station, Model 3600. Carbonyl absorbance was monitored in the region 1700–1740 cm^{-1}. Crystallinity was monitored using DSC from a Perkin–Elmer Model DSC attached to a System 4 microcomputer controller. Changes in molecular weights and distributions were recorded by GPC from a Waters Model 150C interfaced with a 730 data module. The scanning electron microscope used in this work is a Joel JSM-840 operating at 20 kV. An Instron universal testing machine, Model 4301, was used to find the change in tensile strengths.

The details of natural exposure sites are presented in Table I. The five geographic locations are considered to be the representative exposure sites in Saudi Arabia.[4] Exposure sites and racks were designed according to ASTM Standard D-1435 "Outdoor Weathering of Plastics." Aluminum alloy was used for fabrication of racks and frame holders and the racks are designed so that the exposed surfaces of the samples are at an angle of 45 degrees to the horizontal.

The instrument used for artificial weathering was the Atlas Ci65 Xenon Arc weatherometer. The light source in this instrument is a long arc, water-cooled xenon lamp equipped with inner and outer filters. Test conditions were set according to the ASTM D-2565. The weatherometer was set on the automatic irradiance control mode with an irradiance level of 0.35 w/m^2 at 340 nm.[5]

Table I   Details of Exposure Sites

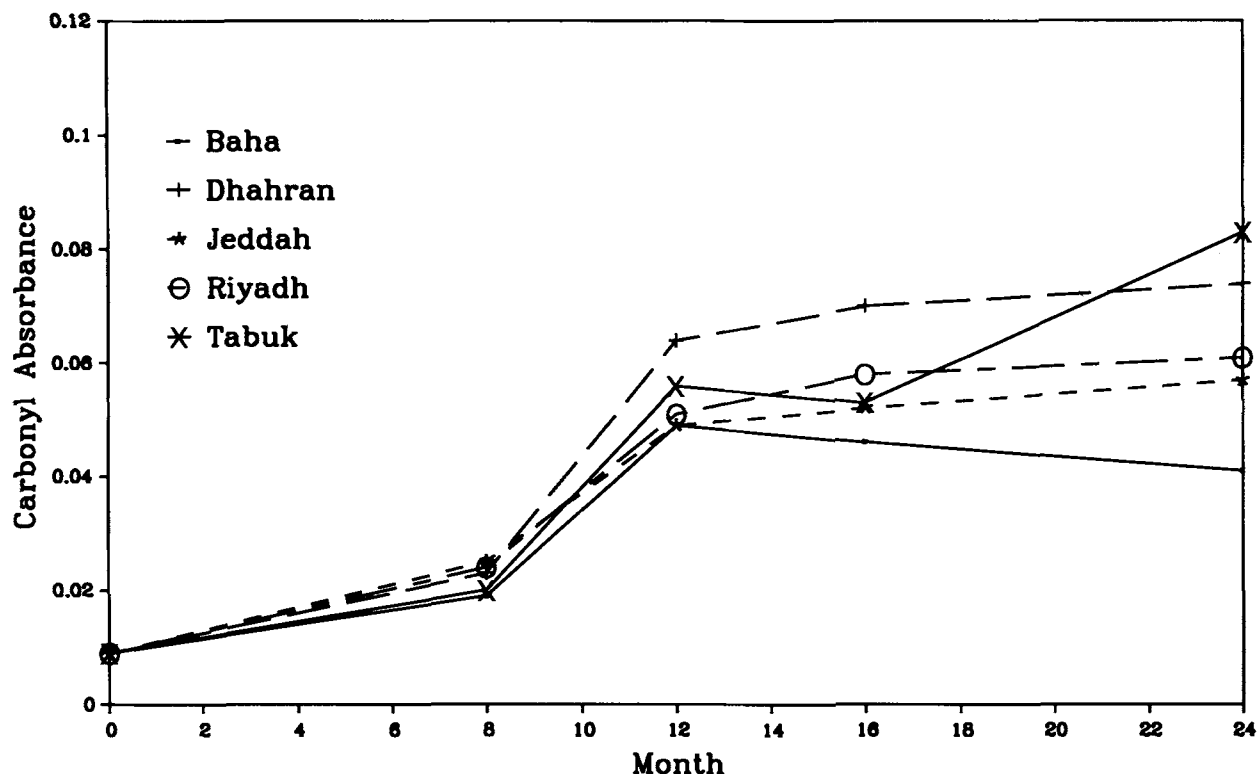| Exposure Sites	Zone	Latitude	Max. Temp. in Last 10 Years (°C)	Max. Monthly Mean Solar Radiation (Langleys)	Max. Monthly Relative Humidity (%)
Dhahran	Coastal Eastern	26.32°	49.5	480	90
Riyadh	Central	25.51°	48.0	575	77
Jeddah	Coastal Western	21.29°	48.0	520	86
Tabuk	Northern	28.23°	44.9	475	68
Baha	Southern	18.13°	38.6	555	60

Figure 1   Change in carbonyl absorbance of polyethylene samples as a function of exposed time.

RESULTS AND DISCUSSION

Low-density polyethylene (LDPE) samples studied in this work are mainly used for greenhouse film applications in the agriculture industry. Antioxidants and hindered amine light stabilizers (HALS) are incorporated into the polymer to give stability in outdoor conditions. The structural modifications of exposed samples were noted in the FTIR spectra, particularly in the carbonyl region (1700–1750 cm^{-1}). The growth in the carbonyl absorbance is presented in Figure 1 for the samples exposed at five different geographical sites. The strongest carbonyl absorption bands are attributed to ketonic $C = O$ moieties. During the exposure trials, chain scission and crosslinking reactions take place simultaneously.[6] The rate of crosslinking is found to be higher at initial stages as compared to chain scission. However, chain scission is found to be dominate during the later stages.[7] The figure indicates a step change in carbonyl growth after eight months of exposure, which can be attributed to the role of UV stabilizers during the early stages of natural weathering. Almost constant carbonyl absorbance during first eight months

can be attributed to the deactivation of excited ketonic carbonyls in polyethylene by HALS.[8] The increasing trend in carbonyl absorbance is obvious in samples exposed at five different sites. However, maximum growth is exhibited for samples exposed in Dhahran region. This can be attributed to the climatic conditions prevailing in this region.

Thermal analysis results of naturally exposed samples are determined using DSC. The results are presented in Figures 2 and 3 for changes in crystalline melting temperature (T_m) and percent crystallinity, respectively. An almost consistent behavior is exhibited in terms of T_m for samples exposed for two solar cycles in different climatic locations. However, an increasing trend in percent crystallinity can be observed for all locations (Fig. 2). Crystallinity increase is also observed by Gee and Melin[9] and it has also been indicated that the imperfect crystalline regions of LDPE are believed to degrade because of crosslinking, whereas chain scission predominates in the amorphous matrix.[10] This leads to secondary crystallization in an amorphous matrix which is later inhibited by the decreasing mobility of the chains due to branching and crosslinking. In
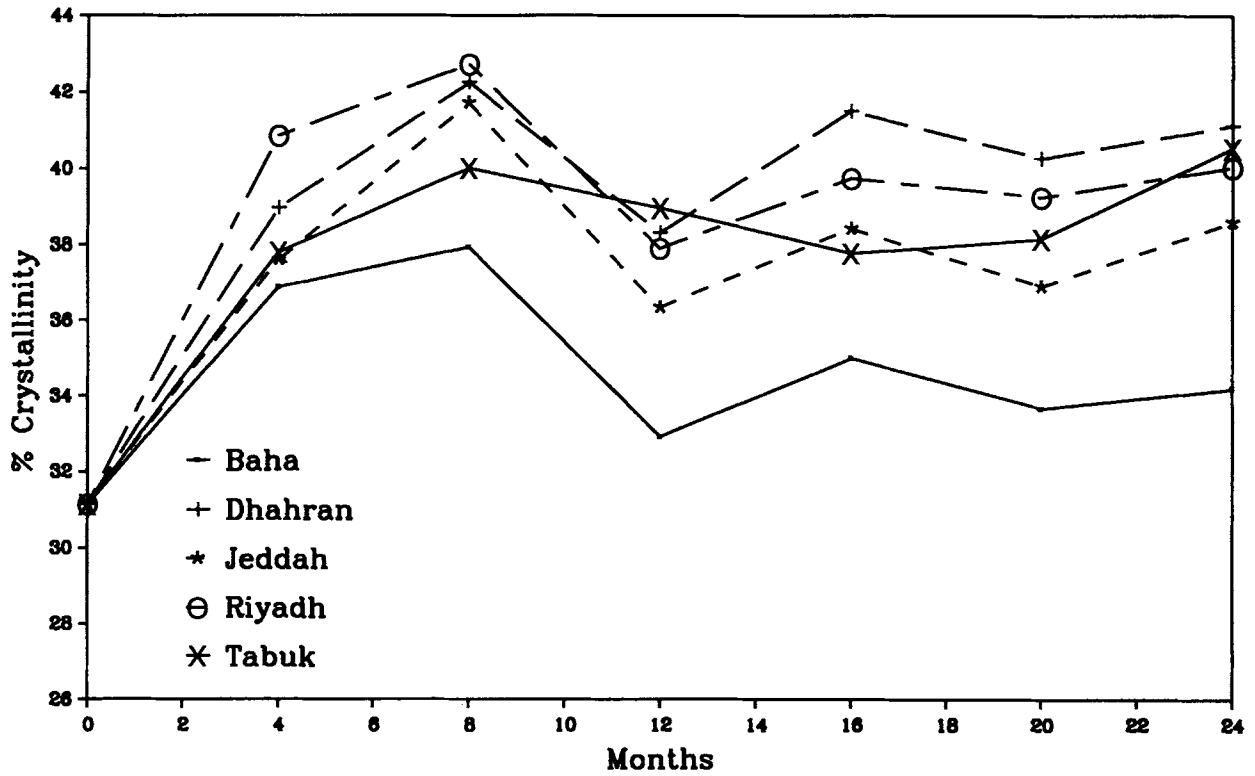
Figure 2 Change in % crystallinity of polyethylene samples as a function of exposure time.
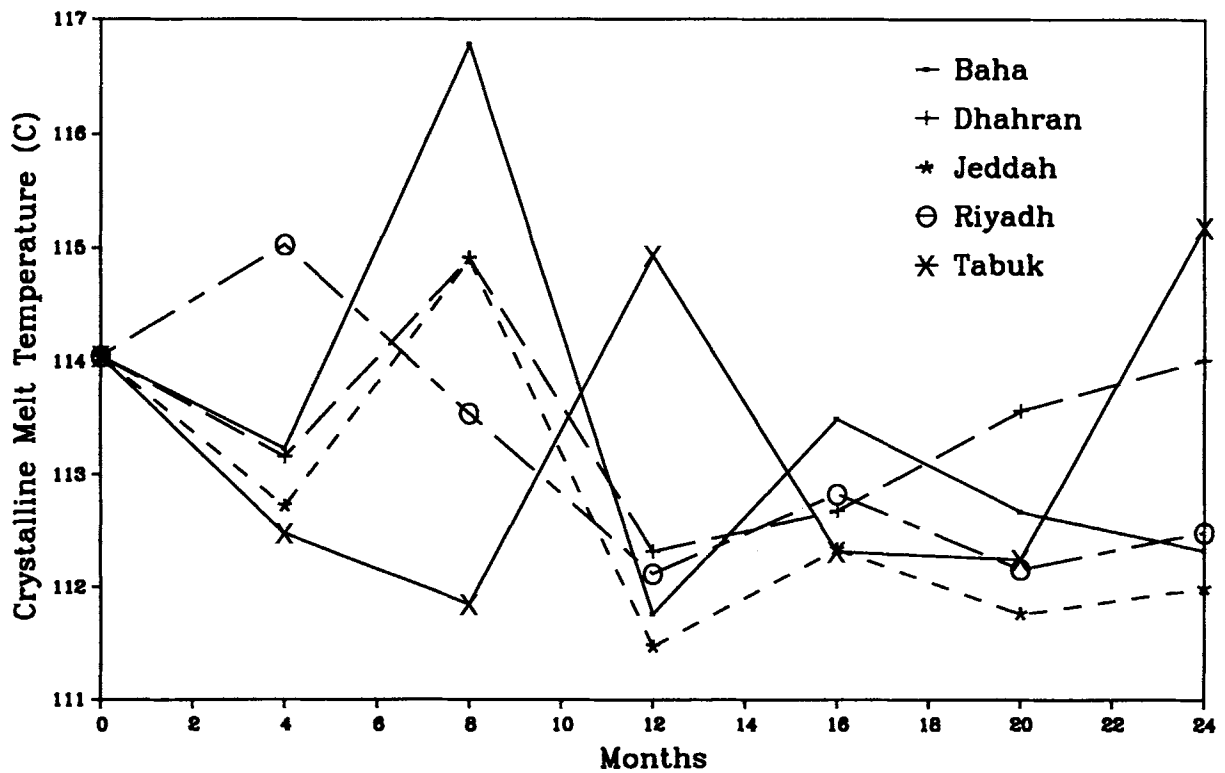

Figure 3 Change in crystalline melting temperature (T_m) of polyethylene samples as a function of exposed time.

Table II   Drop in Peak Molecular Weight (M_p) of Samples Exposed at Jeddah Site

| Exposure Month	Peak Molecular Weight (M_p)
0	179371
9	159465
12	159465
24	126107

one of the studies, an increase in crystallinity was found to be accompanied by an increase in crystalline melting temperature (T_m).[11] It was proposed that irradiation severed tie molecules traversing the amorphous region, allowing the existing crystalline lamellae to increase in perfection, not in thickness, and new lamellae to grow. The increase in crystallinity is generally attributed to the degradation of the ultra-long chains, which is caused by chain scission due to radiation-induced reactions.[12]

Changes in molecular weight were determined using GPC analysis; results from one of the exposure sites are presented in Table II. A drop of 30% of the initial value of M_p is observed for the samples exposed for two years. The drop in molecular weight is a direct consequence of chain scission reaction taking place in the polymers during exposure trials. The SEM micrographs of unexposed samples and those exposed for 24 months at the Dhahran exposure site are presented in Figures 4 and 5, respectively. A comparison of these two figures indicates the breaking up of small particles on the sample surface. Small, rod-shaped particles are observed in samples exposed at Dhahran and microcracks are

apparent on samples from the Baha exposure site. This surface behavior indicates that the degradation reactions initiate from the surface and then move into the bulk, thereby damaging the bulk properties, mainly the mechanical strength.

Mechanical properties of the polyethylene samples used as greenhouse covering are of utmost practical importance, as they are the performance characteristics of polymer. Almost all of the changes in polymer detected by characterization techniques (spectroscopic, calorimetric, micrographic, and chromatographic) have an effect on changes in mechanical property. Changes in percent strain at break are presented in Figure 6 for the samples exposed in the Dhahran region. The plot indicates a slight increase in mechanical properties during the early stages of exposure and later a continuous decline. The increase can be due to the dominance of crosslinking reactions over chain scission during early stages.[13] The drop in mechanical properties over 24 months is not very severe. This indicates appropriate stabilization (HALS benzophenone-type), which has resulted in significant retention in mechanical properties.

The changes in mechanical properties were also monitored for the samples exposed in the artificially accelerated weatherometer. These results are presented in Figure 7. An accelerated test should give perfect correlation to the natural test if all possible parameters are considered. Since this is not practically possible, the idealistic view of perfect correlation is very rarely attained. This is because each material responds differently to the accelerating parameters of the weathering environment.[14]
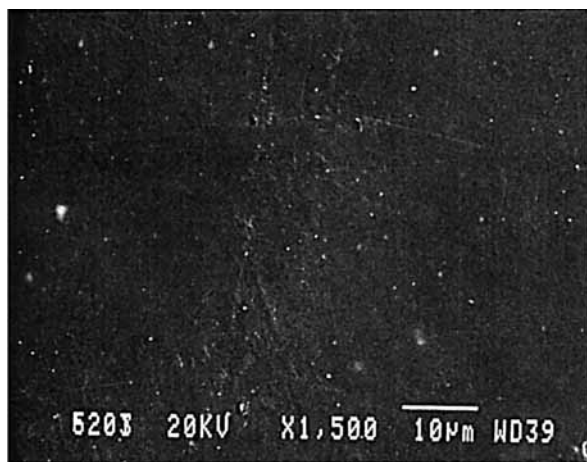
Figure 4   SEM micrograph of unexposed polyethylene samples.
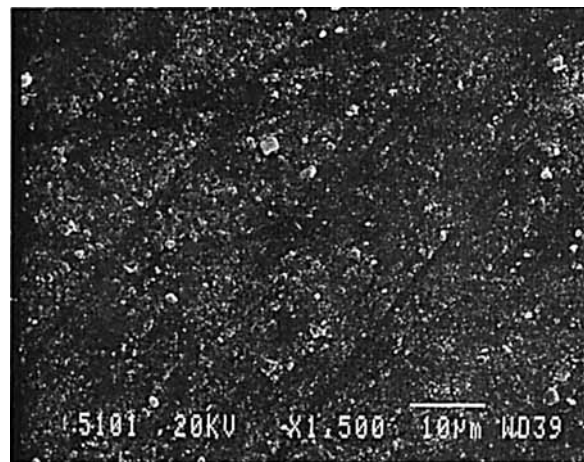
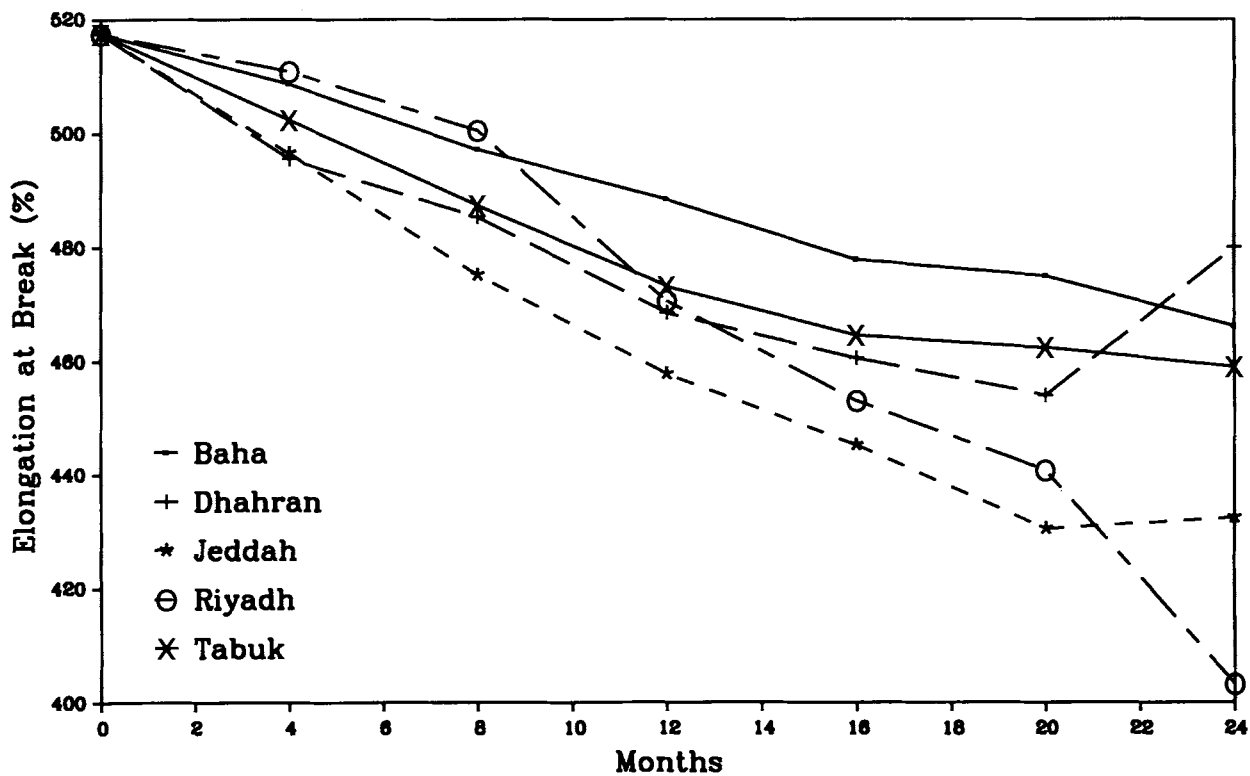**Figure 5**   SEM micrograph of exposed polyethylene samples.

Figure 6   Change in elongation at break of polyethylene as a function of exposure duration.
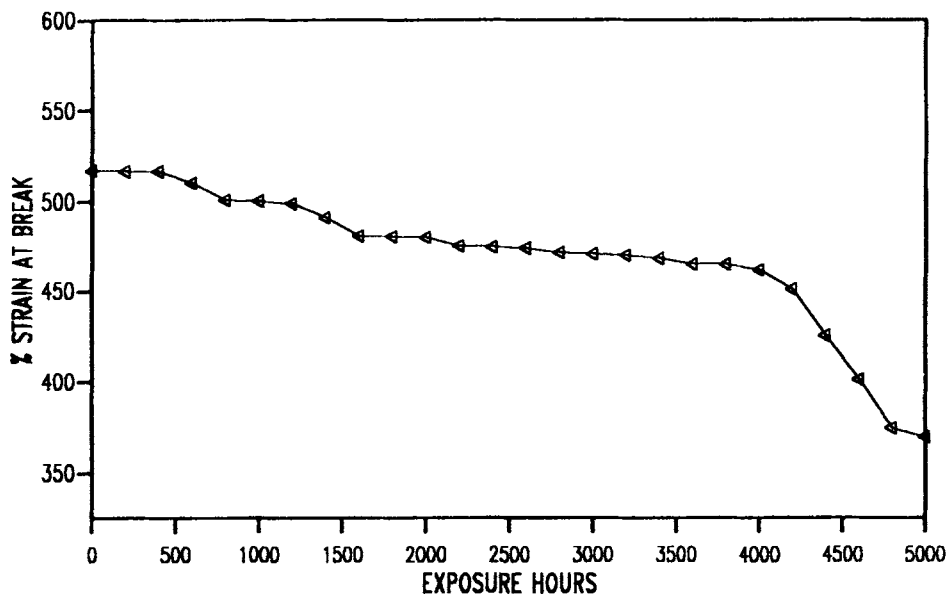

Figure 7   Drop in % strain at break of polyethylene sample exposed in an artificial weatherometer.

General Linear Models Procedure

Number of observations in data set = 26

General Linear Models Procedure

Dependent Variable: YN

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	52573.52111526	26286.76055763	1755.29	0.0001
Error	23	344.44234628	14.97575419		
Corrected Total	25	52917.96346154			

R-Square	C.V.	Root MSE	YN Mean
0.993491	0.872881	3.86985196	443.34230769

Source	DF	Type I SS	Mean Square	F Value	Pr > F
XN	1	52404.88595043	52404.88595043	3499.32	0.0001
XN*XN	1	168.63516484	168.63516484	11.26	0.0027

Source	DF	Type III SS	Mean Square	F Value	Pr > F
XN	1	5147.82309589	5147.82309589	343.74	0.0001
XN*XN	1	168.63516484	168.63516484	11.26	0.0027

Parameter	Estimate	T for H0: Parameter=0	Pr > |T|	Std Error of Estimate
INTERCEPT	523.2407814	247.72	0.0001	2.11225970
XN	-0.0100755	-18.54	0.0001	0.00054343
XN*XN	0.0000001	3.36	0.0027	0.00000003

Observation	Observed Value	Predicted Value	Residual
1	517.50000000	523.24078144	-5.74078144
2	517.00000000	516.03718193	0.96281807
3	518.20000000	508.93504762	9.26495238
4	500.00000000	501.93437851	-1.93437851
5	496.60000000	495.03517460	1.56482540
6	490.50000000	488.23743590	2.26256410
7	480.50000000	481.54116239	-1.04116239
8	479.60000000	474.94635409	4.65364591
9	460.20000000	468.45301099	-8.25301099
10	460.00000000	462.06113309	-2.06113309
11	450.30000000	455.77072039	-5.47072039
12	448.20000000	449.58177289	-1.38177289
13	444.20000000	443.49429060	0.70570940
14	440.10000000	437.50827350	2.59172650
15	430.00000000	431.62372161	-1.62372161
16	425.10000000	425.84063492	-0.74063492
17	425.00000000	420.15901343	4.84098657
18	415.50000000	414.57885714	0.92114286
19	407.30000000	409.10016606	-1.80016606

General Linear Models Procedure

Observation	Observed Value	Predicted Value	Residual
20	407.00000000	403.72294017	3.27705983
21	401.80000000	398.44717949	3.35282051
22	390.80000000	393.27288400	-2.47288400
23	390.00000000	388.20005372	1.79994628
24	381.00000000	383.22868864	-2.22868864
25	380.00000000	378.35878877	1.64121123
26	370.50000000	373.59035409	-3.09035409

Sum of Residuals	0.00000000
Sum of Squared Residuals	344.44234628
Sum of Squared Residuals - Error SS	-0.00000000
First Order Autocorrelation	-0.13676714
Durbin-Watson D	2.15012652

Figure 8 Computer output (SAS) of general linear model (GLM) procedure applied to natural weathering results.

An attempt was made to find a correlation model which can best describe the relationship between mechanical properties and exposure time for the samples exposed in natural and artificially accelerated weather.

The following probable models were examined:

1. Straight line: $y = a + bx$
2. Parabolic: $y = a + bx + cx^2$

General Linear Models Procedure

Number of observations in data set = 26

General Linear Models Procedure

Dependent Variable: YA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	33509.38502991	16754.69251496	78.96	0.0001
Error	23	4880.58150855	212.19919602		
Corrected Total	25	38389.96653847			

	R-Square	C.V.	Root MSE	YA Mean
	0.872868	3.100770	14.56705859	469.78846154

Source	DF	Type I SS	Mean Square	F Value	Pr > F
XA	1	30893.62260684	30893.62260684	145.59	0.0001
XA*XA	1	2615.76242308	2615.76242308	12.33	0.0019

Source	DF	Type III SS	Mean Square	F Value	Pr > F
XA	1	15.58275647	15.58275647	0.07	0.7888
XA*XA	1	2615.76242308	2615.76242308	12.33	0.0019

Parameter	Estimate	T for H0: Parameter=0	Pr > |T|	Std Error of Estimate
INTERCEPT	507.2585470	63.80	0.0001	7.95105631
XA	0.0019956	0.27	0.7888	0.00736423
XA*XA	-0.0000050	-3.51	0.0019	0.00000142

Observation	Observed Value	Predicted Value	Residual
1	517.50000000	507.25854701	10.24145299
2	517.10000000	507.45786325	9.64213675
3	517.00000000	507.25756410	9.74243590
4	510.60000000	506.65764957	3.94235043
5	501.10000000	505.65811966	-4.55811966
6	500.60000000	504.25897436	-3.65897436
7	499.20000000	502.46021368	-3.26021368
8	491.30000000	500.26183761	-8.96183761
9	480.90000000	497.66384615	-16.76384615
10	480.60000000	494.66623932	-14.06623932
11	480.10000000	491.26901709	-11.16901709
12	475.30000000	487.47217949	-12.17217949
13	474.80000000	483.27572650	-8.47572650
14	474.10000000	478.67965812	-4.57965812
15	471.60000000	473.68397436	-2.08397436
16	470.90000000	468.28867521	2.61132479
17	470.10000000	462.49376068	7.60623932
18	468.30000000	456.29923077	12.00076923
19	465.00000000	449.70508547	15.29491453

General Linear Models Procedure

Observation	Observed Value	Predicted Value	Residual
20	465.00000000	442.71132479	22.28867521
21	461.80000000	435.31794872	26.48205128
22	451.20000000	427.52495726	23.67504274
23	425.30000000	419.33235043	5.96764957
24	401.20000000	410.74012821	-9.54012821
25	374.40000000	401.74829060	-27.34829060
26	369.50000000	392.35683761	-22.85683761

Sum of Residuals	0.00000000
Sum of Squared Residuals	4880.58150855
Sum of Squared Residuals - Error SS	-0.00000001
First Order Autocorrelation	0.80303902
Durbin-Watson D	0.26538760

Figure 9 Computer output (SAS) of GLM procedure applied to artificial weathering results.

3. Exponential: $y = ax^b$
4. Cubic: $y = a + bx + cx^2 + dx^3$

The criteria for selecting a model was the value of r^2 (coefficient of determination), which is the measure of what percentage of data is explained by the model. The best model is that which has r^2 approaching 1.[15] The statistical analysis system (SAS) was for all computational analysis.

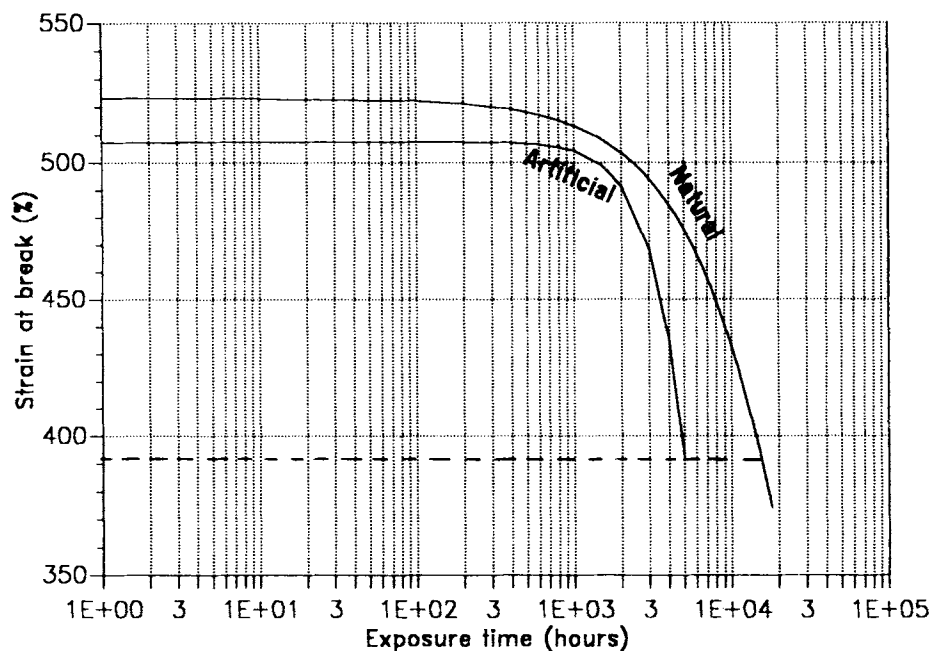The SAS general linear models (GLM) proce-

Figure 10 Change in mechanical properties of polyethylene samples exposed in natural and artificially accelerated environments.

dures were used to examine probable models; results of natural weathering are presented in Figure 8 and Figure 9 shows artificially accelerated weathering results. The results showed that parabolic models had the maximum value of r^2, which implies a higher reliability of the model. Since the cubic model has the same values as the parabolic model, therefore the parabolic model was selected. The values are:

$$YN = 523.241 - 10075 \times 10^{-6}XN + 1.0 \times 10^{-7}XN^2$$

$$r^2 = 0.9935$$

$$YA = 507.258 + 19956 \times 10^{-7}XA - 5.0 \times 10^{-6}XA^2$$

$$r^2 = 0.8782$$

where

YN = % strain-at-break values for natural weathering

YA = % strain-at-break values for artificial weathering

XN = Natural exposure time

XA = Artificial exposure time

Figure 10 presents a plot of change in mechanical properties for both natural and artificial exposure trials. The correlation factor determined by this analysis reveals that the acceleration factor in the artificially accelerated weatherometer is about three

times that of natural weathering trials (5,000 hours of artificial weathering = 14,000 hours of natural weathering).

CONCLUSION

The decay of significant polymer properties during natural and artificially accelerated exposure trials is the direct consequence of changes in structural, thermal, and molecular characteristics. The drop in mechanical properties and the evolution of degradation peaks (carbonyls) in exposed samples are accompanied by a slight increase in crystallinity. This effect indicates that the oxidation, followed by the growth or carbonyl functions, occurs in the amorphous region of semi-crystalline polyethylene morphology. These results are complemented by the drop in peak molecular weight, as determined by GPC analysis. The deterioration of surface characteristics as indicated by SEM micrographs confirms that the degradation reaction starts from the surface and then migrates to the bulk. This, in turn, affects the bulk properties of the polymer, which are primarily reflected in the mechanical strength.

The drop in mechanical properties from artificially accelerated weathering can be considered as a quick means of predicting the polymer's lifetime. An acceleration factor of about three times has been calculated for polyethylene samples exposed in

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