

Modeling of Degradation of Unstabilized and HALS-Stabilized LDPE Films Under Thermo-Oxidation and Natural Weathering Conditions

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ABSTRACT: Mathematical models are proposed to predict degradation of unstabilized low density polyethylene (LDPE) films and those stabilized with hindered amine light stabilizers (HALS) under both thermo-oxidation at 90°C and natural weathering conditions. The degradation was measured by change in percent elongation at break (ϵ_r) with time. The mathematical approach developed was multiple linear regression analysis (MLRA). The reliability of the selected models was analysed using four statistical criteria, residual variance, coefficient of determination (r^2), Student test and Fisher-Snedecor test. The linear systems that resulted from the MLRA were resolved by the Cholesky method. The results obtained indicated that the polynomial models developed to predict elongation at break were reliable for both unstabilized and HALS-stabilized samples under thermo-oxidation at 90°C and natural weathering conditions. This was also confirmed by the comparison of the half-life time (HLT) values predicted from the models with those observed experimentally. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3284–3292, 2001

Key words: LDPE; modeling; degradation; elongation at break.

INTRODUCTION

The prediction of polymer aging under normal service conditions from accelerated tests performed in the laboratory is a difficult task due to the complexity of the photo-oxidation process and to the many factors that influence its course.^{1,2} Several critical reviews dealing with the correlations between natural and accelerated weathering of polymers are available in the literature.^{3–6} However, there is still much controversy and a

sense of the empiricism about the topic.² Two different approaches are mainly reported.^{1,7,8} In the first approach, the kinetics of the oxidation reactions responsible for degradation, and the change in concentrations of both intermediate and final oxidative products in the polymer are determined with respect to the whole chemical reactions involved in the process. In this way, the results obtained are extrapolated to the real lifetime of the material. This method, based on photo-oxidation mechanisms, assumes that the sample in solid state is a homogeneous reactor. However, many experimental data contrast this hypothesis, as reported by Arnaud et al.¹ For example, hydroperoxides, which are the primary

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photo-products, are formed in heterogeneous manner in the polymer chains. This becomes more complicated when considering the formation of both associated and free hydroperoxides under different oxidation rates.^{1,9} The alternative approach is based on the experimental observations of accelerated aging using analytical techniques. In this case, the amount of degradation is evaluated by measuring the drop in mechanical properties, such as elongation at break, stress at break, secant modulus, etc. Mechanical properties are examined because they are the most sensitive to changes occurring during degradation, with ϵ_r being the most sensitive.¹⁰ Thus, it has become almost a rule to consider that the half-life time of the polymer is the time when the elongation at break drops to 50 % of its original value.^{10,11} The data obtained from accelerated aging tests are correlated with natural weathering by using mathematical models.^{3,6,12} In this respect, regression analysis can be used to develop models which can describe well degradation process in significant properties of the polymer as a function of weathering parameters.³

Therefore, the objective of this article is to propose mathematical models to predict elongation at break of unstabilized and HALS-stabilized LDPE films under both thermo-oxidation at 90°C and natural weathering conditions.

The study was carried out assuming that the variation in (ϵ_r) with time is linear with respect to parameters of the selected models, i.e., C_j . The most common general linear models (GLM) used were derived from the following equation:^{12,13}

$$Y = \sum_{j=1}^m C_j \cdot F_j(X) \quad (1)$$

where, Y is an aging parameter, X is the exposure time and C_j , the model coefficients to be calculated. The modeling procedure was performed using both Fortran language and methods of statistical analysis.

MATHEMATICAL AND STATISTICAL ASPECTS

The most common approach to modeling the physico-chemical phenomena is the general linear models (GLM).¹² Thus, any change occurring in the system is described by a function (Y) which is

itself depending on one variable (X). Therefore, the model $Y = Y(X)$ may be expressed by eq.(2):

$$Y = F(X) = C_1 \cdot F_1(X) + C_2 \cdot F_2(X) + \dots + C_m \cdot F_m(X) = \sum_{j=1}^m C_j \cdot F_j(X) \quad (2)$$

where C_j ($j = 1..m$) are the coefficients of the model, and $f_j(j = 1..m)$, the regular functions which may be in the form of :

$$\text{- monomes: } f_j(X) = X^{j-1} \quad (3)$$

$$\text{- exponential: } f_j(X) = \alpha_j \cdot \exp(\beta_j \cdot X) \quad (4)$$

$$\text{- trigonometric: } f_j(X) = \alpha_j \cdot \sin(\beta_j \cdot X) + \gamma_j \cdot \cos(\gamma_j \cdot X) \quad (5)$$

or any other mathematical functions.

In this work, (X) is the exposure time and (Y), the ϵ_r . The procedure assessed for the model development to predict elongation at break was based on the linear multiple regression analysis (LMRA). The resolution of the linear systems resulting from LMRA was carried out by using the Cholesky method.¹⁴

The principle of modeling consisted of changing the parameter m in the range [1, max] to obtain different linear models Y_m ($m = 1..max$). However, the best model (Y) with reasonable accuracy should satisfy four different statistical criteria defined as residual variance, coefficient of determination (r^2), Student test, and Fisher-Snedecor test.

Both Student and Fisher-Snedecor tests were performed assuming 95% confidence limit, as supported by the following hypotheses:

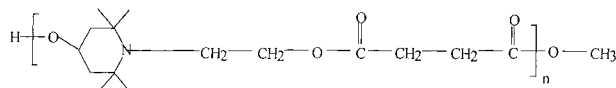
for Student test:

$$H_0''C_j = 0'' \text{ against } H_1''C_j \neq 0'', j = 1 \dots m \quad (6)$$

and for Fisher-Snedecor test:

$$H_2''C_1 = C_2 = \dots = C_m = 0'' \quad (7)$$

We also make the assumption that the experimental results obtained fitted well with Gaussian law.¹²



Scheme 1 Tinuvin 622 ($M_n > 2500$).

EXPERIMENTAL

Materials

The LDPE used is manufactured by the Algerian Company ENIP (Shikda, Algeria) under the trade name of B24/2. The main physical characteristics of the polymer are as follows: density = 0.923 g/cc and melt flow index (MFI) = 0.3g/10 min.

A mixture of two HALS, Tinuvin 622 and Chimassorb 944 provided by Ciba-Geigy (Basel, Switzerland), was added to the polymer. The commercial mixture of HALS is known as Tinuvin 783. The stabilizer concentration used was 0.6%w/w.

The chemical structure of the stabilizers and their molecular weight are given in Scheme 1 and 2.

Sample Preparation

Films of 80 μm thick were prepared by blown extrusion process. A Battenfeld SFB 400 extruder with a ratio $L/D = 24$ was used. The temperature in the extruder varied from 160 to 180°C along the barrel, while in the die, it decreases from 180 to 160°C. The films were stretched in the air after leaving the die at a pulling speed of 6 m/min. They were cooled by air passing through the die into the bubble. Finally, the films were cooled with a large volume of air upward over the surface of the bubble.

Exposures

Natural Weathering

Natural weathering of unstabilized and HALS-stabilized LDPE films was carried out according to ASTM D 1435. The samples, in the form of rectangular bands (30 x 20 cm) were mounted on racks, facing south. The natural exposure was carried out at Bejaia (5° 4' E longitude and 36° 43' N latitude) from December 1996. The average radiation in the experimental period was 160 Kcal/cm² per year. The average temperature varied between 15°C (winter) and 25°C (summer). The humidity level varied between 48% (winter) and 94% (summer). The amount of rain was 760 mm/year.¹⁵ The unstabilized samples were ex-

posed up to 170 days whereas, the stabilized ones up to 650 days.

Thermo-Oxidation at 90°C

The unstabilized and HALS-stabilized films were placed in an oven-aging at 90°C with air circulation up to 40 days and 630 days, respectively. The exposed samples were removed regularly for tensile measurements.

Tensile Measurement

The measurement of the elongation at break was carried out using an Adhamel Lhomargy DY 25 testing machine according to ASTM D 882. The elongational speed was 100 mm/min. An average of five tests was performed to confirm the experimental results.

The ϵ_r was calculated according to the following relation:¹⁶

$$\epsilon_r = \frac{L - L_0}{L_0} \cdot 100 \quad (8)$$

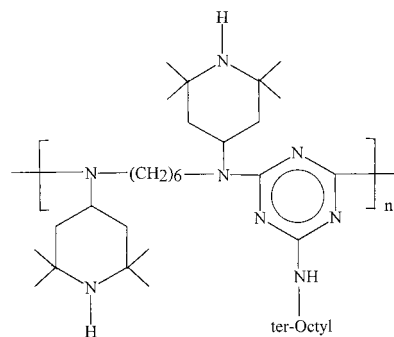
where ϵ_r is the elongation at break, L_0 is the initial length of the sample and L , the length at break.

RESULTS AND DISCUSSION

Unstabilized LDPE Film

Physico-chemical Analysis of Degradation

Figure 1 shows the variation in ϵ_r as a function of exposure time for unstabilized LDPE films under both thermo-oxidation at 90°C and natural weathering conditions. In thermo-oxidation, the figure exhibits a classic sigmoidal shape, fre-



Scheme 2 Chimassorb 944 ($M_n > 2500$).

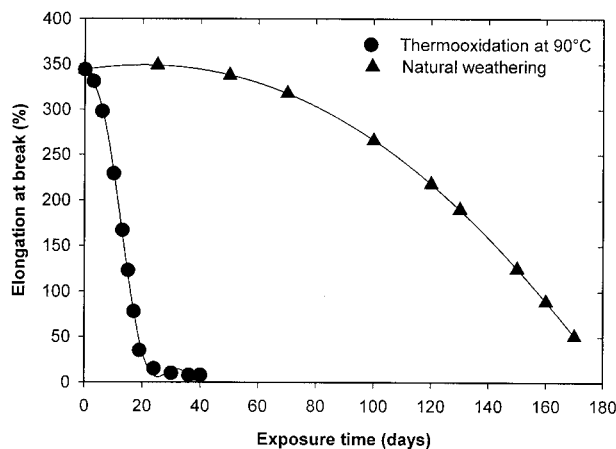


Figure 1 Elongation at break as a function of time for unstabilized LDPE film under both thermo-oxidation at 90°C and natural weathering conditions.

quently described in literature.^{7,17} The first period in which the elongation at break remains almost constant is known as the induction period.¹⁸ This corresponds to the time necessary for accumulation of a critical number of radicals which later lead to the reactions of chain scissions in the amorphous phase. The second period is characterized by a fast drop in elongation at break. This is generally attributed to the auto-oxidation mechanism responsible for chain scissions. The literature¹⁹ reported that the decrease in elongation at break is often accompanied by a rapid growth in carbonyl groups, mainly ketones, resulting from the hydroperoxide decomposition. Finally, the last period is associated with the brittle state of the material.

In natural weathering conditions, the figure shows a quasi plateau during almost the first 50 days of exposure, followed by a gradual decrease in elongation at break up to 170 days. According to the literature,^{20,21} the photo-oxidation mechanism is responsible for the degradation of polyethylene films. Essentially, the chain scission in the amorphous phase is responsible for inducing brittleness in polymers.¹⁷ Under UV exposure, the chain scission mechanism is due to Norrish type I and II reactions resulting from the photolysis of macroketones.²²

Modeling

This article presents the models based on Bejaia data. The percent elongation data obtained under both thermo-oxidation at 90°C and natural weathering for unstabilized and HALS-stabilized

LDPE films were analyzed and used for the development of the models. Before initiating the work on the model development, an attempt was made to find a correlation model which can best describe the relationship between ($\% \epsilon_r$) and exposure time for both unstabilized and HALS-stabilized samples under natural and thermo-oxidation conditions. Several models were investigated, mainly those listed in eqs.(3), (4) and (5). The main parameter which determines the selection of any probable model is the coefficient of determination (r^2).¹² This coefficient indicates the percentage of data that is explained by the model. The best model is that which has (r^2) approaching the unity.⁸ Based on the experimental data (X_i, Y_i) _{$i=1..(p \geq 10)$} carried out in Bejaia for both unstabilized and HALS-stabilized samples and the applicability of the models listed above, the results obtained have shown that the model of eq.(3) has the maximum value of (r^2) and thus, higher reliability. Accordingly, the polynomial model of eq.(3) was selected. Furthermore, the determination of the degree ($m - 1$) of the best polynomial model text math $Y_m(X) = \sum_{j=1}^m C_j \cdot X^{j-1}$ was carried out by varying m in the range [1, (max = 8)]. For each value of m , there is a corresponding polynome $Y_m = Y_m(X)$ with a coefficient of determination (r^2). The selection of m was based on that which has r^2 close to the unity. Moreover, the reliability of the selected model might satisfy three other statistical criteria, i.e, residual variance, Student test and Fisher-Snedecor test.

All the numerical results were calculated assuming that the functions f_j ($j=1..m$) are $f_j(X) = X^{j-1}$ in eq.(2) and using at least ten observations.

Thermo-Oxidation at 90°C. The observed and predicted values of elongation at break as a function of time for unstabilized LDPE films are shown in Table I. The residual values determined by the difference between the observed and the predicted values of elongation at break are also presented to evaluate the goodness of fit.

The selected model used has the following form:

$$Y = 344.2490 - 527.7585 \cdot 10^{-3} X - 139.5116 \cdot 10^{-2} X^2 + 298.7601 \cdot 10^{-4} X^3 \quad (9)$$

where Y is the elongation at break in (%) and X , the exposure time in days.

Table I Observed and Predicted Elongation at Break for Unstabilized LDPE Films^a

Time (days)	Observed (% ϵ_r)	Predicted (% ϵ_r)	Residual Values
0	344	344.2340	-0.2340
3	331	330.9525	0.0475
6	298	297.3403	0.6597
10	229	229.2866	-0.2866
13	167	167.1097	-0.1097
15	123	123.0516	-0.0516
17	78	78.5856	-0.5856
19	35	35.1498	-0.1498
20	15	14.2676	0.7324
40	3	3.0218	-0.0218

^a The proposed model in thermo-oxidation at 90°C was used.

The accuracy of this model to predict elongation at break under thermo-oxidation at 90°C is supported by the validity of the statistical criteria, i.e., residual variance, coefficient of determination (r^2), Student, and Fisher-Snedecor tests. The data are shown in Table II. They indicate low value of residual variance = 0.2485 and a maximum value for $r^2 = 99.999\%$. Moreover, the calculation of the model coefficients using both Student and Fisher-snedecor tests results in higher values than the tabulated ones. Therefore, the calculated values have very good approximations. The model appears capable of describing the ϵ_r of LDPE films during the thermo-oxidative degradation process. Table III shows the comparison between the observed and the predicted HLT values calculated from the model. The results show that the predicted HLT is 13 days while the observed one is almost 14 days. Within the limits of the experimental errors, the model describes well the variation of ϵ_r with time. However, if the accuracy of the model is statistically established, the physical meaning of eq.(9) demonstrates that this model is most likely valid during the first 20 days

Table III Comparison Between the Observed and the Predicted HLT for Unstabilized LDPE Films^a

Exposures	Observed HLT (days)	Predicted HLT (days)
Thermo-oxidation at 90°C	14	13
Natural weathering	140	136

^a Under thermo-oxidation at 90°C and natural weathering conditions.

of exposure. Because the thermo-oxidative degradation induces a drastic reduction in ϵ_r , it leads to visible physical effects such as discoloration and embrittlement of the samples. At this stage of degradation, negligible changes in ϵ_r are observed.

Natural Weathering. Table IV shows the observed and the predicted values of the ϵ_r for unstabilized LDPE films under natural weathering conditions. The residual values are also reported. The selected model to predict the ϵ_r has the following form:

$$Y = 343.6124 + 573.1188 \cdot 10^{-3} X - 135.1263 \cdot 10^{-4} X^2 \quad (10)$$

The validity of the selected model is analyzed using the statistical criteria presented in Table V. The results obtained indicate low value of the residual variance (0.2391) and a maximum value for (r^2) which is 99.998%. The calculation of the model coefficients from Student and Fisher-Snedecor tests gives higher values than the tabulated ones and so implies the accuracy of the model. Moreover, the adequacy of the selected model is also confirmed by the data reported in Table III. The predicted HLT and the experimental one have comparable values. It is found 136 days for

Table II Unstabilized LDPE Films in Thermo-Oxidation at 90°C

Residual Variance	(r^2) (%)	Student Test ^b Calculated Values:				Fisher-Snedecor Test
		$T(C_1)$	$T(C_2)$	$T(C_3)$	$T(C_4)$	
0.2485	99.999	779.163	3.814	149.428	186.942	Tabulated value = 6.59 Calculated value = 209591

^a Statistical criteria analysis using the proposed model to predict elongation at break.

^b Tabulated value: $T(n - m, \alpha/2) = 2.77$.

Table IV Elongation at Break for Unstabilized LDPE Films^a

Time (days)	Observed (% ϵ_r)	Predicted (% ϵ_r)	Residual Values
0	344	343.6124	0.3876
25	349	349.4968	-0.4968
50	338	338.4902	-0.4902
70	318	317.5237	0.4763
100	266	265.8049	0.1951
120	218	217.8131	0.1869
130	190	189.7634	0.2366
150	125	125.5565	-0.5565
160	89	89.3993	-0.3993
170	51	50.5395	0.4605

^a The proposed model in natural weathering was used.

the predicted HLT while the experimental one, is approximately 140 days. This slight difference in the HLT values is acceptable within the limits of the experimental errors. The applicability of the selected model is however, limited to an exposure period not to exceed 182 days, as % ϵ_r predicted from the model indicates zero value. At 170 days, the samples become brittle as evidenced by surface cracking.

HALS-Stabilized LDPE Film

Physico-Chemical Analysis of Degradation

The variation in ϵ_r as a function of time for HALS-stabilized LDPE films under both thermo-oxidation at 90°C and natural weathering conditions is presented in Figure 2. In thermo-oxidation, the plot exhibits an induction period for approximately 100 days, and is followed by a slow decrease in elongation at break up to 630 days of exposure. This behavior shows clearly the effectiveness of Tinuvin 783 as a thermo-oxidative stabilizer for LDPE films.^{15,23} The literature²⁴ reported that the stabilizing activity of HALS is due to the piperidinoxyl radicals and their deriva-

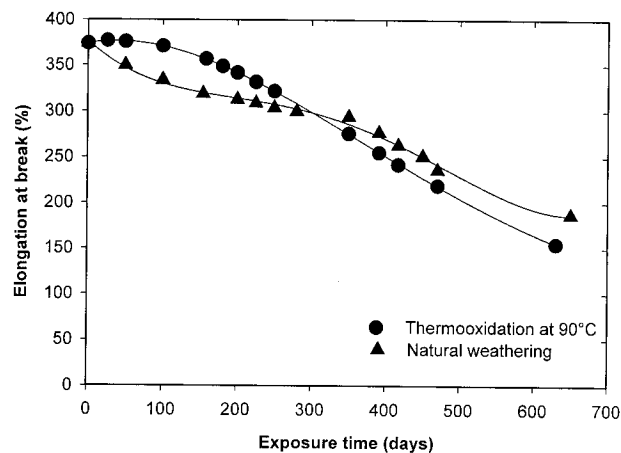


Figure 2 Elongation at break as a function of time for HALS-stabilized LDPE film under both thermo-oxidation at 90°C and natural weathering conditions.

tives, i.e., hydroxylamines and macroalkylhydroxylamines which participate in catalytic photoantioxidant processes. These oxidized species are capable of inhibiting propagation and chain branching during thermo-oxidation by trapping the free radicals, such as macroalkyl, hydroxyl and hydroperoxyl radicals. In natural weathering conditions, the Figure shows a continuous but slow decrease in elongation at break with time. The plot reveals that the decline in ϵ_r starts at the beginning of exposure without showing any induction period. The effectiveness of Tinuvin 783 as a long term photostabilizer is evidenced by a significant retention in elongation at break. The photostabilization mechanism of HALS in LDPE films under natural weathering conditions is attributed to the formation of stable piperidinoxyl radicals in the polymer matrix according to the well known regeneration process, as reported in the literature.²⁵ The synergistic effect between the two HALS components, i.e., Chimassorb 944 and Tinuvin 622, in the polymer matrix should also be considered through the probable recombination of the fragmented oligomers due to chain scissions.

Table V Unstabilized LDPE Films in Natural Weathering^a

Residual Variance	(r^2) (%)	Student Test ^b Calculated Values:			Fisher-Snedecor Test
		$T(C_1)$	$T(C_2)$	$T(C_3)$	
0.2392	99.998	836.226	52.383	223.568	Tabulated value = 4.74 Calculated value = 235248

^a Statistical criteria analysis using the proposed model to predict elongation at break.

^b Tabulated value: $T(n - m, \alpha/2) = 2.36$.

Table VI Elongation at Break for HALS-Stabilized LDPE Films

Time (days)	Observed (% ϵ_r)	Predicted (% ϵ_r)	Residual Values
0	374	375.1695	-1.1695
26	377	376.3897	0.6103
50	376	375.8242	0.1758
100	371	369.9112	1.0888
158	357	356.1115	0.8885
180	349	349.2248	-0.2248
200	342	342.2847	-0.2847
225	332	332.7977	-0.7977
250	322	322.5226	-0.5226
350	276	275.9794	0.0206
391	255	255.6280	-0.6280
417	242	242.7184	-0.7184
470	219	217.0472	1.9528
630	155	155.3911	-0.3911

^a Using the proposed model in thermo-oxidation at 90°C.

Moreover, it has been found that a certain amount of piperidinoxyl radicals is covalently attached to the polymer backbone, as reported by many authors.²⁵⁻²⁸ This would imply a permanent photoprotection toward the LDPE film by improving the durability or service life of the material.

Modeling

The same preliminary procedure as the one described in the previous section dealing with unstabilized samples was applied to select the best models capable of describing the relationship between the ϵ_r and the exposure time under both thermo-oxidation at 90°C and natural weathering conditions.

Thermo-Oxidation at 90°C. Table VI shows the observed and the predicted elongation at break for HALS-stabilized LDPE films under thermo-oxidation at 90°C. The residual values are also

Table VIII Comparison Between the Observed and the Predicted HLT for HALS-Stabilized LDPE Films^a

Exposures	Observed HLT (days)	Predicted HLT (days)
Thermo-oxidation at 90°C	540	541
Natural weathering	650	650

^a Under thermo-oxidation at 90°C and natural weathering conditions.

reported. The selected model has the following form:

$$Y = 375.1694 + 852.7749 \cdot 10^{-4} X - 150.8698 \cdot 10^{-5} X^2 + 13.0095 \cdot 10^{-7} X^3 \quad (11)$$

The validity of the model is assessed on the basis of the data obtained from the statistical criteria analysis, presented in Table VII. The results indicate the low value of the residual variance = 0.9664 and a maximum value for r^2 which is 99.984%. The model coefficients calculated by Student and Fisher-Snedecor tests show higher values than the tabulated ones, implying a very good approximation of the model. Table VIII compares the HLT values predicted from the model with the observed ones. The results indicate 540 days for the predicted HLT while the experimental one, is approximately 541 days. This confirms the adequacy of the selected model to predict the elongation at break of the stabilized samples under thermo-oxidation at 90°C. However, the model is most likely applicable in the exposure period, not exceeding 740 days. Beyond this, the calculation of the ϵ_r from the model leads to unreliable values indicating a sudden increase in this ultimate property with time. It is well established that a consequence of oxidation chain scis-

Table VII HALS-Stabilized LDPE Films in Thermo-Oxidation at 90°C

Residual Variance	(r^2) (%)	Student Test ^b				Fisher-Snedecor Test
		Calculated Values:				
0.9664	99.984	$T(C_1)$ 529.806	$T(C_2)$ 8.067	$T(C_3)$ 36.491	$T(C_4)$ 29.732	Tabulated value = 3.86 Calculated value = 21778

^a The proposed model to predict elongation was used.

^b Tabulated value: $T(n - m, \alpha/2) = 2.26$.

Table IX Elongation at Break for HALS-Stabilized LDPE Films

Time (days)	Observed (%ε _r)	Predicted (%ε _r)	Residual Values
0	374	375.0911	-1.0911
50	350	348.9001	1.0999
100	334	331.8209	2.1791
154	319	319.1705	-0.1705
180	313	314.0816	-1.0861
200	309	310.3027	-1.3027
225	304	305.5051	-1.5051
250	300	300.4281	-0.4281
280	294	293.7275	0.2725
350	277	274.5953	2.4047
391	263	260.9856	2.0144
420	251	250.4761	0.5239
450	236	239.1052	-3.1052
650	187	186.8051	0.1949

^a The proposed model in natural weathering was used.

sion is the decrease in ε_r leading to material embrittlement.²⁹

Natural Weathering. Table IX shows the observed values of elongation at break for HALS-stabilized LDPE film and those predicted from the model under natural weathering conditions. The residual values are also reported. The selected model to predict elongation at break has the following form:

$$Y = 375.0911 - 644.533110^{-3}X + 273.356510^{-5}X^2 - 668.334110^{-8}X^3 + 509.910^{-11}X^4 \quad (12)$$

The data generated by the statistical criteria analysis, presented in Table X, indicate the accuracy of the selected model. In fact, the calculation of the residual variance gives 3.5969, while for r² it is 99.890%, close to unity. The calculation of the

model coefficients using both Student and Fisher-Snedecor tests leads to good approximations with the calculated coefficients higher than the tabulated ones. Furthermore, the comparison between HLT calculated from the model and the observed one indicates the same value of 650 days. However, the applicability of the model is most likely exhibited in the interval of time (0–660 days). After 660 days of exposure, the ε_r predicted from the selected model shows a deviation toward the end of the test period. In fact, the calculation of % ε_r from the model indicates an increase in the values which is not possible due to the dominance of chain scission at long exposure time.

CONCLUSION

From this study, the following conclusions can be drawn. The different polynomial models developed to describe the changes in the ε_r with time under both thermo-oxidation at 90°C and natural weathering conditions for unstabilized and HALS-stabilized LDPE films are reliable. This is confirmed by the statistical criteria analysis which has led to very good approximations. The results indicate low residual variance, coefficient of correlation close to unity and very high values of the model coefficients calculated by both Student and Fisher-Snedecor tests. Furthermore, the adequacy of the proposed models is validated by the HLT parameter, which has an important role on the oxidation rate. In the case under study, the HLT value predicted from the model is very close to that obtained experimentally for all the tested materials. The models developed predict the general experimental behavior. However, their applicability is most likely valid only in an interval of time which depends on both the formulation type of LDPE films and the exposure conditions. This requires the knowledge of aging mechanisms and kinetics to predict a realistic lifetime model. Further investigations into the variations of the de-

Table X HALS-Stabilized LDPE Films in Natural Weathering

Residual Variance	(r ²) (%)	Student Test ^b					Fisher-Snedecor Test
		Calculated Values:					
3.5969	99.80	T(C ₁)	T(C ₂)	T(C ₃)	T(C ₄)	T(C ₅)	Tabulated value = 3.86 Calculated value = 2110
		210.988	13.871	7.948	7.659	7.379	

^a The selected model to predict elongation at break was used.

^b Tabulated value: T(n - m), α/2) = 2.26.

veloped models with UV accelerated conditions also need to be performed.

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