

# Natural and Accelerated Photoaging of Linear Low-Density Polyethylene: Changes of the Elongation at Break

ADAMS TIDJANI,<sup>1</sup> RENÉ ARNAUD,<sup>2,\*</sup> and ANICET DASILVA<sup>1</sup>

<sup>1</sup>Laboratoire des DSTN, Faculté des Sciences, Université CAD de Dakar, Dakar-Fann, Sénégal; <sup>2</sup>Laboratoire de Photochimie (U.R.A. C.N.R.S. 433), Université Blaise Pascal de Clermont II, F-63177 Aubière cedex, France

## SYNOPSIS

The photoaging of different linear low-density polyethylenes (LLDPEs), namely, ethylene-butene (EB) and ethylene-hexene (EH), has been studied. Experiments have been carried out under natural and accelerated UV exposure. We focused our investigation on the changes of elongation at break and the modifications in the chemical structure (measured by the IR technique) occurring over the photoaging process. Our results showed that the changes of elongation at break were different under the two modes of irradiation from the very beginning of UV exposure; in contrast, the comparison of stoichiometry displayed a small difference in the later stage of UV irradiation. That pointed out the difficulty of establishing a relationship between the buildup of carbonyl groups and the mechanical changes due to UV irradiation, which has been usually attempted. In addition, it appeared that the density, oxygen permeability, and the type of  $\alpha$ -olefin of the polymer might have an effect upon the elongation-at-break changes. From our data, it can be suggested that the prediction of weathering resistance of polymers can be based on both mechanical changes and modifications in chemical structure to minimize erroneous prediction. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

During a service life, linear low-density polyethylene (LLDPE) films may be subjected to several aging factors such as UV radiation, humidity, and temperature fluctuations. These factors induce irreversible structural changes in the long run. The direct consequence of these changes is the dramatic deterioration of mechanical properties of the films. For a long time, it was believed that the loss of mechanical properties can be easily assessed by the buildup of carbonyl groups by monitoring through IR spectroscopy. Torikai et al.<sup>1</sup> indicated that the change in mechanical properties can be estimated by the modifications in the chemical structure during the accelerated photodegradation of polyethylene (PE); they found a relationship between the development of carbonyl groups and the changes of elongation and strength at break. In contrast to this ap-

proach, Akay et al.<sup>2</sup> reported that no simple correlation exists between the buildup of carbonyl species and the change of mechanical properties such as stress or strain at break or elastic modulus under natural weathering of LDPE. By investigating the environmental degradation of stabilized LDPE, Severini et al.<sup>3</sup> backed this idea. They also mentioned in this study that the decay of the mechanical properties could not be related to the variation in the concentration of vinyl species and in crystallinity. Later, Földes et al.<sup>4</sup> also indicated that the physical and mechanical properties of LLDPE revealed only poor dependence on crystallization conditions and changes in the chemical structure. But the work of La Mantia<sup>5</sup> did not lead to the same direction with regard to the relationship between crystallinity and mechanical properties. He obtained some correlations between the elastic modulus, strength, and elongation at break and changes of crystallinity (or density) in naturally weathered LDPE films.

The discrepancies existing between the experimental results of several researchers using different irradiation sources prompted us to carry out natural

\* To whom correspondence should be addressed.

and accelerated photoaging on different LLDPEs. In this paper, we tested the elongation at break of different LLDPE samples after accelerated and natural photoaging. The influence of some physical parameters on the elongation at break has also been examined.

## EXPERIMENTAL

### Materials

Studied LLDPEs are commercial polymers with only processing antioxidants, provided by Exxon. For a few samples, the antioxidant was extracted with chloroforme in a Soxhlet device. The further comparison of the photooxidation results on washed or initial samples showed that the processing antioxidant does not have a significant effect on the oxidation rate. Ethylene-butene (EB) and ethylene-hexene (EH) copolymers have been employed. The melt index and the density of the films (measured by the supplier) are listed in Table I. In Table II, oxygen permeability values evaluated using a Lyssy apparatus (Model GPM 200) based on gas chromatographic analysis<sup>6</sup> are reported.

### Methods

All the employed samples have been subjected to natural (outdoors) photoaging and accelerated photoaging.

### Accelerated Photoaging

Samples were irradiated in a Sepap 12-24 device that has been described elsewhere.<sup>7</sup> In this apparatus, the incident polychromatic beam was filtered using appropriate cutoff filters to eliminate the radiation

of wave lengths  $\leq 300$  nm. All experiments were conducted at  $60 \pm 2^\circ\text{C}$ .

### Natural (Outdoor) Photoaging

Natural exposure to the environmental conditions was carried out under a tropical climate at Dakar, Sénégal. Without any stress, the films were fixed in wood racks inclined at  $15^\circ$  to the horizontal, oriented southwest to get the maximum sunlight. The racks were placed on the top of a Dakar University building at about 30 m above ground level. During the exposure, ambient and sample average temperatures measured were found to be varied between  $25^\circ\text{C}$  (in January) and  $32^\circ\text{C}$  (in July). The average daily sunshine time is around 10 h.

### Analytical Measurements

After different exposures, films were removed for the analysis to estimate the effects of accelerated and natural photoaging. A Nicolet 510 FTIR spectrometer was used to monitor the damages caused by UV irradiation on the chemical structural changes in the films.

The measurement of the elongation at break proved to be the more discriminatory test to measure the mechanical changes caused by photoaging. Tests have been done at ambient temperature  $25 \pm 0.2^\circ\text{C}$  using an Adamel Lhomargy DY 22 testing machine. The elongational velocity was 100 mm/min; the initial gauge length was 50 mm. In all the cases, several experiments (average five tests) have been performed to confirm the results.

## RESULTS AND DISCUSSION

### Accelerated Photoaging

Throughout the course of the photooxidation, no oxygen starvation in the films was noted. Changes in the mechanical properties allow an indirect macroscopic measure of the chemical structure modifications of polymeric materials through UV exposure. Lifetime measured in terms of accumulation of carbonyl groups at  $1715\text{ cm}^{-1}$  has been used to monitor these modifications. Since the structural changes in LLDPE during irradiation in Sepap 12-24 may provoke a change in the mechanical behavior, we have attempted to correlate the carbonyl content with the elongation at break. Figures 1 and 2 displayed the obtained curves. In the beginning of irradiation, the elongation at break remained almost constant. Most authors explained it by the predominance of

**Table I** Characteristics of LLDPEs Studied

Samples	Melt Index (g/10 Min)	Density (g/cm <sup>3</sup> )
EB1	1.0	0.918
EB2	0.7	0.925
EB3	2.0	0.918
EB4	2.8	0.918
EB5	1.0	0.935
EH1	2.8	0.917
EH2	0.8	0.921
EH3	0.8	0.926
EH4	1.8	0.920

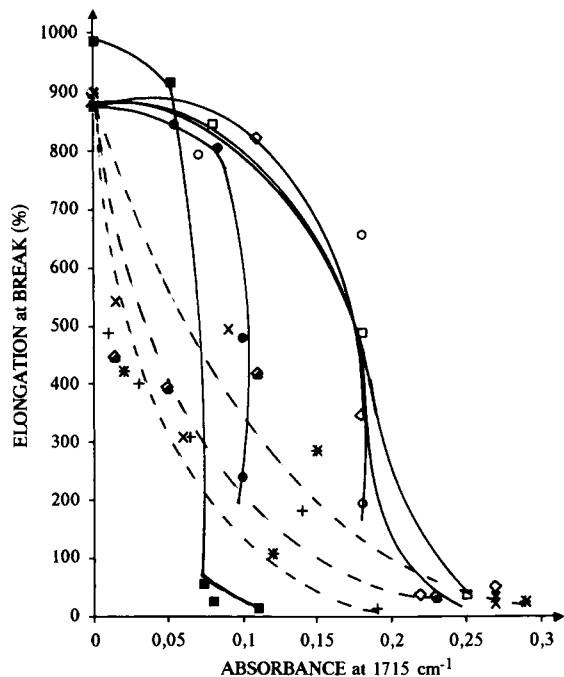
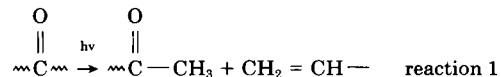
**Table II Oxygen Permeability Values and Absorbance at 1715  $\text{cm}^{-1}$  Corresponding to the Loss of 50% ( $A_{50}$ ) of Elongation at Break of LLDPE Samples under Accelerated and Natural Photoaging**

Samples	Oxygen Permeability [ $1 \text{ m}^{-2} \text{ atm}^{-1} (25 \text{ h})^{-1}$ ]	$A_{50}$ Values in Accelerated Photoaging	$A_{50}$ Values in Natural Photoaging
EB1	$1.20 \pm 0.1$	0.15	0.04
EB2	$0.84 \pm 0.01$	0.10	0.02
EB3	$0.83 \pm 0.09$	0.16	0.02
EB4	$1.16 \pm 0.05$	0.18	0.03
EB5	$0.52 \pm 0.02$	0.03	0.02
EH1	$1.05 \pm 0.15$	0.09	0.05
EH2	$1.26 \pm 0.09$	0.12	0.03
EH3	$0.77 \pm 0.03$	0.09	0.02
EH4	$1.20 \pm 0.1$	0.11	—

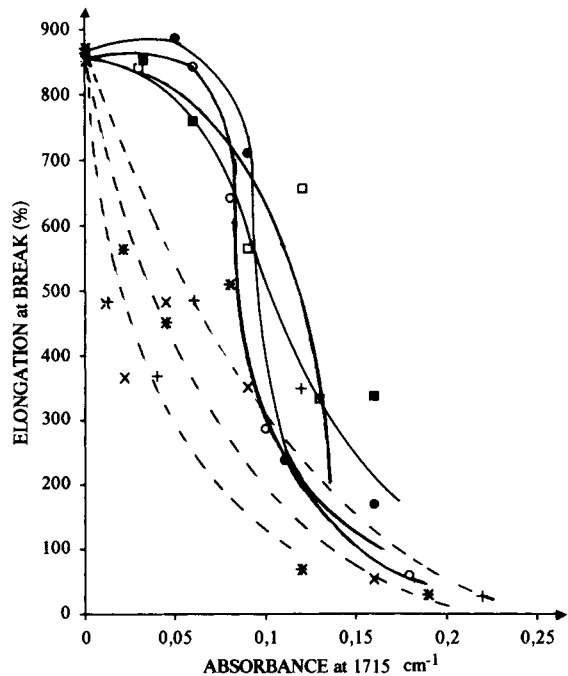
cross-linking reactions over chain scission as well as by the changes of crystallinity. This tendency was reversed as we observed a dramatic decrease of the elongation at break.

The formation of vinyl unsaturations at  $910 \text{ cm}^{-1}$ , which represent the more evident photoproducts of

the chain scission reactions during PE photooxidation, has been followed. Remember that these photoproducts are believed to issue from the Norrish type II reaction on ketones:

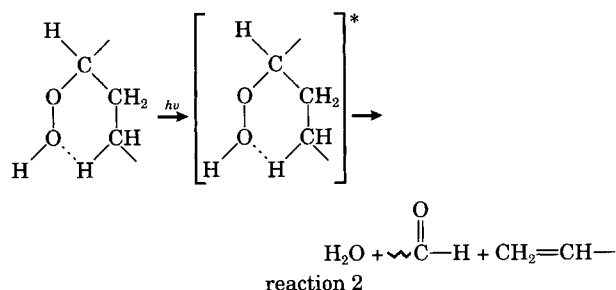


**Figure 1** Variations of the elongation at break vs. the absorbance at  $1715 \text{ cm}^{-1}$  of EB copolymers under accelerated and natural photoaging: (○, ◆) EB1; (●, +) EB2; (◇, \*) EB3; (□, X) EB4; (■) EB5. To ease the examination of the figure, accelerated photoaging curves and natural one are plotted using solid and dashed lines, respectively.



**Figure 2** Variations of the elongation at break vs. the absorbance at  $1715 \text{ cm}^{-1}$  of EH copolymers under accelerated and natural photoaging: (○, \*) EH1; (■, +) EH2; (●, X) EH3; (□) EH4. As in Figure 1, the meanings of the lines are the same.

Recently, the formation of vinyl unsaturations by an intramolecular decomposition on secondary hydroperoxides leading to ketone and vinyl groups has been proposed<sup>8</sup>:



The absorbance at  $1715\text{ cm}^{-1}$  against the one at  $910\text{ cm}^{-1}$  is depicted in Figure 3. To avoid overloading the figure, we have shown only the curves of two typical samples of each type of copolymer; but all of them show a similar trend. We did not observe any linear relationship between the vinyl and carbonyl formations during the irradiation time. At the beginning of UV irradiation, the formation of the vinyl unsaturations seems to be favored, which does not support the observed unchanged elongation at break. The predominance of cross-linking reactions over chain scissions, previously mentioned, was emphasized through the above observation.

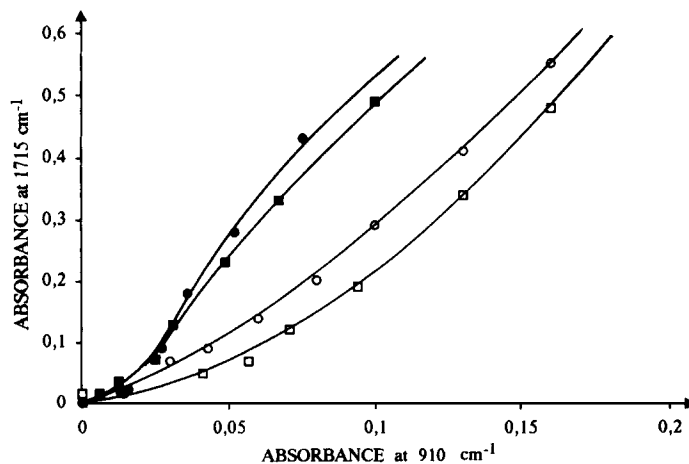
Reviewing Figures 1 and 2, a point is worthy of mention: The absorbance at  $1715\text{ cm}^{-1}$  required to reach 50% loss of the elongation at break ( $A_{50}$ ) differs from one sample to another. This effect is more pronounced on EB copolymers. In Table II are listed the values of  $A_{50}$  recorded with the initial oxygen permeability. The density and the oxygen perme-

ability are physical parameters that we believed to have an important role on the rate of oxidation—hence, upon the loss of mechanical properties after UV exposure.

We have noted that for samples with higher oxygen permeability the  $A_{50}$  values were found to be higher. The EB3 sample is an exception to this behavior, which we cannot explain. Except for EB3 in spite of an apparent high oxidizability, the most oxygen-permeable samples were found to maintain their initial mechanical properties for a longer period. It can be argued that oxygen facilitated the cross-linking reactions during the photooxidation of LLDPE, and according to Torikai et al.,<sup>9</sup> the samples having a greater amount of tie molecules were able to reach the higher oxidation product buildup without causing great damage in the elongation at break.

The changes of the  $A_{50}$  values against the initial density are more difficult to explain. The samples having the highest density are most crystalline and should be the most stable ones against photoirradiation since the oxidation process takes place mainly in the amorphous phase as per the observation of several authors (e.g., see Ref. 10). Even though one can expect a better ultimate stress from these samples, we have not observed this. In addition, the different behavior observed for EB and EH copolymers complicated the problem. For EB copolymers, the  $A_{50}$  values are high for samples of low density and vice versa. The obtained results are in good agreement with the work of Torikai et al.<sup>9</sup>

Oppositely, we observed no significant changes for EH copolymers, which makes us point out the role that the type of  $\alpha$ -olefin used in the copolymer



**Figure 3** The absorbance at  $1715\text{ cm}^{-1}$  against the one at  $910\text{ cm}^{-1}$  during photoaging for two samples: (○, ●) EB1; (□, ■) EH2. Open and closed symbols refer, respectively, to accelerated and natural photoaging.

may play. No significant effect of the melt index on the changes of elongation at break in both copolymers has been observed.

### Natural Photoaging

Under natural aging, the situation is totally different. The trend is clearly demonstrated in Figures 1 and 2, displaying variation of the elongation at break vs. the absorbance at  $1715\text{ cm}^{-1}$ : The samples lost quite rapidly their mechanical properties, as indicated by the decreasing of the elongation at break. The  $A_{50}$  values (ranging from 0.015 to 0.05) were much lower than those obtained under accelerated photooxidation (Table II). That would mean that the chain scission reactions outweighed the cross-linking reactions from the early moment of the natural exposure. In this case, the curves representing the absorbance at  $1715\text{ cm}^{-1}$  vs. the one at  $910\text{ cm}^{-1}$  (Fig. 3) under natural photoaging supported this idea. At the later stage of the natural photoaging, the shape of these curves was different from the ones plotted in accelerated photoaging. These results suggested that some stoichiometry differences might take place under both modes of irradiation.

One may assume that the change in behavior of the elongation at break in natural photooxidation is due to the rapid depletion of the processing antioxidant that no longer protects the polymer. Under these conditions, it is well known that the loss of the stabilizer is not only governed by its chemical action but also by other influencing physical factors. But the kinetic study in both photooxidation conditions did not prove this point. In fact, on displaying

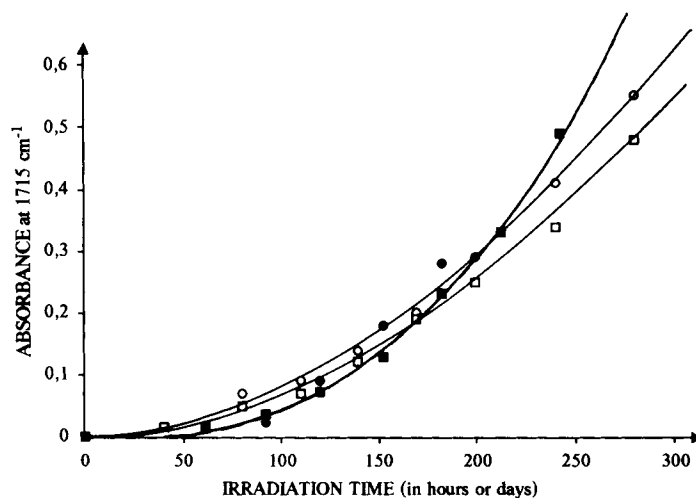
the variation of photoproduct absorbance at  $1715\text{ cm}^{-1}$  throughout the course of natural and accelerated photooxidation (Fig. 4), we did not note any difference in the shape of the curves.

We suspect the flux of the photon and the temperature to be the main reasons for the behavior difference of the elongation at break under the two ways of irradiation: In the accelerated device, the high temperature may favor the mobility of radicals generated in high quantity by the unceasing radiation and great flux of photons compared to the natural exposure. All of that can favor the cross-linking reactions over the chain scission under accelerated irradiation, which are not occurring under natural exposure. Our conclusion was supported by the reported effect<sup>11</sup> of the natural weathering of blends of LDPE and LLDPE, which indicated the alterations in molecular weights resulting mainly from chain scission.

### Acceleration Factor

From the laboratory and natural tests, the usual criteria used to predict the service life of polymers outdoors are the elongation at break and/or the formation of photoproducts, especially carbonyl species. In this part, we assess the acceleration factor using two different criteria: the first one based on the time required to attain a chosen value of the absorbance at  $1715\text{ cm}^{-1}$ , and the second one, on the time corresponding to the loss of 50% of elongation at break for samples of  $100\text{ }\mu\text{m}$  thick.

The observed data are presented in Table III. The



**Figure 4** Variations in the absorbance at  $1715\text{ cm}^{-1}$  during the natural (irradiation time in days) and accelerated photooxidation (irradiation time in hours). Symbols have the same meaning as in Figure 3, and the values of the absorbance at  $1715\text{ cm}^{-1}$  have been corrected for  $100\text{ }\mu\text{m}$  to ease the comparison.

**Table III Acceleration Factor  $F$  Values Calculated at 0.1 and 0.2 Absorbance at  $1715\text{ cm}^{-1}$  and at 50% Loss of the Elongation at Break**

Samples	$F$ at 0.1 Absorbance at $1715\text{ cm}^{-1}$	$F$ at 0.2 Absorbance at $1715\text{ cm}^{-1}$	$F$ for 50% Loss of the Elongation at Break
EB1	27	23	15
EB2	30	26	18
EB3	36	27	14
EB4	30	27	17
EB5	28	25	18
EH1	27	25	17
EH2	26	23	13
EH3	32	26	14
EH4	25	24	—
Average value	$29 \pm 3$	$25 \pm 2$	$16 \pm 3$

Remember that the acceleration factor is the ratio between the times estimated under natural and accelerated photoaging to get these points.

average values determined by the first technique at two different values of the absorbance at  $1715\text{ cm}^{-1}$  ( $25 \pm 2$  and  $29 \pm 3$ ) were higher than the one obtained using elongation at break criteria ( $16 \pm 3$ ), taking into account experimental errors. The difference is not as large as we could have expected. But at this point, it is quite difficult to claim which criteria should have been chosen. To do so, an exhaustive statistical study on different polyolefins may be necessary.

## CONCLUSION

The results presented in this work clearly demonstrate that it is not easy to establish a simple correlation between the development of carbonyls and the elongation at break, which is the most common mechanical property studied. The deterioration of the elongation at break of the photooxidized LLDPEs seems strongly dependent on the initial oxygen permeability and density and maybe on the type of  $\alpha$ -olefin copolymer. Our experiments, which have been carried out at Dakar (Sénégal), indicated that the oxidation reaction of the LLDPEs proceeded in different ways during the accelerated and natural photoaging with respect to the changes of the elongation at break. The variation of the absorbance at  $1715\text{ cm}^{-1}$  vs. the one at  $910\text{ cm}^{-1}$  supported this point at the later stage of the photooxidation.

The prediction of weathering resistance of polymers based on the only mechanical changes or chemical structural alterations may lead to drastic

errors, as confirmed by the divergence recorded in the calculation of the acceleration factor using two different criteria: the loss of elongation at break and the degree of oxidation measured by the absorbance at  $1715\text{ cm}^{-1}$ . To minimize erroneous prediction, a good combination of both criterion may be a better solution.

## REFERENCES

1. A. Torikai, A. Takeuchi, S. Nagaya, and K. Fueki, *Polym. Photochem.*, **7**, 199 (1986).
2. G. Akay, T. Tincer, and H. E. Ergöz, *Eur. Polym. J.*, **16**, 601 (1980).
3. F. Severini, R. Gallo, S. Ipsale, and N. Del Fanti, *Polym. Deg. Stab.*, **14**, 341 (1986).
4. E. Földes, M. Iring, and F. Tüdös, *Polym. Bull.*, **20**, 89 (1988).
5. F. P. La Mantia, *Eur. Polym. J.*, **20**, 993 (1984).
6. J. L. Philippart and J. L. Gardette, *Makromol. Chem.*, **187**, 1639 (1986).
7. G. Penot, R. Arnaud, and J. Lemaire, *Angew. Makromol. Chem.*, **117**, 71 (1983).
8. F. Gugumus, *Polym. Deg. Stab.*, **27**, 19 (1990).
9. A. Torikai, H. Shirakawa, S. Nagaya, and K. Fueki, *J. Appl. Polym. Sci.*, **40**, 1637 (1990).
10. N. C. Billingham and P. D. Calvert, in *Developments in Polymer Stabilisation*, Part 3, G. Scott, Ed., London, Applied Science, 1980, p. 139.
11. A. Daro, A. Trojan, R. Jacobs, and C. David, *Eur. Polym. J.*, **26**, 47 (1990).

Received November 4, 1991

Accepted March 3, 1992