

# Natural and Artificial Weathering of Low-Density Polyethylene (LDPE): Calorimetric Analysis

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## SYNOPSIS

Studies of the thermal and photodegradation of two commercial polymers, stabilized and unstabilized low-density polyethylene, show the effects of weathering on differential scanning calorimetry (DSC) curves. The shape and the size of the melting peak vary significantly in thermal aging and in accelerated photoirradiation, but no change was observed in natural weathering, implying that the crystallinity remains steady in outdoor exposures. The melting temperatures remain steady for all exposure tests. The fall of mechanical properties and the evolution of chemical structure, followed by IR spectroscopy results, especially near the carbonyl regions, were also observed. The resistance to UV light irradiation as probed by deformation at break was superior in stabilized LDPE compared to unstabilized LDPE. Simple correlations observed between the fall of mechanical properties, the rate of oxidation, and morphology. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

When the polyethylene films for greenhouse covering are exposed to heat, UV light in the presence of oxygen, they became brittle, and visual signs of deterioration are apparent. Degradation and embrittlement of those films can be related to the evolution of chemical structure and morphology (i.e., the crystallinity, size, and perfection of the crystallites, the deformation of amorphous regions, etc.). It is now well established that the primary mechanism of degradation of polyethylene when exposed to heat and/or UV light involves the process of thermal and/or photooxidation.<sup>1,2</sup> Those reactions lead to the buildup of a vinyl group and of a variety of oxygen-containing groups such as various carbonyl functions. The photochemical degradation of PE results from competing reactions of crosslinking and chain scission.<sup>3,4</sup> At first stages of exposures, the crosslinking reactions may predominate, leading to an increase of the Young's modulus.<sup>5,2</sup>

Polyethylene is a semicrystalline polymer. Its

structure can be considered as an alternating crystalline and amorphous layers (two-phase system). Neighboring crystalline lamellae are connected by tie molecules, passing through the amorphous interlamellar regions.<sup>6</sup> It was assumed that oxidation was restricted to the amorphous regions.<sup>7,4</sup> Oxidation damage at the tie molecule region can be responsible of the sudden loss of mechanical properties, especially elongation at break.<sup>8,9</sup> It was assumed that the crystallinity increase with oxidation. It seems that this effect is due to the replacement of C—H bonds by C=O bonds in the amorphous regions.<sup>7</sup>

Natural weathering studies were conducted by exposing stabilized LDPE samples.<sup>10,11</sup> It was concluded that the observed slight increase in crystallinity could not be attributed to the formation of crosslinked structure because of the complete solubility of the sample.

During photooxidation, LDPE, is well known to undergo changes of molecular weight.<sup>10,11</sup> Other works on high pressure crystallization of PE<sup>12</sup> have shown that the heat of fusion decreases with molecular weight and the number of peaks of DSC curves near the melting temperature increases with decreasing molecular weight.

The aim of this work was the study of the relation

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between the mechanical properties and the evolution of the chemical structure and the morphology of the exposed polymers. The durability of polymers was evaluated by tests under thermal aging, outdoor exposures, and accelerated UV photoirradiation.

## EXPERIMENTAL

### Material

The polymers used in the present study are two commercial low-density polyethylene (LDPE) films for greenhouse covering identified as Riblene type without stabilizers (El-Kurty, Algeria) and stabilized Lotrene type (Atochem, France). The thickness of the films were 0.20 mm for the unstabilized polymer (sample A) and 0.18 mm for the stabilized polymer (sample B).

### Exposures

The natural exposure tests were started at the end of January 1990 at Laghouat, Algeria (38°48' N) and Bandol, France (43°16' N). The samples were mounted on a wooden panel, facing south and inclined at 45° (NF T51-165).

The accelerated UV photoirradiation exposures tests were carried out with a medium pressure mercury lamp at 60 ± 1°C regulated drying oven made in our laboratory and in SEPAP 12-24 at CNEP (University of Clermont-Ferrand).

The thermal aging exposures tests were carried out in a 70 ± 1°C regulated drying oven.

### Instrumental

The tensile test datas for both exposed and unexposed films were measured using an Instron 1186 machine. All tests were conducted at 20 <  $T^{\circ}\text{C}$  < 25 and 40 < RH (%) < 45. The rate of strain was 170 and 1.70 min<sup>-1</sup> for the calculations of the deformation at break and the Young's modulus, respectively (NF T54-102).

The IR spectra were recorded using a Perkin-Elmer 683 spectrometer attached to a CDS data station Model 3500.

The thermal properties of the samples were obtained from a Mettler TA 3000 differential scanning calorimeter attached to a microcomputer controller. Indium was used as a standard for calibrating the temperature axis. The polymers films were cut finely and were put in an aluminum pan. The temperature

of the samples was raised, together with an empty reference sample holder, at a constant rate of 10°C/min. The differential power input was recorded as a function of the temperature.

The samples were cycled two times between -150 and 200°C to determine the transition temperatures. The first- and the second-order transition temperatures, i.e., melting ( $T_m$ ) and glass-transition ( $T_g$ ) temperatures, respectively, were well defined and reproducible.

The change of crystallinity was followed by X-ray diffraction and DSC techniques, and the percentage crystallinity may be calculated from DSC results by the following relation:

$$X(\%) = (\Delta H_f / \Delta H_f^c) * 100$$

where  $\Delta H_f$  is a heat of fusion of the sample and  $\Delta H_f^c$  is a heat of fusion of the 100% crystalline sample;  $\Delta H_f^c = 285 \text{ J/g}$ .<sup>13</sup>

## RESULTS AND DISCUSSION

### Natural Weathering

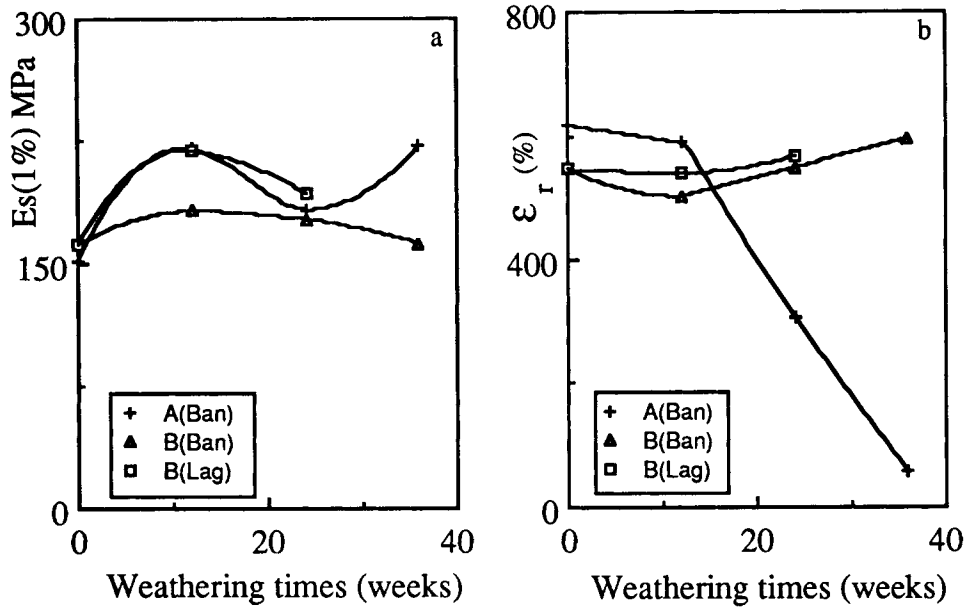
The secant Young's modulus (at 1% strain) and deformation at break for both polymers have been plotted against weathering time in Figures 1(a) and 1(b), respectively. A slight increase in the value of the secant modulus is related to the crosslinking reactions. There is a sudden loss in the value of the elongation at break for sample A after 16 weeks of exposure at Bandol. Within 24 weeks almost 50% of the value of this property was lost, but for the stabilized polymer (sample B), the elongation at break practically remains steady after 36 weeks of exposures at Laghouat and at Bandol.

A significant change in the carbonyl functional groups, for sample A, was observed from IR spectroscopy results, when no change was observed for sample B [Fig. 2(a)].

### Thermal Aging

The polymers have been observed to undergo changes similar to those found in photoirradiation except that during thermal aging vinyl groups are not observed, and the carbonyl groups constitute a smaller fraction that are formed in outdoor exposures, especially for sample A [see Fig. 2(a)].

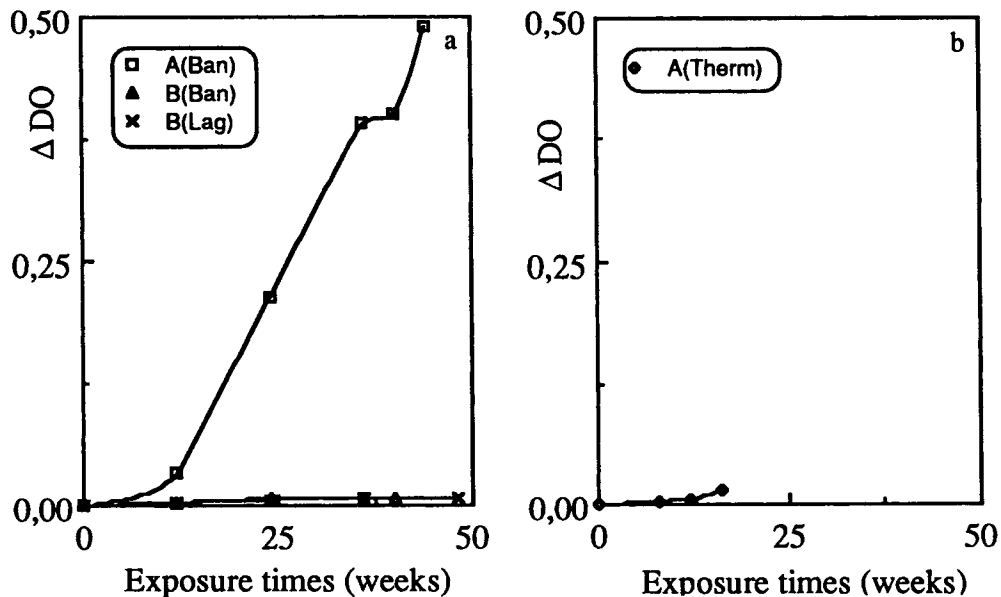
An increase in the secant Young's modulus was also observed for both materials [Fig. 3(a)], indi-



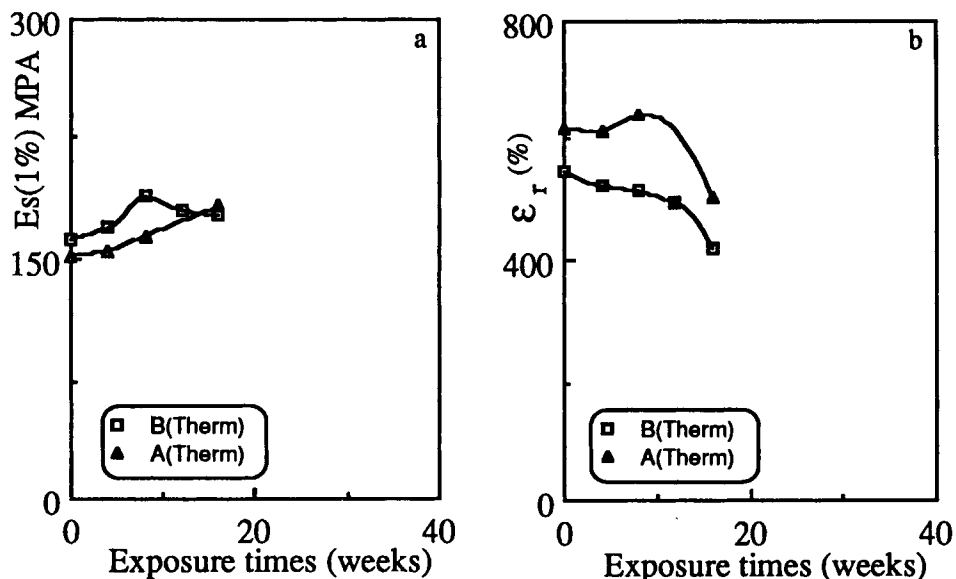
**Figure 1** Exposure time dependence of (a) secant modulus and (b) deformation at break; samples A and B exposed at Bandol and at Laghouat [(Ban) and (Lag), respectively].

cating the predominance of crosslinking reactions. A slight increase of the carbonyl group concentration for sample A [Fig. 2(b)], and no change in this region for sample B was observed. The deformation at break for unstabilized polymer decreases more

weakly than in natural weathering. The decrease of this property, for sample B, in this aging type when it remains steady in natural weathering [Fig. 1(b)] and practically in accelerated photoirradiation [Fig. 4(b)] has not been elucidated.



**Figure 2** Exposure time dependence of the relative optical density of carbonyl groups: (a) samples A and B exposed at Bandol and at Laghouat [(Ban) and (Lag), respectively]; (b) sample A in thermal exposure [A(Therm)].



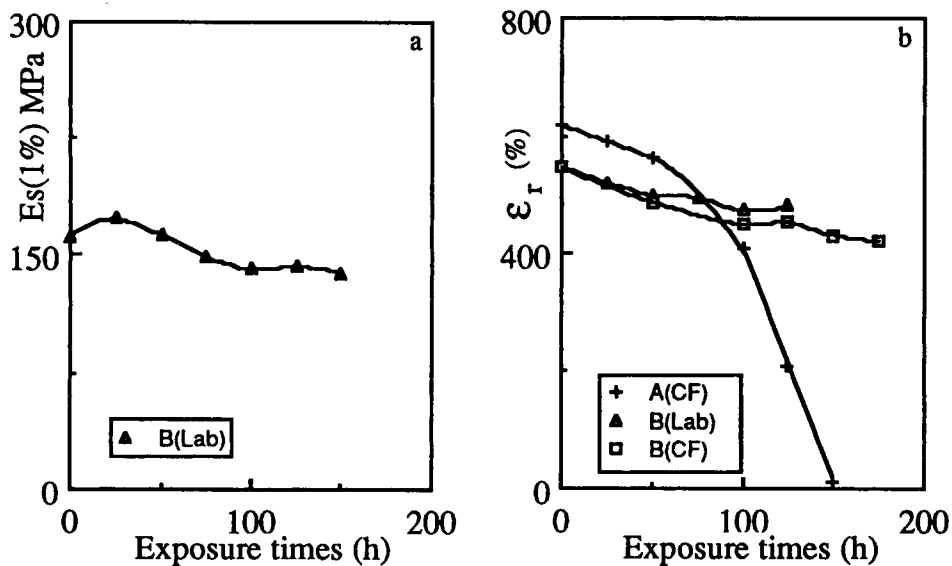
**Figure 3** Exposure time dependence of (a) secant modulus and (b) deformation at break for both polymers [A(Therm) and B(Therm), respectively] in thermal ageing.

**Accelerated Photoirradiation**

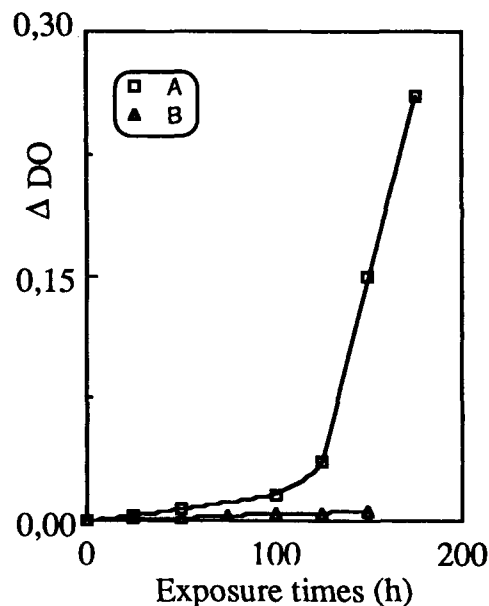
The same evolution as in natural weathering was observed in mechanical and chemical properties for both samples (Figs. 4 and 5). Fifty percent of the value of the deformation at break was reached after almost 100 h of exposure for sample A, whereas it remains steady for the same period for sample B [Fig. 4(b)].

**Calorimetric Results**

The spectral DSC curves were reported for all exposures. The melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_f$ ), glass-transition temperature ( $T_g$ ), relaxation temperature ( $T_r$ ), and percentage crystallinity ( $X\%$ ) are listed in Table I for both starting materials. It seems<sup>14</sup> that this relaxation temperature is sensitive to the thermal treatments of pro-



**Figure 4** Exposure time dependence of (a) secant modulus and (b) deformation at break for sample A in SEPAP 12-24 [A(CF)] and for sample B in SEPAP 12-24 [B(CF)] and in our laboratory's regulated drying oven [B(Lab)].



**Figure 5** Exposure time dependence of the relative optical density of carbonyl groups for samples A and B in SEPAP 12-24.

cessing. It should correspond to the liberation of intermolecular attraction.

The analysis of those curves suggests the following remarks:  $T_m$  and  $T_g$  remain steady for all exposure times with the previous ones within experimental errors. No change also was observed for the

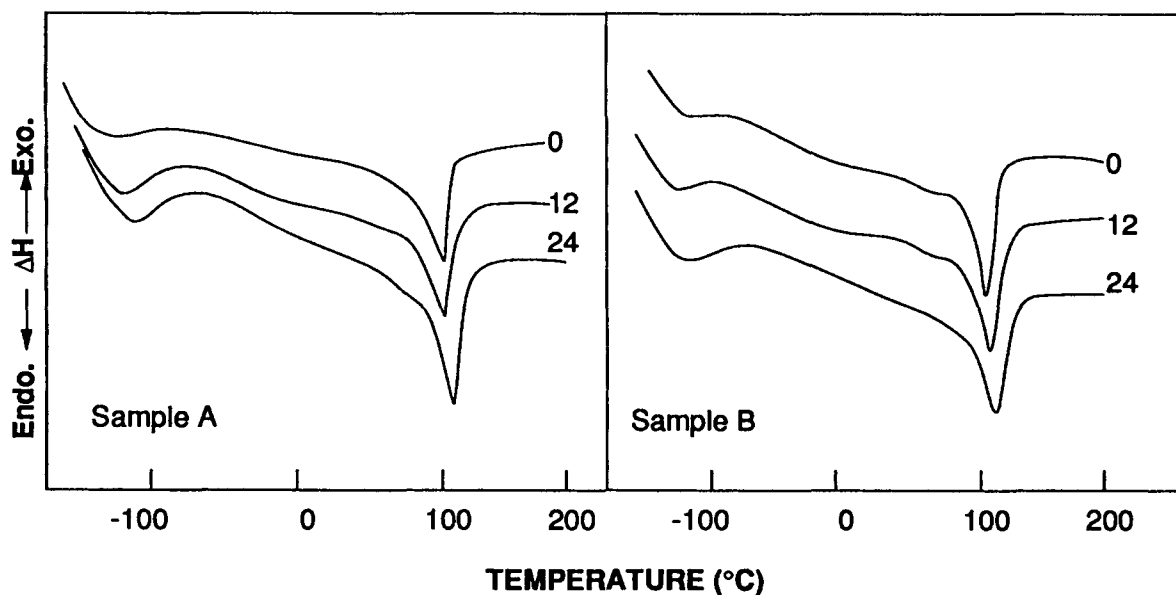
**Table I** Thermal Characteristics and Percent Crystallinity for Both Starting Polymers

	Samples	
	A	B
$T_m$ (°C)	111.6	109.7
$T_g$ (°C)	-125	-130
$T_r$ (°C)	48-50	48-50
$\Delta H_f$ (J/g)	99.3	84.8
$X$ (%)	34.8	29.7

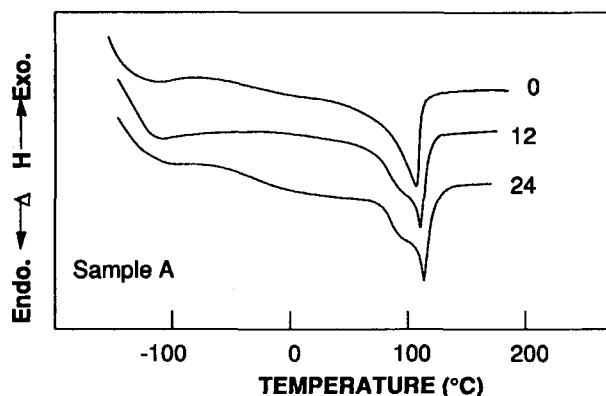
value of relaxation temperature  $T_r$ , but in the second time of heating this peak always disappears.

Any difference in DSC curves in the temperature range below the melting point was observed in natural weathering for both polymers (Fig. 6) and in thermal aging for sample A (Fig. 7). This effect was attributed to the fact that, below the melting temperature, the specific heat of both amorphous and crystalline phases are not very different.<sup>15</sup> However, in accelerated photoirradiation, the DSC curves showed the perturbations of this regions after 200 h of exposure for sample A (Fig. 8). It seems equally reasonable to suggest that this effect is due to the presence of the great amount of carbonyl groups in the amorphous regions [see Fig. 5(a)].

Some major differences occur in the DSC curves near the melting point between the different aging types:



**Figure 6** Change in DSC curves in natural weathering at Bandol.



**Figure 7** Change in DSC curves for unstabilized polymer: thermal aging.

- i. In accelerated photoirradiation, with increasing time of exposure the melting peak becomes larger and broader, especially for sample A, but the melting temperature remains steady for both polymers.
- ii. In thermal aging, after 20 weeks of exposure, the widening of the melting peak was the most apparent effect for sample A.
- iii. In natural weathering, no change in the size and the shape of the melting peak, within experimental errors, was observed for both materials.

It seems that the increase in the melting peak and when the melting temperature remains steady, there is a secondary crystallization.<sup>15</sup> This effect is attributed to the formation of C=O groups.<sup>2,7</sup> We suggest that, in addition to this chemical effect, there

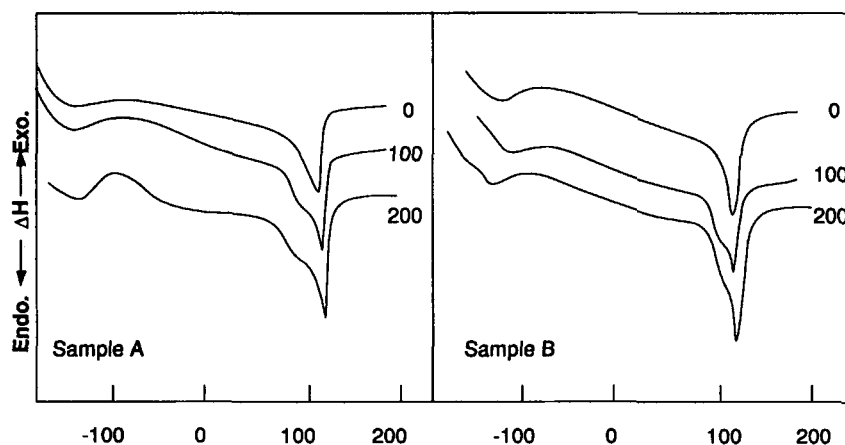
is a "physical" effect related to the widening of the melting peak (presence of different sizes of lamellae). The local melting of smallest sizes may occur before the one of thickest sizes.<sup>12</sup>

## CONCLUSION

The decay of mechanical properties and the evolution of IR spectrum of unstabilized polymer was not connected with crystallinity which remains steady in natural weathering. This effect confirms that the oxidation, followed by the buildup of carbonyl functions, occurs in amorphous phases. The rate of oxidation was similar in natural weathering and in accelerated photoirradiation, indicating that UV light is a more predominant factor than the temperature in degradation processes.

The widening of DSC curves near the melting point in accelerated photoirradiation and in thermal aging, when the formation of carbonyl groups was very weak in the latter, suggests that this evolution of the shape of the DSC curves is due to physical aging, which may occur simultaneously with the chemical aging in the exposed polymers. For natural weathering there is no change in the shape and the size of melting peak for both polymers. We think that the alternating of a day and a night may play a nonnegligible role on morphology. This has to be verified.

Simple correlations were not observed between the fall of mechanical properties (deformation at break) and the evolution of chemical structure and morphology for both polymers.



**Figure 8** Change in DSC curves in accelerated photoirradiation.

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