

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

M. SEBAA,<sup>1,\*</sup> C. SERVENS,<sup>2</sup> and J. POUYET<sup>1</sup>

<sup>1</sup>Laboratoire de Mécanique Physique, URA CNRS 867, 351 Cours de la Libération 33405 Talence Cedex, France, and <sup>2</sup>Institut du Pin, 351 Cours de la Libération 33405 Talence Cedex, France

## SYNOPSIS

Studies of the thermal and photodegradation of two commercial polymers, stabilized and unstabilized low-density polyethylene (LDPE), show the effects of weathering in 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 especially near the carbonyl regions, was also performed. The resistance to UV light irradiation as probed by deformation at break was superior in stabilized LDPE compared to unstabilized LDPE. Simple correlations were not observed between the fall of mechanical properties, the rate of oxidation, and the morphology.

## INTRODUCTION

When the polyethylene (PE) films for greenhouse covering are exposed to heat and UV light in presence of oxygen, they become brittle and visual signs of deterioration are apparent.

Degradation and embrittlement of these films can be related to the evolution of chemical structure and morphology (i.e., the crystallinity, the size, and the 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 carbonyls 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 the increase of the Young's modulus.<sup>2,5</sup>

The 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>4,7</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 increases 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 low-density polyethylene (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.

\* To whom correspondence should be addressed.

The aim of this work was the study of the relation 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 ageing, outdoor exposures, and accelerated UV photoirradiation.

## EXPERIMENTAL

### Material

The polymers used in the present study are two commercial LDPE films for greenhouse covering identified as Riblene type without stabilizers (Elkurty, 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' North) and Bandol, France (43° 16' North). 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 ageing exposures tests were carried out in a 70 ± 1°C regulated drying-oven.

### Instrumental

The tensile test data for both exposed and unexposed films were measured using an Instron 1186 machine. All tests were conducted at 20 < T°C < 25 and 40 < RH(%) < 45. The rate of strain was 170 min<sup>-1</sup> 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. In the following ΔOD is the difference of the intensity values between the exposed sample and the starting sample. The intensity was measured at the maximum absorption band.

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 finely

cut and put in an aluminum pan. The temperature of the samples is raised, together with an empty reference sample holder, at a constant rate of 10°C/mm. The differential power output 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:

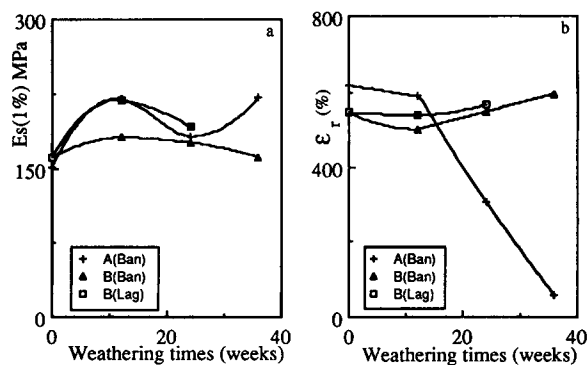
$$X(\%) = (\Delta H_f / \Delta H_f^c) 100$$

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>

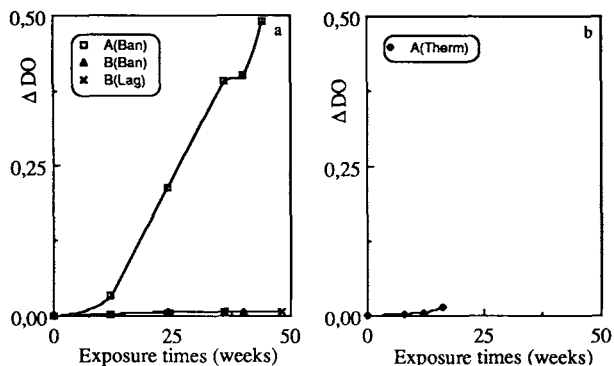
## RESULTS AND DISCUSSION

### Natural Weathering

The secant Young's modulus (at 1% strain) and deformation at break for both polymers have been plotted against weathering time in Figure 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.



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



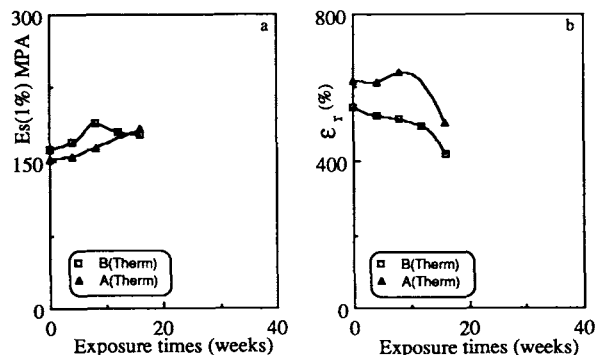
**Figure 2** Exposure time dependence of the relative optical density of carbonyl groups: (a) samples A and B exposed at Bandol and at Laghouat [(Ban) and (Lag), respectively], (b) sample A in thermal exposure [A(Therm)].

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)].

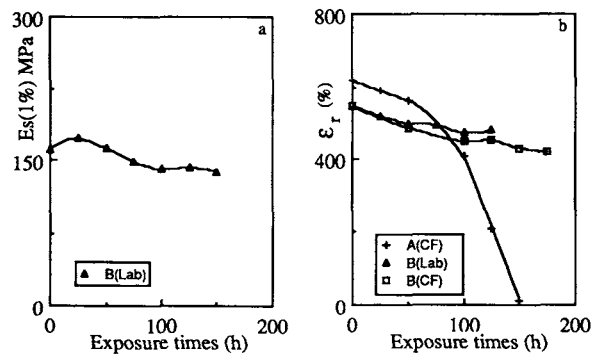
**Thermal Ageing**

The polymers have been observed to undergo changes similar to those found in photoirradiation except that during thermal ageing 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)] indicating the predominance of crosslinking reactions. A slight increase of the carbonyl group concentration for sample A [Fig. 2(b)] and no change in this regions for sample B was observed. The deformation at break for unstabilized polymer decreases more



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



**Figure 4** Exposure time dependence of the (a) secant modulus, (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)].

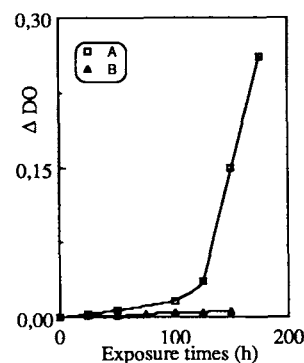
weakly than in natural weathering. The decrease of this property, for sample B, in this ageing type when it remains steady in natural weathering [Fig. 1(b)] and practically in accelerated photoirradiation [Fig. 4(b)] has not been elucidated.

**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 fu-



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

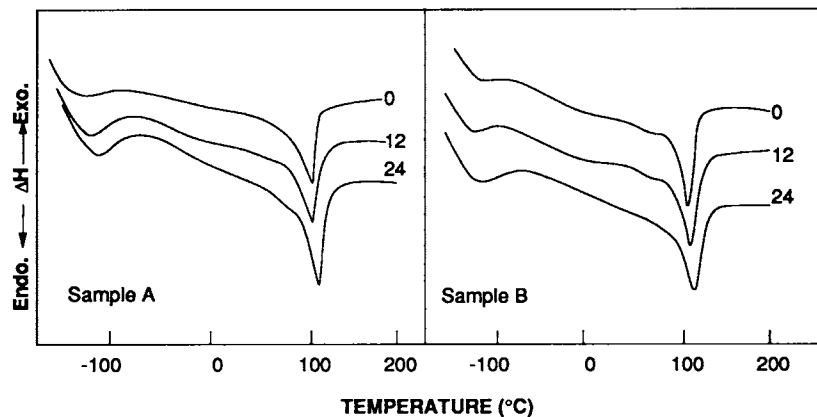


Figure 6 Change in DSC curves in natural weathering at Bandol.

sion ( $\Delta H_f$ ), 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 processing. 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 was observed for the 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 ageing 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 ageing types:

1. 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.
2. In thermal ageing, after 20 weeks of exposure, the widening of the melting peak was the most apparent effect for sample A.
3. 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

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

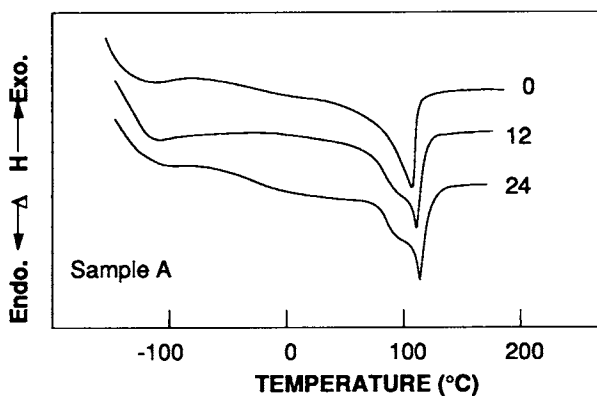


Figure 7 Change in DSC curves for unstabilized polymer: thermal ageing.

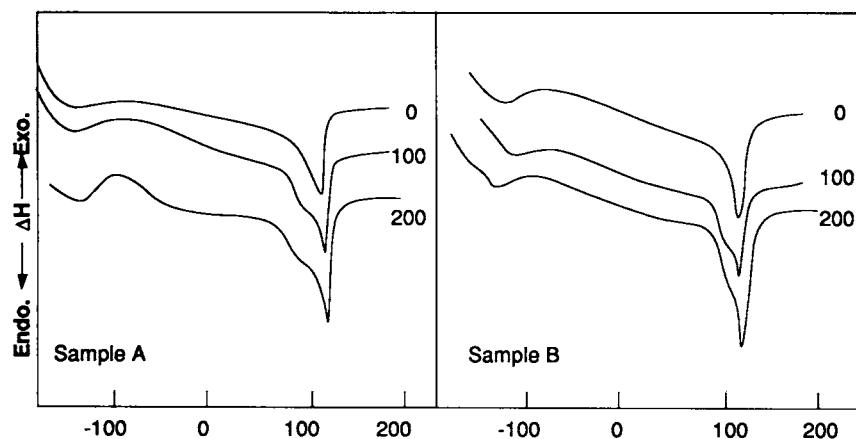


Figure 8 Change in DSC curves in accelerated photoirradiation.

suggest that in addition to this chemical effect there is a "physical" effect related to the shoulder appearing in the DSC profile in the region near and below 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 ageing when the formation of carbonyl groups was very weak in the later suggests that this evolution of the shape of the DSC curves is due to physical ageing, which may occur simultaneously with the chemical ageing 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 alternance 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.

The authors are indebted to Dr. J. Lemaire (CNEP-University of Clermont Ferrand II) and Mr. M. Beraud (Sta-

tion d'essais de vieillissement naturel de Bandol) for allowing us to carry out the artificial exposures in SEPAP 12-24 and the natural exposures at Bandol, respectively.

## REFERENCES

1. P. E. Cassidy and T. M. Aminabhavi, *J. Macromol. Sc.-Rev. Macromol. Chem.*, **21**(1), 89-133 (1981).
2. J. Verdu, *Vieillessement des plastiques*, Afnor Techniques, Paris, 1984.
3. S. H. Hamid, A. G. Maadhah, F. S. Qureshi, and M. B. Amin, *Arabian J. Sc. Eng.*, **13**(4), 503-531 (1988).
4. F. H. Winslow, W. Mareyek, and A. M. Trozollo, *Polym. Preprint, ACS Div. Polym. Chem.*, **10**(2), 1271-1280 (1969).
5. J. E. Guillet, *Pure Appl. Chem.*, **52**, 285-294 (1980).
6. C. G. Vonk, *J. Polym. Sci. Phys.*, **28**, 1871-1872 (1990).
7. N. C. Billingham, P. Prentice, and T. J. Walker, *J. Polym. Sci. Symp.*, **57**, 287-297 (1976).
8. A. Torikai, H. Shirakawa, and S. Nagaya, *J. Appl. Polym. Sci.*, **40**, 1637-1646 (1990).
9. A. Torikai, R. Geetha, and S. Nagaya, *J. Polym. Sci. Chem.*, **28**, 3639-3646 (1990).
10. F. Severini, R. Gallo, S. Ipsale, and N. Del Fanti, *Polym. Degrad. Stab.*, **14**, 341-350 (1986).
11. F. Severini, R. Gallo, S. Ipsale, and N. Del Fanti, *Polym. Degrad. Stab.*, **17**, 57-64 (1987).
12. M. Yasuniwa, S. Tsubakihara, and C. Nakafuku, *Polym. J.*, **20**(12), 1075-1082 (1988).
13. B. Wenderlich and C. M. Cormier, *J. Polym. Sci. Part A-2*, **5**, 987-988 (1967).
14. F. Rocaboy, *Comportement thermique des polymers synthétiques*, Vol. 1, Masson & Cie, Paris, 1972.
15. S. H. Hamid, F. S. Qureshi, M. B. Amin, and A. G. Maadhah, *Polym. Plast. Technol. Eng.*, **28**(5,6), 475-492 (1989).

Received March 21, 1991

Accepted September 4, 1991