

# CHANGES IN THE MECHANICAL PROPERTIES AND THERMAL BEHAVIOUR OF LDPE IN RESPONSE TO ACCELERATED THERMAL AGING

P. Budrugaec<sup>1</sup> and E. Segal<sup>2</sup>

<sup>1</sup>EUROTEST S.A., Splaiul Unirii Nr. 313, P.O. Box 4-77, Bucharest 73204

<sup>2</sup>Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest  
Bd. Republicii 13, Bucharest, Roumania

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## Abstract

The accelerated thermal degradation of low-density polyethylene (LDPE) was studied in air at atmospheric pressure and temperatures of 70, 80, 90 and 100°C. The changes in elongation at break, traction resistance and density as a result of accelerated thermooxidative degradation were followed. Thermal analysis curves (TG, DTG and DTA) of non-aged and thermally aged LDPE were recorded, and the thermal analysis results were compared with those relating to the variations in the elongation at break, the traction resistance and the density as a consequence of accelerated thermal aging.

**Keywords:** accelerated thermal aging, LDPE, mechanical properties, thermooxidative degradation

## Introduction

The use of polymeric materials requires a knowledge of their behaviour under the given environmental conditions (heat, light, humidity, nuclear radiation, etc.). To obtain this information rapidly, materials of particular interest are subjected to accelerated aging, with observation of the time dependence of mechanical properties (elongation at break, compression, traction resistance, residual deformation under constant deflection, etc.) or/and electrical properties (dielectric strength, resistivity, etc). In suitable cases, these results allow an evaluation of the lifetime under the operating conditions. The thermal lifetime is predicted by the procedure recommended by IEC-216 [1].

As far as thermal aging is concerned, when the acceleration factor is chosen, the accelerated degradation mechanism for the material should be identical to that of the degradation under the operating conditions. At the same time, in the interpretation of results obtained by accelerated aging, the mechanism of degradation should be taken into account so that the extrapolation to the operating conditions may lead to realistic values of thermal lifetimes. In order to attack these

problems, the methods of thermal analysis (TG, DTG, DTA or DSC) are useful, as they allow determination of the temperature range of thermal stability [2–8], the non-isothermal kinetic parameters of the degradation [8–15] and the changes undergone by the polymer as a consequence of accelerated aging [3, 16–18].

The thermooxidative degradation of polyethylene has been extensively investigated [19, 20]. Nevertheless, controversial results have been reported on the changes in mechanical properties due to thermooxidative degradation. A comparison of the results obtained by using physico-chemical methods on the same sort of polyethylene was recently reported [21].

The present paper reports the results of an accelerated thermal aging investigation of LDPE. The changes in elongation at break, traction resistance and density were determined. Thermal analysis (TG, DTG and DTA) was also performed on non-aged and thermally aged samples. The results obtained by processing the thermal analysis diagrams are correlated with those obtained from the variation in mechanical properties as a result of thermal aging.

## Experimental

The LDPE used was synthesized in the Petrochemical Company Brazi (Romania). The main properties of this material are  $MW=30\,500$ ;  $T_m=105^\circ\text{C}$ ; and density  $=0.915\text{ g cm}^{-3}$ .

The accelerated thermal aging of the test specimens was performed in a WSU-200 oven with forced air circulation, in which the temperature was kept constant with an accuracy of  $\pm 2^\circ\text{C}$ .

The elongation at break and traction resistance of the initial test specimens and of the specimens submitted to accelerating aging were determined with an accuracy of  $\pm 1\%$  by using a universal Monsanto T-10/E machine.

The test specimens (dumbbell-shaped) were prepared from LDPE according to ASTM D-412 requirements.

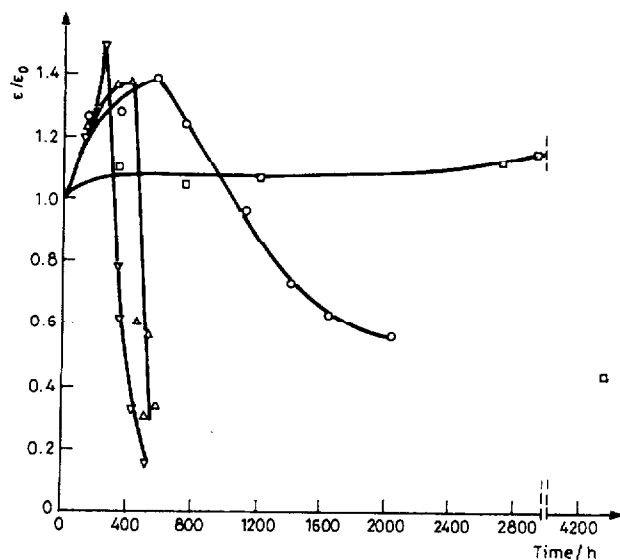
The density of the whole sample was determined by weighing in heptane and in air.

Thermal analysis curves (TG, DTG and DTA) of powdered samples were recorded with a Q-1500 D (MOM, Budapest) Paulik-Paulik-Erdey derivatograph in static air atmosphere in the temperature range  $20\text{--}500^\circ\text{C}$  at a heating rate of  $2.50^\circ\text{C min}^{-1}$ .

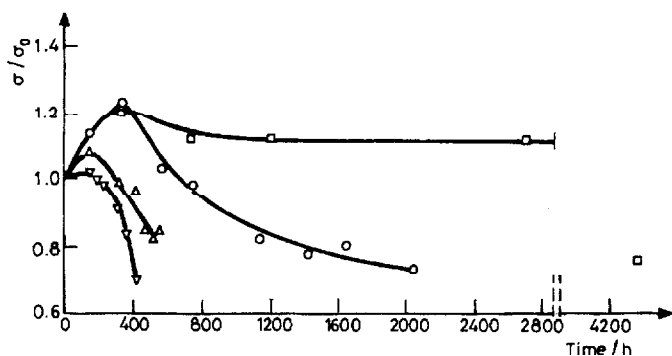
## Results and discussion

### *Isotherms showing changes in mechanical properties*

Figures 1 and 2 depict the change in the relative elongation at break ( $\epsilon/\epsilon_0$ ), here  $\epsilon_0$  is the initial value of this property, with current value  $\epsilon$ , and also that in the relative traction resistance of  $\sigma/\sigma_0$  LDPE subjected to accelerated aging in air at atmospheric pressure and at temperatures of 70, 80, 90 and  $100^\circ\text{C}$ .



**Fig. 1** Variation with time of the relative elongation at break for thermally aged LDPE in air:  
 □ - 70°C; ○ - 80°C; △ - 90°C; ▽ - 100°C



**Fig. 2** Variation with time of the relative traction resistance for thermally aged LDPE in air:  
 □ - 70°C; ○ - 80°C; △ - 90°C; ▽ - 100°C

Each isotherm exhibits two portions, an initial one in which the relative property increases with the duration of accelerated thermal aging, followed by another one in which the property decreases with the duration of aging.

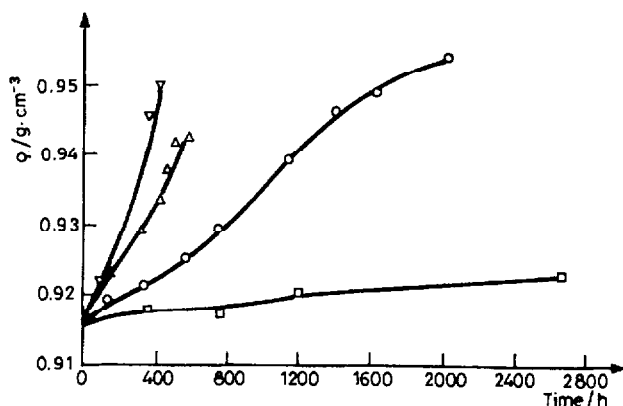
In the first portion, the relative property is higher than unity. Figures 1 and 2 demonstrate that an increase of temperature leads to a shorter time until the position of the maximum in the isotherm.

As far as the second portion is concerned, the mechanical degradation of the material decreases with the duration and the temperature of thermal degradation.

The initial increase in the relative property can be assigned to the initial cross-linking of LDPE. The subsequent decrease is due to the thermooxidation of LDPE. In order to confirm this finding, experiments on LDPE degradation in air at pressures higher than 1 atm were carried out. Earlier results [22] demonstrated that the mechanical degradation of LDPE is strongly accelerated by an increase of the oxygen partial pressure.

### *Isotherms showing change in density*

Figure 3 presents isotherms for LDPE subjected to thermally accelerated aging in air at atmospheric pressure and the temperatures at which the isotherms of the changes in the mechanical properties were recorded



**Fig. 3** Variation with time of the density for thermally aged LDPE in air:  $\square$  – 70°C;  $\circ$  – 80°C;  $\triangle$  – 90°C;  $\nabla$  – 100°C

The density of LDPE increases with the temperature and the duration of thermally accelerated aging. The increase in density exhibits a tendency towards the crystal density of PE ( $\approx 1 \text{ g cm}^{-3}$ ). The 80°C isotherm in the first portion ( $t < 350 \text{ h}$ ) reveals a slow increase of density with time, while the increase is more rapid in the second portion ( $t > 350 \text{ h}$ ). The other isotherms exhibit similar trends. The initial slow increase can be assigned to the LDPE cross-linking which occurs at relatively short durations of aging. At higher durations of thermal aging, the LDPE density increase can be explained in terms of the thermooxidation of LDPE [21].

### *TG, DTG and DTA data*

Figure 4 depicts TG, DTG and DTA curves for the initial LDPE. The DTA curve displays a first-order phase change (melting or softening) through the minimum I at  $\approx 100^\circ\text{C}$ . At higher temperatures, the melted polyethylene under-

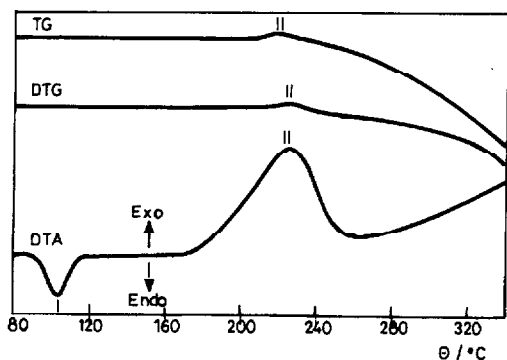


Fig. 4 TG, DTG and DTA curves of non-aged LDPE in static air atmosphere at a heating rate of  $2.5^{\circ}\text{C min}^{-1}$

goes an exothermic change (peak II in the DTA curve), accompanied by a slight increase in mass. In order to account for this, a DTA curve of LDPE was recorded in argon. This curve no longer exhibits peak II. Thus, the exothermic peak corresponds to the thermooxidation of LDPE with the generation of solid products, probably hydroperoxides, due to the attack of singlet oxygen ( $^1\text{O}_2$ ,  $^1\Delta_g$ ) on the methylene groups from the monomeric units [23]. At higher temperatures, thermooxidative degradation with the generation of volatile products occurs. Such a thermooxidative degradation characterized by two kinds of oxidation (one accompanied by a mass increase and the other by the release of volatile compounds) was previously reported in connection with the thermooxidative degradation of certain polymeric materials [13, 15, 24–27].

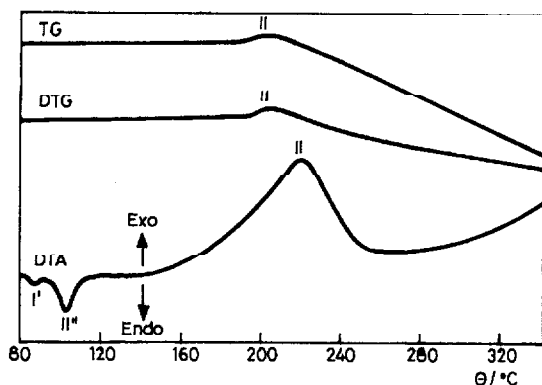


Fig. 5 TG, DTG and DTA curves of aged LDPE ( $100^{\circ}\text{C}$ , 192 h) in static air atmosphere at a heating rate of  $2.5^{\circ}\text{C min}^{-1}$

Figures 5 and 6 show TG, DTG and DTA curves for thermally aged LDPE samples.

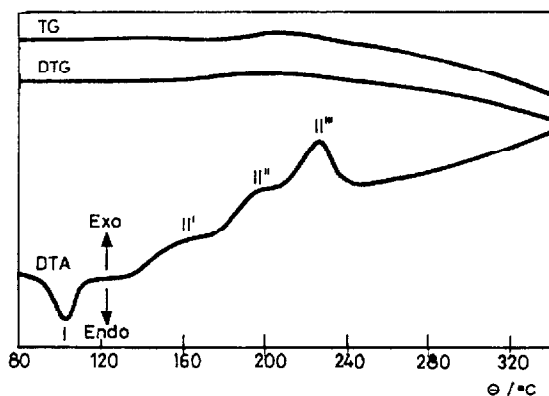


Fig. 6 TG, DTG and DTA curves of aged LDPE (80°C, 750 h) in static air atmosphere at a heating rate of 2.5°C min<sup>-1</sup>

Figure 5 reveals that thermal aging of LDPE for 112 h at 100°C results in splitting of the melting minimum into two minima, located at 85 and 105°C. This phenomenon, which is common for all LDPE samples subjected to thermally accelerated aging at 90 and 100°C, can be explained by the scission of some of the material chains leading to a mixture of two materials with different melting points.

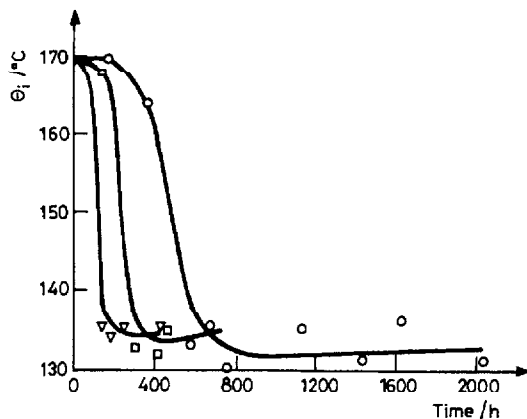


Fig. 7 Variation in temperature at which the non-isothermal thermooxidation of LDPE begins as a function of the duration of accelerated thermal aging ◦ – 80°C; ◻ – 90°C; ▽ – 100°C

As shown in Fig. 6, on thermal aging at 80°C for 750 h, the thermooxidative peak corresponding to the formation of solid products is split into three peaks. The splitting of peak II (Fig. 4) was evidenced for some of the thermally aged samples (80°C, 577 h; 80°C, 750 h; 80°C, 1344 h; 90°C, 316 h; 90°C, 408 h and

90°C, 456 h). The splitting of exothermic peak II can be attributed to the scission and cross-linking which accompany the thermal aging and which determine the generation of various oxidation centres with different reactivities.

Figure 7 shows the variation in the temperature at which the thermooxidation with the generation of solid compounds begins ( $\theta_i$ ) as a function of the duration of thermal aging. After short periods of aging, significant changes in this temperature can be observed. The subsequent thermal aging causes practically no further change in the value of  $\theta_i$ . The decrease in the initial temperature of thermooxidation can be assigned to the initial cross-linking of LDPE leading to tertiary carbon atoms. It is well known that the chemical reactivity of the carbon atoms of the polymer increases with the degree of substitution [23, 27].

## Conclusions

Results relating to the changes in the elongation at break, the traction resistance and the density of LDPE as a consequence of accelerated thermal aging have been reported. Thermal analysis experiments have also been carried out. The changes in the thermal behaviour of LDPE following accelerated thermal aging have been established. It has been demonstrated that accelerated thermal aging in air atmosphere is accompanied by cross-linking, scission of the macromolecular chain and thermooxidation.

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