

*Dedicated to the memory of Professor
I.G. Murgulescu (1902–1991)*

THE USE OF HIGH PRESSURES IN ORDER TO ACCELERATE THERMO-OXIDATIVE AGING OF LDPE

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The accelerated thermal degradation of low-density polyethylene (LDPE) was studied in air at 80°C and at the pressures of 1-6 atm. The changes in elongation at break and traction resistance as a result of accelerated thermo-oxidative 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 elongation at break and the traction resistance as a consequence of accelerated thermal aging.

INTRODUCTION

The practical use of polymeric materials requires the knowledge of their behaviour under given environmental conditions (heat, light, humidity, nuclear radiation, etc.). To obtain this information rapidly, materials of particular interest are submitted to accelerated aging, with recording of the time dependence of mechanical properties (elongation at break, compression, traction resistance, residual deformation under constant deflection, etc.), electrical properties (dielectric strength, resistivity, etc.) or/and weight loss. 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 the IEC-216 Standard.¹ According to this procedure, which consists in thermal aging in air, at atmospheric pressure, the assessment of a material requires approximately 10-12 months of accelerated aging. In previous papers²⁻⁹ it was shown that a decrease of the experiment time for prediction of the thermal lifetime could be realized through accelerated thermal aging in oxygen or air at supraatmospheric pressures. The analysis of the obtained results for ethylene-propylene rubber,^{2,3} nitrile-butadiene rubber⁵ and glass-reinforced epoxy resin⁴ led to the conclusion that the oxygen or the air pressure are accelerating factors for thermal degradation. A kinetic equation for the change of the property in terms of the air or the oxygen pressure, temperature and time was derived. The problem that arises is whether this equation could be applied for other classes of polymeric materials too.

This paper reports the results of accelerated thermal aging of LDPE, in air, at 80°C and $P \geq 1$ atm. The changes in elongation at break and traction resistance were determined. Thermal analysis curves (TG, DTG and DTA) were also carried out 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 at the Petrochemical Company Brazi (Roumania). The main properties of this material are: MW = 30500, $T_m = 105^{\circ}\text{C}$ and density 0.915 g.cm^{-3} .

The air-accelerated aging ($P = 1 \text{ atm}$) was performed within a WSU-200 chamber with air-forced circulation and temperature stabilization accuracy within the limits of $\pm 2^{\circ}\text{C}$.

The block diagram of the unit used for accelerated thermal ageing under air pressure and the operation of the unit were shown in a previous paper.²

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

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

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 of $20\text{-}500^{\circ}\text{C}$ and a heating rate of 2.5 K.min^{-1} .

RESULTS AND DISCUSSION

Isotherms showing changes in mechanical properties

In order to show the accelerating effect of air pressure on the thermo-oxidative degradation of LDPE, the accelerated aging was studied at air pressures 1 atm, 4 atm, 5 atm and 6 atm, and 80°C .

Figs. 1 and 2 depict the changes in time of the relative elongation at break ($\frac{\epsilon}{\epsilon_0}$, here ϵ_0 is the initial value of this property, with current value ϵ) and of the relative traction resistance ($\frac{\sigma}{\sigma_0}$).

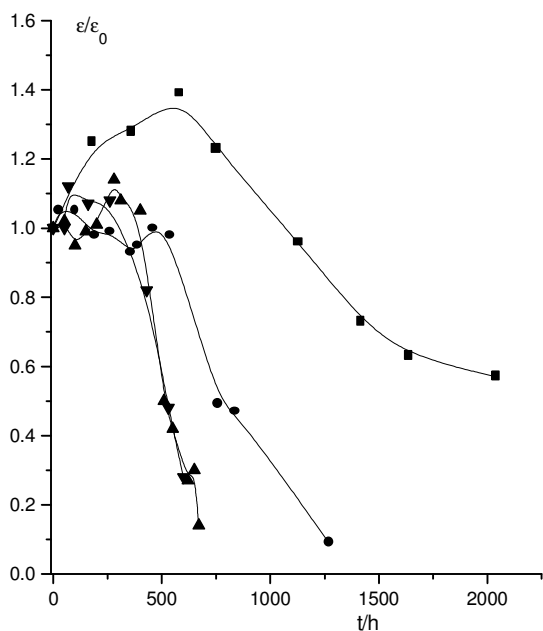


Fig. 1 – Change in time of the relative elongation at break for thermally aged LDPE in air, at 80°C .
 ■ 1 atm; • 4 atm; ▲ 5 atm; ▼ 6 atm.

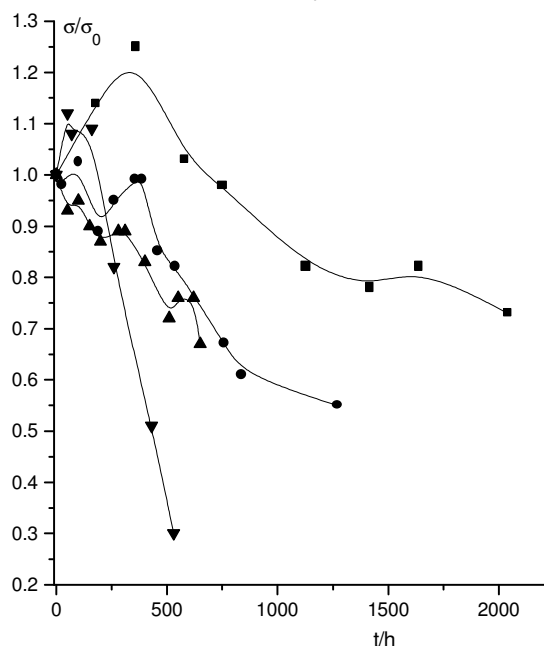


Fig. 2 – Change in time of the relative traction resistance for thermally aged LDPE in air, at 80°C .
 ■ 1 atm; • 4 atm; ▲ 5 atm; ▼ 6 atm.

Each isotherm exhibits two portions, an initial one characterized by one or two peaks, followed by another one in which the property decreases with the duration of aging. In the first portion there are many points where the relative property is higher than unity. For $\frac{\epsilon}{\epsilon_0}$ vs. t as well as for $\frac{\sigma}{\sigma_0}$ vs. t , the isotherm

recorded at $P = 1$ atm exhibits only one maximum while the isotherms recorded at higher pressures exhibit two maxima. Single maximum isotherms were reported in a previous paper¹⁰ where the results obtained on the investigation of accelerated thermal degradation of LDPE in air, at various temperatures, and $P = 1$ atm were presented. The existence of these two portions of the thermal degradation isotherms is characteristic for the thermal degradation of some composites which contain epoxidic resins too.^{4,9} According to Tsotsis *et al.*,⁹ such a behaviour could be explained by the occurrence of two parallel processes undergone by the material during heating, namely cross-linking and chain scission due to the oxidation reaction. Cross-linking trends to stiffen the polymer by creating additional bonds between polymer chains. The relative rate of chain extension due to cross-linking to the rate of scission due to the oxidation reaction dictates whether properties increase or decrease. Furthermore, as exposure times increase, the number of potential reactive sites for cross-linking decreases as they are consumed, so that chain scission will eventually have a much higher effect relatively to cross-linking. As far as the second portion of the isotherms is concerned, the mechanical properties of the material decrease with the duration of thermal degradation and the air pressure. In this portion the thermo-oxidation process which occurs with scission of the macromolecular chain prevails.

For $P = 5$ atm and $P = 6$ atm, the isotherms $\frac{\epsilon}{\epsilon_0}$ vs. t practically coincide. Such a coincidence was not

put into evidence for the isotherms $\frac{\sigma}{\sigma_0}$ vs. t . This shows that at relatively high values of the pressure, at high values of the time of degradation, the scission of macromolecular chains occurs without the breaking of the bonds between chains generated during cross-linking which occurs at lower duration of thermal aging.

In previous papers²⁻⁶ we derived the dependence of the property of some polymeric materials on temperature, air or oxygen pressure and the duration of thermal aging. The derivation was based on the assumption that during thermal degradation only one process prevails and can be considered as rate limiting. Obviously, such a treatment cannot be applied for LDPE that exhibits a complex mechanism of degradation.

TG, DTG and DTA data

Fig. 3 depicts the TG, DTG and DTA curves for the initial (non-aged) LDPE. The DTA curve displays a first-order phase change (melting or softening) through the minimum I at $\approx 105^\circ\text{C}$. At higher temperatures, the melted LDPE undergoes an exothermic change (peak II in the DTA curve), accompanied by a slight increase in mass. By comparison of the DTA curve obtained in air atmosphere with that obtained in argon atmosphere, it was demonstrated¹⁰ that the exothermic peak II corresponds to the thermo-oxidation of LDPE with generation of solid products, probably hydroperoxides. At higher temperatures, thermo-oxidative degradation with generation of volatile products occurs. Such a thermo-oxidative degradation characterized by two kinds of oxidation (one accompanied by a mass increase and the other by release of volatile compounds) was previously reported in connection with the thermo-oxidative degradation of certain polymeric materials.¹¹⁻¹⁵

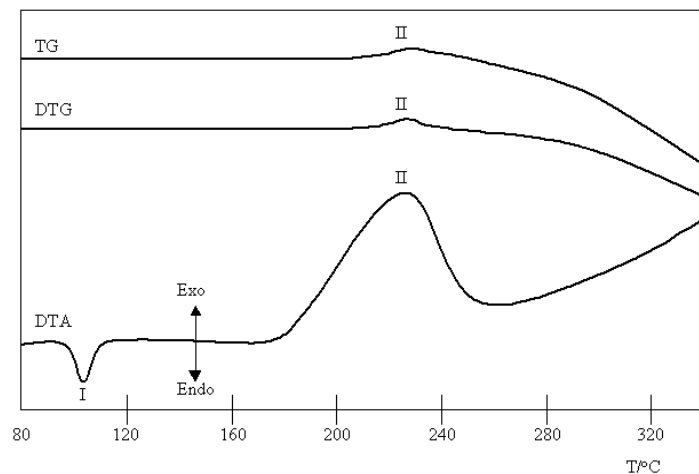


Fig. 3 – TG, DTG and DTA curves of non-aged LDPE in static air atmosphere, at a heating rate of $2.5 \text{ K}\cdot\text{min}^{-1}$.

The TG, DTG and DTA curves corresponding to thermally aged LDPE at $P > 1$ atm are similar with those obtained for the LDPE samples aged in air at $P = 1$ atm, reported in a previous paper.¹⁰ It was obtained that:

- the beginning temperature of process II (T_I) decreases sharply at aging times corresponding to the beginning of the second portion of the curves $\frac{\mathcal{E}}{\mathcal{E}_0}$ vs. t and $\frac{\sigma}{\sigma_0}$ vs. t . For example, at $P = 5$ atm, $T_I = 160-170^\circ\text{C}$ for $t < 500$ h and $T_I = 127^\circ\text{C}$ for $t = 668$ h.
- some peaks of the thermo-oxidation with oxygen absorption exhibit two steps; these steps belong to the first portion of the curves $\frac{\mathcal{E}}{\mathcal{E}_0}$ vs. t (or $\frac{\sigma}{\sigma_0}$ vs. t). The splitting of the exothermic peak II can be attributed to the scission and cross-linking which accompany the thermal ageing and which determine the generation of various oxidation centers with different reactivities.

CONCLUSIONS

Results concerning to changes in the elongation at break and the traction resistance of LDPE as a consequence of thermal aging in air, at 80°C and different pressures ($P \geq 1$ atm) were reported. Thermal analysis experiments were carried out. It was demonstrated that cross-linking and scission of the macromolecular chain by thermo-oxidation accompany accelerated thermal aging in air. This study reveals the importance of air pressure as an accelerating factor in thermal degradation of LDPE.

REFERENCES

1. IEC 216/1990, *Guide for determination of thermal endurance properties of electrical insulating materials*, Ed. Bureau Central de la Commission Electrotechnique Internationale, Genève, Suisse, 1990.
2. S. Ciutacu, P. Budrugaec, G. Mares and I. Boconcios, *Polym. Deg. Stab.*, **1990**, 29, 321.
3. G. Mares and P. Budrugaec, *Elastomer technology Handbook*, Ed. N. P. Cheremisinoff, CRC Press, Boca Raton, Ann Arbor, London, Tokyo, **1993**, Ch. 10.
4. S. Ciutacu, P. Budrugaec and I. Niculae, *Polym. Deg. Stab.*, **1991**, 31, 365.
5. P. Budrugaec, *Polym. Deg. Stab.*, **1995**, 47, 129.
6. P. Budrugaec, *die Angewandte Makromolekulare Chemie*, **1997**, 247, 19.
7. T. K. Tsotsis, *J. Comp. Mat.*, **1995**, 29, 410.
8. T. K. Tsotsis, *J. Comp. Mat.*, **1998**, 32, 1115.
9. T. K. Tsotsis, S. Keller, J. Bardis and J. Bish, *Polym. Deg. Stab.*, **1999**, 64, 207.
10. P. Budrugaec and E. Segal, *J. Thermal Anal.*, **1998**, 53, 801.
11. M. Iring, Z. H. Laslo, T. Kelen and F. Tudos, *Proc. 4th ICTA Budapest*, **1975**, Vol. 2, p. 127.
12. F. G. Will and D. W. McKee, *J. Polym. Sci., Polym. Chem. Ed.*, **1983**, 21, 3479.
13. L. Slusarski, *J. Thermal Anal.*, **1984**, 29, 905.
14. E. Segal, P. Budrugaec and S. Ciutacu, *Thermochim. Acta*, **1990**, 164, 161.
15. P. Budrugaec, *Polym. Deg. Stab.*, **1992**, 38, 165.