Chemical changes in ethylene–propylene elastomers during salt thermal ageing

Traian Zaharescu
ICPE SA, Laboratory 68, 313 Splaiul Unirii, Bucharest, RO 74204, Romania
(Received 18 April 1994)

The isothermal degradation of ethylene–propylene elastomers, ethylene–propylene rubber and ethylene–propylene–diene terpolymer, in four NaCl aqueous solutions (0%, 0.1%, 1.0% and 10%) was investigated. The film specimens were examined by i.r. spectroscopy to detect the evolution of oxygenated group content. It was shown that the lower the salt concentration, the more oxidative damage takes place in the polymer. There is a large discrepancy between the carbonyl and hydroxyl formation rates of these two materials. The ethylene–propylene copolymer is more oxidatively stable than its corresponding terpolymer.

(Keywords: ethylene–propylene copolymers; thermal ageing; degradation)

Oxidative degradation experiments on polymers during their thermal treatment in salt solutions represent a check on their stability under environmental stress. For example, in the case of electrical wire and cable insulation, the stability of ethylene–propylene copolymer upon oxidation is an important parameter to consider when recommending it for any outdoor application.

Some recent papers have studied the oxidation of cable-grade material (polyethylene, crosslinked polyethylene[1], low-density polyethylene[2] and ethylene–propylene rubber (EPR)[3]) by means of accelerated tests, and looked at the consequences on service time of the electrical insulation or commercial article. This type of experiment successfully predicts the stability and lifetime of most practical polymers.

In order to study the response of ethylene–propylene elastomers, EPR and ethylene–propylene–diene terpolymer (EPDM), to the aggressive attack of NaCl solutions, a short study on their thermal stability in these solutions was performed at 90°C in the uncompounded state.

The test materials had a propylene content of 30%. Ethylene norbornene was the added diene in the terpolymer structure. The film specimens (30 μm thick) were prepared by solvent removal from $CHCl_3$ solutions. Before heating, the samples were irradiated to a total dose of 100 kGy with a ^{60}Co source. Thermal degradation was carried out by film immersion in four aqueous NaCl solutions with salt concentrations of 0%, 0.1%, 1.0% and 10%. The full i.r. spectra were recorded.

Although there have been numerous studies on the thermal ageing of polyolefins in air, there have been fewer studies on polymer degradation in an aqueous environment. Stability tests are required by both suppliers and manufacturers, because they qualify the outdoor lifetime of products.

During thermal ageing of elastomers in NaCl aqueous solutions, the preirradiated films exhibit changes mainly in the 1720 and 3350 cm^{-1} absorption bands, providing evidence of the oxidative attack of external chemical agents. Thus, some features of this process may be emphasized.

The initial radicals formed after any energy action on the polymers preferentially abstract the molecular oxygen dissolved in the polymer mass, or diffuse towards its inner layers to generate peroxy radicals $RO_2^{\bullet}$ and finally, stable oxygenated molecules.

At the early stage of ageing, the C=O and C–OH formation rates are not dependent on salt concentration, and the curves are close together (*Figures 1a* and *2a*). The concentration of oxygen-containing groups increases in the same manner, which demonstrates their simultaneous and competitive formation; the rate of carbonyl group accumulation is higher than that of hydroxyl groups. This fact is explained by several formation routes, according to the reaction mechanism[4].

Later, the development of the oxygenated molecule concentration is quite different: while the carbonyl concentration tends to reach increasingly high levels, the hydroxyl concentration reaches a steady state after a certain time (*Figures 1* and *2*). This means that the hydroxyl groups participate to a larger extent in the formation of ketones, acids, esters and ethers (measured within the 1720–1750 cm^{-1} band) than in generating alcohols (3350 cm^{-1} band).

The presence of ethylidene norbornene in EPDM promotes its greater ageing relative to EPR copolymer tested under the same conditions. The radical uptake time required by the EPDM is half that of EPR. This behaviour is expected, because of the higher susceptibility of the terpolymer to be oxidized by any oxidative environment[5,6].

The effect of salt on the ethylene–propylene elastomers is revealed by the increased oxidation rates for both materials. The lower the salt concentration, the greater the polymer degradation. It may be supposed that the chloride ion reaction with the hydroperoxyl present yields the intermediate entities $RO^{\bullet}$ and HO^{-}, which sub-

0032-3861/94/17/3795–02

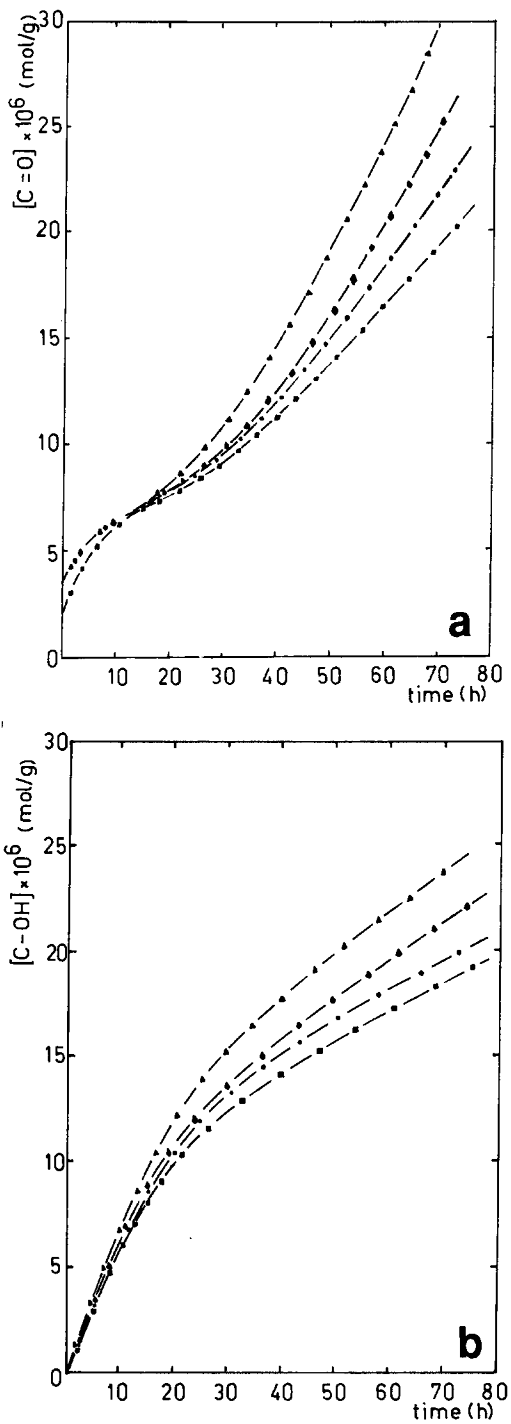

Figure 1 Changes of the oxygenated group concentrations for ethylene–propylene copolymer degradation: (a) C=O evolution; (b) C–OH evolution. ■, 0% solution; ▲, 0.1% solution; ◆, 1% solution; ●, 10% solution

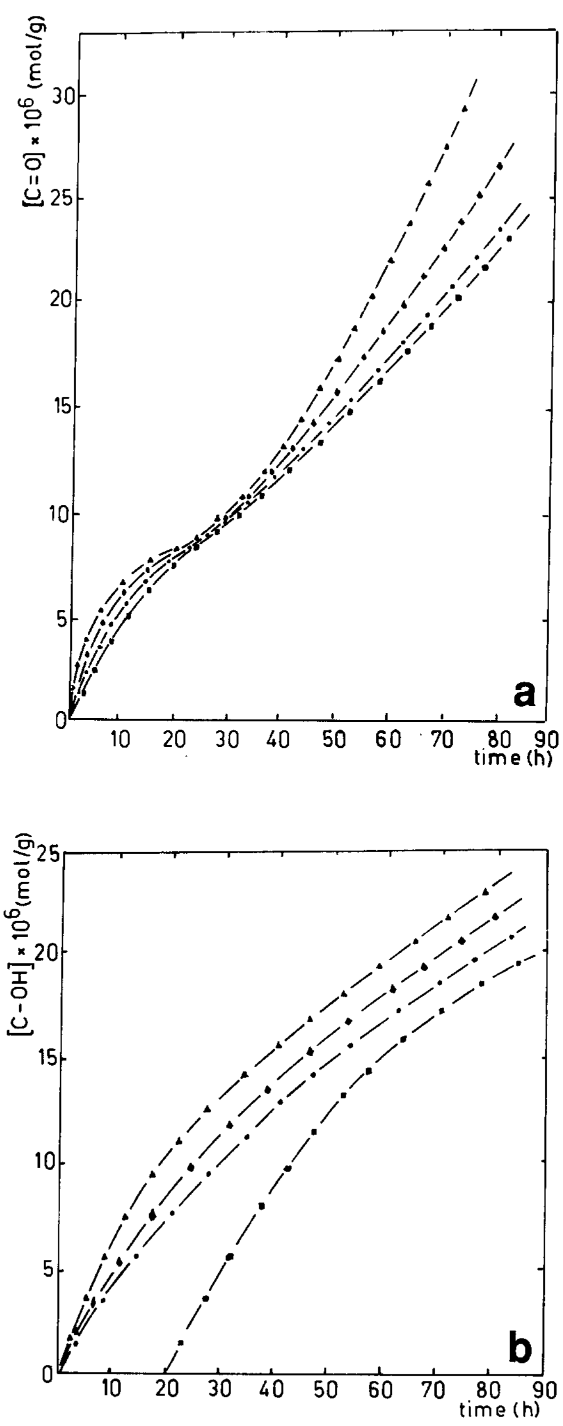

Figure 2 Changes of the oxygenated group concentrations for the ethylene–propylene–diene copolymer degradation: (a) C=O evolution; (b) C–OH evolution. Symbols as in *Figure 1*

sequently act as reactive species to form the final stable products, according to the following equation:

$$\mathrm{ROOH+Cl^- \rightarrow RO^{\cdot}+HO^- +Cl^{\cdot}}$$

Moreover, the chlorine atoms may generate new radicals by hydrogen abstraction from the polymer macromolecules, the propagation step of the chain reaction being thus ensured.

The presence of low NaCl concentrations in a wet outdoor environment, together with other salts, causes severe oxidative degradation of polymers, which decreases the product lifetime to a great extent.

References

1 Densley, R. J., Banji, S. S. and Crine, J. P. International Symposium on Electrical Insulation, Toronto, 1990, p. 178
2 Panel, B. and Gueguen, V. Proceedings of 7th Symposium on Electrets, Berlin, 1991, p. 944
3 Henry, J. L., Ruaya, A. L. and Garton, A. *J. Polym. Sci., Part A, Polym. Chem.*, 1992, **30**, 1693
4 Carlsson, D. J., Chmela, S. and Lacoste, J. *Macromolecules* 1990, **23**, 4934
5 Zaharescu, T., Setnescu, R. and Giurginca, M. *Rev. Roum. Chim.* in press
6 Seguki, T., Arakawa, K., Haiakawa, N., Watanabe, Y. and Kuiryama, I. *Radiat. Phys. Chem.* 1982, **19**, 821