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Oxygen consumption in EPDM irradiated under different oxygen pressures and at different LET

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Abstract

We conceived a novel set-up for measuring the radiochemical yields of oxygen consumption in polymers. The measurement is based on a sampling of the gas mixture with a mass spectrometer, before and after irradiation. We irradiated an ethylene, propylene and 1,4-hexadiene terpolymer (EPDM) with 1 MeV electron and 10.75 MeV/A carbon beams. Samples were irradiated under oxygen within a wide range of pressure (5–200 mbar). The yields under C irradiation are four times smaller than the yields under electron irradiation. This shows that radiooxidation is very sensitive to the linear energy transfer of the projectiles and hence to the heterogeneity of the energy deposition. The oxygen consumption yields do not vary significantly in the range of pressure investigated; even at 5 mbar, the kinetics is still governed by the bimolecular recombination of peroxy radicals.

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1. Introduction

Under the presence of oxygen in the irradiation atmosphere, ionising radiation generates in polymers a well-known degradation process called radiooxidation. Radiooxidation is induced by the reaction of molecular oxygen dissolved in the material with the radiation-induced macroradicals. Consequently, oxygen is consumed with a radiochemical yield ($G(–O_2)$); the sign minus stands for consumption in contrast to production. Oxidised products are generated within the polymeric chains and some oxygen containing molecules as CO, CO_2 and H_2O are released from the irradiated samples. As the Henry low is generally followed in polymers in the range of pressure of interest here, the molecular oxygen concentration $[O_2]$ is proportional to the oxygen partial pressure in the

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irradiation atmosphere ($P(O_2)$). When the oxygen consumption rate ($r(–O_2)$) is high, this proportionality is not true any more within the full thickness (d) of the sample. Oxygen does not diffuse fast enough to compensate the O_2 consumption in the inner part of the sample. This is the so-called diffusion-limited oxidation regime characterised by an oxidation profile in depth. In our work, we have carefully chosen the experimental conditions to avoid being in this diffusion-limited oxidation regime. The quantification of the oxidation level generated in the sample can be carried on either by measuring the oxidised groups enclosed in the film or by directly measuring $r(–O_2)$.

The dosage of oxidised groups is generally done by Fourier Transform Infrared Spectroscopy (FTIR). However an alternative interesting study by solid-state Nuclear Magnetic Resonance has recently been done using polymers aged under $^{17}O_2$ [1]. The first difficulty of FTIR quantification is the presence of many different species having common chemical groups and giving bad-resolved IR bands. For instance in polyolefins, hydroperoxides, alcohols and acid contribute to the broad hydroxyl stretching band; the carbonyl stretching band cover vibrations from ketones, esters, acids, aldehydes and peracids. To differentiate this species, derivation reactions were developed [2,3]. They mainly use gaseous reactants that penetrate the solid. The calculation of $G(–O_2)$ from FTIR measurements is obviously not very accurate as the many molar extinctions coefficients needed are not precisely known and because it is impossible to be exhaustive in measuring all the products, including the gaseous ones. If the measurement of carbonyl and hydroxyl band intensities can be performed on-line [4], this is obviously not the case for derivation reactions. The dosage of the oxidised groups generally includes post-irradiation effects.

The direct measurement of $G(–O_2)$ is always based on the measurement of the decrease of $P(O_2)$ during irradiation of samples in a closed cell. The radiation-induced variation of the cell pressure is a balance between a decrease of $P(O_2)$ and an increase due to radiation-induced production of small molecules that are released from the samples. In addition to the yet mentioned molecules containing oxygen atoms, molecular hydrogen is usually abundantly produced. Therefore, the different teams have discarded to base their estimation of $G(–O_2)$ on the plain variation of the cell pressure. One of the pioneering measurements of $G(–O_2)$ was done by Decker [5] by measuring total pressures before and after condensation of the heaviest molecules at 77 K, and by removing O_2 in a Cu + CuO furnace. The others active groups in the field (Sandia Laboratories in USA [6] and Takasaki in Japan [7,8]) have used gas chromatography. For our work we have developed a method based on mass spectrometry (MS).

2. Radiooxidation kinetics

The simplest kinetic model used in polyolefins for describing radiooxidation considers two radical species (the macro radical $P^\bullet$ and the peroxy $POO^\bullet$) and four steps [9]. First step (a) is the radiation inducing of $P^\bullet$ with the concomitant H_2 generation; (b) is oxidation of $P^\bullet$ giving $POO^\bullet$; (c) is propagation which induces the chain reaction $POO^\bullet \rightarrow POOH + P^\bullet$; (f–h) are the bimolecular termination steps involving respectively the reactions $P^\bullet + P^\bullet$, $P^\bullet + POO^\bullet$ and $POO^\bullet + POO^\bullet$. Irradiations times are generally long enough to ensure that radicals reach their stationary level. The relative importance of the three bimolecular terminations greatly depends on $[O_2]$. Basically, at sufficiently high $[O_2]$, it is only necessary to consider reaction (h) ($POO^\bullet + POO^\bullet$). When $[O_2]$ decreases, only (g) and (f) successively operates. In fact, scanning $[O_2]$ within a wide range allows to sequentially turn on and off each of the three recombination regimes. This clearly decreases the number of unknown parameters and greatly helps to experimentally determine the kinetic constants. Moreover, the three termination regimes are characterised by different dependences with respect to $[O_2]$. When step (h) dominates (highest $[O_2]$), $G(–O_2)$ does not depend on $[O_2]$. When step (g) dominates (intermediate values of $[O_2]$), the dependence of the yield with $[O_2]$ is given by $G(–O_2) = A + B\sqrt{[O_2]}$, A and B being constants. When step (f) dominates (lowest $[O_2]$), $G(–O_2)$ shows a linear