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Determination of long-term radiation ageing in polymers

**Part 1. Techniques for monitoring
diffusion-limited oxidation**

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National foreword

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INTRODUCTION

It is usually necessary to estimate the anticipated lifetime of a polymeric material in various use environments. For extended lifetimes (years), this often requires the application of accelerated ageing techniques which typically involve the modelling of results obtained at higher-than-ambient environmental stress levels. For many practical applications, air is present during environmental exposures – this usually implies that important oxidation effects underlie the degradation of the material. Unfortunately, exposure of polymers to air during ageing often results in inhomogeneously oxidized samples, a complication which affects attempts both to understand the oxidation process and to extrapolate accelerated exposures to long-term conditions.

The most important inhomogeneous oxidation complication involves diffusion-limited oxidation. The significance of this complication in various environments, including thermal [1]* radiation [2 to 4] and ultraviolet [5] has been recognized for many years. Diffusion-limited oxidation can occur whenever the rate of oxygen consumption in a material is greater than the rate at which oxygen can be resupplied to the interior of the material by diffusion processes from the surrounding air atmosphere. Such instances result in a smooth drop in the oxygen concentration from its equilibrium sorption value at the sample surfaces to a diminished or non-existent value in the sample interior. This will usually lead to a heterogeneity in the oxidation across the material, with equilibrium oxidation (e.g. corresponding to air-saturated conditions) occurring at the sample surfaces, and reduced or little oxidation in the interior.

The importance of the effect will clearly depend upon the material geometry, coupled with the oxygen consumption rate, the oxygen permeability coefficient and the oxygen partial pressure surrounding the sample [5 to 8]. Since the oxygen consumption rate will typically depend upon the environmental stress level (e.g., temperature, radiation dose rate) and both the consumption rate and the permeability coefficient may change as the material degrades [9, 10], the importance of diffusion-limited oxidation will also vary with stress level and degradation. This often implies that the percentage of the sample which is oxidized under accelerated (higher-level) environmental conditions is substantially lower than the percentage oxidized under lower-level application conditions [5 to 7, 10 to 16]. Thus, as has been clear for many years, in order to confidently extrapolate shorter-term accelerated simulations to long-term, air-ageing conditions, a critical requirement is the ability to monitor and quantitatively understand diffusion-limited oxidation effects.

Since a great deal of progress has recently been made in this area, this goal is now realistic. The purpose of this report is to review this area. Clause 2 will describe experimental profiling methods which can be used to monitor diffusion-limited oxidation. Theoretical descriptions of the phenomenon will be briefly given in clause 3. Since the shapes of the theoretical profiles depend upon the oxygen permeability coefficient and the oxygen consumption rate, these quantities must be measured or estimated in order to quantitatively validate the theories. Many experimental methods have been developed for measuring permeability coefficients and a large number of experimental values are

* Figures in square brackets refer to annex B.

available in the literature. Clause 4 will introduce some of the important literature. Experimental methods for estimating oxygen consumption rates will briefly be reviewed in clause 5. Experimental data supporting the theoretical treatments is presented in clause 6. Once confidence in the theoretical treatments exists, the theories can be used either to choose experimental ageing conditions so that diffusion effects are unimportant, or to predict the importance of such effects. If it is impossible to eliminate diffusion effects under air ageing conditions, increasing the oxygen pressure surrounding the sample during ageing may, in certain instances, be used to achieve the desired goal, as outlined in clause 7 on the oxygen overpressure technique.

Part 2 will be published as a separate report and will describe procedures for predicting radiation ageing at low dose-rates.

DETERMINATION OF LONG-TERM RADIATION AGEING IN POLYMERS

Part 1: Techniques for monitoring diffusion-limited oxidation

1 Scope

When oxygen is present during ageing of polymers in various environments including temperature, radiation or ultraviolet, inhomogenous ageing effects caused by diffusion-limited oxidation are often encountered. These effects make it difficult to understand the ageing process and to extrapolate accelerated exposure to long-term conditions. This document reviews experimental techniques to quantitatively monitor these effects and provide theoretical equations to estimate their importance.

2 Profiling techniques to monitor diffusion-limited oxidation

The presence of diffusion-limited oxidation effects implies that various properties related to the amount of oxidation will depend upon spatial location in the material. Thus, any technique which can profile (map) these spatial variations will allow diffusion-limited oxidation to be monitored. Since polymer geometries utilize cross-sections down to a few millimetres or less, and since diffusion-limited oxidation effects are operative over such small dimensions, a useful profiling technique must have a resolution of at least 100 μm . An additional problem related to sensitivity is the observation that severe polymer degradation typically corresponds to less than 1 % of the polymer being oxidized. Thus, a useful profiling technique must have reasonable resolution, good sensitivity to the small chemical changes which occur, wide applicability, and relative ease of operation and analysis. A number of particularly useful techniques are briefly described in this clause.

2.1 *Infra-red profiling techniques*

Because of the ability to provide detailed chemical information on thin film samples, infra-red spectroscopy has been used to monitor diffusion-limited oxidation effects for more than 25 years [17]. Any oxidation-sensitive infra-red peak that can be monitored, either as a function of sample thickness, or as a function of sequentially microtomed slices, will yield information on oxidation heterogeneities. Many of the studies to date have concentrated on the carbonyl region (approx. $1\,720\text{ cm}^{-1}$) of polyolefin materials, such as polyethylene and polypropylene, since infra-red peaks in this region are characterized by high extinction coefficients (high sensitivities) and are usually absent from these materials when unaged. Since the carbonyl region typically represents a superposition of a number of oxidation products (e.g. ketones, aldehydes, esters, acids) of differing extinction coefficients at slightly different wavelengths, simplifying assumptions are often needed to extract semi-quantitative information. In most cases, either the maximum height of the hybrid carbonyl peak or its area is chosen. It should be noted that additives present in commercially formulated materials (e.g. antioxidants, fire retardants) often absorb in the carbonyl region, thereby complicating attempts to use FTIR spectrometry for these materials.

An example of an infra-red profile obtained after microtoming slices off an aged material is shown in figure 1 [18]. A polyolefin material was aged in air for 6 days at 100 °C and the relative oxidation (the absorbance of the carbonyl peak) is plotted versus the depth away from the air-exposed sample surface. The oxidation drops with depth with an approximate exponential dependence; similarly shaped profiles are often observed for heat-aged materials [10, 13, 14].

A second infra-red approach is to create multilayer samples by packing thin films together under mechanical pressure. After ageing, the individual films are separated, then individually analysed. Carbonyl profiles obtained in this fashion for gamma-radiation ageing in air of an unstabilized low-density polyethylene material are shown in figure 2 [19]. The profiles are symmetrical, since both surfaces of the multilayer samples were exposed to air. For these samples, the profiles show a fairly abrupt transition between completely oxidized and unoxidized regions, quite different behaviour from the "exponential" shape observed in figure 1.

Another interesting advance is the use of micro FTIR spectroscopy as a profiling method. Jouan and co-workers [20, 21] pioneered this approach and have used it in photo-oxidation studies to profile the carbonyl peak of a PVC material [20], and product profiles for styrene-butadiene (SBR) and nitrile rubbers [21]. Figure 3 shows product profiles for an SBR film photo-oxidized for 100 h and surrounded on both sides by air [21]. In this case, the drop-off in oxidation away from the surface is similar in shape to the result shown in figure 1.

2.2 *Modulus profiling*

The modulus profiling technique [14, 15] allows one to obtain rapidly and accurately more than 20 quantitative tensile compliance (D) measurements per millimeter of sample cross-section ($1/D$ is closely related to the tensile modulus of the material). This technique is especially useful for elastomers, since the modulus of such materials is very sensitive to scission and cross-linking events and therefore to processing and ageing.

The instrument, which is based on modifications of a thermomechanical analyser, is shown schematically in figure 4. The apparatus measures the indentation of a tiny, paraboloidally-tipped indenter into the sample. A tiny vice (shown in the figure), is used to hold the cross-sectioned samples. After the vice assembly is metallographically polished, indentation measurements under a chosen load are made at selected locations across the cross-sectioned surface. An optical microscope and an X-Y-Z linear positioner are used to quantify the measurement locations. For samples of rectangular cross-section, three samples are held in the vice in a sandwich arrangement with the profiling done across the middle sample. This avoids edge artefacts caused by the high-modulus aluminum plates used as part of the vice. The accuracy (within better than ± 10 % of conventional modulus measurements), reproducibility (typically better than ± 5 %) and linearity (with load) of the apparatus have been demonstrated on a variety of elastomeric materials [14].

Figures 5 to 7 show modulus profile results for 1,68-mm thick sheets of a commercial Viton^{®1)} rubber (Parker V747-75), which were gamma-radiation aged in air at 70 °C at three different dose rates. The data are plotted on a normalized thickness basis in which the ordinate, P , represents the percentage of the distance from one air-exposed surface of the sample to the opposite air-exposed surface. These profiles have shapes that appear to be intermediate between the "exponential" or "U-shaped" profiles shown in figures 1 and 3 and the "step-shaped" profiles shown in figure 2. For unaged Viton[®], the modulus is independent of cross-sectional position and equal to 5,4 MPa; this result is denoted by the horizontal line labelled "unaged". At the highest radiation dose rate of 5,49 kGy/h (figure 5), spectacular heterogeneity, caused by diffusion-limited oxidation, develops with ageing. Oxidative scission occurs near the air-exposed sample surfaces, leading to rapid decreases in modulus. Ageing occurs under essentially anaerobic (inert) conditions in the sample interior, yielding a cross-link-dominated increase in modulus. Since the heterogeneity can be observed after less than 0,04 MGy, which corresponds to relatively moderate changes (10 % to 20 %) in ultimate tensile properties [6, 7, 11], modulus profiling can clearly be sensitive to the earlier stages of ageing. Figure 6 gives results at a six times lower dose rate of 0,9 kGy/h, where diffusion-limited oxidation effects are reduced but still evident. Finally, at 0,14 kGy/h (figure 7), oxidation has been slowed down sufficiently to assure homogeneous oxidation throughout the sample. At high dose rates characteristic of typical accelerated radiation ageing conditions, cross-linking dominates the overall (i.e. macroscopically observed) degradation whereas, under long-term, low dose-rate ageing conditions, scission will predominate. Such results clearly underscore the danger that occurs whenever important diffusion-limited oxidation effects exist for accelerated environments, if the accelerated results are used to make predictions under long-term, low-level environments.

Modulus profiling results [10] for 1,9 mm thick chloroprene rubber samples after ageing in an air-circulating oven at 150 °C and 100 °C are shown in figure 8. Significant and complicated diffusion-limited oxidation effects are evident. At the higher temperature of 150 °C (left plot), diffusion effects exist at the earliest stages of ageing. At the lower temperature of 100 °C (right plot), diffusion effects appear to be less important. In fact, at the early stages of ageing, the oxidation appears to be essentially homogeneous. In the later stages of ageing, however, important diffusion effects become apparent. This phenomenon, of increasingly important diffusion-limited effects with ageing time, is common for elastomers which are thermally aged in air. It is often caused by substantial decreases in oxygen permeation rate which occur as the polymer hardens (modulus increases) with progressive ageing. Other factors contribute [10], for example, the rate of oxygen consumption may increase with ageing time. Sorting out these complicated diffusion-limited effects is clearly necessary if results from accelerated temperature exposures are used to make long-term predictions at much lower temperatures.

1) Viton[®] is the trade name of a product supplied by DuPont de Nemours. This information is given for the convenience of users of this Report and does not constitute an endorsement by IEC of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2.3 *Density profiling*

The density profiling technique [13] is based on the use of a density gradient column to obtain the density of successive thin slices cut across a sample. It depends on the fact that oxidation reactions often lead to substantial and easily measurable increases in polymer density. Although a number of methods are available for measuring density, only the density gradient column can yield accurate results on the extremely small samples necessary for achieving the required spatial resolution. To use the density profiling approach, one has to find liquids for the column that are not significantly absorbed by the polymer, since swelling of the material will complicate the interpretation of the data. Since absorption of water by most polyolefins is small, density profiling has been successfully applied to these materials using aqueous salt solutions. Some example density profiling data are plotted in figure 9 for two thicknesses of a commercially formulated EPDM rubber material after radiation ageing in air to 0,32 MGy at 6,65 kGy/h and 70 °C [22]. Since the amount of oxidation is approximately linearly related to the density increase, density changes are plotted as crosses versus cross-sectional position. The vertical span of each cross represents the estimated experimental uncertainty of the measurement, whereas the horizontal span denotes the position and thickness of each slice. The shape of these profiles again lies in the regime that is intermediate between "U-shaped" and "step-shaped". As expected, diffusion-limited oxidation effects become less important as the sample thickness is reduced.

Since density profiling is a much more difficult and time-consuming technique than modulus profiling, the latter technique is generally preferred where applicable, especially for elastomers. However, under certain ageing conditions, elastomers may degrade with an approximate balance between scission and cross-linking events, implying little sensitivity of modulus to ageing. In such instances, density profiling may prove helpful.

2.4 *X-ray microanalysis*

Another recently developed technique for monitoring diffusion-limited oxidation effects involves the use of X-ray microanalysis (XMA) [24]. During oxidation, common products which result on the polymer chain are carboxyl containing groups and peroxide groups. After ageing, a cross-sectional slice of the material is exposed and dipped in a 0,1 N KOH-isopropanol solution in order to convert these groups to potassium-containing species. After conversion, the profile of potassium will therefore represent the oxidation profile for these two oxidation species. The potassium distribution is measured using an electron probe X-ray microanalyser [24].

Figure 10 shows some representative results for an EPDM material which was radiation-aged in air at 1 kGy/h and room temperature. The results indicate that the thickness of the oxidized region is reasonably constant up to doses of at least 330 kGy, implying that the oxygen consumption rate and the oxygen permeability coefficients are reasonably constant up to this dose. Figure 11 shows XMA profiles for this same material after various thermal ageing exposures. It is interesting to note from the 70 °C results that homogeneous oxidation occurs for ageing times up to 4 000 h, but that heterogeneous behaviour becomes significant at longer times. This clearly indicates that the permeability and/or the consumption rate change significantly with ageing time. It is also interesting to note the very different profile shapes observed for the two different ageing environments (radiation versus thermal). In fact the general shapes observed with all of the profiling techniques for thermal ageing exposures (see figures 1, 8 and 11) and for radiation exposures (see figures 2, 5, 6, 9 and 10) are similar.

2.5 Miscellaneous profiling techniques

A number of other techniques have shown some promise as profiling tools. For soluble materials, Bowmer and co-workers [25] have used gel permeation chromatography as a method to derive profiles for scission and cross-linking. Another technique sensitive to cross-linking involves the use of nuclear magnetic resonance pulsed field gradient measurements of a material's self-diffusion constant to profile diffusion-limited oxidation effects [26]. Figure 12 shows some results for low-density polyethylene samples radiation aged in air and vacuum. Wilski and co-workers [27, 28] pioneered the use of viscosity profiles to show the importance of diffusion effects for gamma-irradiated polyethylene, polypropylene and PVC. Kuriyama *et al.* [29] obtained gel fraction profiles versus dose rate for gamma-irradiated polyethylene. Chemiluminescence has been successfully applied to gamma-irradiated polypropylene samples by Yoshii *et al.* [30]. Figure 13 shows some of their results. A recent review has been written on experimental methods for monitoring heterogeneous oxidation and covers in more detail many of the above profiling techniques as well as a number of other potentially useful experimental approaches [6].

3 Theoretical treatments of diffusion-limited oxidation

Diffusion-limited oxidation can result whenever oxidation reactions in a material use up oxygen faster than it can be replenished by diffusion effects from the air surrounding the material. Thus, theoretical modelling of diffusion-limited oxidation profiles necessitates combining diffusion equations with expressions for the rate of oxygen consumption, the latter derived from the kinetics appropriate to the oxidation of the material. A particularly useful theoretical treatment of diffusion-limited oxidation for slabs of material of thickness, L , was originally formulated by Cunliffe and Davis [5] using oxidation kinetics which are terminated by bimolecular reactions. More recently, Gillen and Clough [6, 7, 22, 23] showed that very similar theoretical results occur for oxidation kinetics which are terminated by unimolecular reactions. Details of the derivations are given in annex A to this section.