IEC TS 61244-1

Edition 2.0 2014-08

TECHNICAL SPECIFICATION

SPECIFICATION TECHNIQUE

colour inside

Determination of long-term radiation ageing in polymers –
Part 1: Techniques for monitoring diffusion-limited oxidation

Détermination du vieillissement à long terme sous rayonnement dans les polymères –
Partie 1: Techniques pour contrôler l'oxydation limitée par diffusion

IEC TS 61244-1:2014-08(en-fr)

IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
Fax: +41 22 919 03 00
info@iec.ch
www.iec.ch

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DETERMINATION OF LONG-TERM RADIATION AGEING IN POLYMERS –

Part 1: Techniques for monitoring diffusion-limited oxidation

FOREWORD

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Technical specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 61244-1, which is a technical specification, has been prepared by IEC technical committee 112: Evaluation and qualification of electrical insulating materials and systems.

This second edition cancels and replaces the first edition published in 1993 and constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

a) numerical simulation of DLO is much improved;

b) geometry of samples has been expanded from only the case of the infinite plane to the cylindrical and the spherical cases.

The text of this specification is based on the following documents:

Enquiry draft	Report on voting
112/287/DTS	112/304/RVC

Full information on the voting for the approval of this technical specification can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 61244 series, published under the general title *Determination of long-term ageing in polymers*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- transformed into an International standard,
- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

It is usually necessary to estimate the anticipated lifetime of a polymeric material in various usage 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] [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 specification is to review this area. Clause 2 describes experimental profiling methods which can be used to monitor diffusion-limited oxidation. Theoretical descriptions of the phenomenon are 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 are 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 available in the literature. Clause 4 introduces some of the important literature. Experimental methods for estimating oxygen consumption rates is briefly 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 is published as a separate specification and describes procedures for predicting radiation ageing at low dose rates.

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1 Figures in square brackets refer to the Bibliography.

DETERMINATION OF LONG-TERM RADIATION AGEING IN POLYMERS –

Part 1: Techniques for monitoring diffusion-limited oxidation

1 Scope

This part of IEC TS 61244, which is a technical specification, reviews experimental techniques to quantitatively monitor the effects 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 and provide theoretical equations to estimate their importance. These effects make it difficult to understand the ageing process and to extrapolate accelerated exposure to long-term conditions.

It is widely known that mechanical properties degrade prior to electrical properties.These changes are consequences of chemical changes such as oxidation. In this technical specification, only mechanical or chemical monitoring techniques are of interest.

This technical specification does not deal with electrical monitoring techniques.

2 Profiling techniques to monitor diffusion-limited oxidation

2.1 General

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 has to 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 shall 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.

2.2 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 (approximately 1 720 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].

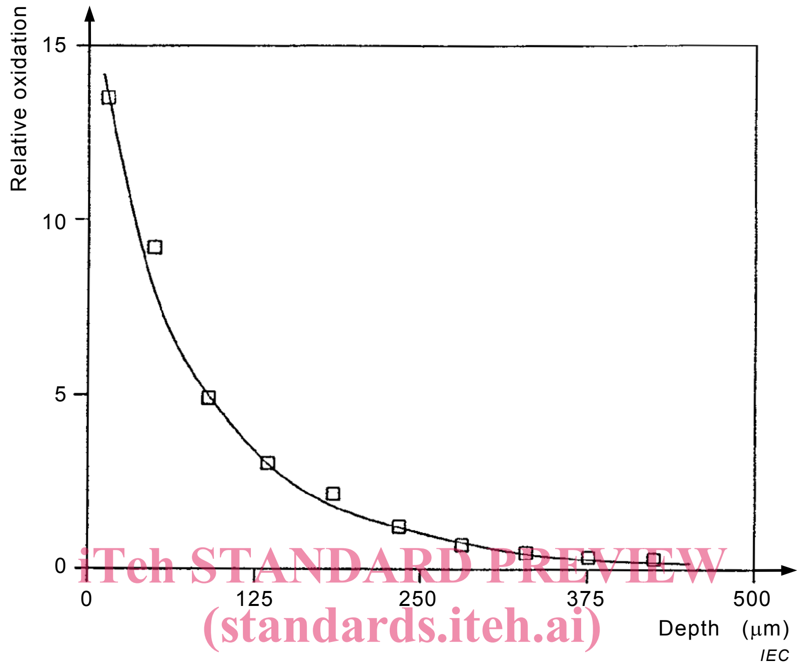
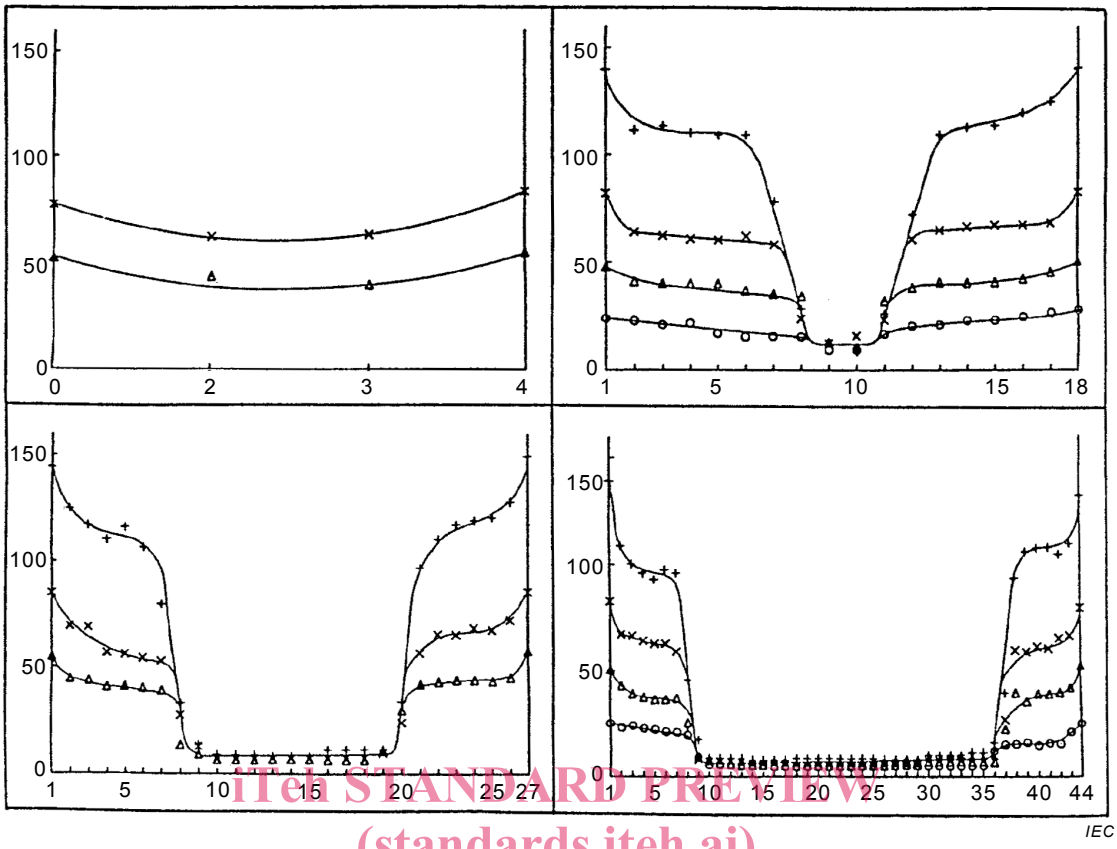


Figure 1 – Relative oxidation as determined from the carbonyl absorbance versus depth away from air-exposed surface of polyolefin material after ageing for 6 days at 100 °C (from [18])

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.

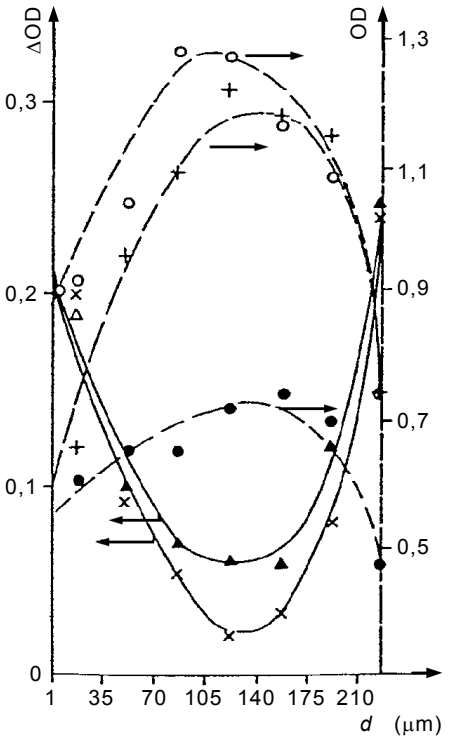
Another interesting advance is the use of micro FTIR spectroscopy as a profiling method. Jouan and co-workers [20, 21] pioneered this approach and have used it in photo-oxidation studies to profile the carbonyl peak of a PVC material [20], and product profiles for styrene-butadiene (SBR) and nitrile 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.



Key

○	0,14
Δ	0,30
×	0,45
+	0,60 MGy (from [19])

Figure 2 – Depth distribution of carbonyl groups in irradiated (0,69 Gy/s) multilayer samples composed of 4, 18, 27 and 44 films of 22 μm thickness



Key

▲	carbonyl at 1 717 cm^{-1}	+	1,4-*trans* at 962 cm^{-1}
×	hydroxyl at 3 440 cm^{-1}	●	1,2 at 910 cm^{-1}
○	1,4-*cis* at 700 cm^{-1}	*d*	represents the width of the slice (from [21])

Figure 3 – Micro-FTIR spectrophotometric determination of photoproduct and of residual double-bond profiles in a SBR film photooxidized for 100 h

2.3 Modulus profiling

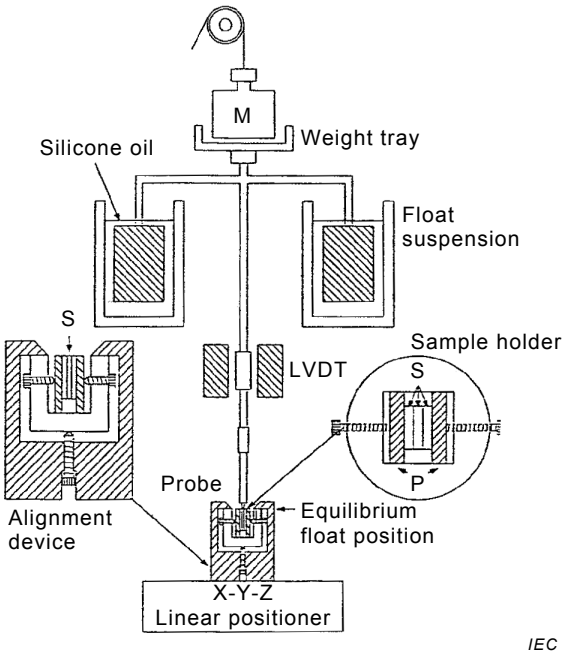
The modulus profiling technique [14, 15] allows one to obtain rapidly and accurately more than 20 quantitative tensile compliance (*D*) measurements per millimeter of sample cross-section (1/*D* is closely related to the tensile modulus of the material). This technique is especially useful for elastomers, 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 indentor 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, 6 and 7 show modulus profile results for 1,68 mm thick sheets of a commercial fluoro elastomer rubber, 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 commercial fuoro elastomer, 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. When high dose-rate is adopted for radiation ageing, which is typically in accelerated ageing conditions, cross-linking is macroscopically dominant; on the other hand, in the case of low dose-rate and long-term radiation ageing, scission is dominant. 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.



NOTE The detailed top view of the sample-holder shows three samples labelled with an S held between metal plates P. The detail to the left shows a side view of the sample-holder held in the alignment device (from [14, 15]).

Figure 4 – Schematic diagram of modulus profiling apparatus

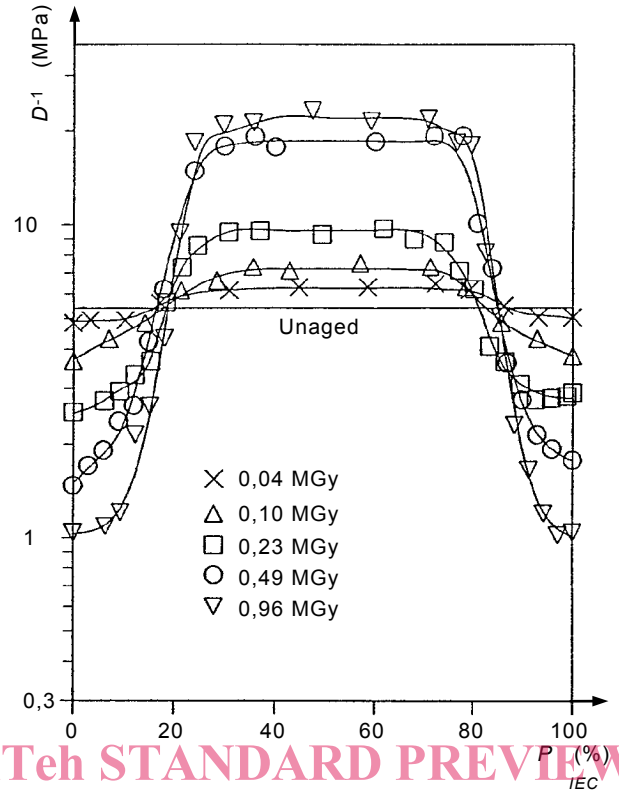


Figure 5 – Modulus profiles of 1,68 mm thick commercial fluoro elastomer samples after air ageing at 5,49 kGy/h and 70 °C to the indicated radiation doses (from [15])

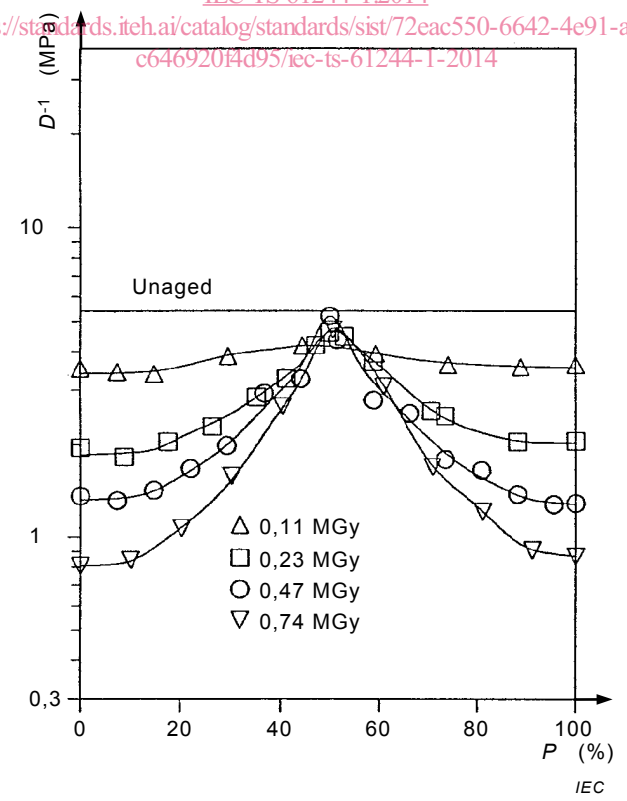


Figure 6 – Modulus profiles of 1,68 mm thick commercial fluoro elastomer samples after air ageing at 0,90 kGy/h and 70 °C to the indicated radiation doses (from [15])

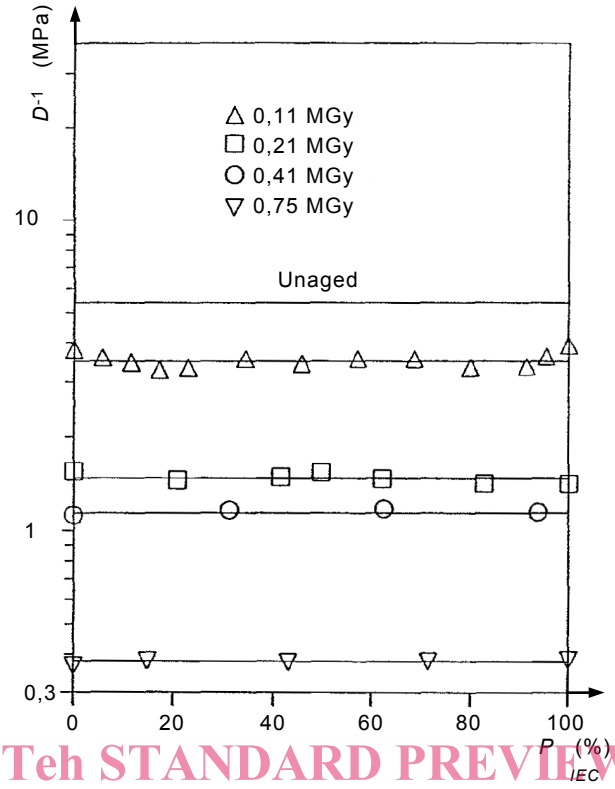


Figure 7 – Modulus profiles of 1,68 mm thick commercial fluoro elastomer samples after air ageing at 0,14 kGy/h and 70 °C to the indicated radiation doses (from [15])

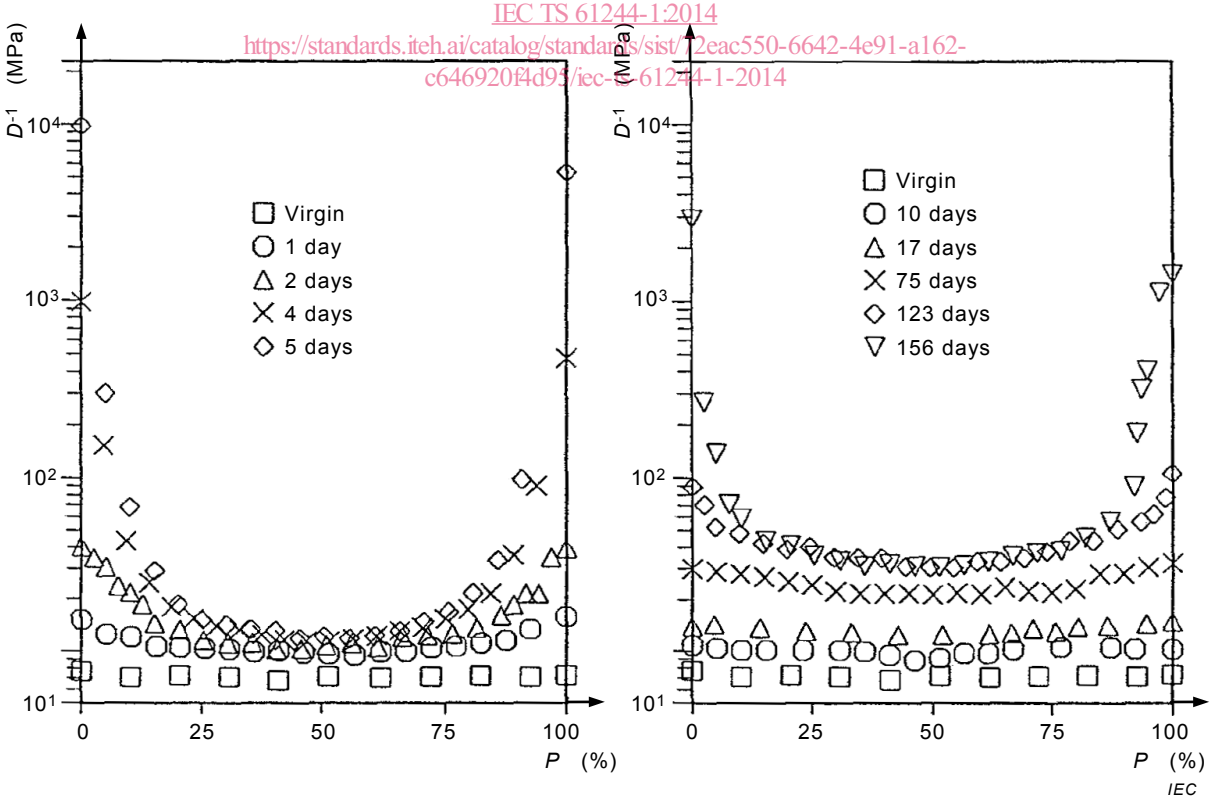


Figure 8 – Modulus profiles of 1,9 mm thick chloroprene rubber samples following elevated temperature exposures in the presence of air at 150 °C, left plot, and 100 °C, right plot (from [10])