

Determination of long-term radiation ageing in polymers —

Part 2: Procedures for predicting ageing at low dose rates

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- Adhesive Tape Manufacturers' Association
- British Capacitor Manufacturers' Association
- British Industrial Ceramic Manufacturers' Association
- British Telecom plc
- Electrical and Electronic Insulation Association (BEAMA Ltd.)
- Electricity Association
- Rotating Electrical Machines Association (BEAMA Ltd.)

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- AEA Technology
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National foreword

This Part of BS 7816 has been prepared by Subcommittee GEL/15/5. It is identical with IEC 1244-2:1996 *Determination of long-term radiation ageing in polymers, Part 2: Procedures for predicting ageing at low dose rates*, published by the International Electrotechnical Commission (IEC).

IEC 1244-2:1996 was issued in the type 2 technical report series of publications (according to G.4.2.2 of Part 1 of the IEC/ISO Directives) as a “prospective standard for provisional application” in the field of insulating materials because there was an urgent requirement for guidance on how standards in this field should be used to meet an identified need.

IEC 1244-2:1996 is not to be regarded as an “International Standard”. It is proposed for provisional application so that information and experience of its use in practice may be gathered. A review of the technical report, IEC 1244-2:1996, will be carried out not later than three years after its publication, with the options of either extension for a further three years, or conversion to an International Standard, or withdrawal.

This British Standard implements IEC 1244-2:1996, and as such it is a technical report and is not to be considered to be a “provisional standard” subject to the outcome of the above mentioned review.

Any comments on the content of this British Standard should be sent to the British Standards Institution, marked for the attention of the Secretary to Technical Committee GEL/15.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 22, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Introduction

The behaviour of polymers under irradiation is strongly influenced by the atmosphere in which they are irradiated, particularly the presence of oxygen. When polymers are irradiated in oxygen-containing atmospheres, it is often observed that the irradiation dose required to reach a particular level of degradation changes with dose rate. The existence of such dose rate effects in the radiation ageing of polymeric materials has been recognised for many years but only recently has a sufficient understanding been achieved of the processes involved to enable predictive methodologies to be developed. The types of dose rate effects which are seen in polymers are illustrated schematically in Figure 1 [1]¹⁾, where DED (dose to equivalent damage) is defined as the dose required to reach a specific level of a damage parameter (such as elongation at break, tensile strength, compression set, etc.).

Figure 1 illustrates behaviour that is commonly seen in most, but not all, polymers. In an inert atmosphere, represented by curve I, degradation is independent of dose rate over a wide range of dose rates. When dose rates are small enough for thermal degradation effects to dominate, curve I will approach the line representing thermal ageing under inert conditions. On a log-log plot like Figure 1, this thermal ageing will be represented by a straight line of slope equal to one.

In the presence of oxygen, dose rate effects can arise from several processes including diffusion-limited oxidation and time-dependent chemical reactions. At high dose rates, diffusion limited oxidation becomes important (Figure 1); in this region DED tends to increase with increasing dose rate. It should be noted that Figure 1 is schematic and is only indicative of the types of behaviour that can occur. The diffusion-limited region in particular is very dependent on the type of polymer, its thickness, the permeation rate for oxygen and the sensitivity of the material to surface properties. The observed degradation is strongly influenced by the thickness of the oxidation layer. At high enough dose rates, oxidation will only occur in a thin surface layer which does not affect the bulk properties of most polymers. In this case, the degradation observed is similar to that seen in an inert atmosphere and DED approaches the inert ageing line. The dose rate above which heterogeneous oxidation occurs can be determined theoretically or by the use of profiling techniques. These procedures are discussed in detail in report IEC 1244-1. In the homogeneous oxidation region, dose rate effects are reduced for many polymers; the slope of the log-log DED versus dose rate plot remains constant or nearly constant with decreasing dose rate (curve II in Figure 1), until the dose rate is sufficiently low for thermal degradation to become dominant. In type II behaviour, the slope of the DED plot against dose rate is determined by the reaction rate of the dominant chemical reaction. If the reaction rate is high relative to the initiation rate, the slope is small and may approach zero; whereas at low reaction rates, the slope is higher but < 1 .

¹⁾ Figures in square brackets refer to annex A.

In a few polymers irradiated in oxygen-containing environments, more complex dose rate effects are observed in the homogeneous oxidation region (e.g. curve III in Figure 1). A well documented example of type III behaviour is seen in PVC; this is believed to arise from the breakdown of intermediate hydroperoxide species produced by irradiation [2-4]; this is illustrated in more detail in 4.5.

1 General

1.1 Scope and object

This part of IEC 1244 is a technical report of type 2 which applies to procedures for predicting ageing at low dose rates.

The object of this report is to present three methods which have been used to extrapolate data obtained from high dose rate experiments to the low dose rates typical of service conditions. These methods assume that homogeneous oxidation has been achieved under the test conditions. The techniques described in the following clauses are research methods which have been found to be useful for a range of elastomeric and thermoplastic materials and some thermosets, and are subject to continuing research. The procedures require a considerable number of test data to enable predictions to be made under low dose rate conditions. The power law extrapolation method (clause 2) has mainly been used for isothermal data whereas the superposition methods (clauses 3 and 4) can make use of data obtained over a range of temperatures.

1.2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of IEC 1244. At the time of publication, the editions indicated were valid. All normative documents are subject to revision, and parties to agreements based on this part of IEC 1244 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

IEC 544-1:1994, *Guide for determining the effects of ionizing radiation on insulating materials — Part 1: Radiation interaction and dosimetry.*

IEC 544-2:1991, *Guide for determining the effects of ionizing radiation on insulating materials — Part 2: Procedures for irradiation and test.*

IEC 544-4:1985, *Guide for determining the effects of ionizing radiation on insulating materials — Part 4: Classification system for service in radiation environments.*

IEC 1244-1:1993, *Determination of long-term radiation ageing in polymers — Part 1: Techniques for monitoring diffusion-limited oxidation.*

2 Power law extrapolation method

2.1 Introduction

This method is based on the extrapolation of test data obtained under isothermal conditions in air or in oxygen overpressure over a range of dose rates. The upper limit to the dose rate is such that homogeneous oxidation conditions are achieved (but see 2.4). The test data obtained at the different dose rates are used to determine endpoint criteria which are extrapolated graphically to the service dose rate.

2.2 Test procedure

The maximum dose rate at which homogeneous oxidation will occur in the test material shall be assessed. Information in the literature may be used to estimate the maximum dose rate, or the oxidation layer thickness may be calculated (IEC 1244-1). Once the maximum dose rate has been established, at least two (preferably three) other dose rates should be selected, each dose rate being at least one order of magnitude lower than the previous value.

The general guidelines of IEC 544-2 should be used in the selection of specimen types, radiation source, dosimetry, and temperature control. All irradiations should be carried out in air or at constant oxygen overpressure, although as noted in IEC 1244-1, oxygen overpressure techniques entail some risk of over-ageing the samples. The homogeneity of oxidation through the specimen thickness should be checked using profiling techniques such as those described in IEC 1244-1. The test report should include details of the irradiation source, dose rate, atmosphere, temperature, sample type and thickness.

2.3 Evaluation and extrapolation

For the types of materials for which this procedure is recommended (i.e. elastomers and thermoplastics), elongation at break e is generally the property measured; for some materials, tensile strength or other criteria may be more useful. Using elongation as the measured parameter, to establish the endpoints at each dose rate, the relative elongation e/e_0 is plotted against absorbed dose (e_0 is the initial value of the elongation at break). A number of endpoint criteria can be interpolated from the graph (Figure 2); typical endpoint criteria might be $e/e_0 = 0,75, 0,5$ or $0,4$. A sufficient number of absorbed doses shall be used to enable the endpoint criterion to be established without extrapolation.

The dose at which the endpoint criterion is reached, i.e. the dose to equivalent damage DED, is plotted against the dose rate in a log/log plot (Figure 3). This plot is found to be linear in some materials, e.g. some polyolefins, enabling extrapolation to lower dose rates. The endpoint dose is then given by

$$\text{DDE} = K \cdot \dot{D}^n \quad (1)$$

where

$\dot{D}$ is the dose rate;

K and n are empirical constants specific to the material tested.

2.4 Limitations

This procedure can be a useful method for estimating the behaviour of some polymers at low dose rates but reference to Figure 1 immediately shows its potential limitations. For all materials it must break down at dose rates low enough for thermal ageing to become dominant (Figure 1). On a log-log plot of DED versus dose rate used for extrapolation, the thermal ageing limit would be represented by a line of slope = 1, i.e. constant time conditions, whereas the slope of the extrapolated data is generally < 1 . Extrapolation to dose rates within the thermally dominated region would give unrealistically high values for the predicted DED (Figure 4a). This problem can be partially accounted for if separate thermal ageing data are available; these would allow determination of the appropriate thermal only result. If the additional data indicate that thermal effects will dominate, the thermal results can be used for predictions. The power law extrapolation method also cannot be used for materials which exhibit complex dose rate effects in the homogeneous oxidation region (type III curve in Figure 1). In these materials, data obtained in the “knee” region of the type III curve would give misleading results when extrapolated to lower dose rates (Figure 4b).

Although the linear extrapolation method assumes that homogeneous oxidation conditions have been obtained in all of the experiments, it appears to be useful in some materials at dose rates where heterogeneous oxidation would be expected to occur. For example the behaviour of XLPE shown in Figure 7, the two higher dose rates used are likely to give rise to heterogeneous oxidation but the plots are linear in this dose rate range with the same slope as at lower dose rates. This may arise because cracks generated in the thin oxidised layer can then propagate through the bulk unoxidised material, so that the observed macroscopic properties are determined by degradation in the oxidised surface layer or by enhanced embrittlement from crosslinking.

2.5 Examples

Some examples of the use of the linear extrapolation method are given for several types of polyolefins, as follows.

Polypropylene

This material was tested over a dose rate range of 4,45 Gy/h to 2 000 Gy/h. In Figure 5, plots of relative elongation at break e/e_0 are shown for polypropylene monofilaments irradiated in air [5]. Using an end-point criterion of $e/e_0 = 0,5$, the values of the end-point dose DED can be interpolated from these plots. These DED values are shown in Figure 6; it can be seen that over this dose rate range there is a linear relationship between $\log(\text{DED})$ and $\log(\text{dose rate})$, with a slope of 0.26.

For this material, homogeneous oxidation was obtained at all dose rates because of the thickness (0,4 mm) of the samples.

Crosslinked polyethylene

For this XLPE cable material [7], tested over the dose rate range 100 Gy/h to $1,8 \cdot 10^5$ Gy/h, data for $e/e_0 = 0,5$ are shown in Figure 7. This is an example where heterogeneous oxidation would have occurred at the two highest dose rates. However, for this material, the slope of the plot remains the same at all dose rates.

Polyolefin

This is an example (Figure 8) of a polyolefin cable material where heterogeneous oxidation would have occurred at the two higher dose rates. However, in this case, there is a marked change in slope of the plot and the power law extrapolation method cannot be used on these data.

3 Superposition of time dependent data

3.1 Introduction

The second procedure which can be used to extrapolate to lower dose rates makes use of additional data obtained at elevated temperatures under irradiation. The method uses the superposition principle which has been used extensively for thermal ageing (time-temperature superposition) and here is expanded to time-temperature-dose rate superposition for combined thermal-radiation environments [8, 9].

The superposition procedure in thermal ageing uses time dependent data taken under isothermal conditions at different temperatures. The higher temperatures are assumed to accelerate the degradation of properties in a uniform manner so that data can be shifted on the time axis to a single curve at the reference temperature by the application of a multiplicative shift factor (Figure 9a). In combined thermal-radiation environments, a similar procedure can be used to shift time dependent data obtained under constant temperature and constant dose rate; this is shown schematically in Figure 9b. By using elevated temperatures to accelerate degradation, data are obtained which are relevant to dose rates lower than those which are accessible experimentally.

In thermal ageing, the functional relationship between the shift factor $b(T)$ and the temperature often takes a simple form, such as the Arrhenius relationship. The empirically derived activation energy from such a functional relationship represents an effective activation energy for the overall thermal degradation. For combined thermal-radiation ageing, the shift factors $a(T,D)$ which are determined from the time dependent data do not always show a simple functional relationship with temperature and dose rate. In some cases, an empirical relationship can be determined [8, 9] which enables extrapolation to lower dose rates to be carried out. Some examples of polymers where this procedure has been used are given in 3.5.

3.2 Test procedure

The general guidelines of IEC 544-2 should be used in the selection of specimen types, radiation source, dosimetry, and temperature control. All irradiations should be carried out in air or at constant oxygen overpressure, although as noted in IEC 1244-1 oxygen overpressure techniques entail some risk of over-ageing the samples. The damage parameter used should reflect the use that is to be made of the material; for example, for a seal material, compression set would be an appropriate parameter whereas, for a cable material, elongation at break would be more suitable. The homogeneity of oxidation through the specimen thickness should be checked using profiling techniques such as those described in IEC 1244-1. The test report should include details of the irradiation source, dose rate, atmosphere, irradiation temperatures, sample type and thickness and the damage parameter measured.

Data should be obtained at a minimum of three dose rates and at least two, preferably three, temperatures at each of these dose rates. For each of these temperature-dose rate conditions, measurements should be made at a minimum of three times. In addition, similar data on unirradiated material shall be obtained for at least three temperatures. This is the minimum data set for this method; more accurate assessment of the shift factors will be obtained if more data are available.

3.3 Evaluation

The first stage in the evaluation is to superpose plots of the damage parameter versus log (time) obtained at constant temperature conditions on unirradiated material to yield a master curve (Figure 10). The values of the shift factor $b(T)$ at each temperature are determined and used to superpose the data. These values can then be plotted versus $1/T$, where T is the temperature in kelvins (Figure 11). The activation energy for thermal-only degradation is determined from the slope of the straight line plot using the Arrhenius relationship:

$$b(T) = \exp \{-E/R (1/T - 1/T_{\text{ref}})\} \quad (2)$$

where

$b(T)$ is the shift factor;

E is the activation energy;

R is the gas constant (8,314 J.kmol⁻¹.K⁻¹);

T_{ref} is the reference temperature i.e. the temperature at which $b(T) = 1$. For ease of assessment, T_{ref} is usually chosen to be one of the temperatures used in the combined thermal-radiation ageing measurements.

In the second stage of the evaluation, the time dependent data obtained under combined thermal-radiation ageing conditions are superposed on the master curve as shown in Figure 12. The shift factors $a(T,D)$, at temperature T and dose rate D , required to superpose the data are determined for each temperature-dose rate condition. At this stage of the evaluation, values of $a(T,D)$ are known for the matrix of temperatures and dose rates used.

The following empirical relationship between the shift factor $a(T,D)$ and the temperature and dose rate [9] can be used for a number of polymers:

$$a(T,D) = \exp \{-E/R (1/T - 1/T_{\text{ref}})\} [1 + k \cdot \dot{D}^x \cdot \exp \{Ex/R(1/T - 1/T_{\text{ref}})\}] \quad (3)$$

where

T is the temperature in kelvins;

T_{ref} is the reference temperature;

$\dot{D}$ is the dose rate;

E , k and x are the model parameters. The parameter E is the value of the activation energy for thermal-only ageing (Figure 11). The parameters k and x are determined by fitting the values of $a(T,D)$ obtained experimentally to the empirical equation above.

When $T = T_{\text{ref}}$, the equation simplifies to

$$a(T_{\text{ref}}, D) = 1 + k \cdot \dot{D}^x \quad (4)$$

The parameter x usually takes the value $x \leq 1$. This is shown in Figure 13; the parameter x is the limiting value of the slope of the plot at high dose rates. The parameter k determines the position of the curve on the dose rate axis.

Having determined the parameters E , k and x from the experimental data, the empirical model can be used to calculate the DED at lower dose rates or temperatures. This can be determined using the equation:

$$\text{DED} = \dot{D} \cdot t_m / a(T, D) \quad (5)$$

where

t_m is the time required to reach the selected damage level at the reference conditions of $T = T_{\text{ref}}$ and $D = 0$,

$a(T,D)$ is calculated from equation (3). This is shown in Figure 14; the limiting slope of the log-log plot of DED versus dose rate is $(1-x)$ at high dose rates.