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SHORT-TERM EVALUATION OF THE THERMAL ENDURANCE CHARACTERISTICS OF POLYMERIC MATERIALS BY TA

A. Motori [1*], *G. C. Montanari* [1], *A. Saccani* [1] *and F. Peruzzotti* [2]

[1]University of Bologna, Viale Risorgimento 2, 40136 Bologna, Italy
[2]Pirelli Cavi e Sistemi SpA, Milano, Italy

Abstract

Two thermal analysis techniques (isothermal differential calorimetry and isothermal thermogravimetric analysis) are used as analytical methods for short-term thermal endurance characterization of polymeric materials, used for electrical insulation. These techniques are applied to commercial grade ethylene-propylene rubber and polyvinyl chloride. It is shown that thermogravimetric analysis provides very satisfactory results, independently of the degradation reactions which take place in the material. Calorimetry proves to be effective only for polymers (such as polyolefins) in which oxidation is the largely prevailing degradation mechanism in the test and service temperature ranges.

Keywords: electrically insulating polymers, isothermal differential calorimetry, isothermal thermogravimetric analysis, temperature index

Introduction

IEC 216 Standard describes a conventional long-term procedure for the determination of the thermal endurance parameters of polymeric insulating materials [1]. These parameters are: *i*) the Temperature Index (TI), defined as the temperature at which the material is able to withstand thermal stress for 20000 h, still keeping a certain amount of its original properties which would ensure serviceability; *ii*) the Halving Interval (HIC), i.e. the temperature increase necessary to halve this time. Once a diagnostic property has been chosen (tensile strength, electrical strength, mass, etc.), material samples are aged at least at three temperatures and tested at selected times till a significant change of the diagnostic property is reached. As this procedure is both time consuming and expensive, IEC 1026 Standard recommends a short-term method [2], which is based on analytical techniques combined with a conventional aging test at a temperature, which must provide a failure time longer than 300 h. This procedure is very useful when the aim is the comparison of several materials, which may have different technological features (additives, curing, structure, etc); in fact, it allows quickly to select the best performing material as well as to arrange further technological improvements. In this paper, the short-term thermal endurance of chemically dif-

* Author for correspondence: E-mail: antonio.motori@mail.ing.unibo.it

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Akadémiai Kiadó, Budapest

ferent polymers is evaluated resorting to two analytical procedures: the former relies upon oxidative stability measurements by isothermal differential calorimetry (IDC) [3, 4]; the latter refers to the mass loss determined by isothermal thermogravimetric analysis (ITA) [5]. In this paper, it is shown that both techniques can provide comparable results, i.e. values of TI and HIC, which are close to those obtained by the conventional procedure, when they are applied to nearly pure polyolefins, for which oxidation is the largely prevailing degradation reaction both in the service and in test temperature range. If applied to polymers for which degradation reactions other than oxidation superimpose, only ITA seems to provide results which fit well those derived from long-term conventional life tests.

Experimental

Materials

The following commercial grade materials were investigated:

- ethylene-propylene rubber (EPR), used for medium and high voltage applications;
- polyvinyl chloride (PVC), used for low voltage insulation.

For IDC and ITA tests, polymer slices were cut from unaged cables. Slices were about 0.25 mm thick and an overall mass of 5 mg was used for each test. Specimens were kept in dry environments until testing, but no particular thermal conditioning was applied.

Procedures

Both IDC and ITA tests were performed under a pure oxygen flow of 50 mL min^{-1}, from 160 to 200°C for EPR and from 110 to 140°C for PVC. In the last case, temperature values were selected below 150°C, in order to avoid, or to limit, the sudden decomposition of the polymer with production of chloridic acid. At least three specimens were tested at each temperature in order to estimate measurement variance and calculate confidence intervals.

According to the procedure described elsewhere [3, 4], IDC tests were continued until the exothermic peak, generated by the oxidation reaction, was observed; the time corresponding to the maximum of the peak, i.e. the oxidation maximum time (OMT), was chosen as the property for the application of the analytical technique.

In ITA measurements, tests were continued until a characteristic point in the mass loss *vs*. time curve was detected (e.g., a maximum or the point corresponding to a sharp slope change), or a suitable mass loss was reached. The time corresponding either to the characteristic point or to the selected mass loss was chosen.

Results and discussion

Ethylene-propylene rubber

An example of the ITA curves, obtained for EPR at 190°C, is reported in Fig. 1. After an initial, slight decrease, mass remains almost constant till a sudden, sharp change in the

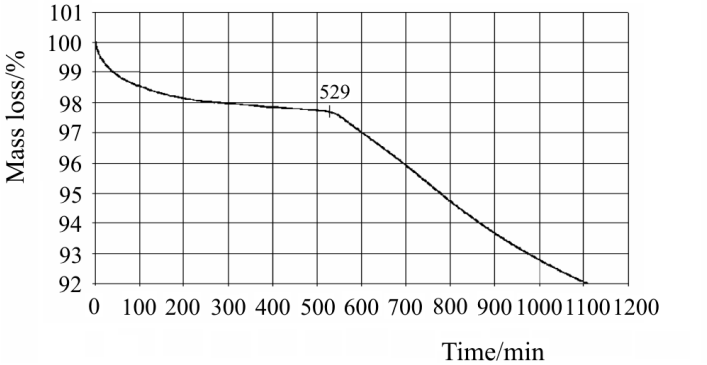

Fig. 1 ITA plot at 190°C for EPR

slope takes place; afterwards, a continuous mass decrease is observed until the end of the test. Therefore, a characteristic time, i.e. the slope change time (SCT) is envisaged in ITA curves. The result of the IDC test performed at the same temperature is shown in Fig. 2. A clear oxidation peak can be observed, with a maximum time (OMT). Therefore, both the peak in the IDC curves and the region of the slope change in the ITA curves can be related to the thermo-oxidative reaction of the polymer. The mean values of the SCT and OMT, obtained at different test temperatures, are reported in Figs 3 and 4, respectively; confidence intervals refer to the 90% of probability.

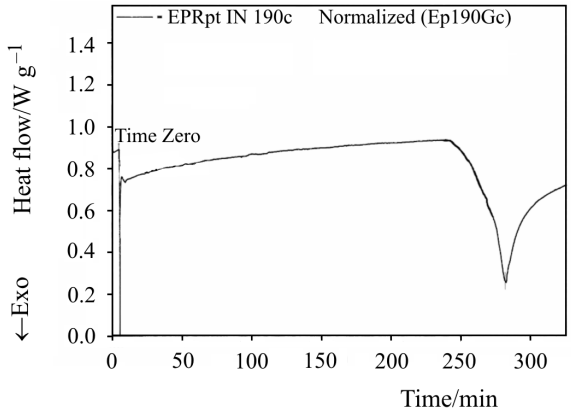

Fig. 2 IDC plot at 190°C for EPR

The slope of the line obtained by the fitting of the experimental points in both plots provides the activation energy of the oxidation process for EPR, as well as the slope of the thermal endurance line in the thermal life plot [3]. According to IEC 1026 Standard [2], the location of the thermal endurance line can be obtained resorting to a conventional test, which must provide a failure time longer than 300 h.

The thermal life plot of Fig. 5 was drawn using the slope of the regression line of Fig. 3 and the failure time provided by a conventional life test at 150°C, considering the electric strength as diagnostic property and 0.5 (i.e., its 50% decrease) as end-

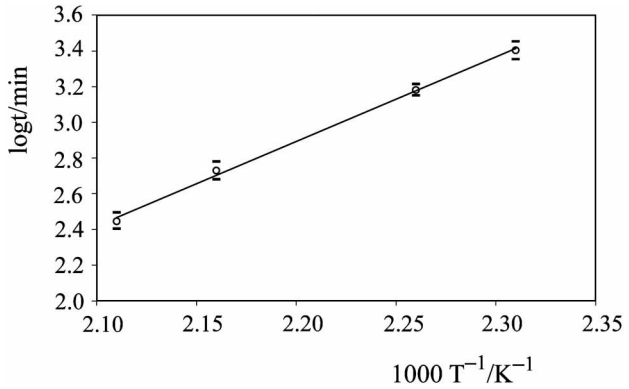

Fig. 3 Mean values of the SCT as a function of the reciprocal absolute temperature

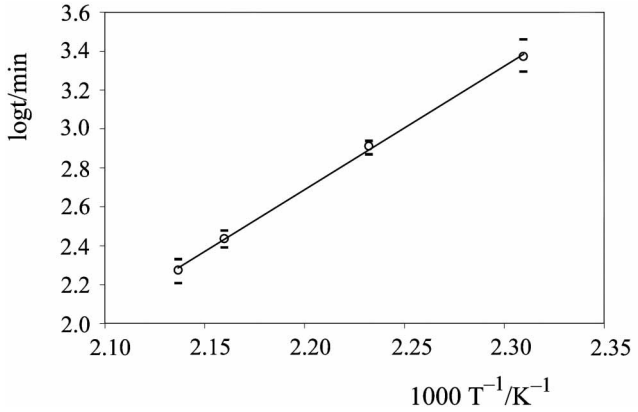

Fig. 4 Mean values of the OMT as a function of the reciprocal absolute temperature

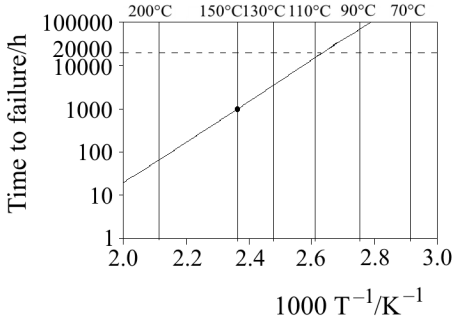

Fig. 5 Thermal endurance graph for EPR (diagnostic property: electrical strength; end–point: 0.5)

point [3]. The thermal endurance parameters TI and HIC were finally derived from this graph [1, 2]. Other values of TI and HIC were obtained on the basis of the life test at 150°C, using different diagnostic properties and failure criteria: (*i*) mass and its decrease to 0.995, (*ii*) tensile strength and its decrease to 0.5.

The same procedure was applied to draw the thermal endurance graph from IDC measurements (not reported for the sake of brevity); in this case, the slope was provided by the OMT data of Fig. 4, while the conventional test data were the same previously reported for the procedure based on ITA tests.

In Figs 6 and 7, the values of TI and HIC provided by IDC and ITA tests, resorting to the different diagnostic properties and end-points, are reported and compared with those obtained by the long-term conventional procedure (C), which was carried out between 120 and 160°C, elsewhere reported [6].

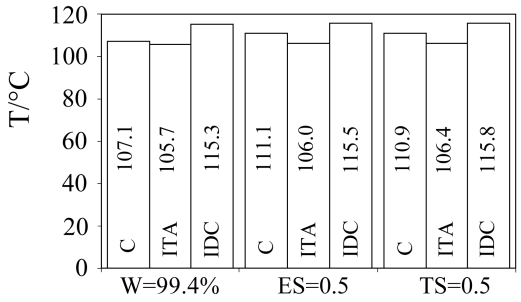

Fig. 6 TI values obtained by analytical techniques using ITA and IDC and conventional life test (the times to failure provided by the conventional test at 150°C and the indicated properties and end-points were used)

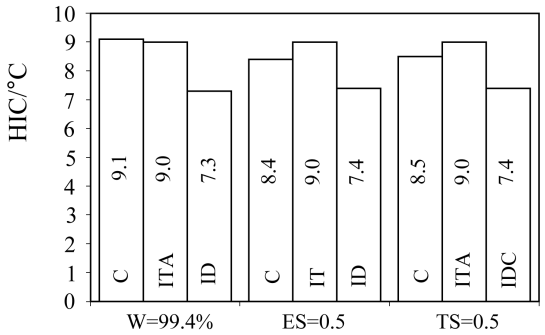

Fig. 7 HIC values obtained by analytical techniques using ITA and IDC and conventional life test (the times to failure provided by the conventional test at 150°C and the indicated properties and end-points were used)

As can be observed, the results derived from the three methods are almost comparable, thus proving, in this case, the effectiveness of both the proposed analytical techniques. Indeed, if compared with the IDC method, the ITA procedure provides thermal endurance indices, which are slightly closer to those obtained with the long-term conventional tests.

Polyvinyl chloride

As regards PVC, the oxidative stability tests by IDC did not provide useful results, as no clear oxidation peak was observed in the heat flow *vs.* time curves (which are,

therefore, not reported). On the contrary, the procedure based on ITA measurements provided mass *vs*. time curves like that reported in Fig. 8, where a continuous mass decrease with time can be observed. In this case, as no characteristic point was detectable, a suitable mass loss and the corresponding time (time to a selected residual mass, TRM) were selected for the application of the analytical technique.

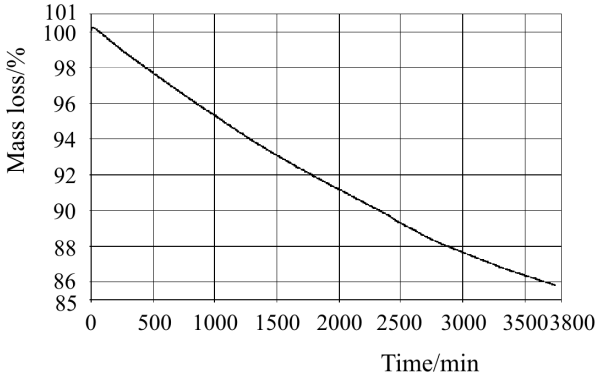

Fig. 8 Example of ITA plot at 130°C for PVC

The mean values of the TRM at 0.98 (i.e., 98% of residual mass), obtained at different test temperatures, are reported as a function of the reciprocal absolute temperature in Fig. 9.

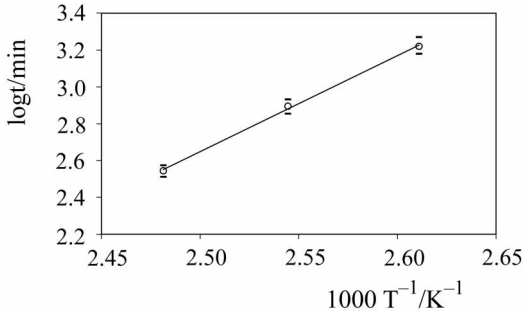

Fig. 9 Mean values of the TRM at 0.98 as a function of the reciprocal absolute temperature

Again, a linear fitting of the experimental points provides the activation energy of the degradation process, as well as the slope of the thermal endurance line. Other mass loss values may be selected for the calculation of the activation energy: Table 1 shows the slope values obtained with the TRM data provided by different residual masses (0.99, 0.985 and 0.98); no significant slope changes are observed in this range of mass loss. For the analytical procedure, the mean value of the slopes of Table 1 was used.

The thermal endurance line location in the life graph of Fig. 10 was obtained resorting to a conventional tests at 100°C with elongation at break as diagnostic property and 0.5 as end-point.

Table 1 Slope values obtained from TRM data provided by different residual mass (end-points 0.99, 0.985 and 0.98)

End point	Slope
0.990	5210
0.985	5260
0.980	5220

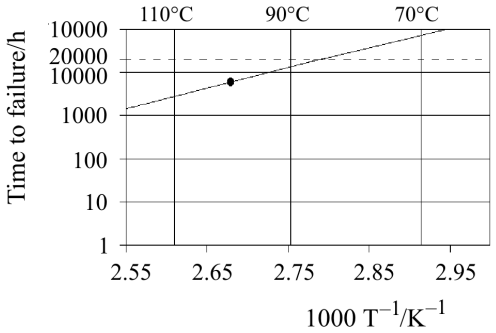

Fig. 10 Thermal endurance graph for PVC (diagnostic property: elongation at break; end–point: 0.5)

Table 2 compares the values of TI and HIC derived from both the conventional life tests (provided by the manufacturers) and the ITA technique. A good agreement of the thermal endurance indices can be observed.

Table 2 TI and HIC values obtained with different methods

Method	TI/°C	HIC/°C
Conventional	89.0	7.9
ITA	86.2	7.4

Conclusions

Isothermal differential calorimetry and isothermal thermogravimetric analysis in oxygen flow were applied for the short-term thermal endurance characterization of polymers for electrical insulation. Both the analytical techniques provide comparable results, which are in good agreement with those obtained by the long-term conventional procedure, if they are applied to nearly pure polyolefins, for which oxidation is the largely prevailing degradation mechanism in service conditions.

In polymers different from polyolefins (e.g., polyvinyl chloride), which are usually filled and contain additives like flame retardants, other reactions or degradation mechanisms can superimpose and prevail on oxidation; for these materials, only isothermal thermogravimetric analysis seem to provide satisfactory results.

References

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