

THE APPLICATION OF THE THERMOGRAVIMETRIC ANALYSIS (TGA) AND OF THE DIFFERENTIAL THERMAL ANALYSIS (DTA) FOR RAPID THERMAL ENDURANCE TESTING OF ELECTRICAL INSULATING MATERIALS

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abstract: The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were applied to investigations of aging processes in some electroinsulating polymeric materials (glass reinforced epoxy resin, NBR (two sorts), styrenated unsaturated polyester resin, hydrogenated NBR (T80), polychloroprene rubber , EPR) and to the measurement of aging reaction rates. It is shown that thermal analysis curves (TG and DTA) can be used for planning thermally accelerated aging experiments which are used for the thermal lifetime evaluation by the method given in IEC 216. Some results concerning isothermal and non-isothermal aging of the above mentioned materials are presented and discussed. The obtained results show that, except EPR, for each investigated material, the value of activation energy corresponding to isothermal degradation of a mechanical property is close to the value of activation energy rapid evaluated from TGA or DTA data. The rapid method for thermal lifetime evaluation which consists in the rapid determination of the activation energy from thermal analysis data and the plotting of only one isotherm of accelerated aging, corresponding to the maximum admitted temperature for accelerated aging, was checked. The results presented in this work show that the TGA and DTA methods should be included among the analytical methods used for thermal endurance testing of insulating materials.

Introduction

The practical use of the polymeric electroinsulating materials requires the knowledge of their thermal lifetime corresponding to a certain end-point criterion and the operating temperature. According to the method recommended by IEC 216 [1], in order to predict the thermal lifetime, the polymeric material is submitted to accelerated aging (at temperatures higher than the temperature of use) by following the changes in time of a property of interest (mechanical property, electrical property, weight loss). Through extrapolation of the so obtained results at the temperature of use, the thermal lifetime of the polymeric material can be estimated. In order to apply this method, one has to choose the temperatures of thermal accelerated aging. In this paper it will be shown how the thermal analysis methods, like TG, DTG and DTA, can be used in order to estimate these temperatures.

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According to IEC 216 Standard [1], the thermal endurance characterization of an insulating material requires about 1 year. As is suggested in IEC 1026 Standard [2], the time of experiments necessary for thermal lifetime prediction can be shortened by using some analytical techniques (gas chromatography, mass spectrometry, isothermal differential calorimetry). This Standard does not recommend the use of the rapid non-isothermal techniques (such as thermogravimetric analysis (TG) and differential thermoanalysis (DTA)) since these methods lead to extrapolation of test results over a large temperature span, which may lead to erroneous conclusions. However, the results reported by some investigators [3 – 8] show that a careful kinetic analysis of the non-isothermal data lead to the value of the activation energy which can be used in order to rapid prediction of the thermal lifetime. In this paper, the results obtained in the study of the isothermal and non-isothermal thermal degradation of some polymeric materials will be presented. In addition, the possibility of using of the thermal analysis methods in order to rapid thermal endurance characterization of these materials will be discussed.

The use of thermal analysis (TG, DTA) in the selection of the temperatures of accelerated thermal aging

According to IEC 216 Standard [1], for thermal degradation, the acceleration factor has to be chosen so that the mechanism of accelerated degradation of the polymeric material should be identical with that of the degradation under practical conditions of use. The minimal and maximal temperatures of accelerated aging should belong to the so-called range of chemical stability of the material; i.e. the temperature range in which for the relatively short time of several hours, no chemical changes are detected in the material [7]. It is obvious that one has to account for the phase changes (softening, glass transition). The range of chemical stability, as well as the temperatures corresponding to the phase transitions can be determined by thermal analysis methods (TG, DTG, DTA, DSC).

Below, some examples concerning the use of thermal analysis methods in order to select the temperatures of accelerated aging will be given.

The thermograms (TG, DTG and DTA curves) were recorded using a Q-1500 D – MOM – Budapest – type Paulik-Paulik-Erdey derivatograph, in static air atmosphere, in the temperature range 20 – 500°C.

Thermal degradation of low density polyethylene (LDPE)

In a recent paper [9], the results concerning the changes in mechanical properties (elongation at break, traction resistance) and thermal behaviour of LDPE in response to accelerated thermal aging were presented. The thermal analysis (TG, DTG, DTA) of LDPE shows that, at the progressive heating of this material, the following processes take place:

1. a first order phase change (melting or softening) at $\approx 105^{\circ}\text{C}$;
2. an exothermic change, accompanied by a slight increase in mass;
3. a thermo-oxidative degradation with the generation of volatile products. The corresponding range of chemical stability is 20 – 170°C. According to these results, the temperatures of accelerated aging were: 70°C, 80°C, 90°C and 100°C.

Thermal degradation of polycarbonate

The thermal analysis of polycarbonate shows that this material exhibits a glass transition around 135°C and a range of chemical stability of 20 – 235°C. The values of the

mechanical properties of the thermal aged material at 100°C , 120°C and 130°C exhibit a significant statistical scattering. This result can be explained by the inadequate selection of the temperatures of accelerated aging which are close to the glass transition temperature.

Thermal degradation of polychloroprene rubber

For this material, accelerated thermal aging was studied by measuring the residual deformation under constant deflection in air [10,11]. The thermogram shows that up to 325°C a single exothermal degradation process takes place, which is accompanied by a release of volatile products (mainly hydrogen chloride). The temperatures of accelerated aging which were selected, 70°C , 80°C ,90°C and 100°C, are substantially lower than the maximum temperature of the range of chemical stability. In the choice of these temperatures we have into account the recommendation of IEC 216 [1] according to which an aging temperature that yields predictive information in less than 100 h is too high.

Thermal analysis and the rapid thermal endurance characterization of polymeric materials

Considering that at thermal degradation a polymeric material undergoes a single main chemical reaction, and the change of the property of material is dependent on the degree of conversion (quasichemical approximation), Dakin [12, 13] derived the following kinetic equation:

$$-\frac{d\varepsilon}{dt} = Af(\varepsilon)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

where ε is the property of interest (mechanical property, electrical property, weight loss) , $f(\varepsilon)$ is the differential function of degradation, A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

If the activation parameters do not depend on ε , the integration of eqn. (1) leads to:

$$F(\varepsilon) = At \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where: $F(\varepsilon) = -\int_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon}{f(\varepsilon)}$; ε_0 is the initial value of ε .

The logarithmic form of eqn. (2) is:

$$\ln t = a + \frac{b}{T} \quad (3)$$

where:

$$a = \ln F(\varepsilon) - \ln A \quad (4)$$

$$b = \frac{E}{R} \quad (5)$$

A polymeric material can be used until the value of the relative property decreases at a certain value, $\frac{\varepsilon_L}{\varepsilon_0}$ = end-point criterion, when $t = L$ = *thermal lifetime*. Thus, according to eqn. (3):

$$\ln L = a_L + \frac{b}{T} \quad (6)$$

Equation (6) is the *thermal lifetime equation*, and the corresponding straight line $\ln L$ vs. $(1/T)$, for a certain end-point criterion, is the *thermal endurance line* [1]. Through extrapolation of this straight line at the temperature of use, T_U , the thermal lifetime is evaluated. In some cases [1], the thermal endurance of a polymeric material is expressed in a abbreviated form through the *temperature index, TI*, which is the temperature, in °C, at which the end-point criterion is reached in 20000 h. From relationship (6), one obtains the following formula in order to calculate *TI* :

$$TI = \frac{b}{-a_L + \ln 20000} - 273 \quad (7)$$

For a certain end-point criterion, it is also possible to use the following formula in order to calculate the lifetime of the polymeric material:

$$\ln L_u = \ln L_a + b \left(\frac{1}{T_u} - \frac{1}{T_a} \right) \equiv \ln L_a + \frac{E}{R} \left(\frac{1}{T_u} - \frac{1}{T_a} \right) \quad (8)$$

where the subscripts *u* and *a* correspond to aging at the temperature of use and at temperature of accelerated aging, respectively. Thus, in order to determine the thermal lifetime, L_a and E should be known.

The main assumption made in the analytical test methods for thermal lifetime evaluation is that the activation energy of the degradation process can be derived in a short time by analytical techniques. The thermal endurance line location is provided by an experimental point, which is derived by a conventional life test, corresponding to the maximum admitted temperature for accelerated aging (≈ 300 h of thermal aging).

In the following we will show that in many cases, the correct evaluation of the parameters from thermal analysis data leads to the value of activation energy which is close to that obtained from thermal endurance line.

Table 1. Comparison between the isothermal and non-isothermal values of activation energy

Material	Isothermal Property	Non-isothermal method ^a		
		E kJ.mol ⁻¹	E kJ.mol ⁻¹	
Glass reinforced epoxy resin	Flexural strength	69.4	68.1– 73.2	F-W-O(iso) [14,15]
Styrenated unsaturated polyester resin	Weight loss	155.3 – 164.0	160.7–174.9	F-W-O(iso) [14,15]
NBR (I) ^b	Elongation at break	85.7	88.2	Kissinger [16]
NBR (II)	DRC ^c	71.5	74.4	Kissinger [16]
Hydrogenated NBR	Elongation at break	67.3 – 69.4	69.4	Flynn (low degree of conversion) [17]
Polychloroprene rubber	DRC	80 – 140	70 - 130	Friedman [18]
Ethylene-propylene rubber	Elongation at break	52.7	105.8	Kissinger [16]

^aF-W-O (iso) , Flynn-Wall-Ozawa method for isoconversion ; ^b NBR (I) and NBR (II) are two sorts of nitrile-butadiene rubber; ^cDRC, residual deformation under constant deflection;

^dE varies with the degree of degradation

The results listed in Table 1 shows that, except ethylene-propylene rubber, the two values of the activation energy (isothermal and non-isothermal ones) are in satisfactory agreement.

The polychloroprene rubber exhibits the change of the activation energy with the degree of degradation. According to the previous theoretical considerations [19], in this case, in both isothermal and non-isothermal conditions the dependence of the activation energy on the degree of degradation was evaluated by differential isoconversional methods. The isothermal and non-isothermal values of the activation energy are practically in the same range and increase with the degree of degradation [11].

For the ethylene-propylene rubber, there is a discrepancy between the two values of the activation energy. This can be accounted for by taking into account that the isothermal degradation is limited by diffusion of oxygen in the polymeric material.

Tables 2 and 3 contain the values of *TI* for hydrogenated NBR and styrenated unsaturated polyester resin, estimated by conventional aging method (CA) (eqn. (7)) and by using the values of activation energy evaluated from thermal analysis data (TA).

Table 2. Comparison between *TI* values estimated by CA and TA, for different end-point criteria of hydrogenated NBR (property is elongation at break)

End-point	a _L	b K	TI (°C) (CA)	TI °C (TA)
0.80	-14.9133	8187	57	58
0.75	-14.2909	8054	60	62
0.70	-14.1534	8119	65	66
0.65	-14.4454	8358	70	70

Table 3. Comparison between *TI* value, estimated by CA and TA, for different weight losses values of styrenated unsaturated polyester resin

Weight loss %	A _L	b K	TI °C (CA)	TI ^a °C (TA)	TI ^b °C (TA)	TI ^c °C (TA)
17.5	-36.8418	19087	135	137	139	139
20	-35.7003	18705	137	140	142	142
25	-36.3093	18944	144	145	148	146

^{a, b, c} *TI* was evaluated using $\bar{E} = 167.8$ kJ.mol⁻¹ (obtained from non-isothermal data) and the isotherm of thermal degradation recorded at : a. $T_a = 191^\circ\text{C}$; b. $T_a = 200^\circ\text{C}$; c. $T_a = 210^\circ\text{C}$

One can notice a satisfactory agreement between the values of TI evaluated by CA and TA. From Table 3, it results that the TI values provided by TA are relevant to only one value of thermal endurance line slope, and change with the selection of the CA test for thermal endurance line location. However, the differences among the TI values provided by TA, obtained for the three values of T_a , are in the limits of the experimental errors.

These results support the use of the thermal analysis methods for short-time thermal endurance characterization of polymeric materials.

Conclusions

1. It was shown that thermal analysis curves (TG, DTG, DTA) can be used for planning thermally accelerated aging experiments on polymeric materials.
2. Some results concerning isothermal and non-isothermal degradation of some polymeric materials have been presented and discussed.
3. It has been shown that, in some cases, thermal analysis methods can be used for rapid thermal endurance characterization of polymeric materials.

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