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Estimation of the thermal index of electric insulators by non-isothermal thermogravimetry ☆

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Abstract

A method of estimating the thermal index of electric insulators is suggested by its correlation with quantities which can be determined from TG curves: the temperatures required to obtain given fractions of their weight loss; the temperature corresponding to the maximum rate of decomposition; the total energy of activation of thermal decomposition; or the partial energy of activation of process around a given fraction of weight loss. Using five resins with different structures, the optimizing programme applied gave the best correlation of the thermal index with the temperature corresponding to weight loss fractions of 0.14 or 0.15, if one-parameter equations were used.

Keywords: Electric insulators; Non-isothermal TG; Thermal index

1. Introduction

Determination of thermal indices of insulating materials by the method established by the International Commission of Electrotechnics (ICE) requires a long time to test an electric insulating material; it can take as long as nine months. That is why rapid methods for estimating the above property is necessary. This can be done by correla-

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tion with other quantities characteristic of such materials. Even though the obtained values are not very accurate, rapid methods enable the preselection of materials to be subjected to ICE tests.

Mathematical relations between thermal indices determined by the ICE method and quantities determined by non-isothermal thermogravimetry—such as the temperatures corresponding to given weight loss fractions, the temperature of maximum rate of thermal decomposition, the total energy of activation of thermal decomposition or the partial energy of activation of process around a given fraction of weight loss—have been established. Finally, the relationships obtained were applied to calculate the thermal index of a polyester–imide resin and good correlation with that obtained by the ICE method was found.

2. Experimental

The tested electric insulating materials, their structure and the ICE thermal indices are given in Table 1.

The non-isothermal thermogravimetry was carried out with a Derivatograph type C, 1989-MOM Budapest, at a heating rate of $10\,K\,min^{-1}$ in air, using samples of 20–60 mg and temperatures between 25 and 1000°C.

The samples were obtained by mechanical removal from metallic supports on which the insulators were deposited using a steel blade. The crucibles delivered by the producer were used and the samples were settled in the same way.

The kinetic parameters were calculated from thermal analysis data using the well-known equation:

$$\beta(d\alpha/dT) = A \exp(-E_a/RT)\, f(\alpha) \tag{1}$$

where β is the linear heating rate in $K\,s^{-1}$; α, the weight loss fraction; A, the pre-exponential factor in s^{-1}; E_a, the energy of activation in $J\,mol^{-1}$; T, the absolute temperature and $f(\alpha)$, the kinetic function.

The tested $f(\alpha)$ functions which give the lowest deviation for Eq. (1) are summarized in Table 2 together with the rate-controlling process [1].

Linearization of Eq. (1) gives a relationship of the form:

$$Y = C_0 + C_1 X \tag{2}$$

Table 1
Insulating materials, their polymeric structures and their ICE thermal indices

Insulating material	Polymeric structure	ICE thermal index °C
5531 Ez	Alkydo-melamine	140
3330 Ez	Epoxy	147
6665 Ez	Polyester	160
R_3	Polyester-imide	182
R_2	Polyester-imide	184
K_1	Polyimide	220

Table 2
Kinetic functions, $f(\alpha)$, giving the lowest deviations for Eq. (1)

Kinetic function	n	m	Rate controlling process
α^n	0.1–3	–	Nucleation ($n < 1$) or growth of germs ($n > 1$)
$(1-\alpha)[-\ln(1-\alpha)]^n$	0.1–3	–	Growth of germs
$\alpha^n(1-\alpha)^m$	0.1–3	0.1–3	Nucleation or growth of germs in final stage
$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$	–	–	Three-dimensional diffusion (Jander)
α^{-1}	–	–	Uni-dimensional diffusion
$[(1-\alpha)^{-1/3}-1]^{-1}$	–	–	Three-dimensional diffusion (Gindsling–Brounstein)
$[-\ln(1-\alpha)]^{-1}$	–	–	Three-dimensional diffusion
$(1-\alpha)^n$	0.1–3	–	Chemical reaction (Friedman)

where $Y = \ln[\beta\, d\alpha/(f(\alpha)\, dT)]$; $C_0 = \ln A$; $C_1 = -E_a/R$ and $X = 1/T$. The constants C_0 and C_1 were determined by the fitting method in [2].

The following quantities were used as parameters: temperatures T_1 corresponding to weight loss fractions ranging between 0.01 and 0.50; the temperature of maximum rate of decomposition, T_m; total energy of activation of decomposition, E_α; and the energy of activation for weight loss fractions around 0.15, E'_0, for which the best correlations were obtained. The last quantity was considered for the whole process which takes place in that area.

The values of the above-mentioned parameters are given in Table 3.

A Turbo Pascal computer program was used to obtain the optimum correlation of termal indices with the above quantities for the equations listed in Table 4.

3. Discussion

The optimizing program used shows that the best correlation between the ICE thermal indices, Y, and the indicated parameters is obtained for temperatures corresponding to weight loss fractions of 0.14 or 0.15, if one-parameter equations are used, in contrast with literature data [3] which indicate T_0 (initial decomposition temperature) and $T_{.0}$ (temperature for 10% weight loss) among the main criteria for determining the heat stability of polymers with dynamic heating. The equations are of the form:

$$Y = C_0 + C_1/T_{15} \tag{2}$$

with $C_0 = 416.3°C$ and $C_1 = 91122.2(°C)^2$,

$$Y = C_0 \exp(C_1/T_{14}) \tag{3}$$

Table 3
ICE thermal indices (Y/°C), temperature of maximum rate of decomposition (T_m/°C), temperatures corresponding to the indicated fractions of weight loss (T_x/°C), total and partial energies of activation (E_a, E_0^1/k J mol^{-1})

Insulating material	5531 Ez	3330 Ez	6665 Ez	R_3	R_2	K_1
Y	140.0	147.0	160.0	182.0	184.0	220.0
T_m	365.0	360.0	370.0	403.0	405.0	590.0
T_{01}	163.2	136.8	205.8	179.0	190.3	33.0
T_{10}	305.6	335.4	329.8	379.4	376.7	243.0
T_{12}	315.0	342.7	336.5	384.5	380.2	277.5
T_{13}	319.6	346.3	339.8	386.1	382.9	424.3
T_{14}	323.5	349.9	343.1	387.6	384.1	451.6
T_{15}	328.2	353.0	346.4	389.2	386.7	464.7
T_{16}	330.3	355.7	348.8	390.7	389.3	471.4
T_{17}	337.7	358.5	350.5	392.3	391.9	476.8
T_{18}	337.1	361.2	352.3	394.6	393.9	481.5
T_{20}	342.1	366.6	355.8	399.2	397.4	489.9
T_{25}	352.2	380.4	364.5	408.0	405.2	505.5
T_{30}	360.4	395.7	372.8	417.4	411.7	526.4
T_{35}	366.7	413.9	379.3	426.5	419.9	545.2
T_{40}	372.7	436.3	385.7	435.7	428.5	559.5
T_{45}	379.1	474.6	392.2	445.5	437.2	573.6
T_{50}	386.7	523.7	406.1	453.7	446.0	585.1
E_a	43.80	24.87	21.64	13.70	8.55	10.93
E_0'	37.21	39.33	45.52	104.67	121.51	134.57

Table 4
Equations used to correlate ICE thermal indices with selected parameters

$Y = C_0 + C_1 X_1$
$Y = C_0 + C_1/X_1$
$Y = C_0 + X_1 C_1$
$Y = C_0 + C_1 X_1$
$Y = C_0 + C_1 \ln X_1$
$Y = C_0 \exp(C_1/X_1)$
$Y = C_0 \exp(C_1 X_1)$
$Y = C_0 + C_1 X_1^m$, $m = -10$ to $+10$
$Y = C_0 + C_1 X_1 + C_2 X_1^2$
$Y = C_0 + C_1 X_1 + C_2 X_1^2 + C_3 X_1^3$
$Y = C_0 + C_1 X_1 + C_2 X_1^2 + \cdots + C_5 X_1^5$
$\ln Y = C_0 + C_1/X_1$
$Y = C_0 + C_1 X_1 + C_2 X_2$
$Y = C_0 + C_1 X_1 + C_2 X_2 + C_{12} X_1 X_2 + C_{11} X_1^2 + C_{22} X_2^2$
$Y = C_0 + C_1 X_1 + C_2 X_2 + C_3 X_3$
$Y = C_0 + C_1 X_1 + C_2 X_2 + C_3 X_3 + C_{12} X_1 X_2 + C_{13} X_1 X_3 + C_{23} X_2 X_3$

where $C_0 = 703.8°C$ and $C_1 = -523.9°C$ and

$$Y = C_0 + C_1 T_{14} \tag{4}$$

with $C_0 = -63.9°C$ and $C_1 = 0.6$.

The correctness of the selection performed by the computer can be demonstrated by representing simple average deviations from the ICE thermal index, S_{min}, in terms of weight loss fractions for Eqs. (2)–(4) (Fig. 1). As can be seen, the minimum average deviation is obtained for $\alpha = 0.15$ using Eq. (2), followed by Eqs. (3) and (4) with $\alpha = 0.14$.

If equations with two and three parameters are used, the average deviations are substantially reduced but it is very difficult to find a phenomenological correlation between the ICE thermal indices and parameters obtained from TG curves.

The temperature corresponding to the maximum rate of thermal decomposition does not give better correlation than T_{14} or T_{15} for any of the equations with one parameter.

A decrease of the total energy of activation of thermal decomposition with increasing of ICE thermal index can be observed in Table 3, while the partial energy of activation of the whole processes around $\alpha = 0.15$ increases. So the partial energy of activation mentioned correlates better with thermal indices, the errors are greater than those given by Eqs. (2)–(4).

The decreasing of the total energy of activation of thermal decomposition with increasing ICE thermal index can be explained by the preponderance of diffusional processes taking place in the final stages of decomposition, which superimpose over the chemical reactions.

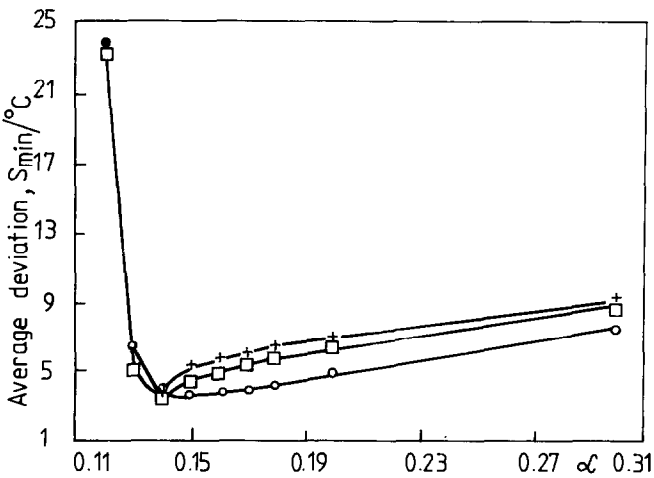

Fig. 1. Average deviation of the obtained thermal indices from ICE ones as a function of weight loss fractions: (○) Eq. (2); (□) Eq. (3) and (+) Eq. (4) etc.

Table 5
Kinetic functions $f(\alpha)$, giving the lowest deviations for Eq. (2)

Insulating material	Kinetic function	Rate controlling process
5531 Ez	$(1-\alpha)^n$	Chemical reaction
3330 Ez	$(1-\alpha)^n$	Chemical reaction
6665 Ez	$(1-\alpha)^n$	Chemical reaction
R_3	$\alpha^n(1-\alpha)^m$	Nucleation
K_1	$\alpha^n(1-\alpha)^m$	Nucleation

The $f(\alpha)$ functions (Table 2) which give the lowest deviations for Eq. (2) are shown in Table 5 together with the process controlling the rate of thermal decomposition.

In Table 5 it can be seen that electroinsulating materials with high thermal indices have rates of decomposition controlled by physical phenomena (nucleation), while those with low thermal indices are controlled by chemical processes. In this way, the earlier conclusion [4, 5] that the total energy of activation of thermal decomposition can be used only for a qualitative estimation of the heat resistance of an electroinsulating material is confirmed.

A better correlation between thermal indices and total energies of activation of thermal decomposition is expected in the case of the insulating materials having similar chemical structure, because of the very similar decomposition processes, which can determine the compensation effect between the pre-exponential factor and the energy of activation. As concerns the use of this effect as a selection criterion and determination of kinetic parameters, the literature data are inconsistent: it is considered to be present in all kinetic processes [6] or only in the case of chemical reactions of compounds having similar structure [7].

The validity of Eqs. (2)–(4) was checked for polyester–imide resin R_2 from Table 1, for which the ICE thermal index was determined, and the average deviation was found to be ± 4°C. This recommends Eqs. (2)–(4) as useful equations for selecting electroinsulating materials, the temperature corresponding to a weight loss fraction of 0.14 or 0.15 being easily determined from TG curves.

The results given by Eqs. (2)–(4) could be improved if lower rates of heating and more electroinsulating materials were used and the degree of grinding of the material was more carefully controlled.

4. Conclusions

1. The ICE thermal index of an electroinsulating material can be rapidly estimated from TG data.
2. The parameter which best correlates with the ICE thermal indices is the temperature corresponding to a weight loss fraction of 0.14 or 0.15 using Eqs. (2)–(4).
3. The total and the partial energies of activation give less satisfactory correlations with ICE thermal indices.

4. Such correlations can be improved using more electroinsulating materials and lower rates of heating.

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