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# The ageing compensation effect in the thermal degradation of some electrical insulators

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## Abstract

The existence of an ageing compensation effect (ACE) was suggested for the thermally accelerated ageing of some insulating polymeric materials. It was shown experimentally that the usual form of the ACE is found when an isokinetic temperature exists on the Arrhenius plots.

## INTRODUCTION

Experimental data concerning accelerated thermal ageing of polymeric materials used as electrical insulators are commonly described by the linear relationship [1]

$$\ln t = a + \frac{b}{T} \tag{1}$$

where $t$ is the time of thermal ageing and $T$ is the temperature; the constants $a$ and $b$ can be obtained as the intercept and the slope of the straight line ($\ln t$, $1/T$) respectively.

The constants $a$ and $b$ are characteristic of a given series of related reactions.

Recently [2,3], the following linear relationship between the constants $a$ and $b$, valid for some insulating polymeric materials, was suggested:

$$a = \alpha + \beta b \tag{2}$$

where the constants $\alpha$ and $\beta$ could also be determined as coefficients of a linear regression.

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Equation (2) describes the so-called ageing compensation effect (ACE) and expresses in a specific way the usual compensation effect (CE) from chemical kinetics, which consists of, for instance, a linear dependence between $\ln A$ and $E$, where $A$ and $E$ are the pre-exponential factor and the activation energy respectively [4–6].

In order to demonstrate this statement we shall use the so-called chemical approximation [7,8] according to which for a chosen physical property $P$ (which changes with time during the thermal degradation) the rate of change is given by

$$-\frac{\mathrm{d}P}{\mathrm{d}t}=kf(P) \tag{3}$$

where $t$ is the time, $k$ is the rate constant and the function $f(P)$ is usually considered in the framework of the "reaction order" model

$$f(P)=P^n \tag{4}$$

The exponent $n$ is the overall reaction order of the thermal degradation. As far as the rate constant $k$ is concerned, its temperature dependence is given by the Arrhenius equation [9]

$$k=A\exp(-E/RT) \tag{5}$$

From eqn. (3) by variable separation and taking into account eqns. (4) and (5) and integrating one obtains

$$F(P)=At\exp(-E/RT) \tag{6}$$

where $F(P)$ is the integral ageing function.
From eqn. (6) we obtain

$$\ln A=\ln F(P)-\ln t+E/RT \tag{7}$$

From the eqns. (1) and (7) we obtain

$$b=E/R \tag{8}$$

and

$$\ln A=\ln F(P)-a \tag{9}$$

From eqns. (2), (8) and (9) we obtain

$$\ln A=\ln F(P)-\alpha-(\beta/R)E \tag{10}$$

or

$$\ln A=\alpha^*+\beta^*E \tag{11}$$

where

$$\alpha^*=-\alpha+\ln F(P) \tag{12}$$

and

$$\beta^*=-\beta/R \tag{13}$$

Equation (11) is an expression of the known compensation effect from chemical kinetics. Equation (11) shows that $\alpha^*$ is constant, but according to eqn. (12), $\alpha^*$ depends on the degree of thermal degradation. Experimentally it will be shown that $\alpha^*$ is constant and thus ln $F(P)$ is practically constant or negligible.

From eqn. (5) and taking into account eqn. (8) we obtain

$$\ln k = \ln A - b/T \tag{14}$$

or, taking into account eqn. (9)

$$\ln k = \ln F(P) - a - b/T \tag{15}$$

Introducing the notation

$$\ln k^* = \ln k - \ln F(P) \tag{16}$$

eqn. (15) becomes

$$\ln k^* = -a - b/T \tag{17}$$

Equation (17) shows that when $T = T_i$ all the Arrhenius straight lines intersect at a point, i.e. all the related reactions from the given series are characterized by a common value of the rate constant. The temperature $T_i$ is called the isokinetic temperature. The existence of an intersection point of the Arrhenius straight lines is another criterion for a time compensation effect. This criterion was suggested by Agrawal [5].

It is easy to show that [4–6]

$$T_i = 1/R\beta^* = -1/\beta \tag{18}$$

In the following, some compensation effect shown by the kinetic data in the thermally accelerated ageing of some electrically insulating polymeric materials is presented.

## EXPERIMENTAL

In Table 1 the thermal ageing temperatures as well as the measured properties of the insulating polymeric materials investigated are given.

The accelerated thermal ageing of the test specimens occurred in a VSU-200 oven with forced air circulation, in which the temperature was kept constant with an accuracy of ±2°C.

The manufacture and the measurement of the properties of the test specimens were performed according to ASTM testing recommendations.

## RESULTS AND DISCUSSION

### *The dependence of constants* a *and* b *(eqn. (1)) on the degree of thermal degradation*

The constants $a$ and $b$ for various values of the degree of thermal degradation were determined for all the materials listed in Table 1.

TABLE 1

The materials investigated, the measured properties and the accelerated ageing temperatures

| Material | Main component | Measured property | Temperatures of accelerated ageing (°C) |
|---|---|---|---|
| PVC | Polyvinyl chloride | Elongation at break | 120, 135, 145 |
| EPDM | Compound EPDM chemically reticulated | Elongation at break | 100, 120, 135, 145 |
| TVC-70 | Compound EPDM | Deformation under constant deflexion | 85, 100, 115 |
| Polychloroprenic rubber 8050-PC50 | Polychloroprene | Deformation under constant deflexion | 70, 80, 90, 100 |
| Rubber PF-60B | Nitrile–butadiene rubber | Deformation under constant deflexion | 90, 105, 120 |
| Rubber 3061 [a] | Nitrile–butadiene rubber | Elongation at break<br>weight loss<br>Deformation under constant deflexion | 90, 105, 120 |
| Rubber 3090 [a] | Nitrile–butadiene rubber | Weight loss<br>Elongation at break | 80, 90, 105 |
| Rubber B12/2 [a] | Nitrile–butadiene rubber | Weight loss | 80, 90, 105, 120 |
| | | Deformation under constant deflexion | 90, 105, 120 |

[a] The rubbers PF-60B, 3061, 3090 and B12/2 differ in their acrylonitrile and black carbon contents.

According to the results obtained, the materials investigated can be classified as follows:

(1) materials for which *a* and *b* change with the degree of thermal degradation (PVC, TVC-70 and polychloroprenic rubber, with the properties mentioned in Table 1);

(2) materials for which *a* and *b* do not change with the degree of thermal degradation (rubbers PF-60B, 3061, 3090 and B12/2, with the properties mentioned in Table 1);

(3) EPDM, which exhibits two degradation ranges, namely the range of low values of the degree of thermal degradation, with variable *a* and *b* values, and the range of high values of the degree of thermal degradation, with constant *a* and *b* values.

For the materials classified in group (1), and for EPDM in its first degradation range, eqn. (2) was checked (Fig. 1).

Using the least-squares method, we obtained the values of the constants $\alpha$ and $\beta$ shown in Table 2.

Agrawal's criterion describes in a satisfactory way the kinetic behaviour

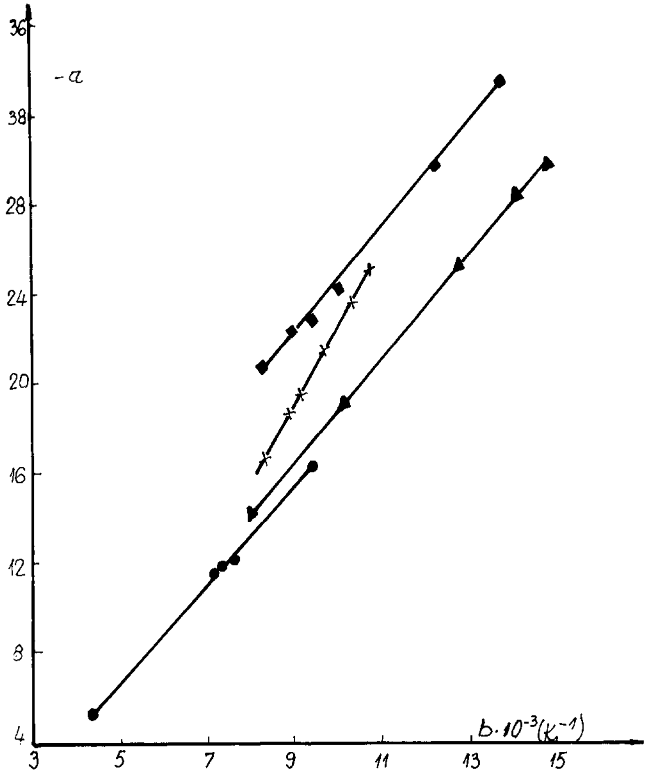

Fig. 1. The correlation of ACE regression coefficients *a* and *b* for the following: ×, TVC-70 (deformation under constant deflexion); ▲, PVC (elongation at break); ■, polychloroprenic rubber (deformation under deflexion); ●, EPDM (elongation at break).

of those materials for which *a* and *b* are dependent on the degree of thermal degradation (Figs. 2–5).

Nevertheless, with the exception of PVC, the Arrhenius straight lines do not intersect at a single temperature, but over a narrow range of tempera-

TABLE 2

The values of the regression parameters $\alpha$ and $\beta$ for the ACE relation

| Material | Property | $\alpha$ | $-\beta \times 10^3$ (K$^{-1}$) | $-r$ [a] |
|---|---|---|---|---|
| TVC-70 | Deformation under constant deflexion | 12.00 | 3.45 | 0.9997 |
| PVC | Elongation at break | 4.03 | 2.30 | 0.9997 |
| Polychloroprenic rubber 8050-PC50 | Deformation under constant deflexion | −0.80 | 2.38 | 0.9981 |
| EPDM | Elongation at break | 4.25 | 2.20 | 0.9987 |

[a] *r* is the correlation coefficient of the linear regression.

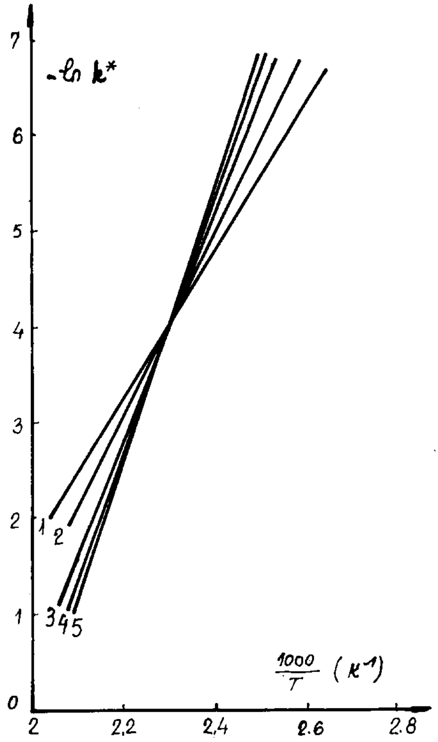

Fig. 2. Arrhenius plots for thermal degradation of PVC at the following relative elongations at break: 1, 0.50; 2, 0.55; 3, 0.50; 4, 0.45; 5, 0.40.

tures. This behaviour could be assigned to the quasi-inconstancy of ln $F(P)$. Table 3 lists the values of the isokinetic temperatures for those materials investigated which exhibit ACE. Besides $T_i$ for PVC, the graphically determined values of $T_i$ show a narrow range, corresponding to the intersection range of the Arrhenius straight lines. The $T_i$ values for TVC-70 are not realistic because this material undergoes thermal degradation at temperatures higher than 40°C. This is why its compensation effect could be only apparent.

## *The ACE for the nitrile–butadiene rubbers PF-60B, 3061 and B12/2*

In one of the attempts to explain the compensation effect in heterogeneous processes [10] it is assumed that the common characteristic of the related reactions is the existence of a main reaction which remains unaltered and a parameter (considered as a secondary factor) which alters the way the reaction rate changes with temperature. Thus the constants $a$ and $b$ should be correlated through ACE for the thermal degradation of materials with similar structures. As shown in Fig. 6, such a correlation has

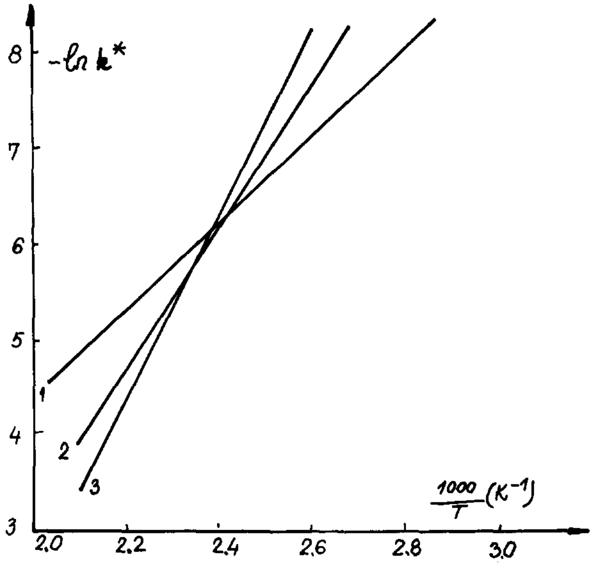

Fig. 3. Arrhenius plots for thermal degradation of EPDM at the following elongations at break: 1, 0.55; 2, 0.45; 3, 0.42.

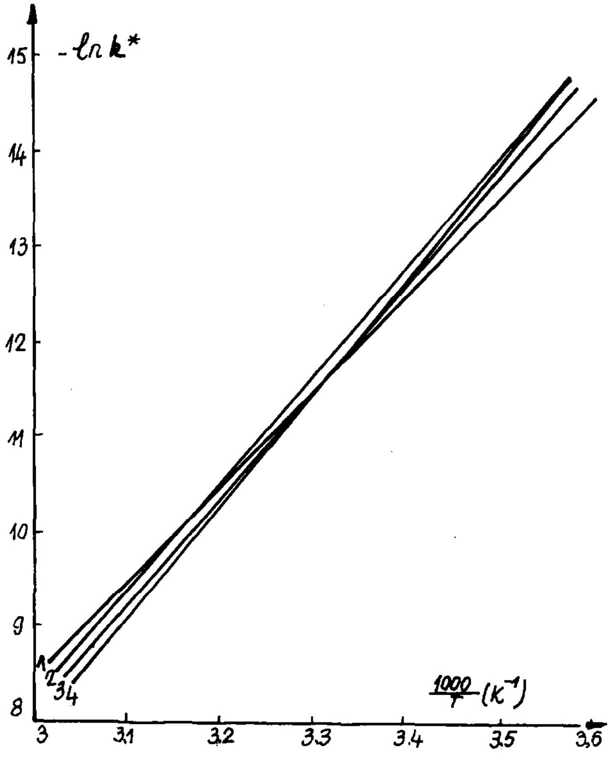

Fig. 4. Arrhenius plots for thermal degradation of TVC-70 at the following deformations under constant deflexion: 1, 0.55; 2, 0.50; 3, 0.45; 4, 0.40.

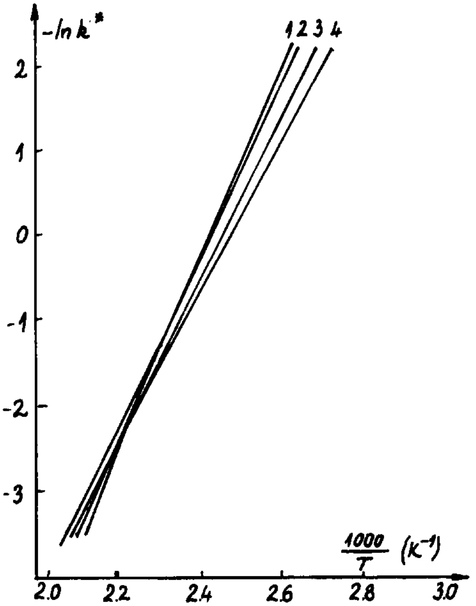

Fig. 5. Arrhenius plots for thermal degradation of polychloroprenic rubber at the following deformations under constant deflexion: 1, 0.35; 2, 0.30; 3, 0-.25; 4, 0.20.

been suggested for the PF-60B, 3061 and B12/2 rubbers. All these rubbers contain nitrile–butadiene as their main component and differ in their contents of acrylonitrile and black carbon (for these materials the residual deformation under constant deflexion was followed).

For the straight line from Fig. 6, the following values of $\alpha$ and $\beta$ have been obtained: $\alpha = 5.67$; $\beta = -2.54 \times 10^{-3}\ \mathrm{K}^{-1}$.

For TVC-70 and polychloroprenic rubber (investigated experimentally in a similar way) the values of $a$ and $b$ do not lie on the straight line shown in Fig. 6. The explanation for this can be found in the difference in composi-

TABLE 3

Isokinetic temperature for materials which exhibit ACE

| Material | $T_i$ (°C) | |
|---|---|---|
| | Calculated according to eqn. (18) | Graphically determined |
| PVC | 162 | 164 |
| EPDM | 182 | 137–150 |
| TVC-70 | 17 | 20– 39 |
| Polychloroprenic rubber 8050-PC 50 | 146 | 142–182 |

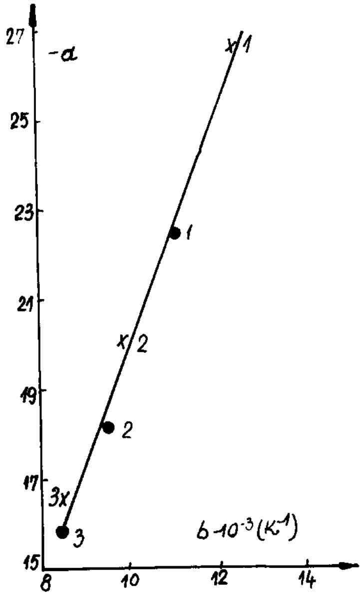

Fig. 6. The correlation of ACE regression coefficients *a* and *b* for the deformation under constant deflexion (●, $(1-D)=0.5$; × $(1-D)=0.6$) of the following rubbers: 1, PF-60B; 2, B12/2; 3, 3061.

tion (Table 1) and implicitly in the difference in the mechanism of thermo-oxidative degradation of these materials compared to the nitrile–butadiene rubbers.

The intersection of the Arrhenius straight lines ($\ln k^*$, $1/T$) in the case of nitrile–butadiene rubbers, for $(1-D)=0.5$ (Fig. 7) and for $(1-D)=0.6$

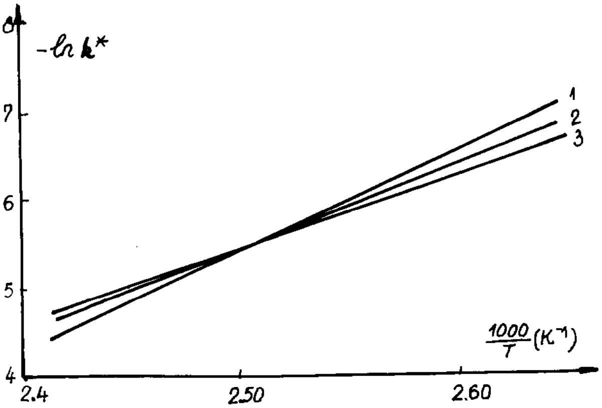

Fig. 7. Arrhenius plots for deformation under constant deflexion ($(1-D)=0.5$) of the following rubbers: 1, PF-60B; 2, B12/2; 3, 3061.

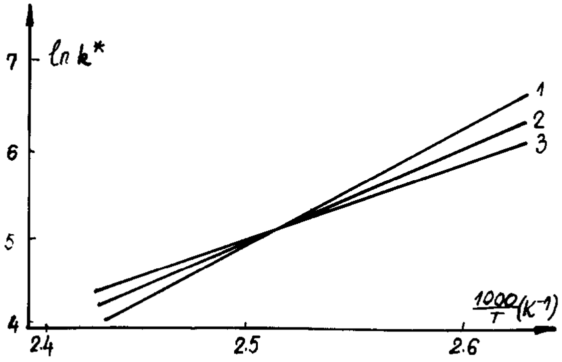

Fig. 8. Arrhenius plots for deformation under constant deflexion ($(1-D)=0.6$) of the following rubbers: 1, PF-60B; 2, B12/2; 3, 3061.

(Fig. 8), where $D$ is the residual deformation under constant deflexion, show that Agrawal's criterion for the compensation is fulfilled.

The isokinetic temperature was evaluated from the slope of the straight line in Fig. 6, and from the value of $1/T$ corresponding to the intersection of the Arrhenius straight lines from Figs. 7 and 8. The values 120°C, 125°C and 126°C were obtained, showing once again the existence of an ACE in the thermal degradation of rubbers PF-60B, 3061 and B12/2.

## CONCLUSIONS

(1) The linearity of the relationship between the coefficients $a$ and $b$ (the ACE) has been checked for thermal accelerated ageing of eight insulating solid polymeric materials.

(2) The ACE is practically a normal chemical compensation effect. This was demonstrated by checking Agrawal's criterion concerning the intersection of the Arrhenius straight lines.

(3) The isokinetic temperature values obtained by two methods are in good agreement.

(4) Until now it was considered that the coefficients $a$ and $b$ were not sensitive to the degree of thermal degradation. Our results partly contradict this statement for some materials which exhibit ACE. From this, the necessity arises for developing a methodology for determining the lifetime of these materials, taking into account the existence of the ACE.

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