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The compensation effect in the non-isothermal degradation of polychloroprene rubber

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Abstract

The results of an attempt to evaluate the non-isothermal kinetic parameters for the thermal degradation of polychloroprene rubber are presented. The non-isothermal kinetic parameters exhibit a compensation effect.

INTRODUCTION

Kinetic investigations of heterogeneous solid–gas decompositions often reveal the validity of the following relationship between the pre-exponential factor A and the activation energy E

$$\ln A = aE + b \tag{1}$$

where a and b are constant coefficients for a series of related reactions [1–10]. Relationship (1) reflects a compensation effect between the exponential and pre-exponential factors in the Arrhenius equation.

Recently [9, 10], relationship (1) has been confirmed for the non-isothermal degradation of a nitrile-butadiene rubber previously submitted to accelerated thermal ageing, as well as for the non-isothermal thermal degradation of various kinds of nitrile-butadiene rubbers.

A compensation effect, known as the "ageing compensation effect" (ACE), has been shown to exist for the accelerated thermal degradation of some electro-insulating polymeric materials [11–14]. In a recent investigation of polychloroprene rubber [13], it was shown that the activation energy depends on the degree of degradation.

This work is a detailed analysis of the TG, DTG and DTA curves of

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polychloroprene rubber in order to obtain the values of the non-isothermal kinetic parameters. The results concerning the existence of a compensation effect will be compared with previous results [13] obtained from the isothermal degradation of the same material following an alteration of the residual deformation under constant deflexion (DRC).

EXPERIMENTAL

Polychloroprene rubber (CATC-Piteşti-Romania) whose isothermal degradation of DRC was previously investigated [13] was used.

The heating curves of powdered samples were recorded on a Q-1500 D MOM Budapest-type Pualik–Paulik–Erdey derivatograph in static air atmosphere in the temperature range 20–500°C, at heating rates of 0.73, 1.48, 3.08 and 6.20 K min^{-1}.

METHODS OF ANALYSING THE EXPERIMENTAL DATA

The following methods were used to estimate the non-isothermal kinetic parameters: the Coats–Redfern [15], the Coats–Redfern modified by Urbanovici and Segal [16], the Flynn–Wall for constant heating rate [17] and the Flynn–Wall for isoconversion [18]. Programs written in BASIC [19, 20] were used to analyse the experimental data, using a TIM-S computer.

RESULTS AND DISCUSSION

Figure 1 shows the derivatogram of polychloroprene rubber recorded at a heating rate of 1.48 K min^{-1}. Similar derivatograms were obtained at all

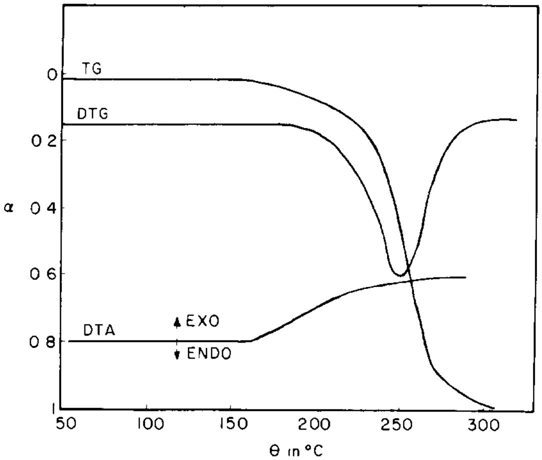

Fig. 1. Derivatogram corresponding to the thermal degradation of polychloroprene rubber at the heating rate of 1.48 K min^{-1}.

the other heating rates. Up to 325°C, a single exothermal degradation process takes place, accompanied by the release of volatile products.

When the above-mentioned integral methods were used to evaluate the non-isothermal kinetic parameters, the results obtained, such as negative values for the apparent reaction order, were physically meaningless. Therefore, the non-isothermal kinetic analysis was carried out using the Flynn–Wall method for isoconversion [18] which enables the activation energy to be evaluated without a detailed knowledge of the heterogeneous reaction mechanism. Straight lines were obtained on plotting $\ln\beta$ against $1/T$, where β is the heating rate, using this Flynn–Wall isoconversion method: for $\alpha = 0.025$ and $\alpha = 0.05$, where α is the degree of conversion, correlation coefficient values $r = 0.9715$ and 0.9666 were obtained. For α values in the range $0.075 \leqslant \alpha \leqslant 0.90$, all the correlation coefficient values were higher than 0.992. As shown in Fig. 2, the activation energy changes with the degree of conversion. In the range of conversion values $0.025 \leqslant \alpha \leqslant 0.35$, the activation energy increases from 10.2 to 25.6 kcal mol^{-1}. For the range $0.35 \leqslant \alpha \leqslant 0.90$, the activation energy decreases from 25.6 to 19.3 kcal mol^{-1}.

A similar increase in activation energy values for degradations below 40% was obtained when investigating the isothermal change of the residual deformation under constant deflexion as a consequence of accelerated

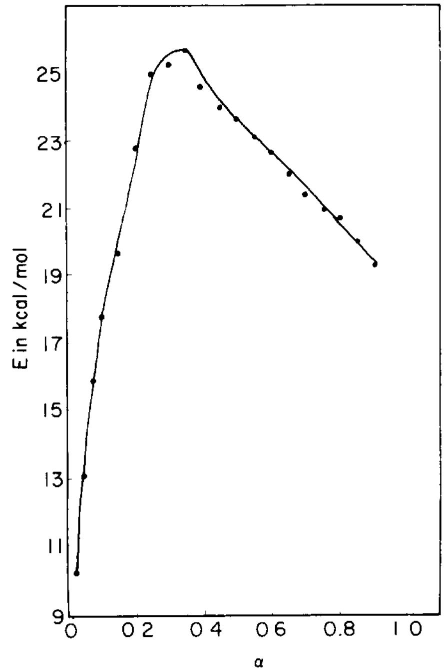

Fig. 2. The activation energy of the non-isothermal degradation of polychloroprene rubber versus the degradation degree.

thermal ageing [13]. Thus, the thermal degradation with release of volatile products is responsible for the decrease in the mechanical property as a consequence of heating.

In order to verify the existence of a compensation effect, the values of the pre-exponential factor for various degrees of conversion and heating rates should be known. The general rate equation of non-isothermal kinetics

$$\frac{d\alpha}{dT}=\frac{A}{\beta}f(\alpha)\exp(-E/RT) \qquad (2)$$

where $f(\alpha)$ is the conversion function, was used to obtain values of the pre-exponential factor with difference α and β values.

For

$$f(\alpha)=(1-\alpha)^n \qquad (3)$$

where n is the apparent reaction order, eqn. (2) in its logarithmic form can be written

$$\ln A=\ln\frac{d\alpha}{dT}+\ln\beta+\frac{E}{RT}-n\ln(1-\alpha) \qquad (4)$$

From eqn. (4), the $\ln A$ values for given values of the degree of conversion α and heating rate β, can be estimated using the value of E determined from the Flynn–Wall method for isoconversion, the value of $d\alpha/dT$, obtained from the DTG curve, and the value of n. From data published concerning the isothermal degradation of polychloroprene rubber [21], $n=1$. However, whatever the value of n, the contribution of the last term in eqn. (4) is negligible with respect to the other terms. Calculations were carried out for the $0.04\leqslant\alpha\leqslant0.14$ range, in which the DTG curves are well-defined for all the heating rates. As shown in Figs.

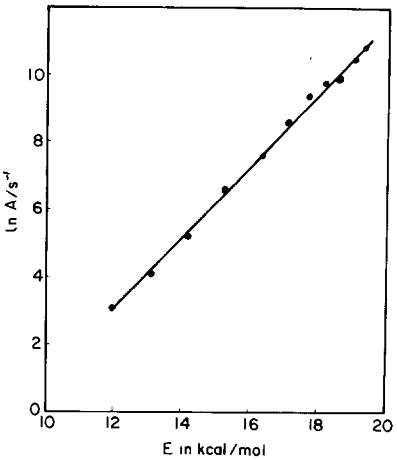

Fig. 3. The plot of $\ln A$ versus E for the thermal degradation of polychloroprene rubber. Heating rate, $\beta=0.73$ K min^{-1}.

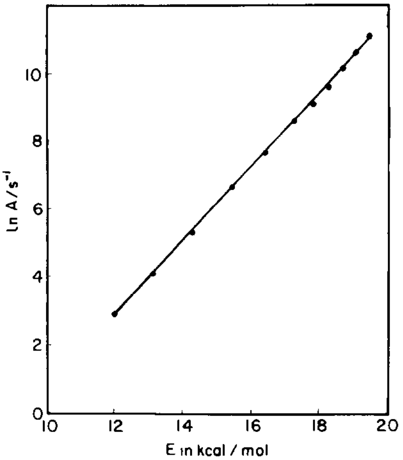

Fig. 4. The plot of ln A versus E for the thermal degradation of polychloroprene rubber. Heating rate, $\beta = 1.48\ \mathrm{K\ min^{-1}}$.

3–6, the ln A values change linearly with the activation energy values, thus suggesting the existence of a compensation effect.

Table 1 gives the values of the a and b parameters of eqn. (1), as well as the values of the isokinetic temperatures, calculated from the relationship [8]

$$T_i = \frac{1}{Ra} \tag{5}$$

It should be noted that there is a satisfactory agreement among the values obtained for the various heating rates. The slight differences in the

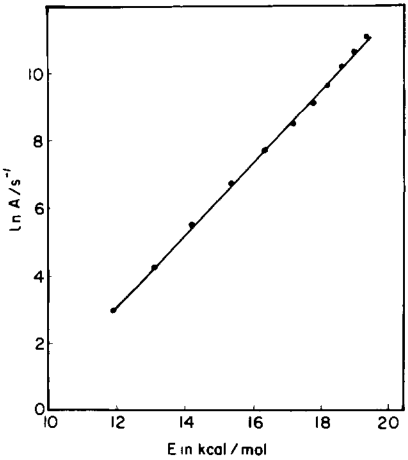

Fig. 5. The plot of ln A versus E for the thermal degradation of polychloroprene rubber. Heating rate, $\beta = 3.08\ \mathrm{K\ min^{-1}}$.

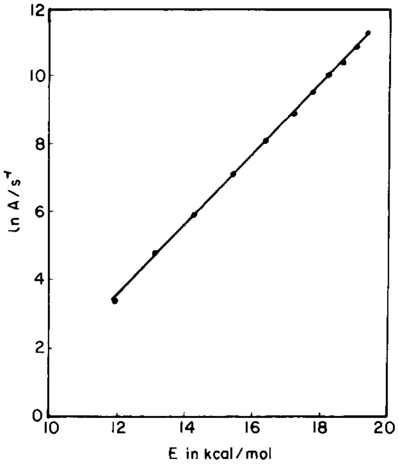

Fig. 6. The plot of ln A versus E for the thermal degradation of polychloroprene rubber. Heating rate, $\beta = 6.20\ \mathrm{K\ min^{-1}}$.

values of the b parameter are probably due to errors in the evaluation of $\mathrm{d}\alpha/\mathrm{d}T$ from the DTG curves. The values of the a parameter in Table 1 are all close to the value $a = 1.2000\ \mathrm{mol\ kcal^{-1}}$, obtained from the data for the isothermal thermomechanical degradation of polychloroprene rubber [13]. This result, as well as the similar change in activation energy with the degree of conversion, suggests that the mechanical ageing of polychloroprene rubber is mainly due to the formation of volatile products (mainly hydrochloric acid [22]).

In order to demonstrate the weak dependence of the a and b parameters on n, their values were estimated for low values of the degree of conversion ($0.04 \leq \alpha \leq 0.08$). In such conditions, $\ln(1-\alpha) \approx -\alpha$, and the activation energy changes linearly with α

$$E = \alpha E_1 + E_0 \qquad (6)$$

with $E_0 = 7.4\ \mathrm{kcal\ mol^{-1}}$ and $E_1 = 114\ \mathrm{kcal\ mol^{-1}}$.

TABLE 1

The parameters of the compensation effect for the non-isothermal degradation of polychloroprene rubber ($A/(\mathrm{s^{-1}})$)

$\beta/(\mathrm{K\ min^{-1}})$	$a/(\mathrm{mol\ kcal^{-1}})$ [a]	$-b$ [a]	r [b]	T_i/K [c]
0.73	1.0546	9.6449	0.9987	477
1.48	1.0876	10.1415	0.9997	463
3.08	1.0611	9.6841	0.9998	474.5
6.20	1.0379	8.9172	0.9998	485

[a] Coefficients of the linear regression. [b] Correlation coefficent of the linear regression. [c] Isokinetic temperature.

TABLE 2

The parameters $(aE_1 - n)$ and $(aE_0 + b)$ obtained from the straight lines of $u(\alpha)$ versus α for the non-isothermal degradation of the polychloroprene rubber

$\beta/(\mathrm{K\,min^{-1}})$	$aE_1 - n$	$-(aE_0 + b)$	r
0.73	115.351	1.6567	0.9992
1.48	119.276	1.8916	0.9993
3.08	117.139	1.6768	0.9989
6.20	116.453	1.1958	0.9980

Taking into account these approximations, from relationships (1) and (4), one obtains

$$u(\alpha) \equiv \ln\frac{\mathrm{d}\alpha}{\mathrm{d}T} + \frac{E}{RT} + \ln\beta = (aE_1 - n)\alpha + (aE_0 + b) \qquad (7)$$

From the straight line of $u(\alpha)$ versus α for $0.04 \leqslant \alpha \leqslant 0.08$ plotted in steps of $\alpha = 0.01$, values for $(aE_1 - n)$ and $(aE_0 + b)$ were obtained, see Table 2.

Using these values, the compensation parameters a and b for $n = 0.5, 1.0, 1.5$ and 2.0 were estimated, see Table 3; for a given heating rate, the a and b values are practically independant of the value of n. Moreover, the calculated a and b values are quite close to those given in Table 1.

Concerning the compensation effect, Garn [2] noticed that the common element of the processes it describes is a main reaction which remains unaltered and in which a parameter considered as a secondary factor changes the variation of the reaction rate with temperature. In our case, the release of hydrochloric acid from polychloroprene rubber can be considered as the main reaction. While it occurs, the structure of the

TABLE 3

The values of the parameters of the compensation effect for the non-isothermal degradation of polychloroprene rubber $(A/(\mathrm{s^{-1}}))$ calculated from the regression coefficients of the straight line of $u(\alpha)$ versus α (eqn. (7))

n	Heating rate $\beta/(\mathrm{K\,min^{-1}})$							
	0.73		1.48		3.08		6.20	
	a	$-b$	a	$-b$	a	$-b$	a	$-b$
0.5	1.0162	9.1768	1.0507	9.6665	1.0319	9.3129	1.0259	8.7875
1.0	1.0206	9.2093	1.0550	9.6986	1.0363	9.3455	1.0303	8.8199
1.5	1.0250	9.2418	1.0594	9.7314	1.0407	9.3779	1.0347	8.8524
2.0	1.0294	9.2742	1.0638	9.7639	1.0451	9.4104	1.0391	8.8848

macromolecular chain changes continuously, thus resulting in the continuous and compensated change of the pre-exponential factor and the activation energy.

CONCLUSIONS

An investigation into the non-isothermal degradation in static air atmosphere of polychloroprene rubber was carried out. Up to 325°C, the material undergoes a single reaction which consists mainly in the release of hydrochloric acid. The non-isothermal kinetic parameters of the reaction depend on the degree of conversion and exhibit a compensation effect.

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