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The compensation effect in the thermo-oxidative degradation of some nitrile butadiene rubbers

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Abstract

The authors present the results of a non-isothermal kinetic analysis of the thermo-oxidative oxidation, accompanied by evolution of volatile compounds, of three kinds of nitrile-butadiene rubbers. A compensation effect characterising the common matrix of the three rubbers was demonstrated.

INTRODUCTION

In homogeneous kinetics, it is widely accepted that the dependence of a specific reaction rate constant on temperature is given by the well known Arrhenius equation

$$k = A\exp\left(-\frac{E_A}{RT}\right) \tag{1}$$

where the terms have their usual meanings.

Equation (1) has been extended to heterogeneous reactions in solid–gas systems, although for these cases the meanings of A and E_A are questionable (the Maxwell–Boltzmann distribution of energy is not established instantaneously in solids). In such heterogeneous systems, a linear relationship of the form

$$\log A = aE_A + b \tag{2}$$

is frequently met [1–8]. Relationship (2) reflects a compensation effect between the exponential and pre-exponential factors in the Arrhenius equation. Thus the validity of relationship (2) for a set of related reactions characterises the existence of a compensation or isokinetic effect. The second term derives from the fact that the validity of relationship (2) presumes the existence of an isokinetic temperature corresponding to the intersection of the Arrhenius straight line plots [6,7]. Also, this temperature can be calculated according to [6,7]

$$T_i = \frac{1}{2.303Ra} \tag{3}$$

Concerning the compensation effect, Garn [8] noticed that the common element of the processes it describes is a main reaction which remains unaltered and in which a parameter, considered a secondary factor, changes the variation of the reaction rate with temperature. This statement is illustrated by our kinetic data, as it will be shown below.

EXPERIMENTAL

Three vulcanized nitrile-butadiene rubbers, denoted B, C and D, produced by CATC, Jilava, Romania, were used. Rubbers B and C contain 38% acrylonitrile, whereas rubber D contains 40% acrylonitrile. All the rubbers contain various amounts of carbon black and plastifiers. Rubber D also contains antioxidants.

The heating curves of the powdered samples were recorded using a Q-1500 D MOM Budapest-type Paulik–Paulik–Erdey derivatograph in static air atmosphere and in the temperature range 20–500 ° C at a heating rate of 2.8 K min^{-1}.

METHODS OF WORKING THE EXPERIMENTAL DATA

To evaluate the non-isothermal kinetic parameters, three methods were used: the Coats–Redfern [9], the Coats–Redfern modified by Urbanovici and Segal [10] and the Flynn–Wall for constant heating rate [11]. The experimental data were processed automatically using BASIC programs [12,13] run on a TIM-S computer.

RESULTS AND DISCUSSION

The TG, DTG and DTA curves for sample B are shown in Fig. 1. Samples C and D give similar curves. Figure 1 shows that there are two changes, α and β, accompanied by weight loss. At a temperature between these two changes, there is an exothermic event (peak I on the DTA curve).

In the case of sample B, peak I is accompanied by a slight increase in weight. For all three investigated samples, peak I is located at practically the

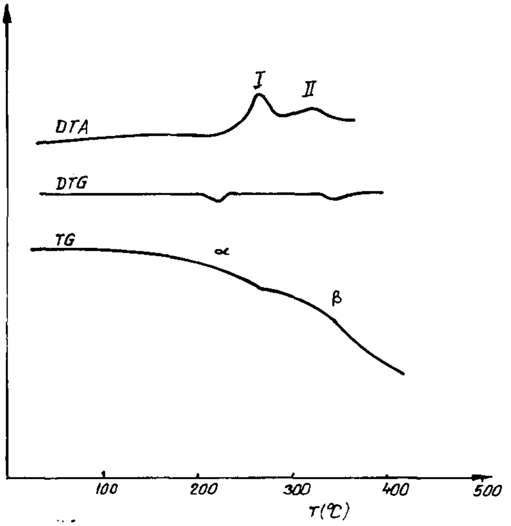

Fig. 1. Derivatogram of nitrile-butadiene rubber B in static air atmosphere at $a = 2.8$ K $\min^{-1}$.

same temperature (between 250 and 255 °C). Therefore, this peak has been assigned to the same oxidation reaction which yields solid products. Similar reactions have been found in the thermo-oxidation of some elastomers [14] and of the compound EVA [15]. In such oxidation reactions, hydroperoxides are mainly generated, probably as a result of singlet oxygen ($^1O_2$, $^1\Delta_g$) attack on the methylene groups of diene monomeric units [16].

The exothermic peak II is located at practically the same temperature (between 300 and 320 °C) for all the samples. This peak corresponds to the change β which occurs with generation of volatile products.

The values of the non-isothermal kinetic parameters for changes α and β are given in Table 1. There is quite good agreement among the values of the non-isothermal kinetic parameters obtained by the different applied methods.

For all the investigated samples, change α has practically the same reaction order value, in the range 1.4–1.6. The values of the activation energy and of the pre-exponential factor differ from sample to sample and are not correlated through relationship (2); thus change α is not characterised by a compensation effect. This can be explained by the fact that change α corresponds to volatilisation of the ingredients (plastifiers, auto-oxidants, etc) which vary in the investigated rubbers. Moreover, rubber samples which have been submitted to accelerated thermal ageing in isothermal conditions at temperatures higher than 80 °C, loose all their volatile ingredients. The derivatograms of such samples do not exhibit change α [17].

Change β is characterised by practically the same reaction order value around 2. The activation energy and the pre-exponential factor values, which

TABLE 1

Values of non-isothermal kinetic parameters for processes α and β of the thermo-oxidative degradation

Rubber	Process	Coats–Redfern				Modified Coats–Redfern				Flynn–Wall ($a = ct$)			
		E_A [a] (kcal mol^{-1})	n [b]	A [c] (s^{-1})	$-r$ [d]	kE_A (kcal mol^{-1})	n	A (s^{-1})	$-r$	E_A (kcal mol^{-1})	n	A (s^{-1})	$-r$
B	α	19.8	1.6	1.676×10^4	0.9988	20.5	1.6	5.881×10^4	0.9988	20.6	1.6	5.542×10^4	0.9990
	β	35.5	2.1	1.991×10^{10}	0.9939	35.4	2.0	1.965×10^{10}	0.9936	36.0	2.1	3.241×10^{10}	0.9947
C	α	12.9	1.6	7.329×10^2	0.9913	13.2	1.6	1.131×10^3	0.9916	13.7	1.5	3.641×10^3	0.9934
	β	41.2	2.0	3.583×10^{12}	0.9942	40.1	1.8	1.264×10^{12}	0.9939	41.4	2.0	4.439×10^{12}	0.9948
D	α	9.7	1.5	2.711×10	0.9675	10.1	1.5	5.292×10	0.9705	10.6	1.4	2.284×10^2	0.9763
	β	25.7	2.1	1.912×10^6	0.9907	25.7	2.0	1.9505×10^6	0.9906	26.1	2.0	3.379×10^6	0.9923

[a] E_A activation energy.

[b] n, apparent reaction order.

[c] A, pre-exponential factor.

[d] r, correlation coefficient of the linear regression.

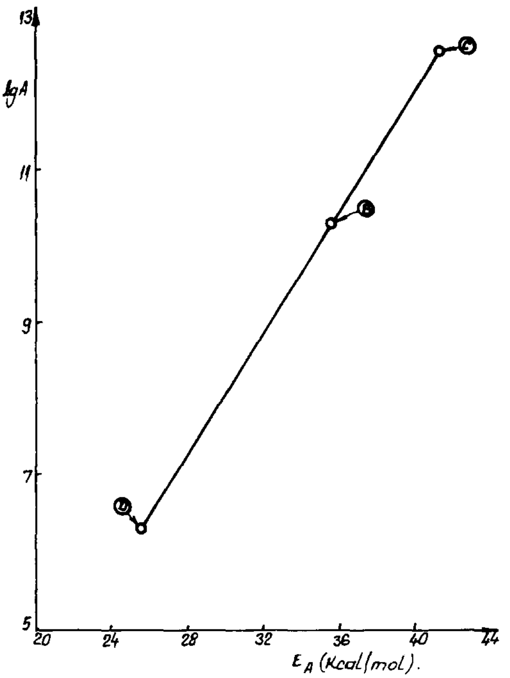

Fig. 2. Plot of log A versus E_A for process β.

differ from sample to sample, are nevertheless correlated through relationship (2); thus in this case a compensation effect is indicated (Fig. 2).

From the straight line plot of log A against E_A, the following values have been obtained for the constants a and b: $a = 0.40409$ mol kcal^{-1} and

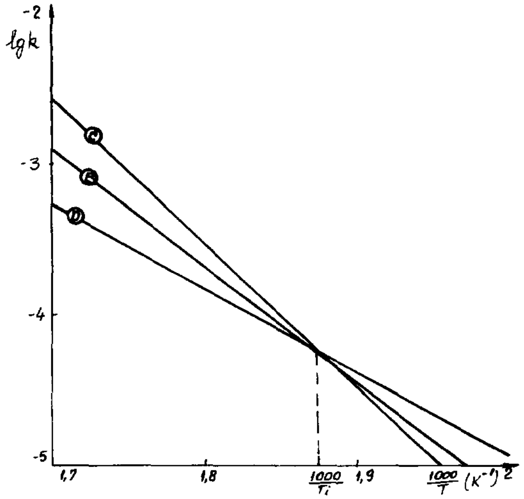

Fig. 3. Arrhenius plots for process β.

$b = -4.0881$. Using this value of a, the isokinetic temperature was calculated using relationship (3): $T_i = 268\,^\circ C$. From the intersection of the three Arrhenius straight lines corresponding to the three investigated samples (Fig. 3), $T_i = 260\,^\circ C$, in satisfactory agreement with the previous value.

The compensation effect seen for change β characterises the common matrix of the investigated rubbers. The differences in the values of E_A and A are mainly due to the varying contents of acrylonitrile and carbon black in the investigated samples.

CONCLUSIONS

The non-isothermal kinetic parameters of the thermo-oxidative degradation of three kinds of nitrile-butadiene rubbers have been determined using three methods which have yielded results which are in satisfactory agreement. A compensation effect has been demonstrated for the change in β that occurs with weight loss.

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