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DSC ANALYSIS OF THE INDUCTION PERIOD IN THE VULCANISATION OF RUBBER COMPOUNDS

P. Šimon[1] *and A. Kučma*[2]

[1]Department of Physical Chemistry, Faculty of Chemical Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava
[2]Research Institute of Rubber, Matador joint stock company, 020 32 Púchov, Slovak Republic

Abstract

Vulcanisation of rubber compounds was studied by DSC under isothermal and non-isothermal conditions. The parameters of an Arrhenius-like equation describing the temperature dependence of induction period have been obtained both from isothermal and non-isothermal measurements. A new method for obtaining the kinetic parameters from non-isothermal measurements, based on the dependence of onset temperature of vulcanisation peak on heating rate, is presented. Also, a procedure for the evaluation of temperature difference between the furnace and sample is proposed. It has been shown that the treatment of non-isothermal DSC measurements gives the kinetic parameters free of systematic errors. The new method can also be used for studying other reactions exhibiting the induction period.

Keywords: differential scanning calorimetry, induction period, kinetics, vulcanisation

Introduction

Curing of rubber compounds occurs in two stages [1]. In the first one, called the induction period, seemingly no chemical reaction takes place. At the end of the induction period the second stage, i.e. the vulcanisation itself, begins. Accurate determination of the induction period is of utmost importance for the rubber technology since this is the point where the physico-chemical and mechanical properties of the rubber compounds change irreversibly as a consequence of the start of crosslinking. The curing is an exothermic process and the reaction heat evolved makes it possible to employ the differential scanning calorimetry (DSC) for its study [1–3]. The vulcanisation is also accompanied by a change in the rheological properties of the compound. Rheometers are the devices used most widely to determine the induction periods and to follow the kinetics of curing.

Kinetic description of the vulcanisation resides in finding the kinetic equations characterising the process and obtaining the values of kinetic parameters (rate constants, activation energies, pre-exponential factors, etc.) appearing in the equations. Knowing this, modelling of the vulcanisation process is possible. The modelling leads to better understanding of the process and it gets the practical importance in optimising the vulcanisation process [4].

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The determination of induction periods from isothermal DSC measurements is quite problematic mainly at lower temperatures since the exothermic peak of curing is flat and its onset can hardly be determined unambiguously. On the other hand, at higher temperatures where the induction periods are below 1 min, the periods are comparable with the time of establishing the steady state of DSC apparatus and a correct determination of the induction period cannot be carried out. When studying the vulcanisation at various heating rates we realised that, contrary to the isothermal measurements, the peak of vulcanisation is distinct in these non-isothermal measurements and the onset temperature can be read accurately and unambiguously. Hence, in this paper a new method is proposed for obtaining the kinetic parameters of induction periods from the onset temperatures of non-isothermal DSC runs with linear increase of temperature. The results obtained are compared with the induction periods obtained by Rheometer.

Experimental

Two techniques were employed to study the curing of the rubber compounds:

1. Differential scanning calorimeter DSC-7 Perkin-Elmer. The temperature scale was calibrated using the standards In and Zn. The samples of 3–4 mg were crimped in standard aluminum pans. The purge gas used was nitrogen.

2. Rheometer MDR-2000 E from Alfa Technologies (Monsanto). The frequency of oscillations was 1.67 Hz, the amplitude was 0.5°. The induction periods were determined as t_{02}.

Theoretical

Dependence of the induction period on temperature can be expressed by an Arrhenius-like relationship [1]:

$$t_i = A\exp[B/T] \tag{1}$$

where A and B are constants and T is the absolute temperature. The constants A and B are mostly obtained from the logarithmic transformation of Eq. (1):

$$\ln t_i = \ln A + B/T \tag{2}$$

For non-isothermal vulcanisation, the induction period can be calculated according to the Eq. (1)

$$1 = \int_0^t \frac{dt}{t_i(T)} \tag{3}$$

where the dependence of t_i on temperature is given by Eq. (1). In case of the linear increase of temperature, the furnace temperature can be expressed as

$$T_f = T_o + \beta t \tag{4}$$

where T_f is the furnace temperature, T_o is the starting temperature of the measurement and β stands for the coefficient of temperature increase (scan). If one assumes that the temperature of the sample equals that of the furnace, combination of Eqs (1), (3) and (4) gives the result

$$\beta = \int_{T_o}^{T_i} \frac{dT}{A\exp[B/T]} \tag{5}$$

where T_i is the temperature of the end of induction period, i.e. the onset temperature of the vulcanisation peak. As Eq. (5) indicates, when increasing the rate of heating, the onset temperature also increases.

When deriving Eq. (5) an assumption has been adopted that the temperature of the sample equals that of the furnace. In DSC non-isothermal measurements, the thermal resistance between the pan and furnace is eliminated by temperature calibration. However, a temperature difference between the bottom of the pan and the sample can exist. For the case that the temperature gradient within the sample and between the sample and the pan are insignificant compared with the difference between the pan and the furnace, a simple method has been proposed for estimation of the temperature lag between the sample and the furnace [3]. We modified the method in order to obtain the correct onset temperature of vulcanisation.

For the power-compensated DSC calorimeters, the signal registered by the apparatus is a difference of powers for heating the sample and the reference, respectively:

$$P = P_s - P_r \tag{6}$$

where P is the DSC signal with respect to the baseline. The powers for heating the sample and the reference, P_s and P_r, can be expressed as

$$P_s = \kappa(T_f - T) \tag{7}$$

$$P_r = m_p C_p \beta \tag{8}$$

where κ is the overall heat transfer coefficient, m_p and c_p stand for the mass and heat capacity of the pan. The overall heat transfer coefficient has been determined from the slope of the peak of In melting to be κ=35.5 mW/K. Combining Eqs (6)–(8) one can get:

$$T = T_f - \frac{P + m_p c_p \beta}{\kappa} \tag{9}$$

Equation (9) enables to calculate the correct values of the sample temperature, so that the kinetic parameters obtained from Eq. (5) are free of systematic errors caused by the different temperatures of furnace and sample.

Results and discussion

Induction periods have been measured for two rubber compounds denoted as KIN1 and KIN2; their composition is summarised in Table 1. The kinetic parameters describing the induction period have been obtained both for isothermal and non-isothermal measurements.

Table 1 Composition of the rubber compounds under study [phr]

Compound	KIN1	KIN2
synthetic polyisopren	100	100
ZnO	4.98	4.98
stearin	1.98	1.98
soot N-330	34.97	34.97
sulphur milled oiled	2.22	2.22
sulfenax CBS/MG	0.96	1.20

The dependences of induction periods on temperature obtained from isothermal measurements are shown in Fig. 1. It can be seen that the curves obtained by DSC are not smooth due to the uncertainties in the determination of onset times for the flat vulcanisation peaks. The kinetic parameters of the induction period, A and B, have been obtained by a direct comparison of experimental and theoretical values of induction periods, where the theoretical values are given by Eq. (1). The minimisation of the sum of squares between experimental and theoretical values has been made by the simplex method [5]. The kinetic parameters have been determined also by the other procedure, i.e. the determination of $\ln A$ and B as the intercept and slope of the linear dependence $\ln t_i = f(1/T)$ given as Eq. (2). The values of A and B obtained by both procedures are listed in Table 2.

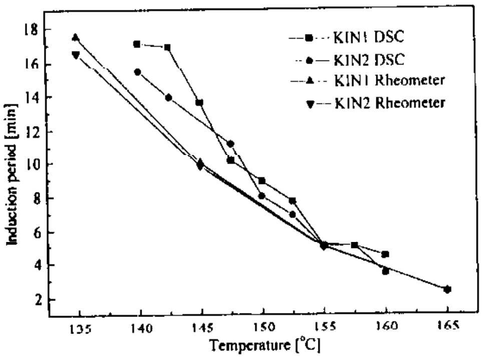

Fig. 1 Isothermal measurements of induction periods by DSC and Rheometer

Table 2 Values of the kinetic parameters A and B obtained by various methods

Sample	Method	10^{14} A/min^{-1}	10^{-3} B/K
KIN1	iso-DSC Eq. (1)	49.8	12.9
	iso-DSC Eq. (2)	12.1	13.5
	non-iso-DSC	2.17	14.1
	non-iso-DSC corrected	2.03	14.1
KIN2	iso-DSC Eq. (1)	315.0	12.1
	iso-DSC Eq. (2)	13.2	13.4
	non-iso-DSC	2.03	14.1
	non-iso-DSC corrected	2.41	14.0

Onset temperatures of vulcanisation for non-isothermal measurements with various scan rates are listed in Table 3. Table 3 also shows the onset temperatures corrected by Eq. (9). The parameters A and B in Eq. (5) have been obtained by minimising the sum of squares between experimental and theoretical values of heating rate by the simplex method [5]. The integration indicated in Eq. (5) has been carried out by the trapezium method. The kinetic parameters are given in Table 2.

Table 3 Onset temperatures (in °C) of vulcanisation for various scan rates

Compound		KIN1	KIN2
Method		DSC original/corrected	
heating rate/ K min^{-1}	2.5	152.11/152.08	152.24/152.21
	5.0	161.92/161.86	161.23/161.16
	7.5	166.84/166.75	167.29/167.19
	10.	171.39/171.26	171.04/170.89
	15.	177.46/177.25	176.20/175.99
	20.	180.86/180.60	180.66/180.37
	30.	183.56/183.18	184.49/184.07

It can be seen from Table 2 that the values of kinetic parameters A and B, describing the dependence of induction period on temperature, differ greatly for isothermal and non-isothermal measurements. In isothermal measurements, the time of heating the sample from ambient temperature to the temperature of measurement taking 30–60 s represents a systematic error. Addition of this constant term to the induction periods leads to lower values of both kinetic parameters. The sum of squares between experimental values of induction periods and those calculated using the kinetic parameters, obtained by a treatment of the isothermal data using Eq. (2) is several times higher than when using Eq. (1). However, we do not consider correct the treatment based on Eq. (2), since the logarithmic transformation obviously brings about a deformation of the distribution of errors and, consequently, the values of A and B are also deformed so that they do not correspond to the true minimum of the sum of squares.

From the original and corrected values of onset temperatures listed in Table 3 it can be seen that the thermal lag between the bottom of the pan and the sample is very small in non-isothermal measurements (up to 0.4 K) even for the highest scan rate. Also, the values of kinetic parameters obtained from the original and corrected temperatures are very close (Table 2). The kinetic parameters obtained with the inclusion of temperature correction should be free of systematic errors. The temperature dependences of induction periods calculated by using the data of Table 2 are shown in Fig. 2 for the compound KIN1. It can be seen that the differences of induction periods for original and corrected non-isothermal data are less than 0.5 min. The induction periods calculated using the parameters obtained from isothermal measurements are longer than those from non-isothermal ones. For 140°C, the difference can reach as much as 5 min which is an apparent consequence of the time delay existing in isothermal measurements.

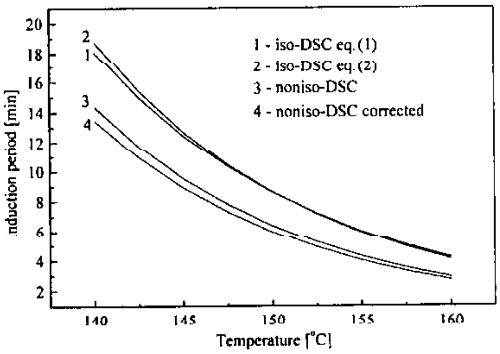

Fig. 2 Temperature dependences of induction period calculated from the data of Table 2 using Eq. (1) for the compound KIN1

Comparison of induction periods obtained by DSC and Rheometer shows that, as a rule, DSC gives longer induction periods than Rheometer (Fig. 1). This difference between DSC and Rheometer data is well known [1, 6–8] and it is ascribed to the production of heat in the sample during the measurements in Rheometer due to the dissipation of the mechanical energy of oscillations [8]. It is obvious that, due to the heat generated, the sample temperature in Rheometer reaches higher value than the temperature of the furnace. This increase of sample temperature is responsible for the shorter induction periods in comparison with DSC.

It can be concluded that the isothermal induction periods involve the time delay due to heating the sample from ambient temperature to the temperature of the measurement. These measurements can be used for comparing the induction periods of different samples since the systematic error affects all measured values in the same direction. In the non-isothermal DSC measurements with temperature correction the systematic errors are eliminated. The kinetic parameters *A* and *B* do not convey the effect of heat transfer within the sample so that they are transferrable to be used in modelling the vulcanisation where the effects of reaction kinetics, heat transfer, evolution of reaction heat, etc. are explicitly involved. An undoubted advantage is that the kinetic parameters are obtained using the same equation as is used for the evaluation of non-isothermal induction periods in modelling the vulcanisation. This procedure eliminates the errors brought about by an eventual imperfection of Eq. (5). We believe that the method of the treatment of non-isothermal DSC runs, based on the analysis of onset peak temperature on heating rate, can be employed also for the study of other reactions exhibiting the induction period, such as oxidation of polymers, oils etc.

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