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Multilinear Regression Analysis in TGA Curves of a Copolymer INFINEUM SV 260

Ioana Stanciu

Universitatea Bucuresti, Bd. Regina Elisabeta 4-12, 030018 Bucuresti, Romania
e-mail: ioasta2003@yahoo.uk.com

Abstract

The kinetic parameters (activation energy, reaction order, reaction enthalpy and preexponential factor) of a copolymer INFINEUM SV 260 were determined using the multilinear regression analysis of a TGA curve.
The same procedure is also applied to some experimental TGA curves obtained for the exothermal decomposition of INFINEUM SV 260.

Keywords: *differential scanning calorimetry, kinetic analysis, multilinear regression, kinetic parameters.*

Introduction

The evaluation of hazard of chemical compounds is an important aspect of safety and loss prevention. Among the most common analytical techniques, the differential scanning calorimetry (DSC) is commonly used for monitoring the exothermal processes because it requires a small sample size and a short analysis time [1, 2]. One the major advantages of the DSC method is that the thermodynamic parameter (reaction enthalpy) and kinetic parameters (activation energy, reaction order and preexponential factor) can be evaluated simultaneously.
The present work presents a calculation method of kinetic parameters based of a TGA curve. The methods are based on the linearization of the fundamental kinetic equation. The are relatively efficient for single step processes, where their results are satisfactory.

Experimental details

The following copolymer were used as: hydrogenated poly(isoprene-co-styrene) (Infineum UK LIMITED) – trade name INFINEUM SV 260.
The experimental thermogram was obtained using a differential scanning calorimeter CAHN DSC 912 under following experimental condition: the heating rate 20°C min^{-1} in non-isothermal conditions, the sample mass 10. 2989 mg.
A method of multilinear regression analysis (MLRA) of the kinetic equation was choused for the simultaneous evaluation of the activation energy, frequency factor and reaction order from a TGA curve. Using a computer simulation program, several TGA curves were obtained, provided with different gaussian errors, starting from the evaluated kinetic parameters. Since the

dependent variable varies within maximum one order of magnitude, constant absolute errors simulate best the naturally occurring spread of experimental data.

Results

The kinetic calculations from the experimental data usually proceed from the basic kinetic equation:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where α is the conversion, t the time and T the absolute temperature. Arrhenius equation is generally used for the dependences of rate constant k(T) on the absolute temperature:

$$k(T) = Ae^{-E/RT} \quad (2)$$

where A is the frequency factor, E the activation energy and R the molar gas constant.
The conversion function is dependent on the assumed reaction mechanism. Various from of this function has been published [3-5]. In this work the following from of the conversion function was used:

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

where n is the reaction order with respect to reactant, describing best our experimental data.
Inserting equations (2) and (3) in equation (1), the kinetic equation in the following form is obtained:

$$d\alpha/dt = Ae^{-E/RT}(1 – \alpha)^n \quad (4)$$

Under non-isothermal conditions the explicit temporal dependence in equation (4) is eliminated through the transformation:

$$d\alpha/dt = (A/\beta)e^{-E/RT}f(\alpha) \quad (5)$$

where $\beta = dT/dt$ is the heating rate.
From experimental TGA the weight of temperature can be also determined using for following equation:

$$d\alpha/dt = A\alpha^n(1-\alpha)^m e^{-E/RT} \quad (6)$$

where m is the reaction order.
Starting from experimental TGA curve, the kinetic parameters (E, A, n and m) were evaluated by a multilinear regression method, using the linearized from of equation (6).
The TGA of INFINEUM SV 260 at the specified temperatures and weight are shows in figure 1.
Table 1 shows the values of kinetic parameters for the thermal decomposition of hydrogenated poly(isoprene-co-styrene) at 20°C min^{-1} heating rate, obtained by multilinear regression.

From TGA curve the deriv. of temperature can be also determined using for following equation 4. The kinetic parameters (E, A and n) were evaluated by a multilinear regression method.
Table 2 shows the values of kinetic parameters for the experimental deriv. of temperature curve obtained by multilinear regression.

Table1. The kinetic parameters obtained with equation 6 for the experimental weight-temperature curve of INFINEUM SV 260

Kinetic parameters	MLRA
E / (kJ mol^{-1})	3. 264E+01
A /s^{-1}	7.552E+00
n	0.5050
m	1.0640
Correlation Coefficient	0.9414

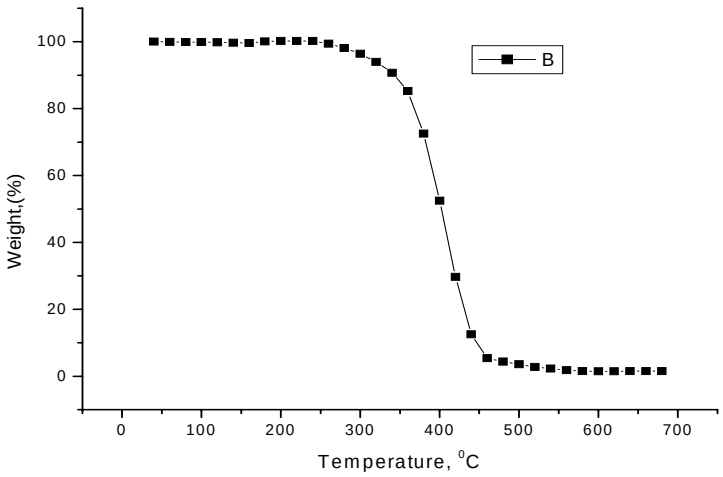

Fig.1. The experimental weight-temperature curve for INFINEUM SV 260

Table2. The kinetic parameters obtained with equation 4 for the experimental derive.-temperature curve of INFINEUM SV 260

Kinetic parameters	MLRA
E / (kJ mol^{-1})	-1.692E+02
A /s^{-1}	2.514E-15
n	2.5190
Correlation Coefficient	0.9035

The TGA of INFINEUM SV 260 at the specified temperatures and derive. are shows in figure 2.

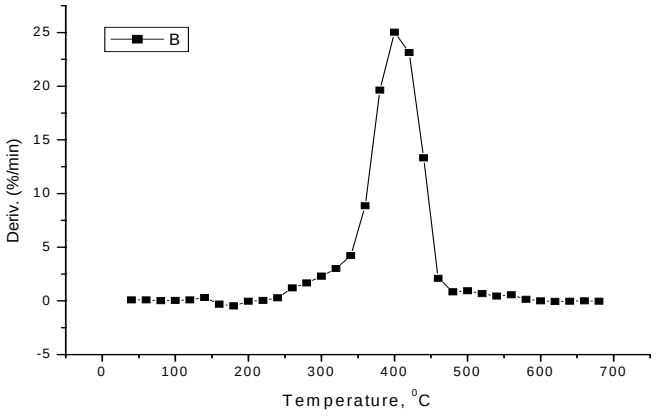

Fig.2. The experimental derive.-temperature curve for INFINEUM SV 260

Conclusions

The results show that a simultaneous calculation of the activation energy, frequency factor and reaction order from a TGA curve from one reaction by multilinear regression of the kinetic equation is a very efficient, direct method which gives good estimates. The method was applied for the evaluation of the kinetic parameters of both the experimental TGA curve for a process. The results of calculations with the values obtained by using multilinear regression analysis [6-10] .

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Regresia multiliniară a curbelor TGA pentru copolimerul infineum SV 260

Rezumat

In cadrul acestui articol sunt prezentate cele mai importante aspecte ale comportării termice ale copolimerului INFINEUM SV 260. Cu ajutorul regresiei multiliniare am determinat parametrii cinetici corespunzători descompunerii termice a copolimerului: energia de activare, factorul preexponențial, ordinul de reacție şi coeficienții de corelație.