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ON THE COMPENSATION EFFECT AT THE FORM OF THE DIFFERENTIAL CONVERSION FUNCTION

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Abstract

From the general form of the rate equation under non-isothermal conditions, some relationships showing the existence of a compensation effect due to the change of the analytical form of the differential conversion function were derived. These relationships were checked for some simulated TG curves, as well as thermogravimetric data corresponding to the degradation of some polymers and to the decomposition of calcium carbonate.

Keywords: compensation effect, non-isothermal kinetic parameters

Introduction

It is well known that in a series of related reactions the activation parameters, preexponential factor (A) and activation energy (E), are correlated through the relationship:

$$\ln A = a + bE \tag{1}$$

where a and b are constants characteristic of the given series [1–19].

The validity of relationship (1) shows the existence of a compensation effect (CE) between the preexponential factor and the activation energy in the Arrhenius equation. In a recent review article, the problem of the compensation effect for the non-isothermal degradation of polymers has been discussed [20].

Literature data reveal that relationship (1) has been checked for various kinetic models applied to the same thermoanalytical curves [9, 10, 17, 19].

This paper is dedicated to a theoretical analysis concerning the compensation effect due to the change of the form of the differential conversion function. The obtained results have been checked for some simulated TG curves, as well as for

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the thermogravimetric data obtained for the thermal degradations of polymeric materials and the decomposition of calcium carbonate.

Theoretical background

By inserting into the general rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the differential conversion function, the condition of linear heating rate:

$$\beta = \mathrm{d}T/\mathrm{d}t \tag{3}$$

and the Arrhenius equation:

$$k(T) = A\exp(-E/RT) \tag{4}$$

one obtains:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} \equiv \ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \ln A - \frac{E}{RT} + \ln f(\alpha) \tag{5}$$

Choosing arbitrarily various kinetic models characterized by various differential functions ($f_1, f_2, ...f_i$), the activation parameters (A_1, E_1; A_2, E_2; ...A_i, E_i) are obtained. It has been shown [9, 10, 17, 19] that these parameters are correlated by the compensation effect relationship (1).

Obviously, for a given temperature T, unique values of α and $\mathrm{d}\alpha/\mathrm{d}T$ are obtained from the corresponding TG curve. Thus, for two kinetic models characterized by two differential conversion functions, $f_1(\alpha)$ and $f_2(\alpha)$, at a given temperature T, the reaction rate has the same values. Consequently:

$$\ln A - \frac{E_1}{RT} + \ln f_1(\alpha) = \ln A_2 - \frac{E_2}{RT} + \ln f_2(\alpha) \tag{6}$$

where the indices 1 and 2 correspond to the two kinetic models considered.

For the activation parameters correlated by the CE (relationship (1)), from relationship (6) one obtains:

$$b = \frac{1}{RT} - \frac{\ln[f_1(\alpha)/f_2(\alpha)]}{E_1 - E_2} \tag{7}$$

On the other hand, the integration of the non-isothermal Eq. (5) using Doyle's approximation for the temperature integral [11] leads to:

$$\frac{1}{RT}=\frac{1}{1.052E_1}\ln\frac{A_1E_1}{\beta R}-\frac{\ln F_1}{1.052E_1}-\frac{5.068}{E_1} \tag{8}$$

where $F_1(\alpha)=\int_0^{\alpha}[\mathrm{d}\alpha/f_1(\alpha)]$ is the integral conversion function.

By inserting this last result into Eq. (7), the following expression is obtained:

$$b=\left[\frac{1}{1{,}052E_1}\ln\frac{A_1E_1}{\beta R}-\frac{5.068}{E_1}\right]-\left[\frac{1}{1.052E_1}\ln F(\alpha)+\frac{\ln[f_1(\alpha)/f_2(\alpha)]}{E_1-E_2}\right]=C-G(\alpha) \tag{9}$$

where C is the term independent of α and $G(\alpha)$ is the term dependent on α.

By inserting into Eq. (9) the following differential functions:

$$f_1(\alpha)=(1-\alpha)^{n_1} \tag{10}$$

$$f_2(\alpha)=(1-\alpha)^{n_2} \tag{11}$$

and the integral conversion function corresponding to $f_1(\alpha)$:

$$F_1(\alpha)=\frac{1-(1-\alpha)^{(1-n_1)}}{1-n_1} \tag{12}$$

the condition for an extremum of $G(\alpha)$:

$$\frac{\mathrm{d}G(\alpha)}{\mathrm{d}\alpha}=0 \tag{13}$$

leads to the following value of α for which b takes its minimum value:

$$\alpha^*=1-\left[\frac{g}{c(1-n_1)+g}\right]^{1/(1-n_1)} \tag{14}$$

where

$$c=\frac{1}{1.052E_1} \tag{15}$$

$$g=\frac{n_1-n_2}{E_1-E_2} \tag{16}$$

Through elimination of the term $1/RT$ between relationship (7) and the similar relationship with the functions $f_1(\alpha)$ and $f_3(\alpha)$, the following result:

$$f_2(\alpha)=f_1(\alpha)^{(1-\gamma)}f_3(\alpha)^{\gamma} \tag{17}$$

with

$$\gamma = \frac{E_1 - E_2}{E_1 - E_3} \tag{18}$$

is obtained.

If $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ correspond to the 'reaction order' model, it is easy to show that:

$$n_2 = n_1(1 - \gamma) + n_3\gamma \tag{19}$$

It can be shown that if $f(\alpha)=\alpha^n$, relationship (19) is still valid.

Relationship (17) cannot be checked for any set of three kinetic models chosen arbitrarily. Generally, an equation in α is obtained and the problem which arises is to find an α value for which this equation is verified. In these cases, the compensation effect still exists because the contribution of the first term from relationship (7) is higher than the contribution of the second one.

A working formula for the calculation of b can also be derived using the integral forms of the rate equations. Thus, according to the Coats-Redfern approximation [11]:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{E} - \ln F(\alpha) - \frac{E}{RT} \tag{20}$$

For two kinetic models characterized by the integral conversion functions $F_1(\alpha)$ and $F_2(\alpha)$, and considering the existence of a compensation effect, we obtain:

$$b_{\mathrm{CR}} = \frac{1}{RT} + \frac{1}{E_1 - E_2}\ln\frac{E_1F_1(\alpha)}{E_2F_2(\alpha)} \tag{21}$$

On the other hand, for Doyle's approximation:

$$\ln F(\alpha) = \ln\frac{AE}{\beta R} - 5.3314 - 1.052\frac{E}{RT} \tag{22}$$

a similar procedure leads to

$$b_{\mathrm{D}} = \frac{1.052}{RT} + \frac{1}{E_1 - E_2}\ln\frac{E_2F_1(\alpha)}{E_1F_2(\alpha)} \tag{23}$$

According to relationships (7), (21) and (23), the value of the parameter b depends on the heating rate, as for a given α the corresponding T increases with this operational parameter. Thus, one expects that parameter b should decrease with increasing heating rate.

Applications

Relationships (7), (21) and (23) for the evaluation of the compensation parameter b will be applied to:

- the thermogravimetric data from reference [21] generated for: $f(\alpha)=1-\alpha$; E=83.6 kJ mol^{-1}; $A=1.67\cdot10^{10}$s^{-1} and the heating rates of 1, 2, 5, 10, 50 and 100 K min^{-1};
- the thermogravimetric data concerning the thermooxidative degradation of a glass reinforced epoxy resin (GRER), presented in an earlier work [22];
- the thermogravimetric data concerning the thermal degradation in an argon flow of a resin R obtained by heating for 18 h 150°C of a mixture of equivalent amounts of a highly reactive resin DINOX 010S (produced by Polycolor-Bucharest Romania) and DDS (diamino-dimethyl-sulfone).

Relationship (19) will be checked for:

- GRER;
- resin R;
- the results of Madarász *et al.* [19] concerning the decomposition of $CaCO_3$;
- the results obtained by Mincheva *et al.* [23] concerning the effect of a retardant (bromine compound) on the degradation of polyethylene terephthalate (PET).

Evaluation of the compensation parameter b

Thermogravimetric data given in reference [21]

The kinetic models corresponding to the conversion functions listed in Table 1 were considered.

Table 1 The analytical forms of the conversion function

Mechanism	Code	$f(\alpha)$
Avrami-Erofeev (m=2)	AE2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
Diffusion mechanism	D1	α^{-1}
Diffusion mechanism	D2	$[-\ln(1-\alpha)]^{-1}$
Reaction order	R0.9	$(1-\alpha)^{0.9}$
Reaction order	R1	$1-\alpha$
Reaction order	R1.5	$(1-\alpha)^{1.5}$

Table 2 Values of the kinetic parameters obtained by using theoretical simulated thermogravimetric data from reference [21], for reaction mechanisms listed in Table 1

	β=1 K min^{-1}			β=10 K min^{-1}			β=100 K min^{-1}		
Mechanism	E/ kJ mol^{-1}	ln$A$/ A/s^{-1}	r	E/ kJ mol^{-1}	ln$A$/ A/s^{-1}	r	E/ kJ mol^{-1}	ln$A$/ A/s^{-1}	r
AE2	42.6	8.92	0.9967	41.4	9.55	0.9958	41.0	10.54	0.9956
D1	128.7	38.61	0.9944	127.9	37.13	0.9956	128.0	36.03	0.9956
D2	143.8	44.32	0.9978	143.0	42.48	0.9985	143.0	41.02	0.9985
R0.9	84.0	23.61	0.9993	–	–	–	82.7	23.22	0.9993
R1	86.9	24.85	0.9992	86.1	24.39	0.9990	85.9	24.31	0.9990
R1.5	105.7	31.04	0.9976	102.2	30.19	0.9967	102.2	29.71	0.9966

r is the correlation coefficient of the linear regression

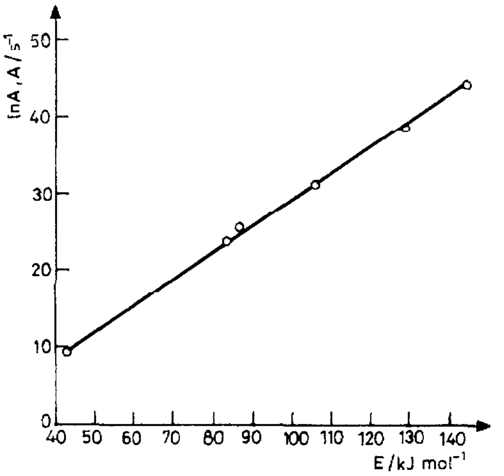

Fig. 1 The straight line ln$A$ *vs.* E for the data listed in Table 2; β=1 K min^{-1}

Table 3 The compensation parameters evaluated using the data from Table 2

β/K min^{-1}	b/mol kJ^{-1}	a	r
1	0.347	–5.624	0.9998
10	0.322	–3.460	0.9992
100	0.296	–1.319	0.9991

The kinetic parameters for each conversion function were evaluated from the parameters of the straight line: $\ln\left[\frac{\beta(\mathrm{d}\alpha)/(\mathrm{d}T)}{f(\alpha)}\right]$ *vs.* $1/T$ as shown in an earlier paper

[24]. The results are listed in Table 2. As seen from this Table, all the considered conversion functions lead to high values of the correlation coefficient.

For each considered heating rate, the straight lines ln*A* *vs.* *E* were drawn. Such a straight line for $\beta=1$ K min^{-1} is shown in Fig. 1.

The values of the compensation parameters obtained from such straight lines are listed in Table 3.

The data in Table 3 show clearly the existence of the compensation effect ($r>0.999$). As expected, the value of the b parameter decreases with the heating rate.

Table 4 shows the values of b, b_{CR} and b_D calculated with relationships (7), (21) and (23) for different pairs of conversion functions and values of α in the range $0.1\leq\alpha\leq0.6$.

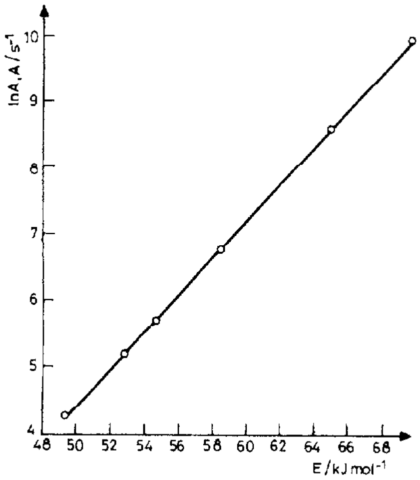

Fig. 2 The straight line ln*A* *vs.* *E* for GRER; $\beta=2.97$ K min^{-1}

For the same pair of conversion functions, the values of b, b_{CR} and b_D appear to be close (practically equal). The b values for $0.1\leq\alpha\leq0.6$ are practically independent of the degree of conversion. Finally, the calculated b values are close to those obtained from the slope of the straight line ln*A* *vs.* *E* (Table 3). The differences can be assigned to the fact that relationship (17), which is a kind of condition imposed by the existence of the CE, cannot be checked for all the considered kinetic models. In order to confirm this statement, let us consider: $f_1(\alpha)=1-\alpha$; $E_1=86.9$ kJ mol^{-1}; $f_2(\alpha)=(1-\alpha)^{1.5}$; $E_2=1105.7$ kJ mol^{-1}; $f_3(\alpha)=\alpha^{-1}$; $E_3=128.7$ kJ mol^{-1}. Inserting into relationship (17) the value obtained for γ obtained by means of Eq. (18) ($\gamma=0.45$), the following relationship:

$$0.95\ln(1-\alpha)=-0.45\ln\alpha \qquad (24)$$

should be verified. But such a result is not valid for $0<\alpha<1$, as its left side <0 while its right side >0.

Table 4 Values of b, b_{CR} and b_D calculated by means of relationships (7), (21) and (23) using the data in Table 2

	$f_1=1-\alpha$ $f_2=[-\ln(1-\alpha)]^{-1}$			$f_1=\alpha^{-1}$ $f_2=[-\ln(1-\alpha)]^{-1}$			$f_1=1-\alpha$ $f_2=(1-\alpha)^{1.5}$			$f_1=1-\alpha$ $f_2=\alpha^{-1}$		
α	b/	b_{CR}/ mol kJ^{-1}	b_D/	b/	b_{CR}/ mol kJ^{-1}	b_D/	b/	b_{CR}/ mol kJ^{-1}	b_D/	b/	b_{CR}/ mol kJ^{-1}	b_D/
0.1	0.342	0.340	0.342	0.387	0.393	0.399	0.387	0.396	0.395	0.326	0.320	0.321
0.2	0.345	0.345	0.346	0.382	0.387	0.392	0.381	0.389	0.387	0.331	0.327	0.328
0.3	0.346	0.344	0.346	0.381	0.385	0.389	0.379	0.385	0.384	0.333	0.330	0.330
0.4	0.345	0.345	0.346	0.382	0.384	0.388	0.377	0.383	0.381	0.332	0.331	0.331
0.5	0.344	0.345	0.346	0.384	0.383	0.388	0.381	0.382	0.380	0.329	0.331	0.331
0.6	0.342	0.344	0.345	0.387	0.384	0.388	0.384	0.382	0.380	0.325	0.330	0.330

Table 5 Vaues of the non-isothermal kinetic parameters for the thermooxidative degradation of GRER

β=1.45 K min^{-1}				β=2.97 K min^{-1}			
n	E/ kJ mol^{-1}	ln$A$/ A/s^{-1}	r	n	E/ kJ mol^{-1}	ln$A$/ A/s^{-1}	r
0.8	46.8	3.23	0.9947	0.5	49.7	4.24	0.9932
1.2	51.6	4.69	0.9980	0.7	53.1	5.19	0.9963
1.5	55.6	5.87	0.9987	0.8	54.8	5.70	0.9972
1.8	59.8	7.13	0.9979	1.0	58.5	6.79	0.9977
2.0	62.9	8.015	0.9966	1.3	65.0	8.58	0.9944
				1.5	69.8	9.89	0.9908

Table 6 The compensation parameters for the data listed in Table 5

β/ K min^{-1}	b/ mol kJ^{-1}	a	r
1.45	0.297	−10.666	0.9999
2.97	0.283	−9.807	0.9998

Table 7 Values of b, b_{CR} and b_D calculated by means of relationships (7), (21) and (23) using data in Table 5

β=1.45 K min^{1} $f_1=(1-\alpha)^{0.8}$; $f_2=(1-\alpha)^2$				β=2.97 K min^{-1} $f_1=(1-\alpha)^{0.5}$; $f_2=(1-\alpha)^{1.5}$			
α	b/	b_{CR}/ mol kJ^{-1}	b_D/	α	b/	b_{CR}/ mol kJ^{-1}	b_D/
0	0.013	–	–	0	0.289	–	–
0.034	0.292	0.309	0.287	0.035	0.280	0.296	0.276
0.067	0.285	0.301	0.278	0.066	0.273	0.288	0.269
0.113	0.280	0.294	0.271	0.109	0.268	0.282	0.262
0.195	0.279	0.289	0.266	0.172	0.265	0.277	0.257
0.279	0.279	0.285	0.262	0.246	0.263	0.273	0.252
0.380	0.282	0.283	0.259	0.351	0.265	0.271	0.255
0.492	0.291	0.285	0.261	0.444	0.266	0.268	0.251
0.606	0.304	0.290	0.265	0.561	0.273	0.270	0.247
0.738	0.327	0.300	0.275	0.667	0.281	0.281	0.249
				0.772	0.296	0.276	0.254

As expected, not only the *b* values but the b_{CR} and b_D values for a given α decrease with increasing heating rate.

Thermogravimetric data concerning the thermooxidative degradation of GRER

The TG curve obtained for the heating rates 1.45 K min^{-1} and 2.97 K min^{-1} [22] will be analyzed.

We shall consider that the differential conversion function is given by the 'reaction order' model Eqs (10) and (11). The values of the obtained kinetic parameters are listed in Table 5.

For both heating rates used, the plots ln*A* *vs.* *E* are linear. Figure 2 shows the straight line corresponding to β=2.97 K min^{-1}.

The parameters of the straight lines ln*A* *vs.* *E* are listed in Table 6.

In Table 7 the values of *b*, b_{CR} and b_D calculated using relationships (7), (21) and (23) considering pairs of conversion functions are given. As one can see, by using relationships (7) and (21), the *b* values are close to those obtained from the slope of the straight line ln*A* *vs.* *E*.

Higher deviations (maximum 12.8%) are obtained when using relationship (23) based on Doyle's approximation. As shown in Fig. 3, *b* exhibits a minimum value for 0.27<α<30. Using Eq. (14) for β=2.97 K min^{-1}, the value α^*=0.296 is obtained, in satisfactory agreement with the one obtained from Fig. 3. Similar

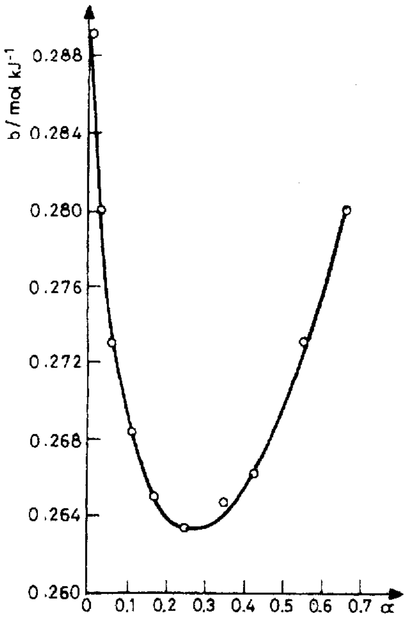

Fig. 3 The change of *b* parameter calculated using relationship (7) with the conversion degree for GRER (β=2.97 K min^{-1})

calculations for β=1.45 K min^{-1} show a good agreement between α^* calculated by means of relationship (14) and α^* obtained from the curve *b vs.* α.

Thermogravimetric data obtained for the thermal degradation of resin R

The investigation of the thermal degradation of resin R in an argon flow (10 l h^{-1}) at β=2.62 K min^{-1} evidenced a single step which occurs in the temperature range 292°C–425°C and with a total mass loss of 70.4%. The maximum degradation rate corresponds to a temperature of 381°C. Considering that the kinetics of degradation is described by 'reaction order' conversion functions, by changing the values of *n*, we obtained the results shown in Table 8.

Table 8 Values of non-isothermal kinetic parameters for the thermal degradation of resin R

n	*E*/kJ mol^{-1}	ln*A*/*A*/s^{-1}	*r*
0.5	137	18.27	0.9889
0.6	143	19.42	0.9918
0.8	155	21.95	0.9962
1.1	177	26.40	0.9991
1.3	194	29.80	0.9982
1.5	213	33.53	0.9951

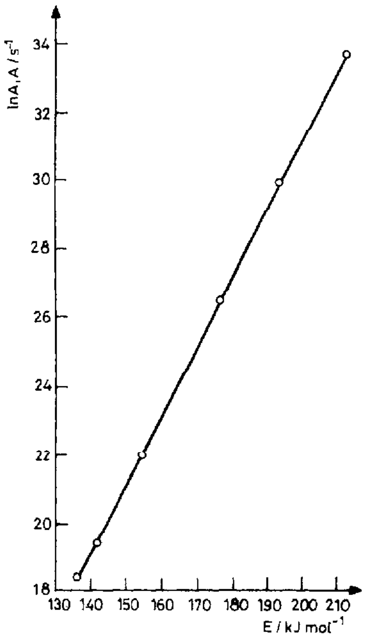

Fig. 4 The straight line ln*A vs. E* for resin R

Figure 4 shows the straight line ln$A$ *vs.* E which has the following parameters:

b=0.200 mol kJ^{-1}; a=–9.078 (A expressed in s^{-1}) with r=0.9999.

Table 9 Values of b, b_{CR} and b_D calculated by means of relationships (7), (21) and (23) using the data in Table 8

$f_1=(1-\alpha)^{0.6}$; $f_2=(1-\alpha)^{1.1}$				$f_1=(1-\alpha)^{0.6}$; $f_2=(1-\alpha)^{1.5}$			
α	b/ mol kJ^{-1}	b_{CR}/ mol kJ^{-1}	b_D/ mol kJ^{-1}	α	b/ mol kJ^{-1}	b_{CR}/ mol kJ^{-1}	b_D/ mol kJ^{-1}
0	0.213	–	–	0	0.213	–	–
0.024	0.201	0.207	0.205	0.024	0.201	0.207	0.206
0.038	0.199	0.205	0.203	0.038	0.199	0.205	0.203
0.094	0.197	0.202	0.200	0.094	0.199	0.202	0.200
0.108	0.196	0.202	0.199	0.108	0.196	0.201	0.199
0.145	0.195	0.200	0.198	0.145	0.195	0.200	0.198
0.178	0.194	0.199	0.197	0.178	0.194	0.199	0.197
0.225	0.194	0.198	0.195	0.225	0.193	0.197	0.196
0.282	0.193	0.197	0.194	0.282	0.193	0.196	0.195
0.380	0.194	0.197	0.194	0.380	0.193	0.196	0.194
0.445	0.194	0.196	0.193	0.445	0.193	0.195	0.194
0.591	0.197	0.197	0.194	0.591	0.195	0.195	0.194
0.638	0.198	0.196	0.193	0.638	0.196	0.195	0.193
0.751	0.199	0.197	0.194	0.751	0.199	0.196	0.194
0.836	0.203	0.199	0.196	0.836	0.203	0.197	0.195
0.897	0.211	0.200	0.197	0.897	0.208	0.199	0.197
0.939	0.218	0.202	0.199	0.939	0.213	0.201	0.199

Table 10 Checking of relationship (19) for GRER and resin R

	GRER β=1.45 K min^{-1}					GRER β=2.97 K min^{-1}					resin R		
n_1	1.2	0.8	1.8	1.5	1.0	0.8	0.8	0.5	1.0	0.8	1.1	1.1	0.5
n_3	1.8	2.0	1.5	2.0	1.3	0.5	1.5	0.7	1.3	0.7	1.5	1.3	0.8
n_2	0.8	1.8	2.0	1.2	0.8	1.3	1.3	1.5	0.7	1.0	0.8	0.6	1.3
γ	–0.59	0.805	–0.75	–0.54	–0.60	–2.00	0.67	6.00	–0.87	–2.25	–0.62	–2.02	3.14
n_2^*	0.85	1.8	2.0	1.3	0.8	1.4	1.3	1.7	0.7	1.0	0.85	0.7	1.4

n_2^* is the value of n_2 calculated by means of relationship (19); γ was calculated using the values of the activation energy listed in Table 5 for GRER and Table 8 for resin R

Table 11 Checking of relationship (19) for the decomposition of $CaCO_3$ [19] and degradation of PET [23]

	Decomposition of $CaCO_3$						Degradation of PET			
n_1	0.4303	0.4557	0.4814	1.097	0.9383	0.8768	0.5*	1.0*	0.5**	0.5**
E_1/kJ mol^{-1}	150.06	155.00	159.97	265.10	240.16	230.17	192.13	311.37	91.94	91.94
n_3	0.7343	0.6991	0.5878	0.7569	0.7346	0.8158	1.5	2.0	1.5	2.0
E_3/kJ mol^{-1}	206.16	200.02	179.99	210.03	206.21	220.04	430.40	549.94	349.89	478.89
n_2	0.5347	0.5878	0.5347	0.9383	0.8158	1.0640	1.0	1.5	1.0	1.0
E_2/kJ mol^{-1}	170.11	179.99	170.11	240.16	220.04	259.94	311.37	430.40	220.94	220.94
γ	0.3574	0.5551	0.5065	0.4529	0.5926	−2.9388	0.5004	0.4985	0.5000	0.3334
n_2^*	0.5390	0.5908	0.5353	0.9430	0.8175	1.0560	1.0	1.5	1.0	1.0

For the meaning of n_2^* and γ see Table 10

* 0% retardant

** 5% retardant

Table 9 shows the b, b_{CR} and b_D values calculated using relationships (7), (21) and (23) for two pairs of differential conversion functions. In this case, for the entire α range, the values calculated for b are close to the value of the slope corresponding to the straight line ln$A$ *vs.* E. One can equally notice that the b values listed in Table 9 exhibit a minimum.

Checking equation (19) for the 'reaction order' model

As shown for $f(\alpha)=(1-\alpha)^n$ with different values of n, the existence of the CE requires the validity of relationship (19). Tables 10 and 11 show how relationship (19) is checked for:

– the thermooxidative degradation of GRER;

– the thermal degradation of resin R in an argon flow;

– the decomposition of $CaCO_3$ with the kinetic parameters according to Madarász *et al.* [19];

– the thermal degradation of PET with the kinetic parameters according to Mincheva *et al.* [23].

A good agreement can be observed between the imposed n_2 values (round the optimum value given by the computing program) and the values calculated using Eq. (19).

Conclusions

Taking into account the existence of the compensation effect due to the change of the analytical form of the conversion function:

– three relationships for the evaulation of the b parameter were derived;

– a relationship between differential conversion functions which lead to activation parameters correlated by compensation effect was equally derived.

The obtained relationships are well verified by the experimental data.

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