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Compensation effects in the thermoxidative decomposition of polymers

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SUMMARY

Are presented some aspects of the non-isothermal kinetics of the thermoxidative decomposition of poly(methylmethacrylate), poly(vinylchloride), poly(vinylacetate) and poly(vinylalcohol). Both the apparent activation energies and the pre-exponential factor depend on conversion and exhibit a pseudo-compensation effect.

INTRODUCTION

In our previous papers /1-3/ it has been suggested that the apparent activation energy of the thermal and thermoxidative decomposition of polymers depend on the heating rate (hr), the sample mass, the athmosphere, the conversion degree, the molecular weight and on other operational and structural parameters.

In this paper we have reanalysed our former data in order and to evaluate the pre-exponential factor and the reaction order and to establish if there acts or not a compensation effect in polymer decomposition reactions.

EXPERIMENTAL

The thermoxidative decomposition of the following polymers has been studied: Poly(methylmethacrylate) - PMMA - (radicalic, M_w=108,000; 11% iso-, 50% syndio- and 38.5% atactic); poly(vinylchloride) - PVC - (suspension, 56.1% Cl, M_n=29,000 and 52,000, respectively; fractionated and unfractionated samples); poly(vinylacetate) - PVAc - (100% acetate groups, M_w=170,000 and 480,000) ; poly(vinylalcohol) - PVA - (alkaline hydrolysis of PVAc , 98-99% degree of hydrolysis; M_n=76,000 and 108,000).

As it has been already mentioned /1-3/, the thermal decomposition was studied using a Paulik, Paulik - Erdey type Derivatograph, at different hr between 2 and 40^{o}C/min. The sample weight was of 20 mg either as film (of 0.03 mm thickness for PVC and PVAc and of 0.06-0.08 mm for PVAc) or as powder (granulation of 0.06-0.07 mm). Al_2O_3 freshly calcinated at 1200^{o}C was used as DTA reference material.

The kinetic parameters have been computed by coupling in a FORTRAN IV programm the differential method of Swaminathan /4/ with the isoconversional method of Friedman /5/. As a result the following equation was used:

$$\ln B \, d\alpha/dT = \ln A - E/RT + n \ln(1-\alpha)+m \ln\alpha+p \ln[(-\ln(1-\alpha)] \qquad (1)$$

$\alpha = W_t/W_\infty$ is the degree of conversion given by the ratio of the weight loss at time "t" and at the end of the process; T the temperature in K; B the hr; A the

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*To whom offprint requests should be sent pre-exponential factor; E the activation energy and m,n,p reaction orders. The last three terms are included in the "conversion function", noted by f(α).

The Swaminathan method is applied to a single TG curve and leads to average or overall values; the method of Friedman uses Tg curves obtained at different hr and gives kinetic parameters for different conversion degrees in the supposition that these are identical for all hr used.

For a good reliability of the computed parameters a minimum of 30 equidistant weight loss points were found to be necessary for the evaluation of each individual Tg curve. These reading procedure has been repeated for 3 times, increasing thus the number of data points up to 155. dα /dT has been evaluated by numerical method.

The equations were solved by the least square method. The solutions were tested by evaluating both the difference $(d\alpha/dT)_{exp}-(d\alpha/dT)_{calc}$ and the mean square error for each experimental point of the DTG and TG curves, respectively.

RESULTS and DISCUSSION

Using equ.(1) it was possible to test the known 17 mechanistic functions of the kinetic laws of the solid-gas decomposition reactions /6/ and all the related functions with different values of the reaction orders m, n and/or p.

The obtained average values (for different hr, numbers of read out points, film or powder samples) of the kinetic parametres vary in large limits (see Fig.1). For each of the studied polymer a particular correlation has been obtained between the computed pre-exponential factors and apparent activation energies, represented by an iso-kinetic relation of the form:

$$\ln A = a_1 + a_2E \qquad (2)$$

In Table 1 are presented some of the results concerning the evaluation of the kinetic parameters of the thermoxidativ decomposition of PMMA at a hr of 10°C/ min. Were tested the various f(α) functions for different numbers of reading out points.

Table 1. Kinetic Parameters for the Thermoxidative Decomposition of PMMA, hr = 10°C/min

Number of read out points	Exponents of f(α)			Symbol for f(α)	ln A	E (Kj/mol)
	n	m	p			
154	1.719	0	0	I	25.43	125.54
	0	1.634	0	II	-31.29	-147.08
	0	0	2.06	III	-53.05	-249.67
	0	1.196	0.569	IV	-37.44	-176.09
	0.630	0	1.439	V	-27.14	-126.22
	0.218	1.456	0	VI	-24.43	-114.19
	1.407	-2.261	3.493	VII	-24.73	-113.19
75	1.703	0	0	I	25.405	125.46
	0	1.681	0	II	-31.63	-148.89
	0	0	2.116	III	-53.97	-254.24
	0	1.12	-0.711	IV	-39.33	-185.28
	0.588	0	1.56	V	-30.42	-142.11
	0.133	1.572	0	VI	-27.50	-129.12
	1.775	-3.498	4.793	VII	-28.23	-129.44

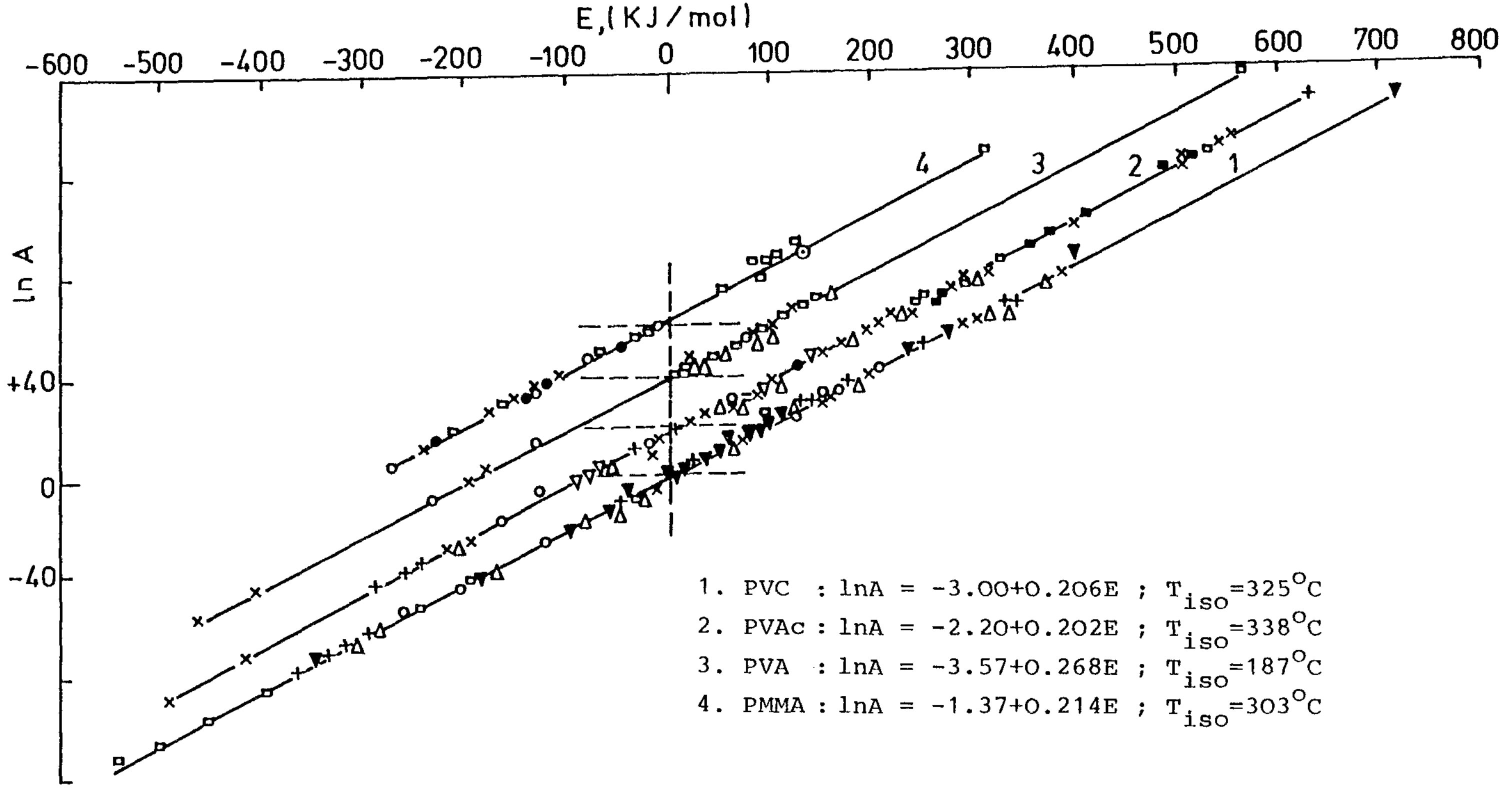

Fig.1 The interdependence between lnA and E for: 1 - PVC, 2 - PVAc, 3 - PVA and 4 - PMMA The curves of the last three are shifted along the ordinate by 20, 40 and 60 units, respectively. (⊙) - theoretical value. x, o, and ● - 155, 75 and 30 read out points; ▼, △ different molecular weights; ■, ▽ different hydrolysis degrees and ☐ different hr. All seven f(α) equations shown in Table 1 were used for each polymer

It is evident, that only the form (I) of the conversion function, i.e.

$$\ln \beta \, d\alpha /dT = \ln A - E/RT + n \ln(1-\alpha) \qquad (3)$$

with n=1.7 assures a good reproductibility. Negative values of ln A and/or E are meaningless from the kinetic point of view. Positive values of the kinetic parameters might thus be used as a criterion for choosing the most probable conversion function.

A supplementary criterion could be a good reproductibility of the kinetic parameters by using a decreasing number of experimental points. A good agreement between values obtained by various differential and/or integral methods and those obtained in isothermal reaction condition support supplementary the correctness of the choosen conversion function.

In the case of PMMA which obeys the relatively simple depolymerization mechanism a good agreement was obtained between published values of A and E /7/ and the computed values by using form (I) i.e. equ. (3) of the conversion function.

The results shown in Fig.2 do not confirm that a selected best conversion function is valid for the whole TG range. Similar all the other tested functions show a minimum error for only the restricted middle part of the TG curves, that means for about 30% (to maximum 60% for other vinyl polymers) of the whole decomposition range.

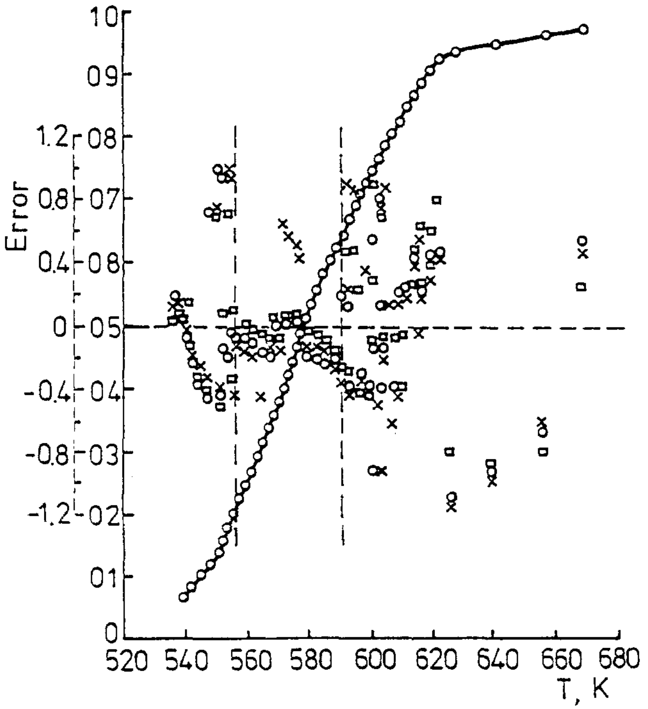

Fig. 2 Magnitude of errors in each individual point of the TG curve of PMMA decomposition. Errors evaluated for kinetic parameters evaluated for the conversion functions of form: I - □ ; V - x and VI - o , respectively.

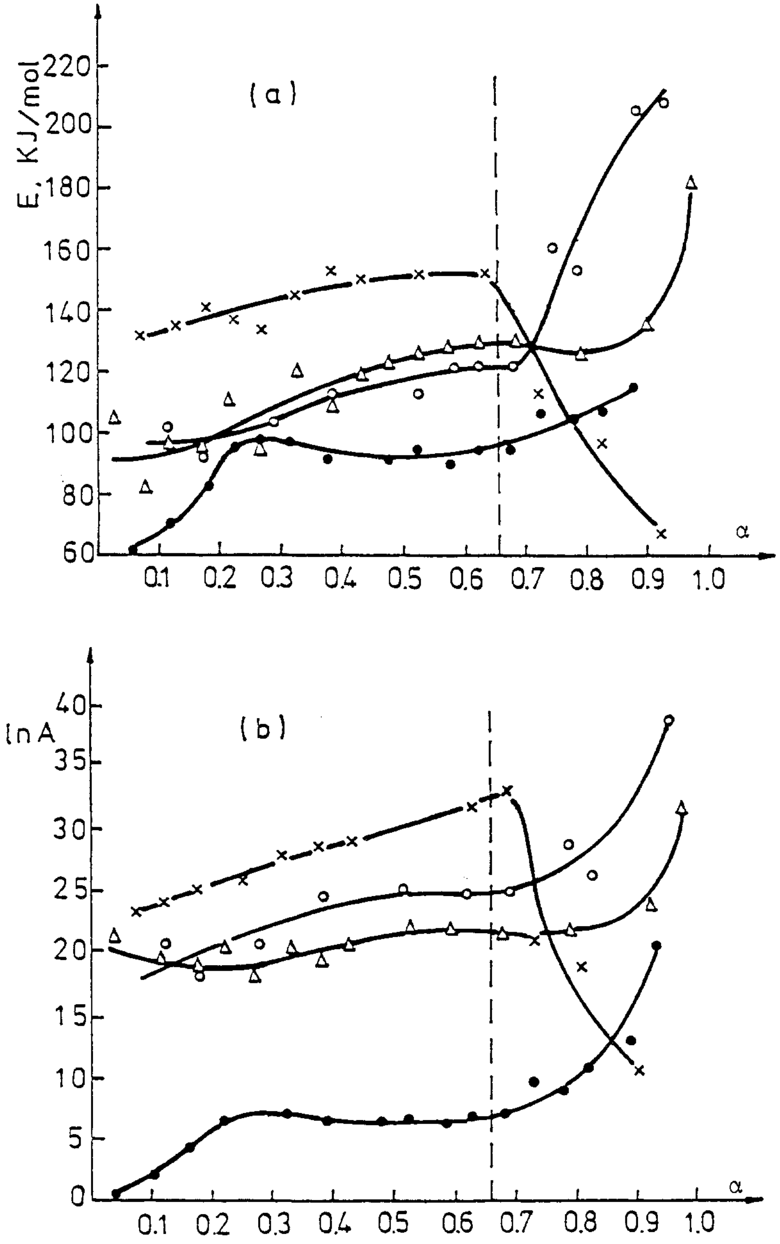

Fig.3 Composition Dependence of the Kinetic Parameters
a - E vs. α and b - lnA vs. α for the thermoxidative decomposition of: x - PVC ; o - PVAc ; - PVA and o - PMMA. f(α) given by equ.(3)

Table 2. Kinetic Parameters for the Thermoxidative Decomposition of Polymers at different heating rates

Polymer	hr ^{o}C/min	ln A	E Kj/mol	Reaction orders			ln k	Decomposition range, ^{o}C
				n	m	p		
PMMA	10.50	25.43	125.54	1.714	0	0	13.13-13.67	267 - 346
	26.40	18.16	90.78	1.312	0. 196	0	14.21-14.81	271 - 369
	28.10	22.30	110.31	1.503	0	0	17.55-18.24	278 - 372
PVAc	5.50	19.46	106.87	0.804	0	0	14.98-15.46	293 - 360
	25.00	24.63	118.97	0	6.56	-0.532	19.94-20.40	330 - 396
PVA K_W=30	2.60	18.21	91.79	0.86	0	0	13.64-14.36	205 - 295
	5.96	19.30	101.10	1.64	0	0	14.37-15.74	215 - 402
K_W=70	2.81	33.80	164.79	0	3.46	-4.15	25.57-27.45	203 - 344
	14.20	21.39	118.07	7.53	- 1.63	0	170.44-173.1	373 - 415

(K_W : K - Wert, technical measure of molecular weight)

The large errors at the begining and the end of the TG curves are due on the one hand to the non-linear increase of the sample temperature because of the reaction heat and on the other hand to the possible invalidity in these ranges of the choosen conversion function. Supplementary it is generally hard to differentiate between the various conversion functions by using the mean square error method . The respective values vary in a too narrow range.

The use of the Agrawal's criterion /8/ to account for the possible validity of the compensation rule is not advisable because the higher the hr the TG curves are shifted towards higher temperatures. The overall rate constants, k, vary correspondingly (Table II).

But only for unique chemical decomposition processes the TG curves are shifted parallel each other towards higher temperatures and no conversion dependence of the kinetic parameters is observed. These is generally not valid for polymer decomposition. The results are in agreement with those published by Adonyi and Körösi /9/ and other authors /10,11/.

It is well known /1/ that the isoconversional method is most suitable for the study of polymer degradation because changes in reaction mechanism can be evidenced.

The Friedman method can be applied in two variants: either by addapting the optimal conversion function for each conversion interval or by using a fixed form of the conversion function for the whole decomposition range. The latter posibility was used in our case. Thus the conversion function equ.(3) has been used with $n \in [1.5, 1.7]$.

In both cases nearly the same E values were obtained. The dependence of these E values on the conversion degree, α, is presented in Fig. 3a. A similar dependence is observed for ln A (Fig. 3b).

On the contrary, if the conversion function is optimized for each conversion interval, no compensation effect is observed (see Fig.4).

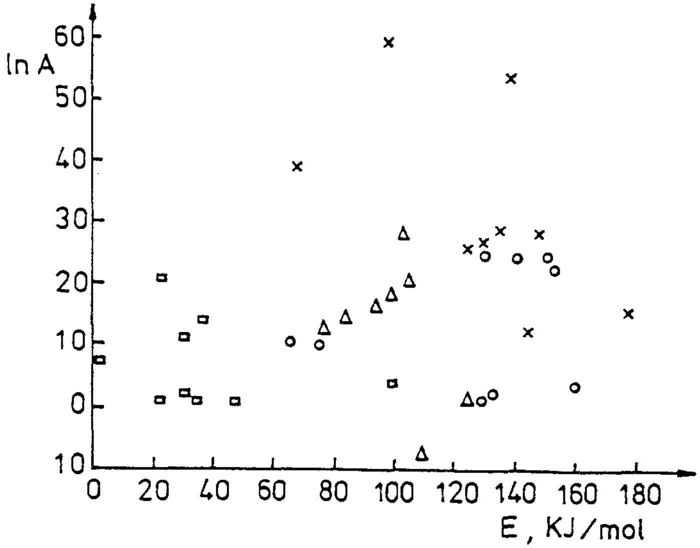

Fig. 4 lnA vs E for the Thermoxidative Decomposition of : x - PVC ; o - PVAc ; $\triangle$ - PVA and ☐ - PMMA. Conversion function used for different decomposition interval see Table 3.

From Fig.3 it can bee observed supplementary that there are only small variations of the E values for a relatively large conversion range. Hence the studied polymers obey a relatively simple oxidativ decomposition mechanism. For $\alpha > 0.65$ the deviations are higher, probabely the conversion functions used are not more valid in this range /12/.

It can be concluded that the occurence of the compensation effect depends on the data set and the computing procedure used. The latter is related supplementary to the choosen conversion function. It can thus be considered only as an apparent compensation effect.

The best fit of the TG curves is obtained by using for each conversion range the adapted optimal conversion function. These can be realized only by using many TG curves recorded at different hr.

For the studied polymers we have found optimal conversion functions shown in Table 3.

To establish the best values of the reaction orders n,m and p, at least ten TG curves at different hr are required.

Table 3. Conversion Function used for Polymer Decomposition

Polymer	Conversion interval	Most probable Conversion function
PVC	0.00 - 0.32	$(-\ln(1-\alpha))^p$
	0.32 - 0.70	$(1-\alpha)^n$
PVAc	0.00 - 0.20	α^m
	0.20 - 0.60	$(1-\alpha)^n$
	0.60 - 0.9o	$\alpha^m(-\ln(1-\alpha))^p$
PVA	0.00 - 0.70	$\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p$ complex mechanism
PMMA	0.00 - 0.25	$\alpha^m(-\ln(1-\alpha))^p$
	0.25 - 0.80	$(1-\alpha)^n$

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