

**DETERMINATION OF THE ACTIVATION ENERGY  
OF THE DECOMPOSITION OF FLAME RETARDED  
HIPS UNDER SPECIAL CONSIDERATION  
OF THE COMPENSATION EFFECT**

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**Abstract:** The kinetic triplet of high impact polystyrene (HIPS) and fire retarded HIPS was determined using a new method which eliminates the compensation effect after the calculation of the activation energy and the pre-exponential factor using the Kissinger and the Ozawa method. It was found that the change in the pre-exponential factor has a strong impact on the degradation. The degradation follows nucleation kinetics described by Avrami-Erofeev kinetics and power-laws.

## **1. Introduction**

In order to improve the flammability of High Impact Polystyrene (HIPS), which is frequently used for injection molding applications, brominated fire retardants, such as decabromo diphenyl ether (DPE) and decabromodibenzyl (DDB), are used. The effect of these fire retardants can be improved by adding  $Sb_2O_3$  as a synergist. However, the thermal decomposition (e.g. during combustion or thermal recycling processes, such as pyrolysis) of fire retarded HIPS causes the release of brominated dibenzo dioxins and furans. Since these compounds are a threat for health and environment, the behavior of the decomposition of HIPS is under investigation for a long time[1-4]. One important aspect of the degradation is the determination of the activation energy  $E_A$ , the pre-exponential factor  $k_0$  and the kinetic model, since this information allow conclusions about the pathway of the degradation. However, the results depend strongly on the method used. One reason for this behavior is the so called compensation effect[5], which is visible in a linear relationship between the  $k_0$  and  $E_A$ . The invariant kinetic parameter (IKP) method was found to be sufficient for the elimination of the compensation effect from the method of Coats and Redfern [6-7].

We will show that the compensation effect observed in the calculation of kinetic parameters from iso-conventional methods (i.e. Kissinger or Ozawa) can be successfully eliminated. The results of this procedure are close to those obtained by the IKP method, however, applicable for a wider decomposition range.

## 2. Experimental

For this investigation, five samples were used: HIPS, HIPS+DPE (DPE-Sb(0)), HIPS+DPE+Sb<sub>2</sub>O<sub>3</sub> (DPE-Sb(5)), HIPS+DDB (DDB-Sb(0)), HIPS+DDB+Sb<sub>2</sub>O<sub>3</sub> (DDB-Sb(5)), with contents of 13 wt% fire retardant and 5 wt% Sb<sub>2</sub>O<sub>3</sub>. A Seiko TG/TDA6200 was used in a temperature range between 50 °C and 700 °C with helium gas flow of 200 ml min<sup>-1</sup>.

Initially, the  $E_A$  and  $k_0$  values were calculated for 99 weight losses in a weight loss range between 1 and 99 wt% by two methods, Kissinger[8] and Ozawa[9]. Four of these data pairs were used to determine the compensation effect parameters  $\alpha$  and  $\beta$  using eq. 1, resulting in 24 pairs of  $\alpha$  and  $\beta$ :

$$\lg k_0 = \alpha + \beta * E_A \quad \text{eq. 1}$$

These  $\alpha$  and  $\beta$  pairs formed again a straight line, which was used to calculate the invariant kinetic parameters  $k_0^*$  and  $E_A^*$ :

$$\alpha = \lg k_0^* - E_A^* * \beta \quad \text{eq. 2}$$

However, it was observed that the degradation process is in general described by more than one kinetic triplet. The kinetic triplets obtained were used to model the degradation of the samples.

## 3. Results and Discussion

The degradation of HIPS took place between 350 and 450 °C. The thermal stability was slightly reduced by the addition of a fire retardant and strongly affected in the presence of Sb<sub>2</sub>O<sub>3</sub>, visible in an early degradation step prior to the main degradation (Fig.1). However, the degradation was nearly independent from the fire retardant used.

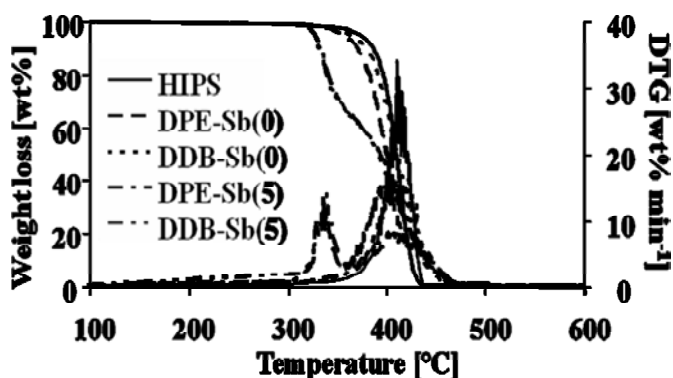


Fig. 1 TGA and DTG of the degradation of HIPS at 5 K min<sup>-1</sup>

## PART I PYROLYSIS

As it can be seen in Fig. 2a (HIPS) and Fig. 2b (DDB-Sb(5)), the calculation of  $E_A$ , using the methods of Kissinger and Ozawa, suggests the change of the  $E_A$  with the weight loss. It can also be seen that there is a linear dependency of  $k_0$  from  $E_A$  (Fig. 2c, Fig. 2d). This compensation effect is actually an indication that the  $E_A$  observed is not the real one. As it can be seen in Fig. 2e and Fig. 2f, the points, obtained from eq. 1 are located close to a common regression line; however, a closer look reveals that for each sample three degradation regions can be named.

As it can be expected from Fig. 2a, the changes in the  $E_A$  for the different regions were quite small (Tab. 1); however, also for the other samples it was found that the variation in  $E_A$  was much smaller than it would be expected from the plot of  $E_A$  over the weight loss. For any of the fire retarded samples, the  $E_A$  changed little in a range of about 80 wt%. The degradation, however, was much more influenced by the change in  $k_0$ . As it can be seen in Tab. 1, this is often accompanied by a change in the kinetic model. This might be caused by changes in the properties of the material.

Tab. 1 Activation energies  $E_A^*$ , pre-exponential factors  $k_0^*$ , and regression coefficients  $r$ , calculated from compensation effect parameters and their weight loss range.

Sample	range [wt%]	Kissinger			Ozawa			Reaction model
		$E_A^*$ [kJ mol <sup>-1</sup> ]	$\lg k_0^*$	$-\lg(1-r^2)$	$E_A^*$ [kJ mol <sup>-1</sup> ]	$\lg k_0^*$	$-\lg(1-r^2)$	
HIPS	1-96	202	15.1	3.29	202	15.1	3.84	
	1-12	161	12.6	2.81	171	13.4	3.81	A3/2
	13-52	198	14.9	3.78	199	15.0	3.73	A3
	53-96	200	14.4	4.83	201	14.6	4.91	P2
DPE-Sb(0)	1-96	143	10.6	2.85	147	11.0	2.99	
	1-48	145	11.0	3.17	148	11.3	3.34	A2
	49-80	144	10.4	3.54	148	10.8	3.63	P2
	81-96	216	15.5	3.07	218	15.6	3.20	F1/3
DDB-Sb(0)	1-96	167	12.3	2.61	169	12.5	2.98	
	1-45	166	12.5	3.90	168	12.7	3.95	A3/2
	45-84	172	12.5	3.50	175	12.8	3.38	P3
	85-96	304	22.0	3.49	305	22.1	2.80	P4
DPE-Sb(5)	1-96	147	11.5	1.99	149	11.7	1.97	
	1-40	148	12.2	3.14	151	12.4	3.12	A2/A3
	41-72	151	11.2	2.70	154	11.5	2.79	A2
	73-96	211	15.1	2.10	211	15.1	2.12	F1/3
DDB-Sb(5)	1-96	125	9.8	1.40	129	10.2	1.46	
	1-36	145	12.0	2.21	148	12.3	2.30	A3
	37-84	150	11.1	2.54	154	11.5	2.54	A2
	85-96	254	18.2	2.90	247	17.4	3.08	F0

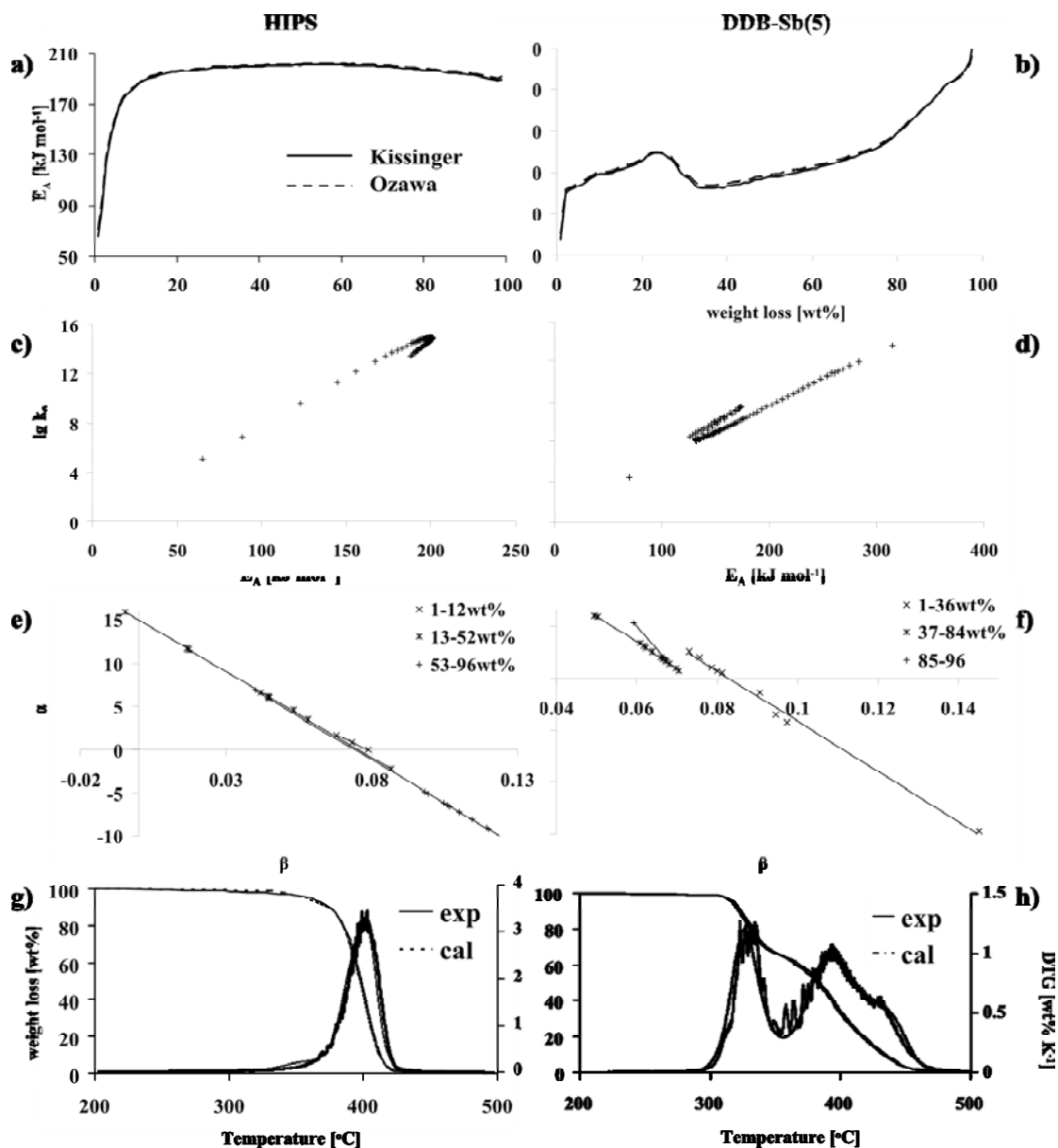


Fig. 2 Degradation of HIPS (left side) and DDB-Sb(5) (right side). a) and b)  $E_A$  versus weight loss, c) and d)  $k_0$  versus  $E_A$ , e) and f) compensation effect parameters  $\alpha$  and  $\beta$ , g) and h) experimental and calculated TG and DTG plots.

The kinetics of each sample can be described by mechanisms after Avrami-Erofeev (A3/2, A2, A3) or power-laws (P2, P3, P4). This indicates that HIPS and fire retarded HIPS decomposes by the formation of a small number of centers, where initially radicals are formed. From these centers the reaction approaches by radical propagation. The results of the modeling are shown in Fig. 2g and 2h. The kinetic triplets used show a good agreement with the experimental data.

### 4. Conclusion

Kinetic parameters of the degradation of fire retarded HIPS were successfully gained by a new method, allowing the elimination of the compensation effect from iso-conventional methods. The modeling of the TG and DTG plots showed the validity of the obtained data.

These data can be helpful for the investigation of the behavior of HIPS at high temperature. They can be used for the calculation of the residence time of HIPS in different reactors during thermal processes; or with a deeper knowledge of the degradation behavior, a way of minimizing the evolution of brominated organic compounds might be found.

### References

- [1] B. L. Joesten, E. R. Wagner. *J. Appl. Polym. Sci.* **1977**, *21*, 2675.
- [2] R. Luijk, H. A. J. Govers, G. B. Eijkel, J. J. Boon *J. Anal. Appl. Pyrolysis.* **1991**, *20*, 303.
- [3] S. Hamm, M. Strickeling, P. F. Ranken, K. P. Rothenbacher *Chemosphere.* **2001**, *44*, 1353.
- [4] E. Jakab, Md. A. Uddin, T. Bhaskar, Y. Sakata *J. Anal. Appl. Pyrolysis* **2003**, *68-69*, 83.
- [5] A. I. Lesnikovich, S. V. Levchik *J. Therm. Anal.* **1985**, *30*, 677.
- [6] B. Jankovic, B. Adnadevic, *Int J. Chem. Kinet.* **2007**, *39*, 462.
- [7] A. W. Coats, J. P. Redfern *Nature.* **1964**, *201*, 68.
- [8] T. Akahira, T. Sunose Research Report Chiba Institute, *Technology*, **1971**, *16*, 22.
- [9] T. Ozawa Bull. *Chem. Soc. Jpn.* **1965**, *38*, 1881.