

Distributed activation energy model (DAEM) of the thermal degradation of flame retarded HIPS

Guido Grause^{1),*}, Jun Ishibashi¹⁾, Tomohito Kameda¹⁾, Thallada Bhaskar²⁾,
Toshiaki Yoshioka¹⁾

¹⁾ Graduate School of Environmental Studies, Tohoku University

²⁾ Catalytic Conversion Process Division (CCPD), Indian Institute of Petroleum (IIP), India

The distributed activation energy model (DAEM) of the degradation of high impact polystyrene (HIPS) showed the effect of fire retardants and Sb_2O_3 . The addition of these compounds led to the broadening of the activation energy range. While pure HIPS degraded to 70% in a range between 200 and 210 kJ mol^{-1} , there was no favored activation energy region in the presence of Sb_2O_3 .

Introduction

Plastics are used in almost all areas of life. Since they consist mainly of carbon and hydrogen, they also show a high flammability. In order to prevent plastics from burning fire retardants are added. Many common fire retardants contain brominated compounds. These compounds are very helpful in the prevention of fires, however, cause trouble after use. Brominated fire retardants have to be removed during the recycling process in order to obtain a valuable product that can be used as a feedstock in the chemical industry.

There are many studies concerning the degradation of fire retardants [1], however, few investigations were carried out studying the degradation behaviour from the point of view of the activation energy. The DAEM is a powerful tool for the determination of the kinetic properties of a material. It allows the identification of different degradation steps and also the determination of the activation energies of these steps. It is possible to use the kinetic data obtained to recalculate the weight loss for any temperature profile. Combined with the knowledge of the evolved products (e.g. brominated products) at any stage allows the improvement of existing dehalogenation processes.

Experimental

The development of a DAEM is shown in this presentation using HIPS with and without fire retardant as an example. Two different fire retardants, decabromodiphenylether (DPE) and decabromodibenzyl (DDB), were added to the HIPS. The effect of Sb_2O_3 was also investigated.

HIPS was degraded by TGA at four different heating rates (2.5, 5.0, 7.5 and 10.0 K min^{-1}). The activation energy E_A and the frequency factor k were determined after the method of Miura [2] using an interval of 1% weight loss.

Results and Discussion

It was observed for all samples, that $\log k$ showed a linear dependence on E_A . However, E_A was not rising over the whole temperature range. In certain areas of the degradation, E_A was decreasing. The inflections can be used to determine the degradation steps of the material.

HIPS degraded in a single degradation step with a peak at 210 kJ mol^{-1} (Fig. 1). 70 wt% of the material was degraded between 200 and 210 kJ mol^{-1} . Therefore, E_A was smaller than for polystyrene [3] or butadiene rubber [4].

The addition of DPE or DDB showed similar effects on the degradation of HIPS. The degradation was slightly delayed in the beginning due to a scavenger effect of the fire

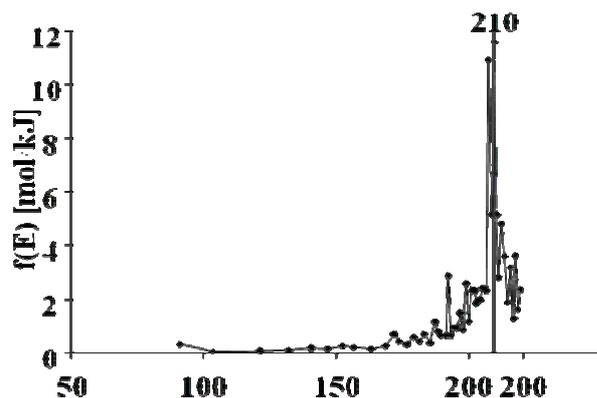


Fig. 1 DAEM of HIPS

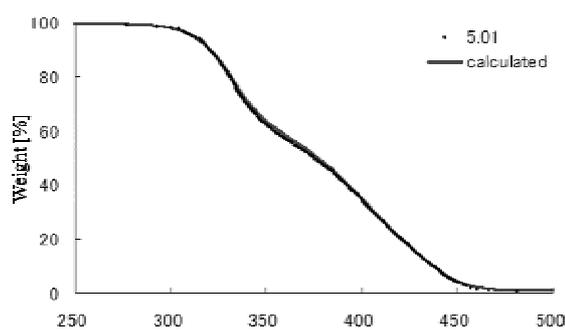


Fig. 2 Experimental and calculated TGA plot of HIPS in the presence of DDB and Sb_2O_3

retardant. When the fire retardant itself started to degrade, HIPS underwent a radical induced degradation. Since weak links were degraded during the early stage, the degradation was terminated at a higher temperature than for pure HIPS. About 25 wt% were degraded during a single peak at 178 and 192 kJ mol^{-1} for DPE and DDB, respectively.

The addition of Sb_2O_3 amplified the effect of the fire retardant. The degradation of the fire retardant was accelerated. The end of the HIPS degradation shifted even more to a higher temperature. A main E_A as for the Sb_2O_3 free samples was not observed anymore. The DAEM showed a broad distribution of E_A .

The kinetic data were used for the recalculation of the TGA plot. The discrepancy between experimental and calculated data was in general below 2.7 K. Just in the presence of DDB and Sb_2O_3 , the maximum discrepancy rose to 5.6 K.

Conclusions

The DAEM was a powerful tool in the investigation of the degradation of HIPS with and without fire retardant. It was shown that the material did not degrade homogeneously, but accompanied by the change of the E_A . However, 70 wt% of HIPS and about 25 wt% in the presence of DPE or DDB were degraded in a narrow E_A range. The addition of Sb_2O_3 led to the broadening of E_A distribution without significant E_A peak.

It is obviously that the change in the reaction mechanism caused also the change in the slope of the $E_A/\lg k$ relationship. This fact can be used to identify the range of reaction steps more precise as it is possible by TGA/DTA.

References

- [1] E. Jakab, Md. A. Uddin, T. Bhaskar, Y. Sakata: Thermal decomposition of flame-retarded high-impact polystyrene, *J. Anal. Appl. Pyrolysis* 68-69 (2003) 83.
- [2] K. Miura, T. Maki: A Simple Method for Estimating $f(E)$ and $k_0(E)$ in the Distributed Activation Energy Model, *Energy Fuels* 12 (1998) 864.
- [3] A. K. Burnham, R. L. Braun: Global Kinetic Analysis of Complex Materials, *Energy Fuels* 13 (1999) 1.
- [4] P. T. Williams, S. Besler: Pyrolysis-thermogravimetric analysis of tyres and tyre components, *Fuel* 74 (1995) 1277.