Using Distributed Activation Energy Model (DAEM) to Predict Mass Loss Rates in PMMA

FIRE TOOLS

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Introduction

Flame retardants are used as additives in polymeric plastics to inhibit and suppress the flammability characteristics. Depending on their nature, they can act physically or chemically inside the condensed phase during the heating process and interfere with the material decomposition rate [1]. Thus, it is difficult to determine an accurate reaction mechanism for most polymeric materials due to complicated reactions occurring between virgin material and flame retardant additives. For performing robust fire safety engineering calculations, it is important to be able to predict mass loss rates (MLR) using a pyrolysis model without going into very detailed reaction mechanism of these polymers. Distributed Activation Energy Model (DAEM) is one such multi-reaction model which performs prediction of mass loss rates(MLRs) and computation of chemical kinetic parameters (A, Ea). It assumes that the thermal decomposition of complex polymeric materials having heterogeneous chemical composition may be described by infinite number of parallel occurring reactions, whose chemical kinetic parameters can be described by a statistical distribution function such as a Gaussian bell curve. In this work Miura Maki Integral method [2] has been used to evaluate these parameters and predict MLR of PMMA using DAEM approach. The model has been validated against already published results of Verdugo [3] and Sonobe [4].

Experimental

PMMA Sample → **STA- (TGA-DTG)** → **DAEM Code**

DAEM model equation

$$1 - \frac{V}{V*} = \int_0^\infty \exp(-k_o \int_0^t e^{\frac{-E_a}{RT}} dt) * f(E_a) * dE_a$$

DAEM Multi-reaction Scheme

Heat → M → Rxn. i
Rxn. i+1
Rxn. i+n

Gaussian distribution function For Ea

$$f(Ea) = \frac{1}{\sqrt{2\pi}} exp^{[-\frac{E_a - E_{ao}}{2\sigma^2}]}$$

Nomenclature :
V/V* =   De-volatalization rate
Ea_0 =   Mean Activation Energy (kJ/mol)
F(Ea)=   Distribution function for activation energy
k0 =   Frequency factor corresponding to Ea value (1/s)
σ=   Standard deviation
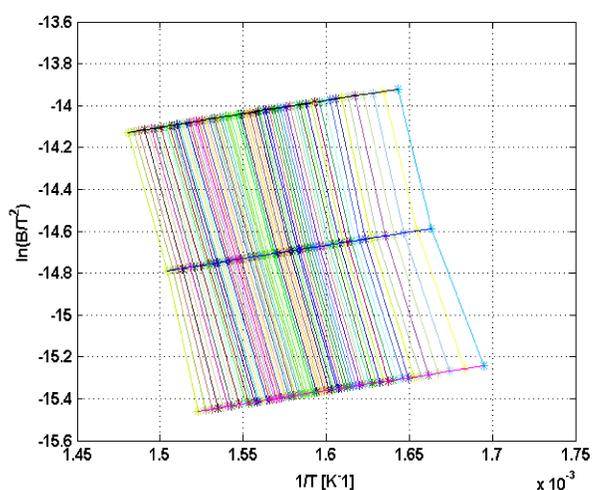
Results and Discussions

Fig. 1 Arrhenious fittings for TGA data (75 conversion levels)
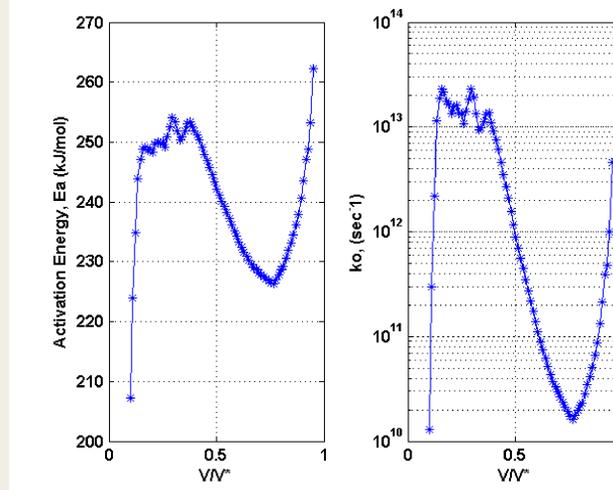

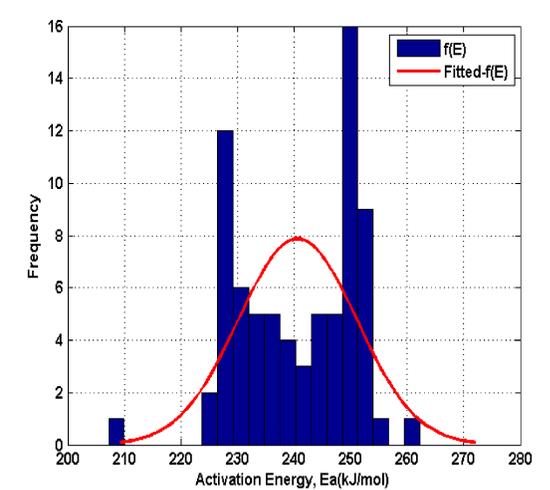**Fig. 2 Chemical kinetic parameters (Ea, k0)**

Fig 3. Frequency distribution curve

Table 1. Summary of chemical kinetic parameters fitted for PMMA

Kinetic Parameters	Range	Mean	Standard Deviation
Activation Energy (Ea-kJ/mol)	207-262	240.63	10.47
Pre-Exp. Factor (ko -1/s)	$1.286*10^{10}$- $2.324*10^{13}$	$5.35*10^{12}$	$7.13*10^{12}$

- For DAEM model computations a MATLAB® code was written having the ability to read experimental TGA data obtained at three different linear heating rates and fit the model equations to produce the simulation results (Fig 1-4). Numerical methods were used in calculations.
- For all computations the Miura Maki Integral method [2] was used. The code was validated against the data published by Verdugo [3] and Sonobe [4] by manually digitizing already published results.
- Figure 1 shows the Arrhenious fittings of the mass loss data of the PMMA material in the inert atmosphere follows a linear profile.
- Figure 2 shows the plot of chemical kinetic parameters (Ea,ko) corresponding to each de-volatalization rate. These values are distributed in the range of 207-262 kJ/mol over the conversion range.
- Figure 3 shows the normalized frequency distribution curve of PMMA material and it is compared with the MATLAB fitted (in red) curve. The fitted curve can be characterized with a mean and standard deviation as shown in the Table 1. The f(Ea) curve doesn't follow the exact Gaussian bell curve profile as hypothesized earlier in the model, however it is compared with the fitted curve of the MATLAB ®.
- Figure 4 shows the model predictions for the de-volatlization rate for PMMA under different linear heating rates and its comparison with experimentally obtained data. There is a slight over prediction error ranging from 0.3-0.8 %
- From the literature search it is apparent that the PMMA material decomposes in a two steps reaction, and it was also corroborated from the DTG results. However for this work, simulations related to the most prominent peak of the DTG thermo-gram was considered. The initial peak as shown by DTG has not been modelled
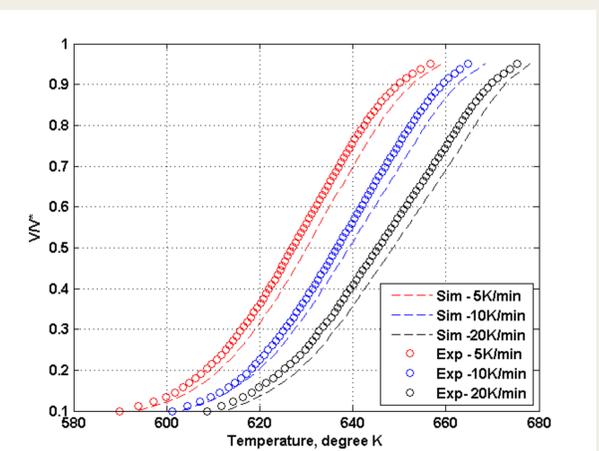

Fig 4. De-volatalization Rate Model Predictions Vs Experimental Data

References
[1] J. Troitzsch, Plastics Flammability Handbook - Principles, Regulations, Testing, and Approval (3rd Edition), Hanser Publishers, 2004.
[2] Miura, K. & Maki, T. A Simple Method for Estimating f(E) and k0(E) in the Distributed Activation Energy Model. Energy & Fuels 864–869 (1998).
[3] A. Soria-Verdugo, N. Garcia-Hernando, L.M. Garcia-Gutierrez, U. Ruiz-Rivas, Analysis of biomass and sewage sludge devolatilization using the distributed activation energy model, Energy Convers. Manag. 65 (2013) 239–244.
[4] T. Sonobe, N. Worasuwannarak, Kinetic analyses of biomass pyrolysis using the distributed activation energy model, Fuel. 87 (2008) 414–421.