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Pyrolysis modeling of PVC and PMMA using a distributed reactivity model

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ABSTRACT

The thermal decomposition kinetics of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) was studied by thermogravimetry using non isothermal experiments. A detailed kinetic analysis was done using the isoconversional methods (model-free) (including Friedman, Kissinger-Akhaira-Sunose (KAS) and Kissinger methods) and distributed reactivity model (model-fitting). The overall aim was to retrieve kinetic parameters of the model describing the differential thermogravimetric (DTG) curve. For distributed reactivity models, both double and multi-Gaussian methods were used to explain the thermal decomposition process in these polymers. Apparent kinetic parameters were retrieved using optimization calculations with a newly developed computer code using MATLAB® involving pattern search algorithm. Modeling results were compared with the experimental data obtained in a simultaneous thermal analyzer (STA). Agreement between experimental tests and simulations showed good results for fire modeling applications for these polymers.

1. Introduction

In the last couple of decades, there has been an increase in the production of polymeric plastic materials on a global scale. The world plastic production is estimated to have reached 299 million tons in the year 2013 as compared to 204 million tons in 2002 [1]. In Europe, building and construction sector is the second largest application area, this constitutes 20.3% of the total plastic demand. Traditional materials such as bricks, concrete, glass, cement and wood now have plastic alternatives due to their excellent physical properties. The main advantages of using plastics are durability, low maintenance costs, corrosion resistance and good insulation properties. PVC and PMMA are two of the many polymers used in this sector. PVC is used in piping work, electrical cabling, roof sealing, floor, wall and ceilings coverings and window profiling. PMMA is used as a lightweight replacement for glass and finds applications in doors, windows, canopies, balustrades and illumination applications. Other polymers used in modern buildings for insulation purpose include poly(urethanes) (PUR), poly(isocyanurate) (PIR), expanded poly(styrene) (EPS), extruded poly(styrene) (XPS). Fire safety of such polymers is an important issue. In case of fire, the heat released and toxic smoke produced poses a potentially fatal hazard to the building occupants. Hence, many studies deal with the thermal degradation of polymers to assess their suitability for real life applications.

Computer simulation on the fire behavior of plastic materials has gained significant attention in the last decade [2]. There has been an increasing number of studies demonstrating that one-dimensional numerical pyrolysis models can be used to predict the outcomes of a standard cone calorimeter test (ISO 5660) [3–5]. One of the main sub-models used in such calculations is the chemical kinetic model. Its function is to mathematically describe the mass loss rate (MLR) and heat generated in the material due to ongoing chemical reactions leading to conversion of solid mass into volatiles, char and smoke. It enables the modeling of the chemical heat source term for the overall solution of the heat transfer equation. The chemical kinetic model and the heat transfer equation are solved simultaneously to compute the heat release rate (HRR) from the material subject to appropriate boundary conditions. The current state of the art methodology for retrieving kinetic input parameters for fire simulation is to perform microscale thermogravimetric analysis (TGA) on the sample followed by computations using isoconversional (model free) or non-linear

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least square (model fitting approach) [6,7]. Retrieved kinetic parameters can be used as input values for the overall solution of the pyrolysis model. Several studies have shown that, there are a number of chemical kinetic models available in the literature to describe different types of chemical reactions occurring in solids e.g. power laws, nucleation and diffusion models [6]. As a consequence of this, the results vary considerably from one study to another for the same set of materials depending upon the choice of the reaction model [8–11]. Stoliarov et al. [4] found that the extent of this variation leads to discrepancies in the prediction of HRR and its magnitude was found to be far more in case of charring polymers than the non-charring ones. They further add that the main cause for such discrepancies is the gap in the understanding of the thermo-chemistry of different materials. The FIRETOOLS project investigates the possibilities to predict real scale fire behavior of building products, content and barriers by means of using material data on successively increasing scales [12].

Recently, two different studies were conducted by Vyazovkin et al. [13,14] which aim to provide recommendations for collecting experimental thermal analysis data and perform kinetic computations on them. It provides a pragmatic approach to perform kinetic model fitting calculations. For materials, degrading in single step, isoconversional methods were recommended, while for materials degrading in multiple reaction steps non-linear regression methods and distributed reactivity models were suggested. In this study a preliminary analysis using isoconversional methods was performed followed by a detailed analysis using distributed reactivity concept.

The main aim of this study is to compare the quantitative aspects of the thermal decomposition process in two different polymer specimens (PVC and PMMA) by employing isoconversional approaches and multiple step parallel reaction models. Previous studies have shown that these materials decompose in two or more steps [9–11,15,16]. Therefore, a distributed activation energy model (DAEM) was considered for this study. It is one of the more comprehensive pyrolysis models that has been applied to complex materials such as coal, biomass and sewage sludge, all of which exhibit thermal decomposition in multiple reaction steps [17–21]. As newly manufactured plastics become increasingly complex due to impregnation of several additives and flame-retardants, it is important to investigate the multiple reactions occurring in them during the pyrolysis process. In the first part of the study, TG analysis is undertaken, while in the second part; results of kinetic simulations are presented. The modelling results are compared with the test results from the TG and DTG curves.

2. Theory

2.1. DAEM model

The main assumption in the DAEM reaction model is the thermal degradation of material occurs in multiple parallel overlapping steps. Each reaction step is assumed to consist of an infinite number of simultaneously occurring parallel reactions having different activation energies (E_a) and frequency factors (k_o). In this study, the distribution function of the activation energy has been modeled by a Gaussian function. Recently, Cai et al. [22] and Zhang et al. [20,23,24] have applied this model to explain pyrolysis kinetics of biomass and municipal solid waste but very few studies are reported regarding its application to fire behavior of building materials. In a previous study Bhargava et al. [25,26] used this concept in the form of distribution free approach, however in this study the distribution fitting approach is used.

DAEM uses the thermal decomposition data obtained in a dynamic TG experiment to retrieve the chemical kinetic parameters using an optimization technique. For non-isothermal TGA runs, where temperature is a linear function of time, the temperature function can be modelled as equation (1), where T is the absolute temperature (K), β is the heating rate (K/s) and t is the time (s).

$$T(t) = T_0 + \beta x t \tag{1}$$

The degree of conversion for a sample material is calculated by equation (2). In this equation, α (T) is the degree of conversion at temperature T (K), m_0 (mg) is the initial weight, m_T (mg) is the weight at temperature T (K) and m_f (mg) is the final weight

$$\alpha(T) = \frac{m_0 - m_T}{m_0 - m_f} \tag{2}$$

$$\alpha(T) = \int_0^{\infty} \{1 - \varphi(E_a, T)\} \, x \, f(E_a) \, x \, dE_a \tag{3}$$

$$\varphi(E_a, T) = \exp\left(\frac{-k_0}{\beta} \int_0^{\mathbf{T}} e^{-E_a/RT} \, dT\right) \tag{4}$$

$$f(E_a) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{E_a - E_{a0}}{2\sigma^2}\right] \tag{5}$$

Equations (3)–(5) show the change in amount of volatiles represented in the terms of DAEM model. In equation (3), $\varphi(E_a,T)$ is the term comprising of temperature integral and $f(E_a)$ is the probability distribution function of the activation energies having the conversion at temperature T (K). In equation (4), k_0 (1/s) is the pre-exponential factor corresponding to the activation energy value, E_a (kJ/mol), β (K/s) is the heating rate, R is the real gas constant having a fixed value of 8.314×10^{-3} kJ mol^{-1} K^{-1}. In equation (5), E_{a0} (kJ/mol) is the mean activation energy and σ (kJ/mol) is the standard deviation. The derivative form of equation (3) can be written as shown in equation (6)

$$\frac{d\alpha(T)}{dT} = \frac{1}{\sigma\sqrt{2\pi}} \int_0^{\infty} \frac{k_0}{\beta} \exp\left[-\frac{E_a}{RT} - \frac{k_0}{\beta} \int_0^{T} \exp\left(-\frac{E_a}{RT}\right) dT - \frac{(E_a - E_{a0})^2}{2\sigma^2}\right] dE_a \tag{6}$$

Previous studies [21,27–30] have shown that other forms of DAEM equation exist in the literature in which the distribution of activation energy is modeled using several forms of probability distribution functions such as weibull, logistic or delta dirac distribution. The primary reason for such an assumption is the fact that activation energies of real materials are rarely symmetric. Hence, other types of distributions are discussed to account for asymmetry. Other authors have also considered single nth order DAEM equation instead of first order assumption [30,31]. However, for simplicity the analysis in this work is based on the assumption of first order having Gaussian distribution of activation energies.

Since there is no analytical solution for the inner temperature integral (dT) in equation (6), a large number of approximations that intend to approximate the values of temperature integral have been discussed in the literature [32,33]. But numerical integration for its evaluation is preferred. Hence, in our computations we have used adaptive quadrature method to evaluate the temperature integral. The algorithm of evaluation of DAEM is shown in the flowcharts below (Figs. 1 and 2).

The two ways of evaluation depend upon the choice of equation used for the formulation of the objective function (O.F.) by the