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Application of genetic algorithm to pyrolysis of typical polymers

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ABSTRACT

In order to apply genetic algorithm to kinetic calculation and degradation study of polymers, extruded polystyrene (XPS) and rigid polyurethane (PU) were selected to perform a series of thermogravimetry (TG) analysis with four heating rates (5, 10, 15, and 20 °C/min) in nitrogen. XPS showed one-step degradation. Three commonly used isoconversional methods and genetic algorithm were used to calculate the activation energy of XPS. Calculation results by genetic algorithm were very close to those by isoconversional methods. Furthermore, a three-step reaction modeling was created to describe the degradation of PU. Agreement between experimental data and predicted values justified the accuracy of genetic algorithm calculation. Mass evolutions of reactants, intermediates, and products were separated from total mass loss. Then Fourier transform infrared (FTIR) and thermogravimetry–mass spectrometry (TG–MS) were employed to verify the validation of calculation results, which showed that temperature region and variation tendency were in good accordance with calculation by genetic algorithm.

1. Introduction

Developing environmental-friendly, permanent, and effective handling methods for polymer refuse has been on global priority list. In the past few decades, demands for polymers have increased rapidly, along with increasingly prominent contradiction with disposal of waste polymers. Inappropriate processing of wastes could result in environmental contamination and natural gas emissions [1]. Accumulations of most polymers would cause a fire hazard [2], due to their flammable feature. For example, on July 1st, 2013, a fire disaster caused at least 100,000 tons polymers burning, taking place at a wasteyard of Smethwick in England.

Nowadays, waste polymer is mainly disposed by landfill, incineration, and degradation recycling [3]. The former two methods are much cheaper, but pollute environment. For the third method, degradation recycling for materials, it could not only deal with these waste polymers friendlily to environment, but also generate hydrocarbon for energy storage. This is the reason why so many researchers study thermal degradation of different polymers and/or biomass [4–15,18–21]. Gasification and pyrolysis are now regarded as promising ways to change solid polymers to gas fuel and fuel oil.

Many researchers have conducted studies on thermal degradation of polymers. Aboulkas and Bouadili [8] studied pyrolysis and kinetic behavior of polyethylene (PE) and polypropylene (PP), and evaluated their accuracies with different kinetic models. Eventually, PE was described by "Contracting Sphere" model, and PP by "Contracting Cylinder" model. Kiran et al. [7] studied the liquid and gaseous degradation products of PE and polystyrene (PS) on Gray-King apparatus. Chrissafis [11] studied the kinetics of HDPE (high density polyethylene) degradation, using three isoconversional methods and sixteen different models. Jiao et al. [9] explored the kinetics and volatile products of three commonly used thermal insulation polymer materials, extruded polystyrene (XPS), expandable polystyrene (EPS), and polyurethane (PU). Then Jiao et al. [10] studied the reaction mechanism of PU degradation in nitrogen, dividing PU degradation into four reactive phases according to degradation temperature regions.

All studies mentioned above involve kinetic reaction modeling or kinetic parameter calculation. The first step to study material degradation is to calculate kinetic triplet, where E is the activation energy, A is the pre-exponential factor, and n is the reaction order. There are several commonly used methods for kinetic triplet calculation [8,11], for example, Kissinger–Akahira–Sunose (KAS) method [24,25], Flynn–Wall–Ozawa (FWO) method [22,25], and Friedman method [23,25]. However, these methods are not able to confirm three kinetic parameters simultaneously. Besides, for some complex multi-step reactions, such as PU, coal, and biomass [26], these methods are not suitable.

In this study, two commonly used polymers, XPS and PU, were selected to research chemical kinetics of one-step and multi-step degradations, respectively. Thermal degradation of PU in nitrogen should be a three-step reaction mechanism [10,12]. For each reaction, it should own its corresponding kinetic triplet. For this kind of complex degradation, traditional isoconversional methods are obviously unreasonable. So in this study, genetic algorithm would be studied to obtain kinetic triplet of multi-step reaction. Degradation of PU is divided into three reactions, and each reaction would be calculated to obtain kinetic triplet.

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Fourier transform infrared (FTIR) and thermogravimetry–mass spectrometry (TG–MS) are employed to monitor temperature variation tendency of reactants and products, which would prove the reliability of genetic algorithm. The aim of this work is to use genetic algorithm to obtain accurate kinetic triplet of multi-step pyrolysis reaction [13]. Only accurate determination of chemical kinetics could promote bench scale degradation to industrial production.

2. Experimental

2.1. Materials

XPS we used was produced by Zhengbang Newly Building Material Co. Ltd., Anhui Province, China. PU was produced in laboratory. The formula was typical for thermal insulation materials, composed of polyols, isocyanates, blowing agent, and catalysts by one step synthesis. The isocyanate index was 1.1. Before testing, PU and XPS foams were grinded to powder.

2.2. TG

Thermogravimetry (TG) testing was conducted on a SDT Q600 by TA Instruments. A sample of powder with 6.0 mg was placed in an aluminum oxide crucible. Sample was heated from 25 to 800 °C with four heating rates (5, 10, 15, and 20 °C/min). Pure nitrogen gas was used as a purge gas with a flow rate of 20 mL/min.

2.3. FTIR

Changes in functional groups during degradation process were recorded on a Nicolet 8700 FTIR spectrometer. PU specimens were heated from 25 to 500 °C with a heating rate of 15 °C/min in nitrogen. KBr pressed-disk technique and CaF_2 window were adopted, and the FTIR spectrum range was 4000–1000 cm^{-1}.

2.4. TG–MS

On-line testing of volatile products obtained during thermal degradation was performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer coupled with Clarus SQ 8T MS to monitor the variation of characteristic fragment ions. Sample was heated from 25 to 800 °C with a heating rate of 15 °C/min in helium, and the gas flow rate was 75 mL/min.

3. Kinetic methods

TG provides an ideal environment of controllable atmosphere and heating rate, with negligible thermal gradient and transport effects during degradation of small solid sample. Mass loss rate (MLR) could be expressed as product of two functions. One function is about reaction temperature, T, and the other is about conversion percent, α. So MLR could be written as:

$$d\alpha/dt = \beta(d\alpha/dT) = k(T)f(\alpha) \quad (1)$$

where β is the heating rate, α is the conversion percent, t is the time, and T is the temperature. $k(T)$ is the reaction rate, which could be described by the Arrhenius law, so Eq. (1) could be changed to

$$d\alpha/dt = A\exp[-E/(RT)]f(\alpha) \quad (2)$$

where E is the activation energy, and A is the pre-exponential factor.

Isoconversional method is a commonly used way to calculate kinetic parameters by using temperature and derivative thermogravimetry (DTG) data at the same conversion with different heating rates. Three most commonly used ones are KAS method, FWO method, and Friedman method.

3.1. Flynn–Wall–Ozawa method (FWO) [22,25]

FWO method is an integral isoconversional method which is based on the following expression:

$$\ln\beta = -1.0516E/(RT) + \text{const.} \quad (3)$$

At a certain conversion α, plotting $\ln\beta$ against $1/T$ at different heating rates could get the straight line slope of $-1.0516E/R$ by which the apparent activation energy could be obtained.

3.2. Friedman method [23,25]

This differential isoconversional method is suggested by Friedman based on the expression:

$$\ln[\beta(d\alpha/dT)] = \ln A + \ln f(\alpha) - E/(RT). \quad (4)$$

The activation energy could be obtained from the slope of the straight line by Eq. (4). At a particular value α, the intercept $\ln A + \ln f(\alpha)$ should be constant without effects of activation energy.

3.3. Kissinger–Akahira–Sunose method (KAS) [24,25]

KAS method is based on the expression:

$$\ln\left(\beta/T^2\right) = \ln(AR/E) - E/(RT). \quad (5)$$

Plotting $\ln(\beta/T^2)$ against $1/T$ obtained from data at different heating rates should be a straight line which could give us the value of activation energy.

If the calculated activation energy is the same for different conversion, existence of single step reaction could be proved, such as degradation of XPS, EPS, PP, and PE [7–10] in non-oxidizing or oxidizing atmosphere. Conversely, changing of activation energy values with different conversions indicates complexity of multi-step reaction mechanism which invalidates above three methods, such as degradation of PU [9,10], biomass materials [20], and coal [14,26].

3.4. Model fitting method

Model-fitting method involves fitting different models to TG data and simultaneously determining activation energy and pre-exponential factor. So many models are usually used, such as n-order reaction models, diffusion models, phase boundary reaction models, and nucleation and nuclei growth models. In the following work, n-order reaction model, the simplest and most commonly used one, was selected to calculate kinetic triplet.

4. Genetic algorithm

Genetic algorithm is a heuristic scientific method based on Darwin's biological evolutionism [13], which has been widely applied to solve high dimensional optimization problem for parameter optimization in engineering and science areas, such as building construction [27] and biotechnology [28]. Meanwhile, it has also been applied to the optimization of chemical reaction mechanisms and kinetic triplet calculation [16,17]. A brief introduction about genetic algorithm is described in the following sections.