



Thermal degradation kinetic study of polystyrene/organophosphate composite

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ABSTRACT

A polystyrene/bis (2, 4-dicumylphenyl) pentaerythritol diphosphate (DPP) composite (PS-DPP) with a DPP loading of 10% (w/w) was prepared by the melt-compounding method. Results indicated that DPP had a thermal destabilization effect at temperatures below 380 °C. A comparative degradation kinetic analysis was performed employing the Kissinger method and the isoconversional methods of Friedman, Starink and Advanced Isoconversional Method (AICM). Variation of activation energy with extent of conversion (α) results from all the isoconversional methods showed that activation energy did not vary significantly with α for both pure PS and PS-DPP. Activation energies obtained from the Starink method above 380 °C were very close to those obtained from AICM consistent with activation energy values not varying significantly with α . The $y(\alpha)$ master plots and the Friedman methods were used to identify the reaction model and calculate the frequency factor respectively. The Sestak-Berggren model was identified as the most appropriate model to describe the thermal degradation of both PS and PS-DPP. The overall results indicates that activation energies of the composite were not significantly higher than those of pure PS at low conversion ($\alpha < 0.2$) where DPP had a destabilizing effect but became higher when DPP had a stabilization effect.

1. Introduction

Polymer composites have been researched extensively in view of formulating polymeric materials that have enhanced physical, flammability, and thermal properties [1–6]. The use of these composite materials has increased in recent years principally due to their light weight, corrosion resistance and easy of processing in addition to their enhanced flammability and thermal properties. The enhanced physical properties, thermal stability and low flammability of polymer composites have made them materials of choice for domestic and industrial applications [7]. Halogenated compounds were found to be very effective filler materials in polymer composites, resulting in greatly improved thermal and flammability properties. However, due to environmental concerns of halogenated fillers, the development of new non-halogenated fillers has become an active area of research [2,3,5]. Non-halogenated filler materials include metal oxides, metal hydroxides, lamella compounds such as clays and zirconium phosphate, and phosphorus containing compounds among other materials [8]. Phosphorus containing materials have been shown to be effective as filler materials for a variety of polymers [9,10].

The effects of filler materials on the thermal stability of polymer

composites is routinely investigated by conducting thermal degradation kinetics making use of thermogravimetric (TG) and differential scanning calorimetry [11–14]. In addition to parameterizing the reaction rate as a function of system parameters, kinetic measurements also provides insight into reaction mechanisms of chemical and physical transformations [15]. The kinetics of many solid state transformations can be characterized adequately by the general kinetic equation shown in Eq. (1) [14];

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

in which the extent of conversion at any given time (t) is represented by α , $k(T)$ is the temperature dependent rate constant, and $f(\alpha)$ is the functional form that represent the reaction model that contains information about the reaction mechanism. Thermal degradation kinetics of a variety of materials have been routinely carried out by making use of isoconversional methods [13,14,16]. For non-isothermal processes, isoconversional methods can be divided into differential methods, notably the Friedman method (Eq. (2)) and integral methods [17]. For processes studied under a linear heating rate program integral methods can be represented by Eq. (3);

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$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha}] - \frac{E_a}{RT_{\alpha,i}} \quad (2)$$

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left[-\frac{E_a}{RT}\right] dT \quad (3)$$

with the parameters E_a and $g(\alpha)$, being the activation energy and the integral form of the reaction model, respectively. A is the pre-exponential factor, t is the time taken to reach a certain conversion, T is the absolute temperature, β is the heating rate, and R is the molar gas constant. The integral in Eq. (3), the so-called temperature integral, has no analytical solution and can be solved by numerical integration or by using approximations. A number of approximations have been applied in the regular integral isoconversional methods. The use of approximations lead to simple linear equations of the general form shown in Eq. (4) [17] which greatly simplifies the estimation of the activation energy.

$$\ln\left(\frac{\beta}{T_{\alpha,i}^{\kappa}}\right) = \text{Const} - C\left(\frac{E_a}{RT_{\alpha,i}}\right) \quad (4)$$

In the above equation, κ and C are parameters connected to the approximations employed in the method. The regular integral isoconversional methods do not take into account the variation of the activation energy with the extent of conversion, thus they are not applicable when there is significant variation of E_a with extent of conversion. To account for the variation of E_a with extent of conversion and simultaneously increasing accuracy, methods which utilize numerical integration in solving the temperature integral have been developed [15,18–20].

It has been recently shown that an organophosphate {bis (2,4-dicumylphenyl) pentaerythritol diphosphate, referred herein as DPP}, results in improved thermal stability of polystyrene at a loading of 10% [21]. Since kinetic analysis have been employed frequently in the determination of the effects of filler materials on thermal stability of polymers, degradation kinetics study of PS and PS-DPP composites may provide an insight into the effects of DPP on the thermal stability of PS. The main aim of this study was to utilize thermal degradation kinetics to evaluate the effects of DPP on the thermal stability of PS. The Kissinger method, together with isoconversional methods would be used to evaluate the activation energies of the degradation process making use of thermogravimetry.

2. Materials and methods

2.1. Materials

Bis (2,4-dicumylphenyl) pentaerythritol diphosphate, trade name Doverphos S9228, was obtained from Dover Chemical company in Dover Ohio. Polystyrene (PS, molecular weight $\approx 230\,000\text{ g mol}^{-1}$, $M_n \approx 140\,000\text{ g mol}^{-1}$, softening point $107\text{ }^{\circ}\text{C}$ Vicat, ASTM D1525 melt index 7.5 g per 10 min) was purchased from Aldrich Chemical Co.

2.2. Methods

2.2.1. Instrumentation

Thermogravimetry analysis was conducted on an SDT 2960 simultaneous DTA-TGA instrument using alumina pans in N_2 atmosphere, at a flow rate of 60 ml min^{-1} . Polymer samples with initial sample weight in the range of 3.5–4.0 mg were heated from 50 to $600\text{ }^{\circ}\text{C}$ at heating rates of 5, 10, 15, 20 and $25\text{ }^{\circ}\text{C min}^{-1}$. The recorded TG data (change in sample mass with time and temperature) at the different heating rates were converted into extent of conversion (α) in which $\alpha = [(w_0 - w)/(w_0 - w_{\infty})]$. Activation energy variation data were computed for $0.1 \leq \alpha \leq 0.9$ range with a 0.05 step. The 5th order Savitzky-Golay smoothing algorithm was used to pre-process the TG

signal for the Friedman method.

2.2.2. Sample preparation

The polystyrene/DPP composite was prepared via melt blending as previously reported [21]. In brief, melt blending was conducted at a temperature of $180\text{ }^{\circ}\text{C}$ and a screw speed of 60 rpm in a Brabender Plasticorder with a residence time of 7 min. A sample of pure PS was also treated in the same manner to serve as a control. The polymer (PS) and the corresponding amounts of the additives (DPP) were mixed together to give the required 10 percent loadings of the additives in the composite referred herein as PS-DPP.

2.2.3. Kinetic models and mathematical treatment of kinetic data

Thermo-kinetic methods of analysis have been classified into model free and model fitting methods which can be carried out under isothermal or non-isothermal conditions. The disadvantage of the isothermal methods is that the sample requires time to reach the prescribed temperature such that during the temperature ramping period, the sample might undergo transformations that are likely to affect the results. In this regard, isothermal processes are restricted to low temperatures. The assessment of the variation of activation energy with extent of conversion was accomplished using three isoconversional methods; Two integral methods viz. the Starink method [17], and the advanced isoconversional method (AICM) by Vyazovkin [15,20], and one differential method, the Friedman method [22]. The Starink method is a regular integral isoconversional method that utilizes approximations while AICM utilizes numerical integration to evaluate the temperature integral in Eq. (3). The Starink method was chosen for this study as it has been considered as one of the most accurate methods among the regular isoconversional integral methods [23]. In addition to the three isoconversional methods, the Kissinger method [24] was also incorporated into the study as it gives a single global value of the activation energy. The single global E_a value would provide a useful comparison since the decomposition of polystyrene has been shown by numerous authors to be a single step process [21,25,26].

AICM is based on the minimization of Eq. (5), and the activation energy at any α value is obtained by determining the value of E_a that minimizes the equation. The method has been shown to reduce the systematic errors which characterize the regular integral isoconversional methods when there is significant variation of E_a with conversion. AICM has been largely recognized as one of the most accurate methods for evaluation of activation energy from thermogravimetry data [27].

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_a, T_i(t_{\alpha})]}{J[E_a, T_j(t_{\alpha})]} \quad (5)$$

In Eq. (5), the subscripts i and j represent ordinary numbers of two experiments conducted under different heating programs. $J[E_a, T_i(t_{\alpha})]$ is the temperature integral which is given by Eq. (6).

$$J[E_a, T_i(t_{\alpha})] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_{\alpha}} \exp\left[-\frac{E_a}{RT_i(t)}\right] dt \quad (6)$$

In the present study, the Bernardes macro was utilized in the implementation of AICM [28]. In the Starink method, the parameters κ and C in Eq. (4) take the values of 1.92 and 1.0008, respectively, leading to Eq. (7) [17].

$$\ln\left(\frac{\beta}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008\left(\frac{E_{a,\alpha}}{RT_{\alpha,i}}\right) \quad (7)$$

From Eq. (7), the activation energy is obtained from the plot of $\ln(\beta/T_{\alpha,i}^{1.92})$ vs $1/T_{\alpha,i}$. The Friedman method is the most widely used differential isoconversional method for the calculation of E_a and is based on Eq. (8).

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