



Material behaviour

Thermal decomposition kinetics of polypropylene composites filled with graphene nanoplatelets

J.Z. Liang^{a, b, *}, J.Z. Wang^a, Gary C.P. Tsui^b, C.Y. Tang^b^a Research Division of Green Function Materials and Equipment, School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou, 510640, PR China^b Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Kowloon, Hung Hom, Hong Kong, PR China

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ABSTRACT

Three polypropylene (PP) composites filled separately with different sizes of graphene nano-platelets (GNPs) were prepared using a melt blending method. Thermal gravimetric analysis of the samples was conducted to investigate the effects of the GNP size on the thermal decomposition behavior. Some probable thermal decomposition mechanism parameters were determined through the Malek method, and then the most probable thermal decomposition mechanism functions of these composite systems were obtained using the Achar and Coats–Redfern methods. The thermal decomposition kinetics equation with integral form of the thermal degradation mechanism function for these composites was $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. The thermal degradation mechanism was a phase boundary controlled reaction (contracting volume). The calculated activation energies of the three composites were, respectively, 277.4, 283.1 and 300.5 kJ/mol. This indicated that the GNPs could improve the activation energy of PP composites, and the activation energy increased with increasing the GNP lateral dimension. Moreover, the thermal decomposition was simulated by applying the thermal decomposition kinetics equation and the determined function parameters; good agreement was found between the simulations and the experimental values.

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1. Introduction

Graphene nano-platelets are widely used in industry owing to their excellent physical and mechanical properties such as high specific strength and good conductivity. For instance, a small amount of GNPs can significantly improve the mechanical properties [1–4], electrical properties [5–7] and thermal properties [4,8,9] of polymer materials. Polypropylene (PP) is a widely used thermoplastic resin owing to its good processing properties, recyclability and low cost. The thermal stability and flame retardancy of PP can be improved when it is filled with GNPs [10–12], in addition to the mechanical and electrical properties. Thermal properties and thermal stability are important of performance parameter of polymeric materials. Several researchers studied the thermal stability of PP/GNPs composites. Achaby and his co-workers [13] found

that the thermal stability of the composite was significantly improved when PP was filled with 3 wt.% GNPs. Song and his colleagues [14] fabricated graphene-based polypropylene nanocomposites; the results showed that the mechanical and thermal properties were enhanced. GNPs, however, did not always enhance the thermal stability of the polymer composites. Shi and his colleagues [15] studied the thermal stability and smoke suppression of polypropylene composites filled with CuO/graphene nanohybrids, and found that the value of the starting decomposition temperature of the PP composites was lower than that of the unfilled PP resin. The mechanisms of this phenomenon for the PP/GNPs composites should be deeply studied. In addition, the size effects of GNPs on the thermal stability of the PP/GNPs composites should be investigated. However, there have been relatively few comprehensive studies on the thermal stability mechanisms of the PP/GNPs composites.

In general, thermal decomposition reaction mechanisms of polymer materials are complicated [16,17], especially for polymer composites [18,19]. It is, therefore, quite meaningful to understand the thermal decomposition behavior and mechanisms of polymer composites, and to study the thermal decomposition kinetics.

* Corresponding author. Research Division of Green Function Materials and Equipment, School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou, 510640, China.

E-mail address: scutjzl@sohu.com (J.Z. Liang).

When the thermal decomposition kinetics is studied, a method combining experimental data and a kinetics model function is usually used to determine whether the model function can describe this reaction. The effect of the model-fitting and the residual error value are usually determined intuitively, or are determined according to linear regression coefficients. Malek's method is to determine the thermal decomposition kinetics mechanisms through defining a function $y(\alpha)$ and comparing experimental curves and standard curves [20]. However, the experimental curves are usually close to several standard curves, thus it is difficult to judge the best mechanism function. In this case, one can combine other methods to determine the reaction mechanism function, such as single rate scanning methods and multiple rate scanning methods. Among the single rate scanning methods, the Achar method [21] and Coats–Redfern method [22] are classical procedures.

However, there have been relatively few studies on the thermal decomposition kinetics of PP/GNPs composites. The objectives in this study are to investigate the effects of GNPs on the thermal decomposition activation energy of filled PP composites through introducing the Achar and Coats–Redfern methods on the basis of the Malek method to infer the most probable mechanism function; and then to establish a non-isothermal kinetic model using the determined most probable mechanism function. Finally, the comparison between the calculations and the experimental data of the thermal decomposition kinetic model parameters was made to verify the non-isothermal kinetic model.

2. Kinetic analysis of thermal decomposition

2.1. Basic equations

In thermal gravimetric testing of materials, conversion rate (α) can be determined using the following equation:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (1)$$

where W_0 , W_f and W_t are, respectively, the initial quality, the final quality and the quality at moment t of the specimen. The reaction rate ($\frac{d\alpha}{dt}$) is defined as the derivative of the conversion rate to the time. That is

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

where $f(\alpha)$ is the function dependant on decomposition reaction mechanisms. k is the reaction rate constant which can be expressed by the Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where A is the factor related to temperature in min^{-1} , E is the activation energy in kJ mol^{-1} , T is the absolute temperature in K, R is the gas constant in $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

Combining Eqns. (2) and (3), one has the following expression:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(\frac{-E}{RT}\right) \quad (4)$$

If the heating rate of the specimen is constant, then $\beta = \frac{dT}{dt}$, and the reaction rate can be expressed as follows:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \frac{d\alpha}{dT} \quad (5)$$

Combining Eqns. (4) and (5), one has

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (6)$$

Taking the conversion rate (α_0) corresponding to the initial temperature (T_0) as the integral lower boundary, taking the conversion rate (α_p) corresponding to the peak temperature (T_p) as the integral upper boundary, and then integrating Eqn. (6), one obtains:

$$\int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T_p} \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

If T_0 is very small, then a reasonable assumption may be: $\alpha_0 = 0$. In this case, one can consider that there is no reaction between 0 and T_0 . That is

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} \exp\left(\frac{-E}{RT}\right) dT \quad (8)$$

where $g(\alpha)$ is the integral function of conversion rate (α).

In terms of polymers, the integral function $g(\alpha)$ is a S type function or a reduction function. Table 1 lists several common solid state reaction mechanism functions $f(\alpha)$ and $g(\alpha)$ [23]. These functions can be used to speculate the solid state reaction mechanism of the specimens through non-isothermal thermal gravimetric tests.

2.2. Achar method

The Achar method is a type of differential method. First, making transformation of Eqn. (6), and then taking logarithms, one can obtain the following equation

$$\ln\left[\frac{\beta \frac{d\alpha}{dT}}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \quad (9)$$

It can be seen from Eqn. (9) that the relationship between both sides of the equals sign is linear. Substituting different values of $f(\alpha)$, T and $d\alpha/dt$ into Eqn. (9), drawing curves and then making linear regression analysis of these curves, one can determine the corresponding reaction activation energy (E) and factor (A) through the slope and intercept.

2.3. Coats–Redfern method

Coats–Redfern method is a type of integral method. Taking asymptotic approximation to the integral results of Eqn. (8) ($2RT/E \ll 1$), one can obtain the following equation

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (10)$$

Similarly, it can be seen from Eqn. (10) that the relationship between both sides of equals sign is linear. Substituting different values of $g(\alpha)$, T and α into Eqn. (9), drawing curves and then making linear regression analysis of these curves, one can determine the corresponding reaction activation energy (E) and factor (A) through the slope and intercept from these curves.

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