



Evaluation and modeling of thermal kinetic degradation for PVA doped PbS quantum dot

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ABSTRACT

The kinetic analysis of the thermogravimetric curves for the thermal decomposition processes of PVA/PbS was performed. The samples were heated in nitrogen, with three different heating rates: 10, 20 and 30 °C min⁻¹. Various forms of non-isothermal methods of analysis for determining the kinetic parameters were used. The differential and integral models were used to calculate the activation energies. Comparing with pure PVA, the results showed that the maximum activation energy of thermal degradation is achieved for PVA/PbS nanocomposite. Isoconversion model is used for predicting the thermal degradation acceleration. The results showed that the acceleration of thermal degradation for pure PVA was faster than PVA/PbS nanocomposite.

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1. Introduction

The thermal degradation kinetics in polymers is more complicated than in inorganic materials due to the nature of polydispersity of polymer chains. Upon thermal excitation, the covalent bonds in polymer chains undergo complex vibration and rotation motions within their local space. With further excitation these bonds can break to form a variety of fragment radicals or small molecules, which may further mutually recombine or break. Ultimately, the resulting fragments may be vaporized, diffused out, or carbonized. The thermal behavior of materials can be improved if the information about the thermal degradation kinetics and degradation mechanisms can be employed to decrease the thermal degradation rate or increase the heat resistance. Thermogravimetric analysis (TGA) is an excellent tool for studying the kinetics of thermal degradation. It provides information on frequency factor, activation energy, and overall reaction order [1–5]. A precise prediction requires the knowledge of the so called kinetic triplet, namely, the activation energy, the pre-exponential factor and the kinetic model, $f(\alpha)$. This latter parameter, also known as conversion function, is an algebraic expression that is associated with the physical model that describes the kinetics of a solid state reaction [6,7]. Therefore, the kinetic analysis also provides some understanding of the mechanism of the reaction under study [6–8].

Knowledge of the mechanism of thermal degradation of available macromolecules is very helpful in the field of the

thermal stability of polymers [9]. Crystallization kinetics of materials can be described through three kinetic parameters, namely; the activation energy for crystallization, the Avrami exponent which reflects the mechanism of nucleation and the growth process and the frequency factor [10–12]. In calorimetric measurements, isothermal and non-isothermal methods can be used to obtain these parameters. In the isothermal method, the sample is brought quickly to a temperature near the crystallization temperature and the heat produced during the crystallization process at constant temperature is recorded as a function of time. In the non-isothermal method, the sample is heated at a constant heating rate (β), and the heat produced is recorded as a function of temperature or time. Generally, the reaction rate, $d\alpha/dt$, of a solid state reaction can be described by the following equation:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A e^{-E/RT} (1 - \alpha)^n \quad (1)$$

where A is the Arrhenius pre-exponential factor, R is the gas constant, E the activation energy, α the reacted fraction, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α . The kinetic model, $f(\alpha)$ is an algebraic expression which is usually associated with a physical model that describes the kinetics of the solid state reaction [6]. Eq. (1) is a general expression that describes the relationship among the reaction rate, reacted fraction and temperature independently of the thermal pathway used for recording the experimental data. In the case that the experimental data were recorded at a constant heating rate $\beta = dT/dt$, Eq. (1) can be written as follows [13]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1 - \alpha)^n \quad (2)$$

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