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Polymer Degradation and Stability 91 (2006) 1747–1754

Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Kinetics study of thermal decomposition of epoxy resins containing flame retardant components[☆]

Qingfeng Wang, Wenfang Shi*

State Key Laboratory of Fire Science and Department of Polymer Science and Engineering,
University of Science and Technology of China, Hefei, Anhui 230026, PR China

Received 31 October 2005; received in revised form 24 November 2005; accepted 26 November 2005
Available online 18 January 2006

Abstract

Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in different ratios with a commercial epoxy resin to obtain a series of flame retardant resins. The thermal decomposition mechanism of their cured products in air was studied by thermogravimetric analysis and in situ Fourier-transform infrared spectroscopy. The degradation behaviours of epoxy resins containing various flame retardant components were found to be greatly changed. The incorporation of phosphorus and nitrogen compounds improved the thermal stability at elevated temperature. The kinetics of thermal decomposition was evaluated by Kissinger method, Flynn–Wall–Ozawa method and Horowitz–Metzger method. The results showed that the activation energy at lower degree of the degradation decreased by the incorporation of flame retardant components, while increased at higher degree of the degradation.

Keywords: Epoxy resin; Flame retardant; Decomposition kinetics; Activation energy; Polyphosphate ester; Hyperbranched

1. Introduction

Epoxy resins have been extensively used in many industrial applications such as coatings, adhesives, composites, laminates and encapsulants for electronic packaging because of their low cost, good chemical and electrical resistance, superior mechanical properties, low shrinkage upon curing and outstanding adhesion properties. However, the flammability of epoxy resins is a serious limitation in areas requiring high flame retardance. Many different approaches have been reported for improving the flame retardance of epoxy resins [1–4]. Halogen-containing compounds have been reported to be effective flame retardant agents for various epoxy resins. However, they are not always acceptable because of the release of highly toxic and corrosive fumes during combustion [5,6]. Environmental concerns and legislation are driving the search of new, halogen-free flame retardant agents used in epoxy resins. Phosphorus, nitrogen, and silicon compounds are the agents mostly used for replacing halogen-containing compounds in flame retardant epoxy resins. And the combination of different types of these flame retardants can lead to a synergistic improvement in the fire retardance of epoxy resins [7].

Organophosphorous compounds have demonstrated good ability as flame retardants for polymeric materials. They can form a carbonaceous char during combustion, which acts as a physical barrier to insulate heat from the flame and to prevent the diffusion of combustible gases [5]. Therefore, flame retardant epoxy resins can be achieved through the addition of phosphorus-containing oxiranes, and various efforts have been reported in this field. Moreover, flame retardancy can also be obtained with phosphorus-containing curing agents [8]. The incorporation of phosphorus into epoxy systems via curing has the advantage of ensuring that a wide range of epoxy resins can be used. On the other hand, the improvement of flame retardance was also observed by introducing nitrogen

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[☆] Granted by China NKBRSF project, No. 2001CB409600, and NSFC project, No. 50233030.

* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.
E-mail address: wfshi@ustc.edu (W. Shi).

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doi:10.1016/j.polymdegradstab.2005.11.018

into phosphorus flame retardant systems [3,9]. These combined compositions generally exhibit high efficiency in flame retardancy and provide an approach for reducing the amounts of flame retardants used.

Our previous work has described the synthesis of a novel hyperbranched polyphosphate ester (HPPE) used for flame retardant epoxy systems. The incorporation of HPPE into bisphenol-A epoxy resin can improve its thermostability and char yield during the decomposition. The limiting oxygen index value increased to 31 when HPPE was used as a curing agent [10]. In this study, the detailed investigation of thermal decomposition of epoxy resins containing flame retardant components is mainly concerned. From the results of thermogravimetric analysis, the kinetic parameters have been determined by various methods. In situ Fourier-transform infrared spectroscopy (FTIR) was used to examine the changes in the chemical structures of the products during the thermal degradation.

2. Kinetic methods

In the non-isothermal experiments carried out with a thermobalance, the sample mass is measured as a function of temperature. The rate of degradation or conversion, $\mathrm{d}\alpha/\mathrm{d}t$, is a linear function of a temperature-dependent rate constant, k, and a temperature-independent function of conversion, α, that is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{1}$$

The reaction rate constant, k, has been described by the Arrhenius expression

$$k=A\exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

The combination of Eqs. (1) and (2) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{3}$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta=\mathrm{d}T/\mathrm{d}t$, the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the rearrangement of Eq. (3) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}f(\alpha)\exp\left(-\frac{E}{\mathrm{R}T}\right) \tag{4}$$

The integrated form of Eq. (4) is generally expressed as

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E}{\mathrm{R}T}\right)\mathrm{d}T \tag{5}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

Based on the aforementioned equations, different kinetic methods (differential and integral) were applied in this study.

2.1. Differential method

Analysis of the changes in thermogravimetric data brought about by variation of the heating rate, β, is the basis of the most powerful differential method for the determination of kinetic parameters.

Kissinger method involves the maximum temperatures (T_{max}) of the first derivative weight loss curves at multiple heating rates [11]. The activation energy can be determined by the Kissinger's method without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln\left(\frac{\beta}{T_{\mathrm{max}}^2}\right)=\left\{\ln\frac{A\mathrm{R}}{E}+\ln\left[n(1-\alpha_{\mathrm{max}})^{n-1}\right]\right\}-\frac{E}{\mathrm{R}T_{\mathrm{max}}} \tag{6}$$

where T_{max} is the temperature corresponding to the inflection point of the thermodegradation curves which corresponds to the maximum reaction rate, α_{max} is the conversion at T_{max}, and n is the reaction order.

Taking into account the Kissinger's approximation which states that $f'(\alpha_{\mathrm{max}})=n(1-\alpha_{\mathrm{max}})^{n-1}\cong\mathrm{const.}$, the activation energy E can be determined from a plot of $\ln(\beta/T_{\mathrm{max}}^2)$ against $1/T_{\mathrm{max}}$.

2.2. Integral methods

The integral method involves an approximate integration of Eq. (5). Two kinds of integral methods are applied in this article.

Flynn–Wall–Ozawa method [12,13], using the Doyle's approximation [14] for the integration, has been expressed as

$$\log\beta=\log\left[\frac{AE}{g(\alpha)\mathrm{R}}\right]-2.315-0.4567\frac{E}{\mathrm{R}T} \tag{7}$$

Using Eq. (7), the linear representation of $\log\beta$ versus $1/T$ allows us to determine the activation energy with a given value of the conversion.

Horowitz–Metzger method [15] simplifies the exponential integral, obtaining the following equation

$$\ln\left[\ln(1-\alpha)^{-1}\right]=\frac{E\theta}{\mathrm{R}T_{\mathrm{max}}^2} \tag{8}$$

where θ is the difference between T and T_{max}. The activation energy can be determined from a linear fit to the plot of $\ln[\ln(1-\alpha)^{-1}]$ versus θ.

3. Experimental

3.1. Materials

HPPE was prepared in our laboratory and the details were described elsewhere [10]. Phenolic melamine (PM) was synthesized according to the reported method [16]. The structures of these two compounds are shown in Fig. 1. Bisphenol-A