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Isothermal curing kinetics of a flame retardant epoxy resin containing DOPO investigated by DSC and rheology

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ABSTRACT

The isothermal curing kinetics of a flame-retardant epoxy resin containing DOPO (1.5 wt% of phosphorus) with hardener DICY was investigated using differential scanning calorimetry and oscillatory shear rheometry. The glass transition temperature T_g increased with conversion α measured by DSC. When the curing temperature is lower than $T_g{}^{\infty}$ of the completely cured epoxy, the curing kinetics at high α became diffusion-control due to that cured epoxy restricted the diffusion of the reactants to decelerate curing. The modified Kamal model including the diffusion factor described curing conversion rate curves quite well. The curing degree θ was established with relative storage modulus, which was measured by the cyclic frequency sweep, and revealed that the transition from liquid to solid during curing appeared later with a slower rate than that for the conversion change, because the network began to form after formation of branched polymer chains. At the modulus transition time, the epoxy samples cured at different temperatures had the same conversion of 0.409, indicating that above this conversion of reactants the effective network was formed to bear the stress.

1. Introduction

Epoxy resins have been widely used in adhesive, laminated composite, surface coating, and semiconductor encapsulation due to the advantages in strong adhesive force to many substrates, excellent chemical resistance, mechanical and electrical performance, and thermal stability [1,2]. However, inflammability is one of the main drawbacks of epoxy resins, which limits their application in electronic industry [3–6]. The flame-retardant property can be gained by covalently incorporating epoxy with flame-retardants, such as a compound DOPO (9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide) and DOPO derivatives [5,7,8]. We have prepared a halogen-free flame retardant epoxy resin consisting of DOPO-based glycidyl ether of cresol formaldehyde novolac and diglycidyl ether of bisphenol A cured by micronized dicyandiamide (DICY) with accelerator U-52 to achieve the UL-94 V-0 grade with 1.0 wt% of phosphorus [9]. Curing reaction kinetics of the flame-retardant epoxy resin was observed by DSC through both non-isothermal and isothermal processes. Three new DOPO derivatives flame-retardants were reported in literature [10].

The curing process begins by formation of short polymer chains, and then the chains were branched, and subsequently cross-linked to form three-dimensional networks. During the isothermal curing, the reactant mixture changes via. gelation and/or vitrification depending on the curing temperature and time, which affects the final composition and properties of the cured resins. The time–temperature–transformation (TTT) curing diagram provides a useful framework for designing the curing process and predicting the material properties after curing for thermoset resins [11]. As the curing reaction proceeds, the molecules are cross-linked, and the glass transition temperature T_g of the resin is increased gradually. There are three T_gs as T_{g0}, $T_{g\infty}$, and ${}_{gel}T_g$ for the cured resin. T_{g0} is the T_g of the uncured resin mixture and $T_{g\infty}$ is the T_g of the completely cured epoxy resin. ${}_{gel}T_g$ is a temperature above which the resin passes the gelation stage first, and then enters the vitrification stage during curing, while below which the resin enters the vitrification stage directly without gelation. After vitrification, the curing process changes from reaction-control to diffusion-control, which obstructs the reactant mobility [12]. Therefore, the desired curing temperature T_{cure} is slightly higher than $T_{g\infty}$ for complete curing without diffusion-control stage. When cured below ${}_{gel}T_g$, a much long curing time is required to compensate the loss in reactant mobility [12].

Some experimental techniques were developed to study curing kinetics, such as Fourier transform infrared spectroscopy (FT-IR)

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[13–15], nuclear magnetic resonance ^{13}C NMR [16], size exclusion chromatography (SEC) [17], and differential scanning calorimetry (DSC) [14,18]. Dynamic mechanical spectrum is a powerful tool to detect the cross-linking and network structure in cured resins, which can monitor the structure change during the curing process [19]. The viscoelastic behavior of polymers relevant to the cross-linking near the sol–gel transition was examined experimentally and theoretically [20–24].

A few researches have been reported for curing kinetics of flame-retardant epoxy resins, despite their special importance today [7,9,25]. In order to observe the cross-linking structure change during isothermal curing with rheometry, the somewhat low curing temperature was desired to keep the epoxy mixture within the rheological fixture during heating. 2-Ethyl-4-methyl-1*H*-imidazole (EMI-2,4) was added to the former formulation for this purpose as the accelerator and hardener. The onset temperature of curing was reduced by 20 °C and the peak temperature was reduced by 10 °C. As we obtain two sets of curing kinetics from DSC and rheometry, the results are compared further to understand the whole process of the curing reaction.

2. Experimental

2.1. Materials

Multifunctional epoxy resin of glycidyl ether of cresol formaldehyde novolac with phosphorus of 3.2 wt% and epoxy equivalent weight (EEW) of 310 g/eq was kindly supplied by Zhongshan Taiguang Electronic Materials Co. (11DB07) [9]. Epoxy resin diglycidyl ether of bisphenol-A (DGEBA) was a commercial product (E51 from Wuxi resin factory) with the EEW of 190 g/eq. Curing agent of micronized DICY and accelerator U-52 from CVC special chemicals were used as received [9]. EMI-2,4 was obtained from Aladdin Reagents (Shanghai) Co., Ltd., DOPO-containing epoxy resin (DOPOER, phosphorus 1.5 wt%) was prepared by mixing 11DB07 and E51 at 118:100 weight ratio and the weight ratio of DOPOER:DICY:U-52:EMI-2,4 was kept at 100:4.6:1.5:1. The hardener DICY was added to the resin DOPOER at 50 °C to decrease viscosity. This DOPOER and DICY mixture was mechanically stirred at room temperature for 10 min, and then degassed using a vacuum pump for 15 min until disappearance of air bubbles. Finally, the catalysts U-52 and EMI-2,4 were added to the mixture under mechanical agitation and degassed again before the ultimate curing.

2.2. Thermal analysis

2.2.1. DSC

The isothermal curing kinetics of the present system was studied with a Netzsch DSC-204 F1 instrument operated in nitrogen atmosphere using aluminum pans. An empty pan and pure indium were used as the reference and standard for calorimeter calibration, respectively. The curing was carried out at several temperatures of 110, 120, 130, 140, and 150 °C according to the dynamic DSC results (see Section 3.1). After the sample pan was settled, the temperature was raised rapidly to a specified value at 40 °C/min. The heat flow was recorded as a function of the curing time. The total heat of the curing reaction ΔH was determined from the non-isothermal DSC curve at 10 °C/min. Dynamic DSC experiments were performed at 10 °C/min to determine T_{g0} and $T_{g\infty}$. T_g was taken as the midpoint between the onset and end of the inflectional tangents on the heat flow curve [26]. The residual enthalpy ΔH_{res} and T_g of the partially cured resin were obtained through the second heating run of the dynamic DSC at 10 °C/min. For the completely cured resin, $T_{g\infty}$ was detected through the second heating run without appearance of ΔH_{res}.

2.2.2. Theoretical background

The curing kinetics study begins with a basic equation of conversion rate $d\alpha/dt$, which is related to the concentration of reactants through a temperature-dependent reaction rate constant $k(T)$. A variety of phenomenological models of rate equation represent the main feature of the curing kinetics, ignoring the reaction details. In common kinetics models [19,27], the conversion rate is generally expressed as:

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

where α is the curing conversion, t is the reaction time, $f(\alpha)$ is a kinetic model-dependent function [28,29]. $k(T)$ is expressed by the Arrhenius equation

$$k(T) = A\exp(\frac{-E_a}{RT}) \tag{2}$$

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

The basic assumption for application of DSC technique to curing kinetics is that the conversion rate $d\alpha/dt$ is proportional to the heat flow rate dH/dt as [27,30]

$$\frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H} \tag{3}$$

ΔH is the total heat of the curing reaction, which was determined from integration of the non-isothermal DSC curve.

For isothermal DSC measurements, the curing kinetics of epoxy resins is often described with the Kamal model [31]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{4}$$

where m and n are the reaction order, k_1 and k_2 are the non-catalytic and autocatalytic reaction rate constant, respectively. This equation was successfully applied to many curing systems, where there was a maximum in the isothermal reaction rate [32,33]. This was characteristics of an autocatalytic process, such as an epoxy resin cured with novolac [34] and DOPO-based flame retardant epoxy resin [9].

T_g of the cured epoxy is increased accompanying with the curing process. When it exceeds the curing temperature T_{cure}, the mobility of the reactants is hindered, and the reaction rate is decreased, causing the reaction controlled by the reactant diffusion. The Kamal kinetic model is necessary to be modified to including this diffusion-control effect. According to the Rabinowitch concept, the total rate constant k_e is expressed with the rate constant k_c of the Kamal model without diffusion effect and the diffusion-control rate constant k_d as [35]

$$\frac{1}{k_e} = \frac{1}{k_c} + \frac{1}{k_d} \tag{5}$$

In this work, we adopted the diffusion factor f_d to describe the curing kinetics with the diffusion-control effect, which was defined as the ratio of measured reaction rate to that of reaction-control one [36]. The curing kinetics with the diffusion-control effect is expressed in the same form as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n f_d(\alpha) \tag{6}$$

and f_d proposed by Chern and Poehlein [37] and by Cole et al. [38] is determined as

$$f_d(\alpha) = \frac{k_e}{k_c} = \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{7}$$

where C and α_c are temperature-dependent fitting constant and critical conversion, respectively. When α is much lower than α_c, f_d