Thermochimica Acta 577 (2014) 11–16

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The influence of tertiary amine accelerators on the curing behaviors of epoxy/anhydride systems

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ARTICLE INFO

Article history:
Received 13 August 2013
Received in revised form 8 November 2013
Accepted 3 December 2013
Available online 12 December 2013

Keywords:
Epoxy resin
Anhydride
Accelerator
Curing behavior

ABSTRACT

Accelerators have significant effects on the curing behaviors of epoxy/anhydride (diglycidyl ether of bisphenol-F/methylhexahydrophthalic anhydride, DGEBF/MeHHPA) systems. Non-isothermal DSC was used to investigate the influence of dimethyl benzylamine (BDMA, 0.2 phr/0.5 phr) and Tris-(dimethyl aminomethyl) phenol (DMP-30, 0.2 phr/0.5 phr) on the curing behaviors of DGEBF/MeHHPA systems, respectively. When the amount of accelerators was kept constant, the activation energy calculated by Kissinger method changed slightly in the presence of either BDMA or DMP-30. And, with increasing the accelerator content from 0.2 phr to 0.5 phr, the value of activation energy decreased from 115 kJ/mol to 85 kJ/mol. Furthermore, the calculation results of Málek method identified that all systems in this study fitted Sesták–Berggren (SB) model and the corresponding model parameters, m and n, were obtained. It was found that the contribution of autocatalytic reaction with low accelerator content (0.2 phr) was far less than that with high accelerator content (0.5 phr).

1. Introduction

The curing of epoxy resins involves very complicated chemical and physical reactions, which leads to sophisticated curing kinetics [1]. The curing mechanism and kinetics of epoxy resins have already attracted extensive attention of scientists and researchers [2–8]. Lots of researchers have done excellent works on epoxy resins cured by amines [4–7]. However, epoxy resins cured by anhydrides usually have better properties, such as, less poisonous [9], higher glass transition temperature, less water absorbent, lower reaction exothermic [10], as well as lower reaction shrinkage [11]. Some researches indicated that instead of reacting with epoxy groups directly, the anhydride, at first, takes ring-opening reaction with hydroxyl groups to form carboxyl groups which then react with epoxy creating diesters and new hydroxyl groups. The direct reaction between anhydride and epoxy can take place only when the temperature is above 200 °C [12]. In general, the accelerators used in epoxy/anhydride curing systems were BDMA and DMP-30 [13–15]. Montserrat et al. studied the influences of accelerator content on the curing reaction of DGEABA/MTHPA systems in detail, and found different peak patterns for different accelerator content in DSC curves. The non-isothermal DSC curves in the study of Montserrat showed two exothermic peaks. The first peak, appeared between 80 and 200 °C, might be attributed to the catalytic curing reaction, and the second peak between 200 and 230 °C appeared only at the circumstance of low accelerator content, which was characterized as non-catalytic curing reaction [13]. Sorokin studied the curing of epoxy resins on a model reaction of phenyl glycidyl ether with phthalic anhydride under catalysis with BDMA. He used n-butyl alcohol as an admixture containing hydroxyl groups. By studying of isolated reactions, he found that two reactions mainly run alcoholysis of anhydride and the reaction of the nascent monoester with the epoxy compound. Both reactions take place with and without a catalyst [14].

As mentioned above, the accelerator has a significant impact on the curing reaction of epoxy/anhydride systems. Although the accelerator was widely used in the curing of epoxy, but the studies elaborating the influences of different accelerator types and content on curing reaction of epoxy/anhydride systems have been seldom reported. In addition, kinetic analysis of epoxy resin is necessary to understand structure/property/processing relationships [16].

To our knowledge autocatalytic models are now the most common models of kinetic models to investigate the curing systems of epoxy and curing agent. Autocatalytic models mainly include SB model which is obtained by non-isothermal DSC and Kamal model which is deduced by isothermal DSC [17]. Gang Sun et al. used SB model to study the curing kinetics and mechanism of a lignin-based-epoxy/maleic anhydride (LEPL/MA) resin system. They found that, the value of $n+m$ obtained by SB model can help us to have a comprehensive and profound understanding of the cure reactions of the LEPL-MA system [18]. As far as we know, the

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0040-6031/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.tca.2013.12.003

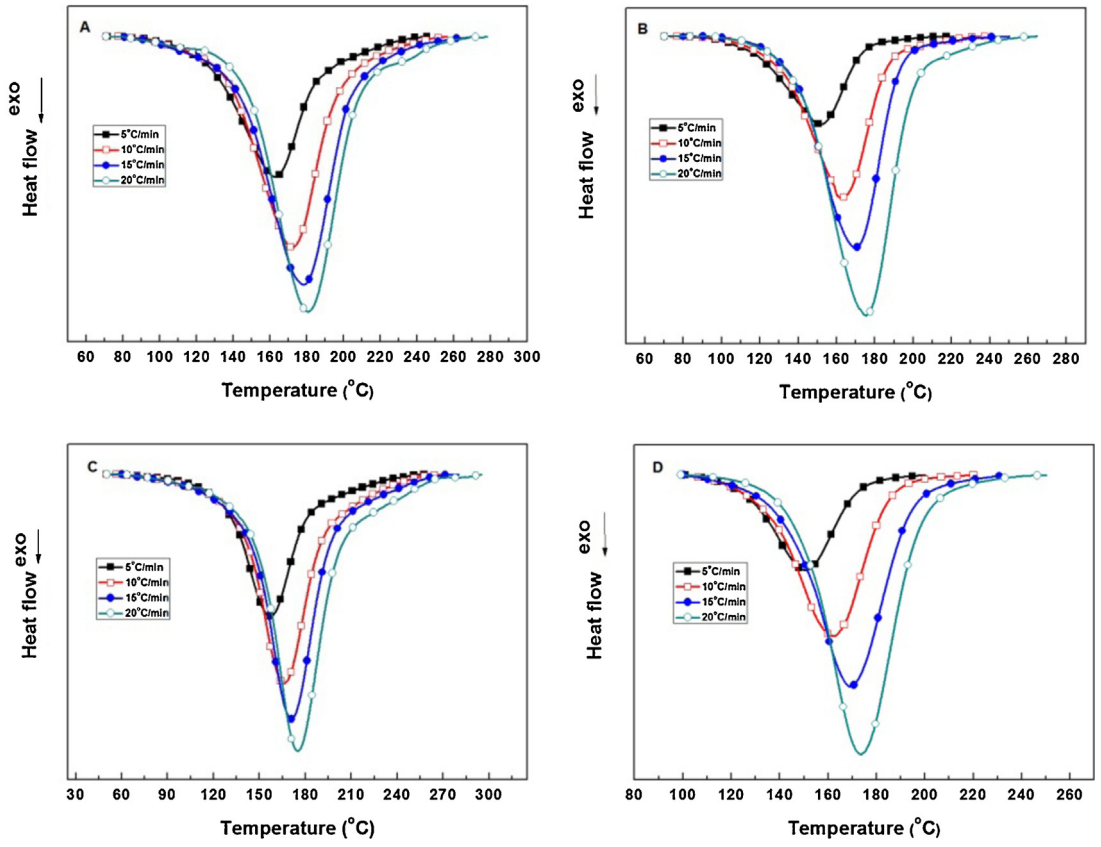

Fig. 1. DSC thermographs for the different non-isothermal reaction systems at heating rates of 5, 10, 15 and 20 °C/min.

studies elaborating the influences of different accelerator types and content on the model parameters (m and n) of epoxy/anhydride systems have not been reported. Actually, the values of m and n stand for autocatalytic reaction and non-autocatalytic reaction of the curing reaction. And the accelerator has a huge impact of the value of m and n by changing the reaction path.

In this paper, the influences of two types of accelerators with different content on DGEBF/MeHHPA systems were investigated by using DSC and the values of activation energy of the curing reaction and the model parameters (m and n) of these systems were discussed.

2. Experimental

2.1. Materials

DGEBF (trade name BPF, equivalent epoxy weight 165.3 g/mol) was purchased from Taiwan NanYa Group Co., Ltd.; MeHHPA (99.4%) was purchased from the Puyang Huicheng Electronic Materials Co., Ltd.; DMP-30 and BDMA were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

2.2. DSC study of cure reaction

Table 1 lists the composition of the DGEBF/MeHHPA formulations with 0.2 wt% and 0.5 wt% of BDMA and DMP-30 respectively.

The non-isothermal reactions of formulations shown in Table 1 were investigated using a Perkin-Elmer DSC. About 5–8 mg fresh resin mixture was accurately weighted, enclosed in an aluminum DSC crucible, and immediately subject to temperature scan from 25 °C to 300 °C with an identical empty crucible as the reference. Dry nitrogen was used as protective gas, and the heating rates were controlled at 5, 10, 15 and 20 °C/min. The DSC exothermic curves were used to evaluate the activation energy and kinetic parameter of the cure reaction.

3. Results and discussion

3.1. Model-fitting kinetics

The DSC curves of systems A, B, C and D are shown in Fig. 1.

When epoxy resin is cured at a constant heating rate β, the relationship of reaction rate and conversion rate can be described as Eq. (1) [19–21], assuming that the reaction exotherms are directly proportional to the fractional conversion.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the rate of reaction; α is the degree of curing reaction; A is the frequency factor; $f(\alpha)$ is the function of the degree of reaction; R is the universal gas constant.

Table 1
The composition of the DGEBF/MeHHPA formulations with 0.2 wt% and 0.5 wt% of BDMA and DMP-30, respectively.

	BPF (g)	MeHHPA (g)	Accelerator (g)	
			BDMA	DMP-30
A	100	105	0.2	
B	100	105	0.5	
C	100	105		0.2
D	100	105		0.5