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Material Behaviour

Effect of tertiary amine accelerators with different substituents on curing kinetics and reactivity of epoxy/dicyandiamide system

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ABSTRACT

Non-isothermal Differential Scanning Calorimetry and gel time measurements were employed to study the effects of four different tertiary amine accelerators with different molecular structure and substituents on the curing behavior and reactivity of epoxy/dicyandiamide (DICY) system. Results showed that the acceleration behavior depends on three factors: the bulkiness, the number of nitrogen atoms in molecular structure and the electron density of accelerator. Among these, the former two factors demonstrated stronger effect. The results of model fitting kinetic demonstrated that Šesták–Berggren model can well simulate the reaction rates especially for the samples accelerated by 2,4,6-tris(dimethylaminomethyl)-phenol and (Dimethylaminomethyl)phenol. The activation energy projected by Flynn-Wall-Ozawa and Kissinger–Akahira–Sunose methods exposed different amounts for each accelerator while both models revealed similar trends. Moreover, 1-methylimidazol-accelerated samples showed shortest storage life and gel time mainly due to the presence of two nitrogen atoms in a compact structure of accelerator.

1. Introduction

Due to their outstanding chemical and mechanical properties, epoxy resins are widely used in different industrial applications such as coatings, adhesives and composites [1–3]. In addition to popular liquid curing agents some latent curing systems have been developed in the solid state to improve the processability of epoxy resins as well as their facility of use. As an example, the dicyandiamide (DICY) could be considered as one of the main curing agents in epoxy based film adhesives and prepregs [4]. Generally, the final properties of a cured epoxy system depend on the degree of crosslinking and the cure behavior. Therefore, the study of curing behavior and kinetics of epoxy systems is crucial for improvement and development of their industrial applications and has already received great attention [5–8]. Sacher [9] studied the curing of several bisphenol-A epoxide/DICY systems in the temperature range between 170 °C and 220 °C. His results showed that fora higher molecular weight epoxy resin, curing reaction caused a more rigid cured epoxy. A number of other published works have focused on accelerator influence on the epoxy/DICY system. Hayaty and coworkers [10] investigated the curing behavior of a commercial glass/epoxy prepreg based on a DICY-cured diglycidylether of bisphenol-A (DGEBA) epoxy resin system containing urone as accelerator. According to their kinetic parameters, the best agreement with the experimental data was obtained in Ozawa's model. Moreover, the influence of other accelerators such as benzyl dimethyl amine (BDMA), 3-(4-chlorophenyl)-1,1-dimethylurea (Monuron) and 2-methyl imidazole on the curing behavior of various epoxy/DICY system was also investigated by this group [11]. Saunders et al. [12] conducted a series of experiments on tertiary amine-catalyzed, epoxy/DICY systems to explain the curing mechanism. They concluded that curing is a two stage mechanism consisting of multiple reactions; an initial exothermic ring opening of oxiran by dicyandiamide imino and amino anionic species followed by a subsequent exothermic reaction of hydroxyl across the nitrile triple bond. Feng et al. [13] modified DICY with phenyl hydrazine to improve the disadvantages of the epoxy/DICY system and reported an improved reactivity and compatibility between the epoxy resin and the curing agent using modified DICY. Zhao et al. [14] studied the curing of epoxidized soybean oil (ESO) in the presence of DICY and different combinations of DICY and accelerators. Their results indicated that carbonyldiimidazole (CDI) acts as a highly efficient accelerator for the ESO-DICY curing system. Liu et al. [15] studied the epoxy/DICY curing system accelerated by N-

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aryl-N′,N′-dialkyl urea to clarify the accelerating mechanism and the effect of molecular structure of the accelerator.

The curing kinetics of epoxy resins is predominantly investigated on the basis of autocatalytic models [16–18]. Yang et al. [19] studied the effect of accelerator's type and contenton the Šesták–Berggren (SB) model parameters, in the epoxy/anhydride system. They found that the contribution of autocatalytic reaction with low accelerator content was far less than that with high accelerator content. Wan et al. [20] used isoconversional methods to study the reaction rate of butyl-glycidyl ether modified poly(-propyleneimine) dendrimers with DGEBA and found good agreement between the SB model and experimental data.

Overall, the slow cure reaction in epoxy/DICY system necessitates the use of accelerators, in particular, the amine-based ones. However, to the best of our knowledge, no comprehensive studies on the influence of different substituents and the content of tertiary amine accelerators on the curing kinetics and model parameters of epoxy/DICY systems have been reported. In this work, the influence of four tertiary amine-based accelerators with different contents is studied on the curing kinetics of DGEBA/DICY systems via differential scanning calorimetry (DSC) and the activation energies of the curing reaction and the model parameters (m and n) of these systems are discussed. Moreover, the characteristic gel time and storage time of these systems are examined to further elucidate the cure behavior. This work is an introductory part of a comprehensive study for preparation of latent accelerators for epoxy/DICY one-pot system with high storage ability and low curing temperature.

2. Experimental

2.1. Materials and sample preparation

Table 1 gives the chemical formula and characteristics of the materials used in this study. Epoxy resin of diglycidyl ether of bisphenol-A (Epikote 828) with an epoxy molar mass of 184–190 g/eq and viscosity of 12–14 Pa.S at 25 °C was supplied by Momentive Co. (Columbus, OH, USA). The curing agent dicyandiamide (DICY) with the melting point of 208–211 °C and average particle size of 150 μm was obtained from Mokarar Co. (Tehran, Iran). Three alkanolamine-type accelerators were purchased from Sigma-Aldrich, Germany (2,4,6-tris(dimethylaminomethyl)-phenol (DMP-30), 2-dimethylaminoethanol and (Dimethylaminomethyl) phenol).1-Methylimidazole (DY 070) was obtained from Huntsman Co. USA.

The samples were prepared via gentle mixing of the resin, curing agent and accelerator at the ambient temperature, while the ingredients were previously dried at 100 °C for 3 h in a vacuum oven under 10 mbar vacuum. Due to fine particle size of DICY all samples were homogenous and stable within the period of experiments. The sample compositions in addition to the sample codes are tabulated in Table 2.

2.2. Characterization

Thermal properties were investigated in a differential scanning calorimeter, DSC (Mettler Toledo DSC1, Switzerland). Each sample was put in an aluminum DSC pan and immediately heated up to 90 °C at a heating rate of 20 °C/min. The sample was then kept at 90 °C temperature for 2 min followed by a cooling step down to 35 °C and reheating up to300 °C at three different heating rates of 5, 10 and 20 °C/min. The glass transition temperature (T_g) was measured in the third run at the heating rate of 10 °C/min for each sample.

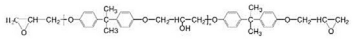
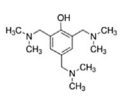
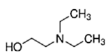
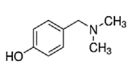
The storage time of the samples at ambient temperature was determined based on the viscosity measurements at 40 °C using a Brookfield RVDV-11 + pro viscometer, which can offer high shear rate with integrated temperature control. Gel time of the samples was determined according to ISO 8130-6 standard test method. The gel time of the samples was recorded at three different temperatures of 110, 120 and 130 °C. During the heating period, samples were stirred continuously with a glass rod. The resin viscosity first decreased and then increased gradually due to heating and cross-linking, respectively, and after a while, it showed an elastic behavior (like a rubber) and reached the gel state. At this time, the timer was stopped and the recorded time was noted as the gel time. The experiment was repeated three times for each temperature.

3. Results and discussion

3.1. Non-isothermal curing reaction kinetics

Fig. 1-(a) illustrates DSC thermograms for ED sample at three different heating rates. As shown in Fig. 1(a), the thermograms shift towards higher temperatures by increasing the heating rate, may

Table 1
Chemical formulae and characteristics of the materials used.

Material	Molecular structure	Supplier	Characteristics
Epikote 828		Momentive Co.	Molar Mass: 184–190 g/eq, Viscosity @25 °C: 12–14 Pa.s
DICY		Mokarar Co.	Melting point: 208–211 °C, Average particle size: 150 μm
DMP-30		Sigma-Aldrich	molar weight = 265.39, Boiling point: 130–135 °C
2-dimethylaminoethanol		Sigma-Aldrich	molar weight = 89.14, Boiling point: 130–135 °C
(Dimethylaminomethyl)phenol		Sigma-Aldrich	molar weight = 151.21
DY 070		Huntsman Co.	Flash point: 92 °C