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Comparative study on the kinetic behavior of neat benzyl thiirane ether and benzyl glycidyl ether reacted with polyether amine

Xiaocun Tan, Yizhou Huang, Xiangyuan Li, Jue Cheng*, Junying Zhang*

The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

The neat episulfide of benzyl thiirane ether (BTE) resin was synthesized by the reaction of benzyl glycidyl ether (BGE) epoxy resin and KSCN under the microwave atmosphere at low temperature. The ring opening kinetic behaviors of neat BGE and neat BTE with polyether amine (D230) as the hardener were comparatively investigated by non-isothermal differential scanning calorimetry(DSC), and analyzed by the model-fitting Málek method and the model free advanced iso-conversional method of Vyazovkin. The results indicated that both BGE/D230 and BTE/D230 systems fitted Šesták–Berggren model well. The activation energy of neat BTE/D230 system (43.2 kJ/mol) was much lower than that of neat BGE/D230 system (58.7 kJ/mol). And, the m value in the Šesták–Berggren kinetic model equation for BTE/D230 system ($m = 0.1902$) is much higher than that for BGE/D230 system ($m = 0.0512$), indicating BTE/D230 system has much more autocatalytic effect and/or a secondary reaction initiated by the sulfhydryl groups, which generated from the ring-open reaction of thiirane groups.

1. Introduction

Episulfide resin refers to a kind of compounds with three-membered ring containing a sulfur atom, whose structures are similar to corresponding epoxide compounds with the only difference between sulfur atom and oxygen atom in the rings [1]. Therefore, episulfide resin and epoxy resin show lots of similar performance, such as excellent chemical resistance, adhesion, heat resistance, mechanical properties, electrical properties and dimensional stability of the cured products. However, episulfide resin also has its advantage, such as: the high reactivity at low curing temperature, good adhesive properties with inert metal, because of its small ring tension. And episulfide resins are widely used as a fast curing matrix at low-temperature and attract extensive attention of scientists and researchers [2,3].

Currently, the study on the episulfide resin mainly focuses on their curing reactions at low temperature. It is reported that bisphenol A-type episulfide resin cured by amide and amine cured at much lower temperature, compared with the corresponding epoxy resin [4]. Chino et al. [5] reported that the mixture of bisphenol F epoxy/episulfide resin with 50% content of episulfide groups can gelate rapidly at the temperature less than 5 °C. Chongfeng Zhang [3] researched the system of the hexahydro-4-methylphthalic anhydride(MHHPA)/diglycidyl 1,2-cyclohexane dicarboxylate (CY184) epoxy/episulfide resin system with the content of 50.5% episulfide groups and found that the activation energy is 67.6 kJ/mol, which is significantly lower than that of the corresponding epoxy system(86.3 kJ/mol). Up to now, to the best of our knowledge, a few literatures on the curing behaviors of episulfide resins are about some mixture systems of thiirane groups and epoxide groups, and the curing kinetic research work on the neat episulfide resin has not been mentioned.

As it is well known, the neat episulfide resin is very difficult to be synthesized because of the reversible reaction of epoxide group and KSCN at 45–50 °C, which leads to the lower conversion of epoxide groups even lasting for a long reaction time [1]. In our work, an unique synthetic process of a microwave [6] process (inducing ring-opening reaction of the epoxy) followed by low temperature thermal process (carrying out the closed loop to form thiirane groups) was used to prepare the neat episulfide model compound. Furthermore, the as-synthesized neat episulfide model compound was reacted by D230 [7] to investigate reaction behavior. Meanwhile, the BGE/D230 epoxy resin system was comparatively investigated as a reference. DSC measurement were used to obtain the reaction curves at various heating rates, and the reaction process parameters was analyzed and calculated by Málek

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* Corresponding authors.
E-mail addresses: chengjue@mail.buct.edu.cn (J. Cheng), zjybuct@gmail.com (J. Zhang).

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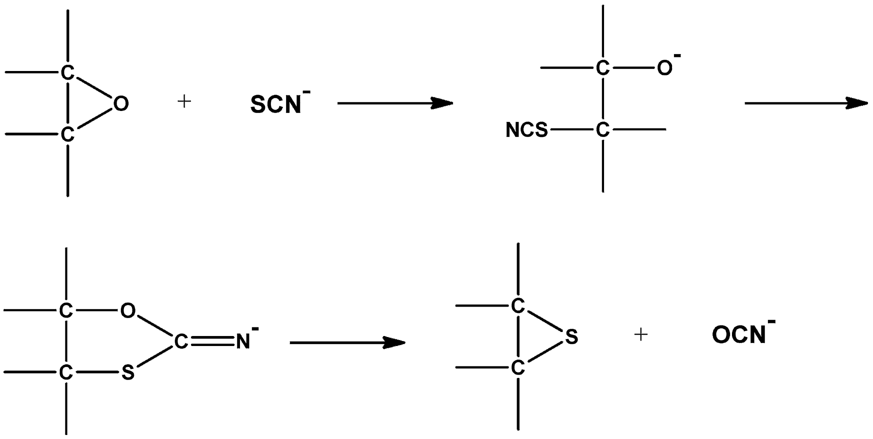

Scheme 1. The reaction mechanism of BGE with KSCN.

method [8,9]. Advanced isoconversional [10–13] was used to analyze the dependence of activation energy on the conversion rate of functional groups.

2. Experimental

2.1. Materials

BGE was purchased from Wuxi Huilong Electronic Materials Co., Ltd., and the epoxy value is 0.41. D230 was purchased from HUNTSMAN with the amine hydrogen equivalent weight by 8.4 meq/g. KSCN and ethanol were analytical agents purchased from Beijing Chemical Works Co., Ltd. All the agents were used as received.

2.2. Synthesis of BTE

First, the BTE was prepared by the reaction between BGE and KSCN under microwave process followed by low temperature thermal process. The reaction mechanism is shown in Scheme 1 [1]. Homogeneous solutions of 50 mL deionized water dissolving 19.4 g (0.2 mol) KSCN and 50 mL ethanol dissolving 16.4 g (0.1 mol) BGE were prepared under the stirring by EUROSTAR 20 digital stirrers, respectively. Both the solutions were charged into a 250 mL three-neck flask equipped with straight condenser and thermocouple probe. The three-neck flask was kept in microwave oven under 100 W at 318 K for 2 h. Then, the three-neck flask was moved to the outside and kept at the room temperature for another 10 days. The product was poured into separating funnel and washed alternatively by toluene and deionized water alternately for three times. The upper layer was separated and dried by anhydrous $MgSO_4$ for 24 h, and then the solvent was removed by rotary evaporation to get light yellow liquid.

2.3. Characterization

2.3.1. FTIR measurement

FTIR spectrum of BTE and BGE was recorded on a Nicolet Nexus 670 FTIR spectrometer (USA) in the range of 4000–400 cm^{-1} using KBr pellet. The result is shown in Fig. 1. Characteristic infrared absorption peak of epoxy group at around 916 cm^{-1} disappeared nearly, and the characteristic infrared absorption peak of episulfide group at around 617 cm^{-1} appeared, which prove that the episulfide monomer had been synthesized.

2.3.2. ^1H NMR measurement

The purified BTE was dissolved in $CDCl_3$ and the test was carried out on Bruker NMR at room temperature. ^1H NMR data (400 MHz, $CDCl_3$, 25 °C, δ, ppm): 7.25 (s, solvent residual), 2.18 (d, 1H, Ha-2), 2.48 (d, 1H, Hb-2), 3.08 (m, 1H, H-3), 3.47 (d, 1H, Ha-4), 3.66 (d, 1H, Hb-4). The serial number of carbon atom is shown in Scheme 2. The content of BTE is 99%, which was obtained by integration.

Table 1
Calorimetric data of BTE/D230 and BGE/D230 systems.

System	β/°C min^{-1}	T_i/°C	T_p/°C	T_f/°C	ΔH/J g^{-1}	ΔH/kJ mol^{-1}
BTE/D230	5	17.7	78.8	138.2	104.6	25.1
	10	17.1	95.3	153.6	97.0	23.2
	15	25.5	103.9	163.0	92.2	22.1
	20	30.6	110.1	166.0	89.4	21.4
BGE/D230	5	45.6	122.7	192.4	338.6	75.7
	10	50.0	137.8	213.3	313.6	70.1
	15	55.2	146.6	224.1	303.3	67.8
	20	58.2	152.0	233.0	293.0	65.5

2.3.4. DSC measurement

BGE and BTE were mixed with D230 (The formula of D230 is shown in Scheme 3) in equivalent respectively, and the non-isothermal reactions were investigated by using differential scanning calorimetry (DSC, Q20, TA instruments). About 6 mg fresh resin mixtures were accurately weighted and enclosed in an aluminum crucible scanned from 273 to 523 K with an identical empty crucible as the reference under the protection of dry nitrogen. The heating rates were 5, 10, 15, and 20 K min^{-1}.

3. Results and discussion

3.1. Non-isothermal reactions of BTE and BGE

The DSC thermographs of non-isothermal reactions of the BTE/D230 and the BGE/230 are shown in Fig. 2. The initial reaction temperature (T_i), peak reaction temperature (T_p), and final reaction temperature (T_f) can be obtained from Fig. 2, which are listed in Table 1. It can be found from Table 1 and Fig. 2 that the initial reaction temperature of BTE/D230 system is about 30 K lower than that of BGE/D230 system; the peak reaction temperature of BTE/D230 system is about 40 K lower than that of BGE/D230 system; and the final reaction temperature of BTE/D230 system is about 60 K lower than that of BGE/D230 system. All the data suggested indeed the higher reactivity of the episulfide monomer. This phenomenon can be explained by the fact that the bond energies of thiocarbonyl bond (S—C) and internal energy of thiirane are far less than those of the oxirane, and the S—C bond is relatively easy to break.