A Study on EDTAD / Epoxy Resin Curing System

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Abstract. A novel and convenient method for the synthesis of epoxy resin curing agent ethylenediaminetetraacetic anhydride (EDTAD) was explored. The curing reaction kinetics of DGEBA/EDTAD/DMP-30 system was studied by non-isothermal differential scanning calorimetry (DSC). The experimental results show that there are two exothermic peaks in the non-isothermal curing reaction curve; the higher the heating rate, the higher the peak temperature, the shorter the curing reaction time; the table of DGEBA/EDTAD/DMP-30 system is obtained by Kissinger and Ozawa methods The apparent activation energies of the DGEBA/EDTAD system were 4.9kJ/mol, 67.8kJ/mol and 7.3kJ/mol, 72.1kJ/mol respectively. The apparent activation energies of 36.1kJ/mol, 44.5kJ/mol and 41.2kJ/mol, 48.9kJ/mol.

1. Introduction

Epoxy shrinks during curing, causing internal stresses in the polymer to form microcracks and micro-fractures, resulting in a change in the volume and size of the cured product due to the inter-molecular Van der Waal distance conversion Price distance. At present, the most widely used method is to reduce the volume shrinkage by adding an expanded monomer, but the types of the expanded monomers are limited to six-membered cyclic carbonates and spirocyclic orthocarbonates, and the application is limited to tooth repair [1-3]. According to the expansion principle of the expanded monomer, it is proposed that epoxy ring-opening reaction with EDTAD can theoretically reduce the volume shrinkage of the material [4]. EDTAD is an important organic compound and pharmaceutical intermediate used as a synthetic raw material for hydrogels, an antidote to toxic metal ions and a paramagnetic contrast agent diagnosed by magnetic resonance [5, 6]. In this paper, starting from the curing agent structure, a simple and easy synthesis of ethylenediaminetetraacetic anhydride synthesis method. The reaction mechanism of DGEBA/EDTAD and DGEBA/EDTAD/DMP-30 was investigated by differential scanning calorimetry (DSC).

2. Experimental Part

2.1. Materials and Equipment

Ethylenediaminetetraacetic acid (EDTA), acetic anhydride, pyridine, ether, dimethyl silicone oil, are of analytical grade, Sinopharm Reagent Co., Ltd.; epoxy resin (DGEBA), Yueyang Baling Petrochemical.

Heat collector thermostat: DF-101S, Gongyi Yuhua Instrument Co., Ltd.; High-speed mixer: JJ-1, Guohua Instrument Co., Ltd.

2.2. Experimental Process

EDTAD and acetic anhydride with the molar ratio of 1: 8 were added in a single-neck round-bottom flask equipped with a spherical condenser containing a drying tube, then, inert gas was continuously put into. The mixture was stirred at 90℃ in water bath until the starting material had completely disappeared about 28h, then stop heating and stirring, the mixture was cooled down to room temperature. The supernatant of crude solution was removed and suction filtered to give a crude product EDTAD. The crude product was dissolved in an Erlenmeyer flask equipped with acetic anhydride, plugged, intermittent oscillation, being suction filtered after 0.5h, the above steps were repeated twice. The product after suction filtration was washed with a certain amount of diethyl ether and then dried in an oven at 120℃. Pure ethylenediaminetetraacetic anhydride product obtained and calculate the yield finally (Figure 1).
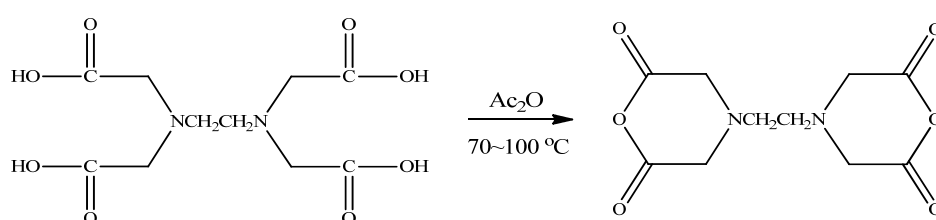
Figure 1. The synthesis reaction equation of EDTAD

2.3. Tests and Methods

Infrared Spectroscopy Test: Infrared spectra of the obtained synthesized product and its epoxy resin cured product were analyzed by Impact 420 Model - Fourier Transform Infrared Spectrophotometer (USA). The KBr tablet had a wavenumber range of 4000-400 cm^{-1}.

DSC Test: The non-isothermal curing reaction of DGEBA/EDTAD system was studied by Differential Scanning Calorimeter (PerkinElmer DSC-7). First, the instrument baseline, temperature and enthalpy were calibrated with high purity, and then a small amount of DGEBA and stoichiometry Of EDTAD quickly mixed evenly at room temperature, weighed about 10mg fresh sample and placed in a sealed aluminum DSC crucible, heated scan it immediately with a sealed empty crucible as a reference. The test temperature is 20-300℃, the heating rate is 5, 10, 15 and 20K·min^{-1}, and the protective gas is dynamically dried high purity N_2 (40mL·min^{-1}).

3. Result and Discussion

3.1. EDTAD FT-IR Analysis

EDTAD and ethylenediaminetetraacetic anhydride infrared spectroscopy, in which a is EDTAD infrared spectroscopy, figure 2 shows: a stronger C=O absorption peak appeared at 1696.65cm^{-1}. b is the IR spectrum of the product. Two absorbtion peaks appeared at 1808cm^{-1} and 1762cm^{-1} because of the two carbonyl couplin vibration. The 1808cm^{-1} peak is stronger than that of 1762cm^{-1} because the ethylenediamine tetraacetic anhydride is the cyclic anhydride. Therefore, the product is EDTAD.
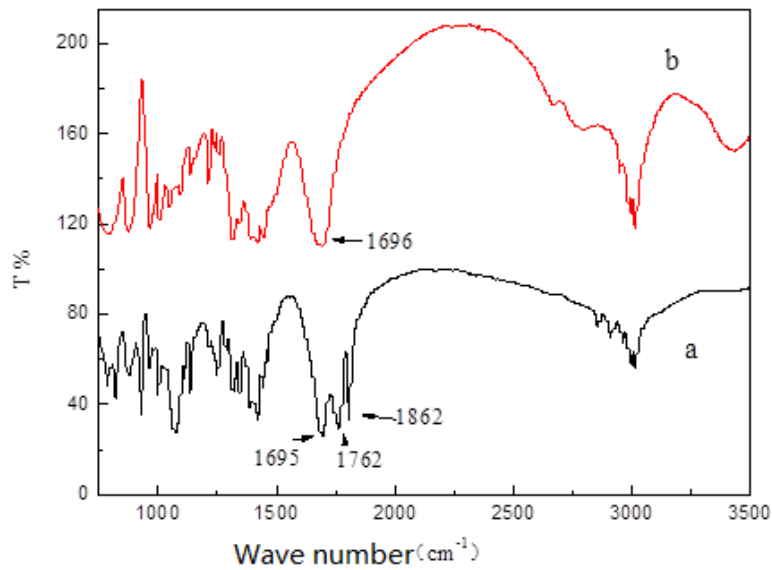
Figure 2. FT-IR of EDTA and Product

3.2. EDTAD / DGEBA Curing Dynamics

3.2.1. Equal-transition Ratio Method. In general, the reaction rate equation in the study of epoxy curing kinetics can be expressed by Equation 1:

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

For non-isothermal curing kinetics, the heating rate is linear with time, Equation 1 can be transformed into the following expression:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} \tag{2}$$

β is the heating rate, K·min-1, k is a reaction rate constant, which is a function of temperature. According to Arrhenius law, f(α) is a function of conversion, represents the reaction model. Equation 1 can be written as the following expression:

$$\beta \frac{d\alpha}{dt} = Ae^{(-E/RT)} f(\alpha) \tag{3}$$

T is the cure temperature, A is the pre-factor, E is the activation energy, and R is the gas constant. The integral form of the rate equation can be expressed as:

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} e^{(-E/RT)} dT = \frac{A}{\beta} P(E, T_\alpha) \tag{4}$$

Which is the integral form of the reaction model. In order to calculate Arrhenius parameters and dynamic conditions, we need to approximate the formula 4, then the following expression:

$$\lg \beta = \lg(\frac{AE}{Rg(\alpha)}) - 2.315 - 0.4567\frac{E}{RT} \tag{5}$$

By changing the bottom formula, we can get the following expression:

$$\ln \beta = const. - 1.0516\frac{E}{RT} \tag{6}$$

For a given conversion, the activation energy can be calculated using the linear relationship between $\ln\beta$ and T^{-1}.

3.2.2. Conversion Rate and Time

As shown in Figure 3, the relationship between the conversion rate and the time of the epoxy resin system was obtained according to the equation (1). At the initial stage of the reaction, the conversion rate α slowly increased, reaching 50%, reaching a plateau (α≈0.4). With the increase of the reaction time, the conversion rate increased rapidly and finally reached a limit (α≈1). At this point the system is almost completely cured. The conversion rate α increased sharply with the increase of time t. Apart from the rise of the reaction temperature, α is also related to the autocatalytic reaction and DMP-30. In the latter part of the curing reaction, the cross-linking density of the curing system is continuously increased while the concentration of the reactive groups is continuously decreased, which makes the conversion rate increase more slowly.
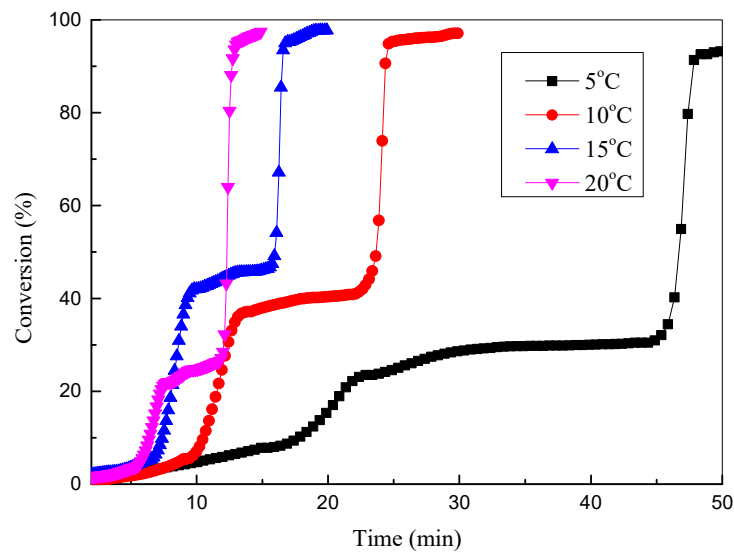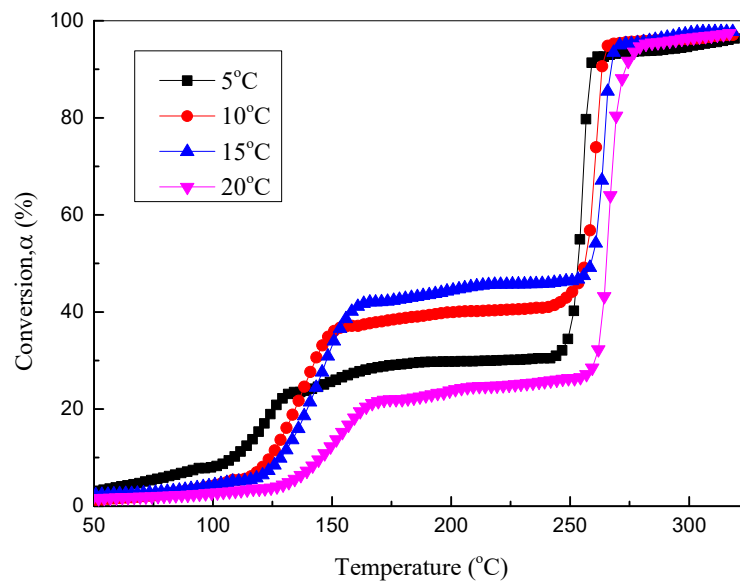

Figure 3. Plots of conversion as a function of curing time for the DGEBA / EDTAD / DMP-30 at different heating rates

3.2.3. Non-isothermal Curing Reaction Conversion Rate and Activation Energy. In general, epoxy curing is a process involves many elementary reactions, accompanied by mass transfer and phase transition. Therefore, the curing reaction mechanism of epoxy resin is so complex that the effective reaction activation energy generally varies with the conversion rate. In this chapter, we use Fredman [7, 8] model-free conversion rate method to discuss the relationship between the effective reaction activation energy and conversion rate which can be described by the following expression:

$$\ln[\beta_i(\frac{d\alpha}{dt})_{\alpha,i}] = \ln[f(\alpha_i)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{7}$$

Where $T_{\alpha,i}$ represents the temperature of corresponding curing reaction at a given conversion rate α and a heating rate β, β_i is the heating rate, subscript i is the thermal analysis experiment number, Eα is the activation energy in the reaction at a given conversion α , R is a universal gas constant.

As can be seen in Figure 4, the higher the cure temperature turns, the conversion curve shifts more to the right, which indicates that the conversion is a function of temperature. Makeing a lnβ to 1/T plot, you can get the slope of each line.
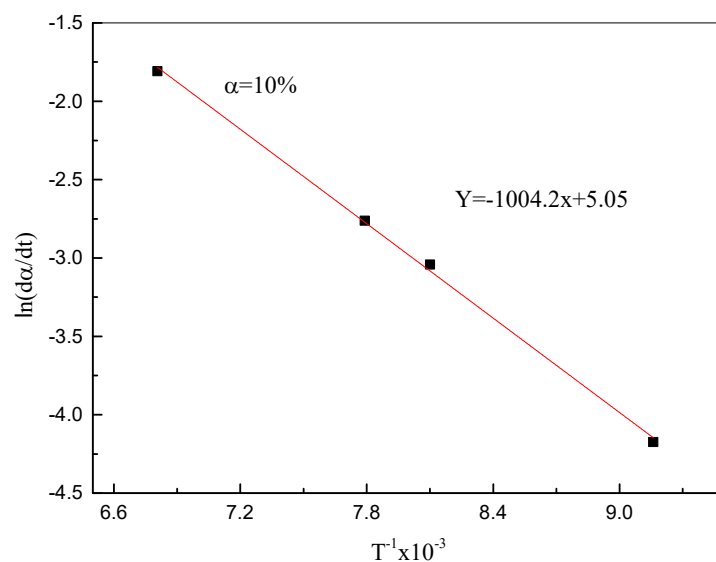

Figure 4. Plots of conversion as a function of curing temperature for the DGEBA / EDTAD / DMP-30 at different heating rates

Figure 5 shows the linear relationship between lnβ and 1/T at 10% conversion with good linearity. As shown in Figure 6, it can be seen that Eα is small when α<0.4, Eαis rapidly increased when 0.4<α<0.5, and Eα is decreased when α>0.5. This is because in the initial stage of the curing reaction, the temperature of the system increases continuously, and the viscosity is low, so the molecular diffusion rate is high, and the thermal movement of the segment is accelerated, the diffusion capability of the active groups of the system is increased and the autocatalytic effect as well, resulting in the decrease of the activation energy of diffusion. In the middle of the curing reaction, with the increase of conversion rate, the molecular weight increases rapidly, the system appears gelation and glass transition, the molecular weight hindered by the continuous movement and the free movement of molecular movement, and the curing reaction will be affected by the diffusion effect resulting in the increasing of viscous flow activation energy.

3.2.4. Non-isothermal Curing Reaction Apparent Activation Energy. As shown in Figure 7, according to the Kissinger method, the linear regression of ln (β/T_p^2) and $1/T_p$ is performed, and the apparent activation energy can be obtained from the slope K of the straight line E=-KR.

According to the Ozawa method, the linear regression of lnβ and $1/T_p$ is performed, and the apparent activation energy can be obtained from the slope K' of the straight line E'=-K'R, Take the average, E= (E+E')/2 to reduce the error. It can be seen that the apparent activation energy corresponding to the first peak of the DGEBA / EDTAD / DMP-30 system is much smaller than the

apparent activation energy corresponding to the second peak due to the decrease of DMP-30 as a promoter during the curing reaction. One peak of the DGEBA/EDTAD system corresponds to a larger apparent activation energy than the DGEBA/EDTAD/DMP-30 system (Table 1).

Figure 5. NonIsothermal reaction rate as a function of T^{-1} at given conversion, 10%
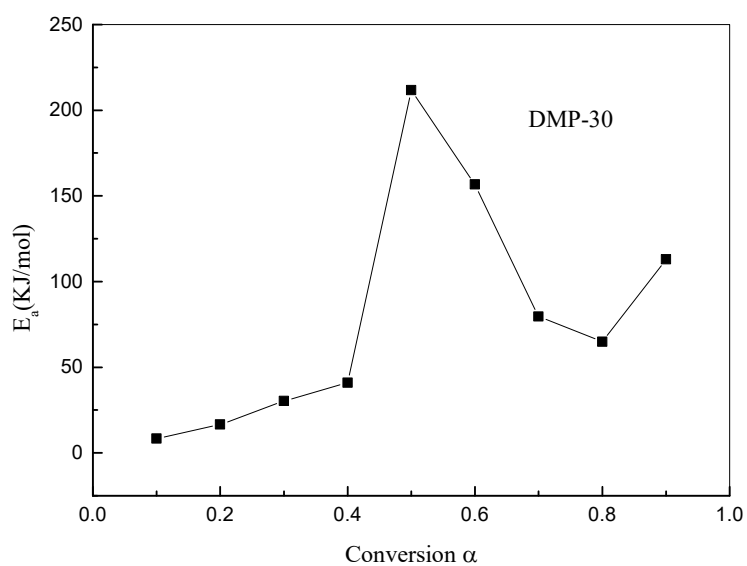
Figure 6. Values of $E\alpha$ obtained at different temperature
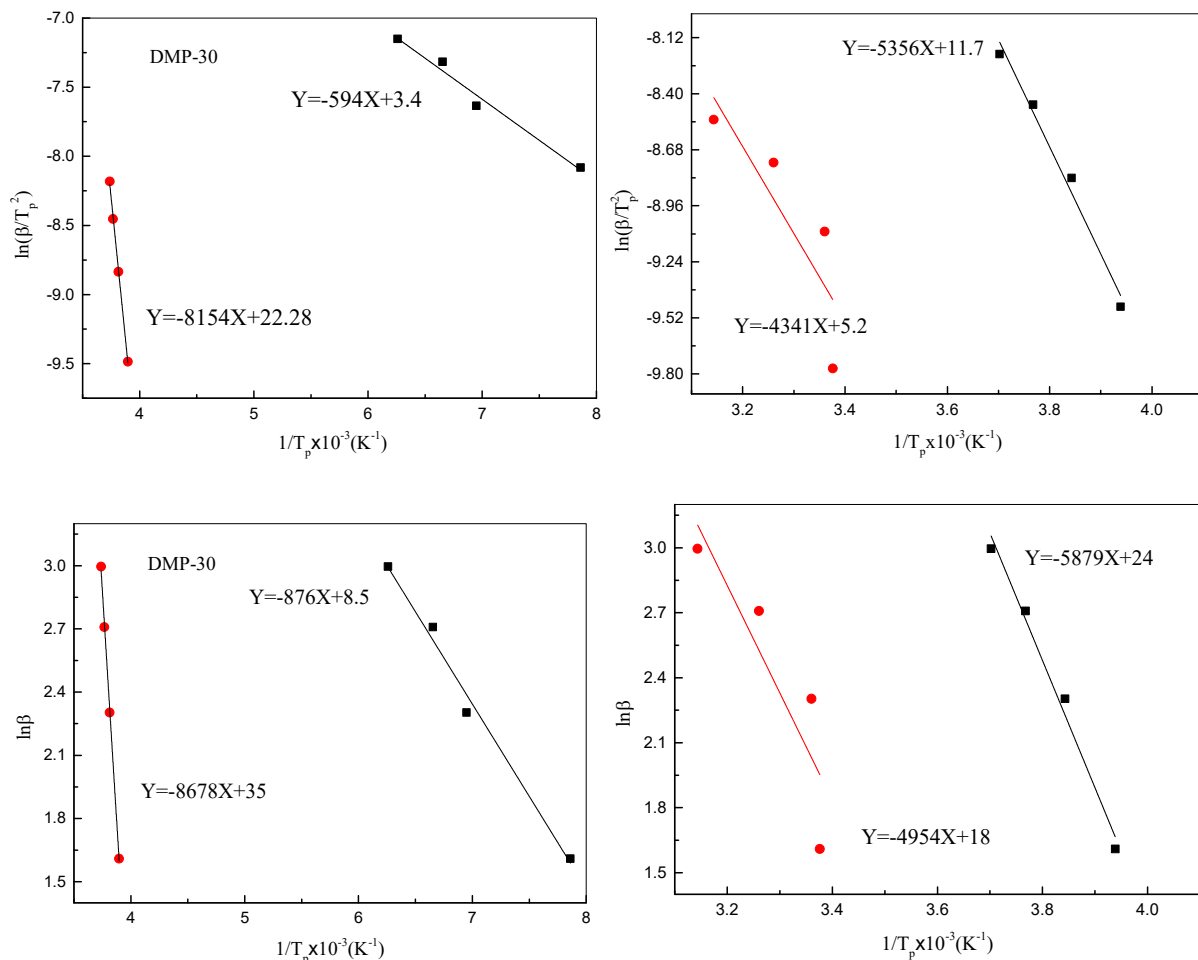
Figure 7. Plots of $\ln\beta/T_p^2$ and $\ln\beta$ vs. T^{-1}

Table 1. Activation energies of different no isothermal reaction systems

system	Activation energy E_1 (kJ / mol)			Activation energy E_2 (kJ / mol)		
	Kissinger method	Ozawa method	Mean	Kissinger method	Ozawa method	Mean
DGEBA / EDTAD / DMP-30	4.9	7.3	6.1	67.8	72.1	70.0
DGEBA / EDTAD	36.1	41.2	38.7	44.5	48.9	46.7

4. Conclusion

A new type of intumescent curing agent (EDTAD) was successfully produced. The kinetics of non-isothermal curing reaction of DGEBA/EDTAD/DMP-30 system was studied according to kinetic analysis. The results show that the curing reaction of the epoxy resin system is accurately described by Kissinger and Ozawa methods.

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