

Study on Synthesis of Thoreau-modified 3, 5-Dimethyl-Thioltoluenediamine Used as Epoxy Resin Curing Agent and Its Performance

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Abstract. A novel curing agent Thoreau modified 3, 5-Dimethyl-thioltoluenediamine was synthesized and its molecular structure was characterized by FTIR and DSC. The curing kinetics of a high toughness and low volume shrinkage ratio epoxy system (modified DMTDA/DGEBA) was studied by differential scanning calorimetry (DSC) under noni so thermal conditions. The data were fitted to an order model and autocatalytic model respectively. The results indicate that in order model deviates significantly from experimental data. Malik's method was used to prove that the curing kinetics of the system concerned follow single-step autocatalytic model, and a "single-point model-free "approach was employed to calculate meaningful kinetic parameters. The DSC curves derived from autocatalytic model gave satisfactory agreement with that of experiment in the range 5K/min~25K/min. As the heating rate increased, the predicted DSC curves deviated from experimental curves, and the total exothermic enthalpy declined owing to the transition of competition relationship between kinetics control and diffusion control.

1. Introduction

Epoxy resin is one of the most important thermosetting resins. The cured epoxy resins are of high crosslinked network that often exhibit high tensile strength and modulus [1], excellent chemical and corrosion resistance [2], and good thermal stability [3]. However, the ordinary epoxy resin cannot crosslink alone without curing agents or accelerant. In order to convert the resins to practical materials, it is necessary to add a curing agent. Most of the epoxy curing agents in common use are poly functional amines [4, 5], tertiary amines, anhydrides and other latent curing agents.

Now with theorem can significantly reduce the curing temperature of epoxy resin, to synthesis a novel curing agent by theorem-polyamine condensation reaction, the study using theorem modified liquid aromatic amine, the expected good mechanical properties of the resin system.

In this paper, 3, 5-Dimethyl-thioltoluenediamine (DMTDA) was used to replace the solid aromatic amines, and the amount of active hydrogen in theorem was more than that of solid urea and polyamine. , After the reaction can improve the reactivity of DMTDA, make it better and more fully with the epoxy resin reaction. The final preparation of low toxicity, faster curing, and epoxy resin easy to mix evenly epoxy curing agent.



The thermodynamic curves of the modified DMTDA / epoxy resin curing system were obtained by non-isothermal DSC scanning [6, 7]. The kinetic parameters of the modified aromatic amine-epoxy resin were obtained by using the n-level model and the autocatalytic model respectively. Contrast to determine its kinetic equation. Finally, the curing process parameters of the resin system were obtained by the measured data and extrapolation method.

2. Experimental Section

2.1. The Synthesis of Theorem-modified 3, 5-Dimethyl-thioltoluenediamine

To a 100 ml clean three-necked flask equipped with an exhaust gas treatment unit were 0.15mol theorem and 0.6mol DMTDA which were added and nitrogen was introduced. Oil bath heating system slowly increased to 135°C temperature, the speed of stirring, constant temperature reaction for 8h, then stop heating and stirring, cooling to room temperature, after pumping the liquid obtained by adding slowly into the beaker containing toluene solution, After stirring, into the separator funnel, to be placed after the separation, the upper layer of liquid in the beaker, after the rotary evaporation, the dark yellow oily liquid. Theorem modified polyamine reaction principle shown in Figure 1 ($n \leq 3$):

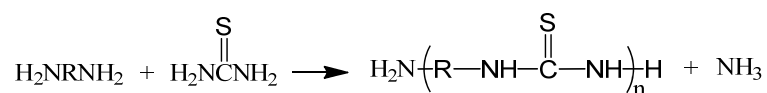


Figure.1 The synthesis reaction equation of theorem modified polyamine

2.2 Study on Curing Kinetics of Modified DMTDA / Epoxy Resin System

2.2.1 Determination of Curing Parameters of Modified DMTDA / Epoxy Resin by DSC The prepared modified DMTDA/epoxy resin(DGEBA) system was vacuum degassed at 40°C and weighed 3~5mg for DSC analysis. The temperature was measured by 5K / min, 10K / min, 15K / min and 20K / min respectively.

The curing reaction heat (ΔH) was determined by integrating the area between the DSC curve and the baseline in units of kJ/mol.

3. Result and Discussion

3.1 FT-IR Analysis of Modified DMTDA

Figure 2 shows the FT-IR characterization of the product after separation and purification of theorem modified DMTDA at 130 °C, 7h, nDMTDA: nthiourea = 4: 1.

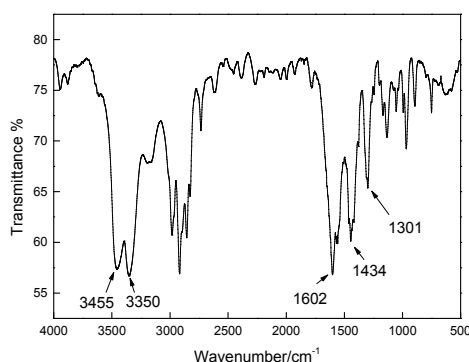


Figure.2 The infrared figure of theorem modified 3, 5-Dimethyl-thioltoluenediamine

The peaks at 3455 cm⁻¹, 3350 cm⁻¹ and 1602 cm⁻¹ can be confirmed as the stretching and bending vibration peaks of -NH₂-, and the presence of primary amino groups ensures that the substance remains as an epoxy resin curing agent use. 1301 cm⁻¹ is the stretching vibration peak of -C=S- in the -CS-N- unit, and 1434 cm⁻¹ is the stretching vibration peak of -CN- in the -CS-N- unit, which indicates that the theorem modified DMTDA.

3.2 Study on Curing Kinetics of Modified DMTDA / Epoxy Resin System

3.2.1 Study on Curing Kinetics of Resin System Based on n - level Dynamic Model Most of the kinetics of resin curing reaction using the n-level dynamic model in the image model:

$$\frac{d\alpha}{dt} = k_0(1 - \alpha)^n \quad (1)$$

Where α is the curing degree; n is the reaction order; k_0 is the reaction rate constant which related by the temperature.

The kinetic parameters of the curing reaction, such as the activation energy and the reaction order, play an important role in understanding the curing reaction kinetics. In general, the Kissinger and Crane equations can be used to process the DSC data obtained at different heating rates. The kinetic parameters such as E_a , n , A and so on can be obtained, and the n-level kinetic model equation of the curing reaction can be determined.

Kissinger equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{RT}{Eg(\alpha)}\right) - \frac{E}{RT} \quad (2)$$

Where β is the heating rate; T_p is the peak temperature; E_a is the apparent activation energy.

Fig. 3 shows the DSC curves at different heating rates. Table 1 shows the exothermic enthalpy ΔH , the initial temperature T_i , the peak temperature T_p and the termination temperature T_f at different heating rates.

At different heating rates, the relationship between $\ln(\beta/T^2)$ and $(1/T_p)$ is shown in Fig. Linear fit can be obtained slope, that is, $-E_a/R$ intercept is $\ln(AR/E_a)$.

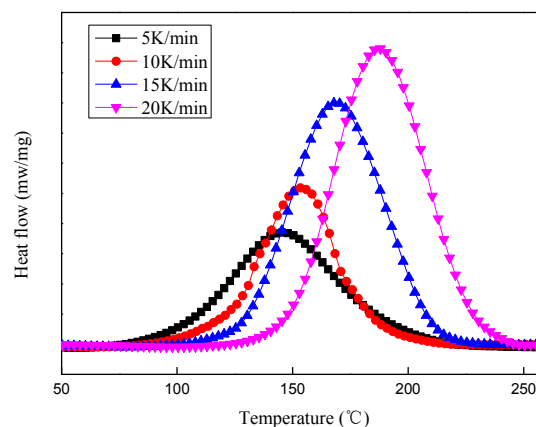
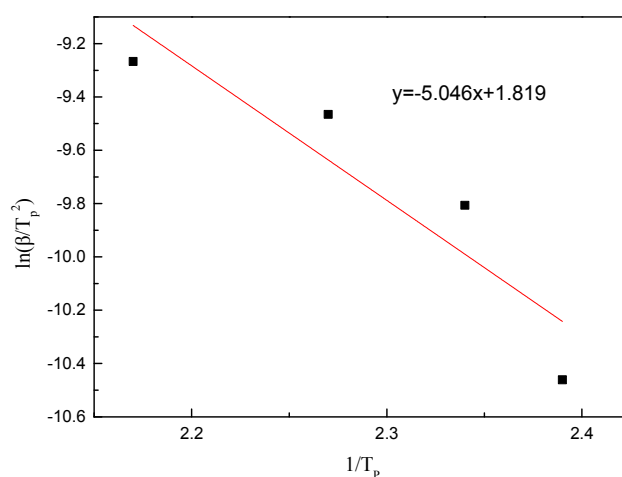


Figure.3 DSC scans of modified DMTDA/DGEBA at different heating rates

Table 1 characteristic parameters of the different reaction systems

$\beta/(\text{K} \cdot \text{min}^{-1})$	$T_i/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_f/^\circ\text{C}$	$\Delta H/(\text{J} \cdot \text{g}^{-1})$
5	95.6	145.4	202	20.72
10	103.5	153.8	208.3	21.47
15	117.3	167.3	217.6	38.15
20	142.4	187.7	232.5	46.40

**Figure.4** the Kissinger equation of DEGBA/modified DMTDA

From Fig. 4, we can get the equation $y = -5.046x + 1.819$, and the apparent activation energy of DGEAB/modified DMTDA system is $E_a = 41.9 \text{ kJ/mol}$ according to the slope.

Crane equation:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\left(\frac{E_a}{nR} + 2T_p\right) \quad (3)$$

When $\frac{E_a}{nR} \geq 2T_p$, the equation can convert to $\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{E_a}{nR}$. At different heating rates, the relationship between $\ln \beta$ and $1/T_p$ is shown in Fig.5, and the linear slope is linear.

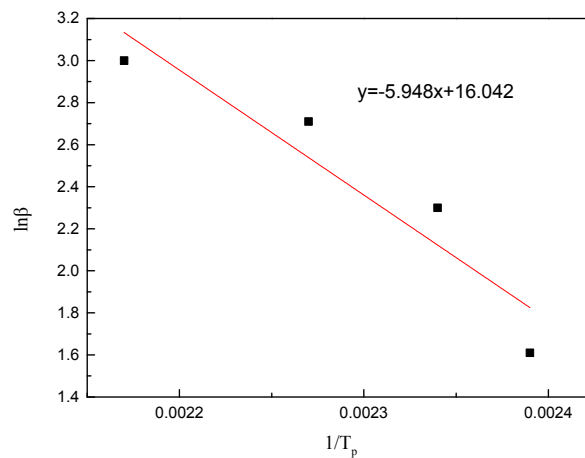


Figure.5 the Crane equation of DEGBA/modified DMTDA

From Fig. 5, we can get that the straight line equation is $y = -5.948x + 16.042$, and the reaction order of DGEAB/modified DMTDA system is 0.84 according to the slope.

3.2.2 Study on Curing Kinetics of Resin System by Autocatalytic Model The autocatalytic model is generally used to study isothermal curing kinetics due to its simultaneous calculation of the complexity of multiple parameters:

In order to further study the curing behavior of DGEBA/modified DMTDA system, the self-catalyzed model is used to determine the appropriate reaction kinetic function. In this paper, that is based on the definition of function $y(\alpha)$ and $z(\alpha)$ to determine $f(\alpha)$.

$$y(\alpha) = \left(\frac{d\alpha}{dt} \right) \exp(\chi) \quad (4)$$

$$z(\alpha) = \pi(\chi) \left(\frac{d\alpha}{dt} \right) \frac{T}{\beta} \quad (5)$$

In the formulas (3-10) and (3-11), χ express E_a / RT it is said that β the heating rate $\pi(\chi)$ is the temperature integral, and the four-level approximation of Senum-Yang is used to represent the temperature integral.

$$\pi(\chi) \approx \frac{\chi^3 + 18\chi^2 + 88\chi + 96}{\chi^4 + 20\chi^3 + 120\chi^2 + 240\chi + 120} \quad (6)$$

Figure 3-6 is the normalization of DGEAB / modified DMTDA system $y(\alpha)$, $z(\alpha)$ and the reaction rate of the reaction with the conversion rate of the relationship between the heating rate of

10K / min-1, $y(\alpha)$, $z(\alpha)$ and curve of the peak Respectively, α_p , α_M , α_p^∞ , detailed parameters as shown in the table.

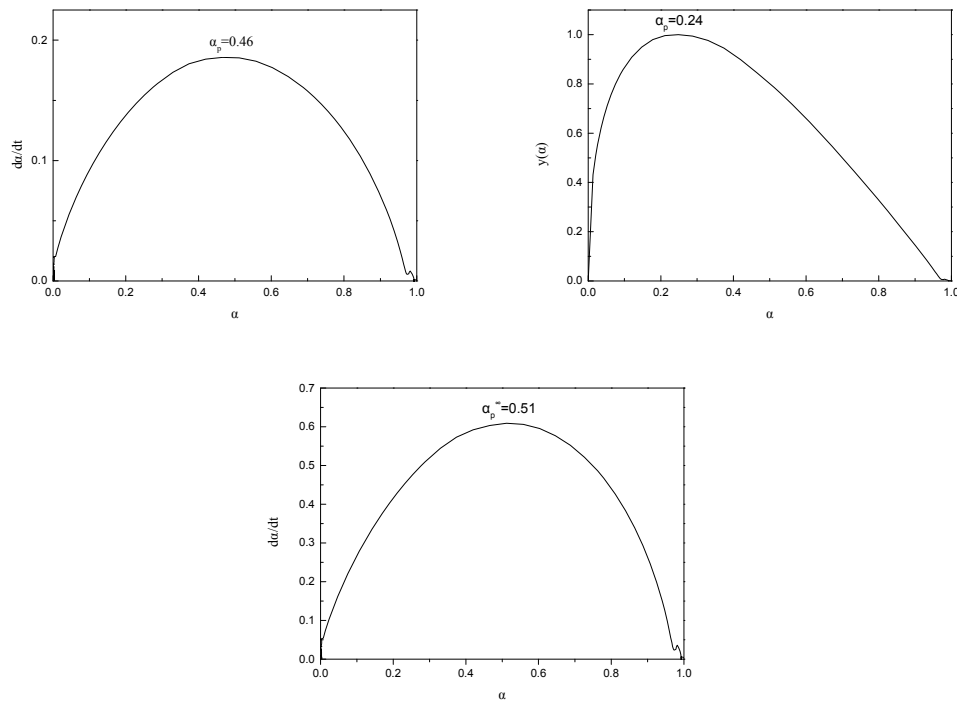


Figure.6 Variation of experimental reaction ($d\alpha/dt$), normalized $y(\alpha)$, and $z(\alpha)$ versus fractional conversion for DGEBA/modified DMTDA (10K·min-1)

Table 2 Peak values of $d\alpha/dt$, $y(\alpha)$, and $z(\alpha)$, along with calculated kinetic parameters

Heating rate/(K·min ⁻¹)	α_p	α_M	α_p^∞	n	m	$\ln A$
5	0.47	0.20	0.51	1.57	1.39	11.52
10	0.46	0.21	0.51	1.50	1.28	12.01
15	0.47	0.27	0.52	1.17	1.04	11.69
20	0.51	0.29	0.49	1.22	1.27	11.68
Average value				1.37	1.25	11.73

It can be seen from Table 2 that $0 < \alpha_M < \alpha_p^\infty$, and $\alpha_p^\infty \neq 0.632$, according to the shape, the eigenvalue determines the kinetic mechanism function closest to the SB (m, n) model.

$$\frac{d\alpha}{dt} = Ae^{-\chi}\alpha^m(1-\alpha)^n \quad (7)$$

Where m, n is the reaction order.

It can convert to,

$$\ln\left[\left(\frac{d\alpha}{dt}\right)\exp(\chi)\right] = \ln A + n \ln[\alpha^{m/n}(1-\alpha)] \quad (8)$$

Where m/n is equal to $\alpha M / (1 - \alpha M)$, so that in the range of $0.2 \leq \alpha \leq 0.9$, $\ln[(\frac{d\alpha}{dt})\exp(\chi)]$ is plotted with $\ln A + n \ln[\alpha^{m/n}(1 - \alpha)]$, and the slope is n , so that the m value can be calculated and the straight line Intercept is $\ln A$, the results shown in Table 2, Figure 7 is when the heating rate of $5K \cdot \min^{-1}$, the system $\ln[(\frac{d\alpha}{dt})\exp(\chi)]$ with $\ln A + n \ln[\alpha^{m/n}(1 - \alpha)]$ changes.

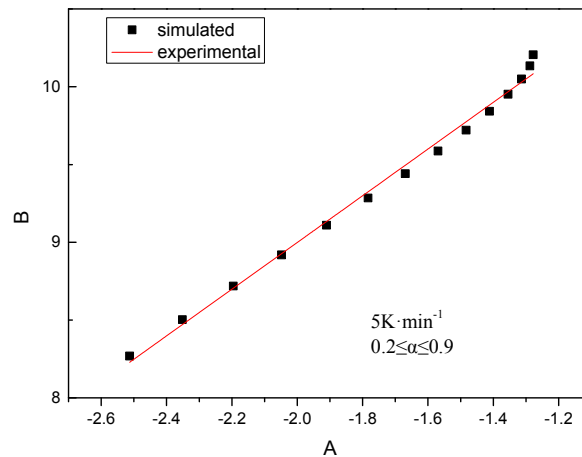


Figure. 7 variation of $\ln[(\frac{d\alpha}{dt})\exp(\chi)]$ versus $\ln A + n \ln[\alpha^{m/n}(1 - \alpha)]$ for DGEBA/modified DMTDA ($5K \cdot \min^{-1}$)

The results of DGEBA / modified DMTDA were as follows:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = 1.24 \times 10^6 \exp\left(\frac{-41900}{RT}\right) \alpha^{1.25}(1 - \alpha)^{1.37}$$

The initial conditions were as follows: $T = 0^\circ\text{C}$, the curing degree α_0 , and the calculation results shown in Figure 8.

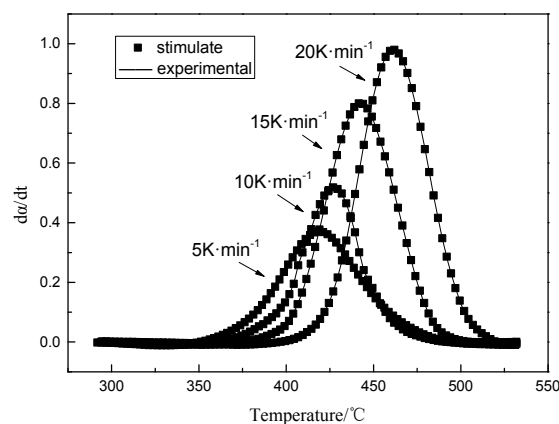


Figure.8 comparison rates of experimental and predicted for DGEBA/modified DMTDA from SB (m, n) model

Figure 8 shows the experimental curve and model calculation curve at different heating rates. As shown in the figure, the model curve agrees well with the experimental curve. However, with the increase of the heating rate, the experimental curve gradually deviates from the model calculation curve. This is because the curing rate of the epoxy resin system depends on the activity and activity of the functional group. The reaction rate between the reaction groups in the initial reaction is much greater than the rate of intermolecular collision, and the curing reaction is controlled by the chemical activity of the reactive groups. With the progress of the reaction, the molecular chain is growing until the system reaches the gel. The crosslinking degree of the further polymerization system is increasing, and the movement of the active group is more and more restricted, and the curing reaction is changed to the diffusion control. With the increase of the heating rate, the initial temperature of the curing reaction increased, the thermal motion of the molecule increased, the time of gelation was gradually shortened, and the influence of the diffusion control on the system became more and more obvious.

In general, the model can be used to describe the curing behavior of modified DMTDA / epoxy resin system in the temperature range of 5K / min ~ 25K / min. This curing model can be used to predict the time required for the system to reach a certain degree of cure at a certain temperature, or to achieve the desired temperature for a predetermined period of time.

4. Conclusion

Increasing the reactivity of DMTDA by polyamine-theorem condensation reaction, effectively reducing its curing temperature as epoxy resin curing agent, determining the product by FT-IR characterization, which provides the modification of DMTDA A new idea. The self-catalyzed model can describe the curing behavior of the modified DMTDA / epoxy resin system, and the model of the ϕ -T curve is calculated by the non-isothermal kinetics. The self-catalyzed model can be used to describe the curing behavior of the modified DMTDA / Epoxy resin system. Values and experimental values are basically consistent. Which provides a theoretical basis for the application of the system as a high-performance resin material and optimizing the curing process.

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