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Curing Reaction Kinetics of the EHTPB-Based PBX Binder System and Its Mechanical Properties

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Abstract: In this research, differential scanning calorimetry (DSC) was employed to compare the curing reaction kinetics of the epoxidized hydroxyl terminated polybutadiene-isophorone diisocyanate (EHTPB-IPDI) and hydroxyl terminated polybutadiene-isophorone diisocyanate (HTPB-IPDI) binder systems. Glass transition temperature (T_g) and mechanical properties of the EHTPB-IPDI and HTPB-IPDI binder systems were determined using the DSC method and a universal testing machine, respectively. For the EHTPB-IPDI binder system, the change of viscosity during the curing process in the presence of dibutyltin silicate (DBTDL) and tin 2-ethylhexanoate (TECH) catalysts was studied, and the activation energy was estimated. The results show that the activation energies (Ea) of the curing reaction of the EHTPB-IPDI and HTPB-IPDI binder systems are 53.8 and 59.1 $\mathrm{kJ \cdot mol^{-1}}$, respectively. While their average initial curing temperatures of the two systems are 178.2 and 189.5 °C, respectively. The EHTPB-IPDI binder system exhibits a higher reactivity. Compared with the HTPB-IPDI binder system, the T_g of the EHTPB-IPDI binder system is increased by 5 °C. Its tensile strength and tear strength are increased by 12% and 17%, respectively, while its elongation at break is reduced by 10%. Epoxy groups and isocyanates react to form oxazolidinones, thereby improving the mechanical properties and thermal stability of polyurethane materials. These differences indicate that the EHTPB-IPDI binder system has better thermal stability and mechanical properties. During the EHTPB-IPDI binder system's curing process, the DBTDL catalyst may ensure a higher viscosity growth rate, indicating a better catalytic effect, consistent with the prediction results obtained using the non-isothermal kinetic analysis method.

Keywords: EHTPB; catalyst; cure kinetics; mechanical properties; DSC

1. Introduction

HTPB-based polyurethane materials have been extensively used as binders for solid composite propellants and polymer bonded explosives (PBXs) [1,2]. Solid composite propellant is a kind of energetic composite material with specific performance. It is the power source of a strategic missile, tactical missile, solid motor of space vehicle and kinetic energy interceptor [3]. Cast PBXs explosive with HTPB isocyanate system as a binder has the characteristics of good fluidity, long service life, high solid content, good adhesion with metal, excellent explosion performance and good safety, it has become one of the main types of solid rocket propellant, large and medium caliber shells, missiles and underwater weapons, and has been widely used at home and abroad [4,5]. For the traditional HTPB binder system, low polarity, poor mechanical properties and weak binding strength limit its development in solid propellants. EHTPB is the introduction of epoxy groups into the molecular chain of hydroxyl-terminated polybutadiene (HTPB), which can effectively improve the polarity of the molecule, the cured epoxy polymer has good physical and chemical properties, low shrinkage, high hardness, which can greatly improve the mechanical properties, and it is used widely for adhesives, sealants, coatings and elastomers [6,7]. EHTPB-based polyurethane elastomer exhibits excellent physicochemical properties, making it a promising binder for solid propellants [8,9]. The kinetic mechanism of the curing reaction reflects the physicochemical properties of the curing products. Therefore, the polyurethane curing reaction kinetics is of great importance for designing and producing high-quality products.

Previous research [10–20] of the HTPB curing reaction kinetics focused on the effects of dibutyltin dilaurate (DBTDL), ferric acetylacetonate (FeAA), triphenyl bismuth (TPB) and tin 2-ethylhexanoate (TECH) on the HTPB/IPDI binder system. DBTDL exhibited a strong catalyzing effect on the reaction between isocyanate and alcohols, so-called a gel catalyst. The application of FeAA as a catalyst yielded a binder system with a relatively short pot life. Cast PBXs explosive and composite solid propellant are composed of a binder system and solid composition. The catalytic effect of the catalyst TPB on the HTPB-IPDI binder system is not obvious, and the viscosity of the binder system increases slowly, which leads to the sedimentation of the solid composition. Compared with DBTDL, TECH is more environmentally friendly, exhibiting lower toxicity and longer pot life when added into a binder system. However, to the authors' best knowledge, research on the EHTPB-based binder system's curing process has not been reported so far.

Thermal analysis is one of the most important methods to determine the kinetics of the curing reaction. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been extensively used to calculate the kinetic parameters [21]. Among these methods, the DSC method has been the most broadly applied. The curing reaction of the EHTPB-based binder system is a continuous exothermic process, so the non-isothermal DSC method can be used to study the curing kinetics of the EHTPB system.

The performance of a polyurethane elastomer relies not only on the chemical composition and preparation technique but also on the curing conditions. Research on the curing reaction kinetics provides more in-depth insight into the curing process. This study investigated the curing kinetics of the HTPB-IPDI and EHTPB-IPDI binder systems using the DSC method. The glass transition temperatures (T_g) of the EHTPB-IPDI and HTPB-IPDI polyurethane elastomers were determined. The mechanical properties of the polyurethane elastomers were tested using a universal testing machine. The curing kinetics of the EHTPB-IPDI system under different catalytic conditions were studied, and the corresponding curing kinetic parameters were determined, such as post-processing temperature and curing time in the gelation. Such as post-processing temperature and curing time in the gelation. These results provide theoretical support for the determination of the optimal curing parameters.

2. Materials and Methods

2.1. Materials

EHTPB (Mn = 3000 g/mol, the hydroxyl value = 0.75 mmol/g, epoxide value = 0.84 mmol/g and moisture content = 0.015%) and HTPB (Mn = 3240 g/mol, the hydroxyl value = 0.67 mmol/g and moisture content = 0.017%) were purchased from Liming Research and Design Institute of Chemical Industry Co., Ltd., the curing agent, IPDI, from BASF SE (Ludwigshafen, Germany), TECH from Shanghai Institute of Organic Chemistry (Shanghai, China) and DBTDL from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). EHTPB and HTPB were dried at 100 °C, first in a vacuum, and then at atmospheric pressure of 0.05 mPa for 4 h before the testing. Subsequently, the dried chemicals were separately stored in dry and sealed bottles.The chemical structures of the HTPB and EHTPB are shown in Figures 1 and 2.

A SNB-1A numeric viscosimeter (Shanghai Fangrui Instrument, Shanghai, China) was used to measure the viscosity of the binder systems, and a DHG303-2 oven (Shanghai Yiheng Instrument, Shanghai, China) was used to dry the samples. Thermal analysis of the samples was conducted using an HCT-1 thermal analyzer (Beijing Yongjiu Instrument, Beijing, China).

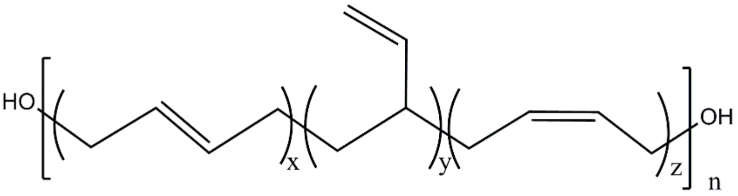


Figure 1. Chemical structure of HTPB.

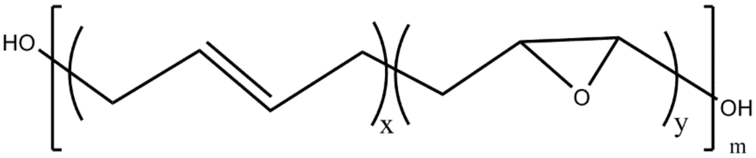


Figure 2. Chemical structure of EHTPB.

2.2. *Sample Preparation*

Each binder system was prepared according to the following procedures:

HTPB-IPDI and EHTPB-IPDI with a weight ratio of R(nNCO/nOH) = 1 were added into a dry beaker. An electrical stirring machine was used to mix the two components for 10 min. The pressure of the mixture was reduced to 100 Pa and kept for 5 min to remove the formed bubbles. Finally, the binder system was obtained and collected.

The films of the binder system were prepared by pouring the as-prepared binder system into polytetrafluoroethylene (PTFE) molds, placing them in a thermostatic oven and curing at 70 °C for 7 days. The thickness of the films is 2 mm.

2.3. *Calculation of the Curing Reaction Kinetics*

Kissinger, Flynn–Wall–Ozawa (F-W-O), Doyle and Crane methods are commonly used to determine the kinetic parameters of a non-isothermal curing process. The kinetics can be expressed by the following equations [22,23]:

$$\frac{\mathrm{d}\partial}{\mathrm{d}t} = Ae^{-E/RT} \times (1-\partial)^n \tag{1}$$

Kissinger equation:

$$\ln\frac{\beta_i}{{T_{pi}}^2} = \ln\left(\frac{AR}{E}\right) - \frac{E}{R}\cdot\frac{1}{T_{pi}} \tag{2}$$

(F-W-O) equation:

$$\ln\beta = \ln\left[\frac{AE}{Rg(\partial)}\right] - 5.330 - 1.0516\frac{E}{RT} \tag{3}$$

Doyle equation:

$$\ln\beta = \ln\left[\frac{AE}{Rg(\partial)}\right] - 2\ln\frac{E}{RT} - \frac{E}{RT} \tag{4}$$

Crane equation:

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}\left(1/T_p\right)} = -\frac{E}{nR} \tag{5}$$

where, T_p and T(K) are the temperatures of the peaks, β (K/min) is the heating rate, R (8.314 J/mol) is the gas constant, E (kJ/mol) is the apparent activation energy and A is the pre-exponential factor, which has the same dimension as the rate constant and depends on the reaction order, n.

2.4. *DSC Testing*

The DSC tests for the analysis of curing reaction kinetics were conducted in a nitrogen atmosphere at a flow rate of 50 mL/min. In a typical experiment, a crucible with 10 mg of sample (propellant slurry) was placed in the heating chamber of the DSC analyzer (HCT-1 thermal analyzer, Beijing Yongjiu Instrument, Beijing, China). The measurements were performed by heating from 25 to 350 °C at four different heating rates (5, 10, 15 and 20 °C/min).

The determination of T_g was performed using the described DSC tests, except that the heating rate was 10 °C/min. That for T_g the cured samples had been tested by DSC and that an increased heat flow (endothermic behavior) shows T_g.

2.5. Mechanical Properties of EHTPB-IPDI and HTPB-IPDI Polyurethane Elastomers

The tensile properties of the EHTPB-IPDI and HTPB-IPDI binder system films were tested with an EMT-C universal material testing machine.

According to the Chinese standard: GB/T 528-1998 [24], rubber, vulcanized or thermoplastic, we determined the tensile stress–strain properties. The tensile strength and elongation at break of the specimens were measured by setting the gauge length of the specimens and the tensile speed at 25 mm and 50 mm/min, respectively. Five samples were cut from each type of the binder system film, and further analyzed. Figure 3 represents the dumbbell-shaped specimens. The data recorded in the five tests of the same binder system film were collected. The mean value of the indexes obtained from the five measurements was set as the final test result.

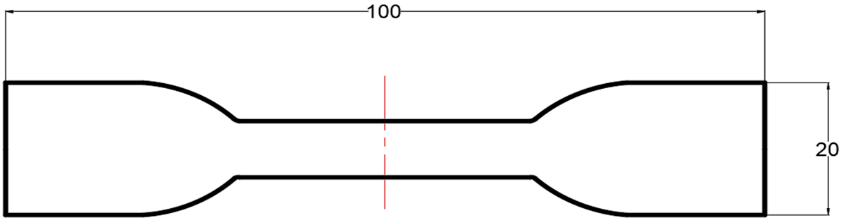


Figure 3. The dumbbell-shaped specimens.

According to the Chinese standard: GB/T 529-2008 [25], Rubber, vulcanized or thermoplastic, we determined tear strength. Tearing properties of L-shaped specimens (Figure 4) were also tested with an EMT-C universal material testing machine at room temperature (25 °C). The gauge length of the specimens was fixed at 25 mm, and the tensile speed was 50 mm/min. Each group of the binder system films was tested for at least 5 times to assess the experiment's reproducibility.

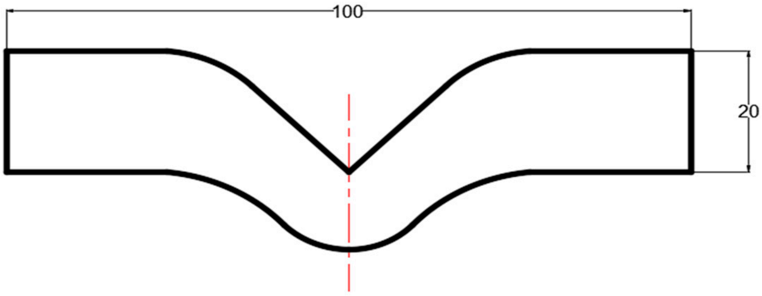


Figure 4. L-shaped specimens.

2.6. Viscosity Monitoring Experiment

An SNB-1A digital viscometer was used to monitor the EHTPB-IPDI binder system's viscosity changes in the presence of DBTDL and TECH catalysts during the curing process. The binder system was stirred by a 29# size rotor, with a rotating speed of 0.5 rpm at 25 °C.

3. Results and Discussion

3.1. Determination of the Activation Energy of EHTPB-IPDI and HTPB-IBDI Binder Systems

A non-isothermal DSC method with multiple scanning rates was selected to determine the curing kinetics of the systems. Figure 5 shows the non-isothermal curves of the HTPB-IPDI system recorded at different heating rates. As the heating rate increased, the exothermic peak temperature shifted to the right, while the shape of the exothermic peak gradually widened. With the increase of heating rate, not all the reactants have a curing reaction, and the crosslinking degree of curing reaction was not high. Thermal decomposition occurs between the reactant and the cured crosslink, and the exothermic peak of decomposition overlaps with the exothermic peak of the curing reaction. Therefore, there will be a baseline shift in the DSC curve. The total heat output increased in the same manner, while the corresponding curing time decreased with the heating rate increase. These changes indicate that the curing reaction of the HTPB-IPDI system was not only thermodynamically but also a kinetically controlled process.

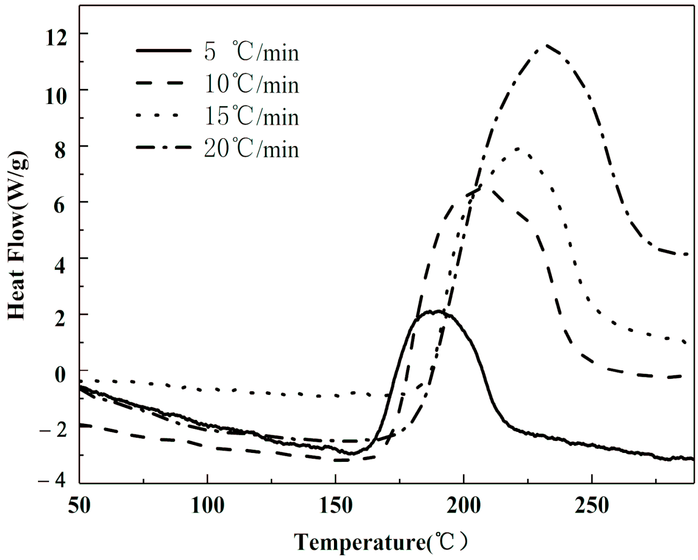


Figure 5. Non-isothermal differential scanning calorimetry (DSC) curves of the HTPB-IPDI system at different heating rates.

Figure 6 shows the non-isothermal curves of HTPB-IPDI and EHTPB-IPDI systems at a heating rate of 5 °C/min. It can be seen from Figure 6 that the initial temperature and peak temperature of exothermic peak of the curing reaction of the EHTPB-IPDI system were lower than that of the HTPB-IPDI system.

The corresponding peak temperatures, T_p, of the binder systems at different heating rates, listed in Table 1, were linearly fitted. $\ln(\beta/T_p^2)$ vs. $1/T_p$ (Figure 7) was plotted according to the Kissinger method Equation (2), and the pre-exponential factor, A, and activation energy, E, were calculated from the slope and intercept of the fitting linear curves. The values of the determined pre-exponential factor, A, and activation energy, E, of the two binder systems are listed in Table 2.

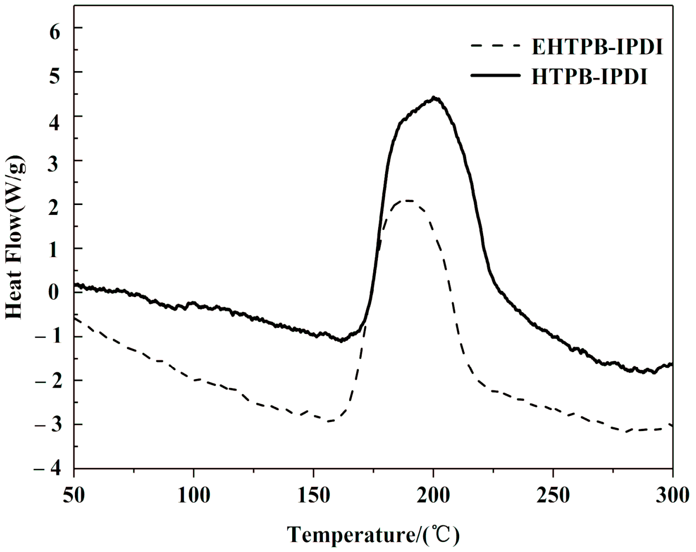


Figure 6. Non-isothermal DSC curves of the HTPB-IPDI system and HTPB-IPDI system a scanning rate of 5 °C min^{-1}.

Table 1. Data of the EHTPB-IPDI and HTPB-IPDI systems.

β/°C·min^{-1}	T_{1i}/°C	T_{1p}/°C	T_{1f}/°C	T_{2i}/°C	T_{2p}/°C	T_{2f}/°C
5	167.4	190.4	212.7	174.5	200.1	223.3
10	174.8	207.8	239.6	189.5	221.1	247.4
15	181.4	222.4	255.6	196.4	232.7	263.1
20	189.1	234.2	270.2	197.7	241.9	277.4

β: heating rate; T_i: initial temperature; T_p: peak temperature; T_f: final temperature; T_1 and T_2: curing reaction temperatures of the EHTPB-IPDI and HTPB-IPDI systems.

Table 2. Kinetic parameters of the curing reactions of the EHTPB-IPDI and HTPB-IPDI systems.

System	E/kJ·mol^{-1}	A/s^{-1}
EHTPB-IPDI	53.8	1.79×10^5
HTPB-IPDI	59.1	5.29×10^5

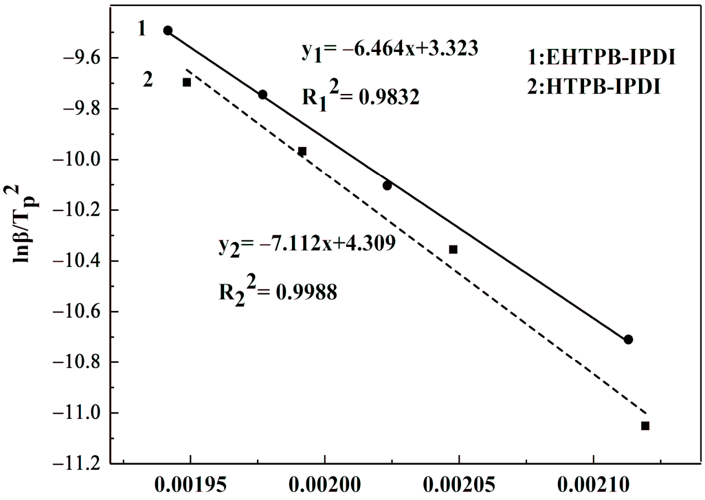


Figure 7. Determination of activation energy, *E*, of the EHTPB-IPDI and HTPB-IPDI systems, using the Kissinger method.

The activation energy of the EHTPB-IPDI binder system was lower than that of the HTPB-IPDI binder system, indicating the curing reaction of the EHTPB-IPDI binder system was more likely to occur.

3.2. Analysis of the Glass Transition Temperature, T_g

The glass transition temperature (T_g) of polyurethane elastomer reflects its thermal stability and thermal degradation properties. The T_g value is related to the cross-linking density and chemical structure of the polyurethane elastomer. Figure 8 indicates that due to epoxy groups' introduction, T_g of the EHTPB-IPDI polyurethane elastomer increased by 5 °C, and the thermal stability also improved to a certain extent. These effects originated from the reaction of the introduced epoxy groups that react with isocyanate and generate oxazolidinone (Figure 9) during the polyurethane elastomers' curing process. There are three positions of C=C in the molecular structure of HTPB (Figure 1). In the epoxidation reaction, the double bond may be opened to form an epoxy group. With the curing reaction going on, a large number of oxazolidinones can be produced by the reaction of epoxy group and isocyanate radical. The existence of oxazolidinone in the binder system may improve the performance of polyurethane elastomers [26]. The presence of oxazolidinone in polyurethane can increase the glass transition temperature of polyurethane, which is consistent with the experimental results of Yu et al. [27], polyurethane material was prepared by the reaction of diglycidyl terephthalate and toluene diisocyanate. The glass transition temperature was 110 °C, and it had good thermal stability. Besides, the reaction between isocyanate and epoxy groups will branch the EHTPB-IPDI binder system and increase its cross-linking density, improving the elastomer's thermal stability.

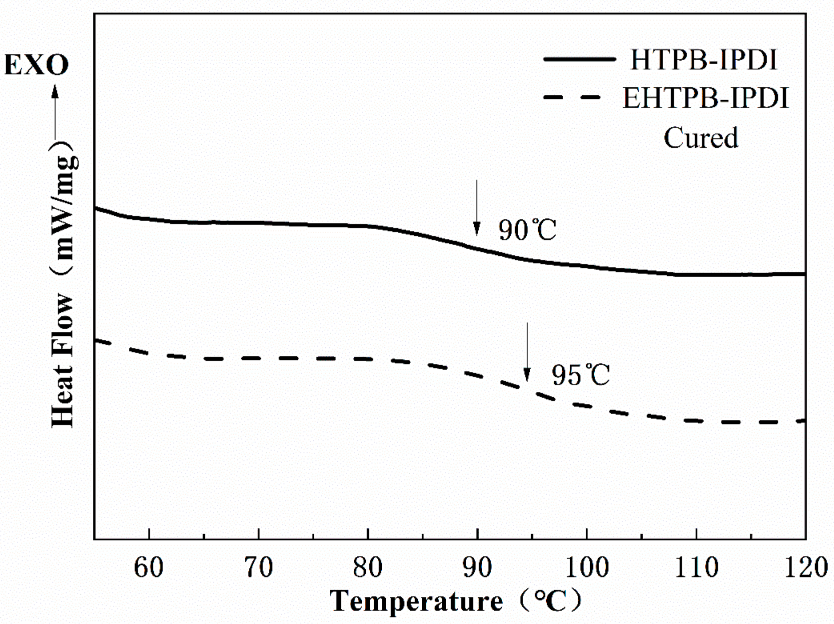


Figure 8. Glass transition temperature (T_g) determined by the DSC thermograms at a scanning rate of 10 °C min^{-1} for the EHTPB-IPDI and HTPB-IPDI systems.

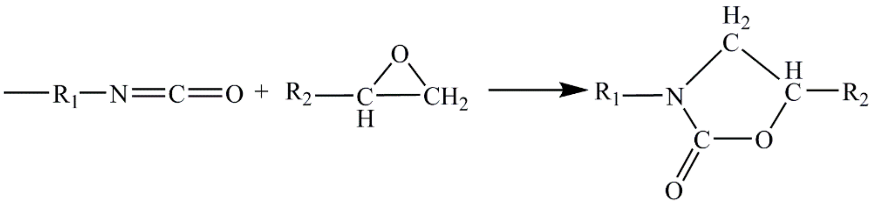


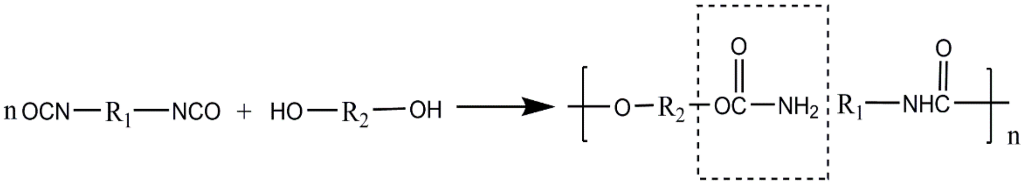
Figure 9. The reaction between –NCO and epoxy groups.

3.3. Determination of Mechanical Properties

Table 3 shows that the tensile strength of the EHTPB-IPDI polyurethane elastomer was 12% higher than that of the HTPB-IPDI elastomer. Besides, compared with EHTPB-IPDI, the tear strength of HTPB-IPDI increased by 17%, while its elongation at break was reduced by 10%. These changes can be attributed to the fact that besides the carbamate formation (Figure 10) via the reaction with hydroxyl groups, isocyanate in the EHTPB-IPDI elastomer can also react with epoxy groups and form oxazolidinone (Figure 9). Oxazolidinone can improve the mechanical properties of polyurethane [28]. As a result, more branched chains (Figure 11) were generated in the elastomer, yielding the increased cross-linking density of the polyurethane elastomer and enhancing its tensile and tearing strength, which is consistent with the experimental results of Yang et al. [29], EHTPB-modified epoxy resin exhibited excellent mechanical properties than that of neat epoxy resin. Moreover, the increase of the cross-linking density may block the sliding and movement of the molecular segments, resulting in a lower fracture growth rate, which is consistent with results from a study by Shen et al. [30].

Table 3. Mechanical properties of the EHTPB-IPDI and HTPB-IPDI systems.

System	Tensile Strength (mPa)	Elongations at Break (%)	Tear Strength (N/mm)
HTPB-IPDI	1.25 ± 0.05	473 ± 23	2.78 ± 0.07
EHTPB-IPDI	1.40 ± 0.03	429 ± 18	3.27 ± 0.05



$$n\,OCN{-}R_1{-}NCO + HO{-}R_2{-}OH \longrightarrow \left[O{-}R_2{-}O\overset{O}{\overset{\|}{C}}{-}NH_2\, R_1{-}NH\overset{O}{\overset{\|}{C}} \right]_n$$

Figure 10. The reaction between –NCO and –OH.

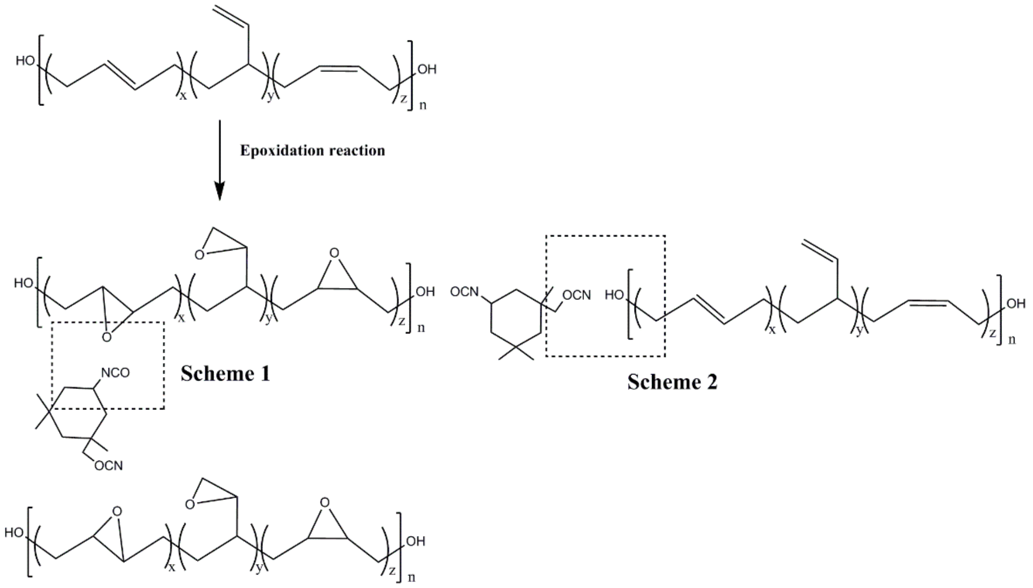


Figure 11. The curing reaction of EHTPB-IPDI binder system forms a network structure.

Compared with the HTPB-IPDI binder system, the EHTPB-IPDI binder system had lower E_a and better thermal stability and mechanical properties. Therefore, the EHTPB-IPDI binder system was selected for further research in this paper.

3.4. Calculation of the Average Activation Energy of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH Binder Systems

3.4.1. Kissinger Method

The peak temperature, T_p, of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH systems at different heating rates (Table 4) was plotted as ln (β/T_p^2) vs. $1/T_p$ according to the Kissinger method (as shown in Figure 12) and linearly fitted.

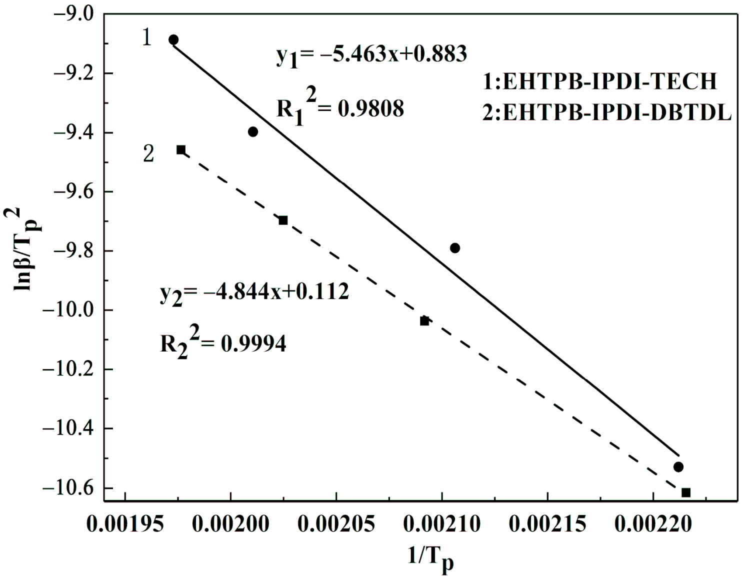


Figure 12. Fitting of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH systems by the Kissinger equation.

Table 4. DSC data of the TECH-catalyzed and DBTDL-catalyzed EHTPB-IPDI curing reaction.

β/°C·min^{-1}	T_{1i}/°C	T_{1p}/°C	T_{1f}/°C	T_{2i}/°C	T_{2p}/°C	T_{2f}/°C
5	159.5	199.5	216.9	164.2	178.2	199.0
10	169.1	220.9	241.7	174.7	204.9	233.8
15	180.9	242.0	265.8	181.1	220.7	251.8
20	182.7	250.8	279.0	187.1	232.8	264.4

β: heating rate; T_i: initial temperature; T_P: peak temperature; T_f: final temperature; T_1 and T_2: curing reaction temperatures of the TECH-catalyzed and DBTDL-catalyzed EHTPB-IPDI curing reaction.

As Figure 12 shows, the linear correlation coefficients, R_1^2 and R_2^2 , of the two fitting lines were 0.9808 and 0.9994, respectively, indicating a good correlation of the linear fitting curves. The activation energies of the two systems, E_1 and E_2, were 45.4 and 40.3 kJ/mol, respectively. The pre-exponential factors of two systems, A_1 and A_2, were 1.32×10^5 and 5.42×10^3 s^{-1}, respectively.

3.4.2. F-W-O Method

The peak temperature, T_p, of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH systems obtained at different heating rates (Table 4) was plotted as lnβ vs. $1/T_p$ (Figure 12) then linearly fitted.

As Figure 13 shows, the linear correlation coefficients of the two fitting lines, R_1^2 and R_2^2, were 0.9865 and 0.9995, respectively, indicating a good correlation of the two linear fitting curves. From the F-W-O equation, Equation (3), the activation energy of the systems can be calculated from the slope and intercept of the fitting line. The determined activation energies of the two systems, E_1 and E_2, were 51.0 and 45.8 kJ/mol, respectively.

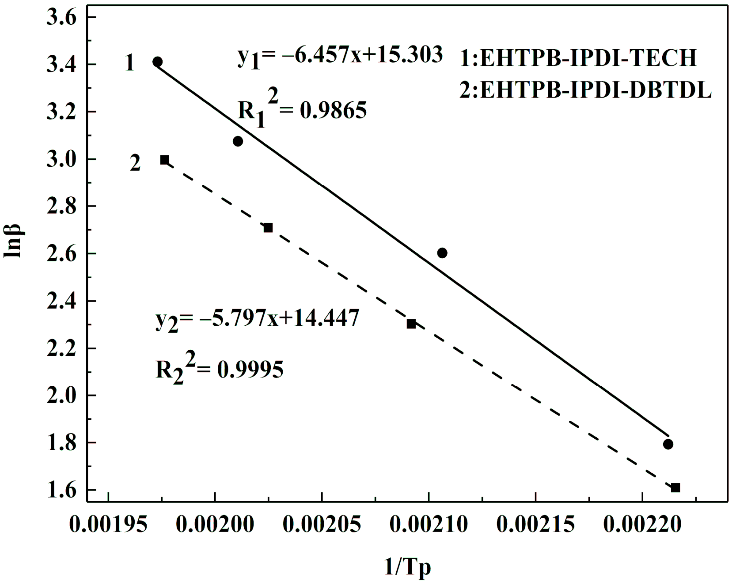


Figure 13. Linear fitting of lnβ vs. $1/T_p$ for the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH systems by the Flynn–Wall–Ozawa (F-W-O) equation.

The activation energy obtained by the FWO method was slightly higher than that calculated using the Kissinger method, the reason for the slightly higher activation energy is that there is a certain difference in the formula fitting between the FWO method and the Kissinger method, but this does not affect the accuracy of the result, which is consistent with results from other studies, e.g., the studies by Lee et al. [31] and Liu et al. [32]. The difference in the activation energy could originate from the limitations of the used equations. Still, it is not related to the characteristics of the studied systems. Therefore, the kinetics of the curing reaction of the EHTPB-IPDI-TECH and EHTPB-IPDI-DBTDL binder systems can be fitted with the nth-order reaction model.

3.4.3. Doyle Method

The DSC data listed in Table 3 were analyzed using the Doyle method. lnβ vs. $1/T_p$ was plotted (Figure 13) and linearly fitted. The linear correlation coefficients of the two fitted lines, R_1^2 and R_2^2, were 0.9808 and 0.9994, respectively, which indicates a good linear correlation. The activation energies E_1 and E_2 of the two systems, calculated from the fitted lines' slopes, were 44.9 and 40.8 kJ/mol, respectively.

3.4.4. Average Activation Energy

Table 5 shows the average activation energy calculated using the Kissinger, F-W-O and Doyle methods. The average activation energy values, ΔE_1 and ΔE_2, of the two systems were 47.1 and 42.3 kJ/mol, respectively. The results show that the average activation energy of the EHTPB-IPDI-DBTDL binder system was lower, and the initial reaction temperature was lower and the reaction activity was higher. It has reference value for the design of curing formula at room temperature.

Table 5. E_a and R^2 of the curing reaction calculated by Kissinger, F-W-O and Crane equation.

Binder System	**E_a (kJ/mol)**			**Correlation Coefficient R^2**		
-	**Kissinger**	**F-W-O**	**Doyle**	**Kissinger**	**F-W-O**	**Doyle**
HTPB-IPDI-TECH	45.4	51.0	44.9	0.9808	0.9865	0.9865
EHTPB-IPDI-DBTDL	40.3	45.8	40.8	0.9994	0.9995	0.9995

3.5. Monitoring of Viscosity

The viscosity, or precisely the viscosity growth rate of the EHTPB binder system, increases with the progress of the curing reaction. It grows rapidly around the gelation point of the system and approaches infinity when the system is completely cured. In this research, it is not completely cured, which is the early stage of curing reaction. The temperature of exothermic peak of curing reaction can be obtained from the DSC curve, full chemical curing can not be seen from finalization of the DSC peak. It can be seen from the FTIR spectrum, the disappearance of reaction groups and the formation of new groups.

Figure 14 shows the viscosity increase of the EHTPB-IPDI binder system in the presence of two catalysts, DBTDL and TECH, at the curing temperature of 25 °C. The pot life of the binder system for solid rocket propellants and PBXs is usually defined as the consumed time when the system viscosity increases to 20,000–25,000 mPa·s [33,34]. From the results of viscosity build-up measurement under the same curing temperature, it is possible to conclude that the pot-life of EHTPB-IPDI-TECH system was longer than that of EHTPB-IPDI-DBTDL system. The viscosity growth rate (first derivation of the viscosity curve in Figure 14) of the EHTPB-IPDI binder system was higher for DBTDL than for TECH, indicating a higher catalytic activity of DBTDL, which is consistent with the results obtained from DSC tests. EHTPB-IPDI-DBTDL binder system had higher reaction activity and faster viscosity growth. For the curing reaction of EHTPB-IPDI binder system, the catalytic effect of DBTDL was better than that of TECH, which is consistent with the experimental results of Ma et al. [15].

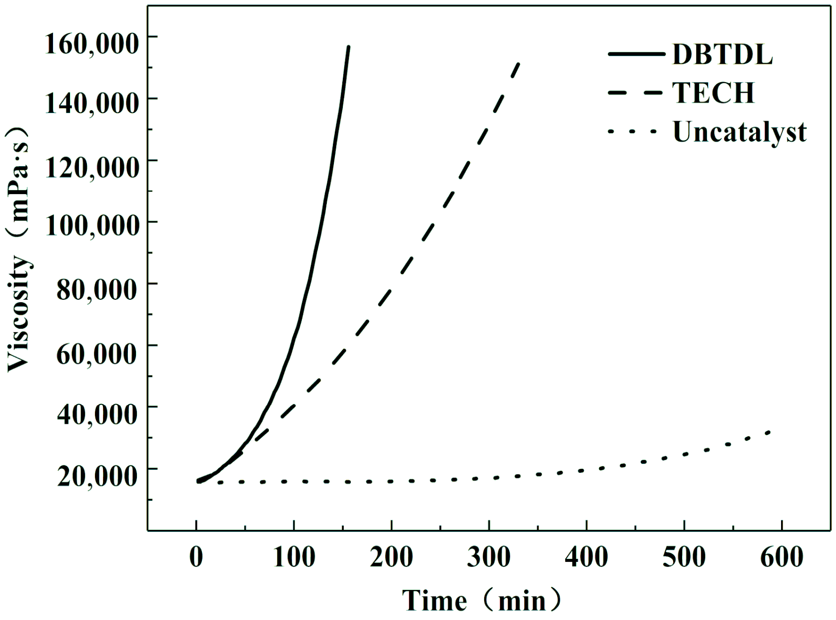


Figure 14. Change of viscosity of the EHTPB-IPDI binder system at the curing temperature of 25 °C.

3.6. Curing Reaction Kinetic Equations of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH Binder Systems

After determining the ΔE of the systems, the curing reaction's order can be obtained using the Crane equation (Equation (5)). lnβ vs. $1/T_p$ was plotted and linearly fitted. The equations of the two fitted lines obtained using the F-W-O method, $y1 = -6.457x + 15.303$ and $y2 = -5.797x + 14.447$, were substituted into Equation (5). The curing reaction orders of the two systems (n_1 and n_2) were calculated to be 0.95 and 0.95, respectively. Since the reaction orders for the two systems are both non-integers, the reaction rate of curing reaction is not only related to the concentration of reactants, but also depends on other factors, so it is a complex reaction. The equations of the curing reaction kinetics of the binder systems can be expressed as follows:

$$\text{EHTPB-IPDI-DBTDL}: \frac{\mathrm{d}\partial}{\mathrm{d}t} = 1.32 \times 10^5 \mathrm{e}^{-5.7 \times 10^3/T} (1 - \partial)^{0.95} \tag{6}$$

$$\text{EHTPB-IPDI-TECH}: \frac{\mathrm{d}\partial}{\mathrm{d}t} = 5.42 \times 10^3 \mathrm{e}^{-5.1 \times 10^3/T} (1 - \partial)^{0.95} \tag{7}$$

3.7. Parameters Optimization in the Curing Process

DSC curves show that when the system was cured by a dynamic heating method, the curing temperature varied with the heating rate. Besides, the peak temperature also changed, so the determination of the actual curing temperature was challenging. To obtain a reliable curing temperature, the characteristic curing temperature at a zero heating rate was obtained by the extrapolation method. Specifically, the initial (T_i), peak (T_p) and final (T_f) temperatures of the curing process at the-zero heating were obtained by extrapolating the heating rate to zero (Table 6). As shown in Figures 15 and 16, when the heating rate of the EHTPB-IPDI-TECH binder system was extrapolated to zero, T_i of the curing process was 153 °C, T_p of the exothermic peak was 185 °C and T_f of the curing process was 198 °C; when the heating rate of the EHTPB-IPDI-DBTDL binder system was extrapolated to zero, T_i of the curing process was 158 °C, T_p of the exothermic peak was 164 °C and T_f of the curing process was 184 °C.

Table 6. Initial, Peak and Final temperatures of EHTPB-IPDI-TECH and EHTPB-IPDI-DBTDL.

System	Initial Temperature (°C)	Peak Temperature (°C)	Final Temperature (°C)
EHTPB-IPDI-TECH	153	185	198
EHTPB-IPDI-DBTDL	158	164	184

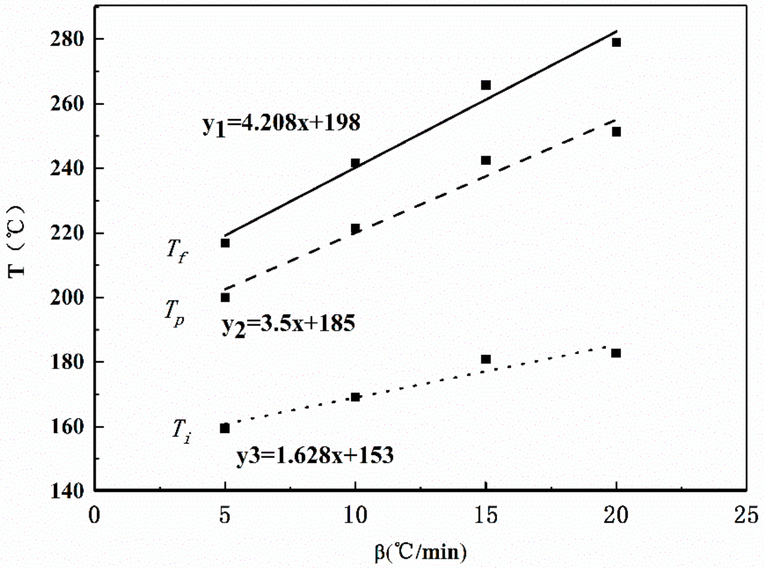


Figure 15. Extrapolation diagram of the curing reaction temperature at a zero heating rate for the EHTPB-IPDI-TECH system.

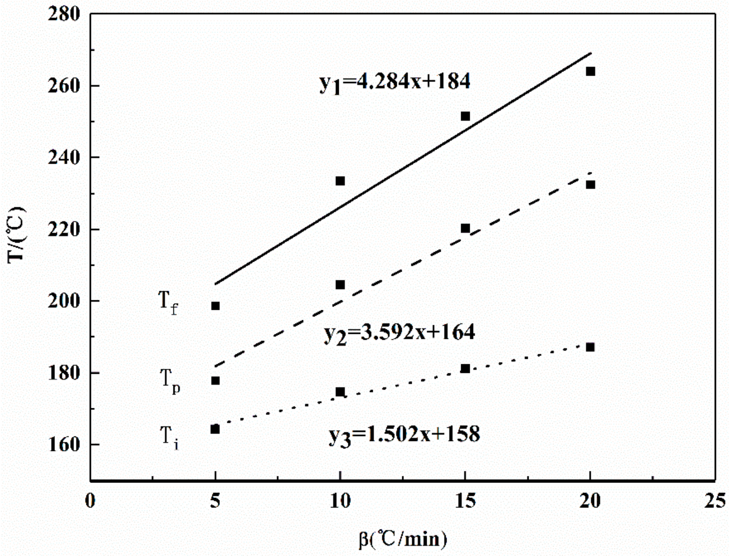


Figure 16. Extrapolation diagram of the curing reaction temperature at a zero heating rate for the EHTPB-IPDI-DBTDL system.

The curing time can be expressed by the curing degree (∂) relative to the curing speed. According to the calculation results, assuming ∂ was 99%, the curing times of the two systems were 4 and 19 h. The curing temperature and the curing time of EHTPB-IPDI-DBTDL were lower than those of EHTPB-IPDI-TECH. The cured thermosetting materials of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH binder systems were obtained under the curing conditions listed in Table 7.

Table 7. Analytical expressions for curing rate and curing time, and the values of the curing time of the EHTPB-IPDI-DBTDL and EHTPB-IPDI-TECH systems.

System	Curing Rate (d∂/d*t*)	Curing Time (*t*)	Curing Time (h)
EHTPB-IPDI-DBTDL	$0.31(1-\partial)^{0.95}$	$t = \frac{\partial}{\mathrm{d}\partial/\mathrm{dt}} = \frac{\partial}{0.31(1-\partial)^{0.95}}$	4
EHTPB-IPDI-TECH	$0.08(1-\partial)^{0.95}$	$t = \frac{\partial}{\mathrm{d}\partial/\mathrm{dt}} = \frac{\partial}{0.08(1-\partial)^{0.95}}$	19

4. Conclusions

In this paper, the curing kinetics of EHTPB-IPDI and HTPB-IPDI binders were studied by the DSC method, and the related mechanical properties were measured. The initial temperature, T_i, and activation energy, E_a, of the EHTPB-IPDI curing reaction were lower than those of the HTPB-IPDI system. Compared with the HTPB-IPDI binder system, the T_g of the EHTPB-IPDI binder system was increased by 5 °C, indicating better thermal stability of the EHTPB-IPDI binder system. The tensile strength and breaking strength of the EHTPB-IPDI system were increased by 12% and 17%. In comparison, its elongation at break was decreased by 10%, indicating better mechanical properties of the EHTPB-IPDI binder system. When DBTDL and TECH were used as catalysts in the EHTPB-IPDI system, the Ea of the EHTPB-IPDI-DBTDL binder system was lower than that of the EHTPB-IPDI-TECH binder system. This indicates that the EHTPB-IPDI-DBTDL system had a higher reactivity, and its curing process occurred at lower temperatures. In summary, the EHTPB-IPDI binder system had a lower reaction initiation temperature, higher reactivity and was more prone to curing reaction at room temperature. This is of reference value for the design of the room temperature curing formula of polyurethane materials. Due to the introduction of epoxy groups, the cured film of EHTPB-IPDI had good mechanical properties and thermal stability. It can be used for composite solid propellant and solid rocket motor insulation and lining materials, and has a wide range of application prospects.

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