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Kinetic studies on the cure reaction of hydroxyl-terminated polybutadiene based polyurethane with variable catalysts by differential scanning calorimetry

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Abstract: This paper employs differential scanning calorimetry (DSC) to investigate the reactions of hydroxyl-terminated polybutadiene (HTPB) binder and isophorone isophorone diisocyanate (IPDI) with two different cure catalysts, namely, dibutyl tin dilaurate (DBTDL) and stannous octanoate (TECH). This study evaluates the effects of two cure catalysts (i.e. DBTDL and TECH) on rate constants of the polyurethane cure reactions. Throughout the study, the kinetic parameters and the curing reaction rate equations are obtained. The present work concludes that both catalysts had a catalytic effect on the HTPB-IPDI system, but that the catalytic effect of DBTDL was higher than that of TECH. The binder system with the TECH catalyst displayed a longer pot-life and lower toxicity compared with the DBTDL. Additionally, this study investigates the binder system’s viscosity build-up at 35°C and the viscosity build-up results were in agreement with the DSC analysis results.

Keywords: catalyst; cure kinetics; DSC; HTPB; viscosity.

1 Introduction

Hydroxyl-terminated polybutadiene (HTPB) liquid pre-polymer is widely used as a binder in preparing castable polymer bonded explosives (PBXs) and solid composite propellants (1–3). The polyurethane elastomer provides polymer-bonded explosives with better dimensional stability and structural integrity (3–5).

In previous reports (6–13), studies on the curing kinetics of HTPB-isophorone diisocyanate (IPDI) binder system were focused mainly on the effects of dibutyl tin dilaurate (DBTDL), ferric tris-acetylacetonate (FeAA), triphenyl bismuth (TPB), etc. DBTDL has powerful catalytic effects on the reaction between isocyanate and alcohol, and is known as a gel catalyst. However, DBTDL is harmful for human beings and ecosystems (14–18). The pot-life of the binder system is relatively short when FeAA is used as a catalyst. Moreover, solid settling may occur as the curing process is relatively slow when TPB is used as a catalyst. To the best of our knowledge, no investigations thus far have explored the catalytic effect of TECH in the HTPB-IPDI binder system. Compared with DBTDL, TECH is more environmentally friendly, less toxic, and exhibits a longer pot-life when used in a binder system.

Out of a variety of methods for studying curing kinetics (6, 9, 10, 19–21), thermal analysis is one of the most important. Thermo gravimetric (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have been widely used to calculate kinetic parameters in thermal analysis (22). Of these methods, the DSC method has the broadest applicability. The curing reaction of the HTPB-based binder system is a continuous exothermic process. Therefore, the non-isothermal DSC method can be used to study the curing kinetics of the HTPB-based system. And viscometer was utilized to measure the viscosity changes and verify the DSC results.

In this study, the DSC and viscosity build-up methods are utilized to investigate the curing kinetics of HTPB-IPDI binder systems when DBTDL and TECH are used as
catalysts. Kinetic parameters, which are crucial for deducing the curing kinetics equation of the binder system, were obtained. Once the curing kinetics equation is solved, it is possible to establish a relationship between curing degree and curing time, which plays a key role in binder system formula design.

2 Experiment

2.1 Materials

HTPB (number-average molecular weight = 2700 g/mol, hydroxyl value = 45.2 mg KOH/g) was obtained from the Liming Research Institute of the Chemical Industry (China). The curing agent IPDI was supplied by BASF Corp (Germany). The catalyst stannous isooctoate (TECH) was purchased from the Shanghai Institute of Organic Chemistry (China). DBTDL was provided by the Tianjin Guang Fu Institute of Fine Chemicals (China). Prior to the test, the HTPB was dehydrated in a vacuum for 2 h at 100°C and 0.05 Mpa, and then put in a dry, sealed bottle.

The SNB-1A digital viscometer was obtained from the Shanghai Fang Rui Instrument Co (China). The DHG303-2 oven thermostat was obtained from the Shanghai Yi Heng Scientific Instrument Co (China). The HCT-1 integrated thermal analyzer was obtained from the Beijing Permanent Scientific Instrument Factory (China).

2.2 Experimental method

The binder system was prepared by mixing HTPB prepolymer and IPDI curing agent with two different cure catalysts viz. DBTDL and stannous octoate (TECH). The mix ratio was 100/9.25/0.109 parts by weight (pbw). About 10 mg of the sample mixture was placed into aluminum crucibles. The DSC operated in a temperature range between room temperature and 350°C under a nitrogen atmosphere with a ventilation of 50 ml/min. Four different heating rates (2.5, 5, 10 and 15°C/min) were employed in the DSC analysis.

2.3 DSC cure kinetics

The non-isothermal DSC kinetics analysis methods have two main components (22): an exothermic curve analysis must be used exclusively; exothermic peak temperature along with heating rate change must be used to analyze the kinetic parameters. This paper adopted the second method for its analysis. Four different peak temperatures were utilized to calculate the kinetic parameters activation energy $E$, pre-exponential factor $A$, and relation order $n$ through the Kissinger (23), Ozawa (24), and Crane methods (25).

Kissinger method:

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

where $\beta$ is the heating rate; $E$ is activation energy; $A$ is the pre-exponential factor; $R$ is the gas constant $8.314 \text{ J·mol}^{-1} \cdot \text{K}^{-1}$; and $T$ is the absolute temperature.

A plot of $\ln \left( \frac{\beta}{T^2} \right)$ vs. $T^{-1}$ from several DSC curves gave a straight line with a slope equal to $-\frac{E}{R}$, where $R$ is the gas constant $8.314 \text{ J·mol}^{-1} \cdot \text{K}^{-1}$ and has an intercept equal to $\ln \frac{AR}{E}$.

Ozawa method:

$$
\log \beta = \log \left( \frac{AE}{RG(a)} \right) - 2.315 - 0.4567 \frac{E}{RT}
$$

where $\beta$ is the heating rate; $E$ is activation energy; $A$ is the pre-exponential factor; $R$ is the gas constant $8.314 \text{ J·mol}^{-1} \cdot \text{K}^{-1}$; $G(a)$ is the mechanism function and $T$ is the absolute temperature.

A plot of $\log \beta$ vs. $T^{-1}$ from several DSC curves gave a straight line with a slope equal to $-0.4567 \frac{E}{R}$.

Crane method:

$$
\frac{d(\log \beta)}{d(T^{-1})} = -\frac{E}{nR} + 2T
$$

If $\frac{E}{nR} \gg 2T$, so

$$
\frac{d(\log \beta)}{d(T^{-1})} = -\frac{E}{nR}
$$

where $\beta$ is the heating rate; $E$ is the activation energy; $A$ is the pre-exponential factor; $R$ is the gas constant $8.314 \text{ J·mol}^{-1} \cdot \text{K}^{-1}$; $n$ is the reaction order and $T$ is the absolute temperature.

A plot of $\log \beta$ vs. $T^{-1}$ from several DSC curves gave a straight line with slope equal to $-\frac{E}{nR}$ when $\frac{E}{nR} \gg 2T$. 
The Kissinger method assumes that the mechanism function agrees with the n-order reaction model, whereas the Ozawa method does not need to assume the mechanism function. If the calculated activation energies from both methods are very close, it demonstrates that they agree with the n-order reaction mechanism function model.

There are two basic types of thermosetting resins mechanism functions (22):

**n-level reaction model:**

Differential expression

\[ f(a) = (1-a)^n \]  

Integral expression

\[ g(a) = \begin{cases} -\ln(1-a) & n = 1 \\ \frac{1-(1-a)^{1-n}}{1-n} & n \neq 1 \end{cases} \]

**Autocatalytic reaction model:**

Differential expression

\[ f(a) = a^n(1-a)^n \]  

From the previous report (26), the curing reaction mechanism function of a hydroxyl terminated polybutadiene (HTPB) and the isocyanate complies with the n-level reaction model.

Curing reaction kinetic equation:

Differential expression

\[ \frac{da}{dt} = k(1-a)^n \]  

Integral expression

\[ \frac{-\ln(1-a)^n}{1-(1-a)^{1-n}} = kt \]  

where \( f(a) \) is the differential expression function mechanism; \( g(a) \) is the of the integral expression function mechanism; \( t \) is the reaction time and \( k \) is the reaction rate constants that obey the Arrhenius equation.

\[ k = A \exp \left( \frac{-E}{RT} \right) \]

where \( A \) is the pre-exponential factor; \( E \) is the activation energy; \( R \) is the universal gas constant 8.314 J·mol⁻¹·K⁻¹ and \( T \) is the absolute temperature.

### 2.4 Viscosity build-up

In the curing process of HTPB-isocyanate binder system, viscosity increased as the reaction progressed. As curing degree increased, the binder system viscosity growth rate also increased. Moreover, viscosity increased rapidly near the gel point, and approached infinity when fully cured.

Because of these characteristics, an SNB-1A digital viscometer is employed to measure the viscosity build-up during the curing process of the HTPB-IPDI binder system in the absence of any catalyst, and in the presence of DBTDL and TECH as catalysts. Then, the results were compared with the DSC results.

### 3 Results and discussion

Table 1 shows the HTPB-IPDI system with DBTDL or TECH as a catalyst under cure reaction temperatures at different heating rates. The DSC reactions showed smooth exothermic curves. From Table 1, it can be seen that as the heating rate increased, the exothermic peak temperature shifted to a higher temperature, the exothermic peak steepened, the curing time shortened, and the heat release of the system increased. The reason for this phenomenon is that as temperature increases, heat release increases per unit time, total released heat is reduced, the exothermic peak becomes steeper, and the curing time is shortened. Additionally, the peak temperature shifts to a higher temperature (27).

As for the HTPB-IPDI-DBTDL system, the Kissinger and Ozawa plots were utilized to compute the activation energies from DSC data, as Figure 1 shows. The value of activation energy \( E \) was 55.02 kJ·mol⁻¹ from the Kissinger method and 59.33 kJ·mol⁻¹ from the Ozawa method, and the value of the pre-exponential factor \( A \) was about 5.99 × 10⁵ s⁻¹. The correlation coefficients of the Kissinger and Ozawa plots were about 0.9939 and 0.9926, respectively. The reaction rate constant at 35°C equaled 2.79 × 10⁻⁴ s⁻¹. The two activation energies were comparatively close, so it can be concluded that the function mechanism was accurate, and that the reaction conformed to the n-level reaction model.
The Crane plot was obtained from the liner fit of ln(β) vs. 1/T, as Figure 2 shows. The correlation coefficient was approximately 0.9940. From Figure 2 and the Crane method, the kinetic order of reaction was found to be about 0.95.

The curing kinetic equation of the HTPB-IPDI-DBTDL system can be written as:

\[
1 - \left(1 - a_1 \right)^{0.05} = \int_0^{t_1} 5.99 \times 10^5 \times \exp \left( \frac{-55.02}{8.314 \times T_1} \right) d_t 
\]  

where \( a_1 \) is the cure degree; \( T_1 \) is the absolute temperature; \( t_1 \) is the curing time and \( k_1 \) is the reaction rate constant at temperature \( T_1 \).

As for the HTPB-IPDI-TECH system, Kissinger and Ozawa plots were also used to calculate the activation energy and pre-exponential factor \( A \), as Figure 3 shows. The activation energy value was approximately 57.19 kJ·mol\(^{-1}\) (Kissinger method) and 61.57 kJ·mol\(^{-1}\) (Ozawa method), and the value of pre-exponential factor \( A \) was \( 7.55 \times 10^5 \) s\(^{-1}\). The correlation coefficients of the Kissinger and Ozawa plots were about 0.9982 and 0.9979, respectively. The reaction rate constant at 35°C equaled \( 1.51 \times 10^{-4} \) s\(^{-1}\). The two activation energies were comparative close, so it is possible to conclude that the function mechanism was accurate, and this reaction conformed to the n-level reaction model.

Similarly, the reaction order of the HTPB-IPDI-TECH system was about 0.95, as Figure 4 shows. The results confirm that the reaction mechanism function of the HTPB-IPDI binder system obeyed an n-level reaction model. The reaction order was 0.95. The addition of a catalyst did not change the reaction mechanism function (28, 29).

Therefore, the curing kinetics equation of the HTPB-IPDI-TECH system can be written as:

\[
1 - \left(1 - a_2 \right)^{0.05} = \int_0^{t_2} 7.55 \times 10^5 \times \exp \left( \frac{-57.19}{8.314 \times T_2} \right) d_t \]  

\[
1 - \left(1 - a_2 \right)^{0.05} = k_2 t_2 \]
where $a_{2}$ is the cure degree, $T_{2}$ is the absolute temperature, $t_{2}$ is the curing time, and $k_{2}$ is the reaction rate constant at temperature $T_{2}$.

Generally, activation energy $E$ represents the required minimum reacted energy. As the activation energy declined, the reaction rate increased. However, this observation is not constant. In some conditions, as the activation energy declined, the reaction rate declined. This variation occurs due to a kinetic compensation effect that exists between activation energy $E$ and pre-exponential factor $A$ (7). Therefore, it is not feasible to make a comparison using the kinetic compensation amended $E$ values to determine the reaction rate size (6). Measuring the value of curing reaction rate constant is a reasonable way to compare the catalytic effect of different catalysts for an HTPB-IPDI system.

As can be seen in Table 2, the reaction rate for $K_{\text{DBTDL}} = 2.79 \times 10^{-4} \text{ s}^{-1}$ (when the catalyst is DBTDL) and for $K_{\text{TECH}} = 1.51 \times 10^{-4} \text{ s}^{-1}$ (when the catalyst is TECH). Therefore, the catalytic effect of DBTDL was higher than that of TECH in the curing reaction of the HTPB-IPDI system.

Figure 5 shows the viscosity build-up of the HTPB-IPDI binder system with DBTDL and TECH as catalysts at a curing temperature of 35°C. It can be found that the curing system’s viscosity build-up grew faster when DBTDL, rather than TECH, was added. For the HTPB-IPDI system, the catalytic activity of DBTDL was greater than that of TECH. The result is consistent with the DSC test results. In prior literature (11), the pot-life of the binder system is defined as the time it takes for the curing system to reach a viscosity level of 20,000 mPa-s. Using this definition, and under a curing temperature of 35°C, the pot-life of the HTPB-IPDI-DBTDL system is approximately 16 min, while the pot-life of HTPB-IPDI-TECH is approximately 114 min. When compared with DBTDL, it is evident that the pot-life of the HTPB-IPDI binder system is longer when TECH is added as a catalyst. Moreover, these results confirm the DSC analysis results.

### Table 2: Kinetic parameters of catalyzed cure reactions of HTPB-IPDI system.

<table>
<thead>
<tr>
<th>System</th>
<th>Catalyst</th>
<th>E/kJmol⁻¹</th>
<th>A/s⁻¹</th>
<th>K(at 35°C)/S⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTPB-IPDI</td>
<td>DBTDL</td>
<td>55.02</td>
<td>5.99×10⁵</td>
<td>2.79×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>TECH</td>
<td>57.19</td>
<td>7.55×10⁵</td>
<td>1.51×10⁻⁴</td>
</tr>
</tbody>
</table>

4 Conclusions

In this study, DSC and viscosity build-up methods are utilized to study the cure reactions of HTPB-IPDI-based polyurethane binder systems with different catalysts. The results of DSC analysis illustrate that the curing reactions of HTPB and IPDI, in the presence of catalysts DBTDL and TECH, follow n-level reaction kinetics. The addition of each catalyst did not alter the reaction mechanism function. Once the curing kinetics equations are solved, a functional relationship between curing degree and curing time is established. The results from DSC and viscosity methods confirm that the catalytic activity of DBTDL was greater than that of TECH in the cure reaction of the HTPB-IPDI binder system. From the results of viscosity build-up measurement under the same curing temperature, it is possible...
to conclude that the pot-life of HTPB-IPDI-TECH system was much longer than that of HTPB-IPDI-DBTDL system.

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References