Study on catalysis effect of TEPB on the curing reaction of HTPB binder system

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Abstract: The catalysis effect of tri (exoxyphenyl) bismuthine (TEPB) on the curing reaction of HTPB binder system was studied by using DSC method. The curing peak temperatures of the catalyst systems were measured to calculate kinetic parameters by using Kissinger and Crane methods, respectively. Two curing reaction kinetic equations were established. The results show that TEPB has high catalytic activity and can decrease the curing temperature of HTPB binder system, down to 35°C, in which the optimum volume of TEPB is 0.5% of HTPB binder system.

1. Introduction
Hydroxyl-terminated polybutadiene (HTPB) is a kind of telechelic polymer. It has low viscosity, oil resistant, aging resistant, good low temperature performance, and machining performance. Many kinds of polyurethane materials have been made by the cross-linking reaction of HTPB with toluene diisocyanate (TDI). Due to the convenience for casting and manufacturing, it has been applied to cast PBX binder [1-2].

The binder of HTPB imparts dimensional stability and structural integrity to the grain for appropriate mechanical properties. However, the reaction rate of hydroxyl functional groups of HTPB with isocyanates is usually low, leading to a high curing temperature and long manufacturing period [3]. When the casting PBX is cured, its internal residual stress could reduce the mechanical property of PBX after it is cooled to ambient temperature. High manufacturing temperature increase the danger of cast PBX productive process and increases the production cost, too.

Therefore, more and more attention has been paid to reduce the curing temperature of HTPB. The catalyst is the best choice to decrease curing temperature and shorten curing time[4]. Dibutyltin dilaurate (DBTDL), ferric tris (acetyl acetonate) (Fe(AA)₃) and triphenyl bismuth (TPB) are usually used as catalysts. The catalytic activity and mechanism have been investigated by using various techniques. However, the high curing temperature still was not solved after by using these catalysts [5-7]. In order to decrease the curing temperature and increase the mechanical properties, in this work, the catalysis effect of TEPB on HTPB binder system curing reaction was investigated.

2. Experimental
2.1. Formulation composition
HTPB binder system is made up of HTPB and DOA by the proportion of 1:1, with a certain amount of curing agent TDI. TEPB is put in additionally. HTPB is made by Shandong zibo qilu ethylene
chemical co., LTD, with a hydroxyl value of 0.77-0.82 mmol/mg. DOA is made by Liaoning yingkou tianyuan chemical co., LTD. TEPB was supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, with a purity of 99.54%.

2.2. Method
By adding different amount of TEPB to HTPB binder system, the catalysis action may be assessed through testing its curing hardness. Catalyst influence of TEPB content on HTPB binder system was investigated at 0.3%, 0.5%, 0.7%. The curing reaction of HTPB binder system was studied at various heating rates, viz., 5, 10, 15 and 20 °C·min⁻¹. Heating rates were varied for determining the kinetics by Kissinger and Crane methods, respectively. A certain amount of catalyst was put in the HTPB binder system. The mixture of about 20 mg was taken in alumina pans and subjected to DSC analysis in a Setaram DSC131 in nitrogen atmosphere at a flow rate of 50 mL·min⁻¹. The heating temperature was in the range of 20 ~ 300 °C.

3. Results and discussion
3.1. The catalysis Effect of TEPB conten on HTPB binder system
HTPB binder system is one of the carbamates by the reaction of the hydroxyl group with isocyanate. Catalyst can reduce the reaction activation energy of HTPB binder system and accelerate reaction rate, leading to a shortened curing time. Catalyst and isocyanate may generate intermediate complex, which can react with hydroxyl compounds to generate polyurethane. The mechanism of reaction [8] is as follows:

\[
\text{NCO—R—NCO + Bi} \xrightarrow{\text{catalyst}} \text{NCO—R—N≡C—Bi}^+ \xrightarrow{\text{O}^-} \text{NCO—R—N≡C—Bi}^+ \xrightarrow{\text{H}⁻} \text{NCO—R—N—C—O—R'—OH} \xrightarrow{\text{Bi}} \text{NCO—R—N—C—OR'OH + Bi}
\]

The curing property of HTPB binder system could be improved by the reaction of carbamate catalyst. Figure 1 shows the effect of curing hardness about different content TEPB on HTPB binder system. From Figure 1, when TEPB contents are 0.3%, 0.5%, and 0.7%, the curing hardness is higher than that without catalyst. The addition of catalyst accelerated reaction rate of HTPB binder system. As TEPB addition 0.5%, the hardness may reach to 35 HA after 72 h.

![Figure 1. Hardness curve with the time change.](image-url)
3.2. TEPB Catalyst to HTPB binder system

The curing reaction rates of HTPB binder system with TEPB and without catalyst were measured by the DSC method. Test results were shown in Figure 2. TEPB catalyst decreases the reaction temperature and makes exothermic peak of DSC curve translate forward. Two apparent exothermic peaks were found in the HTPB-TDI curing system with the catalyst TEPB.

According to the research on catalytic mechanism, TEPB could be combined with hydroxyl. The possible mechanism is through the activation on the isocyanate-hydroxyl complex, which speeds up the reaction proceeds. The first exothermic peak is due to that the combination of TEPB with hydroxyl hydrogen increases the nucleophilicity ability of the adjacent oxygen in the hydroxyl group. Therefore, the catalyzed reactions of hydroxyl with isocyanate may be suggested to involve the initial formation of a TEPB-hydroxyl intermediate, which reacts with isocyanate as a subsequent reaction. Thus, the urethane is formed. The catalyst is regenerated, leading to the formation of the second exothermic peak.

Table 1 and Table 2 give the initial curing temperature($T_i$), the peak curing temperature ($T_p$) and the end curing temperature($T_f$) from the DSC curves of the uncatalyzed and TEPB catalyzed HTPB-TDI curing system.

![Figure 2. DSC curves of different curing system at 15°C·min⁻¹.](image)

**Table 1.** DSC data of HTPB-TDI curing reaction.

| $\beta/°C·min^{-1}$ | $T_i/°C$ | $T_p/°C$ | $T_f/°C$ |
|---------------------|---------|---------|---------|
| 5                   | 153.6   | 195.6   | 209.8   |
| 10                  | 187.6   | 212.9   | 238.1   |
| 15                  | 200.9   | 232.8   | 245.2   |
| 20                  | 212.5   | 239.9   | 261.2   |

Note: $\beta$: heating rate; $T_i$: the initial curing temperature; $T_p$: the peak curing temperature; $T_f$: the end curing temperature.

There’re apparent early and later stages in the DSC curve of TEPB catalyzed HTPB-TDI curing system. The peak temperature of the early stage was reduced 90°C compared to uncatalyzed curing system. And the curing reaction peak temperature gradient ($T_f-T_i$) was decreased from 50°C to 30°C. Above data shows that TEPB can decrease the curing reaction temperature and shorten reaction time.
The high peak temperature of later stage indicates that TEPB-isocyanate-hydroxyl associate or complex is quite stable. Although there’re significant differences in catalytic mechanism of different catalysts, the reaction rate gets faster and catalytic activity gets higher when transient state is more stable. It shows the high catalytic activity of TEPB from the reaction mechanism.

Table 2. DSC characteristic temperature of early and later stage of TEPB catalysed HTPB-TDI reaction.

| \( \beta/\text{°C} \cdot \text{min}^{-1} \) | early stage reaction | later stage reaction |
|---|---|---|
|   | \( T_{i}/\text{°C} \) | \( T_{p}/\text{°C} \) | \( T_{f}/\text{°C} \) | \( T_{i}/\text{°C} \) | \( T_{p}/\text{°C} \) | \( T_{f}/\text{°C} \) |
| 5  | 91.1 | 109.5 | 121.3 | 234.2 | 243.2 | 259.8 |
| 10 | 109.1 | 138.9 | 204.7 | 254.1 | 265.3 |
| 15 | 121.9 | 153.6 | 243.6 | 265.8 | 270.9 |
| 20 | 131.2 | 162.4 | 247.2 | 274.6 | 288.2 |

3.3. Kinetics of TEPB catalyzed HTPB binder system curing

Kinetic parameters of curing reaction are calculated by Kissinger and Crane method.

Kissinger formula:

\[
\frac{d\ln\left(\frac{\beta}{T_p^2}\right)}{dT_p^{-1}} = -\frac{E_a}{R}
\]

Crane formula:

\[
\frac{E_a}{nR} > > 2T_p, \quad \frac{d\ln\beta}{dT_p^{-1}} = -\frac{E_a}{nR}
\]

Where \( \beta \) is the heating rate, and \( E_a \) is the activation energy of curing reaction, and \( R \) is the universal gas constant, and \( T \) is the absolute temperature, and \( n \) is the order of reaction. HTPB-TDI curing system abide n order reaction model according to the research on the curing reaction mechanism of HTPB [9,10], it’s reaction kinetic model equation is:

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

Where \( \alpha \) is the degree of reaction, and \( t \) is the reaction time, and \( da/dt \) is the reaction rate, and \( k \) is the reaction rate constant which following the Arrhenius formula \( k = A\exp(-Ea/RT) \). For all the values of \( n \) except \( n=1 \).

Figure 3 Linear fitting of -\( \ln\beta \) and \( \ln(\beta/T_p^2) \) with \( 1000/T_p \) for uncatalysted curing system
Figure 3 and 4 show the fit linear plots of ln(β/T_p^2) and -lnβ vs.1000/T_p for uncatalyzed curing system and the early stage of TEPB catalyzed system, respectively. \( E_a \), pre-exponential factor (\( A \)) and \( n \) can be calculated by Kissinger and Crane methods.

The kinetic parameters of uncatalyzed HTPB-TDI curing system are \( E_a=51.29 \text{ kJ} \cdot \text{mol}^{-1} \), \( A=7.7\times10^4 \text{ s}^{-1} \), \( n=0.86 \); those in the early stage of TEPB catalyzed reaction are \( E_a=40.14 \text{ kJ} \cdot \text{mol}^{-1} \), \( A=5.2\times10^3 \text{ s}^{-1} \), \( n=0.85 \); those in the later stage are \( E_a=93.12 \text{ kJ} \cdot \text{mol}^{-1} \), \( A=6.0\times10^8 \text{ s}^{-1} \), \( n=0.91 \). Above parameters are substituted into the reaction kinetic model equation(3).

The kinetic equation of HTPB-TDI curing system is:

\[
\frac{d\alpha}{dt} = 7.7\times10^4 \exp \left(-\frac{6169}{T}\right) (1 - \alpha)^{0.86}
\]

The early stage kinetic equation of HTPB-TDI-TEPB curing system is:

\[
\frac{d\alpha}{dt} = 5.2\times10^4 \exp \left(-\frac{4828}{T}\right) (1 - \alpha)^{0.85}
\]

The later stage kinetic equation of HTPB-TDI-TEPB curing system is:

\[
\frac{d\alpha}{dt} = 6.0\times10^8 \exp \left(-\frac{11199}{T}\right) (1 - \alpha)^{0.91}
\]

TEPB decreases the activation energy of curing reaction, which is the reason that TEPB can lower the reaction temperature. The reaction orders of two curing systems is similar and approximate 1, which shows that catalyst do not change the elementary reaction of HTPB-TDI and curing reaction abide \( n \) order reaction model correspondingly.

### Table 3. Rate constants under different temperature.

| Catalyst System | \( 30^\circ\text{C} \) | \( 60^\circ\text{C} \) | \( 100^\circ\text{C} \) | \( 105^\circ\text{C} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Null            | 1.11E-04        | 6.93E-04        | 5.06E-03        | 6.29E-03        |
| TEPB_early      | 6.25E-03        | 2.63E-02        | 1.24E-01        | 1.48E-01        |
| TEPB_later      | 5.33E-08        | 1.48E-06        | 5.48E-05        | 8.15E-05        |

Note: Null: uncatalyzed HTPB-TDI curing system.

The kinetic equations show that there is a linear relationship between reaction rate constants and reaction temperatures. Reaction rate constants decide the reaction rate under the certain temperature. Some reaction rates of uncatalyzed and TEPB catalyzed curing reactions under certain temperature are shown in Table 3. The curing temperature of HTPB is 60\(^\circ\text{C}\) in actual production, and the reaction rate constant under this temperature is barely 6.93\(\times\)10\(^4\) \text{ s}^{-1}. It causes the long curing period and low production efficiency of HTPB. And the reaction rate constant of TEPB catalyzed curing system under...
35°C is $6.25 \times 10^{-3}$ s$^{-1}$, which is equal to that of uncatalyzed system under 105°C. The curing temperature of polyurethane is usually below 100°C. High temperature promotes isocyanate groups reacting with carbamic acid ester or urea linkages or generating cross bond, which decreases the properties of PU. High manufacture temperature reduces the safety of HTPB binder system curing process. This is just the reason that catalysts are added to decrease the manufacture temperature. TEPB can make the curing reaction rate reach the value at ambient temperature. Above data proves that the TEPB is available for ambient catalyst based on the reaction kinetic.

4. Conclusions

- The catalytic activity of TEPB increases with the concentration, and reaches the maximum when concentration is 0.5%. The appropriate concentration of TEPB is 0.5%.
- TEPB may decrease the curing reaction temperature and shorten reaction time by its high catalytic activity. The peak temperature using TEPB was reduced 90°C compared to uncatalyzed curing system.
- HTPB-TDI-TEPB system curing reaction kinetic equation is obtained. The reaction rate constant at 35°C reaches the value of uncatalyzed system at 105°C. TEPB can catalyze HTPB-TDI curing reaction at ambient temperature.

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