Rheokinetic analysis on the curing process of HTPB-DOA-MDI binder system

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Abstract. Polymer bonded explosives (PBXs) are a kind of rubbery explosives, in which the explosive components are bound together by a polymeric binder. The hydroxyl terminated polybutadiene (HTPB)-based polyurethane binder systems possess a unique combination of properties, including superior adhesion, excellent mechanical properties and have been widely used in rocket propellants, PBXs and other weapons. The cure reaction between HTPB and diisocyanates in the castable PBXs plays an important role in the adjustment of process parameters as well as properties of explosive formulations. In this paper, viscosity measurements were carried out at different temperatures (15°C, 25°C, 35°C, 45°C, 55°C) to a series of systemic studies on the viscosity build-up and rheological reaction rate constant during the curing process of the of HTPB- dioctyl adipate (DOA)-diphenyl methane diisocyanate (MDI) binder system, discovered and explained the phenomenon that the pot-life of the binder system was prolonged when the curing temperature raised and the curing reaction rate was accelerated. And the rheology kinetic model of the HTPB-DOA-MDI binder system was established.

1. Introduction
Polymer bonded explosives (PBXs) are kinds of particulate composites, which usually consist of explosive crystals cured together by a macromolecular binder. For the PBXs decreased the risk of accidental detonations during storage, utilizing and transportation, PBXs have been drawn high degree of attention by the governments and scientists around the world in the fields of insensitive munitions (IM) [1-3]. The hydroxyl terminated polybutadiene (HTPB)-isocyanates binder systems possess a unique combination of properties, including high solid loading, long pot life, good flow-ability, superior adhesion, which impart dimensional stability, structural integrity and excellent mechanical properties to the grain, and have been widely used in PBXs, ballistic missiles, launch vehicle, composite solid propellant, nuclear warhead detonating device and underwater weapons [4-6]. There is no doubt that, the formulation of polymeric binder and the properties of the cured polymer matrix have significant impact on the properties of the PBXs product.

Currently, castable PBXs based on HTPB typically require curing under high temperature conditions (60°C~80°C), and the curing time usually takes 5 to 7 days [1]. Because the cross-linking reactions between HTPB and isocyanates curing agents are exothermic reactions, therefore, it is easily lead uneven distribution of the cross-linking density under high temperature curing. Moreover, during the cooling of the casted grain from high temperature to ambient temperature, it usually generates a
thermal stress (i.e. shrinkage stress), which leads to a substantial decline in the performance of the explosive product. The reaction mechanism and rheokinetic of the cure process determine the morphology of the polyurethane network, which in turn affects the physical, mechanical and explosive properties of the cured product [7-14]. Therefore, an understanding of the rheokinetics of polyurethane network formation is of vital importance to improve the safety of the curing process, improve the mechanical properties of the grain and the explosion performance of the cured product.

In this paper, viscosity measurements were carried out to a series of systemic studies on the viscosity build-up and rheological reaction rate constant during the curing process of HTPB- dioctyl adipate (DOA)-diphenyl methane diisocyanate (MDI) binder system. And the rheology kinetic model (i.e. Arrhenius model and Eyring model) of the HTPB-DOA-MDI binder system was established.

2. Experimental

2.1. Materials
Hydroxyl terminated polybutadiene (HTPB) was supplied by Liming Research Institute of Chemical Industry (China). The curing agent, diphenyl methane diisocyanate (MDI) was purchased from Bayer (Germany). Plasticizer, dioctyl adipate (DOA) was obtained from Sinopharm Chemical Reagent (China).

HTPB was dried under vacuum (1-2 mm Hg) at 100°C for two hour, and then put under a nitrogen atmosphere prior to use. MDI and DOA were dehydrated with 4-Å molecular sieves for 3 days before use.

2.2. Sample preparation
For the preparation of the samples studied in the experiment, HTPB and MDI were precisely weighed with a stoichiometric ratio (r = n[NCO] : n[OH] = 1.0). The weight ratio of HTPB:DOA is 5:1 in all the tests. Firstly, HTPB and DOA were thoroughly mixed for 30min, then, mixed and homogenized for 5 minutes by a mechanical stirrer at high-speed stirring (1,000 rpm). The materials were mixed at room temperature. Having completely mixed all materials, samples were utilized for immediate rheokinetic test.

2.3. Viscosity build-up measurement
The rheokinetic analysis of the HTPB-DOA-MDI binder system was investigated by monitoring the viscosity build-up of the curing reaction in the SNB-1A Rotational Viscometer (Shanghai FangRui Instrument, China). The samples measured in the viscosity build-up test were kept in a water bath in the range of 15°C~55°C with an accuracy of ± 0.5°C. And the viscosity data of the binder system were recorded every 2 min by the software automatically.

3. Results and discussion

3.1. Determination of the rate constants and the pot-life of the binder
Figure 1 shows the viscosity build-up of the HTPB-DOA-MDI binder system under different curing temperatures. From the figure, we can find that curing temperature has significant impact on the reaction rate of the curing process. As the curing reaction temperature rise, the viscosity build-up of the binder system grew significantly faster. The reasons may be that, with the increase of the curing temperature, the rate of formation of urethane groups from –NCO groups and –OH groups was speed up, which accelerated the viscosity build-up of the binder system.
Figure 1. Viscosity build-up of the HTPB-DOA-MDI binder system under different curing temperatures.

The pot-life of the binder system is usually defined as the time interval that the viscosity was increased to a specific value (for example, 20,000 mPa·s). The pot-life of the HTPB-DOA-MDI binder system under different temperature was analyzed and summarized in Table 1. From the table, when the curing temperature was in the range of 15°C~35°C, the pot-life of the HTPB-based binder system was increased from 30min to 48min; and in the range of 35°C~55°C, the pot-life of the HTPB-based binder system was decreased from 48min to 34min. From the enlarged partial view of Figure 1, we can find that the initial viscosity of the binder system was decreased from about 6,000 mPa·s to 1,000 mPa·s with the temperature increased from 15°C to 55°C. And the reason for this phenomenon is mainly due to the inherent nature of HTPB, i.e. as the temperature increases, the viscosity of HTPB decrease.

The rheokinetic parameters of the HTPB-DOA-MDI binder system were calculated by applying different single linear regressions, as shown in Figure 2. The corresponding data, such as reaction rate constant (k_ƞ), correlation coefficient, and the ratio of k_ƞ(T_c) / k_ƞ(T_15) are shown in Table 1. From the data in Table 1, one can find that the reaction rate constant (k_ƞ) increase from 0.01362 min^{-1} to 0.07594 min^{-1} with the increase of curing temperature from 15°C to 55°C. What’s more, k_ƞ(T_c) / k_ƞ(T_15) increase from 1.34 to 4.65, this result indicates that with the increase of the curing temperature, the formation of urethane network was significantly accelerated. And the similar phenomena were reported in the literature of Lucio [14], Sekkar [15], Jiahu [16], et al.
Figure 2. ln $\eta$ versus curing time at different curing temperatures for the HTPB-DOA-MDI binder system.

Table 1. Rate constants and pot-life for the curing process of HTPB-DOA-MDI binder system at different isothermal curing temperatures.

| Curing temperature T (°C) | Curing temperature T (K) | Rate constant $k_\eta$ (min$^{-1}$) | Correlation coefficient | $k_\eta(T_{c}) / k_\eta(T_{15})$ | Pot-life (min) |
|--------------------------|--------------------------|------------------------------------|------------------------|---------------------------------|----------------|
| 15                       | 288.15                   | 0.01632                            | 0.9742                 | —                               | 30             |
| 25                       | 298.15                   | 0.02187                            | 0.9972                 | 1.34                            | 40             |
| 35                       | 308.15                   | 0.03047                            | 0.9951                 | 1.87                            | 48             |
| 45                       | 318.15                   | 0.04194                            | 0.9972                 | 2.57                            | 38             |
| 55                       | 328.15                   | 0.07594                            | 0.9889                 | 4.65                            | 34             |

3.2. Kinetic and thermodynamic studies

To calculate the thermodynamic parameters, e.g., pre-exponential factor (A) and activation energy ($\Delta E_\eta$) are computed from the Arrhenius formula (1). Correspondingly, activation entropy ($\Delta S_\eta$) and activation enthalpy ($\Delta H_\eta$), are computed from the Eyring equation (2):

$$\ln k_\eta = -\frac{\Delta E_\eta}{RT} + \ln A$$

(1)
where $k_\eta$ is the rheo-reaction constant and $T$ is the curing temperature (K).

From the Arrhenius diagram (Figure 3) for the HTPB-DOA-MDI cure reaction, the pre-exponential factor ($A$) and activation energy ($\Delta E_\eta$) are calculated with a first-order liner regression. An analogous evaluation of the rheokinetic data in the Eyring diagram (Figure 4) is carried out to calculate the value of activation enthalpy ($\Delta H_\eta$) and activation entropy ($\Delta S_\eta$). The values of $\Delta E_\eta$, $A$, $\Delta H_\eta$ and $\Delta S_\eta$ are calculated and shown in Table 2.

From the Arrhenius diagram (Figure 3) and Table 2, we can find that activation energy of the curing reaction is rather low ($\Delta E_\eta = 28.96 \text{ kJ} \cdot \text{mol}^{-1}$), which is related to a fast urethane reaction rate. And the pre-exponential factor $A$ (also is called frequency factor) is equal to 2687.37.

It is well known that activation enthalpy ($\Delta H_\eta$) and activation entropy ($\Delta S_\eta$) are two thermodynamic parameters which are very important to reveal the reaction mechanism. From the Eyring diagram (Figure 4) and Table 2, the activation enthalpy ($\Delta H_\eta$) is equal to 26.41 kJ·mol⁻¹. And the activation entropy ($\Delta S_\eta$) is equal to -187.83 J·K⁻¹·mol⁻¹. According to transition state theory, activation entropy is usually regarded as the degree of disorder in the reaction system [17]. In this work, large negative values of $\Delta S_\eta$ are found, which demonstrate of an associative mechanism in the transition states.

From the above data, the Arrhenius model and Eyring model for the curing reaction of the HTPB-DOA-MDI binder system can be written as:

$$\ln \frac{k_\eta}{T} = -\frac{\Delta H_\eta}{RT} + \frac{\Delta S_\eta}{R} + \ln \frac{R}{Nh}$$  \hspace{1cm} (2)

$$\ln \frac{k_\eta}{T} = -\left(\frac{26.41}{RT}\right) - \left(\frac{187.83}{R}\right) + \ln \left(\frac{R}{Nh}\right)$$  \hspace{1cm} (3)

where $k_\eta$ is the reaction constant and $T$ is the curing temperature (K).

**Figure 3.** Arrhenius diagram for the curing reaction of the HTPB-DOA-MDI binder system.
Figure 4. Eyring diagram for the curing reaction of the HTPB-DOA-MDI binder system.

Table 2. Rheokinetic parameters for the curing reaction of the HTPB-DOA-MDI binder system.

| $\Delta E_\eta$ (kJ mol$^{-1}$) | $A$ (L mol$^{-1}$ s$^{-1}$) | $\Delta H_\eta$ (kJ mol$^{-1}$) | $\Delta S_\eta$ (J K$^{-1}$ mol$^{-1}$) |
|-------------------------------|-----------------|-------------------------|----------------|
| 28.96                         | 2687.37         | 26.41                   | -187.83       |

4. Conclusions
In this study, viscosity measurement was utilized to monitor the curing reaction of the HTPB-DOA-MDI binder system. Curing temperature showed significantly influence on the reaction rate constant and the pot-life of the binder system. Kinetic and thermodynamic parameters, e.g., activation energy ($\Delta E_\eta$), activation enthalpy ($\Delta H_\eta$) and activation entropy ($\Delta S_\eta$) are computed from the Arrhenius formula and Eyring equation. The results of which were $\Delta E_\eta = 28.96$ kJ mol$^{-1}$, $\Delta H_\eta = 26.41$ kJ mol$^{-1}$ and $\Delta S_\eta = -187.83$ J K$^{-1}$ mol$^{-1}$, respectively.

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