ABSTRACT: In this work, a promising propellant binder using the energetic branched glycidyl azide polymer (B-GAP) as a matrix and the low-toxic dimer acid diisocyanate (DDI) as a curing agent was prepared, under the catalysis of dibutyl tin dilaurate. The curing kinetics considering the thermal diffusion effect and the reaction endpoint of B-GAP/DDI were investigated by the thermal analysis method and a newly proposed variance method, respectively. Moreover, the buildup of microstructures during curing and the tensile and dynamic mechanical performance of this binder were respectively explored. Results show that there exists an obvious induction period in the beginning of the curing reaction, and the autocatalytic model shows that thermal diffusion can effectively describe the curing process. Shore A hardness of sample stabilizes around 40.78 in the end of curing, and the reaction endpoint of B-GAP/DDI is in the time range of 156−168 h. There exist cross-linking, suspension, and free chains during the whole curing process, and the cross-linking density of the binder reaches approximately 4.0 × 10⁻⁴ mol·cm⁻³ when the curing completes. Hydrogen bonding (H-bond) is found to be a strong binder: 53.3% of the carbonyls participates in forming the H-bond. Furthermore, this binder has better mechanical performance and lower glass-transition temperature than the GAP/N100 binder.

1. INTRODUCTION

Nowadays, the sophisticated weapon system places greater demands on the comprehensive performance of the propellants charged in solid rockets or missiles; furthermore, the performance of the propellant depends mainly on the binder matrix; then, improvement for the binder may cause the development or innovation of the solid propellant.¹,² The glycidyl azide polymer (GAP) has drawn great attentions and started to be applied in high-energy propellants and explosives due to its high enthalpy of formation, high density, low burning temperature, and clear exhaust.³−⁶ However, for the linear GAP we generally used, a few defects actually restrict its promotion and application. More specifically, low functionality and the reactivity of hydroxyl on linear GAP easily result in an incomplete curing conversion.⁷ Moreover, there exists more physical entanglement of the linear molecular chains in GAP, thus increasing the viscosity of this polymer and the slurry of GAP propellant. Finally, weak mobility of the terminal groups on linear GAP may lead to high glass-transition temperature and poor mechanical performance.⁸−¹⁰ Fortunately, the branched GAP (B-GAP) has been synthesized and became a focus of research because of its excellent performance.¹¹−¹³ Because of the small hydrodynamic volume and weak entanglement among the branched chains, B-GAP has better rheological and low-temperature performance. Furthermore, more hydroxyl groups on the branched chains can not only increase the oxygen content, which is required by the propellant, but also make the polymer easier to form curing networks. Most importantly, the controllable scale of molecular weight of B-GAP is wider than that of GAP. Then, this branched polymer is expected to replace linear GAP as the energetic binder of the propellant.

The polyurethane curing agent toluene diisocyanate (TDI) is always used in propellant, but it has strong toxicity and is easily volatile under atmospheric pressure, thus being detrimental to the health of researchers.¹⁴,¹⁵ Moreover, TDI has been proved to be extremely sensitive to moisture, which may affect the curing reaction and deteriorate the performance of propellant. Then, developing a substitute for TDI as the curing agent of propellant becomes necessary. The compound dimeryl disiocyanate (DDI) has attracted researchers’
 attentions gradually mainly because of its low toxicity and insensitivity to moisture, and it is reported that the DDI presents a lower vapor pressure than the TDI and the isophorone disocyanate (IPDI). Moreover, the ester groups on the side chains of DDI could plasticize the generated curing networks of the propellant, reducing the cohesion of polar groups and enhancing the mechanical performance under low temperatures. Finally, DDI has excellent aging resistance, which concerns the service life of the propellant. Therefore, DDI is demonstrated to be a promising curing agent in the propellant.

Once the relevant problems of the GAP and TDI were recognized, focus of our research shifts to the newly emerged materials mentioned above. In this paper, B-GAP and DDI were combined to form a low-toxic energetic binder B-GAP/DDI by the catalysis of dibutyl tin dilaurate (DBTDL). Then, the kinetics considering the diffusion effect of the polyurethane reaction was investigated by thermal analysis. Moreover, the reaction endpoint of this binder was determined by a proposed methodology. We also explored the microstructures including cross-linkage and hydrogen bonding of this binder during the curing process. Finally, the tensile and dynamic mechanical performances of this binder were measured. The concerned studies in our work can lay a foundation for the application of the B-GAP/DDI binder in solid propellant.

2. EXPERIMENTS

2.1. Materials and Preparations. The B-GAP resin has a hydroxyl group content of 0.097 mmol·g⁻¹ and an average molecular weight of 3.11 × 10⁴ g·mol⁻¹. Curing agent DDI has an NCO mass content of 14–15%, industrial pure. The B-GAP resin and DDI curing agent were purchased from Liming Research Institute of Chemical Industry, Henan, China. Curing catalyst dibutyl tin dilaurate (DBTDL) was dissolved in dioctyl sebacate (DOS) with a mass fraction of 1%; these reagents were produced by Institute of Chemistry Chinese Academy of Sciences in Shanghai, China. B-GAP was dried in vacuum for 2 days at 60 °C before use. The B-GAP resin and curing agent were accurately weighed with a curing parameter (R) of 1.0, and 0.5 wt % catalyst solution was used to catalyze the urethane reaction. All of these reagents and catalysts were mixed thoroughly in a poly(tetrafluoroethylene) (PTFE) beaker for 10 min. Then, the mixture was evacuated for 1 h under 40 °C to remove the entrapped air and moisture, which may influence the hardness measurement. Subsequently, a small amount of the mixture was used for differential scanning calorimetry (DSC) measurements; a certain amount of the mixture was injected into the NMR tube for cross-linkage testing in the whole curing process, and the remaining was cast into a 5 mm deep PTFE mold and a 2 mm deep mold for curing under a constant temperature of 60 °C. The reaction process is shown in Figure 1.

2.2. Measurements. The kinetic curing reactions of B-GAP/DDI were investigated by DSC910s (TA Instruments, Inc.) with heating rates (β) of 2.5, 5, 10, and 15 °C·min⁻¹, respectively. Moreover, DSC measurements were performed in a nitrogen atmosphere (40 mL·min⁻¹). The hardness of B-GAP/DDI samples during the curing process was measured by a Shore A hardness durometer (Beijing Times Technology Co., Ltd.) according to GB/T 531.1-2008 standard. Noting that the hardness measurements should be started until these samples were not sticky, the time interval for measuring is 6 h. Meanwhile, the film cured in the 2 mm deep mold was sampled for infrared spectrum testing by a Nicolet 8700 Fourier transform infrared spectrometer. The cross-linking density of the sample cured in the NMR tube was tested using a VTMR2010V-T low-field NMR spectrometer (Shanghai Niumai Corporation). The tensile mechanical properties were tested using an Instron 26022 universal testing machine in accordance with GB/T 528-1998, and the strain rates for loading were set at 100 mm·min⁻¹. Dynamic mechanical performance was measured by dynamic mechanical analysis (DMA; DMA 2980, TA Instruments), the loading frequencies were set at 1, 5, and 10 Hz, and a constant heating rate of 5 °C·min⁻¹ was used.

3. RESULTS AND ANALYSIS

3.1. Diffusion-Related Curing Kinetics. Various means have been used for investigating the kinetics of polyurethane reaction. In situ infrared spectrometry can be employed to detect the concentration variation of reactant groups due to its accuracy and synchronicity, however, for a low rate of reaction, it consumes long time to monitor. The isothermal DSC method can be adopted to measure the reaction heat at a constant temperature, but it is necessary to determine appropriate reaction temperature before measurement. In addition, for some reactions to occur at high temperatures, the process of elevating the temperature before experiments may cause testing errors. Then, the nonisothermal DSC method was adopted in this work for understanding the curing kinetics.

The DSC nonisothermal thermograms of the B-GAP/DDI reaction at various heating rates from 2.5 to 15 °C·min⁻¹ are exhibited in Figure 2. For further comparing the results and
investigating the rule of peak shifts, the initial temperature, peak temperature, and final temperature of exothermic peaks were named $T_i$, $T_p$, and $T_f$ respectively. The total heat of curing reaction $\Delta H$ is obtained by integrating the heat flow over time. All of these data were extracted from DSC curves and are listed in Table 1.

Table 1. DSC Data at Different Heating Rates

| $\beta$ (°C·min$^{-1}$) | $T_i$ (°C) | $T_p$ (°C) | $T_f$ (°C) | T (min) | $\Delta H$ (J·g$^{-1}$) |
|-------------------------|------------|------------|------------|---------|--------------------------|
| 2.5                     | 100.18     | 117.33     | 130.97     | 12.32   | 85.91                    |
| 5                       | 107.36     | 125.62     | 146.28     | 7.78    | 76.06                    |
| 10                      | 113.26     | 136.58     | 160.04     | 4.68    | 67.96                    |
| 15                      | 118.74     | 143.33     | 170.72     | 3.46    | 76.82                    |

Several observations can be made from Figure 2. First, with increasing temperature, the heat generated during per unit time increases to its peak and subsequently declines because the polyurethane reaction can be accelerated with increasing temperature and tends to complete at high temperatures. Second, locations of the exothermic peaks shift obviously toward high temperatures with increasing heating rate, as shown in Table 1, and $T_i$, $T_p$, and $T_f$ of these peaks increase with varying degrees but the reaction time $t$ is shorted. The reason for this phenomenon can be ascribed to chemical thermodynamics; an increasing heating rate results in more heat release during unit time($\Delta H/dt$), thus increasing the thermal inertia and the temperature differential between reaction center and external environment. Then, these exothermic peaks may shift to the high-temperature zone for compensation. Variation of $\Delta H$ with the increasing $\beta$ has no obvious regularity.

Subsequently, kinetic analysis will be performed to explore the kinetic model of the curing reaction. During detailed analysis, it is necessary to assume that the released heat at specific time ($\Delta H_\alpha$) has a linear relationship with the curing reaction rate ($\frac{d\alpha}{dt}$)\textsuperscript{23}

$$\alpha = \frac{\Delta H_f}{\Delta H}$$

$$\Delta H_f = \int_0^\alpha \left(\frac{dH}{dt}\right) dt / \Delta H$$

where $\alpha$ represents the curing conversion, $\Delta H$ is the total reaction heat of curing, and $dH/dt$ denotes the rate of heat transfer, which is measured by a thermocouple. Transforming the thermal data in Figure 2 to eq 2, the degree of conversion ($\alpha$) as a function of temperature is shown in Figure 3. In addition, the relationship between $da/dt$ and $\alpha$ was computed and the curves are presented in Figure 4.

As can be seen from Figure 3 that the relations of $\alpha$ with $T$ are close to sigmoid curves, i.e., $\alpha$ increases rapidly in the middle but slowly in the beginning and end. Moreover, with an increase of $\beta$, the initial reaction temperature and $\alpha \sim T$ curves shift to high temperatures obviously. A possible explanation for the sigmoid curve is that there exists an induction period\textsuperscript{24} in the beginning of reaction, the active-site Sn atom in DBTDL could coordinate with hydroxyl or isocyanate, enhancing the reaction activity of hydrogen in hydroxyl and the electron-negativity in isocyanate, complexation of DBTDL with reactants can be formed, and the rate of polyurethane reaction seems rather slow but it increases rapidly (shown in Figure 4). In the middle, chemical cross-linking point and polyurethane can be formed easily by nuclear reaction of the complexation mentioned above; then, the conversion in Figure 3 increases linearly. At the end of the reaction, the concentration of the curing agent becomes lower; in addition, highly cross-linked curing networks inhibit the diffusion of curing agent, the reaction rate may slow down gradually, and $\alpha$ tends to 1.

Considering that the relation between $\alpha$ and $T$ in Figure 3 is the typical characteristic of the autocatalytic reaction, to be specific, a significant induction period exists at the beginning and the highest conversion rate is observed in the middle.
region. The autocatalytic model was therefore employed to describe the curing process of B-GAP/DDI. The kinetic equation can be rewritten as

$$\frac{da}{dt} = A \exp \left( -\frac{E_a}{RT} \right) \alpha^n(1 - \alpha)^m \tag{3}$$

where \( m + n \) is the overall order of reaction.

By taking the logarithm of eq 3

$$\ln \frac{da}{dt} = \ln A - \frac{E_a}{RT} + n \ln(1 - \alpha) + m \ln \alpha \tag{4}$$

The curing rate at conversion \((1 - \alpha)\) can also be expressed as

$$\ln \frac{d(1 - \alpha)}{dt} = \ln A - \frac{E_a}{RT} + m \ln(1 - \alpha) + n \ln \alpha \tag{5}$$

eqs 4–5

value 1 = \((n - m)\ln \left( \frac{1 - \alpha}{\alpha} \right) \tag{6}

value 1 = \ln \left( \frac{\alpha}{1 - \alpha} \right) + \frac{E_a}{RT} - \ln \left( \frac{1 - \alpha}{dt} \right) - \frac{E_a}{RT} \tag{7}

eqs 4 + 5

value 2 = 2 \ln A + (m + n) \ln(\alpha - \alpha^2) \tag{8}

value 2 = \ln \left( \frac{\alpha}{1 - \alpha} \right) + \frac{E_a}{RT} + \ln \left( \frac{d(1 - \alpha)}{dt} \right) + \frac{E_a}{RT} \tag{9}

Here, the thermal data at a heating rate of 10 °C-min\(^{-1}\) were taken to calculate these kinetic parameters. The value of \( n - m \) could be obtained from the slope of the plot of value 1 versus \( \ln [(1 - \alpha)/\alpha]; \) furthermore, the values of \( m + n \) and \( 2 \ln A \) could be deduced by calculating the slope and intercept of the plot of value 2 versus \( \ln(\alpha - \alpha^2), \) respectively. Finally, \( m, n, \) and \( A \) were calculated by the graphic method and solving equations, and the curing kinetic equation of B-GAP/DDI can be expressed as

$$\frac{da}{dt} = 6.17 \times 10^8 \exp \left( -\frac{6.7 \times 10^8}{RT} \right) (1 - \alpha)^{1.15} \alpha^{0.6} \tag{10}$$

Figure 5a,b presents the comparisons between experimental data and the fitted results of \( f(\alpha, T) \sim da/dt, \) which were illustrated in the three-dimensional coordinate.

Comparing the experimental and predicted results in Figure 5, great fitting errors mainly exist in the high conversion regions, especially in the case of \( \beta = 10, S, \) and 2.5 °C-min\(^{-1}\), that is, the higher reaction conversion has some effects on the polyurethane reaction rate, or the proposed autocatalytic model lacks consideration for the restriction of highly cross-linked networks on the reaction rate; as a result, the predicted \( da/dt \) becomes slightly higher than the test results in the \( \alpha \) range of 0.8–1.0. The main reason for the fitting error of eq 10 is that, in the later of reaction, \( da/dt \) is controlled not only by the curing reaction but also by the thermal diffusion because the generated curing-cross-linking networks could restrict the reagents from diffusing into themselves, thus decreasing the reactive collisions among reagents and the corresponding reaction rate. This restriction becomes stronger when the reaction reaches a higher conversion; then, the diffusion control in curing reaction should be considered. When the curing degree reaches a critical value \( \alpha_c, \) the diffusion-controlled rate constant \( K_d \) can be expressed by a semiempirical relation

$$K_d = K_e \exp[-C(\alpha - \alpha_c)] \tag{11}$$

where \( K_e \) denotes the rate constant of chemical kinetics and \( C \) is an empirical constant. Moreover, the total effective rate constant \( K_e \) has a relation with \( K_d \) and \( K_c \)

$$\frac{1}{K_e} = \frac{1}{K_d} + \frac{1}{K_c} \tag{12}$$

A diffusion factor \( f(\alpha) \), which could quantitatively measure the influence of thermal diffusion on the reaction rate, can be obtained by combining eqs 11 and 12

$$f(\alpha) = K_c \frac{K_e}{K_d} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{13}$$

where \( \alpha_c \) represents the critical curing degree over which the reaction is mainly controlled by thermal diffusion. It can be deduced from eq 13 that if \( \alpha \ll \alpha_c, f(\alpha) \approx 1 \), the reaction is dominated by the chemical kinetics. When \( \alpha \) approaches to \( \alpha_c, \) the influence of thermal diffusion on the reaction becomes apparent and \( f(\alpha) \) decreases gradually. While if \( \alpha \gg \alpha_c, f(\alpha) \approx 0, \) the reaction is mainly controlled by the diffusion so that it is almost complete. As can be concluded here that the thermal diffusion effect in the later reaction should be considered, then the curing model involving thermal diffusion could be established through using eq 13 as a diffusion multiplier in the autocatalytic model. Based on the experimental results, these parameters in eq 13 can be evaluated through performing...
a multivariate nonlinear regression analysis, $C = 1.26, \alpha = 0.87$. Then, the curing kinetic model containing diffusion item can be obtained by combining eqs 10 and 13

$$\frac{da}{dt} = 6.17 \times 10^8 \exp\left(-\frac{6.7 \times 10^4}{RT}\right)(1 - \alpha)^{1.15} \alpha^{0.6}$$

$$\frac{1}{1 + \exp[C(\alpha - \alpha_c)]}$$

(14)

The predicted results by eq 14 and the test data are presented in Figure 6 for comparative analysis.

As can be seen from Figure 6 that most predicted results are generally satisfactory with the experimental results, demonstrating that the diffusion-related autocatalytic chemical model is appropriate to describe the curing reaction of B-GAP/DDI catalyzed by DBTDL in the whole $\alpha$ range. Therefore, the diffusion factor $f(\alpha)$ could reflect the restriction of cross-linking networks on the reaction in the later of reaction.

3.2. Curing Reaction Endpoint. There have been multiple effective ways for investigating the curing reaction degree of polyurethane, such as spectroscopy and DSC, but these methods have limitations, including high transmission, and reflectivity of sample are required for spectroscopy measurement and extensive repetitive operations are necessary for the DSC testing for avoiding the sampling error. Moreover, the aforementioned methods are only employed for testing, and there needs to be a method to analyze the reaction endpoint because the testing data vary gradually and there are no obvious time limits between the curing and cured samples. The endpoint determination should be a combination of measurement and analysis; the former concerns a series of performance tests and the latter involves the methodology used for analyzing the tested data. Considering this, a combination of hardness measurement and variance analysis was proposed to investigate the curing reaction endpoint of B-GAP/DDI.

The hardness of the polyurethane samples increases continuously with increasing number of cross-linking points till the reaction completes, then, the Shore A hardness of the B-GAP/DDI samples was tested during curing to reflect the performance variation. Furthermore, the variance analysis method was employed here to investigate the deviation among datasets, thus magnifying the recognition among testing data and contributing to determining the reaction endpoint. It is worth noting that this analysis method could minimize the interference of sample thickness, testing site, random errors, etc. Therefore, the reaction endpoint of B-GAP/DDI was analyzed using the variance analysis method, the foundation of which was detailed synchronously.

Shore A hardness data with error bar of samples during curing were gathered and the relation of hardness versus curing time is graphed in Figure 7.

As shown in Figure 7, the average value of Shore A hardness of B-GAP/DDI samples varies dramatically in a wide range of curing time, but its variation rate does not keep a constant at different stages, hardness of the samples finally stabilized at approximately 40. At the beginning of curing, although the cross-linking points are rapidly generated from the polyurethane reaction, the sample has a lower cross-linking density and strong resistance to external pressure; then, the hardness proves to be lower. The increase rate of hardness tends to decline in the middle and is close to 0 in the later for the reason that the three-dimensional network was gradually refined and the reaction rate decreases with a lower concentration of reagent. Next, the test data in Figure 7 were processed for further analysis.

Shore A hardness test data with an interval of 12 h was defined as $x_{11}, x_{21}, \ldots, x_{n-1}, x_{n}$. Thus, variance of $x_{1}, x_{2}, x_{3}$, and $x_{4}$ can be expressed as
\[
\sigma_i^2 = \frac{\sum_{j=1}^{4} (x_i - \bar{x})^2}{4}, \text{ sample size } J = 4
\] (15)

Similarly
\[
x_{2} \sim x_{5}: \sigma_2^2 = \frac{\sum_{j=2}^{5} (x_i - \bar{x})^2}{4}, J = 4
\] (16)

\[...
\]
\[
x_{n-3} \sim x_{n}: \sigma_{n-3}^2 = \frac{\sum_{j=n-3}^{n} (x_i - \bar{x})^2}{n - i + 1}, J = 4
\] (17)

The collection sequence of \(\sigma^2\) and \(J\) in eqs 15–17 is illustrated in Scheme 1. Considering the test cost and the simplicity request for this method, it is appropriate to take the value of \(J\) as 4.

Scheme 1. Collection Sequence of \(\sigma^2\) and \(J\) in Analysis

![Diagram of Scheme 1](image)

The difference of variance between dataset \([x_i \sim x_{i+3}]\) and the adjacent set \([x_{i+1} \sim x_{i+4}]\) could significantly reflect whether a gradual transformation or a step change occurs from test data \(x_{i+3}\) to \(x_{i+4}\). For this work, the \(\sigma_i^2\) and \(J_i\) values of each dataset were computed and collected. However, it is difficult to describe the variation tendency of \(x_i\) using \(\sigma_i^2\) and \(J_i\) because of their discrete characteristics. Therefore, the cubic spline approximation \(S(J)\) for the curve of \(\sigma_i^2 \sim J_i\) was performed to achieve a smooth transition section (see Figure 8), noting that \(J_i\) are ordered by subscript rather than by its numeric value.

It can be observed from Figure 8 that \(\sigma_i^2\) of datasets decreases dramatically with the ordinal of \(J_i\) (range 1–9) for the reason that shore A hardness of sample inclines rapidly during the corresponding time. However, \(\sigma_i^2\) fluctuates slightly in the middle and tends to zero in the later, indicating the reaction rate decreases gradually. As can be concluded from the analysis above, reaction endpoint of B-GAP/DDI should locate in the later region of \(J_i\) and can be represented by the tendency of function \(S(J)\), and hence it is difficult to recognize a critical point, behind which none of \(\sigma_i^2\) has step change for observation; then the first derivative of \(S(J)\) was computed to reflect the tendency of \(S(J)\) in the later. The curve of \(dS/dJ_i\sim J_i\) is presented in Figure 9.

![Image of Figure 9](image)

The slope of interpolation function \(S(J)\) from \(J_5\) to \(J_{16}\) can be reflected by the first derivative curve in Figure 9. The peaks in the beginning and middle of the curve result from the changing \(\sigma_i^2\) in this region. In comparison to the \(dS/dJ_i\) in the range of \(J_1\) to \(J_{17}\), the value of \(dS/dJ_i\) behind \(J_{15}\) fluctuates slightly (within \(\pm 5 \times 10^{-2}\)) around zero, demonstrating that the data point \(x_i\) included in \(J_{15}\) and the later tends to a constant because the curing of sample is complete. Therefore, \(x_{15}\) can be considered as the first hardness data of the cured B-GAP/DDI sample, considering the discontinuity of sampling in our testing; the endpoint of the reaction was demonstrated to locate in the time range of 156–168 h, and a precise range could be obtained by shortening the sampling interval. Meanwhile, by calculating the average of \(x_{15} \sim x_{20}\) the shore A hardness of the cured B-GAP/DDI sample was proved to be 40.78.

To verify the method for determining the reaction endpoint above, we also prepared a B-GAP/DDI film, which has the same curing condition as the sample for hardness testing. Moreover, the infrared spectra of the film were tested with a time interval of 20 h; then, the local spectra around 2271 cm\(^{-1}\) (−NCO characteristic peak) were collected for analysis (see Figure 10).

![Image of Figure 10](image)

As can be seen from Figure 10 and its local sight that the characteristic peak of the isocyanate group declines with increasing time because the −NCO groups were consumed during the curing process. The peak height stabilizes after 160 h with these spectra coinciding with each other, indicating that the curing reaction completes around 160 h. Then, the accuracy of the reaction endpoint analysis can be verified.

3.3. Microstructures Buildup. Macroscopic performances of the polymers are mainly determined by their microstructures, such as the cross-linking networks, hydrogen bonding, entanglement, etc. These structures have gradually built up during the curing and are vulnerable to the curing conditions. Therefore, monitoring the microstructural evolu-
tion of polymer during curing becomes necessary for the control of the structures and performance of polymers.

3.3.1. Cross-Linking Networks. The curing process of the B-GAP/DDI binder can be considered as a gradually evolving process of the cross-linking networks. Moderate cross-linkage could endow the polymers with excellent mechanical performance at high temperatures and lay the foundation for the application of thermosetting binder in solid propellant. Therefore, it is essential to explore the formation of curing networks to control the microstructure reasonably. Here, a low-field NMR instrument was employed to investigate the cross-linkage of the B-GAP/DDI binder. This technique could be easily understood, and due to the various chemical environments, the protons on the polymer chains have different transverse relaxation times ($T_2$), which is generally used to reverse the mobility of the chains quantitatively.31 The XLD model was demonstrated to be an effective method to describe the relaxation characteristics of the polymer chains in the external magnetic field, and it can be expressed as

$$M(t) = A \exp \left( -\frac{t}{T_{20}} \right) - \frac{1}{2} q M_\alpha \star t^2 + B \exp \left( -\frac{t}{T_{21}} \right) + C \exp \left( -\frac{t}{T_{22}} \right)$$

where $M(t)$ is the attenuated signal; $A$, $B$, and $C$ denote the signal proportions of cross-linking, suspension, and free chains, respectively, $T_{20}$, $T_{21}$, and $T_{22}$ refer to the relaxation times of these three chains $q$ represents the anisotropy of the cross-linking chains, and $M_\alpha$ is the dipole moment below the glass-transition temperature. We used eq 18 to regress the relaxation times of the cross-linking, suspension, and the total attenuated signals (see Figure 11).

Figure 11 presents the attenuation process of $T_2$ for the B-GAP/DDI binder in different curing degrees. As can be seen that the decay rate of $T_2$ in system becomes faster as the curing proceeds, resulting in increasing slopes of these curves before turning points, that is, more protons or chain segments are constrained dramatically by the generated cross-linking points. The $T_2$ at the time of 160 h is demonstrated to be 6.5 ms. Furthermore, we use eq 18 to calculate the cross-linking density ($V_c$) of this binder at different curing times.

$$V_c = \frac{\rho \rho_0 N \sqrt{2qM_\alpha}}{3CM}$$

where $\rho$ is the density of material, $N$ denotes the bond number on the backbone chains, and $C$ and $M$ are the bond number in the Kuhn chain unit and the total mass of the repeat unit, respectively. The increase of $V_c$ for the B-GAP/DDI binder is given in Figure 12. Moreover, the percentages of the cross-linking, suspension, and free chains for the binder at different curing times are shown in Figure 13. Noting that the measurement was performed five times, the error’s fluctuation was also added to $V_c$.

Figure 12 clearly shows an increasing cross-linking density of B-GAP/DDI binder in the curing process; the tendency of $V_c$ is generally similar to that of the $\alpha \sim t$ curve because the cross-linkage in the system is positively associated with the curing degree. The $V_c$ value reaches approximately $4.0 \times 10^{-4}$ mol·cm$^{-3}$ after curing, which is proved to be larger than that of the binder using linear GAP as the matrix.32 Considering the relation between the shear modulus ($G$) with $V_c$, $G = V_cRT$, the B-GAP/DDI binder might have a higher modulus than the GAP/N100 binder. Furthermore, the percentages of cross-linking, suspension, and free chains during curing are present in Figure 13. It can be seen that as the curing proceeds, the percentage of cross-linking chains inclines dramatically before 100 h but slowly within 100–160 h, because the conversion rate $da/dt$ at the stage seems so great that most of the branched chains are constrained with the cross-linking points, but the highly cross-linked networks might restrict the reactants from diffusion in the end. Furthermore, there also
exist the suspension and free chains throughout the reaction. The former might be the defects which are the unreacted hydroxyl due to the restriction of networks, or the branched chains without reactive groups; the latter includes the curing agent DDI and a small amount of linear GAP, which is the by-product in the preparation of B-GAP. These two kinds of chains reduce gradually but do not disappear in the end, that is, most of the brand chains include hydroxyl and the DDI may reduce and form the networks, making the networks complete. However, the branched chains without hydroxyl and the linear GAP terminated with methyl may remain, finally turning into the suspension defects and free chains, respectively. Then, these defects still exist after curing.

3.3.2. Hydrogen Bonding. Hydrogen bonding is another strong interaction that contributes significantly to the mechanical performance of polymers. For polyurethane, hydrogen bonding (H-bonded) is mainly formed by the carbonyl (C=O) and imino (−NH−) groups among different molecular chains through σ-hole noncovalent interactions, once this reticulate structure forms, the segments on the adjacent chains could be strengthened. Generally, the hydrogen-bonding interaction can be investigated through monitoring the shifts of infrared absorption spectra of polyurethane, because the infrared absorption peak of these carbonyl groups, which participates in forming the hydrogen bonding, may shift toward a lower frequency. Then, the curing B-GAP/DDI film was used for infrared spectroscopic testing with a time interval of 20 h, and the tested results are presented in Figure 14.

Figure 14 presents a local sight for the infrared spectra of the B-GAP/DDI binder at different curing times. The spectral absorption peak of the carbonyls generally locates in the wavenumber range of 1680−1740 cm⁻¹ in which the peaks of the H-bonded and free carbonyl groups overlap intricately; then, it is difficult to distinguish these two carbonyl groups, respectively. Considering the bathochromic shift in the infrared spectra, the peaks located around 1733 cm⁻¹ are assigned to the free carbonyl, and correspondingly, the peaks that shift in a wide range and high frequency are the characteristic peaks of H-bonded carbonyl. Generally, the peak area of a characteristic group is proved to be the measurement of the concentration of the characteristic group in infrared spectroscopy analysis. Here, we performed a cluster analysis for the overlapped peaks, that is, measuring the peak area of the H-bonded and free carbonyl groups mathematically with the assistance of the Gaussian function. The detailed resolving process and the final results are shown in Figures 15 and 16, respectively.
Figure 16 presents an apparent trend for the percentage of H-bonded and free carbonyls in the B-GAP/DDI binder. As can be seen from the column graph that the percentage of the H-bonded carbonyls increases continuously over time and reaches 53.3% when the curing completes, suggesting that nearly half of the carbonyls contribute to the formation of hydrogen bonding, while the variation of the percentage of free carbonyls does the reverse. With progress of the curing reaction, the concentration of carbamate (−NHCOO−) groups increases gradually and the probability of covalent bonding between the proton donating imino (−NH−) and the carbonyl or the ether group (−O−) also increases. Moreover, the extent to which the absorption peak of carbonyl shifts toward low frequency becomes greater with increasing curing time, demonstrating the gradually enhancing H-bonds among the segments on polymer chains. Thus, the modulus and tensile strength of the B-GAP/DDI binder could be significantly reinforced by this noncovalent interaction.

3.4. Macro-Performance. The B-GAP/DDI binder will be applied in the solid propellant, which is subjected to various loads (shock, vibration, impact, etc.) under a wide range of temperature; thus, excellent mechanical performance of the binder matrix is required. Therefore, we studied the tensile and dynamic mechanical performance of the B-GAP/DDI binder. Moreover, the performance of linear GAP cured with N100 was present for comparison.

3.4.1. Tensile Mechanical Performance. The tensile mechanical performances of B-GAP/DDI and GAP/N100-(polysiocyanate) binder are given in Table 2, including tensile strength (σm), break elongation (εb), and fracture work, which are usually employed to evaluate the tearing resistance or to reflect the toughness of the polymers.

As shown in Table 2, the tensile strength, elongation, and the fracture work of B-GAP/DDI binder are significantly higher than those of GAP/N100, indicating better tensile mechanical performance of the branched GAP binder. There exist many reasons contributing to these results; in comparison to linear GAP, the branched GAP generally has a high molecular weight, then the interaction among these chain segments could be enhanced dramatically. Moreover, the long branched chains are limited by the cross-linkage and therefore have large conformation entropy that favors chain movements, such as crimping, extension, and shrinkage. Then, the entanglement among these chains easily occurs and contributes to the strength and modulus of the binder. Finally, the branched polymers have an excellent relaxation property due to the free volume of chains, and the tensile stress in the polymer chains when loading can be released rapidly. Therefore, the B-GAP/DDI presents better mechanical performance than GAP/N100 binder.

Table 2. Tensile Mechanical Performance of B-GAP/DDI and GAP/N100 Binders

| Binders     | σm (MPa) | εb (%) | fnde (J) |
|-------------|----------|--------|---------|
| B-GAP/DDI   | 0.96     | 142.25 | 0.87    |
| GAP/N100    | 0.68     | 74.62  | 0.34    |

3.4.2. Dynamic Mechanical Performance. Dynamic mechanical analysis was employed to investigate the mechanical response of the B-GAP/DDI binder under dynamic loads of 1, 5, and 10 Hz. Here, the variations of storage modulus (E’), loss modulus (E″), and loss angle tangent (tan δ) versus temperature are illustrated in Figure 17. Correspondingly, the dynamic mechanical performance of the GAP/N100 binder was also present for comparison.

Figure 17 presents the storage and loss moduli of these binders under various loads. It can be seen that the E’ of binders declines for 3 orders of magnitude in the temperature range of around −62 to −34 °C, which indicates that these binders convert from glassy state to high elastic state with the increase of T. The mobility of polymer chains at low temperatures is limited, the binders present a high elastic modulus, an increasing temperature may increase the entropy of system, the motion of polymer chains can also be enhanced, the molecular structures or conformations can be easily modulated under external force, and then E’ decreases rapidly. It is worth noting that the increase of the loading frequency may increase the E’ value of the B-GAP/DDI binder because motions of molecular chains have a dependence on the relaxation time and increasing the loading frequency has a similar effect to reducing the relaxation time on the motions of chains that is, chain motions lag behind the external force and then the E’ value of the binder may increase with frequency. The E’ value of the B-GAP/DDI binder under 1 Hz in a wide temperature range is proved to be larger than that of the GAP/N100 binder, indicating better elasticity of the former (see Table 3).

The peaks on the curves of loss modulus correspond to the glass transitions of binders; here, the stored energy in polymer chains could dissipate due to phase transition. Compared to GAP/N100, which has a glass-transition temperature (Tg) of...
−47.8 °C under 1 Hz, B-GAP/DDI has a lower $T_g$ under the same frequency because more terminal groups on the branched chains enhance the mobility of this binder. Figure 17b presents the tan δ curves of binders, which can be used to reflect the α transition of polymers. In contrast, the peak temperature of B-GAP/DDI under 1 Hz is lower than that of GAP/N100; the former can maintain its high elasticity under a lower temperature, which is desperately needed by the wide-temperature-range propellant. In general, the B-GAP/DDI binder has excellent low-temperature performance and elasticity, it becomes a promising substitute for the generally used linear GAP in solid propellant.

4. CONCLUSIONS

A promising, energetic binder B-GAP was cured using the low-toxic curing agent disocyanate DDI under the catalysis of DBTDL, meanwhile, the curing kinetics, curing reaction endpoint, and microstructures buildup of B-GAP/DDI were thoroughly investigated. Moreover, the tensile and dynamic mechanical performances of this binder were explored. The autocatalytic model involves a diffusion item, which is appropriate to describe the curing behavior of this binder. Based on the Shore A hardness data and the proposed variance method, the endpoint of reaction is determined to be in the time range of 156−168 h. There exist cross-linking, suspension, and free chains in the curing system; the cross-linking density can increase to around 4.0 × 10−4 mol·cm−3; and the suspension and free chains reduce with time but do not disappear after curing. Intermolecular hydrogen bonding can be formed by the imino groups and the carbonyls or ester groups in the binder; about half of the carbonyls participate in forming this interaction till the end of curing. The B-GAP/DDI binder is expected to substitute the linear GAP in propellant due to its excellent mechanical properties and low $T_g$.

AUTHOR INFORMATION

Corresponding Author
Huixiang Xu – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China; orcid.org/0000-0002-7866-6844; Email: xhx204204@163.com

Authors
Song Ma – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Hongjie Fan – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Ning Zhang – Xi’an North Hui An Chemical Industries Co. Ltd., Xi’an 710302, China
Wenfeng Li – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Yonghong Li – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Yang Li – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China

Dianjun Huang – Qingyang Chemical Industry Co. Ltd., Liaoyang 111000, China
Liyuan Zeng – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Xiaobing Shi – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
Xiulun Ran – Xi’an Modern Chemistry Research Institute, Xi’an 710065, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04439

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