Study on the Correlation of Crosslink Network Structure and Tensile Properties of HTPB Binder

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Abstract. To study the crosslink network structure and the correlation with tensile mechanical properties of hydroxyl-terminated polybutadiene (HTPB) binder, tensile test and nuclear magnetic resonance test were introduced, the crosslink data and tensile stress-strain curves were obtained at various temperatures. The results show that the temperature has a significant effect on the crosslink density. When heating the samples from 30°C to 90°C, the crosslink density decreases and the transverse relaxation time increases. From 90°C to 130°C, the crosslink density raises at first and then becomes lower, and the transverse relaxation time keeps increasing. When the temperature rises from 30°C to 90°C, the elastic modulus and tensile strength of the binder are reduced, the elongation at break gets greater, and the tensile strength and the crosslink density has a linear relationship, which can predict the tensile strength of the binder at different crosslink densities.

1. Introduction
The binder is the important part of propellant, and it is not only regarded as the basis of viscoelasticity, but also the determining factor of mechanical properties [1]. Additionally, the quality of the binder itself directly affects the mechanical properties and the storage lifetime of the propellant [2]. HTPB binder is a temperature-dependent viscoelastic material, and the change of external temperature has an important influence on its mechanical properties and the crosslink network structure [3].

At present, researchers have been engaged in related research on the network structure and mechanical properties of binder at home and abroad. V Sekkar et al. [4, 5] studied the elastic modulus at different temperatures and the activation energy at different crosslink densities of HTPB binder, figuring out that the temperature and crosslink density had obvious effect on the mechanical properties of HTPB binder. S. N. Li et al. [6] studied the accelerated aging law of HTPB solid propellant, implying that the reason which caused the deterioration of the mechanical properties is that the Oxidative decomposition of C=C bond in the binder molecule damaged the network structure. H. Yan et al. [7-10] confirmed that the main reason for the poor mechanical properties of the propellant is the imperfect network structure of the binder. By adding the network regulator, the network structure and the mechanical properties of the propellant are improved. These work are mainly focused on traditional tensile and compression tests, and related studies combining nuclear magnetic resonance with tensile test have not been reported.

In this paper, HTPB adhesives were used as the research object. Tensile test and nuclear magnetic resonance (NMR) test were carried out at normal temperature and high temperature. According to the test
data and phenomena, the effect of temperature on the crosslink network structure and tensile properties of HTPB binders was analyzed.

2. Basic Principle Of Crosslink Density Test

Micro-network cross-linking structure of polymer include physical cross-linking and chemical cross-linking. Physical cross-linking refers to physical crosslinking points produced by entanglement between polymer chains, and chemical crosslinking is the connection between elements by chemical bonds. The crosslink network structure of the HTPB binder includes three forms: (a) Crosslinking part, including chemical cross-linking and physical entanglement, which have poor kinematic properties; (b) The pendant chain part, which is free at one end and bound by a crosslinking point at the other end, and its motion performance is better than that of the cross-linking part. (c) Free chain part, this structure is not bound by cross-linking points, and has the best moveability performance.

The state of hydrogen atoms in the polymer is different, and the transverse relaxation time $T_2$ varies. The transverse relaxation time has high sensitivity to the cross-linking state of hydrogen atoms. When the temperature is higher than the glass transition temperature $T_g$ of the HTPB binder, once the material receives the magnetic resonance pulse, the relaxation behavior of microscopic network structures can be described as the basic theoretical functions of tubular models and single molecular chain models:

$$M(t) = A \times \exp\left(\frac{-t}{T_2} - 0.5 \times q \times Mrl \times t^2\right) + B \times \exp\left(\frac{-t}{T_2}\right) + C \times \exp\left(\frac{-t}{T_{2s}}\right) + A_0$$

Where $M(t)$ is the intensity of magnetization, $A$ is the proportion of the cross-linking part (Chemical crosslinking and physical crosslinking), $T_2$ is the transverse relaxation time of crosslinking part and pendant chain part, $q$ is the anisotropy rate of crosslinking part, $Mrl$ is the residual dipole moment of the sample below the glass transition temperature, $B$ is the proportion of the pendant part, $C$ is the proportion of free chain part, $T_{2s}$ is the transverse relaxation time of free chain part, $A_0$ is a fitting parameter and has no physical meaning.

In the HTPB binder material, the signal of the free chain is derived from the relaxation behavior of the sol small molecule. In general, the content of sol molecules in HTPB binder is very small. Thus, in order to simplify the signal fitting process, it is assumed that the signal of the sol molecule in the nuclear magnetic signal is 0. Simplify the equation (1) as

$$M(t) = A \times \exp\left(\frac{-t}{T_2} - 0.5 \times q \times Mrl \times t^2\right) + B \times \exp\left(\frac{-t}{T_2}\right) + A_0$$

By obtaining the nuclear magnetic resonance signal of the sample, the model parameters, the parameters in equation (2) can be fitted.

The crosslink density of polymer is calculated by equation (3):

$$\nu_c = \frac{\rho}{M_C}$$

Where $\nu_c$ is the crosslink density, $\rho$ is the density of the sample, $M_C$ is the average number of the sample, i.e. the molecular weight between adjacent crosslinking points.

The average number of polymer is calculated by equation (4):
Where \( N \) is the number of backbone keys of the repeating unit, \( C \) is the number of keys in the main chain, \( M_n \) is the molar mass of repeating unit.

Bringing equation (4) into equation (3), the equation to calculate crosslink density is simplified as

\[
\nu_c = \frac{5 \rho N \sqrt{q}}{6CM_n}
\]  

(5)

3. Experimental Section

3.1. Uniaxial Tensile Test

The main test equipment was INSTRON 5982 material testing machine. According to the shape and size of the type 3 standard dumbbell test piece in the GB/T 528-2009 standard, the HTPB binders of the same batch were tailored, and four sets of test pieces (five per group) were and four sets of test pieces (five per group) are obtained.

The four sets of samples were placed in an incubator at 30\(^\circ\)C, 50\(^\circ\)C, 70\(^\circ\)C and 90\(^\circ\)C for 1 h. And then at a corresponding temperature, uniaxial tensile tests were carried out at the rate of 10 mm/min. Meanwhile the test data were recorded.

3.2. NMR test

The NMR test was undertaken on the VTMR20-010V-T NMR temperature analysis system (NIU MAG), which was used to get the crosslink density of HTPB binder.

When the NMR test was carried out, the HPTB binders were cut into long strips of 8mm in length, 2mm in width and 2 mm in thickness. And then put them in the 5 numbered test tubes (Φ8.5mm×H200mm). Warming up the samples to 30\(^\circ\)C, 50\(^\circ\)C, 70\(^\circ\)C, 90\(^\circ\)C, 100\(^\circ\)C, 110\(^\circ\)C, 120\(^\circ\)C and 130\(^\circ\)C in turn. At every constant temperature, keep the samples for 1h, and test e at each corresponding temperature. Finally, the sample was tested at 30\(^\circ\)C, which was cooled from 130\(^\circ\)C. Keep them for 1h, and then carry out a set of controlled tests. After the tests, recorded the NMR test data at every test temperature.

4. Analysis Of The Nmr Tests

The average data of the NMR tests at every temperature are shown in Table 1.

| Temperature \( T(\text{\(^\circ\)}\text{C}) \) | Crosslink percentage \( A(\%) \) | Transverse relaxation time \( \tau (\text{ms}) \) | Crosslink density \( \nu_c \times 10^5 \text{mol/ml} \) |
|---|---|---|---|
| 30 | 62.32 | 16.64 | 5.68 |
| 50 | 55.19 | 21.26 | 4.22 |
| 70 | 47.48 | 25.52 | 2.94 |
| 90 | 40.56 | 30.75 | 2.20 |
| 100 | 41.67 | 31.13 | 2.96 |
| 110 | 43.57 | 32.15 | 3.46 |
| 120 | 37.80 | 37.26 | 2.54 |
| 130 | 33.43 | 47.98 | 1.48 |
| 30(controlled test) | 57.68 | 13.81 | 4.91 |
As is shown in TABLE I, raising the temperature from 30°C to 90°C, the crosslinking proportion and crosslink density decreased obviously, while the transverse relaxation time of HTPB binder. The main reason was that heating untied the physical points, the proportion of free and pendant chain part increased, thus the crosslink density become lower. The hydrogen proton in binder got more active, and the degree of freedom turned into larger, so the transverse relaxation time become longer.

Heating the samples from 90°C to 130°C, the crosslinking proportion and crosslink density increased firstly, and the decreased. The speed of growing for the transverse relaxation time become higher. At 130°C, the surface of the samples had been initially melted when touched by tweezers. The viscosity of HTPB binders were enhanced, and began to exhibit viscous flow characteristics. The main reason was that HTPB binder had undergone oxidation at around 110°C, causing the polymerization of C-C double bonds and free chains, so the crosslink density increased. The temperature continued to rise and a series of side reactions would occur, which could break or transfer polymer chains [3], leading the crosslink density decreased. From 90°C to 110°C, the increase of crosslinking density degree lead the binding force enhancement of hydrogen protons. While the temperature rose, the thermal movement got more active, the degree of freedom grew. The range of transverse relaxation time is related with both binding force and degree of freedom, so $T_2$ increased gradually in the whole. From 110°C to 130°C, some side action would emerge, resulting in Molecular chain fragmentation and hydrogen proton binding force reduction, and together with the effect of thermal movement, $T_2$ grew fast.

Cool the samples from 130°C to 30°C as the controlled test. Comparing the results with the original 30°C test results, it was found that the crosslink density and transverse relaxation time had obvious changes, which implied the high temperature caused the irreversible react to HTPB binder. The reason for the changes is that oxidation reaction and high temperature destruction reaction changed the molecular structure above 90°C. Therefore the accelerated aging test of HTPB propellant must be controlled under 90°C.

![Figure 1. Curve of crosslink density with temperature](image1)

![Figure 2. Curve of transverse relaxation time with temperature](image2)

| Contents                  | Temperature  | Fitted curves                                    |
|---------------------------|--------------|--------------------------------------------------|
| Crosslink density $\nu_0$ | 0–90°C       | $\nu_0 = -0.0586t + 7.2760(R^2 = 0.9902)$         |
|                          | 90–130°C     | $\nu_0 = -0.0036t^2 + 0.7765t - 38.4360(R^2 = 0.9788)$ |
| Transverse relaxation time $T_2$ (ms) | 0–90°C       | $T_2 = 0.2330t + 9.5655(R^2 = 0.9992)$          |
|                          | 90–130°C     | $T_2 = 0.0177t^2 - 3.4865t + 201.7500(R^2 = 0.9940)$ |
According to the test data, the curves of crosslink density versus temperature and transverse relaxation time versus temperature are shown in Fig.1 and Fig.2. When the temperature is lower than 90°C, the crosslink density and transverse relaxation time changed linearly with time. During 90~130°C, Crosslink density and transverse relaxation time were parabolic with temperature. TABLE II shows the specific fitted function, the crosslink density and transverse relaxation time of HTPB binder would be predicted based on the relationships.

Another sample was selected for NMR test. The crosslink density was $2.67 \times 10^{-5}$ mol/ml, and the predicted result was $2.588 \times 10^{-5}$ mol/ml, whose error was 3.07%. The transverse relaxation time was 27.63ms, and the fitted value was 28.21ms, while the error was 2.10%. Therefore, the curve obtained by fitting the test data has certain reference significance.

5. Relationship Of Crosslink Density And Tensile Properties

Fig. 3 shows the tensile stress-strain curves of HTPB binder at different temperatures. Temperature had the obvious effect on the tensile properties. Heating lowered the crosslink density, elastic modulus $E$ and tensile strength $\sigma_m$, while the elongation at break $\varepsilon_b$ increase. The phenomenon were due to that high temperature made the polymer molecule more active and the crosslink degree decrease. Thus, the binder become relatively soft, leading the low modulus and strength, while the elongation at break got higher.

![Figure 3. Curves of stress versus strain for HTPB binder at various temperatures](image)

Combining the test data of NMR tests and tensile tests, the relationship between tensile strength and crosslink density is shown in Fig. 4. The $\sigma_m$ varied linearly with the growth of $v_0$, which could be fitted by linear equation (6):

$$\sigma_m = 0.1637 + 0.0594 \times 10^5 v_0 (R^2 = 0.9940)$$ (6)

The verified tensile test was carried at 80°C, using the same batch of samples as the tests above. The tensile strength obtained was 0.3017MPa, and when the crosslink density was $2.67 \times 10^{-5}$ mol/ml, the predicted result by equation (6) was 0.3164MPa, whose error was 4.87%. The verified test explained that equation (6) can be used to predict the tensile strength of HTPB binder.
6. Conclusion

(1) Heating the samples from 30°C to 90°C, the crosslink density decreased and the transverse relaxation time increased. From 90°C to 130°C, the crosslink density get lower first and then higher, and the transverse relaxation kept growing.

(2) When the temperature is higher than 90°C, irreversible oxidation and high temperature destruction reaction would happen to HTPB binder. Therefore the temperature of accelerated aging test must under 90°C.

(3) As the temperature increases, the crosslink density of the HTPB binder decreased, the elastic modulus and tensile strength decreased, and the elongation at break increased. The tensile strength has a linear relationship with the crosslink density, which can be used to predict the tensile strength at different crosslink densities.

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