

Evaluation of Mechanical Properties of Composite Solid Propellant by Genetic Engineering of Materials: Part A.

Wei Zhang,^{*,[a]} Xing Zhou,^[a] Tong Bao,^[a] Lei Deng,^[a] and Dong-lei Gao^[a]

Abstract: The uniaxial tensile constitutive models of a crosslinked polymer and plasticizer were established based on the characteristics of the network and plasticization by genetic engineering of materials. The key factors affecting the mechanical properties of the polymer matrix were chosen as the genomes of materials. The constitutive model for the crosslinked polymer network with no plasticizer was related to the molecular characteristics of the ingredients, such as the flexibility of the binder prepolymer, functionalities of the ingredients, as well as the curing parameters. On the basis of the constitutive relation of the

crosslinked polymer, the constitutive model for the crosslinked polymer and plasticizer was also related to the volumetric fraction of the plasticizer and the interaction of the binder prepolymer and plasticizer molecules. Within the range of viscoelastic deformation in the tensile test, the viscoelastic characteristics of the network were considered in the model. Numeric results showed that the predicted and experimentally measured stress-strain curves were consistent under uniaxial tensile loading, indicating that the model satisfactorily predicted the stress and strain response.

Keywords: Crosslinked polymer network · Plasticization · Tensile mechanical property · Constitutive model · Material genome

1 Introduction

Analysis of the structural integrity of solid propellant grains requires constitutive equations for composite solid propellants. Constitutive models for propellants mainly generated from data processing of mechanical tests. For example, the main curve of the stress relaxation modulus of the propellant is generated from numerous stress relaxation tests conducted at different and constant strains and temperatures in accordance with the time-temperature superposition principle. The main curve of the stress relaxation modulus was then expressed using a mathematical fitting formula, such as the Prony Series. However, as far as the modification of the formulation of the propellant, numerous mechanical tests should be conducted repeatedly to obtain updated constitutive models for the propellant.

In 2002, Ho [1] developed a constitutive model incorporating mechanical damage and nonlinear viscoelastic material response for solid composite propellants under conditions of high strain-rate impact loading. Numerical constants in the model were obtained from Hopkinson bar experiments at strain rates ranging from 103 s^{-1} to 104 s^{-1} . Damage was also considered using an approach based on correcting the viscoelastic function with a stress-softening function. The model satisfactorily predicted the stress response beyond the temperature range for developing the constitutive equation.

In 2016, Marthinus et al. [2] studied the failure mechanism of an ammonium perchlorate/aluminum-/hydroxyl-terminated polybutadiene (AP/Al/HTPB) propellant by in-situ scanning electron microscopy uniaxial tensile testing. Dur-

ing tensile testing, cracks and voids opened up prior to three processes: the creation of new cracks and/or voids in the propellant sample, the debonding of the binder with AP particles, as well as the nucleation and coalescence of voids. On the fracture surfaces of the samples, the binder matrix separated thoroughly from the large AP particles but more strongly bonded with the aluminum particles. These results suggested the importance of good adhesion between the filler and the polymer matrix.

In 2018, Zhang et al. [3] evaluated the tensile mechanical properties and damage mechanisms of AP/Al/HTPB propellants at temperatures within a wide range (-50°C to 70°C) and at varying strain rates. Their numerical simulations used a two-dimensional particle packing model of solid fillers based on the formulation of the propellant. The calculated results indicated that the number of damaged interfaces between particles and the binder, as well as the extent of damage under loading depend on the strain rate. With increased strain rates, the quantity of the damaged interfaces increased as the development of the particle dewetting damage and damage accumulation were delayed. However, the material parameters in the model for the binder and the interfacial damage were fixed, as reported in their previous study [4].

[a] W. Zhang, X. Zhou, T. Bao, L. Deng, D.-l. Gao
College of Aerospace Science and Engineering
National University of Defense Technology
Deyu Road, Kaifu District, 410073, Changsha, P.R. China
*e-mail: wzhang_nudt@nudt.edu.cn

Meanwhile, many theoretical and experimental studies have been conducted on correlations between mechanical properties and polymer networks in composite solid propellants. Their results showed that the curing parameters of the crosslinked polymer system significantly affected the mechanical properties of the propellants.

In 1993 and 1994, Manjari et al. [5,6] evaluated the influence of crosslinking agents and chain extenders on the mechanical properties of HTPB-based propellants, which contain 1,4-butanediol (BD), trimethylolpropane (TMP) and toluene diisocyanate (TDI). To achieve the maximum strain and moderately high tensile strength of HTPB-based propellant, HTPB with low hydroxyl value required higher levels of tri-functional curing agent and high NCO/OH equivalence ratio. Both the diol-triol and NCO/OH ratios were useful tools for controlling the mechanical properties of HTPB-based propellants. Optimal properties can be achieved with high-molecular-weight HTPB by using a crosslinking agent alone at a lower NCO/OH ratio, a chain extender alone at a higher NCO/OH ratio, or a combination of diol-triol at a higher NCO/OH ratio.

In 2003, Sekkar et al. [7] studied the effects of various NCO/OH equivalence ratios (*r*-values) with three diisocyanates on the mechanical properties of HTPB networks by experimentation. They found that crosslink density correlated well with mechanical properties. The tensile strength and equilibrium relaxation modulus of HTPB-based urethane networks increased with increasing *r*-value, whereas the strain decreased.

In 2006, Sekkar et al. [8] studied the modeling of network parameters in HTPB/diisocyanate based allophanate-urethane networks and the correlation between network parameters and mechanical properties. The mechanical and swelling properties of the networks were characterized. The network parameters, such as the fraction of urethane groups involved in the allophanate formation, and the effective chain length were calculated from the experimental crosslink densities determined from the swell data. They used the modified-model and the Gauss chain model to predict the correlation between network parameters and mechanical properties. The mechanical properties and the calculated network parameters exhibited excellent linear correlation.

In 2007, Sekkar et al. [9] investigated experimental approaches to determining the crosslink density (CLD) of urethane networks based on the HTPB/TDI system. They calculated the CLD from the swell data based on the Flory-Rehner relationship. The initial slope of the stress-strain curve (Young's modulus) from the tensile test, equilibrium relaxation modulus from the stress relaxation test, Mooney-Rivlin plots, and dynamic mechanical properties were also used to obtain the CLDs. The results indicated a correlation between the mechanical properties and the CLD.

In 2014, Ahmad et al. [10] evaluated the influence of cross-linking/chain extension structures on the mechanical properties of HTPB-based polyurethane elastomers with iso-

phorone diisocyanate. They found that the elastomer with 1,4-butanediol yielded the maximum tensile strength, elongation, and modulus. The polymer with TMP was found to be stronger than that with hexanetriol.

Considerable efforts, as mentioned above, have been taken in connecting the tensile behavior of polymer network with several macroscopic parameters, such as curative parameters. Some mathematical constitutive equations have been built by fitting with these experimental data. However, these equations could not consider the effects of the polymer network, plasticization, and molecular interactions between binder prepolymer and plasticizer on the mechanical response of the matrix detail.

In recent years, the Materials Genome Initiative (MGI) has been one of the highlights in materials science. MGI ultimately intends [11,12] to usher in a new paradigm/culture of materials research and innovation where materials design is conducted by upfront simulations/predictions followed by key validation experiments, in contrast to the current practice that is heavily based on experimental iterations and experiences. MGI aims to discover, develop, manufacture, and deploy advanced materials at twice the speed than is currently possible. The genome of materials is the composition and structure of the materials, including the arrangement modes of atoms and/or molecules, as well as the multi-scale aggregation states (e.g. microcosmic, mesoscopic, and macrocosmic scales). One of the tasks of genetic engineering of materials is to establish the correlation between the properties of materials and the material genomes.

Two ways of obtaining genomes of materials have been identified. One is to determine material genomes from the material databases by data mining. Another is to define the genomes of materials as the key influencing factors affecting the properties of materials on the basis of research experiences in materials science. In this study, the second method was adopted to identify the material genomes.

The mechanical response of the propellant depends on the mechanical characteristics of the solid fillers, polymer matrix, and interface between the fillers and the polymer matrix. Thus, if the constitutive models of the three parts of composite solid propellants are obtained, the tensile mechanical properties of the propellants can be predicted.

This study mainly focuses on establishing the constitutive equation for the polymer matrix composed of the polymer network and the plasticizer in the second way. Key factors including the molecular characteristics of binder prepolymer, curing agent, crosslinking agent and plasticizer, the curing parameters of the polymer network, and the content of the plasticizer, are defined as the genomes of materials.

Within the framework of genetic engineering of materials, in order to quantitatively analyze the tensile behaviour of polymer matrix from the viewpoint of genome of materials, a mathematical and theoretical tensile constitutive relation of the polymer matrix on the basis of the

characteristics of the network and the plasticizer is established in this study.

2 Constitutive Relations for Cross-linked Polymer and Plasticizer

2.1 Constitutive Relation Based on the Gaussian Chain Model

In accordance with polymer physics [13], a simple polymer chain can be regarded as a Gaussian chain, also called a free joint chain. When tensile load acts on a crosslinked polymer material, the constitutive relation can be expressed as

$$\sigma = \frac{1}{3} \rho_{\text{net}} R_0 T \left[(1 + \varepsilon) - \frac{1}{(1 + \varepsilon)^2} \right] \quad (1)$$

where σ and ε denote the stress and strain of the polymer respectively; R_0 is the universal gas constant; T is the temperature of the sample; and ρ_{net} is the density of the crosslink chains in the network.

The aforementioned formula can also be expressed as

$$\sigma = \alpha \cdot \left[(1 + \varepsilon) - \frac{1}{(1 + \varepsilon)^2} \right] \quad (2)$$

where α is the modulus.

When the distortion of the polymer is non-affine, and steric hindrance between the polymer chains is considered, the modulus of the crosslinked polymer can be expressed as

$$\alpha = \frac{1}{3} \rho_{\text{net}} R_0 T \delta_B^2 \left(1 - \frac{2}{f_{\text{CL}}} \right) \quad (3)$$

where f_{CL} is the functionality in the crosslinking agent.

2.2 Coefficient of Steric Hindrance of the Binder Prepolymer

One of the parameters to characterize the flexibility of polymer chains is the coefficient of steric effect, which can be calculated by computational chemistry.

Materials Visualizer, the core module in the software Materials Studio, was used to establish the molecular chains of PBT, the copolymer of 3,3'-bis-azidomethyl-oxetane (BAMO) and tetrahydrofuran (THF) with a fixed molar ratio of BAMO and THF. The molecular chains were then established, as follows: ① one PBT molecular chain is generated randomly; ② 10 PBT molecular chains are generated simultaneously, and geometry optimization is implemented on the configuration of each molecular chain. The steric hindrance parameter of the polymer chains was calculated with the Synthia module in Materials Studio. The calculated

δ_B^2 of PBT with the equal molar ratio of BAMO and THF was 1.463.

2.3 Modulus of the Crosslinked Polymer Network

We chose the key factors as the material genomes for the crosslinked polymer network. These factors include the flexibility of the binder prepolymer, curing parameters and molecular characteristics of the ingredients in the crosslinked polymer network, and the interaction between molecules.

The PBT crosslinked network consisted of the binder prepolymer B-2OH (e.g., PBT) with two terminated hydroxyl groups, the chain extender CE-2OH (e.g., 1,4-butanediol) with two hydroxyl groups, the crosslinking agent CL-3OH (e.g., glycerol) with three hydroxyl groups, and the curing agent CU-2NCO (e.g., TDI) with two isocyanate groups. The binder prepolymer and the chain extender first reacted with the curing agent to increase the length of the binder. The crosslinking agent then reacted with the curing agent in the aforementioned system to form the end crosslinked polymer network.

In the crosslinked polymer network, the chain density of the polymer is the sum of the density of the chemical crosslink ($\rho_{0,\text{net}-\text{ch}}$) and that of the physical crosslink ($\rho_{0,\text{net}-\text{phy}}$)

$$\rho_{\text{net}} = \rho_{0,\text{net}-\text{ch}} + \rho_{0,\text{net}-\text{phy}} \quad (4)$$

2.3.1 Density of Chemical Crosslink Chains in the Crosslink Network

When three functional groups of a crosslinking agent exist in an ideal crosslink network, the formula is given by

$$f_{\text{CL}} \cdot n_{\text{CL}} = 2N_{\text{net}-\text{ch}} \quad (5)$$

where n_{CL} is the number of moles of the crosslinking agent in the network; $N_{\text{net}-\text{ch}}$ is the number of moles of the crosslinked chains.

Thus,

$$\rho_{0,\text{net}-\text{ch}} = \frac{N_{\text{net}-\text{ch}}}{V_0} = \frac{f_{\text{CL}} \cdot n_{\text{CL}}}{2V_0} \quad (6)$$

where V_0 is the volume of the crosslinked polymer network.

We defined the curing parameters of the system as follows. The first curing parameter ($R_{\text{NCO}/\text{T-OH}}$), the equivalence ratio of the isocyanate groups to the total hydroxyl groups, can be expressed as

$$R_1 = R_{\text{NCO}/\text{T-OH}} = \frac{[\text{NCO}]}{[\text{OH}]_T} \quad (7)$$

where $[NCO]$ and $[OH]_T$ are number of moles of the isocyanate groups and the total hydroxyl groups in the system, respectively. The subscript 1 refers to the isocyanate curing agent.

The total number of moles of hydroxyl groups can be calculated as

$$[OH]_T = [OH]_B + [OH]_{CE} + [OH]_{CL} \quad (8)$$

Where $[OH]_B$, $[OH]_{CE}$, and $[OH]_{CL}$ denote the number of moles of hydroxyl groups in the binder prepolymer, chain extender, and crosslinking agent, respectively.

The second curing parameter, the equivalence ratio of hydroxyl groups in the chain extender to the total hydroxyl groups in the system, is

$$R_2 = R_{CE-OH/T-OH} = \frac{[OH]_{CE}}{[OH]_T} \quad (9)$$

where the subscript 2 refers to the chain extender.

The third curing parameter, the equivalence ratio of hydroxyl groups in the crosslinking agent to the total hydroxyl groups in the system, is

$$R_3 = R_{CL-OH/T-OH} = \frac{[OH]_{CL}}{[OH]_T} \quad (10)$$

where the subscript 3 refers to the crosslinking agent.

The forth curing parameter, the equivalence ratio of hydroxyl groups in the binder prepolymer to the total hydroxyl groups in the system, is

$$R_4 = R_{B-OH/T-OH} = \frac{[OH]_B}{[OH]_T} = 1 - R_2 - R_3 \quad (11)$$

where the subscript 4 refers to the binder prepolymer.

After designing the crosslinked system, which indicates that the four curing parameters have been fixed, we can calculate the mass content of each ingredient in the network by using the following formula.

The mass content of the binder prepolymer in the system can be calculated by

$$m_B = \frac{1}{E_{B-OH}} \cdot [OH]_T \cdot R_4 \quad (12)$$

where E_{B-OH} is the value of the hydroxyl groups of the binder prepolymer.

The mass content of the chain extender, crosslinking agent, and isocyanate curing agent in the network can be calculated using

$$m_i = \frac{M_i}{f_i} \cdot [OH]_T \cdot R_i \quad i = 1, 2, 3 \quad (13)$$

where M_i and f_i are the molecular weight and the functionality of the i th ingredient in the network, respectively.

The volume of the crosslinked network can be calculated using the formula

$$V_0 = \sum_{i=1}^4 \frac{m_i}{\rho_i} \quad (14)$$

where ρ_i is the density of the i th ingredient in the system.

Thus, the initial density of chemical crosslinked chains can be expressed as

$$\rho_{0,net-ch,4} = \frac{R_3}{2 \left(\sum_{i=1}^3 \frac{M_i}{\rho_i \cdot f_i} \cdot R_i + \frac{1}{\rho_4 \cdot E_{B-OH}} \cdot R_4 \right)} \quad (15)$$

Therefore, once the formulation of the crosslinked polymer network is fixed, indicating that the type of ingredients and the curing parameters have been selected, the initial density of chemical crosslinked chains can be calculated.

2.3.2 Density of Physical Crosslinked Chains in the Network

We supposed that the physical crosslink between polymer chains in the crosslinked polymer network consisted of twines among polymer chains and action of hydrogen bonds. Thus, the density of physical crosslinked chains can be expressed as

$$\rho_{0,net-phy} = \rho_{0,twine} + \rho_{0,hydrogen-bond} \quad (16)$$

where $\rho_{0,twine}$ and $\rho_{0,hydrogen-bond}$ are the density of the chain twine points and hydrogen bonds in the network, respectively.

In general, the longer the polymer chain between the adjacent crosslink points and the greater the flexibility of the binder prepolymer molecules, the greater the possibility of chain twines. Thus, the density of twine points in the crosslinked polymer system can be expressed as

$$\rho_{0,twine} = C_{twine} \cdot \frac{\bar{M}_C}{\delta_B \cdot V_0} \quad (17)$$

where C_{twine} is constant, and \bar{M}_C is the average molecular weight of the chains between the adjacent crosslink points.

For the B-2OH/CL-3OH/CE-2OH/CU-2NCO system, the chains between the adjacent crosslink points is formed by the reactions of isocyanate curative with the binder prepolymer and chain extender; thus, \bar{M}_C can be calculated using

$$\bar{M}_C = \frac{1}{N_{net-ch} \cdot V_0} \sum_{i=1}^4 m_i \quad i = 1, 2, 4 \quad (18)$$

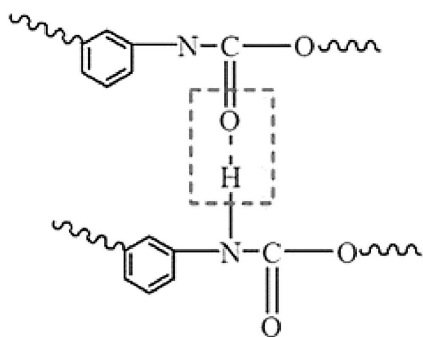


Figure 1. Hydrogen bonds in the B-2OH/CL-3OH/CE-2OH/CU-2NCO system.

The forms of hydrogen bonds in the B-2OH/CL-3OH/CE-2OH/CU-2NCO system are presented in Figure 1.

Therefore, the number of moles of hydrogen bonds is proportional to the content of the isocyanate groups

$$\rho_{0,\text{hydrogen-bond}} = \frac{[\text{OH}]_T \cdot R_1}{V_0} \quad (19)$$

2.4 Effect of the Plasticizer

In the crosslinked polymer and plasticizer system, the plasticizer fulfilled two functions. One was the swelling of the polymer network attributed to the addition of the plasticizer, which reduced the density of the crosslinked chains; the other was to decrease the molecular force between the polymer chains by the plasticizer, which also led to a decrease in the density of twine points in the system.

Thus, in this section, we chose the key factors (the content of the plasticizer and the molecular interaction between the binder prepolymer and the plasticizer) as the material genomes for the plasticizer effect.

The volume of the crosslinked polymer increased when the plasticizer went into the gaps of the crosslinked polymer network because of the swelling action of the plasticizer. The swelling action of the plasticizer depends on the mass ratio of the plasticizer to the binder prepolymer ($R_{p/B}$). The volume fraction of the crosslinked polymer in the crosslink network and the plasticizer (ς_{net}) is calculated using

$$\varsigma_{\text{net}} = V_0 / \left(V_0 + \frac{\sum_{i=1}^4 m_i \cdot R_{p/B}}{\rho_{pi}} \right) \quad (20)$$

where ρ_{pi} is the density of the plasticizer.

If the volume of the crosslinked network without the plasticizer is the unit volume, the volume of the crosslinked polymer and plasticizer system swells to λ_o^3 , which indicates

that the side length of the cube is λ_o . Therefore, the swelling action of the system can be expressed as $\varsigma_{\text{net}}^{1/3}$.

The ability of the plasticizer to decrease the molecular force between the polymer chains depends on the interaction between the polymer and the plasticizer molecules. In the current study, we introduced the interaction parameter (χ_{B-pl}) of the interaction between the polymer and the plasticizer molecules, which can be calculated by Bristow's equation given by

$$\chi_{B-pl} = 0.34 + \frac{\tilde{V}_{pl}}{R_0 T_0} (\kappa_B - \kappa_{pl})^2 \quad (21)$$

where κ_B and κ_{pl} represent the solubility parameter of the binder prepolymer and the plasticizer, respectively, and \tilde{V}_{pl} is the molar volume of the plasticizer, which is equal to the ratio of the molecular weight of the plasticizer to its density.

With Materials Studio, the calculated solubility parameters of PBT and A3 (the mixture of BDNPA and BDNPF with equal mass ratios) plasticizer were 19.96 and 20.90 ($J \cdot \text{cm}^{-3}$)^{1/2} respectively, where BDNPA is (2,2-dinitro-propyl) acetal and BDNPF is (2,2-dinitro-propyl) formal.

Therefore, the density of the crosslinked polymer and plasticizer system can be written as

$$\rho_{\text{net}} = \rho_{0,\text{net-ch}} \cdot \varsigma_{\text{net}}^{1/3} + \rho_{0,\text{net-phy}} \cdot \chi_{B-pl} \quad (22)$$

2.5 Viscoelasticity of the Crosslinked Polymer and Plasticizer

When the strain of the sample is sufficiently large, the viscoelastic characteristic of the polymer system should be considered. From a related theory of polymer physics, such as the Maxwell model for viscoelastic materials, the modulus of the system can be expressed as

$$\alpha = \frac{1}{3} \rho_{\text{net}} R_0 T \delta_B^2 \tau_m \frac{\dot{R}}{L_0} \left(1 - e^{-\frac{L_0}{R \tau_m \dot{e}}} \right) \left(1 - \frac{2}{f_{cl}} \right) \quad (23)$$

where τ_m is the relaxation time, \dot{e} is the strain rate, \dot{R} is the tensile rate in the uniaxial tensile test, and L_0 is the initial length of the sample.

The aforementioned formula considers the actions of both the viscoelastic characteristics of polymer and test conditions, such as tensile rate and temperature.

3 Effect of Parameters on Tensile Properties of Crosslinked Polymer and Plasticizer System

3.1 Effect of Crosslinking Parameter on Tensile Properties of the System

The crosslinked polymer and plasticizer system in this study is the PBT/A3 system with a mass ratio of 1.

To study the accuracy of the model for predicting the stress-strain curves of the system, formulations with different values for R_3 were designed, as shown in Table 1. The samples were subjected to uniaxial tensile testing at 20 °C and tensile rate of 40 mm·min⁻¹. The stress-strain curves of the systems were calculated using the model. The calculated and experimental results are presented in Figure 2.

Each stress-strain curve was divided into 10 equal intervals. The relative errors of the calculated and experimental stress on the stress-strain curve at each point were calculated, as listed in Table 2.

As shown in Figure 2 and Table 2, the calculated results were highly consistent with the experimental ones. Table 2

Table 1. Formulation of the system with different values for R_3 .

| NO. | R_1 | R_2 | R_3 | R_4 |
|-------|-------|-------|-------|-------|
| PBT-1 | 1.0 | 0 | 0.10 | 0.90 |
| PBT-2 | 1.0 | 0 | 0.20 | 0.80 |
| PBT-3 | 1.0 | 0 | 0.30 | 0.70 |

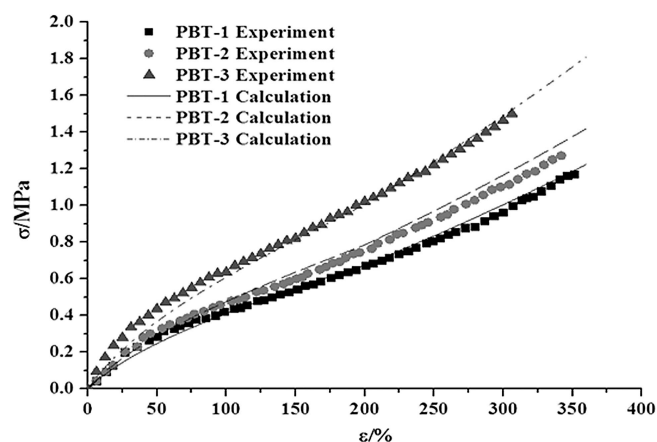


Figure 2. Calculated and experimental stress-strain curves with different chain-extender parameters.

Table 2. Relative errors of calculated and experimental stresses on the stress-strain curves.

| Formulation NO. | Point NO. 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-----------------|----------------|--------|-------|-------|-------|-------|-------|------|------|------|
| PBT-1 | -16.99 | -9.20 | -2.47 | 0.43 | 0.92 | 1.94 | 2.87 | 5.27 | 2.02 | 1.63 |
| PBT-2 | -3.47 | -4.25 | 1.95 | 5.68 | 5.62 | 4.99 | 4.66 | 5.06 | 6.18 | 5.39 |
| PBT-3 | -24.22 | -12.12 | -8.95 | -3.72 | -0.97 | -1.73 | -0.24 | 0.68 | 1.82 | 1.70 |

Table 3. Formulations of the system with different values for R_2 .

| NO. | R_1 | R_2 | R_3 | R_4 |
|-------|-------|-------|-------|-------|
| PBT-4 | 1.0 | 0.57 | 0.08 | 0.35 |
| PBT-5 | 1.0 | 0.66 | 0.07 | 0.27 |
| PBT-6 | 1.0 | 0.75 | 0.05 | 0.20 |

includes 30 data points. Only one of the relative errors was greater than 20%, one was in the 15%–20% range, another was in the 10%–15% range, and 27 were less than 10%. About 93.33% of the relative errors were less than 15%. The strain-softening point and the strain-hardening point were crucial points on the stress-strain curve. At the strain-softening point, the maximum relative errors of stress and strain on the three curves were -10.34% and 17.12%, respectively; at the strain-hardening point, these errors were 25.00% and 18.86%, respectively. The model exhibited satisfactory accuracy for predicting the stress-strain curves of the crosslinked polymer and plasticizer system.

When the crosslinking parameter increased, the crosslink density of the polymer network increased, leading to an increase in the stress of the samples and a decrease in the strain at breakpoint.

3.2 Effect of Chain-extender Parameter on the Tensile Properties of the System

Formulations with different values for R_2 were designed, as listed in Table 3. The stress-strain curves of the systems were generated, and the calculated and experimental results are shown in Figure 3.

As shown in Figure 3, the calculated results were reasonably consistent with the experimental ones.

Meanwhile, when the chain-extender parameter increased, the crosslink density of the polymer network decreased, thereby reducing the stresses of the samples.

On the basis of the model, the effects of the curing parameter, tensile rate, and test temperature on the tensile mechanical responses of the system can also be evaluated. Some results are shown in Figure 4 and 5.

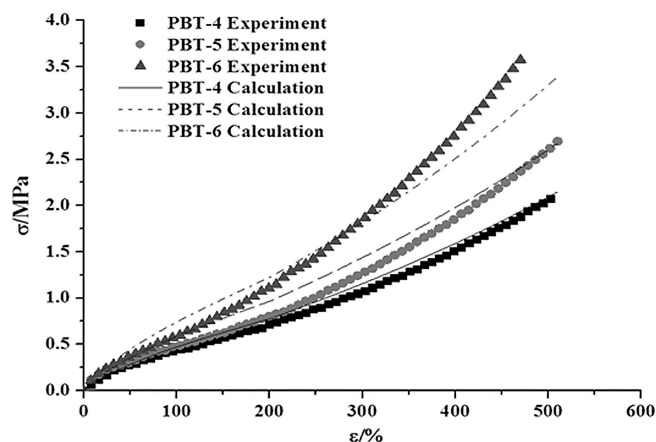


Figure 3. Calculated and experimental stress-strain curves with different crosslink parameters.

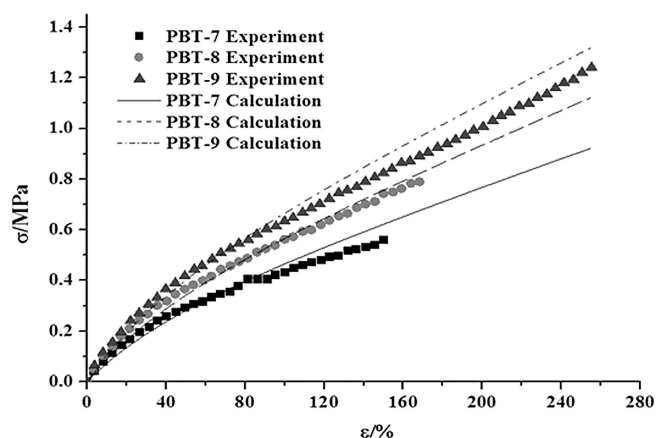


Figure 4. Calculated and experimental stress-strain curves with different values for R_1 .

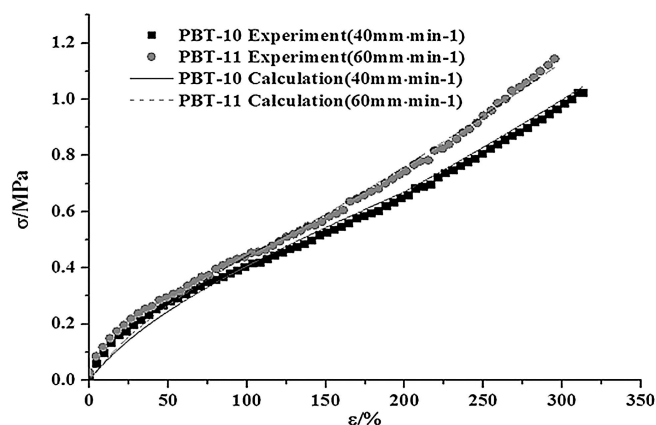


Figure 5. Calculated and experimental stress-strain curves with different tensile rates.

4 Conclusion

Uniaxial tensile constitutive models of the crosslinked polymer and plasticizer were established based on the characteristics of the network and plasticization by genetic engineering of materials. The key factors affecting the mechanical properties of the polymer matrix were chosen as the material genomes. The correlations of the uniaxial tensile properties with the material genomes were obtained.

For the crosslinked polymer with no plasticizer, the constitutive model was related not only to the molecular characteristics of the ingredients, such as the flexibility of the binder prepolymer and the degree of activity of the functional groups in the ingredients, but also the curing parameters. On the basis of the constitutive relation of the crosslinked polymer, the constitutive model of the crosslinked polymer and plasticizer was related to the volumetric fraction of the plasticizer and the interaction between the binder prepolymer and the plasticizer molecules. In the range of viscoelastic deformation during tensile testing, the viscoelastic characteristics of the network were considered in the model.

The predicted and experimentally measured stress-strain curves under uniaxial tensile loading showed consistency. The model satisfactorily predicted the stress and strain response.

References

- [1] S. Y. Ho, High strain-rate constitutive models for solid rocket propellants. *J. Propul. Power*, **2002**, 18 1106–1111.
- [2] M. C. J. van Ramshorst, G. L. Di Benedetto, W. Duvalois, P. A. Hooijmeijer, A. E. D. M. van der Heijden, Investigation of the failure mechanism of HTPB/AP/Al propellant by in-situ uniaxial tensile experimentation in SEM. *Propellants Explos. Pyrotech.*, **2016**, 41, 700–708.
- [3] L. Zhang, S. Zhi, Z. B. Shen, Research on tensile mechanical properties and damage mechanism of composite solid propellants. *Propellants Explos. Pyrotech.*, **2018**, 43, 234–240.
- [4] S. J. Zhi, F. Q. Cao, Z. B. Shen, G. Q. Xing, J. W. Cao, Parameters inversion of particle dewetting damage of composite solid propellants. *J. Prop. Tech.* **2016**, 37, 1977–1983. (In Chinese)
- [5] R. Manjari, U. I. Somasundaran, V. C. Joseph, T. J. Sriram, Structure-property relationship of HTPB-based propellants.II. Formulation tailoring for better mechanical properties. *J. Appl. Polym. Sci.*, **1993**, 48, 279–289.
- [6] R. Manjari, L. P. Pandureng, U. I. Somasundaran, T. J. Sriram, Structure-property relationship of HTPB-based propellants.III. Optimization trials with varying levels of diol-triol contents. *J. Appl. Polym. Sci.*, **1994**, 51, 435–442.
- [7] V. Sekkar, S. Gopalakrishnan, K. Ambika Devi, Studies on allophanate-urethane networks based onhydroxyl terminated polybutadiene: effect of isocyanatetype on the network characteristics. *Eur. Polym. J.*, **2003**, 39, 1281–1290.
- [8] V. Sekkar, K. Narayanaswamy, K. J. Scariah, P. R. Nair, K. S. Sastri, H G. Ang, Studies on urethane-allophanate networks based on hydroxyl-terminated polybutadiene: modeling of network pa-

- rameters and correlation to mechanical properties. *J. Appl. Polym. Sci.*, **2006**, *101*, 2986–2994.
- [9] V. Sekkar, K. Narayanaswamy, K. J. Scariah, P. R. Nair. Evaluation by various experimental approaches of the crosslink density of urethane networks based on hydroxyl-terminated polybutadiene. *J. Appl. Polym. Sci.*, **2007**, *103*, 3129–3133.
- [10] N. Ahmad, M. B. Khan, X. Ma, N. Haq. The influence of crosslinking/chain extension structures on mechanical properties of HTPB-based polyurethane elastomers. *Arabian J. Sci. Eng.* **2014**, *39*, 43–51.
- [11] Materials Genome Initiative for Global Competitiveness [EB/OL]. 2001. http://www.mgi.gov/sites/default/files/documents/materials_genome_initiative-final.pdf.
- [12] J. Zhao, A perspective on the materials genome initiative. *Chinese J. of Nature*, **2014**, *36*, 91–104. (In Chinese)
- [13] F Tanaka. Polymer Physics. *Cambridge University Press*, The Edinburgh Building, Cambridge CB28RU, UK. **2011**.

Manuscript received: December 25, 2018
 Revised manuscript received: March 21, 2019
 Version of record online: August 16, 2019