Experimental investigation and modeling of mechanical behaviors of polyurea over wide ranges of strain rates and temperatures

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Abstract: Theoretical and experimental studies on the compressive mechanical behavior of two formulations of polyurea under uniaxial stress state and quasi-one dimensional strain state are conducted over the temperature range of -40°C -+20°C and the strain rate range of 0.001/s-12000/s. The stress-strain behavior of polyurea samples is established at different strain rates and temperatures, and key mechanical properties of the materials are determined. The experimental results show the significant sensitivity of compressive stress-strain curves of polyurea to strain rate and temperature within and beyond linear viscoelastic regime. In addition, the mechanical properties of PU605 (Versalink P-650 reacted with 105% molar equivalent Isonate 143L) are compared to those of PU105 (Versalink P-1000 reacted with 105% molar equivalent Isonate 143L). Based on the experimental results with confined pressure, a calculation method is presented which is available to study the bulk modulus of polyurea. Finally, a visco-hyperelastic constitutive model is developed to describe the nonlinear mechanical behavior of polyurea over a wide range of strain rates and temperatures.

Key words: Polyurea; Rate-dependence; Temperature-dependent; Confined pressure; Bulk modulus

1. Introduction

Improving the performance of protective structures against failure due to high rate loadings, including but not limited to blast and impact, has been on the forefront of materials research for a long time. However, the use of soft elastomeric coatings for the purpose of minimizing structural collapse, fragmentation, and erosion is comparatively a new endeavor. For example, recent studies have shown that applying a layer of polyurea backing to metal and other stiff plate-like structures significantly enhances the resistance to the impulsive loadings [1-3]. But up to now, the anti-impact mechanism of polyurea is still lack of study in depth and systematically. Only a few speculations include: (1) the elastomer layer delaying the onset of necking behavior of the metal in metal-elastomer bilayer plates [4, 5]; (2) the polyurea layer changing the propagation of stress wave and redirecting the energy [2, 6, 7, 8]; (3) the transition of polyurea between its rubbery-state and its glassy-state under high deformation-rate loading conditions improving the ballistic impact resistance of polyurea-coated structures/test plates [9, 10]. Therefore, the systematic study on the nonlinear mechanical behavior of polyurea at different strain rates has important significance for further design and optimization efforts.

Polyurea is a viscoelastic material; while it demonstrates behavior similar to hyperelastic materials especially at large deformations. With the increasing application of polyurea as coating more scholars have looked at its mechanical properties at high strain rate and large deformations. Yi et al. [11] studied the compressive mechanical properties of one polyurea and three polyurethane samples using the split Hopkinson pressure bar system. These samples demonstrated highly non-linear stress-strain relationships, indicating strong hysteresis and rate dependency. Subsequently, Sarva et al. [12] studied the mechanical properties of polyurea samples over a wide range of strain rates, from 10^{-3} to 10^4 s^{-1} , and found that the stress-strain curves of polyurea indicated a transition from rubber-like behavior at low strain rates to leather-like behavior at high strain rates. Meanwhile, Shim et al. [13] studied the

compressive mechanical properties of polyurea at the strain rate ranges from $10^3/s$ to $10^1/s$, and confirmed the strain rate sensitivity of the compressive stress-strain behavior of polyurea. In addition, Roland et al. [14] carried out the stress-strain measurements of polyurea in uniaxial tension over a range of strain rates from $0.06/s$ to $573/s$, and obtained some available tensile data. More recently, Shim et al. [15] reported the findings of relaxation tests, continuous and multi-step compression tests over a range of strain rates from $10^{-3}/s$ to $10^1/s$, and developed a rate-dependent viscoelastic constitutive model. Amirkhizi et al. [16] also produced a model that separated the volumetric thermo-elastic response from a non-linear viscoelastic shear behavior based on time-temperature superposition and including the pressure effect on shear behavior. However, a comprehensive study on the failure mechanism of polyurea, including multiaxial loading, and coupling effects of strain rate and pressure is still needed.

The present paper examines the compressive mechanical properties of two kinds of polyurea under uniaxial stress state and quasi-one dimensional strain state. To this end, the systematic experiment research on the mechanical behavior of polyurea at the temperature range of $-40^{\circ}C$ - $+20^{\circ}C$ and the strain rate range of $0.001/s$ - $12000/s$ are carried out by a DNS-100 electric universal testing machine and an enhanced split-Hopkinson pressure bar. To ensure the accuracy of experimental results, several important factors that affect the experimental results are studied by numerical simulation and theoretical derivation. Finally, the deformation mechanism and mechanical characteristics of the samples observed in the experiment are analyzed and discussed in this paper.

2. Experimental protocol

2.1. Materials

The polyurea materials tested in this research is fabricated at the Center of Excellence for Advanced Materials, University of California, San Diego and University of Massachusetts, Lowell. The polyurea is formed by the reaction of multifunctional aromatic isocyanate component (Isonate 143L from Dow Chemical; 144.5 g/eq. mol.) and high molecular weight amine-terminated resin blend component (Versalink P-650 or Versalink P-1000; Air Products). Table 1 lists the compositions of polyurea materials in this paper. The chemical compositions for the polyurea materials are changed from sample to sample to provide different hard segment ratios. In theory, a urea group $-(NH)(CO)(NH)-$ is synthesized by the reaction of an isocyanate group $(-NCO)$ and an end amino group $(-NH_2)$. Therefore, the total number of isocyanate functional group should equal the total number of end amino functional group, i.e., the two components should be mixed in a stoichiometric ratio of 1:1. However, in most polyurea formulations, five percent excess of the isocyanate component is used beyond the stoichiometric ratio based on the manufacturers' recommendations. The research shows that this slight excess isocyanate can ensure the completion of reaction between isocyanate component and end amine component [17]. Thus, the component ratio of polyurea materials is selected as 1.05 in this paper. The glass transition temperature of polyurea materials is usually below $-50^{\circ}C$, however, the operating temperature is usually above $-50^{\circ}C$. Therefore, this paper mainly focuses on the mechanical behavior of polyurea materials in the rubbery regime.

Table 1 Polyurea samples composition

Sample	Chain extender			Component molar ratio [NCO/NH ₂]
	Isonate 143L (mol %)	Versalink P650 (mol %)	Versalink P1000 (mol %)	
PU605	51.2	48.8		1.05
PU105	51.2		48.8	1.05

2.2. Experimental techniques

In order to cover a wide range of loading speeds, material tests are conducted on two types of testing machines: (1) an electric universal testing machine for low strain rate tests; (2) an enhanced split Hopkinson pressure bar system (SHPB) for high-rate tests. The finite deformation stress–strain behavior of polyurea at different strain rates is evaluated by unconfined pressure test (uniaxial stress state) and confined pressure test (quasi-one dimensional strain state).

2.2.1. Low strain rate experimental technique

The low rate compression tests are performed using a DNS-100 electric universal testing machine under conditions of constant nominal strain rate. During the loading process, the DNS-100 electric universal testing machine measures the displacements by automatic recording the movement distance of the crossbeam, and acquires the compressive load by high precision pulling and pushing dual-purpose load transducer installed on the crossbeam. The measuring range of compressive load is 2%~100% of the sensor capacity and the precision of the sensor is 0.5%. Specimens are compressed between hardened steel compression platens to overcome any small misalignment along the load train. Lubrication (molybdenum disulfide) is applied on the surfaces of both upper and lower platens to eliminate friction and prevent inhomogeneous deformation. In the quasi-static regime, the assembly diagram of the samples under the unconfined and confined pressure tests is shown in Fig.1. For quasi-static compression testing, the dimension of the samples is designed as cylindrical, with a diameter of 12.7 mm and a length of 5 mm. Based on the collected data from testing machine and the geometric size of specimen, the stress-strain curves of test materials are obtained by mathematical calculation method at low strain rates.

2.2.2. High strain rate experimental technique

The high strain rate compression tests are performed using an enhanced split-Hopkinson pressure bar technique developed by Nemat-Nasser et al. [18]. The SHPB apparatus is shown in Fig.2. The gages for strain history recordings are positioned near the center of the input bar and near the output bar/specimen interface. This system employs chromium-nickel steel pressure incident and transmission bars in order to conduct the high strain rate testing (12.7mm diameter, striker bar length=0.1m, incident bar length=1.2m, transmission bar length=1m). A thin layer of petroleum jelly is applied on both sides of the specimen and the end faces of the incident bar and the transmission bar to lubricate the contact surfaces, so that a homogeneous deformation state is achieved. Copper discs are used as pulse shapers to help improve dynamic equilibrium and also dampen the high frequency

components in the stress pulses thus reducing dispersive effects [12]. The influence of pulse shapers on incident wave is shown in Fig.3. As seen in the figure, the incident wave without pulse shapers contains a large number of higher-frequency vibration components, and accompanied by a serious dispersion effect. The rising time of the incident wave with pulse shapers is 17μs, which is advantageous to realize a uniform stress state of the samples during impact.

The sample thickness used in an SHPB dynamic test is constrained by the need to assure a uniform stress state for accurate and reproducible constitutive data. Previous research illustrates the need to use lower sample aspect ratios (l/d) when studying the entire high-strain-rate constitutive response of low-sound-speed polymer materials [19, 20]. ASM Handbook and the related literatures suggest that the polymer sample aspect ratios range (l/d) of 0.25 to 0.5 can be effective in minimizing wave attenuation while also keeping frictional effects under control [20, 21]. In addition, the inertial effect and frictional effect of the test samples increases as the diameter increases. The wave impedance of the test samples decreases as the diameter decreases, which leads to the low signal-to-noise ratio of transmission signals. Therefore, the diameter of the test samples should be neither too big nor too small. For dynamic compression testing, the dimension of the samples used in unconfined pressure test is designed as Φ6mm×2mm, and the dimension used in confined pressure test is designed as Φ12.7mm×5mm. In order to ensure the internal stress field of the sample to reach the equilibrium state in SHPB dynamic test, the ABAQUS finite element software is used to analyze the stress field of the two kinds of samples. The distribution of the equivalent stress along the thickness of the sample is shown in Fig.4. The stress field distribution depicted in Fig.4 shows the time needed for stress field to reach an equilibrium state is approximate to 14μs in unconfined pressure test, and is approximate to 15μs in confined pressure test. The time under the two conditions is less than the rising time of the incident wave (17μs). Therefore, the samples can reach a stress equilibrium state at the rising stage of the incident wave, which can guarantee the reliability of experimental data.

Assuming wave propagation within the bars is one dimensional, when the stress within a specimen has reached a uniform state, the axial stress and axial strain calculated based on elastic wave theory are given by

$$\sigma_z = \frac{EA}{A_s} \varepsilon_T(t) \quad (1)$$

$$\varepsilon_z = \frac{2C_0}{l_0} \int_0^t [\varepsilon_I(\tau) - \varepsilon_T(\tau)] d\tau \quad (2)$$

where E and C₀ are the Young's modulus and the elastic wave velocity of the input/output bar material, A is the cross-sectional area of the input/output bars, A_s and l₀ are the cross-sectional area and the initial length of polyurea samples, ε_I is the incident pulse in the input bar, and ε_T is the transmitted pulse in the output bar.

2.2.3. Confined pressure test technique

A steel tube with an internal diameter close to the test samples' external diameter plus a very small tolerance is used to restrict the lateral movement of the samples in the confined pressure test. The schematic view of the confining tube device is shown in Fig.2. The material used for the confining tube is 60Si2Mn spring steel (yield

strength σ_s (MPa): ≥ 1176). The post-experiment visual inspection of the confining steel tube shows no permanent damage or plastic deformation of the confining steel. In addition, the experiment data indicate that the maximum stress values of the confining steel tube under different loading conditions are less than 600MPa, far lower than its yield strength. This confined test provides a nearly pure hydrostatic pressure loading condition and a measure of the bulk modulus of polyurea materials.

In the confined test, transverse radial stress is developed in the sample under axial compression due to the Poisson's effect and the presence of the confining steel tube. This stress can be indirectly measured using a hoop strain gage placed on the outside surface of the tube. For an infinitely long tube, elasticity theory gives a closed form for radial stress

$$\sigma_r = \frac{R^2 - r^2}{2r^2} E_c \varepsilon_\theta \quad (3)$$

where R is the external diameter of the confining pressure tube, r is the internal diameter, E_c is the elastic modulus of the confining pressure tube, and ε_θ is the hoop strain on the outer surface of the confining tube. The radial strain of polyurea samples is also given as

$$\varepsilon_r = \frac{\sigma_r}{E_c} \left[1 - \nu_c \frac{R^2 + r^2}{R^2 - r^2} \right] \quad (4)$$

where ν_c is the Poisson's ratio of the confining pressure tube. Chakkarapani et al. [22] used the above theory to evaluate the multiaxial compressive behavior of a polyurea. Qvale et al. [23] used the same theory to evaluate the influence of pressure on the relaxation behavior of polymers. However, when the length of the polyurea sample is small compared to the radius, the relation between the hoop strain at the tube surface and the radial stress in the sample is not trivial. Amirkhizi et al. [24] used LS-DYNA to derive a numerical relationship to correct Eq. (1) for the finite length of the sample. The general form of the relationship between the hoop strain and the radial stress can be expressed as

$$\sigma_r = b E_c \varepsilon_\theta \quad (5)$$

where b is a constant related to sample and tube geometries and the elasticity of the tube. For the experimental conditions in this paper (hoop strain gage width 2mm, steel confinement tube OD=25.4mm, ID=12.7mm, sample nominal length 5mm center aligned with the strain gage), the results of finite element elastic analysis using LS-DYNA indicated that a value of $b=3.245$ should be used. The FE analysis also gives an estimate for average radial strain in the sample which is of 2 orders of magnitude smaller than the axial strain for the current experimental conditions and sample properties and will be neglected in the following analysis.

For the confined compression test, the hydrostatic pressure of polyurea samples can be expressed as

$$\sigma_m = \frac{1}{3} (\sigma_z + 2\sigma_r) \quad (6)$$

where σ_z is the axial stress of polyurea samples. Assuming zero radial strain is a good approximation to the state of

strain, and a similar approach has also been used in [24, 25]. Therefore, the volumetric strain of polyurea samples can be simplified as

$$\varepsilon_m = (1 + \varepsilon_z)(1 + \varepsilon_r)^2 - 1 \approx \varepsilon_z + 2\varepsilon_r \approx \varepsilon_z \quad (7)$$

where ε_z is the axial strain of polyurea samples. The secant bulk modulus of the materials is finally obtained as

$$\kappa = \frac{\sigma_m}{\varepsilon_m} \quad (8)$$

2.2.4. Cryogenic test technology

In order to study the mechanical properties of polyurea from room temperature to the glass transition temperature, a simple and convenient liquid nitrogen refrigeration equipment is designed, which can realize the low temperatures range from -100°C to +20°C. The low temperature environmental test equipment is shown in Fig.5. When the resistance wire in liquid nitrogen jar is connected, the liquid nitrogen is easy to be heated and gasified by the lower boiling point, and then the cold nitrogen gas is communicated into the environmental chamber through a rubber tube. The digital temperature indicator is used to monitor the real-time temperature change in the environmental chamber, and control the nitrogen flow by regulating the voltage at both ends of the resistance wire. Due to the low thermal conductivity of polyurea material, in order to ensure that the internal temperature of the samples is constant, the temperature in the environmental chamber will continue to keep for about 15 minutes after the temperature reaches the set temperature. In this paper, the compression experiments are conducted at the temperatures range from -40°C to +20°C.

3. Results and discussion

3.1. Quasi-static compression properties

The force and displacement time histories of polyurea at low strain rates are obtained from the data acquisition system of the Instron testing system. Subsequently, these data sets are utilized to compute the stress-strain characteristics of the materials. In this paper, true stress-strain is used, where true stress is the load divided by current cross sectional area and true strain is the natural logarithm of the ratio of current height to initial height; current cross-sectional area is calculated based on the assumption that polyurea is a (nearly) incompressible material [11, 36]. In the quasi-static regime, the representative true stress-strain curves for the polyurea samples as obtained from the unconfined and confined pressure test are shown in Figs.6 and 7. The hydrostatic pressure-volumetric strain curves of polyurea at confined pressure are shown in Fig.8. Meanwhile, the bulk modulus, k , for each material is calculated from these tests and listed in Fig.8.

The results show that the quasi-static behavior of polyurea under uniaxial compression is rate dependent and highly non-linear. However, the axial stress-strain relationship for polyurea as obtained from the confined pressure test is weaker on rate dependence and approximately linear. In addition, the quasi-static compressive mechanical properties of PU605 (Versalink P-650 reacted with 105% molar equivalent Isonate 143L) are stiffer than those of

PU105 (Versalink P-1000 reacted with 105% molar equivalent Isonate 143L), as shown in Figs.6 and 7. Under uniaxial stress state, the failure stress of PU605 is two to three times that of PU105. According to the analysis of the stress-strain curves of polyurea at different strain rates, it can be found that the stress value at the same deformation amount increases as the strain rate increases.

The experimental data depicted in Fig.6 shows the uniaxial compressive stress-strain curves of polyurea at low strain rates have the obvious characteristics of three stages, namely the linear elastic stage, the high elastic stage and the densification stage. In the linear elastic regime, the stress increases nearly linearly with the increasing strain. The stress-strain relationship of the materials satisfies approximately Hooke's law. At the end of this regime, there is no obvious yield point observed, but clearly a transition happens to a plateau region. In this region, the materials experience large deformation with a marginal increase in the applied stress. Because the molecular chain of polyurea under compressive deformation tends to gather together. The larger the strain is, the more compact the molecular chain is. When the molecular chain has been very tight; the stress required for continuing to produce deformation has a sharp increase. Therefore, the slope of the stress-strain curve of polyurea in the densification stage becomes increasingly large.

In order to investigate the effect of hydrostatic pressure on the deformation behavior of polyurea, this paper further analyzes the mechanical properties of polyurea at low strain rates and confined pressure, and gives a much stiffer set of stress-strain curves as shown in Fig.7. All curves have contained a small lead region until the specimen makes full radial contact with the confinement chamber; this region is removed from the data shown. According to the analysis of the axial stress-strain curves of polyurea at low strain rates and confined pressure in Fig.7, it can be found that the axial stress-strain curves of the materials have a certain strain rate strengthening effect, and keep ascending nearly linearly. The stress of polyurea at confined pressure is obviously higher than that of the materials at unconfined pressure. It means that the strength properties of the materials in quasi-one dimensional strain state (hydrostatic pressure components) are greatly improved, that is, the effect of confined pressure changes the deformation mechanism of the materials [11]. Based on the mathematical derivation methods in Section 2.2, the hydrostatic pressure-volumetric strain relationship of polyurea at confined pressure is calculated as shown in Fig.8. Meanwhile, the bulk modulus for each material is evaluated and labeled on each plot. Fig.8 shows that the bulk modulus of polyurea at low strain rates and confined pressure is sensitive to strain rate. In addition, for a given strain rate, the bulk modulus of PU605 (Versalink P-650 reacted with 105% molar equivalent Isonate 143L) is close to that of PU105 (Versalink P-1000 reacted with 105% molar equivalent Isonate 143L).

3.2. High strain rate compression properties

Yi et al. and Sarva et al. [11, 12] studied systemically the compression deformation mechanism of polyurea at the strain rate ranges from $10^{-3}/s$ to $10^4/s$, and found that polyurea undergoes transition from a rubbery-regime behavior at the low rates to a glassy-regime behavior at the highest rates. Zhang et al. and Wang et al. [26, 27] studied the compressive behavior of polymer materials at different temperatures, and found that the mechanical

properties of the materials are sensitive to temperature and strain rate in a comparable manner. In addition, the relevant literatures of polymer viscoelasticity showed that polymer would undergo transition from a glassy-regime behavior to a rubbery-regime behavior as the temperature increases [11, 27]. In order to investigate the deformation behavior of polyurea at high strain rates and different temperatures, the dynamic compressive experiments are performed under unconfined pressure (uniaxial stress state) and confined pressure (quasi-one dimensional strain state). For nominal strain rate of 12000/s, the uniaxial compressive stress-strain curves of two kinds of polyurea at different temperatures are shown in Fig.9. The axial stress-strain curves of two kinds of polyurea with the strain rate of 4000/s under different temperatures in the confined configuration are shown in Fig.10.

As seen in a comparison of the experimental data of PU605 and PU105 at different temperatures (Figs.9 and 10), it can be found that the dynamic compressive mechanical properties of PU605 are stiffer than those of PU105. The molecular chain of polyurea is composed of soft segment and hard segment, and the molecular formula of soft segment is $[C_4H_8O]_n$. The n value in the molecular chain of PU605 and PU105 are approximately 9 and 14, respectively. Therefore, compared with that of PU605, the molecular weight of soft segment in the molecular structure of PU105 is higher, which explain that the ability of PU105 to resist external forces is lower. In addition, the stress-strain curves of two formulations of polyurea at different temperatures demonstrate the similar shape feature, as shown in Figs.9 and 10, so this paper mainly uses the deformation curves of PU605 to analyze the compressive mechanical properties of polyurea materials over wide ranges of strain rates and temperatures. Under uniaxial stress state, the typical stress-strain curves of PU605 with the strain rate of 12000/s at four different temperatures are shown in Fig.11. Under quasi-one dimensional strain state, the typical axial stress-strain curves of PU605 with the strain rate of 4000/s at four different temperatures are shown in Fig.12. The hydrostatic pressure-volumetric strain curves of PU605 under different temperatures in the confined configuration are shown in Fig.13. The bulk modulus, κ , for the material is calculated from these tests and listed in Fig.13. In addition, the uniaxial compressive stress-strain curves of PU605 at high strain rates are presented in Fig.14.

The above results show that the stress-strain behavior of polyurea in the high strain rate regime is sensitive to temperature and strain rate. The experimental data depicted in Figs.11 and 12 shows that for the typical given high strain rate, the flow stress value corresponding to the same deformation amount increases as the temperature decreases, and the hardening-resistance behavior becomes more remarkable. It can be found from Fig.11 that when the temperature decreases from +20°C to -40°C, the true stress-strain curves of polyurea hardens significantly. This transition region is observed to be consistent with the glass transition temperature range, measured using dynamic mechanical analysis in [28]. According to the analysis of the confined axial stress-strain curves of polyurea at different temperatures in Fig.12, it can be found that the stress-strain relationship of polyurea under quasi-one dimensional strain state is less sensitive to temperature compared to that of the materials under uniaxial stress state, and yield-like behavior is not observed. In addition, Fig.13 shows the bulk modulus of polyurea at high strain rates and confined pressure is sensitive to temperature. For a given strain rate, the bulk modulus of polyurea

decreases as the temperature increases. Fig.14 plots the uniaxial compressive stress-strain curves of polyurea at different strain rates at constant initial temperature. It can be seen from Fig.14 that the flow stress value corresponding to the same deformation amount increases with increasing strain rate. In addition, according to the comparative analysis of the stress-strain curves of the materials at different strain rates in Figs.6 and 14, it can be drawn that the mechanical behavior of polyurea hardens significantly from low strain rates to high strain rates.

4. Constitutive model

Because of the complexity of the mechanical properties and microstructures of polyurea, the analysis on the anti-impact properties of the materials is increasingly dependent on numerical methods; however, whether or not the numerical method is accurate mainly depends on the constitutive model used. The experimental observations presented in Section 3 indicate that the mechanical behavior of polyurea under finite deformation is rate-dependent, temperature-dependent and highly non-linear. To describe the finite deformation nonlinear mechanical behavior of polyurea, a rate-dependent and temperature-dependent visco-hyperelastic constitutive model is established. Following Yang et al. and Guo et al. [29, 30], the stress-strain response of rubber-like materials arises from a combination of hyperelasticity and viscoelasticity, so the stress response of polyurea under the compressible condition can be represented as

$$\sigma = \sigma_e + \sigma_v \quad (9)$$

where σ is the Cauchy stress tensor, σ_e and σ_v are the hyperelastic part and the viscoelastic part of the Cauchy stress tensor, respectively.

The hyperelastic part of the Cauchy stress tensor can be described by the following constitutive relation

$$\sigma_e = 2I_3 \frac{\partial W}{\partial I_3} + 2 \left[\frac{\partial W}{\partial I_1} + I_1 \frac{\partial W}{\partial I_2} \right] B - 2 \frac{\partial W}{\partial I_2} B^2 \quad (10)$$

where W is the strain energy function, B is left Cauchy-Green deformation tensor, I_1 , I_2 and I_3 are the three invariants of B , which can be defined as

$$\begin{aligned} I_1 &= \text{tr}(B) = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 &= 1/2 \left[I_1^2 - \text{tr}(B^2) \right] = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_1^2 \lambda_3^2 \\ I_3 &= \det(B) = \lambda_1^2 \lambda_2^2 \lambda_3^2 \end{aligned} \quad (11)$$

where λ_1 , λ_2 and λ_3 are the principal stretches of the materials in the loading direction. For the assumption of incompressibility of rubber-like materials, $I_3=1$. Based on the analysis of Brown [31, 37], the strain energy density can be represented as a function of a polynomial series involving (I_1-3) and (I_2-3) . In this paper, the two order strain energy density is considered here with the following form

$$W = C_1 (I_1 - 3) + C_2 (I_2 - 3) + C_3 (I_1 - 3)(I_2 - 3) \quad (12)$$

where C_1 , C_2 and C_3 are the material constants. Considering the loading conditions of the samples, the principal stretches of the materials under uniaxial compression and tension can be expressed as $\lambda_1=\lambda$, $\lambda_2=\lambda_3=\lambda^{-1/2}$, where

$\lambda=1+\varepsilon$. By substituting Eq. (12) into Eq. (10), the constitutive relation for the hyperelastic response can be derived as follows

$$\sigma_e = 2(\lambda - \lambda^{-2}) [C_1 \lambda + C_2 + C_3 (I_1 - 3) + C_3 \lambda (I_2 - 3)] \quad (13)$$

For the viscoelastic part of the Cauchy stress tensor, the stress response depends not only on the current state of strain, but also on the past history of strain. That is to say, the viscoelastic strain energy density depends on the specific time and rate [32, 33]. Following the analysis conclusion obtained by Truesdell and Bernstein [34, 35], the constitutive relation for the viscoelastic response can be derived as follows

$$\begin{aligned} \sigma_v = & 2\lambda^2 \int_0^t \lambda \left[C_4 + C_5 (2\lambda^{1/2} + \lambda^{-1} - 3) \right] \exp\left(-\frac{t-\tau}{C_6}\right) \dot{\lambda} d\tau \\ & + \lambda^{-1} \int_0^t \lambda^{-2} \left[C_4 + C_5 (2\lambda^{1/2} + \lambda^{-1} - 3) \right] \exp\left(-\frac{t-\tau}{C_6}\right) \dot{\lambda} d\tau \end{aligned} \quad (14)$$

where C_4 and C_5 are the material constants, and C_6 is the relaxation factor. The visco-hyperelastic constitutive model of polyurea under finite deformation can be obtained by inserting Eqs. (13) and (14) into Eq. (9).

The experimental results of polyurea at different strain rates are fitted by the above model, and the model parameters are obtained as shown in Table 2. Fig.15 shows a comparison with the experimental results. All comparisons give a reasonable fit to the experimental results, which indicates that the visco-hyperelastic model is suitable to describe the dynamic mechanical response of polyurea over a wide range of strain rates.

Table 2 The optimal model parameters determined by the least square method					
C_1 (MPa)	C_2 (MPa)	C_3 (MPa)	C_4 (MPa)	C_5 (MPa)	C_6 (μ s)
1.29	-0.16	0.062	5.19	4.25	6.8

The experimental results show that temperature has a certain effect on the mechanical behavior of polyurea. In order to further analyze the temperature effect of polyurea material, the stress-temperature relation curves at four different strain levels are obtained, as shown in Fig.16. Through the fitting analysis, it can be seen that the stress-temperature relationship can be described as the following formula

$$\sigma(\varepsilon, \dot{\varepsilon}, T) = \frac{\sigma_{ref}(\varepsilon, \dot{\varepsilon})}{1+a(T-T_{ref})} \quad (15)$$

where a is the material constant related to temperature, σ_{ref} is the stress of the materials at reference temperature, and T_{ref} is the reference temperature. In this paper, $T_{ref}=20^\circ\text{C}$. The thermal-visco-hyperelastic constitutive equation can be obtained by inserting Eq.(9) into Eq.(15). In order to examine the validity of Eq.(15), the dynamic mechanical behavior of polyurea with the strain rate of 12000/s is used as an example. At reference temperature, the material parameters of σ_{ref} can be obtained by Table 2, the material parameter a is determined by the stress-strain curves at other temperatures. The comparison between model predictions and experimental results is shown in Fig.17. The calculated value is: $a=0.0058$.

As shown in Fig.17, the theoretical prediction is in good agreement with the experimental data. Therefore, the

new proposed thermal-visco-hyperelastic constitutive model is suitable to describe the finite deformation behavior of polyurea in a certain temperature range.

5. Conclusions

The systematic experiment research on the mechanical properties of polyurea at the temperature range of -40°C – $+20^{\circ}\text{C}$ and the strain rate range of 0.001/s–12000/s are carried out in this paper. The deformation mechanism and mechanical characteristics of the materials observed in the experiment are analyzed and discussed. Based on the experimental results and mathematical derivation methods, a visco-hyperelastic constitutive model describing the mechanical behavior of polyurea is proposed in this paper, which takes into account the effect of strain rate and temperature. Findings of this study can be summarized as follows:

(1) The uniaxial compressive stress-strain curves of polyurea at different strain rates are rate dependent and highly non-linear. For a given temperature, the flow stress value corresponding to the same deformation amount increases as the strain rate increases. The dynamic mechanical behavior of polyurea is also sensitive to temperature. For a given strain rate, the flow stress value corresponding to the same deformation amount increases as the temperature decreases, and the hardening-resistance behavior becomes more remarkable.

(2) The rate-dependent effect and temperature-dependent effect of polyurea under confined pressure (quasi-one dimensional strain state) are decreased compared to that of the materials under unconfined pressure (uniaxial stress state), and yield-like behavior is not observed. The bulk modulus of polyurea at confined pressure is sensitive to strain rate and temperature. For the typical given strain rate, the bulk modulus of polyurea decreases as the temperature increases.

(3) The compressive mechanical properties of PU605 (Versalink P-650 reacted with 105% molar equivalent Isonate 143L) are stiffer than those of PU105 (Versalink P-1000 reacted with 105% molar equivalent Isonate 143L). For a given strain rate, the bulk modulus of PU605 is close to that of PU105.

(4) A visco-hyperelastic constitutive model is established to describe the finite deformation mechanical behavior of polyurea. The experimental verification and the error analysis show that the model can effectively predict the stress-strain behavior of polyurea over a wide range of strain rates and temperatures.

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Fig.1. Schematic view of the samples in the quasi-static tests.

Fig.2. Schematic view of the enhanced split Hopkinson bar system.

Fig.3. Influence of pulse shapers on incident wave.

Fig.4. Distribution of the equivalent stress along the thickness of the sample.

Fig.5. Schematic view of the liquid-nitrogen refrigerating test device.

Fig.6. Uniaxial compressive stress-strain behavior of polyurea at low strain rates.

Fig.7. Axial stress-strain behavior of polyurea at low strain rates and confined pressure.

Fig.8. Hydrostatic pressure-volumetric strain curves of polyurea at confined pressure. The bulk modulus, k , for each material is obtained from these tests and listed in each plot.

Fig.9. Uniaxial compressive stress-strain curves of the two materials at different temperatures for a certain high strain rate.

Fig.10. True stress-strain curves of the two materials with the strain rate of 4000/s under different temperatures and confined pressure.

Fig.11. Dynamic uniaxial compressive stress-strain behavior of polyurea at different temperatures.

Fig.12. Dynamic compressive stress-strain behavior of polyurea under different temperatures in the confined configuration.

Fig.13. Hydrostatic pressure-volumetric strain curves of polyurea with the strain rate of 4000/s under different temperatures. The bulk modulus, k , for each material is obtained from these tests and listed in each plot.

Fig.14. Dynamic uniaxial compressive stress-strain curves of polyurea at high strain rates.

Fig.15. Comparison between the curves predicted by the visco-hyperelastic model and the experimental data of polyurea at different strain rates.

Fig.16. Stress-temperature relation curves of polyurea at four different strain levels.

Fig.17. Comparison between the curves predicted by the equation and the experimental data of polyurea at different temperatures.