



Free volume based nonlinear viscoelastic model for polyurea over a wide range of strain rates and temperatures

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ABSTRACT

A series of quasi-static and dynamic uniaxial compression experiments over a wide range of temperatures were conducted on polyurea elastomer. The stress-strain response of polyurea exhibits extreme nonlinearity, temperature and strain-rate sensitivity. How to comprehensively describe these complex behaviors regulated by the unique micro-structure of polyurea is still an open question. In this paper, a nonlinear viscoelastic constitutive model for polyurea is developed. The nonlinear viscoelasticity, entropic and energetic elasticity are taken into account, correlated with the interaction of chain segments, the stretch of molecular chains and covalent bonds from the perspective of molecular structure. The viscoelastic response is formulated by the hereditary integral of relaxation modulus and strain rate with time. The real time is accelerated by shift factor, which depends on the free volume. A new mechanism of shear-induced increase of free volume, which gives rise to the nonlinearity of viscoelasticity, is proposed, and the corresponding rate-dependent evolution equation of fractional free volume is developed. Parameters in the model are determined through the compression experiments and DMA test. Comparison with experimental data, as well as the data from references, verifies the ability of the model to predict the nonlinear stress-strain response of polyurea over a wide range of temperatures and strain rates.

1. Introduction

Polyurea, formed through the rapid chemical reaction between isocyanates and amines, is a kind of elastomer which is usually called the microphase-segregated and thermo-plastically linked block copolymer (Grujicic et al., 2011; Holzworth et al., 2013; Li et al., 2018). Because of its excellent mechanical and chemical properties, such as remarkable resilience and yet high dissipation, outstanding impact and shock resistance, excellent adhesion to a wide range of substrates, good abrasion and corrosion resistance (Amini et al., 2010a, 2010b; Amir-khizi et al., 2006; Chevillard et al., 2011; Clifton et al., 2016; Gamonpilas and McCuiston, 2012; Remennikov et al., 2017; Samiee et al., 2013; Xue et al., 2010), it has been used in many engineering fields. Over the past decade, the mechanical behavior of polyurea has been widely investigated by experiments, including quasi-static to high-rate tension and compression even at different temperatures (Amir-khizi

et al., 2006; Chevillard et al., 2011; Guo et al., 2016, 2017; Mohotti et al., 2014; Roland et al., 2007; Sarva et al., 2007; Shim and Mohr, 2011), dynamic mechanical analysis (Holzworth et al., 2013; Nantasetphong et al., 2016b; Qiao et al., 2011), ultrasonic measurements (Nantasetphong et al., 2016a, 2016b; Qiao et al., 2011) and pressure-shear plate impact experiments (Jiao and Clifton, 2014; Jiao et al., 2009). These studies demonstrated the main mechanical features of polyurea, such as highly nonlinear stress-strain behavior, hyper-elasticity with large deformation, significant strain-rate and temperature sensitivity, pressure dependence and cyclic softening (Gamonpilas and McCuiston, 2012; Grujicic et al., 2012; Li and Lua, 2009; Sarva et al., 2007). Like other polymers, polyurea is constructed by long molecular chains with multiple unites in different spatial and temporal scales. Due to strong hydrogen bonding between urea linkages of the neighboring chains or the neighboring portions of the same chain, hard segments in polyurea are typically segregated into hard domains (Choi

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et al., 2012; Das et al., 2007; Li et al., 2018). These hard domains distribute within the compliant/soft matrix composed of isolated hard segments and soft segments, which leads to a special heterogeneous structure of polyurea. The molecular- and domain-level microstructure dominates the highly complex macro-response in polyurea.

Varieties of constitutive models have been proposed to describe the mechanical behavior of polyurea. There are mainly three approaches to model the viscoelastic response of polyurea, including the hereditary integral approach (Amirkhizi et al., 2006; Chevillard et al., 2011; Clifton et al., 2016; Li and Lua, 2009), the framework of multiplicative decomposition of the deformation gradient (Cho et al., 2013; Elsayed, 2008; Jiao et al., 2009; Shim and Mohr, 2011), and the approach via decoupling the strain-dependent term and rate-dependent term (Gamonpilas and McCuiston, 2012; Mohotti et al., 2014). The hereditary integral approach is developed based on the linear viscoelasticity, and is expressed by the integration of relaxation (/memory) function and strain history. Various relaxation functions and fading memory functions are also used in different models through this approach. In the framework of multiplicative decomposition of the deformation gradient, several branches in parallel, such as hyperelastic branch, elasto-plastic branch and viscoelastic branch, are usually adopted to describe the deformation mechanism of materials. The third approach decouples the strain-dependent term and rate-dependent term of stress function (Gamonpilas and McCuiston, 2012) or strain energy density (Mohotti et al., 2014), and then constructs the specific formulas respectively. These former constitutive models achieve great success in describing the mechanical behavior of polyurea in specific cases, and provide an important foundation for a better description of the macro-responses in polyurea.

As the micro-structure of polyurea is the origin of their macro-response, to take into account the micro-structure in the constitutive modeling is essential for a satisfactory description of the complex mechanical behaviors. Polyurea consists of long molecular chains with multiple spatial- and temporal-scaled units similar to other polymers, and what's more, it has the special microphase-segregated structure. From the perspective of molecular structure, there are three levels of micro-processes, namely, the interaction of chain segments, the stretch of molecular chains and covalent bonds. These processes will give rise to different responses. The interaction of chain segments as main reason for viscoelasticity, is greatly influenced by free volume, which is regarded as the difference between the total volume and the occupied volume of polymer chains (Fox and Flory, 1950, 1954). Normally more free volume makes the motion of chain segments easier to take place, and the interactions of chain segments become weaker, indicating a decrease of viscosity macroscopically. The stretch of molecular chains will cause a change of configurational entropy and thus leads to an entropy elastic stress or hyperelastic stress. On a smaller spatial scale of a molecular chain, atoms are connected by covalent bonds that are much stronger than the intermolecular interactions. The small changes of bond length and angle during deformation give rise to an internal energy change, which induces an energy elastic stress. The three micro-processes from intermolecular scale to intramolecular scale coexist and work together in response to external loadings.

So far, how to correlate micro-structure and macro-response by constitutive modeling is still an open issue to be studied for polyurea. Free volume is a vital factor affecting the viscoelastic property of polymers. Besides mechanical property, thermal property and transport property of small molecules through polymer are also strongly influenced by free volume (Budd et al., 2005; Sharma and Pujari, 2017), which means that free volume is an important parameter at micro-structural level in determining the macro-properties of polymers. Doolittle (1951) is the first one who presented an equation establishing the relationship between the free volume and the viscosity of liquids. Later, based on the assumption that the fractional free volume of polymers changes linearly with temperature above the glass transition temperature, Williams et al. (1955) found the consistency of Doolittle

equation and WLF equation. After that, Knauss and Emri (1981) suggested that the fractional free volume should depend on temperature, solvent concentration and mechanically induced dilatation. Based on this idea, they proposed a nonlinear viscoelastic model through hereditary integral approach, which is able to predict the nonlinear stress-strain curve of tension at small strain. Popelar and Liechti (1997) further added a distortional term to the shift factor function in phenomenological way, simply following the form of the dilatational term. The modified model can properly model the nonlinear viscoelasticity of polymers in both dilation-dominated and shear-dominated loading cases. Pressure has also been found to be an important influencing factor on viscoelastic properties, and the dependent relations of free volume on pressure have been proposed (Fillers and Tschoegl, 1977; Tschoegl et al., 2002). Nantasetphong et al. (2016a) developed a constitutive model for polyurea based on WLF equation by introducing the combined effect of pressure and temperature. Obviously, free volume as an internal parameter can naturally bridge the micro-structure and macro-properties. It is known that fractional free volume in polymer materials increases with the decrease of crosslinking density (Ogata et al., 1993). This means new free volume can be produced via breaking crosslinks. However, most crosslinking polymers only possess chemical crosslinks, which are hard to be broken by deformation. Differently, polyurea is a kind of microphase-segregated polymer with hard domains and hydrogen bonds as physical crosslinks. Upon deformation, hard domains and hydrogen bonds break down, as observed by experiments (Choi et al., 2012; Pathak et al., 2008; Rinaldi et al., 2011), which largely decreases the crosslinking density of polyurea and creates lots of free volume. Because of these new traits, to comprehend the free volume evolution mechanism for polyurea and develop a proper description of it are quite necessary.

In this paper, a new free volume evolution mechanism for polyurea is proposed, and based on it, a nonlinear viscoelastic constitutive model is developed for polyurea with application over wide strain-rate and temperature ranges. The total stress response in the model consists of a rate-dependent nonlinear viscoelastic term, a rate-independent entropy elastic term and a rate-independent energy elastic term correlated to the aforementioned three micro-processes respectively, i.e. the interaction of chain segments, the stretch of molecular chains and the small stretch of covalent bonds. Dynamic mechanical analysis (DMA) was performed to exam the linear viscoelasticity of polyurea. Quasi-static and dynamic compression at different temperatures ranging from $-30\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ were implemented to acquire the nonlinear stress-strain curve. The experimental results are used to parameterize the constitutive model. Over a wide range of temperatures and strain rates, the model achieves a satisfactory prediction of the mechanical behavior of polyurea.

The manuscript is organized as follows: Section 2 presents the details of experimental investigation on polyurea. The constitutive model is formulated in Section 3. Parameter identification is shown in Section 4. The model is validated by comparison with experimental data in Section 5.

2. Experiments

2.1. Material and specimen preparation

The specific polyurea used in this research was produced by bulk polymerization of CDMDI-100L (Wanhua Chemical Group Co., Ltd.) and Versalink P1000 (Air Products) with 5% stoichiometry excess CDMDI-100L, which produces a lightly cross-linked polymer according to the references (Amirkhizi et al., 2006; Nantasetphong et al., 2016a). The two components were degassed under 0.1 MPa with continuous stirring for more than 6 h before being mixed. Then they were allowed to react for about 3 min and the mixture was poured into the Teflon molds to form sheets of 3.5 mm in thickness and cylinders of 10 mm and 6 mm in diameter. A curing process at room temperature for 24 h and at $70\text{ }^{\circ}\text{C}$ for 12 h were followed to make sure the complete reaction. The sheets were

then cut into 35 mm × 12.5 mm × 3.5 mm block for DMA test. The two kinds of cylinders were cut into small cylinders with aspect ratio (length/diameter) of 0.5 for quasi-static and dynamic uniaxial compression respectively.

2.2. Dynamic mechanical analysis

A TA Instruments DMA Q800 with a single cantilever clamp test fixture was used to characterize the linear viscoelasticity of polyurea. A controlled strain temperature step/frequency sweep experiment is conducted on polyurea. The specimen was clamped at a free length of 17.5 mm with both ends constrained from rotation. A sinusoidal transverse displacement was applied to one end of the specimen with a 0.05% maximum strain. The temperature range was $-90\text{ }^{\circ}\text{C}$ – $60\text{ }^{\circ}\text{C}$ with temperature step of $3\text{ }^{\circ}\text{C}$, which covers the glass transition zone. The sweeping frequencies at each temperature step were 10, 5.6, 3.2, 1.8 and 1 Hz. At the beginning of each sweep, a soaking time of 5 min was adopted to minimize the temperature gradient in specimen. Liquid nitrogen was used as the cooling source.

Fig. 1 shows the results of DMA tests. The storage modulus decreases monotonically with increasing temperature from glassy region to rubbery plateau, and it increases with the growing frequency. One relaxation peak is observed in loss modulus, which is attributed to the glass transition of the soft segment in polyurea. The more results based on DMA tests will be presented in Section 4.

2.3. Quasi-static uniaxial compression

A servo hydraulic dynamic test system (Instron 8852) with an environmental chamber was used to perform quasi-static uniaxial compression at different temperatures ($-30\text{ }^{\circ}\text{C}$, $-15\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$, $20\text{ }^{\circ}\text{C}$, $40\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$). Cylindrical specimens of 10 mm in diameter and 5 mm in height were used in this experiment. A preliminary experiment was done to exam the proper thermal soaking time, in which a polyurea sample with a thermocouple planted inside was placed between the loading rods. The time used for the sample reaching the setting temperature varies from 15 min to 25 min, depending on the setting temperature. Thus, 30 min was selected as the thermal soaking time to ensure no temperature gradient effect. The nominal strain rate was $4 \times 10^{-3}/\text{s}$. Repeated experiments were performed for every temperature and reasonable results were achieved.

The results are presented in Fig. 2a. The true stress was calculated based on the widely accepted assumption that the volume is conserved during deformation (Amirkhizi et al., 2006; Gamonpilas and McCuiston, 2012; Li and Lua, 2009; Roland et al., 2007; Sarva et al., 2007). The

stress-strain relation is extremely nonlinear, where an initially stiff response is followed by a much more compliant stage, and the stiff response appears again at large strain. Besides, a highly temperature dependence of stress-strain curve is observed: Polyurea exhibits a stiffer behavior with the decrease of temperature. The initial tangent modulus increases from about 60 MPa to 180 MPa when temperature decreases from $60\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$. The flow stress apparently increases with the decrease of temperature. And the rollover of stress-strain curve at a strain of about 0.1 becomes more apparent when temperature decreases, though the stress-strain curves at different temperatures all exhibit a rubbery behavior, which is known from the curves that there is no apparent yield point and strain softening behavior.

2.4. High strain rate dynamic uniaxial compression

The high strain rate compression was conducted on a Split-Hopkinson Pressure Bar (SHPB) apparatus. Considering the low impedance of polyurea, the aluminum bars were used for the experiment and a semiconductor strain gauge was adopted for transmitted bar to get a higher signal to noise ratio. The incident and transmitted bars were 1 m in length and 13 mm in diameter, and the striking bar was 300 mm in length and 13 mm in diameter. Cylindrical specimens of 6 mm in diameter and 3 mm in height were used in this experiment. An environmental chamber was also used for experiments at different temperatures ($-30\text{ }^{\circ}\text{C}$, $-15\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$, $20\text{ }^{\circ}\text{C}$, $40\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$) with similar temperature controlling procedure adopted in quasi-static compression. Repeated experiments were performed and the average true strain rate is about 9000/s.

The results of dynamic compression are presented in Fig. 2b. The temperature dependence is similar to that in quasi-static compression. We can find the rate dependence of stress-strain response by comparing the stress-strain curves at the same temperature in Fig. 2a and b. The dynamic stress-strain curves show a much higher stress level than the corresponding quasi-static ones, especially at the small and intermediate strain.

3. Theory

The experiments in Section 2 indicate that the stress-strain response of polyurea is highly nonlinear, strain-rate and temperature sensitive. Herein, a nonlinear viscoelastic constitutive model is established for polyurea based on free volume concept, in which three basic micro-processes, i.e., the interaction of chain segments, the stretch of molecular chains, and the stretch of covalent bonds, are taken into account.

For solid polymer, the whole molecular chains are not able to slide unless the temperature is higher than the melting point. But the shorter chain segments can rotate to accommodate the imposed deformation as long as the temperature is higher than the glass transition temperature T_g , below which the segment rotation freezes due to the extremely high viscosity and low free volume (Ferry, 1980; Treloar, 1975). When the viscosity is not high enough to freeze the rotation and yet not small enough to enable the fully free motion of the chain segments, a kind of stress is produced due to the interaction of chain segments, which gives rise to the viscoelasticity. The viscosity of polymer is closely related to its free volume. In addition to the motion of chain segments, there are other micro-processes. On the basis of second law of thermodynamic, if no external stress is applied, a molecular chain shall fold itself into random coil to maximize the entropy (Treloar, 1975). Upon deformation, the molecular chains are stretched along the direction of the deformation, which changes the configurational entropy. Thus, the second kind of stress is induced to resist this change, which is usually called entropy elastic stress or hyperelastic stress. On a smaller spatial scale of a molecular chain, covalent bonds among atoms are much stronger than the intermolecular interactions. An internal energy change will be contributed by the small changes of bond length and angle, and then induces an energy elastic stress. Based on the three micro-processes from

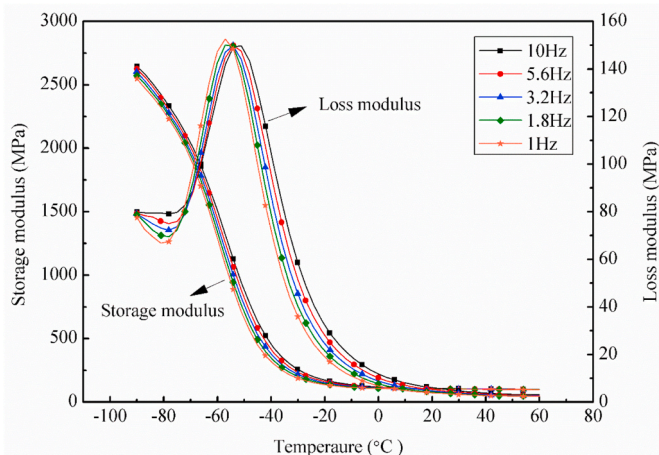


Fig. 1. The Young's storage modulus and loss modulus at different temperatures and frequencies.

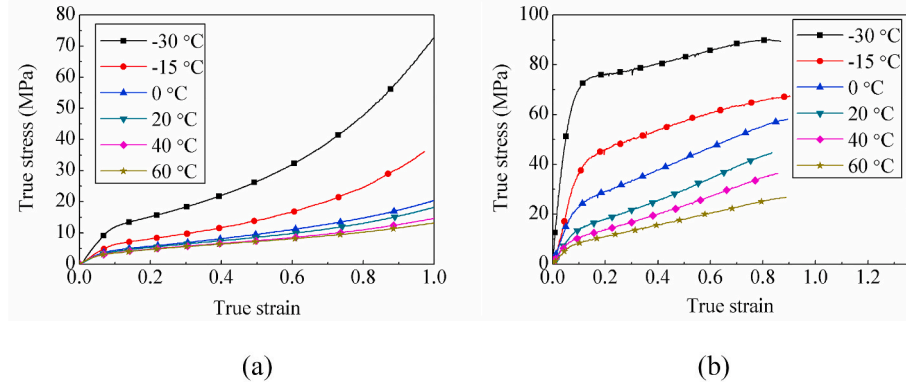


Fig. 2. The stress-strain curves of (a) quasi-static (4×10^{-3} /s) and (b) dynamic compression (9000/s) at different temperatures.

intermolecular scale to intramolecular scale, the overall response of polyurea is thus treated as a combination of a rate-dependent nonlinear viscoelasticity, a rate-independent entropic elasticity and a rate-independent energetic elasticity. Fig. 3 shows the corresponding rheological schematic of the present model.

3.1. General definition

Firstly, we define the deformation gradient tensor as $\mathbf{F} = \partial \mathbf{x} / \partial \mathbf{X}$, which maps the point \mathbf{X} in the reference configuration to the point \mathbf{x} in the deformed configuration. Since the three branches of elements in Fig. 3 are in parallel, the deformation gradient of each branch is equal to the macroscopic deformation gradient,

$$\mathbf{F} = \mathbf{F}^v = \mathbf{F}_1^e = \mathbf{F}_2^e \quad (1)$$

where \mathbf{F}^v , \mathbf{F}_1^e and \mathbf{F}_2^e are the deformation gradient tensors of viscoelastic branch, entropy elastic branch and energy elastic branch respectively. The left Cauchy-Green deformation tensor and the spatial velocity gradient tensor are defined as $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ and $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ respectively. In addition, we decompose the spatial velocity gradient tensor into rate of deformation and spin,

$$\mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T) \quad (2)$$

$$\mathbf{W} = \frac{1}{2}(\mathbf{L} - \mathbf{L}^T) \quad (3)$$

Upon the macroscopic deformation, the stress response of polyurea consists of a viscoelastic stress, an entropy elastic stress and an energy elastic stress,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^v + \boldsymbol{\sigma}_1^e + \boldsymbol{\sigma}_2^e \quad (4)$$

In the following sections, the three kinds of stress will be derived in details.

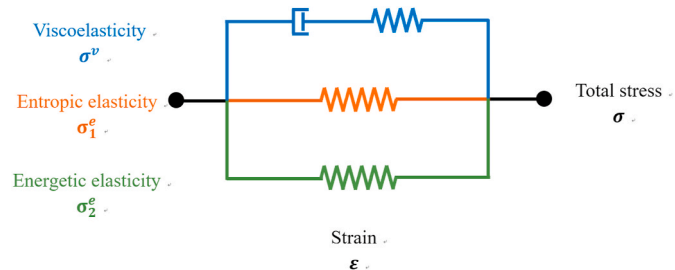


Fig. 3. 1-D rheological schematic of the constitutive model.

3.2. Viscoelastic response

The viscoelastic response can be formulated through Boltzmann superposition principle of linear viscoelasticity, whose mathematical expression is (Amirkhizi et al., 2006)

$$\boldsymbol{\sigma}^v(t) = \int_{-\infty}^t \boldsymbol{\chi}(t-\tau) : \mathbf{D}(\tau) d\tau \quad (5)$$

where \mathbf{D} is the deformation-rate tensor defined by Eq. (2) and $\boldsymbol{\chi}$ is the fourth-order relaxation modulus tensor. Considering that polyurea is isotropic and the volumetric response is nearly rate-independent, we decompose $\boldsymbol{\chi}$ into shear modulus and bulk modulus as

$$\boldsymbol{\chi}(t) = 3K\mathbf{E}^1 + 2G(t)\mathbf{E}^2 \quad (6)$$

where K and $G(t)$ are bulk modulus and shear relaxation modulus respectively and the fourth-order tensor \mathbf{E}^1 and \mathbf{E}^2 are defined as

$$E_{ijkl}^1 = \delta_{ij}\delta_{kl} / 3 \quad (7)$$

$$E_{ijkl}^2 = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) / 2 - \delta_{ij}\delta_{kl} / 3 \quad (8)$$

where δ_{ij} is the Kronecker delta. Since the bulk modulus is time-independent, the stress in Eq. (5) can be decomposed into bulk stress and shear stress,

$$-p = K \ln J / J \quad (9)$$

$$\mathbf{s}^v(t) = \int_{-\infty}^t 2G(t-\tau)\mathbf{E}^2 : \mathbf{D}(\tau) d\tau \quad (10)$$

where p is the hydrostatic pressure, J is the Jacobian of the deformation and \mathbf{s}^v is the shear stress. In addition, we adopt the linear dependence of bulk modulus on temperature as the model of Amirkhizi et al. (2006),

$$K(T) = K_{ref} + m(T - T_{ref}) \quad (11)$$

where T_{ref} is a reference temperature, K_{ref} is the bulk modulus at reference temperature, m is a temperature coefficient. For the shear relaxation modulus, there are several functional forms available. Among them, Prony series are mostly used. However, a large number of parameters are usually needed for good fitting especially when the time range involved is wide which is the case for polyurea. For a simple but reasonable expression, a power law representation is chosen here,

$$G(t) = G_r + \frac{\Delta G}{(1 + t/\tau_0)^q} \quad (12)$$

where G_r is the rubbery modulus at small strain, which is not used in the model but be replaced by the entropy and energy elastic responses discussed below due to the nonlinearity of the elastic response, ΔG is the

difference of glassy modulus and rubbery modulus, τ_0 is the average characteristic relaxation time and q is a constant characterizing the discrete distribution of relaxation times. The relaxation modulus can be obtained through relaxation experiment. But to extend the time range covered, relaxation experiments at different temperatures and the time-temperature superposition are usually adopted. In this paper, we acquire the storage modulus and loss modulus through the DMA test described in Section 2.2 and calculate the relaxation modulus based on the DMA results. The more details are presented in Section 4.

Up to this point, the viscoelastic response is limited to the isothermal case. When temperature rises, the relaxation processes of molecule are more frequently activated due to smaller energy barrier, equivalent to the decrease of characteristic relaxation time τ_0 or the increase of the real time t . A shift factor is used to modify the relaxation modulus,

$$G(t, T) = G\left(\frac{t}{a(T)}\right) = G_r + \frac{\Delta G}{[1 + t/(a(T)\tau_0)]^q} \quad (13)$$

Thus, in more general condition, the shear stress representation can be modified as

$$\mathbf{s}^v(t) = \int_{-\infty}^t 2G(t' - \tau') \mathbf{E}^2 : \mathbf{D}(\tau) d\tau \quad (14)$$

where $t' - \tau'$ is the so-called reduced time, and it is expressed as

$$t' - \tau' = \int_{\tau}^t \frac{d\xi}{a[T(\xi)]} \quad (15)$$

The analytical expression of $a(T)$ is given by Williams et al. (1955) for amorphous polymers,

$$\lg a(T) = -\frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}} \quad (16)$$

where T_{ref} is the reference temperature arbitrarily chosen between the glass transition temperature T_g and $T_g + 100\text{K}$.

Here, the linear viscoelastic model, where the fractional free volume remains constant during deformation, is derived. However, in the nonlinear viscoelastic regime, the fractional free volume changes during deformation. The evolution rule of free volume with strain history is therefore needed. As discussed in Section 1, the viscoelastic stress comes from the interaction of chain segments, and more free volume makes the motion of chain segments easier, indicating an underlying relationship between free volume and shift factor. Doolittle (1951) presented an equation which relates the shift factor to the free volume in materials,

$$\lg a = \frac{B}{2.303} \left(\frac{1}{f} - \frac{1}{f_0} \right) \quad (17)$$

where f is the fractional free volume defined in terms of free volume v_f and occupied volume v_0 of material as $f = v_f / (v_f + v_0)$, f_0 is the fractional free volume at a reference state and B is a constant close to 1. Knauss and Emri (1981) proposed a linear dependence of fractional free volume on temperature T , solvent concentration c and mechanical dilatation θ , which correlates the shift factor with temperature, solvent concentration and mechanical dilatation, and it further affects the time-dependent stress.

Different from that the nonlinearity of viscoelasticity is normally caused by dilatation as those in glassy polymers, the nonlinearity of viscoelasticity is clearly found in polyurea in shear-dominated deformation (Chevellard et al., 2011; Liang and Liechti, 1996; Popelar and Liechti, 1997, 2003). This means that shear exerts an important effect on the free volume evolution and then influences the nonlinear viscoelasticity. Popelar and Liechti (1997) realized the influence of distortion on free volume, and simply introduced this effect similar to the form of dilatation term in shift factor function. Actually, the shear-induced free volume evolution in polyurea should have quite a different mechanism than that of dilatation. As is known, crosslinks firmly connect different

molecular chains, restricting the mobility of chains. The decrease of crosslinking density will cause a growth of free volume, enhancing the mobility of molecular chains. For most crosslinking polymers, they only possess chemical crosslinks which are hard to be destroyed by deformation. However, polyurea has a unique microphase-segregated structure, where hard domains and hydrogen bonds are physical crosslinks. Through shear deformation, these hard domains and hydrogen bonds will break down, which greatly reduces the crosslinking density and improve the content of free volume. Thereby, we propose a new rate-dependent evolution equation for free volume:

$$\dot{f} = \alpha_v \dot{T} + \gamma \dot{c} + \delta \dot{\theta} + \delta_s \dot{\epsilon}_{eff} \quad (18)$$

and

$$\delta_s = \delta_{s0}(f_c - f)^2, \delta_{s0} > 0 \quad (19)$$

where α_v is the volumetric thermal expansion coefficient of free volume, γ is the volumetric expansion coefficient of free volume due to changes in solvent concentration, δ is fractional free volume change per mechanical dilatation, $\dot{\epsilon}_{eff}$ is rate of effective strain and δ_s is fractional free volume change per effective strain and can be an index to measure shear-induced dilatancy. To be noted, δ_s is not a constant but related with the current fractional free volume, as described by Eq. (19). In this equation, δ_{s0} is a constant and f_c is the critical fractional free volume. When the fractional free volume is greater than f_c , no more free volume can be produced by shear strain.

The first three terms in Eq. (18) are the same as the model proposed by Knauss and Emri (1981) but in a rate-dependent form. The fourth term is introduced to characterize the free volume generation caused by shear strain. During shear deformation, some entanglements and crosslinks of the polymer chains are freed or broken due to the relative motion of different chain segments, and the polymer chains are separated, which creates new free volume. For polyurea specifically, break of hard domains and hydrogen bonds by shear deformation makes a considerable contribution to the creation of free volume. We note that, when the fractional free volume becomes more enough, there are plenty spaces for molecular chain motion and the break of crosslinks becomes seldom. Less or even no free volume is then generated by shear deformation.

So far, the bulk response is determined by Eqs. (9) and (11), and the viscoelastic shear response is determined by Eqs. (12) and (14) and (15) and (17)–(19). Firstly, the evolution of fractional free volume is determined by Eqs. (18) and (19). Through Eq. (17), the shift factor is derived which is then used in Eq. (15) to calculate the reduced time. Finally, substitute Eqs. (12) and (15) into Eq. (14) to obtain the viscoelastic shear stress.

3.3. Entropy elastic response

The entropy elastic stress comes from the configurational entropy change due to molecular chains orientation. The non-Gaussian chain based Arruda-Boyce eight-chain model is a suitable choice to describe entropy elastic response, considering that just two parameters are enough to model different loading cases up to large stretch.

The strain energy density of the eight-chain model is (Arruda and Boyce, 1993)

$$W = nk_B T N \left(\frac{\lambda_{chain}}{\sqrt{N}} \beta + \ln \frac{\beta}{\sinh \beta} \right) - CT \quad (20)$$

where $\mu = nk_B T$ is the initial shear modulus of rubbery elasticity, n is the chain density, k_B is Boltzmann's constant, N is the statistic number of rigid links between crosslinks, λ_{chain} is the stretch of polymer chain in eight-chain model which is related to the macroscopic stretch by $\lambda_{chain} = \sqrt{(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)/3}$, C is a constant and β is the inverse Langevin function

($\beta = L^{-1}(\lambda_{chain}/\sqrt{N})$) and the Langevin function is defined as $L(\beta) = \coth \beta - 1/\beta$.

Then the Cauchy stress is obtained by differentiating the strain energy density,

$$\sigma_1^e = \frac{2}{J} \frac{dW}{dI_1} \mathbf{B} - p_1 \mathbf{I} \quad (21)$$

where $J = \det(\mathbf{F})$, \mathbf{B} is the left Cauchy-Green deformation tensor as defined in Section 3.1, I_1 is the first invariant of \mathbf{B} , p_1 is the hydrostatic pressure which can be determined by boundary condition and \mathbf{I} is the second-order identity tensor. For the uniaxial loading case, considering that the volumetric strain is negligible ($J = 1$) and the transversal stress equals to zero, the axial stress is derived as

$$\sigma_1^e = \frac{nk_B T}{3} \frac{\sqrt{N}}{\lambda_{chain}} L^{-1} \left(\frac{\lambda_{chain}}{\sqrt{N}} \right) \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (22)$$

To properly model the entropy elastic response at different temperatures, the dependence of chain density on temperature should be considered. Assuming the total number of chains is conserved, the change of chain density is purely due to the change of specific volume with temperature, which means the chain density is inversely proportional to the specific volume. For polymers, the specific volume increases linearly with temperature above or below the glass transition temperature in different rates. Since the present model is aimed at the temperature ranging from T_g to $T_g + 100\text{K}$, where the linear relation of specific volume with temperature is satisfied, the reciprocal of chain density can be proposed as a linear function of temperature,

$$\frac{1}{n} = k_B (A_1 T + A_2) \quad (23)$$

where A_1 and A_2 are two constants.

3.4. Energy elastic response

Entropy elastic stress of polymers is usually modeled based on the assumption that the internal energy keeps constant during deformation. However, the internal energy does change with strain, and a part of elastic stress comes from the internal energy change (Boyce and Arruda, 2000; McKenna, 2018; Treloar, 1975; Wolf and Allen, 1975). The initial response of polyurea is much stiffer and the rollover of stress-strain curve at strain 0.1 is much more apparent than common rubbery materials, even when the strain rate is very low. This indicates that the segmental motion of polyurea is slightly constrained and is not easy to happen at small strain. Considering the micro-structure of polyurea, hard domains are embedded into soft matrix, and hard domains partly constrain the motion of chain segments. At small strain, the stretch of local covalent bonds may dominate compared with the motion of chain segments, which indicates that energy elastic response of polyurea is non-negligible. Based on this, the elastic stress which monotonically increases with strain and converges to a maximum stress is proposed in the form of:

$$\sigma_2^e = \frac{\sigma_{\max}}{2} \left(1 - \exp \left(- \frac{\varepsilon_{\text{eff}}}{\varepsilon_0} \right) \right) \frac{\ln \mathbf{B}}{\varepsilon_{\text{eff}}} \quad (24)$$

where σ_{\max} is the maximum elastic stress induced by internal energy change, ε_{eff} is the effective strain, ε_0 is a reference strain, and \mathbf{B} is the left Cauchy-Green deformation tensor.

4. Parameter identification

Based on the experiments described in Section 2, a set of parameters for uniaxial loading is determined. Firstly, the parameters of relaxation modulus function (Eq. (12)) are determined by the results of DMA test. The curve fitting of thermal shift factor in DMA test to WLF equation can

provide the fractional free volume at reference temperature (f_0) and the volumetric thermal expansion coefficient of free volume (α_v). Considering no solvent is involved in our experiments and the volumetric strain is negligible, parameters of the second term and the third term in Eq. (18) are not identified here. The difference between dynamic stress and quasi-static stress equals to the difference of viscoelastic stresses in two cases because the entropy elastic stress and energy elastic stress are the same in both cases since they are rate-independent. Therefore, the parameters of the fourth term in Eq. (18) and Eq. (19) are identified by fitting the difference between dynamic stress and quasi-static stress. In addition, we adopt the same values of the parameters in the bulk response as Amirkhizi et al. (2006) but with different reference temperature. Finally, the parameters in entropy elastic response and energy elastic response are determined by fitting the quasi-static stress-strain data with the help of the viscoelastic stress-strain data calculated by the model. All the parameters are listed in Table 1. The more details will be described below.

In Section 3.2, we decompose the overall viscoelastic response into a rate-independent bulk response and a rate-dependent shear response, which means that the shear relaxation modulus needs to be derived. However, since we focus on the uniaxial compression, the Young's relaxation modulus can be used directly to achieve the axial viscoelastic stress by Boltzmann superposition principle of linear viscoelasticity but in one dimensional form, which is

$$\sigma^v(t) = \int_{-\infty}^t E(t' - \tau') \frac{\partial \varepsilon}{\partial \tau} d\tau \quad (25)$$

where σ^v is the axial viscoelastic stress, $E(t)$ is the Young's relaxation modulus and ε is the axial strain. Similar to Eq. (12), the Young's relaxation modulus is analytically represented as

$$E(t) = E_r + \frac{\Delta E}{(1 + t/\tau_0)^q} \quad (26)$$

Time-temperature superposition (TTS) are widely used to acquire the master curve of polymers and the corresponding thermal shift factor (Holzworth et al., 2013; Jia et al., 2016; Qiao et al., 2011; Xiao and Tian, 2019). Firstly, a reference temperature is chosen. Here, we chose 21 °C as reference temperature which is close to the room temperature. Then we modify the storage modulus and loss modulus of multiple temperatures by ET_{ref}/T , where E represents storage modulus or loss modulus. Next, plot the modified storage modulus and loss modulus as a function

Table 1

Parameters of the constitutive model for polyurea with $T_{\text{ref}} = 294\text{K}$

Parameter	Value	Physical meaning
K_{ref} (MPa)	4633	The bulk modulus at reference temperature
m (MPa/K)	-15	Temperature coefficient of bulk modulus
ΔE (MPa)	2616	Difference of glassy and rubbery modulus
τ_0 (s)	4.91×10^{-13}	Characteristic relaxation time
q	0.2068	Exponent of relaxation modulus function
f_0 (%)	4.09	Fractional free volume at reference temperature without deformation
α_v (K ⁻¹)	2.62×10^{-4}	The volumetric thermal expansion coefficient of free volume
δ_{s0}	39.2	The coefficient constant of shear induced free volume evolution
f_c (%)	5.75	Critical fractional free volume
N	2.422	The statistic number of rigid links between crosslinks
A_1 (MPa ⁻¹)	3.084	The first constant in the chain density function of temperature
A_2 (K/MPa)	-723.8	The second constant in the chain density function of temperature
σ_{\max} (MPa)	4.056	Maximum elastic stress induced by internal energy change
ε_0	0.0965	The reference strain in energy elastic stress function

of angular frequency at different temperatures as exemplified in Fig. 4a. Then keep the data of the reference temperature fixed and shift every other line horizontally along the frequency axis to overlap the lines of neighboring temperatures to achieve the master curve. The shifted displacement of each line is the thermal shift factor for the corresponding temperature. Only the data ranging from $-51\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ is used for TTS since the relaxation mechanism changes near and below the glass transition temperature, and the slope of storage modulus with frequency is quite small above $30\text{ }^{\circ}\text{C}$, which may cause large error in shift factor obtained by shifting the data along the frequency axis. Fig. 4b shows the averaged thermal shift factor of storage modulus and loss modulus, and the fit of WLF equation (Eq. (16)), where $C_1 = 10.61$ and $C_2 = 156.24\text{K}$. The corresponding master curves of storage modulus and loss modulus are presented in Fig. 4c. To acquire relaxation modulus, we need to translate the independent variable from angular frequency to time. Ninomiya and Ferry (1959) provided an approximate way,

$$E(t) = E'(\omega) - 0.40E''(0.40\omega) + 0.014E''(10\omega)|_{\omega=1/t} \quad (27)$$

where $E(t)$ is relaxation modulus, $E'(\omega)$ is storage modulus, and $E''(\omega)$ is loss modulus. Using Eq. (27), the relaxation modulus at reference temperature $T_{ref} = 21\text{ }^{\circ}\text{C}$ is obtained, exhibited in Fig. 4d. Then the relaxation modulus data is used to fit Eq. (26), which is also presented in Fig. 4d. The values of the corresponding parameters are listed in Table 1. The value of E_r is not listed because it is not used in the model but be replaced by the entropy and energy elastic responses due to the nonlinearity of the elastic response.

We have mentioned in Section 1 that Williams et al. (1955) found the consistency of WLF equation and Doolittle equation, which is used to acquire the initial fractional free volume at reference temperature and

the volumetric thermal expansion coefficient of free volume. Substituting the linear relation of free volume with temperature as proposed by Eq. (18) or the model of Knauss and Emri (1981) into Doolittle equation (Eq. (17)), we obtained a thermal shift factor function of temperature consistent with WLF equation (Eq. (16)),

$$\lg a(T) = -\frac{B}{2.303f_0} \frac{\Delta T}{f_0/\alpha_v + \Delta T} \quad (28)$$

where $\Delta T = T - T_{ref}$ is the difference between the current temperature and the reference temperature. Considering that B is a constant close to 1 and have no effect on the data fitting, we simply set $B = 1$. Comparing Eq. (16) and Eq. (28), we obtained the values of f_0 and α_v based on the constants of WLF equation from DMA test as $f_0 = 1/(2.303C_1) = 4.09\%$ and $\alpha_v = 1/(2.303C_1C_2) = 2.62 \times 10^{-4}/\text{K}$.

For the viscoelastic response, parameters in the fourth term of Eq. (18) are the last to be determined. To identify these parameters, the stress-strain data of uniaxial compression is used. Since the total stress is composed of a rate-dependent viscoelastic stress, a rate-independent entropy elastic stress and a rate-independent energy elastic stress, which means the latter two kinds of stress are identical for quasi-static and dynamic loading. Therefore, the difference between dynamic stress and quasi-static stress is equal to the difference of viscoelastic stresses in two cases, as exemplified in Fig. 5a of the data and prediction at $0\text{ }^{\circ}\text{C}$. Finally, we fit the difference of dynamic and quasi-static stress-strain data at $-30\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ simultaneously to obtain the parameters in Table 1 and the fitting results are shown in Fig. 5b.

After the identification of parameters in viscoelastic response, there are only the parameters in rate-independent parts, including the entropy elastic response and energy elastic response. Since the rate-independent stress is identical in dynamic loading and quasi-static loading, any one of

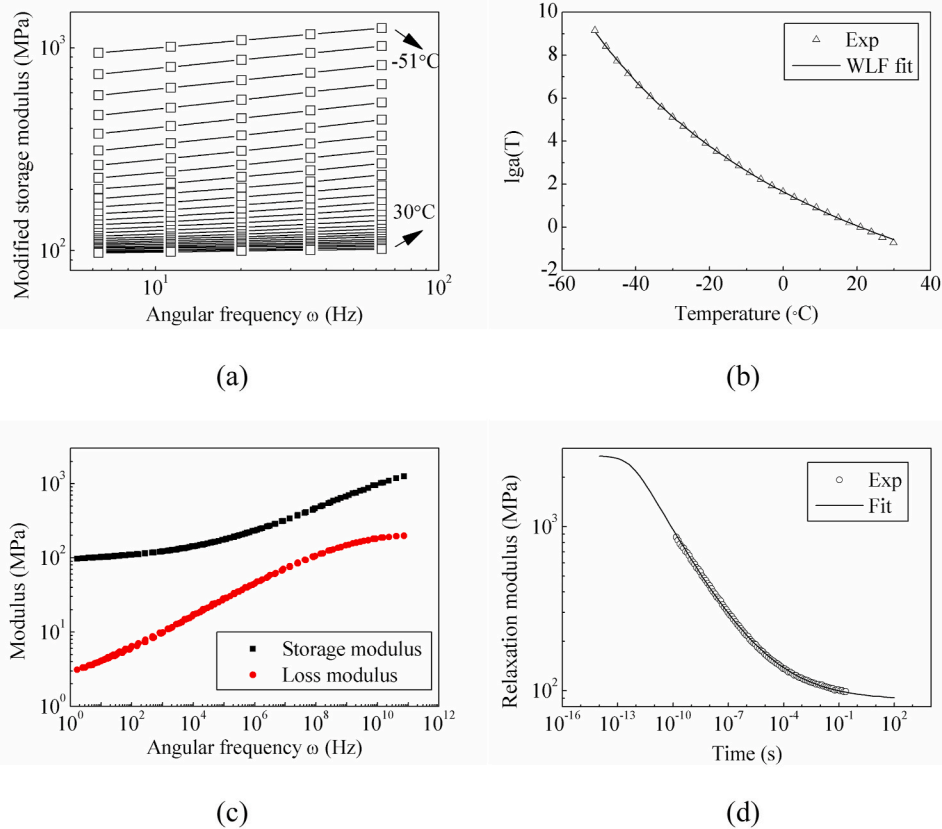


Fig. 4. Parameter identification based on DMA results: (a) the storage modulus as a function of angular frequency at different temperatures, (b) the thermal shift factor from experiment and WLF equation, (c) the master curves of storage modulus and loss modulus, and (d) the relaxation modulus from experiments and fit of Eq. (12).

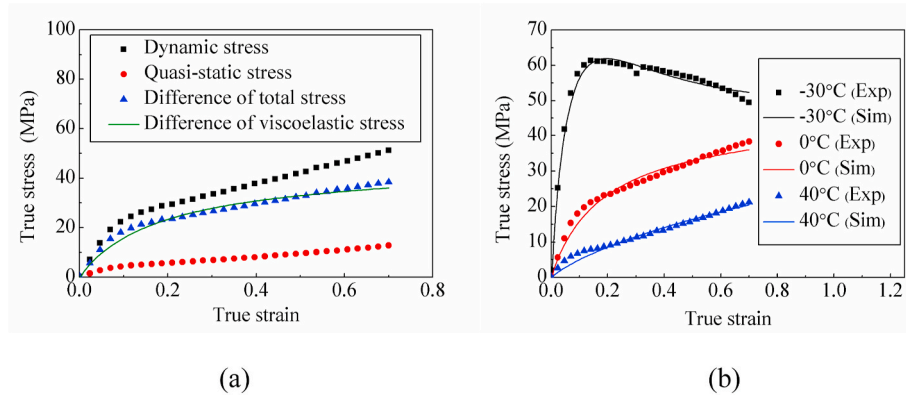


Fig. 5. Fitting of the viscoelastic response: (a) Example data at 0 °C to exhibit the fitting process, (b) Comparison of experimental stress-strain data and fitted viscoelastic response at multiple temperatures.

them can be used to determine the parameters theoretically. However, the rate-independent stress only accounts for a small percentage of the total stress at high strain rate case, which makes the rate-independent stress data from dynamic loading case is not reliable. Thus, we use the difference between quasi-static stress and the corresponding viscoelastic stress calculated by the present viscoelastic model as the corresponding rate-independent stress. Due to the temperature dependence of entropy elastic stress, stress-strain data at multiple temperatures are needed. Eventually, we use Eqs. (22)–(24) together with the viscoelastic stress calculated to fit the quasi-static stress-strain data at all temperatures simultaneously and the parameters are obtained.

5. Results and discussion

The constitutive model of polyurea is used to obtain the stress-strain curves at multiple temperatures and strain rates based on the parameters identified in Section 4. Fig. 6 exhibits the overall comparison between experimental data and prediction of the model, including quasi-static and dynamic compression at multiple temperatures as indicated in the figures. The strain rates of quasi-static and dynamic compression are $4 \times 10^{-3}/s$ and 9000/s respectively. It is apparent that the prediction shows quite satisfactory agreement with the experimental data. The characteristics of the stress-strain curve are well captured by the model. An initially stiff response is followed by a rollover to a more compliant plateau, and eventually the response becomes stiff again due to the limited stretch of polymer chains. The temperature dependence and strain rate dependence of stress-strain response are also well described by the model. Decrease of temperature and increase of strain rate all cause the material stiffer.

Further comparison between the prediction of the proposed model

and the experimental data at intermediate strain rates in references (Sarva et al., 2007) is presented in Fig. 7. Apparently, an excellent agreement is found though these data were not used in parameter identification, which again confirms the fidelity of the model.

With the help of the model, the response of polyurea is able to be analyzed via decomposing the total stress into different parts, which are correlated with different mechanisms respectively. Fig. 8 shows the

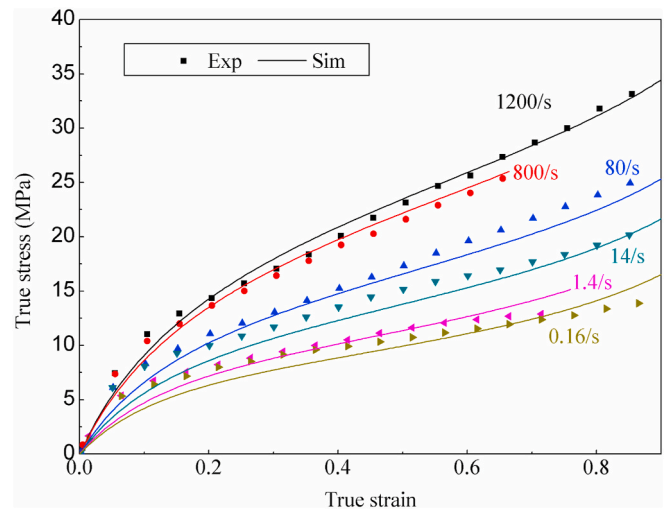


Fig. 7. Comparison with experimental data at intermediate strain rates in the paper of Sarva et al. (2007).

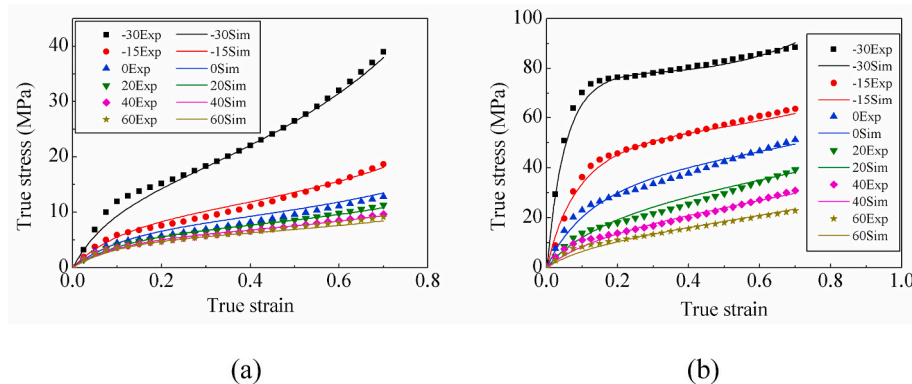


Fig. 6. Comparison between experimental stress-strain curves and model prediction of polyurea compressed at strain rates of (a) $4 \times 10^{-3}/s$, and (b) 9000/s for various temperatures (the numbers in the legend represents the experimental temperature with a unit of °C).

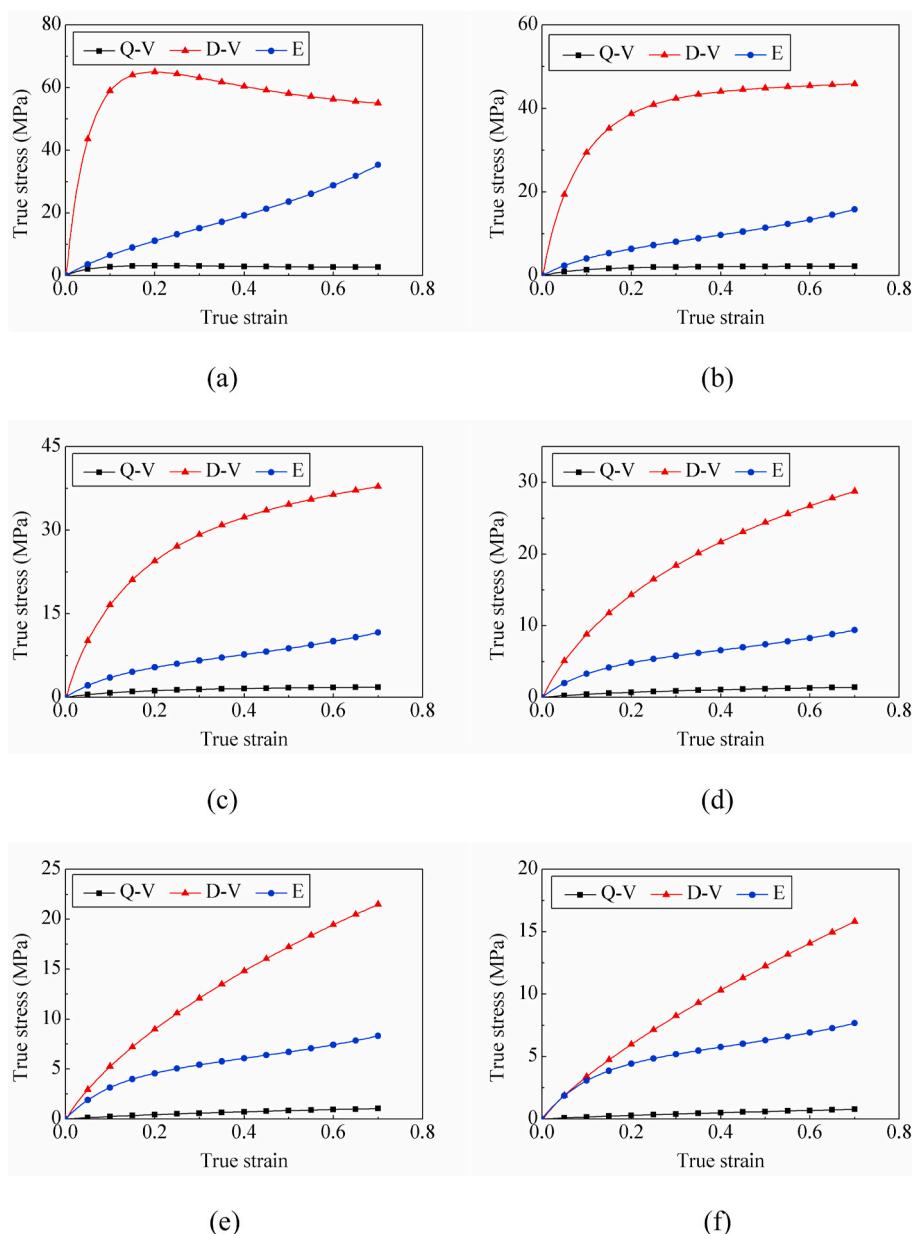


Fig. 8. Rate-dependent viscoelastic stress (V) and rate-independent total elastic stress (E) of dynamic (D) and quasi-static (Q) compression at temperatures of (a) $-30\text{ }^{\circ}\text{C}$, (b) $-15\text{ }^{\circ}\text{C}$, (c) $0\text{ }^{\circ}\text{C}$, (d) $20\text{ }^{\circ}\text{C}$, (e) $40\text{ }^{\circ}\text{C}$, and (f) $60\text{ }^{\circ}\text{C}$.

viscoelastic stress and the sum of two kinds of elastic stress at multiple temperatures and strain rates calculated by the constitutive model. At all temperatures involved, the rate-dependent viscoelastic stress is greater than the rate-independent elastic stress for dynamic compression and the situation is on the contrary for quasi-static compression. This result reveals that the stress response of polyurea at high strain rate is viscoelastic stress dominated and the stress response at low strain rate is elastic stress dominated, which explains the reason why there is a transition in rate-sensitivity at an intermediate strain rate point as found experimentally (Cho et al., 2013; Roland et al., 2007; Sarva et al., 2007).

The fractional free volume of polyurea during deformation at multiple conditions is presented in Fig. 9. For all conditions, fractional free volume monotonically increases with the increasing strain but the slope decreases. This is related to the evolution mechanism of free volume during deformation. Under shear strain, new free volume is produced, due to break of hard domains and hydrogen bonds. As the free volume increases, the interaction of polymer chains becomes weaker and the density of physical crosslinks decreases, resulting in a decrease of the

evolution rate of free volume. The increased amount of fractional free volume at different temperatures varies from 1.35% at $-30\text{ }^{\circ}\text{C}$ to 0.09% at $60\text{ }^{\circ}\text{C}$. As shown in Fig. 9, at the same axial strain ϵ , the fractional free volume of dynamic and quasi-static compression is nearly the same. This is because the increase of fractional free volume is induced by the effective strain, and the effective strain $(\epsilon - \sigma/(9K))$ in uniaxial dilatation inducing free volume) is nearly equal to ϵ since the bulk strain $(\sigma/(3K))$ in uniaxial compression) is negligible compared to the axial strain ϵ . But slight difference can still be observed due to the different bulk strain $(\sigma/(3K))$ in uniaxial compression) in two cases.

To understand how important the mechanism of shear inducing free volume is, we compared the experimental stress-strain data at $20\text{ }^{\circ}\text{C}$ with linear viscoelastic model, nonlinear viscoelastic model (only considering dilatation inducing free volume) and the model proposed, as shown in Fig. 10. The linear viscoelastic model is based on the assumption that free volume does not change with deformation. At small strain, it fits the data well. But the stress level of it become much higher than the experimental data when the strain gets larger. This indicates that the real

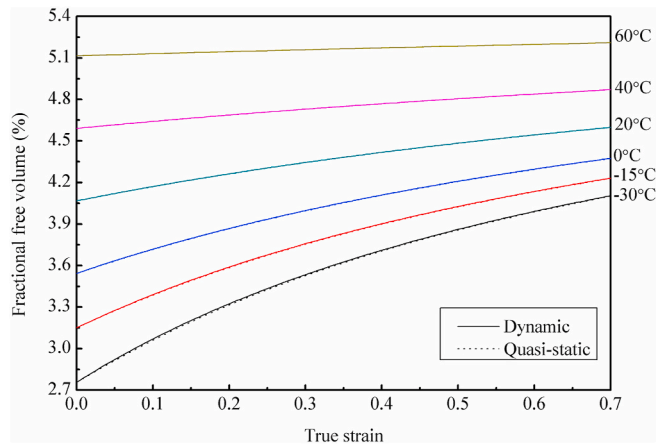


Fig. 9. Fractional free volume of polyurea during deformation.

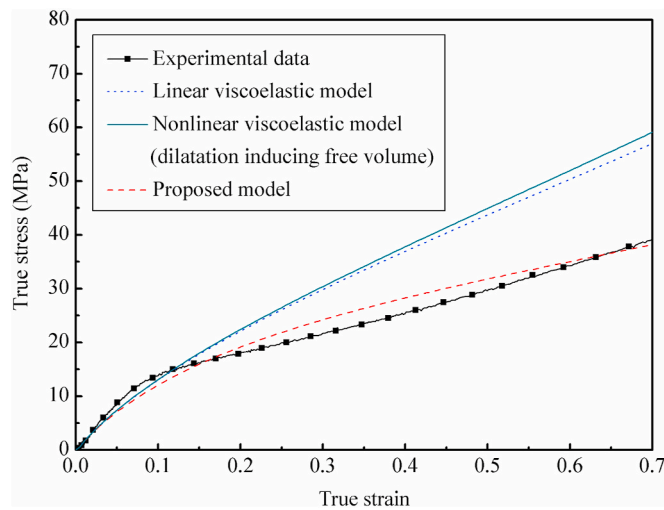


Fig. 10. Comparison of the stress-strain curves from experiment, linear viscoelastic model, nonlinear viscoelastic model (dilatation inducing free volume) and the proposed model.

stress relaxes faster than the linear viscoelastic model due to the increase of free volume with increasing strain. The stress predicted by nonlinear viscoelastic model which only considers dilatation inducing free volume (third term in Eq. (18) with $\delta = 0.1$) is even higher than that by linear viscoelastic model. This is because the bulk strain is negative in compression case, and the free volume decreases with compression, which makes the stress to relax slower even than that happens in linear viscoelastic model. Only the proposed model, which includes the mechanism of shear inducing free volume, fits the experimental data from small to large strain. This again validated the mechanism and evolution equation of free volume proposed.

6. Conclusions

A free volume based nonlinear viscoelastic constitutive model for polyurea has been established to characterize the mechanical behaviors of polyurea, which includes nonlinearity, highly temperature sensitivity and strain rate sensitivity of stress response. Considering the three micro-processes happening within polyurea during deformation, namely the interaction of chain segments, the stretch of molecular chains and the stretch of covalent bonds, the stress response is treated as a combination of nonlinear viscoelasticity, entropic elasticity and energetic elasticity. The nonlinear viscoelastic response of the model is formulated

through the linear viscoelasticity with time accelerated by shift factor, which depends on the free volume of polyurea. A new evolution equation of free volume is proposed from the mechanism that shear strain produces free volume, which enables the model to be used in the shear-dominated case and gives a new insight to the evolution of free volume upon external loading. What's further, a temperature modified eight-chain entropy elastic model and a nonlinear energy elasticity are introduced, describing the rate-independent response of polyurea.

A DMA test has been performed to acquire the linear viscoelasticity of polyurea. Uniaxial compression tests at low and high strain rates for multiple temperatures ranging from $-30\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ have been conducted to explore the rate and temperature dependence of polyurea at large strain. The experimental results are further used to identify the parameters in the model. A fairly satisfactory agreement between model prediction and experimental data validates the fidelity of the proposed model, which means the parameterized constitutive model is able to predict the stress-strain response of polyurea over a wide range of temperatures and strain rates. Pressure sensitivity of polyurea is not discussed much in this work since only uniaxial compression case is considered, where the volumetric deformation is negligible. It is worth noting that, for application of polyurea in high pressure condition, the pressure effect on mechanical behavior shall be pronounced, and the dilatation term in the model will play a vital role, which deserves a further study in our later work.

Author statement

Chencheng Gong: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing-Original Draft, Writing-Review & Editing, Visualization. **Yan Chen:** Conceptualization, Methodology, Resources, Writing-Original Draft, Writing-Review & Editing, Supervision, Project administration, Funding acquisition. **Ting Li:** Methodology, Resources. **Zhanli Liu:** Resources, Writing-Original Draft. **Zhuo Zhuang:** Resources, Writing-Original Draft. **Baohua Guo:** Resources, Writing-Original Draft. **Haiying Wang:** Resources, Writing-Original Draft, Supervision, Funding acquisition. **Lanhong Dai:** Conceptualization, Methodology, Resources, Writing-Original Draft, Writing-Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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