A phenomenological model for dynamic response of double-network hydrogel composite undergoing transient transition

Haibao Lu[a,*], Xiaodong Wang[a], Xiaojuan Shi[a], Kai Yu[b], Yong Qing Fu[c]

[a] Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin, 150080, China
[b] Department of Mechanical Engineering, University of Colorado Denver, Denver, CO, 80217, United States
[c] Faculty of Engineering and Environment, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK

ARTICLE INFO

ABSTRACT

We present a phenomenological model for dynamic deformation and mechanical response of double-network (with short-chained ionic network and long-chained covalent network) hydrogel composite based on theory of transient networks. Molecular structures and stress-strain relations of the hydrogel composite were investigated based on thermomechanical properties of the individual network. Constitutive relations were derived for its nonlinear viscoelastic responses and annihilation/reformation rates of active short chains were determined by means of Eyring formula. An extended Volokh model was proposed to separate effects of large strain hysteresis and anomalous viscoelastic relaxation on the hydrogel composite after strain reversal. Experimental results from rate-independent tests are well in agreement with that of the numerical simulations. This study provides a fundamental simulation tool for modelling and predicting mechanics and mechanisms of viscoelastic response and mechanical responses in double-network hydrogel composite.

1. Introduction

Hydrogels are the embodiment of "soft matter" as they combine the chemomechanical complexity and rheological flexibility [1–3], of which enable them a large entropy change in response to the external stimuli, similar with dielectric elastomer [4,5] and shape memory polymer [6–12].

Hydrogels are a unique class of soft polymeric materials which exhibit nonlinear mechanical responses to external loading with superior stretchability [13]. They have been widely investigated for numerous engineering applications in biomedicine, sensors, actuators due to their excellent properties including large amount of water absorption, high elastic strain, low weight and biocompatibility [14]. Gong and co-workers proposed and synthesized double-network hydrogel composites with both high stiffness and strength compared to those of the conventional single-network hydrogel [15–18]. The double-network hydrogel composites are combined with an ionic network with short chains and a covalent network with long chains [19]. When they are stretched, the ionic network ruptures, thus resulting in a great deal of energy dissipated (a large stress-strain hysteresis) and hydrogels are therefore toughened [20,21]. Whereas during unloading after stretching, the elastic long chains make the hydrogels return back to its initial state owing to the configurational entropy, thus realizing the

large stretchability of hydrogels, this process is vividly shown in Fig. 1(a). In the double-network, the ionic links are adaptive and the rates of annihilation and reformation follow the Eyring formula [22]. For a double network hydrogel composite, it is well-documented that configurational entropy can be neglected and the breakage of the ionic links is sensitive to strain-rate during the loading process [23,24]. However, the mechanical response is not sensitive to the strain-rate because there is no breakage of the adaptive links during the unloading process. Furthermore, the ionic crosslinks without breakage are in process of the elastic stretching [25], this process is displayed in Fig. 1(b).

In this study, a phenomenological model was proposed to study the synergistic effect of ionic network and covalent network on the dynamic mechanical responses of the double-network hydrogel composites based on the theory of transient networks. The molecular structures and stress-strain relations of the double-network hydrogel composites were investigated based on the thermomechanical properties of the individual networks. The nonlinear viscoelastic and mechanical responses of the ionic network was initially modeled based on the theory of transient networks. An extended volokh model was then proposed to separate the effects of large strain hysteresis and anomalous viscoelastic relaxation on the covalent network. Finally, phenomenologically constitutive relations were established to explore the
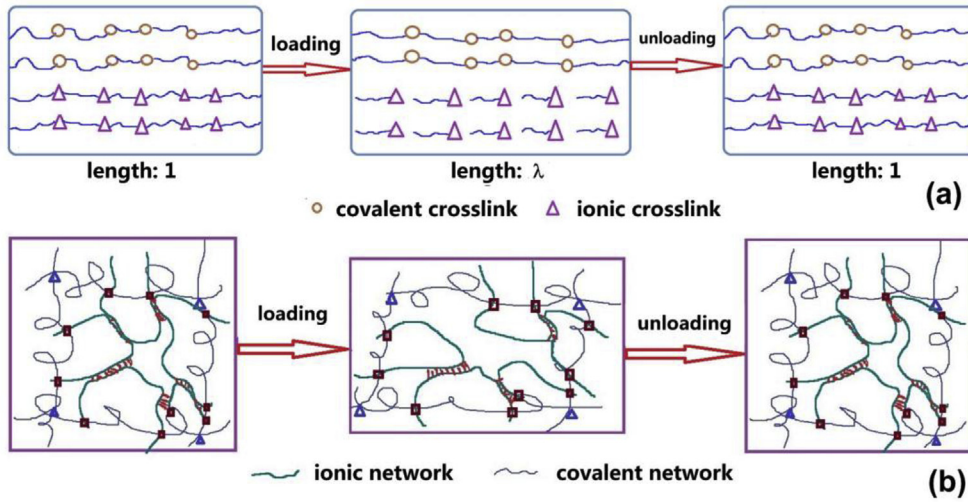

Fig. 1. (a) Dissipation much energy by the breakage of the ionic crosslinks and the configurational entropy of the covalent network makes the hydrogel return to the initial state. (b) The change of the ionic network during the loading and unloading process: some of the ionic crosslinks break, the other is in elastic process. Meanwhile, the elastic long chains have a big deformation during the loading process and return to its initial state during the unloading process.

working mechanism and predict the mechanical behavior of the double-network hydrogel composites.

2. Modelling for ionic network

According to the theory of transient network, the viscoelastic ionic network can be treated as a transient network made from short chains and adaptive links [26]. All the short chains are repeatedly connected via the same adaptive links [27–29]. It is assumed that the short chains of ionic networks lead to annihilation even at a small tensile strain. Therefore, the mechanical response of the ionic network is viscoelastic.

We use the function $\Lambda\left(t, \vec{l}\right)$ to represent the number of adaptive links with respect to the unit vector $\vec{l}$ (per unit mass) existed at time t. The quantity of breakage $\widetilde{\Gamma}\left(t, \vec{l}\right)$ within a constant interval time equals to,

$$\widetilde{\Gamma}\left(t, \vec{l}\right) = -\frac{\partial \Lambda}{\partial t}\left(t, \vec{l}\right)$$
(1)

Here, the constant $\chi\left(\vec{l}\right)$ represents the proportion of permanent links in the ionic network, i.e.:

$$\widetilde{\Lambda}\left(\vec{l}\right) = \Lambda\left(0, \vec{l}\right)$$
(2)

where $\Lambda\left(0, \vec{l}\right)$ is the number of links (peer unit mass) at $t = 0$ with respect to the stretching direction $\vec{l}$. Therefore, the adaptive links exist at time t can be expressed by:

$$\Lambda\left(t, \vec{l}\right) = \chi\left(\vec{l}\right)\widetilde{\Lambda}\left(\vec{l}\right) + Z\left(t, \vec{l}\right)$$
(3)

where $Z\left(t, \vec{l}\right)$ represents the content of the remaining adaptive links at t. The rate of breakage is a function of adaptive links, i.e.:

$$\Gamma\left(t, \vec{l}\right) = \frac{\widetilde{\Gamma}\left(t, \vec{l}\right)}{Z\left(t, \vec{l}\right)} = b$$
(4)

where b is the breakage rate of the ionic network. Different from the

covalent network, the breakage rate of the ionic network is much larger and more sensitive to the tensile rate [21,25]. Here, we can get the differential of $Z\left(t, \vec{l}\right)$ by combining equations (1), (3) and (4),

$$\frac{\partial Z}{\partial t}\left(t, \vec{l}\right) = -b \cdot Z\left(t, \vec{l}\right)$$
(5)

At $t = 0$, the initial condition is $Z\left(0, \vec{l}\right) = \widetilde{\Lambda}\left(\vec{l}\right)\left[\left(1 - \chi\left(\vec{l}\right)\right)\right]$, therefore, we can obtain:

$$Z\left(t, \vec{l}\right) = \widetilde{\Lambda}\left(\vec{l}\right)\left[1 - \chi\left(\vec{l}\right)\right]\exp(-bt)$$
(6)

By substituting equation (6) into equation (3), we can obtain:

$$\Lambda\left(t, \vec{l}\right) = \widetilde{\Lambda}\left(\vec{l}\right)\left\{\chi\left(\vec{l}\right) + \left[1 - \chi\left(\vec{l}\right)\right]\exp(-bt)\right\}$$
(7)

Here, the function $w\left(t, \vec{l}\right)$ is introduced to express the average potential energy of each link of the ionic network with respect to the vector $\vec{l}$, therefore, we can obtain the potential energy of the ionic network (per unit mass) as:

$$W(t) = \int_S \Lambda\left(t, \vec{l}\right)w\left(t, \vec{l}\right)f\left(0, \vec{l}\right)dA\left(\vec{l}\right)$$
(8)

where $f\left(0, \vec{l}\right)$ denotes the density of the ionic link, S is the boundary of a unit sphere with respect to the vector $\vec{l}$. As the ionic networks are considered to be isotropic [19], both the functions $\widetilde{\Lambda}\left(\vec{l}\right)$ and $\chi\left(\vec{l}\right)$ are independent of the guiding vector, and the density of the adaptive link becomes a constant,

$$f\left(0, \vec{l}\right) = a$$
(9)

We use spherical angles φ and ϑ to locate the vectors in the Cartesian coordinate. $\vec{e_i}$ is the unit vector. Accordingly, we can obtain:

$$\vec{l} = \cos\vartheta\,\vec{e_1} + \sin\vartheta(\cos\varphi\,\vec{e_2} + \sin\varphi\,\vec{e_3})$$
(10)

$$dA = \sin\vartheta d\vartheta d\varphi.$$
(11)

Here, we can further write the total equations by substituting equations (7), (9) and (11) into (8),