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Unraveling bio-inspired pre-swollen effects of tetra-polyethylene glycol double network hydrogels with ultra-stretchable yielding strain

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Abstract: Incorporating flexible cross-links into a brittle network for hydrogel not only significantly improves its toughness, but also effectively provides opportunities to design novel double network (DN) hydrogels with targeted properties and multi-functionalities. However, the principles and toughening mechanisms behind many of experimental studies have not been investigated. In this paper we proposed, for the first time, a phenomenological model for the DN hydrogels, which were derived from homogenous tetra-polyethylene glycol (tetra-PEG) first network, molecular stent and flexible polyacrylamide (PAAm) second network, and theoretically and then experimentally studied the pre-swollen effects on their ultra-stretchable yielding strains. Based on the Flory-Huggins solution theory, the pre-swollen effect of polar molecular

stents on the mechanical properties of tetra-PEG/PAAm DN hydrogels was investigated. Finally, the constitutive stress-strain relationships of two-stage loading process were established for the overall response of mechanical behavior, and a good agreement between the numerically simulated results with the experimental ones has been achieved. This study provides a fundamental understanding of the working mechanism of pre-swollen effects and the design guidance for the ultra-stretchable and toughened DN hydrogels.

Keywords: double-network hydrogel; modelling; pre-swollen effect; yielding

1. Introduction

Hydrogels are one of the important soft materials which have many uniquely biomimetic and biocompatible properties, due to their three-dimensional porous network structures and large water content [1-3]. Due to these advantages, multi-stimuli responsive [4] and multi-functional hydrogels [5] have recently been developed with different molecular additives. However, most hydrogels are mechanically weak and unsuitable for many load-bearing applications. In order to solve this problem, double network (DN) gels, which show extremely good toughness, have been proposed. They are generally composed of two types of polymeric networks with interpenetrating structures, e.g., rigid and brittle first network as well as soft and ductile second network [6-9]. Generally, the rigid and brittle ionic network breaks during loading process and dissipates large mechanical energy generated from the fracture of ionic bonds is often used as the soft second network because this hydrophilic polymer shows a large

deformation, and disperses the mechanical energy into the first network by interpenetrating within it [7,8]. These mechanisms enable the DN hydrogels maintaining their good mechanical properties during the large tensile deformation [10,11]. Meanwhile, the soft and ductile covalent network plays an essential role to remember the shape of the DN hydrogels [12]. During the large deformation, hydrogels show irreversible mechanical hysteresis and a lower loading strength [13,14]. Meanwhile, the inhomogeneous first network contributes the high strength of the hydrogels because the fracture of ionic bonds dissipates much mechanical energy in the molecular scale as reported in experimental studies [15-17] and theoretical works [18,19]. Recently, studies showed that the soft and neutral tetra-polyethylene glycol (tetra-PEG) gels become stiff and polarized by adding the molecular stent which has the properties and can be used as the first network of DN gels, and this type of DN gel shows a very small hysteresis resulted from the little breakages of ionic bonds during the large deformation which is quite different from those of the conventional DN hydrogels [21-27]. However, the principles and working mechanisms behind these experimental results have not been explored and investigated in details. Furthermore, the pre-swollen effects on the yielding and toughening mechanisms are critically needed for further designs and fabrications of the DN hydrogels with the targeted properties and multi-functionalities.

In this study, a mixed swelling model is formulated to explain the molecular stents which enable the tetra-PEG polarized and swollen by water, as well as their constraint swelling behavior in the tetra-PEG/PAAm DN hydrogels. The free energy function has

been used to formulate the constitutive stress-strain relationships based on the Flory-Huggins solution theory and quasi-lattice theory [28-30]. A phenomenological model has been presented to study the pre-swollen effect on the mechanical behavior of the hydrogels by means of the worm-like chain theory [31-33], Obukhov model [34,35] and Morse equation [36,37]. Finally, the numerically simulated results obtained from the proposed model are compared with the experimentally obtained data for verifications.

2. Swelling effect of polar molecular stent on DN hydrogels

A hydrogel generally swells from a gel by absorbing a certain amount of water molecules. During the swelling process, the water molecules will infiltrate into the cross-linking network to make gels expanding, thus generating elastic shrinkage energy [28]. The equilibrium condition of swelling can be described using the Flory-Huggins solution theory [28-30]. However, the tetra-PEG gels are not able to attract polar water molecules due to their apparent neutral states [38]. They could become polarized by adding the polar molecular stent [22], and thus enable the tetra-PEG/PAAm DN gel to be swollen by the water molecules [27]. Figure 1 shows a schematic illustration of the pre-swollen effect and stress loading on the DN hydrogels (where λ_3 is one-dimensional pre-swollen ratio, λ is the stretch ratio under an external loading stress, V_0 is the initial volume and V is the swollen volume) [27].

[Figure 1]

When a hydrogel is immersed into the water, the change in the free energy (ΔF) is composed of the mixing free energy (ΔF_M) and the elastic free energy (ΔF_d), which

can be written as [30]:

$$\Delta F = \Delta F_M + \Delta F_d \quad (1)$$

The mixing free energy function for this type of tetra-PEG/PAAm DN hydrogels can be expressed as [39]:

$$\Delta F_M(1) = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_1 n_1 \phi_2 + \chi_2 n_1 \phi_3) \quad (2)$$

where R is gas constant, T is the absolute temperature, and ϕ_1 , ϕ_2 and ϕ_3 are the volume fractions of the tetra-PEG, PAAm and water, respectively. n_1 , n_2 and n_3 are the molar numbers for the components of the tetra-PEG, PAAm and water, respectively. χ_1 and χ_2 are the parameters of the interactions between tetra-PEG and water as well as PAAm and water, respectively, and they are assumed to be the constants.

When the molecular stents have not been incorporated into the tetra-PEG network, equation (2) has the following form without the function of molecular stent ($\Delta F_M(2)$):

$$\Delta F_M(2) = RT(n_1 \ln \phi_1 + n_3 \ln \phi_3 + \chi_2 n_1 \phi_3) \quad (3)$$

Accordingly the influence of molecular stents on the mixing free energy can be expressed as,

$$\Delta F_M = \Delta F_M(1) - \Delta F_M(2) = RT(n_2 \ln \phi_2 + \chi_1 n_1 \phi_2) \quad (4)$$

Based on the quasi-lattice theory [28], we set x_1 and x_2 as the molar volume ratios of molecular stent and tetra-PEG, respectively. Then we can obtain:

$$\phi_2 = \frac{x_1 n_2}{n_1 + x_1 n_2 + x_2 n_3} \quad (5)$$

According to the statistical theory of elasticity, the elastic free energy of the polymer network (ΔF_d) has the form as follows [29]:

$$\Delta F_d = \frac{1}{2} NkT(\lambda_1^3 + \lambda_2^3 + \lambda_3^3 - 3) \quad (6)$$

where N is the number of molecule chains of the DN hydrogels per unit volume, λ_1 , λ_2 and λ_3 are the swelling ratio in three directions.

If we consider one-dimensional swelling condition, the following relationships can be obtained:

$$\lambda_1 = \lambda_2 = 1, \quad V = V_0 \lambda_3 \quad (7)$$

where V is the swollen volume and V_0 is the volume of tetra-PEG/PAAm DN hydrogel.

If we set the reference state of hydrogel without the influence of the molecular stent, equation (6) can be used to describe the changes of the elastic free energy caused by adding the molecule stents:

$$\lambda_3 - 1 = \lambda_3 \phi_2 \quad (8)$$

Combining equations (7) and (8) into (6), we can get:

$$\Delta F_d = \frac{1}{2} NkT (\lambda_3^3 - 1) = \frac{1}{2} NkT \left[\left(\frac{1}{1 - \phi_2} \right)^3 - 1 \right] \quad (9)$$

The equilibrium swelling will occur when the difference of chemical potential ($\Delta\mu$) for water at inside and outside of the hydrogels turns to zero, which can be expressed using:

$$\Delta\mu = \frac{\partial\Delta F}{\partial n_1} = \frac{\partial\Delta F_M}{\partial n_1} + \frac{\partial\Delta F_d}{\partial\phi_2} \frac{\partial\phi_2}{\partial n_1} = 0 \quad (10)$$

Substituting equations (4) and (6) in equation (10), we can get:

$$\frac{\Delta\mu}{RT} = -\frac{\phi_2}{x_1} + \chi_1 \phi_2 - \chi_1 \frac{n_1 \phi_2^2}{x_1 n_2} + \frac{3}{2} \frac{N}{N_a} \left(\frac{1}{1 - \phi_2} \right)^4 \frac{\phi_2^2}{x_1 n_2} = 0 \quad (11)$$

Thus equation (5) can be rewritten as:

$$\frac{n_1}{x_1 n_2} = \frac{1}{\phi_2} - 1 - \frac{x_2 n_3}{x_1 n_2} \quad (12)$$

Substituting equation (12) into (11), we can get:

$$x_1 \chi_1 \phi_2 + \chi_1 \frac{x_2 n_3}{n_2} \phi_2 + \frac{3}{2} \frac{N}{N_a} \left(\frac{1}{1-\phi_2} \right)^4 \frac{\phi_2}{n_2} - 1 = 0 \quad (13)$$

For simplifications, we introduce three constants of A , B and C , e.g.:

$$A = x_1 \chi_1, \quad B = \chi_1 x_2 n_3 \quad \text{and} \quad C = \frac{3}{2} \frac{N}{N_a} \quad (14)$$

Incorporating equation (14) into (13), we can obtain:

$$A \phi_2 + B \frac{\phi_2}{n_2} + C \left(\frac{1}{1-\phi_2} \right)^4 \frac{\phi_2}{n_2} - 1 = 0 \quad (15)$$

According to the equations (8) and (15), we can derive an expression for the changes in molar number of the absorbed water caused by adding the molecular stent:

$$\left(A + \frac{B}{n_2} + \frac{C}{n_2} \lambda_3^4 \right) \left(1 - \frac{1}{\lambda_3} \right) - 1 = 0 \quad (n_2 \neq 0) \quad (16)$$

To verify the accuracy of equation (16), we compared the results obtained from this phenomenological formulation with the experimental data of obtained from the tetra-PEG/PAAm DN hydrogels [27], which are shown in Figure 2. Based on the experimental results [29], we can obtain the constants of $A=0.1$, $B=1.57$ and $C=0.004$. It is found that the increase in 1-D swelling ratio (λ_3) is small while the concentration of molecular stent is below 0.50 %. With a further increase in the concentration of the molecule stent, it gradually has a significant influence on the 1-D swelling ratio (λ_3) of tetra-PEG/PAAm DN hydrogels. The simulation results clearly show that the proposed model is suitable for predicting the constitutive relationship of 1-D swelling ratio (λ_3) as a function of the concentration of molecular stent.

[Figure 2]

On the other hand, the number of molecule chains per unit volume (N) and the interaction parameter between the tetra-PEG and water (χ_1) are two key parameters to characterize the swelling behavior of the DN hydrogels according to equation (14). Figure 3 shows the corresponding numerically obtained results. In Figure 3(a), the simulation results show that the 1-D swelling ratio (λ_3) is gradually increased with the increase in the molar number of molecular stent. With the N increased from $0.1 N$ to $15.0 N$, a higher molar number of molecular stents are required to enable the hydrogel to achieve the same swelling ratio. By increasing the number of molecule chains, the increase in the swelling ratio of hydrogel becomes difficult, and increased numbers of molecular stent are needed to be involved to absorb the water molecule. Meanwhile, a larger molar number of molecular stent is also needed to reach the same 1-D swollen ratio with an increase of interaction parameter (χ_1) from 0.1 to 4.0 as shown in Figure 3(b). As is well known, a higher interaction parameter (χ_1) of the polymer implies that it is more difficult to absorb the water due to the increased free energy for mixing according to the Flory-Huggins solution theory [28], and hence more molecular stents are necessary to achieve the same swelling ratio. Therefore, the swelling behavior is essentially influenced by the interaction parameter. This finding provides a useful approach to change the interaction parameter by using the interactive solvents (i.e., water, pH, ionic strength etc.) in order to design and predict the swelling behavior of the hydrogels. Our simulation results confirm that the 1-D swollen ratio is strongly determined by the number of molecule chains per unit volume (N) of tetra-PEG first network and the interaction parameter (χ_1).

[Figure 3]

3. Modelling of pre-swollen effects on the DN hydrogel

In the previous studies, it was proposed that the swollen tetra-PEG DN hydrogel has a perfect connectivity and a diamond lattice structure [20,27]. The network of tetra-PEG gel is finitely extensible and can be treated as a worm-like chain [40]. It has been found that the tetra-PEG DN hydrogels have experienced a two-stage loading process before their yield points [27]. The first stage is the “soft deformation” along the tensile direction, during which the stretch ratio becomes higher with a lower pre-swollen stress. The second stage is the “stiff deformation” along the tensile direction, which is a combined result from both the strengthened covalent bonds and ionic bonds in tetra-PEG network. The yield stress is gradually decreased when the pre-swollen ratio of tetra-PEG network is increased [27], while the mechanical strength is therefore improved due to the pre-swollen chains in tetra-PEG network [12]. Experimental results revealed that a constitutive relationship of pre-swollen ratio (λ_3) and loading stretching one (λ_{tens}) is $\lambda_3\lambda_{tens}=7.0$ for the tetra-PEG/PAAm DN hydrogel [20,40]. The DN hydrogel becomes tougher and highly stretchable due to the rearrangement of tetra-PEG molecule chains in the pre-swollen process.

3.1 Modelling of pre-swollen effect on tetra-PEG network

The toughness of PAAm second network is negligible compared with one of the tetra-PEG first network before the yielding point of the DN hydrogel [13]. Therefore we can establish the stress-strain relationship of a two-stage loading process mainly based on the first tetra-PEG network.

At the first loading stage, the tetra-PEG chains could be regarded as the worm-like chains (WLC) and has the lattice structure of diamond [20,27]. The nonlinear relationship between force (f) and end-to-end extension (z) is given as [31]:

$$f = \frac{k_B T}{\xi} \left[\frac{1}{4} \left(1 - \frac{z}{L} \right)^{-2} - \frac{1}{4} + \frac{z}{L} \right] \quad (17)$$

where k_B is the Boltzmann constant, ξ is the persistence length and L is the total contour length.

Persistence length (ξ) is introduced here which is an intrinsically mechanical quality for the stiffness (B_s) of a polymer [41]:

$$\xi = \frac{B_s}{k_B T} \quad (18)$$

Here the stiffness (B_s) can be expressed by the Young's modulus (E) [41]:

$$B_s = E \cdot I \quad (19)$$

where I is the moment of inertia.

According to the Obukhov model [34,35], the dependence of Young's modulus on the volume fraction of tetra-PEG has the following form:

$$E = \frac{3\phi_3}{a^3 N} F_{el}^0 \quad (20)$$

where F_{el}^0 is the elastic energy, a^3 and ϕ_3 are the volume and volume fraction of the tetra-PEG chain, respectively.

According to equation (5), ϕ_3 is expressed as follows:

$$\phi_3 = \frac{x_2 n_3}{n_1 + x_1 n_2 + x_2 n_3} = \frac{x' x_2 n_3}{\lambda_3 V_0} \quad (21)$$

where x' is the volume of water molecules.

The elastic energy (F_{el}^0) of a polymer chain can be given as [40]:

$$F_{el}^0 = \left(\frac{\lambda_3 R_0}{R} \right)^2 k_B T \quad (22)$$

where R_0 and R are the root-mean-square end-to-end distances of the chains without and with swollen effect by the water molecules, respectively.

The end-to-end distance of a tetra-PEG chain (R) in the semi-dilute region has the following form [40]:

$$R \cong a(N')^\nu \left(\frac{\phi_3}{\phi^*} \right)^{\frac{2\nu-1}{2(1-3\nu)}} \quad (23)$$

where ϕ^* is the volume fraction of overlapped polymer chains, ν is the exponent of excluded volume effect and N' is the polymerization degree.

By substituting equation (21) into (23), we can get:

$$R \cong aN'^\nu \left(\frac{x' x_2 n_3}{\lambda_3 V_0 \phi^*} \right)^{\frac{2\nu-1}{2(1-3\nu)}} \quad (24)$$

Elastic energy (F_{el}^0) can be further rewritten according to equations (22) and (24),

$$F_{el}^0 = \left[\frac{\lambda_3 R_0}{aN'^\nu} \cdot \left(\frac{x' x_2 n_3}{\lambda_3 V_0 \phi^*} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^2 k_B T \quad (25)$$

By substituting equations (21) and (25) into (20), we can obtain the following form of Young's modulus:

$$E = \frac{3x' x_2 n_3}{a^3 N \lambda_3 V_0} \left[\frac{\lambda_3 R_0}{aN'^\nu} \cdot \left(\frac{x' x_2 n_3}{\lambda_3 V_0 \phi^*} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^2 k_B T \quad (26)$$

A constitutive relationship between the persistence length (ξ) and swollen volume (λ_3) can be further obtained according to equations (18), (19) and (26),

$$\xi = \frac{B_s}{k_B T} = \frac{EI}{k_B T} = \frac{3x'x_2n_3I}{a^3N\lambda_3V_0} \left[\frac{\lambda_3R_0}{aN^{\nu}} \cdot \left(\frac{x'x_2n_3}{\lambda_3V_0\phi^*} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^2 \quad (27)$$

As the x' , x_2 , n_3 , V , I , a , N and R_0 are the given constants, a set of parameters α , β and γ are introduced,

$$\alpha = \frac{3x'x_2n_3I}{a^3NV_0}, \quad \beta = \frac{R_0}{a} \quad \text{and} \quad \gamma = \frac{x'x_2n_3}{\phi^*V_0} \quad (28)$$

Incorporating equations (25) and (28), we can obtain:

$$\xi = \frac{\alpha}{\lambda_3} \left[\frac{\lambda_3\beta}{N^{\nu}} \cdot \left(\frac{\gamma}{\lambda_3} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^2 \quad (29)$$

Furthermore, the constitutive relationship of force (f) and end-to-end extension (z) of a single chain can be obtained from equations (17) and (29),

$$f = \frac{k_B T}{\alpha} \lambda_3 \left[\frac{\lambda_3\beta}{N^{\nu}} \cdot \left(\frac{\gamma}{\lambda_3} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^{-2} \left[\frac{1}{4} \left(1 - \frac{z}{L} \right)^{-2} - \frac{1}{4} + \frac{z}{L} \right] \quad (30)$$

The end-to-end extension (z) can also be expressed as:

$$z = l_0 \sqrt[3]{\lambda_3} (\lambda - 1) \quad (31)$$

where l_0 is the length of the tetra-PEG chains without adding the molecular stents.

Due to the uniform distribution of tetra-PEG chains in DN hydrogel, we can set the number of molecule chains per unit area using the parameter N_a . By combining equations (30) with (31), the stress (σ) and stretch ratio (λ) have the following relationship:

$$\sigma = \frac{N_a k_B T}{\alpha} \lambda_3 \left[\frac{\lambda_3\beta}{N^{\nu}} \cdot \left(\frac{\gamma}{\lambda_3} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^{-2} \left[\frac{1}{4} \left(1 - \frac{l_0 \sqrt[3]{\lambda_3} (\lambda - 1)}{L} \right)^{-2} - \frac{1}{4} + \frac{l_0 \sqrt[3]{\lambda_3} (\lambda - 1)}{L} \right] \quad (32)$$

To verify the accuracy of equation (32), the simulation results of the model are

compared with the experimental data [27] of tetra-PEG/PAAm DN hydrogels with different pre-swollen ratios ($\lambda_3=2.1, 2.3, 3.0, 3.3$ and 3.9), as shown in Figure 4(a). The fitting data are presented in Table 1. It is found that the proposed model well describes and predicts the mechanical behavior of the DN hydrogels. However, they do not show the Mullin effect during the loading process because there is no breakage of the ionic bonds in this stage. Different pre-swollen volumes cause the changes of Young's moduli thus resulting in the DN hydrogels with different mechanical properties.

To investigate the effect of pre-swollen ratio on the mechanical property of DN hydrogel, Figure 4(b) presents the simulation results of the stress as a function of stretch ratio at $\lambda_3=0.1, 1, 2, 3, 4$ and 5 . When the pre-swollen ratio is small (e.g., $\lambda_3=0.1$), the tetra-PEG gels cannot resist to the large force because the amount of absorbed water is far too less to enable it to form a gel. With further increasing of the amount of absorbed water molecules, the DN hydrogel turns to become stiff and shows a classically viscoelastic behavior. At the same stretch ratio, a larger external stress applied on the hydrogel is required. These experimental and theoretical results provide the evidence for the pre-swollen effect of the molecular stent on the strength in the DN hydrogel. The molecular stent plays an essential role in improving and enhancing the mechanical properties by determining the pre-swelling ratio for the tetra-PEG/PAAm DN hydrogels.

[Table 1]

[Figure 4]

Furthermore, it is necessary to separate the effects of the polymerization degree (N') and the exponent of excluded volume (ν) on the stress of tetra-PEG/PAAm DN

hydrogel based on the above-mentioned simulation results. Here the simulations for the hydrogel with a given polymerization degree ($N' = 0.1 N, 1.0 N, 5.0 N, 10.0 N, 15.0 N$ or $20.0 N$) and the exponent of excluded volumes ($\nu = 0.33, 0.34, 0.35, 0.36$ or 0.37) are presented to explore their working mechanisms in influencing the constitutive stress-strain relationship. The results are shown in Figure 5. Numerical results of the stress as a function of the strain for the DN hydrogel are plotted according to the equation (32) as shown in Figure 5(a). It can be seen that the stress is gradually increased with the increase in the polymerization degree, at a given stretch ratio. This is because a higher polymerization degree provides the polymer network to have higher elastic modulus and stiffness [28,29], thus resulting in much higher mechanical energy and stress which are necessary to stretch the hydrogel to a given stretch ratio.

On the other hand, the numerical results for the stress as a function of stretch ratio of the DN hydrogel are shown in Figure 5(b). With an increase in the exponent of excluded volume (ν), the interaction parameter (χ) between the hydrogel and the water is decreased, due to the existence of less water molecules easily absorbed by the hydrogels [30]. With a higher value of exponent of excluded volume (ν), a larger stress is needed for the DN hydrogel to achieve a given constant stretch ratio. These simulation results are contributed to the increased mechanical energy and mixing free energy according to the Flory-Huggins solution theory [28,29]. As the interaction parameter (χ) between the hydrogel and water is decreased, the water molecules are easily absorbed, which will result in the increase of mixing free energy, whereas the stretching free energy is kept a constant at the same stretch ratio. Based on the solution theory [28,29],

the free energy is equal to the mechanical energy of the hydrogel. Therefore, a larger stress is needed owing to the higher mechanical energy, when the stretch ratio keeps a constant.

[Figure 5]

3.2 Modelling of pre-swollen effect on covalent and ionic bonds

After the first loading process, the external stress is mainly applied onto the covalent and ionic bonds of the tetra-PEG first network. Morse potential function is then introduced to formulate the constitutive relations of stress and interatomic potential ($U(x)_c$) for the covalent bonds [36, 37]:

$$\frac{U(x)_c}{D_c} = 1 - [\exp(-2\alpha_c x) - 2\exp(-\alpha_c x)] \quad (33)$$

where D_c is the dissociation energy of the interatomic covalent bond without vibration, α_c is the Morse coefficient and x is the distance of the interatomic bond.

The distance of covalent bonds at the loading process can be expressed using:

$$x = x_0 \lambda_3 (\lambda - \lambda') \quad (34)$$

where λ' is the stretch ratio of the frizzy chains to be unfolding at the first loading process and λ_3 is the pre-swollen ratio. Incorporating equation (34) into (33), the interatomic potential ($U(\lambda)_c$) as a function of stretch ratio (λ) can be obtained:

$$U(\lambda)_c = D_c - D_c \left\{ \exp[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda')] - 2\exp[-\alpha_c \lambda_3 x_0 (\lambda - \lambda')] \right\} \quad (37)$$

Here the mechanical energy (W_c) applied on the covalent bond can be written as:

$$\begin{aligned} W_c &= U(0)_c - U(\lambda)_c \\ &= U(0)_c + D_c \left\{ \exp[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda')] - 2\exp[-\alpha_c \lambda_3 x_0 (\lambda - \lambda')] \right\} - D_c \end{aligned} \quad (38)$$

where $U(0)_c$ is the initial potential of the covalent bond without the applied external

force.

Similarly, the mechanical energy of ionic bonds in the first network is also assumed to follow the same form of the covalent bonds. Equation (38) is therefore rewritten as:

$$\begin{aligned} W_i &= U(0)_i - U(\lambda)_i \\ &= U(0)_i + D_i \left\{ \exp \left[-2\alpha_i \sqrt[3]{\lambda_3} x_0(i) (\lambda - \lambda') \right] - 2 \exp \left[-\alpha_i \sqrt[3]{\lambda_3} x_0(i) (\lambda - \lambda') \right] \right\} - D_i \end{aligned} \quad (39)$$

where $U(0)_i$, α_i , D_i and $x_0(i)$ are the corresponding parameters for the ionic bonds.

For the tetra-PEG networks which are incorporated of covalent bonds and ionic bonds, the overall mechanical energy (W) per unit volume is resulted from both bonds, i.e.,

$$W = (mW_c + nW_i) / (V_0 \lambda_3) \quad (40)$$

where m and n are the molar numbers of the covalent and ionic bonds in the tetra-PEG network, respectively, with a pre-swollen volume of $V = V_0 \lambda_3$ (where V_0 is the initial volume of the DN hydrogel).

According to equations (38), (39) and (40), differentiating equation (40) with respect to the stretch ratio will obtain the following function,

$$\begin{aligned} S = \frac{\alpha W}{\alpha \lambda} &= \frac{2m\alpha_c D_c x_0}{V_0 \lambda_3} \left\{ \exp \left[-\alpha_c \lambda_3 x_0 (\lambda - \lambda') \right] - \exp \left[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda') \right] \right\} \\ &+ \frac{2n\alpha_i D_i x_0}{V_0 \lambda_3} \left\{ \exp \left[-\alpha_i \lambda_3 x_0 (\lambda - \lambda') \right] - \exp \left[-2\alpha_i \lambda_3 x_0 (\lambda - \lambda') \right] \right\} \end{aligned} \quad (41)$$

Here the hydrogel is assumed to be incompressible, thus:

$$\hat{\sigma} = -p \hat{I} + \hat{s} \quad (42)$$

where $\hat{\sigma}$ is the stress tensor, p is the pressure, \hat{I} is the moment of inertia and \hat{s} is the deviatoric stress.

Under a uniaxial extension, the stress tensor $\hat{\sigma}$ can be calculated using [42]:

$$\sigma_1 = -p + S \quad \text{and} \quad \sigma_2 = \sigma_3 = -p - 0.5S = 0 \quad (43)$$

where σ_1 is the stress along the loading direction, σ_2 and σ_3 are the stresses applied perpendicularly to the loading direction.

Submitting equation (41) into (43), we can obtain:

$$\begin{aligned} \sigma_1 = \frac{3}{2}S = & \frac{3m\alpha_c D_c x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_c \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda')] \right\} \\ & + \frac{3n\alpha_i D_i x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_i \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_i \lambda_3 x_0 (\lambda - \lambda')] \right\} \end{aligned} \quad (44)$$

The overall stress also needs to consider the previously pre-swollen effect. The stress σ' is assumed to be equal to the final value of the stress under the first loading. The overall stress (σ) therefore has the following form:

$$\begin{aligned} \sigma = \sigma_1 + \sigma' = & \frac{3m\alpha_c D_c x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_c \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda')] \right\} \\ & + \frac{3n\alpha_i D_i x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_i \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_i \lambda_3 x_0 (\lambda - \lambda')] \right\} + \sigma' \end{aligned} \quad (45)$$

Figure 6 provides the numerical results for the stress values as a function of the stretch ratio of DN hydrogel with different pre-swollen ratios of $\lambda_3 = 2.1, 2.3$ and 3.0 . The experimental data are also plotted for comparisons [27]. Table 2 presents the material parameters of the DN hydrogel used in equation (45). It is found that the simulation results are in good agreements with the experimental ones. With the pre-swollen ratio increased from 2.1, 2.3 to 3.0, a larger stress is needed to stretch the hydrogel to the same stretch ratio. These simulation results confirm that the constitutive relation of stress and stretch ratio is strongly determined by the pre-swollen effect.

[Table 2]

[Figure 6]

Owing to the intrinsic differences of the covalent and ionic bonds, the pre-swollen effects on their stress-stretch ratio relationships are essential to quantitatively separate and identify their working mechanisms. Figure 7(a) plots the curves of stress-stretch ratios for the DN hydrogel at different pre-swollen ratios of $\lambda_3=2.0, 3.0, 4.0, 5.0$ and 6.0 . With an increase in the pre-swollen ratio, the stress is gradually decreased due to the decrease in mechanical energy according to equation (40). On the other hand, it is found that the yielding stress (σ) and strain are both decreased from 1.68 MPa, 1.2 MPa, 0.84 MPa, 0.67 MPa to 0.56 MPa and from $5.0, 3.6, 3.0, 2.6$ to 2.4 , respectively, when the pre-swollen ratio (λ_3) is increased from $2.0, 3.0, 4.0, 5.0$ to 6.0 .

The contribution of covalent and ionic bonds to the yielding behavior of DN hydrogel was further investigated and the results are shown in Figure 7(b). The simulation results reveal that the force is mainly applied onto the covalent bonds of the tetra-PEG network, and this is why little ionic bonds of the tetra-PEG network are broken before the yielding point. The simulation results reveal that the yielding stresses are 5.0 MPa and 4.8 MPa for the hydrogel and the covalent bond in tetra-PEG network, respectively, with the pre-swollen ratio of $\lambda_3=2.0$. While the yielding stresses are 3.6 MPa and 3.0 MPa for the hydrogel and the covalent bond, respectively, with a pre-swollen ratio of $\lambda_3=3.0$. These simulation results reveal that the yielding behavior of the hydrogel is mainly determined by the covalent bonds in the tetra-PEG network, and the pre-swollen ratio has a significant influence on the covalent bonds. It should also be mentioned that there is minor pre-swollen effect on the ionic bonds even as the pre-swollen ratio is

increased from 2.0 to 3.0. The pre-swollen effect on the hydrogel is mainly contributed to that of the covalent bonds.

[Figure 7]

Based on the previous results, it is necessary to characterize the overall response of the mechanical behavior of the tetra-PEG/PAAm DN hydrogel undergoing two-stage loading process. Combining equations of (16), (32) and (45), we could predict the mechanical behavior of the hydrogel using the pre-swollen ratio which is determined by the molar number of molecular stents. The overall response of the mechanical behavior of this DN hydrogel is described by the equation (46). The simulation results have been plotted and compared with the experimental data [27] and the results are shown in Figure 8. A good agreement between the simulation and experimental results has been found. It is confirmed that the theoretical model could well describe and predict the overall response of mechanical behavior for the DN hydrogel with different pre-swollen ratios.

$$\left\{ \begin{array}{l} \left(A + \frac{B}{n_2} + \frac{C}{n_2} \lambda_3^4 \right) \left(1 - \frac{1}{\lambda_3} \right) - 1 = 0 \quad (n_2 \neq 0) \quad \text{controlling pre-swollen ratio formula} \\ \sigma = \frac{\nu k_B T}{\alpha} \lambda_3 \left[\frac{\lambda_3 \beta}{N^{\nu}} \cdot \left(\frac{\gamma}{\lambda_3} \right)^{\frac{2(1-3\nu)}{2\nu-1}} \right]^{-2} \left[\frac{1}{4} \left(1 - \frac{l_0 \sqrt[3]{\lambda_3} (\lambda - 1)}{L} \right)^{-2} - \frac{1}{4} + \frac{l_0 \sqrt[3]{\lambda_3} (\lambda - 1)}{L} \right] \\ \sigma = \frac{3m\alpha_c D_c x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_c \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_c \lambda_3 x_0 (\lambda - \lambda')] \right\} \\ \quad + \frac{3n\alpha_i D_i x_0}{V_0 \lambda_3} \left\{ \exp[-\alpha_i \lambda_3 x_0 (\lambda - \lambda')] - \exp[-2\alpha_i \lambda_3 x_0 (\lambda - \lambda')] \right\} + \sigma' \end{array} \right. \quad (46)$$

[Figure 8]

5. Conclusions

In this study, we proposed a phenomenological model to investigate the pre-swollen

effect and yielding behavior of the tetra-PEG/PAAm DN hydrogels. The proposed constitutive framework provides an effective theoretical approach to characterize the effects of pre-swollen effect on the mechanical behavior and two-stage loading process. The new toughening mechanism (little ionic bonds of the first network break before the yielding point) has been identified because the mechanical energy is mainly on the covalent bonds. It is also found that the pre-swollen effect on the yielding behavior is mainly contributed to the covalent bonds in the tetra-PEG first network. The yielding stress is decreased from 5.0 MPa to 3.6 MPa with the pre-swollen ratio increased from 2.0 to 3.0. Finally the overall response of the two-stage loading process of DN hydrogel has been studied and a good agreement between the simulation results and experimental data has been found. The theoretical model proposed in this study can be further used to help the design of DN hydrogels by means of controlling the degree of polymerization and interaction parameter to reach the required mechanical properties and yielding deformation.

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Tables caption

Table 1. Parameter values used in equation (32).

Table 2. Parameter values used in equation (45).

Table 1. Parameter values used in equation (32).

$N_a k_B T / \alpha$	β / N^v	γ	ν	l_0 / L
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0.005	0.512	0.5954	0.36	0.249
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Table 2. Parameter values used in equation (45).

$3m\alpha_c D_c x_0 / V_0$	$\alpha_c x_0$	$3m\alpha_i D_i x_0 / V_0$	$\alpha_i x_0$
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12.77	0.09	3.92	0.006
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Figures caption

Figure 1. A schematic illustration for the pre-swollen effect and stress loading applied on the DN hydrogel composites.

Figure 2. Comparison between equation (16) and experimental data [27] of one-dimensional swelling ratio for the tetra-PEG/PAAm DN hydrogel composites with various concentrations of molecular stent in the as-prepared state.

Figure 3. (a) The influence of the number of molecule chains of the tetra-PEG gels per unit volume on the swollen property. (b) The influence of the interaction parameter between molecular stent and water on the swollen property.

Figure 4. (a) The comparison between simulation results from equation (32) and the experimental data [27]. (b) Numerical results of stress-stretch ratio curve at different pre-swollen ratios.

Figure 5. (a) Effect of polymerization degree of tetra-PEG (N') on the stress-stretch ratio of DN hydrogel composite. (b) Effect of the exponent of excluded volume effect (ν) on the stress-stretch ratio of DN hydrogel composite.

Figure 6. Comparison between results obtained from equation (45) and experimental data [27] of tetra-PEG/PAAm DN hydrogel composite.

Figure 7. (a) Numerical results of the effect of pre-swollen ratio on the stress-strain relationship of DN hydrogel composites. (b) Separate contributions of ionic and covalent bonds to the stress-strain curve of DN hydrogel composites.

Figure 8. Comparison between results from equation (46) and the experimental curve [27] with the pre-swollen ratio $\lambda_3=2.1, 2.3$ and 3.0 .

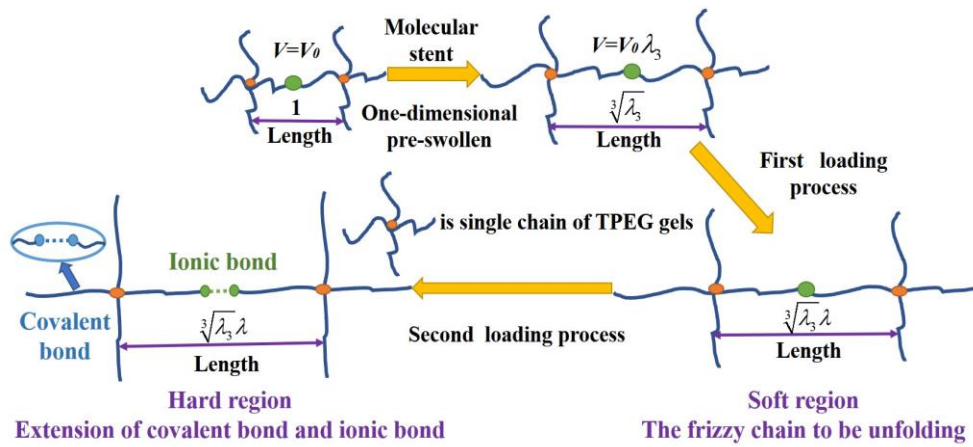


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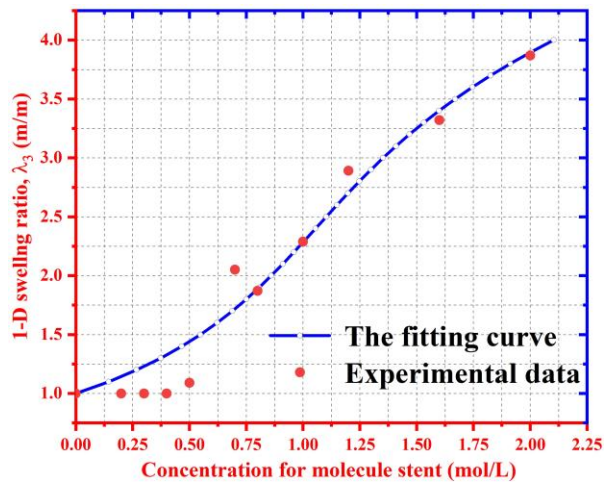


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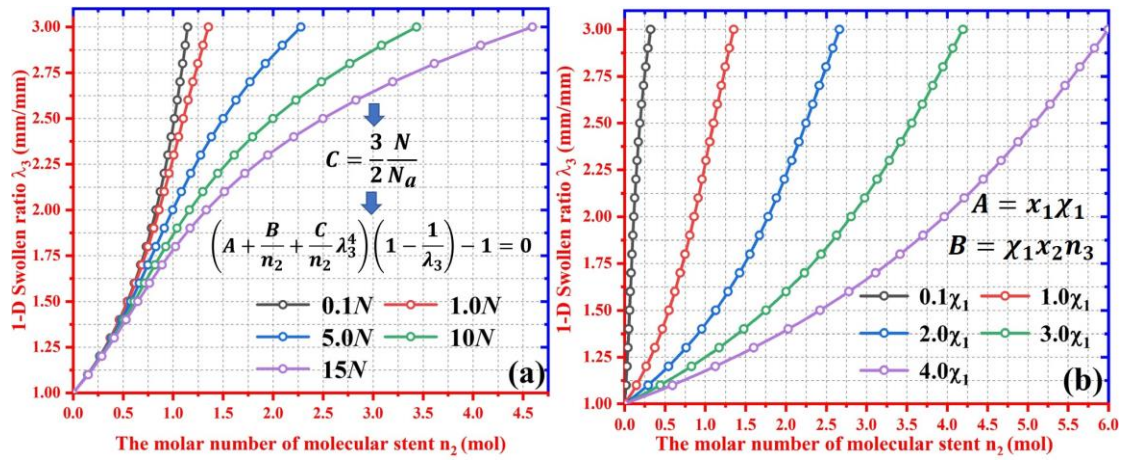


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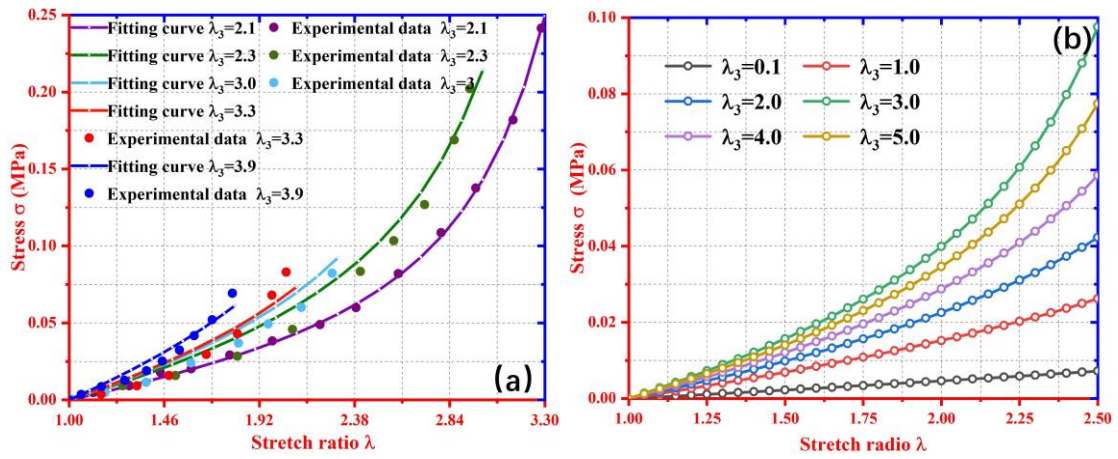


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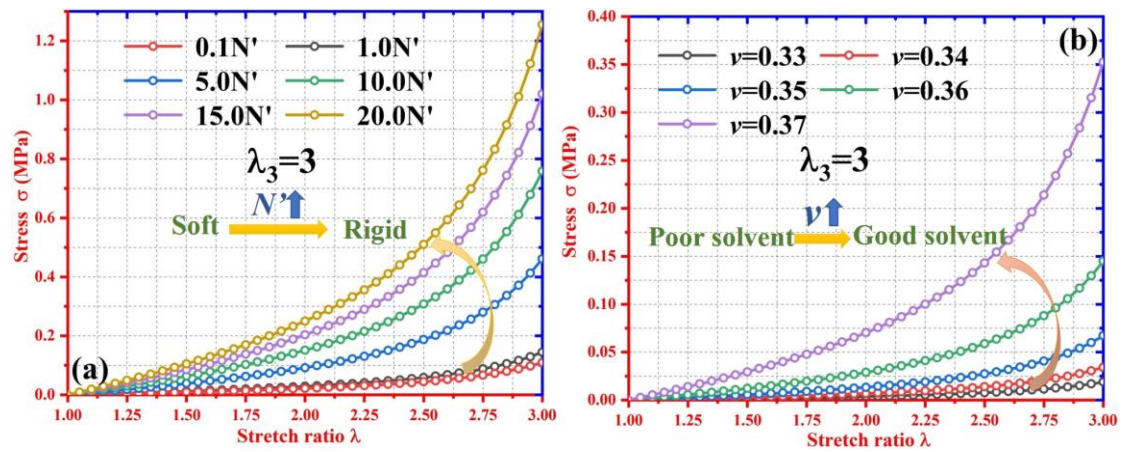


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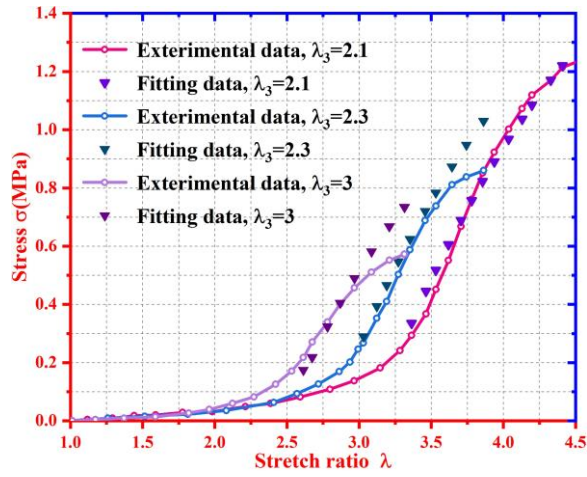


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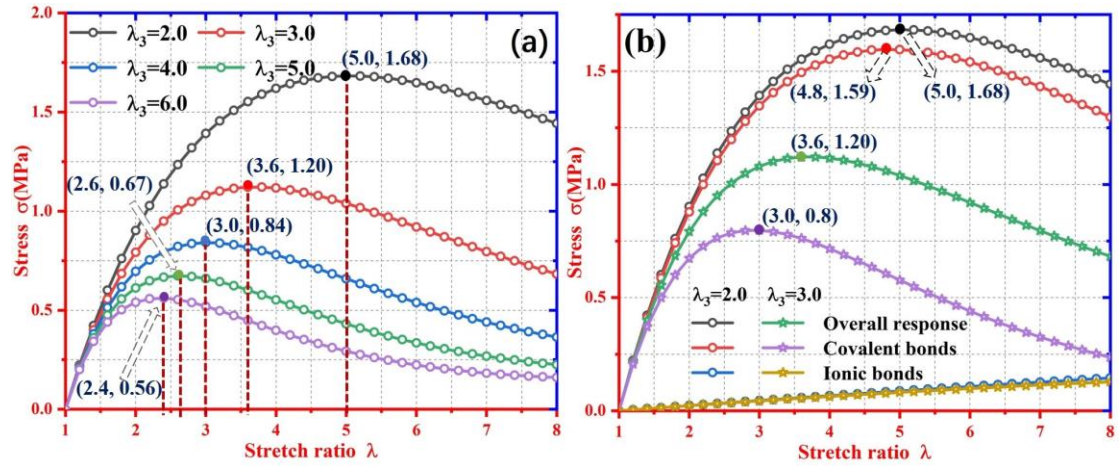


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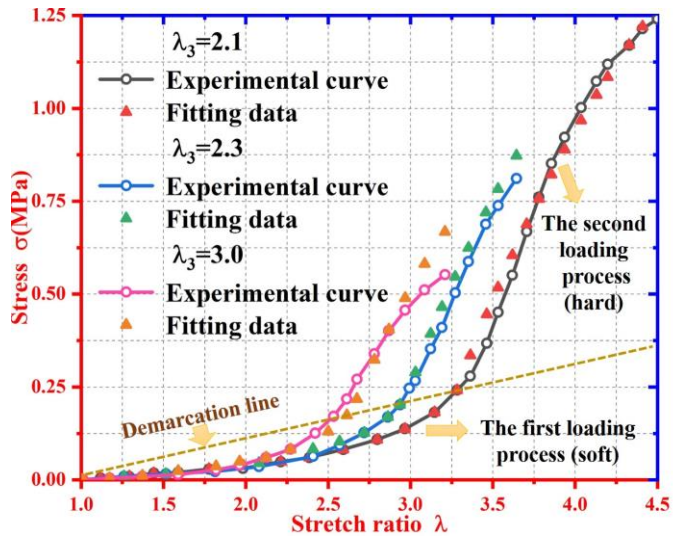


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