Modeling strategy for dynamic-modal mechanophore in double-network hydrogel composites with self-growing and tailorable mechanical strength

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Abstract: Smart materials with self-growing and tailorable mechanical strength have wide-range potential applications in self-healing, self-repairing, self-assembly, artificial muscle, soft robots and intelligent devices. However, their working mechanisms and principles are not fully understood yet and mathematically and physical modeling is a huge challenge, as traditionally synthesized materials cannot self-grow and reconstruct themselves once formed or deformed. In this study, a phenomenological constitutive model was developed to investigate the working mechanisms of self-growing and tailorable mechanical strength in double-network (DN) hydrogel composites, induced by mechanochemical transduction of dynamic-modal mechanophore. An extended Maxwell model was firstly employed to characterize the mechanical unzipping of hydrogel composites, and then mechanochemically induced destruction and reconstruction processes of brittle network in the hydrogel composite were formulated. The enhanced mechanical

strength of brittle network has been identified as the key driving force to generate self-growing and tailorable mechanical strength in the hydrogel composite. Finally, a stress-strain constitutive relationship was developed for the dynamic-modal mechanophorein the hydrogel composite. Simulation results obtained from the proposed model were compared with the experimental data, and a good agreement has been achieved. This study provides an effective strategy for modelling and exploring the working mechanism in the mechanoresponsive DN hydrogel composites with self-growing and tailorable mechanical strength.

Keywords: mechanochemical; modelling; hydrogel composite; self-growing

Nomenclature	
σ	Externally mechanical stress
σ_1 and σ_2	The internal stresses of the brittle and stretchable networks
ϕ_1 and ϕ_2	The dimensional cross-sectional areas of two networks
ε, ε_1 and ε_2	The strains of hydrogel composite, brittle and stretchable networks
η	Viscosity
E_1 and E_2	The moduli of the string components in brittle and stretchable networks
$\dfrac{d\sigma}{dt}$	The stress rate
$\dfrac{d\varepsilon}{dt}$	The strain rate
k_ε	Loading rate for uniaxial tensile testing machine
f_s	The friction force
μ	The frictional coefficient
σ_i	The interactive force between brittle and stretchable networks
E_s	The Young's modulus
ε_s	The Young's strain
$\overline{E}_1$ and $\overline{E}_2$	The Young's moduli of the newly formed brittle and stretchable networks, where $\overline{E}_1 = E_1\phi_1$ and $\overline{E}_2 = E_2\phi_2$
$\overline{\eta}$	The viscosity of newly stretchable network
$\hat{\varepsilon}$	The referenced strain
i	$i = \sqrt{-1}$
τ	The relaxation time
ω	Loading frequency

E'	The storage modulus
$\tan \delta$	The tangent delta parameter
T_g	The glass transition temperature
a_T	The shift factor based on the WLF equation
R^2	The correlation index

1. Introduction

Hydrogel is one of the most popular soft polymeric matters that exhibit a highly stretchable behavior in response to the externally mechanical loading [1-3]. It has highly absorbent polymeric networks and can contain over 90% water [4]. As a stimulus-responsive materials, the response modalities of hydrogels include temperature, pH value, chemical, light and mechanical loading [5-8]. Therefore, the stimulus-responsive hydrogels effectively pave the way for their successful applications in artificial muscle, soft robots and intelligent devices [9-11]. However, conventional hydrogels usually break at a low stress [12,13], and their mechanical properties have been regarded as soft and weak [14]. Recently, double-network (DN) hydrogel composites have been developed and attracted great attention due to their ultrahigh mechanical strength and toughness [12-15]. The DN hydrogel composites are incorporated of two types of polymeric network components which are referred to the brittle and stretchable networks, respectively [14,15]. It was reported that the DN hydrogel composites have mechanical strengths of 1-10 MPa and strains of 1000-2000% under the tensile stress, while their toughness values (tearing fracture energy) are as high as 100-1000 J/m^2 [14]. These excellent mechanical properties of DN hydrogel composites are dramatically different from those of the conventional soft

polymeric materials. Therefore, it presents a great challenge and currently receives extensive interests for the working mechanism of these DN hydrogel composites.

Studies on chemical responses of polymers upon mechanical simulation is crucial for wide-range research areas in polymer science, especially for designs of new types of stress-responsive and energy-transduction polymers [16-18]. Mechanochemistry has been identified as the key reason for DN hydrogels to have both high mechanical strength and toughness, resulted from the mechanochemical transduction at a molecular scale [19]. The mechanochemistry in the DN hydrogel is originated from the breakage of covalent or ionic bonds in a brittle network in response to the mechanical stress [19]. However, the working mechanism in mechanochemical transduction is complex and dramatically different from that of the conventional thermomechanical transduction. There are a few theoretical studies proposed for the mechanical behaviors of the DN hydrogel composites based on the mechanochemistry [20-23], however, due to their complex of mechanics and chemistry, it is critical to formulate new mechanochemical models for the DN hydrogelcomposites in order to explore their working mechanisms and extend their potential applications.

In this study, we formulated a phenomenologically constitutive model for the DN hydrogel composites with mechanically induced dynamic-modal mechanophores, which enable the hydrogel composites to have distinctive capability of self-growing and tailorable mechanical strength. Firstly, an extended Maxwell model was employed to characterize mechanical unzipping of the hydrogel composite. A stress-strain constitutive relationship was then established for the dynamic-modal

mechanophore and mechanochemical behavior of the DN hydrogel composites, and also for their brittle network undergoing a mechanically induced destruction-reconstruction process. Dependences of mechanical properties on Young modulus, cross-sectional areas and viscosity of network component were theoretically investigated. Finally, the simulation results obtained from the proposed model were compared and verified by the experimental data reported in the literature.

2. Dynamic-modal mechanophore in DN hydrogel composite

As reported in Ref. [24], a novel self-growing DN hydrogel was developed in response to repetitive mechanical stress, induced by effective mechanochemical transduction and destruction-reconstruction processes of brittle network. The working mechanism of this self-growing DN hydrogel is similar to that of muscle, which autonomously grows and remodels itself to adapt to its surrounding mechanical environment. A schematic illustration for the destruction-reconstruction and self-growing processes of the DN hydrogel composite is presented in Fig. 1. Its brittle network is considered as a rigid one in response to the mechanical stress, while its stretchable network is considered as a soft one. The mechanochemical transduction of the DN hydrogel is generally incorporated in four steps:

(1) The first step is the yielding of the brittle network, while the mechanical performance is ruled by the classical Maxwell model;

(2) The second step is resulted from the Van der Waals' force of intramolecular friction between brittle and stretchable networks;

(3) The third step is the mechanochemical transduction and structural destruction of

brittle network;

(4) The forth step is the reconstruction of brittle network, whose mechanical behavior is also ruled by the classical Maxwell model.
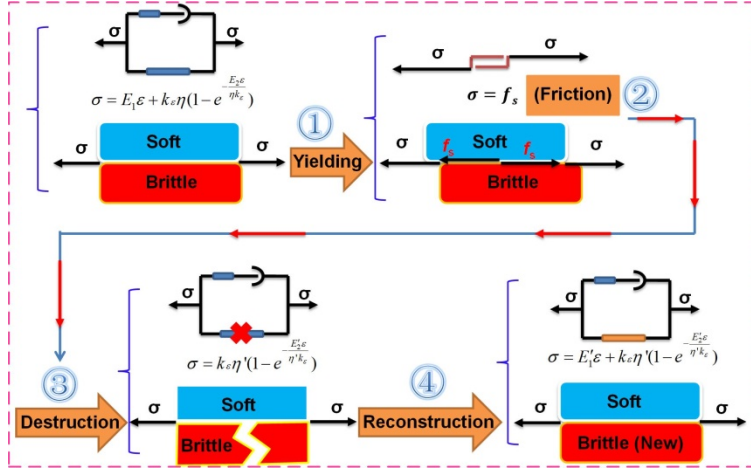

Fig. 1. Illustrations of mechanochemical transduction and mechanical behaviors of DN hydrogel in response to repetitive mechanical stress, including yielding, friction interaction, destruction and reconstruction processes.

The self-growing DN hydrogel composite is incorporated into two types of polymeric networks with totally different mechanical properties, namely the brittle network and the stretchable network. The brittle network generates mechano-radicals that can trigger chemical reactions and functionalizes like a string in response to external mechanical loading. On the other hand, the stretchable network remains intact to preserve the integrity of the bulk hydrogel [25-29] and presents a viscoelastic behavior. Here, an extended Maxwell model is introduced to describe the mechanical behavior of the DN hydrogel composite, where the two networks are in the parallel connection in response to an externally mechanical stress (σ), therefore,

$$\sigma = \phi_1\sigma_1 + \phi_2\sigma_2 \tag{1a}$$

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \tag{1b}$$

where σ_1 and σ_2 are the internal stresses of the brittle and stretchable networks, respectively; ϕ_1 and ϕ_2 are the dimensional cross-sectional areas of two networks, respectively, perpendicular to the direction of deformation; ε, ε_1 and ε_2 are the strains of hydrogel composite, brittle and stretchable networks, respectively.

It is assumed that the cross-sectional areas of two networks are equal to each other, i.e., $\phi_1 = \phi_2 = 0.5$ and $\phi_1 + \phi_2 = 1$, thus, the Maxwell equation of the hydrogel composite [30] can be re-written using the following format,

$$\sigma + \frac{\eta}{E_2}\frac{d\sigma}{dt} = E_1\varepsilon + (E_1 + E_2)\frac{\eta}{E_2}\frac{d\varepsilon}{dt} \tag{2}$$

where η is the viscosity, E_1 and E_2 are the moduli of the string components in brittle and stretchable networks, respectively. $\frac{d\sigma}{dt}$ and $\frac{d\varepsilon}{dt}$ are the stress rate and strain rate, respectively.

Equation (2) can also be expressed as,

$$\sigma = E_1\varepsilon + k_\varepsilon\eta - k_\varepsilon\eta e^{-\frac{E_2\varepsilon}{\eta k_\varepsilon}} \tag{3}$$

where k_ε is a given constant.

With an increase of mechanical loading, there is an intermolecular friction force, which is caused by the Van der Waals' forces generated between the brittle and stretchable networks. At this stage, the mechanical stress is used to overcome this friction force, i.e.,

$$\sigma = f_s = \mu\sigma_i \tag{4}$$

where f_s is the friction force, μ is the frictional coefficient and σ_i is the interactive force between brittle and stretchable networks.

Consequently, the brittle network is then broken with the further increase in the mechanical loading. At this stage, mechanically induced scission of the covalent bonds in the brittle network generates mechano-radicals [31-34]. In other words, when the mechanical stress is applied on the DN hydrogel composite, the covalent bonds have been broken to generate a large number of mechano-radicals at the broken ends of the brittle network, whereas the stretchable network still maintains the integrity of the composite. At this stage, the mechanical energy is mainly used for generating the scission of covalent bond in the brittle network. As the covalent bond is too brittle to break, and the strain is small, the Young's modulus of brittle network is thus assumed to be a constant. Meanwhile, as the strain is very small, the contribution of stretchable network to mechanical energy is insignificant. Therefore, in this step, the constitutive relationship of stress and strain can be written as:

$$\sigma = E_s \varepsilon_s \tag{5}$$

where E_s and ε_s are the Young's modulus and strain of the DN hydrogel composite, respectively.

Finally, the DN network presents a classically viscoelastic behavior in order to resist the external mechanical loading after the structural destruction-reconstruction processes of brittle network. For the brittle network, these mechanically induced mechano-radicals trigger a new type of polymerization of monomers to form a new type of brittle network [24]. The chemical radicals of the newly formed brittle network is different from that of the original one. On the other hand, at this stage, the mechanical behavior of the stretchable network is also different from that of the

original one, due to the induced permanent strain into the DN hydrogel composite. Therefore, the mechanical behavior of the hydrogel composite can be written as:

$$\sigma = \overline{E}_1\varepsilon + k_\varepsilon\overline{\eta} - k_\varepsilon\overline{\eta}e^{-\frac{\overline{E}_2\varepsilon}{k_\varepsilon\overline{\eta}}} \qquad (6)$$

where $\overline{E}_1$ and $\overline{E}_2$ are the Young's moduli of the newly formed brittle and stretchable networks, respectively, and $\overline{\eta}$ is the viscosity of newly stretchable network.

3. Constitutive model and simulation

3.1 Effect of weight fraction on the mechanical behavior

Combining equations (3) and (6), we can see that the mechanical behaviors of the original and newly formed DN hydrogel composite are both ruled by the Maxwell model. Consequently, it is necessary to explore the effect of weight fraction of each single network component on the mechanical behavior of hydrogel composite. Firstly, we assume that there is a mechanochemical transduction in the brittle network, thus, equation (6) can be re-written as,

$$\sigma = E_1\phi_1\varepsilon + k_\varepsilon\overline{\eta} - k_\varepsilon\overline{\eta}e^{-\frac{E_2\phi_2\varepsilon}{\overline{\eta}k_\varepsilon}} \qquad (7)$$

where ϕ_1 and ϕ_2 are the cross-sectional areas perpendicular to the direction of deformation of brittle and soft networks, respectively, and $\phi_1+\phi_2=1$. In comparison with equation (6), it is found that $\overline{E}_1=E_1\phi_1$ and $\overline{E}_2=E_2\phi_2$.

Fig. 2 plots the analytical results of the normalized stress as a function strain for the DN hydrogel composite, calculated using equation (7). For a given cross-sectional area of stretchable network, i.e., ϕ_2=0.2, 0.4, 0.6 or 0.8, the stress applied to the hydrogel composite is gradually increased with an increase in the strain. It is found

that the soft network with a large cross-sectional area experiences a lower stress at a given strain of the hydrogel composite. These simulation results reveal that the mechanical behavior of the DN hydrogel composite is critically determined by the cross-sectional area of the network component.
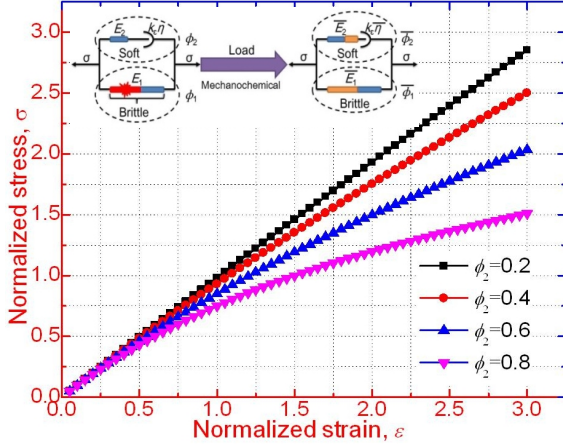

Fig. 2. Numerical results for the effect of cross-sectional areas on the mechanical behavior of DN hydrogel composite at a given ϕ_2 =0.2, 0.4, 0.6 and 0.8, where $k_\varepsilon \eta = k_\varepsilon \bar{\eta}$ =1.

3.2 Effect of viscoelasticity in network components on the mechanical behavior

Due to the dramatically different mechanical properties, it is necessary to investigate the effect of mechanical properties of each network component on the DN hydrogel composite. The obtained constitutive relationship of normalized stress as a function of strain applied to the hydrogel composite is plotted in Fig. 3, calculated based on equation (7). As shown in Figs. 3(a) and 3(b), the stress of the DN hydrogel composite is gradually increased with an increase of the modulus ratio (E_1/E_2 or E_2/E_1) between brittle and stretchable networks. With either increase in the relative modulus ratio (E_1/E_2) of brittle network from 0.1 to 0.5, or increase in that (E_2/E_1) of stretchable one from 1 to 9, the stress of hydrogel composite will be increased

proportionally at the same strain. This clearly reveals that the mechanical properties of the hydrogel composite can be improved by increasing the Young's moduli of both the brittle network and stretchable network.
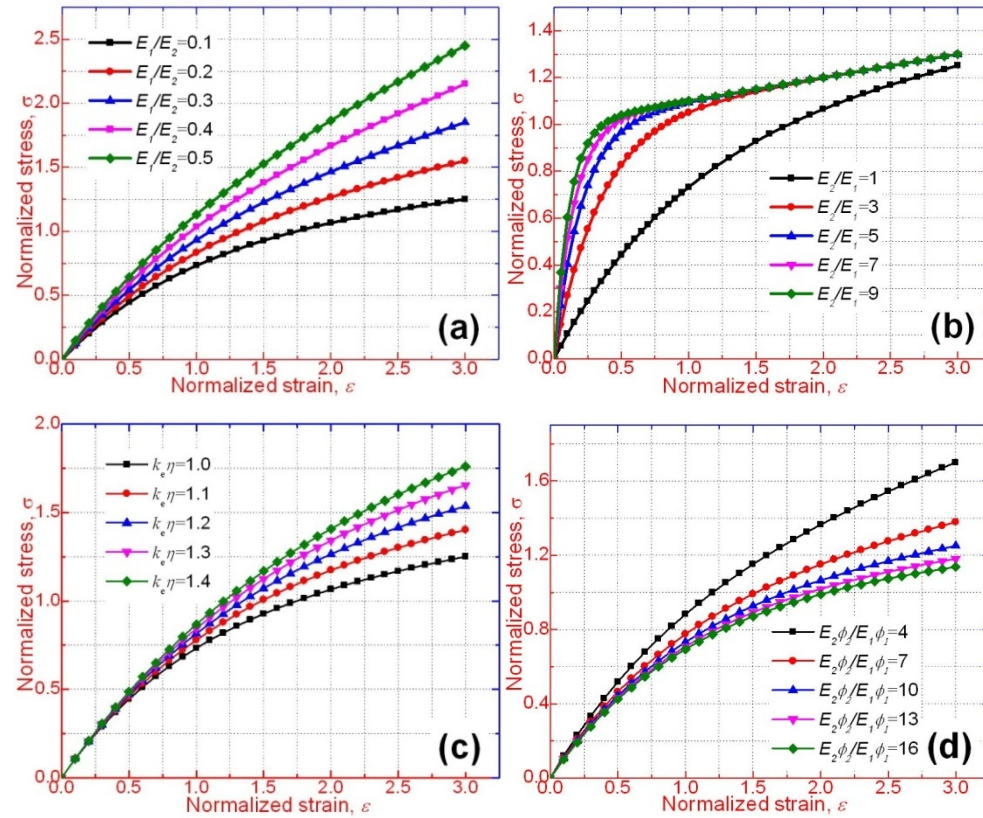

Fig. 3. Numerical analysis results of the stress as a function of strain in the DN hydrogel composite. (a) At a given relative modulus of E_1/E_2 =0.1, 0.2, 0.3, 0.4 and 0.5. (b) At a given relative modulus of E_2/E_1 =1, 3, 5, 7 and 9. (c) At a given relative viscosity of $k_\varepsilon\eta$ =1.0, 1.1, 1.2, 1.3 and 1.4. (d) At a given parameter of $E_2\phi_2/E_1\phi_1$ =4, 7, 10, 13 and 16.

Effect of viscosity of stretchable network on the stress-strain constitutive relationship was further investigated and the results are shown in Fig. 3(c). It is found that the stress of the hydrogel composite is increased with an increase in the relative viscosity ($k_\varepsilon\eta$) of the stretchable network from 1.0 to 1.4. Meanwhile, the

mechanical properties of the newly formed brittle network after the destruction-reconstruction process are also obtained and the results are shown in Fig. 3(d). Clearly, these results are different from that of the original brittle network as already discussed above, which is mainly due to the changes in the cross-sectional areas of the network component. The overall mechanical stress of hydrogel composite is found to gradually decrease with an increase in the proportion of stretchable network ($E_2\phi_2/E_1\phi_1$) from 4 to 16. These numerical results theoretically explain the dependences of Young's modulus, relative modulus, viscosity and cross-sectional areas on the stress-strain constitutive relationship of the hydrogel composite.

3.3 Thermomechanical behavior of DN hydrogel composite

Based on the Maxwell equation, we then further investigated the dynamic thermomechanical behavior of DN hydrogel composite. By introducing a parameter $\hat{\varepsilon}e^{i\omega t}$ [30] to replace ε, equation (2) can be rewritten as,

$$\sigma + \frac{\eta}{E_1}\frac{d\sigma}{dt} = \hat{\varepsilon}e^{i\omega t}[E_2 + (E_1 + E_2)\frac{\eta}{E_1}i\omega] \tag{8}$$

where $\tau = \frac{\eta}{E_1}$, $\hat{\varepsilon}$ is the referenced strain and $i = \sqrt{-1}$. Thus, the storage modulus and tangent delta parameter of the DN hydrogel composite can be obtained [30],

$$E' = \frac{E_2 + \tau^2\omega^2(E_1 + E_2)}{1 + \tau^2\omega^2} \tag{9a}$$

$$\tan\delta = \frac{E''}{E'} = \frac{E_1\tau\omega}{E_2 + \tau^2\omega^2(E_1 + E_2)} \tag{9b}$$

According to equation (7), both the moduli of the brittle and stretchable networks are different from their original ones due to the changes in cross-sectional areas

perpendicular to the direction of deformation, i.e., $\overline{E}_1 = E_1\phi_1$ and $\overline{E}_2 = E_2\phi_2$. Here, the relaxation time of the newly formed DN hydrogel can be expressed as,

$$\overline{\tau} = \frac{\eta}{\overline{E}_2} = \frac{\eta}{E_2\phi_2} = \frac{1}{\phi_2} \cdot \frac{\eta}{E_2} = \frac{1}{\phi_2} \cdot \tau \tag{10}$$

Combining equations (9) and (10), we can obtain,

$$E' = \frac{\phi_1^2\phi_2\overline{E}_2 + \overline{\tau}^2\omega^2(\overline{E}_1\phi_1 + \overline{E}_2\phi_2)}{\phi_1^2 + \overline{\tau}^2\omega^2} \tag{11a}$$

$$\tan\delta = \frac{\overline{E}_1\overline{\tau}\omega}{\phi_2\overline{E}_2 + \overline{\tau}^2\omega^2(\overline{E}_1\phi_1 + \overline{E}_1\phi_2)/\phi_1^2} \tag{11b}$$

According to the time-temperature equivalence principle [35], the constitutive relationship of time $(1/\omega)$ and transition temperature (T_g) can be obtained,

$$E'(T_g, \omega) = E'(T_g', a_T\omega) \tag{12a}$$

$$\tan\delta(T_g, \omega) = \tan\delta'(T_g', a_T\omega) \tag{12b}$$

where T_g' is the reference transition temperature, a_T is the shift factor and it can be determined by the temperature based on the Williams-Landel-Ferry (WLF) equation [30]:

$$\lg a_T = \frac{-17.44(T_g' - T_g)}{51.6 + (T_g' - T_g)} \tag{13}$$

According to equations (12) and (13), the analytical results of storage modulus and tangent delta have been obtained, and the results are plotted as a function of temperature which is shown in Fig. 4. The parameters used in the equations (12) and (13) have been listed in Table 1. As shown in Fig. 4(a), the storage modulus is gradually increased with an increase in the cross-sectional area of the stretchable network (ϕ_2) from 0.2 to 0.8. Meanwhile the peak value of the tangent delta curve

(which is considered as the T_g) is decreased from 307.6 K to 306.3 K with an increase in the cross-sectional area of the stretchable network from ϕ_2=0.2 to ϕ_2=0.8, as revealed in Fig. 4(b). These simulation results clearly show that the thermomechanical properties of the DN hydrogel composite can be adjusted by precisely controlling the component content, including cross-sectional areas of both brittle and stretchable networks.

Table 1. Values of parameters used in equations (12) and (13).

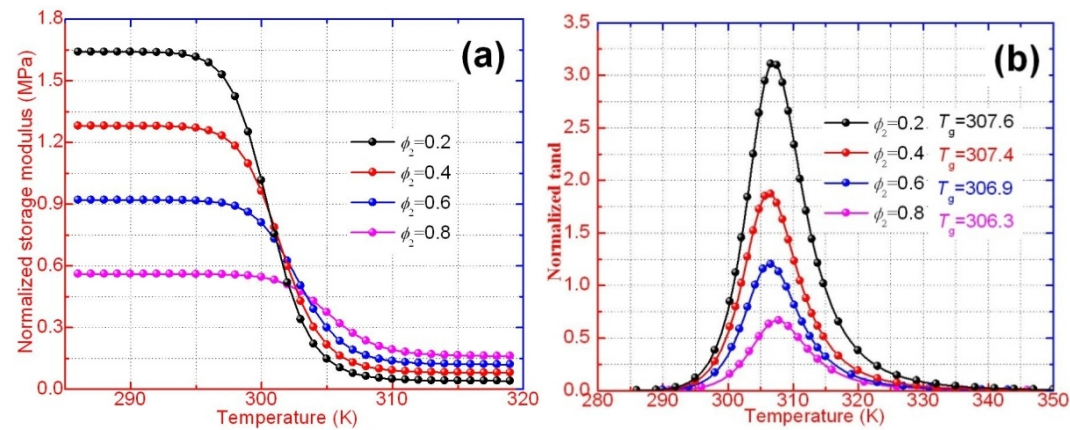| $\bar{E}_1$	$\bar{E}_2$	$\bar{\tau}$	ω	T_g
2	0.2	1	1	300 K

Fig. 4. (a) Numerical analysis of the effect of temperature on the storage modulus at a given ϕ_2 =0.2, 0.4, 0.6 and 0.8. (b) Numerical analysis of the effect of temperature on the tangent delta at a given ϕ_2 =0.2, 0.4, 0.6 and 0.8.

4. Experimental verification

The above theoretical and numerical analysis results has been applied for the studies of loading process of the DN hydrogel composite, and then verified using the experimental results. In combination of equations (3), (4), (5) and (6), a constitutive relationship of stress-strain of the DN hydrogel composite can be obtained for the 1st

mechanical loading cycle,

$$\sigma_{loading}^{1st} = \begin{cases} \sigma_1 = E_1\varepsilon + k_\varepsilon\eta - k_\varepsilon\eta e^{-\frac{E_2\varepsilon}{\eta k_\varepsilon}} & \left(\varepsilon \le \varepsilon_s\right) \\[2mm] \sigma_2 = f_s = \left(\sigma_1\right)_{max} & \left(\varepsilon \le \varepsilon_f \le \varepsilon_s\right) \\[2mm] \sigma_3 = E_s\varepsilon_s \end{cases}$$
$$\sigma_{un} = \bar{E}_1\varepsilon + k_\varepsilon\bar{\eta} - k_\varepsilon\bar{\eta}e^{-\frac{\bar{E}_2\varepsilon}{\bar{\eta}k_\varepsilon}} = \bar{E}_1\varepsilon + C(e^{\frac{\bar{E}_2\varepsilon}{\bar{\eta}k_\varepsilon}} - 1) \tag{14}$$

Furthermore, it is assumed that there is no any friction in the following mechanical loading process, and the bond scission of brittle network has already been induced in the first lading process. In the further mechanical loading process, the constitutive relationship of stress-strain can then be written as,

$$\sigma_{loading}^{ith} = \begin{cases} \sigma_3 = E_s\varepsilon_s & \left(0 \le \varepsilon_s \le \varepsilon\right) \\[2mm] \sigma_1 = E_1\varepsilon + k_\varepsilon\eta - k_\varepsilon\eta e^{-\frac{E_2\varepsilon}{\eta k_\varepsilon}} \end{cases}$$
$$\sigma_{un} = \bar{E}_1\varepsilon + k_\varepsilon\bar{\eta} - k_\varepsilon\bar{\eta}e^{-\frac{\bar{E}_2\varepsilon}{\bar{\eta}k_\varepsilon}} = \bar{E}_1\varepsilon + C(e^{\frac{\bar{E}_2\varepsilon}{\bar{\eta}k_\varepsilon}} - 1) \tag{15}$$

where $C = k_\varepsilon\bar{\eta}e^{-\frac{\bar{E}_2\varepsilon}{\bar{\eta}k_\varepsilon}}$.

According to equations (14) and (15), the analytical results of applied force as a function of length has been plotted to compare with those experimental results reported in Ref. [24], and the results are presented in Fig. 5. The parameters used in the equations (14) and (15) have been listed in Table 2. Fig. 5(a) plots the force-length curves of the 1st loading-unloading cycle, where the force is a combination of viscoelastic force, friction force and the force for mechanochemical transduction of dynamic-modal mechanophore. It is found that the simulation results fit well with the experimental ones, and the proposed model shown in equation (14) can be used to characterize the thermomechanical and mechanochemical behaviors of the DN

hydrogel composite.

Table 2. Values of parameters used in equations (14) and (15) for the different loading cycles for the DN hydrogel composite.

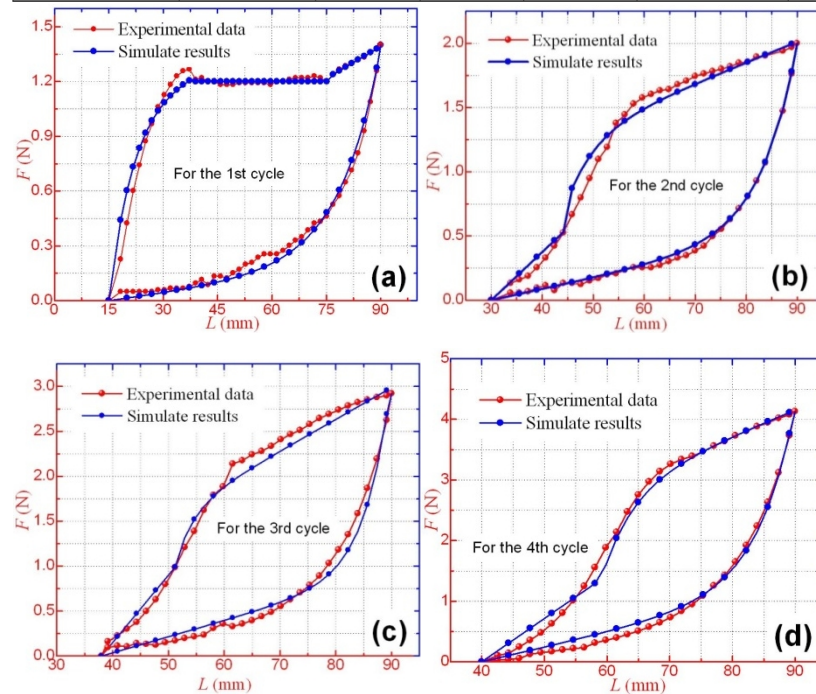|	l_0 (mm)	E_1	E_2	$k_\varepsilon \eta$	C	E_s	$\overline{E}_1$	$\overline{E}_2$
1st cycle	15	0.1	2.4	1.1	1.7×10^{-3}	0.175	0.04	1.44
2nd cycle	30	0.65	8.5	1.2	3.0×10^{-4}	1.5	0.26	5.1
3rd cycle	38	1.7	21	1.5	2.2×10^{-5}	3.6	0.68	12.6
4th cycle	40	2.4	30	2.7	7.2×10^{-4}	4.0	0.96	18

Fig. 5. Force-length curves showing the cyclic loading-unloading behavior of the DN hydrogel composite. (a). For the 1st mechanical cycle. (b), (c) and (d). For the 2nd, 3rd and 4th mechanical cycles, respectively.

On the other hand, the simulation results obtained using the equation (15) were also plotted in order to compare with experimental results, and the results are shown in Figs. 5(b), 5(c) and 5(d). From the simulation results shown in these figures, the proposed model based on equation (15) is suitable for characterizing and predicting

the mechanical behavior of the hydrogel composite in the 2nd, 3rd and 4th mechanical cycles.

Furthermore, the numerical results of DN hydrogel composite obtained using the equations (14) and (15) have been summarized in Fig. 6. Fig. 6(a) presents the force-length curves of cyclic loading-unloading behavior, while Fig. 6(b) presents the force-strain curves of cyclic loading-unloading behavior for the DN hydrogel composite. These simulation results reveal that the strain is gradually decreased from 4.93 to 1.25 with an increase in the number of loading-unloading cycles, while the applied force is gradually increased from 1.38 N to 4.13 N. Therefore, the mechanical strength is significantly improved with an increase in the mechanical cycles, and a gradually increase of the mechanical strength of DN hydrogel composite has been achieved, thus realizing the self-growing and strengthening effects.

The mechanochemical behavior of the DN hydogel composite has been well modelled, but it is also necessary to present a stress-strain consititutive relationship and the working mechanism. Here we will consider the case where the mechanical properties of stretchable network are completely recovered to its original states after the mechanochemical transduction of brittle network, i.e., $E_2 = \overline{E}_2$ and $k_\varepsilon \eta = k_\varepsilon \overline{\eta}$. Meanwhile, we also assume that the mechanochemical transduction from mechanical energy into chemical energy is kept constant when E_s =0.175. It also means that only the mechanical properties of the brittle network has been changed due to the mechanochemical and destruction-reconstruction processes, where the string component of brittle network has been changed from E_1 to $\overline{E}_1$. Furthermore, the

divergences between the numerical and experimental results have been compared based on correlation index (R^2) rating in the Table 3. It is found that the R^2 =0.963624, R^2=0.985157, R^2=0.990649, and R^2=0.992973 for the 1st, 2nd, 3rd, and 4th mechanical loading cycle, respectively. Therefore, it is clear that the proposed model provides an accurate prediction for the experimental results.

Table 3. The R^2 rating for the comparison between numerical and results.

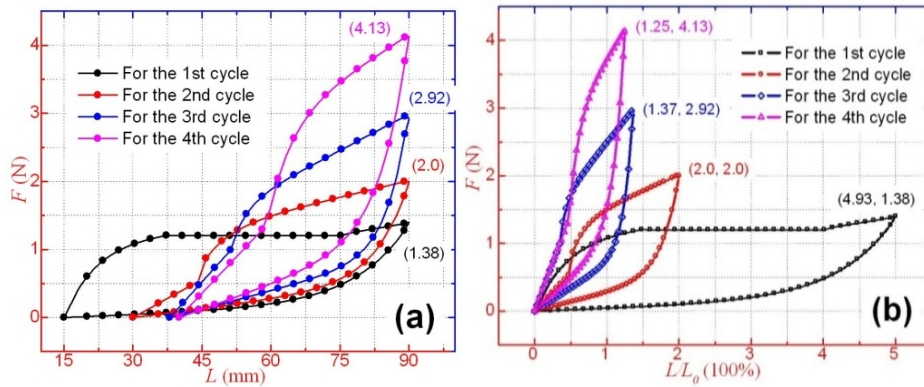|	1st cycle	2nd cycle	3rd cycle	4th cycle
R^2 rating	0.963624	0.985157	0.990649	0.992973

Fig. 6. (a) and (b). Comparison of force as a function of length and strain between the experimental data [24] and simulation results of equations (14) and (15), respectively.

Based on the equations (14) and (15), the obtained analytical results of stress values as a function of strain has been plotted to compare with those experimental results reported in Ref. [24], and the results are presented in Fig. 7. The parameters used in the equations (14) and (15) have been listed in Table 4. It is found that the DN hydrogel composite presents large hysteresis loops due to substantial bond scission of brittle network. Due to the purely elastic nature, the area of the hysteresis loop corresponds to the dissipated energy for the scission of covalent bond of brittle network during mechanical loading. These simulation results are well in agreement

with the experimental data as shown in Fig. 7.

Table 4. Values of parameters used in equations (14) and (15).

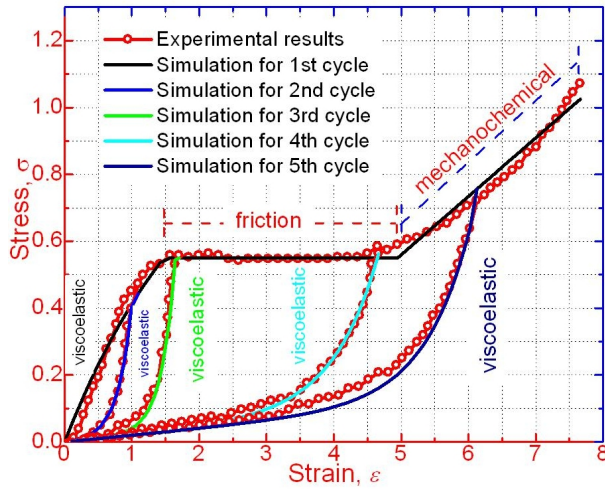|	E_1	$E_2 = \bar{E}_2$	$k_\varepsilon \eta = k_\varepsilon \bar{\eta}$	E_s	$k_\varepsilon \eta e^{-\frac{E_2 \varepsilon}{\eta k_\varepsilon}}$	$\bar{E}_1$
1st cycle	0.5	0.02	1.0	0.175	0.0027	5
2nd cycle	0.5	0.02	1.0	0.175	0.00014	5
3rd cycle	0.5	0.02	1.0	0.175	0.00043	1.5
4th cycle	0.5	0.02	1.0	0.175	0.000062	1.5

Fig. 7. Comparison of stress as a function of strain between the experimental data [24] and simulation results using equations (14) and (15).

5. Conclusion

In this study, a phenomenologically constitutive model was proposed to describe the dynamic-modal mechanophore in DN hydrogel composite with self-growing and tailorable mechanical strength. The improved mechanical strength is mainly due to the driving force generated from the mechanochemical destruction-reconstruction of brittle network which has been formulated by the extended Maxwell principle. The dynamically thermomechanical properties have been systematically modeled and characterized, and dependences of the mechanical properties on the Young's modulus,

viscosity and temperature have been theoretically investigated. Finally, the simulation results were compared and verified by the experimental data reported in the literature, and good agreements between the theoretical and experimental results had been achieved. This study is expected to explore the working mechanism and provide a theoretical guidance to understand and design of DN hydrogel composite with self-growing and tailorable mechanical strength.

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