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Self-assembled topological transition via intra- and inter-chain coupled binding in physical hydrogel towards mechanical toughening

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**Abstract:** Mechanical robustness is one of the challenges for soft hydrogels, which are difficult to repair once fractured, mainly because of their chemical bonds and large binding energies required to heal the fractured surfaces within a reasonable time scale. In this study, an extended Maxwell model is proposed to describe intra-chain ionic bonds and inter-chain hydrogen bonds, coupled in physical hydrogels undergoing self-assembly and mechanical toughening, during both of which the intra-chain and inter-chain bonds are working as sub-entanglement and physical crosslink, respectively. According to the rubber elastic theory, a topology model is formulated to identify the working principle of intra-chain and inter-chain coupled binding in the physical hydrogels. Furthermore, a constitutive stress-strain relationship is developed to understand their self-assembling topology signatures and topological transitions. Finally, effectiveness of the proposed model is verified using molecular dynamic simulations and experimental results of physical hydrogels reported in literature.

**Keywords:** hydrogel; self-assembling topology; intra-chain bond; inter-chain bond
1. Introduction

Hydrogel is a widely used soft matter with an excellent biocompatibility for health care monitoring [1], wearable electronics [2], and human-machine interactions [3]. With their good electrical and self-healing properties, ionic hydrogels [4,5] have also been developed for flexible electronic devices [6], tissue engineering [7], artificial muscle [8], wearable sensors [9] and fluidics [10]. Design of strong and flexible hydrogels has been a crucial issue for their successful applications [11,12].

It has been reported that mechanical and self-healing properties of hydrogels can be optimized by designing their topology structures of networks and chains [13-18], where either hydrogen or ionic bonds play key roles in the strengthening of physical hydrogels. Various binding methods have been developed to achieve toughening of hydrogels by means of entanglements [19-21]. Most of previous studies on the mechanical robustness of physical hydrogels are based on continuum mechanics, which in principle cannot be used to explain the topological signatures and their transitions at molecular scales [22-26]. Understanding the correlation between topology signatures and mechanical properties of physical hydrogels is one of the greatest challenges [27].

On the other hand, different strategies have been utilized to achieve the toughening of hydrogels, through chemical crosslinking from double-network, triple-network and interpenetration of networks [28-32]. When the chemical crosslinks in hydrogels are destroyed, the covalent bonds work as sacrificial bonds undergoing mechano-chemical coupling dissipation [28-32]. However, the hydrogels are often
difficult to repair once fractured, mainly due to their special chemical bonds and large binding energies to heal their fractured surfaces within a reasonable time scale.

In this study, an extended Maxwell model is proposed to describe coupled binding of ionic and hydrogen bonds in physical hydrogels undergoing self-assembling topology and mechanical toughening, during both of which the intra-chain ionic bond and inter-chain hydrogen bond are governed by the sub-entanglement [19-21] and physical crosslink [33,34], respectively. According to the rubber elastic theory [35,36], a self-assembling topology model is formulated to identify the coupling principle of intra-chain and inter-chain bonds in the physical hydrogels. Furthermore, a constitutive stress-strain equation has been developed to describe the effects of self-assembling topology signatures and their topological transitions. Finally, effectiveness of the proposed model has been verified using molecular dynamic simulation results and experimental ones of physical hydrogels reported in literature.

2. Theoretical framework

2.1 Topological transition of intra- and inter-chain coupled binding

The topology structures of physical hydrogels, which are originated from their intra-chain and inter-chain coupled binding, have a decisive influence on their mechanical properties. Their dynamic networks therefore have various topology signatures due to the increase in numbers of chains involved, thus resulting in a distinctly constitutive stress-strain relationship as illustrated in Figure 1. For the physical hydrogels, the intra-chain ionic bonds undergo a molecular sub-entanglement, while the inter-chain hydrogen bonds function as physical crosslinks to resist the
externally mechanical loading. Therefore, it is critical to investigate the dependences of mechanical properties of the hydrogels on the topology signatures and their transitions.

![Diagram](image)

Figure 1. Illustrations of dependences of mechanical behaviors on topology signatures in terms of intra-chain and inter-chain coupled binding in a hydrogel. Topological geometry of intra-chain and inter-chain coupled binding is determined by the number of chains in a crosslinking junction \( f \) and the number of crosslinks within a loop \( l \).

The mechanical behavior of intra-chain topology is incorporated from two parts, i.e., initial elastic unfolding and ionic bond breakage, where the ionic bond breakage is determined by the unbinding of intra-chain sub-entanglement [19-21]. Here, a spring is set to represent the elastic response of the initial elastic unfolding of a polymer chain. Meanwhile, a spring and a pot are set in parallel to characterize viscoelasticity of the intra-chain sub-entanglement, which presents a time-dependent mechanical behavior in response to the external loading [19-21]. Furthermore, the mechanical behavior of inter-chain topology is also incorporated from two parts, i.e.,
slip motion confined by the van der Waals force and slip motion confined by the hydrogen bonding force [36]. Therefore, a spring is set to represent the elastic response of the slip motion confined by the van der Waals force, which is always kept a constant. Meanwhile, a spring and a pot are set in parallel to characterize viscoelasticity of the slip motion confined by the hydrogen bonding force, which is regarded as the crosslink point to presents time-dependent mechanical behavior in response to the external loading force [36].

A constitutive relationship between stress and strain is firstly formulated according to the Maxwell principle [33], of which a three-element system is employed to characterize the elasticity and viscoelasticity of inter-chain bonds, as follows,

\[
\begin{align*}
\frac{d(e - e_{i1})}{dt} & = \frac{1}{E_i} \frac{d\sigma_i}{dt} \\
\sigma_i & = E_{v1}e_{i1} + \eta_i \frac{d\varepsilon_{i1}}{dt}
\end{align*}
\]

where \( e \) is the strain, \( t \) is the time, \( \sigma_i \) and \( E_i \) are the stress and modulus of the hydrogel, respectively, in a tensile loading. \( E_{v1}, \varepsilon_{v1} \) and \( \eta_1 \) are the elastic modulus, strain and viscosity of viscoelastic part, respectively. The equation (1) can be rewritten as a function of strain rate (\( \dot{\epsilon} = \dot{\varepsilon} t \)),

\[
\frac{\sigma_i}{E_i} = \tau_i\phi_i\dot{\varepsilon}[1 - \exp\left(\frac{-\varepsilon}{\tau_i\dot{\varepsilon}}\right)] + (1 - \phi_i)e
\]

\[
\tau_i = \frac{\eta_i}{E_i + E_{v1}}
\]

where \( \tau_i \) is the relaxation time of inter-chain bonds, \( \phi_i = E_{v1}/(E_i + E_{v1}) \) is the proportion of instantaneous elasticity.
On the other hand, the viscoelastic behavior of the intra-chain bonds is similar to that of the inter-chain bonds, while the pre-strain is expected to promote the movement of inter-chain bonds. To present the phase angle ($\delta_2$) of intra-chain bonds, the complex modulus ($E_2^*$) of the hydrogel can be written as,

$$
E_2^* = \frac{1 - \phi_2 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_2^2} + i \frac{\phi_2 \omega \tau_2}{1 + \omega^2 \tau_2^2}
$$

(3)

$$
\tan \delta_2 = \frac{\phi_2 \omega \tau_2}{1 - \phi_2 + \omega^2 \tau_2^2}
$$

(4)

where $\omega$ is the frequency, $i = \sqrt{-1}$, $E_2$ is the modulus of intra-chain bonds, $\tau_2 = \eta_2/(E_2 + E_v2)$ is the relaxation time, and $\phi_2 = E_2/(E_2 + E_v2)$ is the proportion of elasticity of intra-chain bonds. $E_v2$ and $\eta_2$ are the elastic modulus and viscosity of viscoelastic part of the intra-chain bonds, respectively. If under a pre-strain, the viscoelastic behavior of intra-chain bonds can be obtained, where the corresponding complex modulus ($E_p^*$) and phase angle ($\delta_p$) can be written as,

$$
E_p^* = E_{v2} + i \omega \eta_2
$$

(5)

$$
\tan \delta_p = \frac{\omega \eta_2}{E_{v2}}
$$

(6)

Combining equations (4) and (6), the phase angle ($\delta_{2p}$) and relaxation time ($\tau_{2p}$) of the pre-strained hydrogel can be obtained using the following equations,

$$
\tan \delta_{2p} = \tan \delta_p - \tan \delta_2 = \frac{\phi_2 \omega \tau_{2p}}{1 - \phi_2 + \omega^2 \tau_{2p}^2}
$$

(7)

$$
\frac{\tau_{2p}}{\tau_2} = \frac{E_{v2} + \omega^2 \eta_2^2}{E_2 E_{v2}}
$$

(8)

If $\omega \approx 0$, the relaxation time and constitutive stress-strain relationship for the intra-chain bonds can be obtained by substituting equation (8) into equation (2a),
\[ \tau_{2p} = \tau_2 \frac{E_{2p}}{E_2} \quad \text{(9)} \]

\[ \frac{\sigma}{E_{2p}} = \tau_{2p} \phi \dot{\varepsilon} [\exp\left(\frac{\varepsilon}{\tau_{2p} \dot{\varepsilon}}\right) - 1] + (1 - \phi) \varepsilon \quad \text{(10)} \]

where \( E_{2p} \) is the modulus of pre-strained hydrogels.

Combining equations (2a) and (10), the stress function (\( \sigma \)) of the hydrogel, of which the mechanical properties are determined by the intra-chain and inter-chain coupled binding, i.e., \((\sigma=\sigma_1+\sigma_2)\), can be described using the following equation,

\[ \sigma = E_1 \tau_{1p} \phi [1 - \exp\left(\frac{-\varepsilon}{\tau_{1p} \dot{\varepsilon}}\right)] + E_{2p} \tau_{2p} \phi \dot{\varepsilon} [\exp\left(\frac{\varepsilon}{\tau_{2p} \dot{\varepsilon}}\right) - 1] + [E_1 (1 - \phi_1) + E_{2p} (1 - \phi_2)] \varepsilon \quad \text{(11)} \]

According to the rubber elasticity theory \([27,29,30]\), the constitutive relationship of shear modulus (\( G \), where \( E \approx 3G \) for an incompressible material, \( G \) and \( E \) are its shear and Young’s moduli, respectively) and number of chains in a network junction \((f)\) can be formulated to describe the topological transition \([27]\), e.g.,

\[ \frac{G f / k_B T}{N_{el} (f - 2)} = \frac{E f / k_B T}{3N_{el} (f - 2)} = 1 - A_f n_{1,f} - \frac{4(f - 1)}{f^2 (f - 2)} n_{2,f} - \sum_{i=3}^f \frac{4}{f} \left( \frac{1}{(f-1)^{2i-2} + 1} + \frac{1}{(f-1)^{2i-1} - 1} \right) n_{i,f} \quad \text{(12)} \]

where \( k_B = 1.38 \times 10^{-23} \) J/K is the Boltzmann constant, \( T \) is the temperature, \( N_{el} \) \((N_{el} = N_1 + N_{2p})\), where \( N_1 \) and \( N_{2p} \) are the total numbers of inter-chain and intra-chain bonds, respectively) is the number of network junctions per mole, \( A_f \) is a given constant and determined by \( f \), and \( l \) denotes the number of crosslinks within a loop. It is worthwhile to mention that these symbols are different from those defined in the elastic network theory reported in Ref. [27], where \( f \) was defined as the functionality of the network junctions and \( l \) denoted the loop order of the chain.
Figure 2. (a) Illustrations of effect of intra-chain bond on the topology structure under the extrinsic mechanical loading. (b) Schematic diagrams of inter-chain crosslinking undergoing topological transition. (c) Illustrations of the effect of inter-chain bond on the topology structure under the extrinsic mechanical loading. (d) In combination of equations (11) and (13), the constitutive stress-strain curves for the physical hydrogel, of which the mechanical behaviour is resulted from the intra-chain and inter-chain bonds, governed by the sub-entanglement [19-21] and physical crosslink [33,34], respectively.
In combination of equations (11) and (12), the stress values as a function of strain can be obtained, and the results are plotted in Figure 2. Initially, the hydrogel is stretched by the tensile loading, and the molecular structures are changed from $n_{2,3}$ to $n_{4,3}$ as shown in Figure 2(a). Figure 2(b) shows the mechano-responsive transitions of topological structures of one, two and multiple inter-chain crosslinks, which are generally originated from the hydrogen bond or van der Waals force [37,38]. In this case, the topological transition is originated from the intra-chain bonds, and is caused by the dissociation of loops. With the further increase of tensile loading, the topological transition of the hydrogel is then determined by the inter-chain bonds, and the molecular structure is changed from $n_{4,3}$ to $n_{3,4}$ [27], as illustrated in Figure 2(c). Therefore, the working principles of inter-chain and inter-chain bonds in topological transitions have been identified for the hydrogels as summarized in Figure 2.

Based on the transition of topology structure from $n_{4,3}$ to $n_{3,4}$, the equation (12) can be obtained as,

$$\frac{E_1/3}{N_k T} = \frac{f - 2}{f} \left(1 - \frac{81}{4961} n_{3,4} - \frac{192}{8255} n_{4,3}\right)$$

where $\tau_1=\tau_2=1$ s, $\phi_1=\phi_2=0.95$, $\varepsilon=1$ s$^{-1}$, $E_2p=0.01$ MPa in equation (11), while $3N_k T f \frac{\varepsilon - 2}{f} = 0.5$ MPa and $n_{3,4}=n_{4,3}=0.1$, used in equation (13).

2.2 Topological transition of intra-chain bond

In this section, we will characterize the topological transition of intra-chain bonds. We will also quantify the impact of topological transitions (i.e., intra-chain and inter-chain bonds, and intra-chain and inter-chain coupled binding) on the mechanical
properties of the hydrogels. Here, the intra-chain bond is governed by the sub-entanglement theory [19-21] and can be described using,

$$\frac{E_{2p}/3}{N_{2p}k_BT} = \frac{f - 2}{f}(1 - \frac{5}{2}n_{1,3} - \frac{4}{3}n_{1,4} - \frac{8}{9}n_{2,3})$$

(14)

where $A_f(f=3)=5/2$, $A_f(f=4)=4/3$ and $A_f(f\geq5)=2/(f-2)$ [27]. $\tau_1=\tau_{2p}=1s$, $\phi_1=\phi_2=0.95$, $\dot{\varepsilon}=1s^{-1}$, $E_1=1$ MPa in equation (11), while $3N_{2p}k_BT\frac{f - 2}{f} = 5 \times 10^{-3}$ MPa and $n_{1,3}=n_{2,3}=0.01$ in equation (14).

The obtained analytical results of the effect of topological transition of intra-chain bonds on the mechanical behavior of physical hydrogel using the proposed model of equation (14) are plotted in Figure 3. It is revealed that the topology transition is due to the intra-chain bonds in responses to the extrinsic mechanical loading, i.e., from the topology structure of $n_{1,3}$ (or $n_{2,3}$) into $n_{1,4}$, as illustrated in Figure 3(a). The maximum strength of hydrogel is gradually decreased from 3.46 MPa, 2.99 MPa, 2.70 MPa, 2.41 MPa to 2.11 MPa at the same strain of $\varepsilon=6$, with the increase in the concentration of $n_{1,4}$ topology structure from 0% to 40%. By increasing the concentration of $n_{1,4}$, more intra-chain bonds have been involved into the topological transitions, thus lowering the strength of hydrogels at the same strain. The coupled binding of inter-chain and intra-chain bonds [37] is illustrated in Figure 3(b). Intra-chain bonds lead to a topological transition owing to the unbinding of these bonds. Furthermore, the topological transition then turns to influence the inter-chain bonds, resulting into a coupled binding effect.
Figure 3. Illustrations of the effect of intra-chain bond on the topology structure under the extrinsic mechanical loading. (a) The constitutive stress-strain curves for the physical hydrogel, of which the mechanical behaviour is resulted from the coupled binding of inter-chain and intra-chain bonds. (b) Topological transition and coupled binding of inter-chain and intra-chain bonds.

As presented in the previous studies [31-33], topological transition of intra-chain bonds is originated from sub-entanglement of the molecular structures. Therefore, the number of intra-chain bonds ($N_{2p}$) has an indispensable effect on that of the sub-entanglement points ($N_{2p0}$) in the molecular structures, i.e., [31-33],

$$2N_{2p} = fN_{2p0} \exp(-k_p \varepsilon_p)$$

(15)

where $\varepsilon_p$ is plastic strain and $k_p$ is a scaling constant. Under the externally mechanical loading, the topological transition of intra-chain bonds results in a decrease in both the
$N_{2p}$ and $N_{2p}^{0}$. Therefore, both the elastic modulus and strength are decreased according to the equations (11) and (14).

We further use finite element analysis (FEA) to characterize the effect of topological structure and coupled binding of inter-chain and intra-chain bonds on the mechanical properties of the hydrogel, and the results are shown in Figure 4. There are three topology structures, i.e., $f=4$; $f=6$; $f=4$ & $f=6$ (e.g., 4&6, where $l=2$), which have been introduced for comparisons. For the physical hydrogels undergoing intra- and inter-chain coupled binding, the excellent mechanical properties (with both high strength and ultra-high toughness) come from the topology structures including the sub-entanglements (i.e., loops between polymer chains). Therefore, to understand the deformation of the loops is the main challenge to analyze the mechanical properties of hydrogel. However, in the micro-scale level, the deformation of the loops consists of relative sliding, stretching, chains’ drawing, and so forth. The pure theory analysis might ignore such main deformation processes. FEA simulation is more suitable to analyze such a complex coupling deformation. Meanwhile, considering both hydrogel networks undergoing different topological structure are amorphous polymers [33-35], we use the same model and parameters to model their behaviors with different topological structures. The parameters are fitted by a non-linear regression. For the free vibration case, the Poisson's ratio is chosen as 0.4 and density of polymer is 0.9 g/cm$^3$ according to the rubber elastic theory [33-35]. The 8-node hexahedron element, C3D8R, is used to perform the calculation. About 4000 elements are used to model the unit which performs modal analysis and the loading condition is that the strain is
Figure 4. FEA results of the transition of topology structures, at a given \( f=4, 6 \) and \( 4\&6 \) (where \( l=2 \)), and analytical results for the stress as a function of strain of hydrogel with various topology structures.

Figure 4 shows the obtained FEA results of the transition of topology structures, at a given \( f=4, 6 \) and \( 4\&6 \) (where \( l=2 \)), and analytical results for the stresses as a function of strain of hydrogel with various topology structures. Results reveal that only the inter-chain bonds have been found in the hydrogels with topology structures of \( f=4 \) or \( f=6 \). On the other hand, there is a coupled binding of intra-chain and inter-chain bonds in the hydrogels with topology structures of \( f=4 \& f=6 \) (where \( l=2 \)).

The simulation results reveal that the mechanical strength has been improved from 2.97 MPa to 4.04 MPa when the topology structure of hydrogel is increased from \( f=4 \) to \( f=6 \), even though its mechanical property is mainly determined by the inter-chain bonds. Moreover, the mechanical strength is increased from 4.04 MPa to 4.83 MPa due to the coupled binding of intra-chain and inter-chain bonds, when the topology structure of hydrogel is increased from \( f=6 \) to \( f=4 \& f=6 \) (where \( l=2 \)). These simulation results clearly reveal that the mechanical properties of the hydrogel are...
essentially determined by the intra-chain and inter-chain bonds as well as their coupled binding.

2.3 Molecular dynamic simulation verification

In this section, a physical P(SS-co-MPTC) hydrogel, which is incorporated from anionic monomer p-styrenesulfonate (SS) and cationic monomer 3-(methacyloylamino) propyl-trimethylammonium chloride (MPTC) [13]), is chosen to investigate its mechanical behavior using a molecular dynamic (MD) simulation. All the parameters used in the calculation using the equation (11) are listed in Table 1. The chemical structures and atomistic representations of the P(SS-co-MPTC) obtained from the MD simulations are presented in Figure 5(a). The macromolecules consisting of 3 chains with 3996 atoms in total are generated by Amorphous Cell module implemented in the Materials Studio. In the process of MD simulation, 150 monomers of SS and MPTC are set up, and every 50 monomers are formed a polymer chain and connected at the same cross-linking point. Random copolymer is used to simulate the free bonding process [13] without any termination group. The following parameters are set during simulations, e.g., Invert=0, Flip=0, Quality=Medium and Task=Dynamics undergoing Forcefield=Universal. The simulation method is Ewald of electrostatic and Atom based of van der Waals [13], with a time step of 1 fs. In this case, the selected size is capable to reproduce the mechanical properties of hydrogels close to those of bulk cases. After its construction, the hydrogel system is equilibrated in a canonical ensemble (NPT) at a constant temperature of 298.5 K for 50 ps. While another equilibration process is carried out in the isoenergy (NVE) ensemble with a
constant temperature of 298.5 K for 50 ps. The cell size of the model is \(35.83 \times 35.83 \times 35.83\) Å\(^3\).

Table 1. Values used in equation (11) for the MD simulation.

<table>
<thead>
<tr>
<th></th>
<th>(E_1\phi_1) (kPa)</th>
<th>(\tau_1\varepsilon)</th>
<th>(E_{2p}\phi_2) (kPa)</th>
<th>(\tau_{2p}\varepsilon)</th>
<th>(E_1(1-\phi_1) + E_{2p}(1-\phi_2)) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPT</td>
<td>0.199</td>
<td>1.26</td>
<td>9.67 \times 10^{-5}</td>
<td>8.074</td>
<td>0.105</td>
</tr>
<tr>
<td>NVE</td>
<td>0.488</td>
<td>0.692</td>
<td>2.70 \times 10^{-11}</td>
<td>2.264</td>
<td>0.0738</td>
</tr>
</tbody>
</table>

Figure 5. (a) Chemical and atomistic structures of P(SS-co-MPTC) obtained from MD simulations. (b) Topological transition of atomistic structure obtained from MD simulations. (c) The change in cell length as a function of time \((\varepsilon / \dot{\varepsilon})\) for P(SS-co-MPTC). (d) Comparisons of analytical results obtained using equation (11) and MD simulations for P(SS-co-MPTC).
In Figure 5(b), the part 4 is used for a comparison with part 3, and they both have the same equilibrium time. The equilibrium process of amorphous cell length of P(SS-co-MPTC) is shown in Figure 5(c), and the dynamically molecular movement of P(SS-co-MPTC) and its inter-chain and intra-chain bonds are analyzed, and the obtained results are shown in Figure 5(b). In the tensile tests, the simulation cell is deformed in a step-wise manner along \( z \) direction while a constant pressure is applied along the other two directions. The tensile deformation is performed in the canonical ensemble for the as-prepared P(SS-co-MPTC). Meanwhile, the tensile deformation is performed in the isoenergy ensemble after the NPT equilibration at the end of the simulation for the equilibrated P(SS-co-MPTC). The applied stress is \( \sigma=3k_B T \Delta h/h_0^2 \) \((k_B=1.38\times 10^{-23} \text{ J/K}, \ h_0=3.721 \text{ nm for NPT and } h_0=2.534 \text{ nm for NVE})\). The theoretical results obtained using the equation (11) are presented in Figure 5(d), which also compares with those obtained from the MD simulations. Clearly, the analytical results obtained using our proposed model fit well with those MD simulations.

3. Experimental verification

Experimental data reported in Ref. [11] for HAPAA-PANI hydrogel (HAPAA: hydrophobic association poly(acrylic acid) and PANI: pre-infiltrated aniline) have been used to verify the analytical results generated from the proposed model. Figure 6(a) plots the constitutive stress-strain relationships of the HAPAA-PANI hydrogels with various PANI concentrations of 0 mol/L, 0.1 mol/L, 0.15 mol/L and 0.2 mol/L. All the parameters used in the calculation using the equations (11), (13) and (14) are listed in Table 2 at given values of \( n_{1,3}=n_{2,3}=n_{1,4}=n_{3,4}=n_{4,3}=0.01 \) and the initial value of
$f$ is chosen as $f=3$. With an increase in the PANI concentration from 0%, 10%, 15% to 20%, the stress is gradually increased from 0.11 MPa, 0.29 MPa, 0.37 MPa to 0.74 MPa (e.g., an increase rate of 573%), respectively, at the same strain of $\varepsilon=16$. Figure 6(b) shows the divergences between the analytical and experimental results, which were calculated using the correlation index ($R^2$). They are 99.87%, 98.12%, 98.99% and 98.39% for the PANI concentrations of 0%, 10%, 15% and 20%, respectively.

Table 2. Values of parameters used in equation (11) for HAPAA-PANI hydrogel.

<table>
<thead>
<tr>
<th>HAPAA-PANI</th>
<th>$N_i k_BT \phi_i$ (kPa)</th>
<th>$\tau_{1i}\dot{\varepsilon}$</th>
<th>$N_{2i} k_BT \phi_2$ (kPa)</th>
<th>$\tau_{2i}\dot{\varepsilon}$</th>
<th>$N_i k_BT (1-\phi_i) + N_{2i} k_BT (1-\phi_2)$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol/L PANI</td>
<td>19.64</td>
<td>0.962</td>
<td>3.25</td>
<td>14.29</td>
<td>0.35</td>
</tr>
<tr>
<td>0.1 mol/L PANI</td>
<td>11.03</td>
<td>0.00997</td>
<td>5.64</td>
<td>11.11</td>
<td>6.08</td>
</tr>
<tr>
<td>0.15 mol/L PANI</td>
<td>88.24</td>
<td>0.00102</td>
<td>11.16</td>
<td>12.19</td>
<td>0.1</td>
</tr>
<tr>
<td>0.2 mol/L PANI</td>
<td>10.17</td>
<td>0.00983</td>
<td>0.23</td>
<td>2.501</td>
<td>27.5</td>
</tr>
</tbody>
</table>

In the HAPAA-PANI hydrogels, both the intra-chain bonds of HAPAA and PANI undergo topological transitions in terms of disassociation of hydrophobic micelles and internal fracture, respectively. The disassociation of the dynamic inter-chain bonds between HAPAA and PANI can further resist to the extrinsic mechanical loading [11]. Therefore, the toughening mechanism of HAPAA-PANI hydrogels can be well predicted using our newly proposed model of equation (11), i.e., based on the topological transitions of HAPAA intra-chain bond, PANI intra-chain bond and HAPAA-PANI inter-chain bond. As shown in Figure 6(c), the intra-chain bonds undergo a topological transition from $n_{1,3}$ (or $n_{2,3}$) to $n_{1,4}$, whereas the inter-chain bonds are able to dissipate mechanical energy in terms of a topological transition from $n_{4,3}$ to $n_{3,4}$. The topological model and topological transition of HAPAA-PANI hydrogel in the macroscopical scales are presented, where a coupled binding of ionic
bond (intra-chain sub-entanglement) and hydrogen bond (inter-chain crosslink) influences the mechanical property of HAPAA-PANI hydrogel.

Figure 6. Analytical results and experimental data [11] of stress-strain curves of HAPAA-PANI hydrogel, at the various PANI concentrations of 0%, 10%, 15% and 20%. (a) The stress-strain curves. (b) Divergences of analytical and experimental results of stress. (c) Topological transition in HAPAA-PANI hydrogel.

To verify the proposed model based on equation (11) for the characterization of reversibly dynamic topology transition, a group of experimental data of the HAPAA-PANI hydrogels [11] are used to compare with the analytical results. According to equation (11), the obtained simulation results of stress as a function of strain are plotted in Figure 7 for the HAPAA-PANI hydrogels under cycle times of 1
and 20. All the parameters used in the calculation using equations (11), (13) and (14) are listed in Table 3 at given values of $n_{1,3} = n_{2,3} = n_{1,4} = n_{3,4} = n_{4,3} = 0.01$ and $f = 3$.

Table 3. Values used in equation (11) for the HAPAA-PANI hydrogel.

<table>
<thead>
<tr>
<th>HAPAA-PANI</th>
<th>$N_i k_B T \phi_i$ (kPa)</th>
<th>$r_{11} \dot{\varepsilon}$</th>
<th>$N_{22} k_B T \phi_{22}$ (kPa)</th>
<th>$r_{22} \dot{\varepsilon}$</th>
<th>$N_i k_B T (1 - \phi_i)$ + $N_{22} k_B T (1 - \phi_{22})$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading</td>
<td>40.46</td>
<td>0.5314</td>
<td>0.242212</td>
<td>1.13</td>
<td>8.52</td>
</tr>
<tr>
<td>Unloading</td>
<td>6267</td>
<td>0.00105</td>
<td>0.00506</td>
<td>0.415</td>
<td>13.39</td>
</tr>
<tr>
<td>20th</td>
<td>34.12</td>
<td>0.3136</td>
<td>0.00018</td>
<td>100</td>
<td>10.63</td>
</tr>
</tbody>
</table>

Figure 7. Analytical results and experimental data [11] of stress a function of strain of HAPAA-PANI hydrogel, under the loading cycle of 1st loading, 1st unloading to 20th loading. (a) The stress-strain curves. (b) Divergences of analytical and experimental results of stress.

As shown in Figure 7(a), the simulation results fit well with the experimental data. The obtained mechanical stresses are $\sigma = 0.065$ MPa, $\sigma = 0.057$ MPa and $\sigma = 0.049$ MPa for the HAPAA-PANI hydrogels under 1st mechanical loading, unloading and 20th mechanical loading, respectively. These analytical and experimental results reveal that the mechanical strength is gradually decreased from $\sigma = 0.065$ MPa to $\sigma = 0.049$ MPa with the increase of mechanical loading time from 1 to 20, mainly due to the decreases of the intra-chain and inter-chain coupled binding. This clearly indicates that the topology transition of intra-chain and inter-chain bonds is a dynamic process.
This causes that the hydrogel needs enough time to achieve the self-healing effect, even though the intra-chain ionic bonds and inter-chain hydrogen bonds are reversible.

Figure 7(b) shows the divergences between the analytical and experimental results, and the calculated correlation index ($R^2$) are 99.92%, 99.68% and 99.96% at the loading cycle of 1st loading, 1st unloading to 20th loading, respectively.

Furthermore, effects of the ionic and hydrogen bonds on the mechanical behaviors of PAMPS-PAHz-PAAm (PAMPS: poly(2-Acrylamido-2-methyl-1-propanesulfonic acid); PAHz: polyacryloyl hydrazide; PAAm: polyacrylamide) hydrogels, which is crosslinked using poly(ethylene glycol) diacrylate (PEGDA), were investigated in order to identify the working mechanism of topological signature and coupled binding of the hydrogen and ionic bonds [12]. The analytical and experimental results of the PAMPS-PAHz-PAAm hydrogels with various amounts of PEGDA crosslinkers are plotted and compared in Figure 8(a). All the parameters used in the calculations using the equations (11), (13) and (14) are listed in Table 4 at given values of $n_{1,3}=n_{2,3}=n_{1,4}=n_{3,4}=n_{4,3}=0.01$ and $f=3$.

It is revealed that the analytical results fit well with the experimental data.

Experimental results show that the tensile stress is gradually decreased from 2.1 MPa,
1.1 MPa to 0.8 MPa. In these three hydrogels, the amounts of PAMPS and PAHz are kept constants, which mean that the amount of ionic bonds (intra-chain bonds) is also a constant. When the amount of PAAm is increased from 10 mol to 20 mol, the hydrogen bonds (inter-chain bonds) are increased, which results in the increases of tensile stress from 1.1 MPa to 2.1 MPa (e.g., with an increase rate of 91%). On the other hand, the tensile stress is gradually decreased from 1.1 MPa to 0.8 MPa, with an increase in the amount of PEGDA crosslinkers because of the decreases of ionic bonds and hydrogen bonds. Therefore, these experimental results reveal that the toughening mechanism of the PAMPS-PAHz-PAAm hydrogels is originated from both the ionic and hydrogen bonds.

Figure 8. Comparisons of analytical and experimental results [12] for the stress as a function of strain of PAMPS-PAHz-PAAm hydrogels with varying the PEGDA amount. (a) The tensile stress-strain curves. (b) Divergences of analytical and experimental results of tensile stress. (c) Illustrations of topological transition in PAMPS-PAHz-PAAm hydrogel.
The divergences between the analytical and experimental results were calculated, and the obtained correlation index ($R^2$) is plotted in Figure 8(b). The $R^2$ data are 98.85%, 96.58% and 96.86% of 1st, 2nd and 3rd PAMPS-PAHz-PAAm hydrogels, respectively. It is found that the analytical results obtained from the proposed model fit well with the experimental data of PAMPS-PAHz-PAAm hydrogels. Figure 8(c) illustrates the topology transitions of PAMPS-PAHz-PAAm hydrogels with an increase in the PAAm and PEGDA amounts, respectively.

Finally, we have applied the experimental data [13] of P(NaSS-co-MPTC) hydrogel to verify the analytical results obtained using our proposed model. Based on the equation (11), analytical results of their stresses as a function of the strain are plotted in Figure 9. The parameters used in the calculations using the equations (11), (13) and (14) are listed in Table 5 at the given values of $n_{1,3}=n_{2,3}=n_{1,4}=n_{3,4}=n_{4,3}=0.01$ and $f=3$.

Table 5. Values used in equation (11) for P(NaSS-co-MPTC) hydrogels with various monomer concentration ($C_m$(M)) [13].

<table>
<thead>
<tr>
<th>$C_m$(M)</th>
<th>$N_1k_BT\phi_1$ (kPa)</th>
<th>$\tau_1\dot{\varepsilon}$</th>
<th>$N_2k_BT\phi_2$ (kPa)</th>
<th>$\tau_2\dot{\varepsilon}$</th>
<th>$N_1k_T(1-\phi_1)+N_2k_T(1-\phi_2)$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>8.35</td>
<td>0.6468</td>
<td>0.18</td>
<td>4.751</td>
<td>1.35</td>
</tr>
<tr>
<td>1.7</td>
<td>12.54</td>
<td>1.053</td>
<td>0.42</td>
<td>4.096</td>
<td>2.46</td>
</tr>
<tr>
<td>1.9</td>
<td>19.24</td>
<td>0.7068</td>
<td>1.30</td>
<td>3.818</td>
<td>4.61</td>
</tr>
<tr>
<td>2.2</td>
<td>115.97</td>
<td>0.1121</td>
<td>2.08</td>
<td>3.258</td>
<td>12.27</td>
</tr>
</tbody>
</table>

Figure 9(a) presents the stress-strain relationship of the P(NaSS-co-MPTC) hydrogels with different monomer concentrations ($C_m$(M)). It can be clearly seen that the analytical results have shown well agreements with the experimental data. The stress has been significantly enhanced from 0.03 MPa to 0.47 MPa (e.g., an increase rate of 1467%), by increasing monomer concentration ($C_m$(M)) from 1.5 to 2.2, at the
given strain of $\varepsilon=12.5$. The analytical results clearly show that the strengths of inter-chain and intra-chain bonds are significantly improved with an increase in the monomer concentrations. As reported in the previously reported experimental results [13], the inter-chain ionic bond is improved at a high monomer concentration ($C_m(M)$), resulting in an increase of stress. Meanwhile, Figure 9(b) shows the divergences between the analytical and experimental results calculated by using correlation index ($R^2$). The data are 99.86%, 99.92%, 99.93% and 99.96% for the P(NaSS-co-MPTC) hydrogels with monomer concentrations of 1.5, 1.7, 1.9 and 2.2, respectively.

![Graph showing stress-strain curves and correlation index](image)

Figure 9. Comparisons of analytical and experimental results [13] for the stress as a function of strain of P(NaSS-co-MPTC) hydrogels by varying the monomer concentration ($C_m(M)$). (a) The tensile stress-strain curves. (b) Divergences of analytical and experimental results of stress. (c) Topological transition in P(NaSS-co-MPTC) hydrogel.
Figure 9(c) illustrates the topology transitions of the P(NaSS-co-MPTC) hydrogels with an increase in the monomer concentration $C_m(M)$.

4. Conclusions

In this study, a topological framework is established to investigate the working principle of self-assembled topology transition and mechanical robustness in physical hydrogels. The mechanoresponsive topology signature has been investigated to describe the coupled binding of intra-chain ionic and inter-chain hydrogen bonds, in terms of two fractal geometry components ($f$: the number of chains in a crosslinking junction, and $l$: the number of crosslinks within a loop). The sub-entanglement and physical crosslink in the hydrogels have been identified as the driving forces of intra-chain ionic and inter-chain hydrogen bonds, respectively, which determine the topology structures and their transitions. Furthermore, an extended Maxwell model is developed based on the rubber elasticity theory, in order to formulate the constitutive stress-strain relationship. This model can quantify the effects of intra-chain ionic and inter-chain hydrogen bonds on mechanical toughening in the physical hydrogels. Finally, the proposed framework is proved to be able to well predict mechanical behaviors of physical hydrogels, and verified using both the MD simulation results and experimentally obtained data reported in literature. This newly proposed model provides a new toughening mechanism of topological transition and insights into the physical principles which govern the constitutive relationship between molecular self-assembly and mechanical behavior in physical hydrogels undergoing self-assembling topology transition and mechanoresponsive toughening.
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References


