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Local conservation law of rubber elasticity in hydrogel networks undergoing microphase separation and toughening

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Abstract: Thermoresponsive polymer segments have been reported to induce lateral microphase separations due to their switching transitions from a hydrophilic state to a hydrophobic one in hydrogels, which result in shrinkage and collapse of the polymer networks and significantly improved mechanical strength. However, the route from which the hydrophobic segments are assembled into micelles during microphase separations, and their thermoresponsive toughening mechanisms are not fully understood. In this study, a local conservation law of rubber elasticity is firstly formulated to describe the micellization and collapse of polymer networks in hydrogels, during which the thermoresponsive segments undergo a microphase separation. Flory-Huggins theory, interfacial free-energy equation and the extended Maxwell model are then employed to model the thermodynamics of micellization and microphase separations in the hydrogel, in which the polymer networks are composed of both hydrophilic and thermoresponsive segments. The toughening mechanism is further explored and discussed based on the proposed models. Finally, the proposed

models have been verified using the experimental results reported in the literature. This study provides a new mechanism of local conservation law for rubber elasticity in hydrogels and also critical insights into the physical principles which govern the molecular self-assembly.

Keywords: hydrogel; rubber elasticity; microphase separation; micellization

1. Introduction

There is a great interest in developing soft hydrogels which can respond to external stimuli in order to produce mechanical work and activate autonomous motions [1-4]. Various external stimuli are explored including water, chemical solvent, pH change and ionic concentration, but the thermal method is particularly attractive due to its non-invasive nature. To realize different functionalities and expand their applicability, a variety of block hydrogels have been developed [5-7]. These block hydrogels are composed of different molecular structures [1-4,8], which enable them with unique thermodynamics of micellizations and microphase separations [8] for applications in self-assembly [9], liquid crystal [10], nanocomposites [11], and self-healing [12,13].

However, hydrogels normally have poor mechanical properties [14-16], therefore, a lot of studies have been done to introduce various components (including grafts [17,18] and blocks [19-22]) into hydrogels in order to improve their fracture toughness and stiffness. The hydrogel contains two major segments, one of which is a thermoresponsive segment and can be switched from a hydrophilic state to a hydrophobic one at a critical temperature (T_C) [18-22]. Small angle neutron scattering experiments revealed that microstructures of the hydrogel networks are distinctly collapsed during their transitions from a hydrophilic state to a hydrophobic one due to the self-assembly of thermoresponsive segments into micelles [18-20], which plays a key role in improving mechanical toughness of the hydrogel [23-25]. However, the working principle and constitutive relationship between the condensed micelle microstructures and their mechanical properties are not well-understood, due to their scaling effects and complexly thermodynamics [26,27]. Great efforts have been made using theoretical analysis and simulations [28-30], but the working principle has not been well understood.

In this study, a local conservation law of rubber elasticity is firstly formulated to describe micellization and collapse in the hydrogel, of which the thermoresponsive segments undergo microphase separations. A thermodynamic model is then proposed to describe the working principle and toughness mechanism of microphase separation, which determines the molecular structures, swelling behavior and dynamic mechanical properties. Finally, effectiveness of the proposed model has been verified using the experimental results reported in the literature [18-20,31].

2. Rubber elasticity equilibrium of local deswelling

All the conventional hydrogels inevitably swell upon absorption of water, which results in significant degradation of their mechanical properties. However, it was reported that the thermoresponsive segments in the hydrogel are assembled into micelles above a certain critical temperature ($T_{\rm C}$) because of their transition from a hydrophilic state into a hydrophobic one, which enables the hydrogel to undergo microphase separation and thermoresponsive deswelling [17-22]. As shown in Figure 1, the hydrogel network is composed of hydrophilic and thermoresponsive segments, which undergo swelling and deswelling processes, respectively, in response to the water above $T_{\rm C}$. Meanwhile, the thermoresponsive segments become hydrophilic and present a swelling behavior below $T_{\rm C}$. Therefore, the hydrogel shows a local deswelling behavior due to the increase in temperature above $T_{\rm C}$.

Thermoresponsive hydrogel



Figure 1. Schematic illustration of the local deswelling and micellization of thermoresponsive segments in hydrogel above $T_{\rm C}$.

Here, the classical rubber elasticity equation [32] is introduced to characterize the thermodynamics in the hydrogel. The chemical potential is a combination of mixing $(\Delta \mu_M)$ and rubber elastic $(\Delta \mu_{el})$ free-energies as shown in the following equations,

$$\Delta \mu_{M} = k_{B} T (\ln(1 - \phi_{1}) + \phi_{1} + \chi_{HW} \phi_{1}^{2})$$
(1)

$$\Delta \mu_{el} = N_{el} k_B T \nu \phi_1^{1/3} \tag{2}$$

$$\frac{\Delta\mu_M + \Delta\mu_{el}}{k_B T} = \ln(1 - \phi_1) + \phi_1 + \chi_{HW}\phi_1^2 + N_{el}\nu\phi_1^{1/3} = 0$$
(3)

where k_B is the Boltzmann constant, T is the temperature, ϕ_1 is the volume concentration of gel, N_{el} is the cross-linking density of elastic network, and ν is the molar volume ratio of polymer monomer to water molecule. χ_{HW} is the interaction parameter between hydrogel and water, and it plays an essential role to determine the swelling ratio [32].

At $T>T_c$, the hydrogel undergoes a deswelling process (Figure 1) due to the transition of thermoresponsive segments from a hydrophilic state to a hydrophobic one. Small angle neutron scattering experiments [17,19,20] have revealed that there are many micelles of thermoresponsive segments formed during the deswelling process. Meanwhile, microphase separations between the thermoresponsive and hydrophilic segments are presented. The hydrogel network is therefore collapsed due to the micellization of thermoresponsive segments [7,19-21], as illustrated in Figure 2.



Figure 2. Schematic illustrations of the micellization and transition of thermoresponsive segment from a hydrophilic state to a hydrophobic one in hydrogel.

To explore the effects of micellization on the hydrogel network, the diameter of micelle (h_c) can be derived as [7],

$$h_C \propto l_b N_T^{2/3} \left(\frac{\gamma_{HT} l_b^2}{T}\right) \tag{4}$$

where l_b is the length of polymer chain, N_T is the number of thermoresponsive segment and γ_{HT} is interfacial tension between hydrophilic and thermoresponsive

segments. The interfacial tension (γ_{HT}) can be further expressed as [7,33],

$$\gamma_{HT} = \frac{k_B T}{l_b^2} \sqrt{\frac{\chi_{HT}}{6}}$$
(5)

According to the scaling theory [6], the free-energy (F_c) of micelle can be written as,

$$F_C \propto T \frac{h_C^2}{N_T l_b^2} \tag{6}$$

Combining equations (4), (5) and (6), the diameter of micelle (h_c) and the free-energy ratio $r \ (r = \frac{F_c}{F_H})$, where F_H is used for the free-energy of hydrophilic segment in the polymer chain, and r is used to present the content of hydrophilic

segments involved into the micelles) can be obtained using the following equations,

$$h_C \propto k_B l_b N_T^{2/3} \sqrt{\frac{\chi_{HT}}{6}}$$
(7a)

$$\frac{F_C}{F_H} = \frac{h_C^2}{h_H^2} = \frac{\chi_{HT}}{\chi_H}$$
(7b)

where h_H is the mean square terminal distance of hydrophilic segment, and χ_H is the interaction parameter between hydrophilic segment and water.

The interaction parameter (χ_{HW}) between hydrogel and water can be further written as,

$$\chi_{HW} = (1 - \frac{F_C}{F_H})\chi_H + \frac{F_C}{F_H}\chi_T$$
(8)

where χ_T is the interaction parameter between thermoresponsive segment and water. According to the Flory-Huggins theory [5-7], the interaction parameters have the following constitutive relationships as a function of temperature,

$$\chi_T(T) = \frac{A_T}{T - T^*} \tag{9a}$$

$$\chi_{HT}\left(T\right) = \frac{A_{HT}}{T} + C_{HT} \tag{9b}$$

where A_T , T^* , A_{HT} and C_{HT} are material constants. Because $\frac{F_C}{F_H} = r$, the interaction parameter ($\chi_{HW}(T)$) between hydrogel and water can be further written as,

$$\chi_{HW}(T) = (1-r)\chi_{H} + r\chi_{T} = (1-r)[\chi_{H}^{0} + (\frac{A_{HT}}{\chi_{H}^{0}T} + \frac{C_{HT}}{\chi_{H}^{0}})(\chi_{T}^{0} - \chi_{H}^{0})] + r\frac{A_{T}}{T - T^{*}}$$
(10)

where χ_{H}^{0} and χ_{T}^{0} are the interaction parameters of hydrophilic and thermoresponsive segments, respectively.

Substituting equation (10) into (3), the equilibrium equation of hydrogel during swelling can be expressed as,

$$\frac{\ln(1-\phi_1)+\phi_1+N_{el}\nu\phi_1^{1/3}}{-\phi_1^2} = (1-r)[\chi_H^0 + (\frac{A_{HT}}{\chi_H^0 T} + \frac{C_{HT}}{\chi_H^0})(\chi_T^0 - \chi_H^0)] + r\frac{A_T}{T-T^*}$$
(11)

where $\frac{1}{\phi_1} = QQ_0$, in which Q_0 and Q are the initial and final swelling ratios of

hydrogel, respectively [32].

To verify the proposed model and quantitatively separate the effect of temperature on deswelling behavior, a group of experimental data of PEG/PEMGE (PEG: poly(ethylene glycol); PEMGE: poly(ethyl glycidyl ether-co-methyl glycidyl ether)) hydrogels reported in Ref. [20] have been employed to compare with the analytical results using equation (11), where r=0.4. The analytical results of swelling ratios as a function of temperature are plotted in Figure 3. The parameters used in the equation (11) are listed in Table 1. As revealed by both the experimental and analytical results, a two-stage deswelling behavior of the hydrogels is revealed. In the first stage from *T*=5°C to *T*=25°C, the hydrogel is incorporated of two hydrophilic segments, where the thermoresponsive segments undergo a transition from a hydrophilic state into a hydrophobic one in the hydrogel network. The deswelling behavior is sharp and resulted from the micellization process of thermoresponsive segments. On the other hand, there is a stable deswelling process of the hydrogel in the temperature range from *T*=25°C to *T*=40°C. In this stage, the micellization is further increased due to the more thermoresponsive and hydrophilic segments in hydrogel network, instead of slight and local transitions of thermoresponsive segments. As shown in Figure 3, the analytical results are in good agreements with the experimental data [20] of the hydrogels. Furthermore, the swelling ratio is dramatically decreased from 350% to 110% (e.g., a decrease rate of 218.2%) with an increase of temperature from 5°C to 25°C. Meanwhile, the swelling ratio is slightly decreased from 110% to 75% (e.g., a decrease rate of 46.7%), with an increase of temperature from 25°C to 40°C.



Figure 3. Comparison of analytical results and experimental data [20] for the swelling ratio as a function of temperature in the PEG/PEMGE hydrogel.

$N_{_{el}} u$	$\chi^0_{\scriptscriptstyle H}$	χ^0_T	$C_{_{HT}}$
0.006	0.1	0.2	2.8
$A_{HT}(\mathbf{K})$	$A_{T}(\mathbf{K})$	$T^{*}(\mathbf{K})$	Q_0
-800	-3.6	302	400%

Table 1. Values of parameters used in equation (11) for PEG/PEMGE hydrogel.

Furthermore, analytical results of swelling ratios as a function of temperature obtained using equation (11) are plotted in Figure 4(a), which has also included the experimental data of PEG/PEMGE hydrogels with various content ratios (r) of PEMGE to PEG reported in Ref. [19]. In this case, the PEG/PEMGE hydrogel is consisted of PEG and a four-armed PEMGE segment. The PEMGE and PEG are corresponding to the thermoresponsive and hydrophilic segments, respectively. All the parameter values used in equation (11) are listed in Table 2. It is found that the simulation curves fit well with the experimental data. When the temperature is within the transition temperature region from 10°C to 25°C, the swelling ratio is dramatically decreased with respect to the temperature. With an increase in the r from 0.1 to 0.5, the swelling ratio is decreased from 247.9% to 79.9% at $T_{\rm C}$ =25°C. This indicates that more thermoresponsive segments are involved in the micellization process, which achieves a higher deswelling ratio due to the increase of content ratios of PEMGE to PEG in the hydrogel. It is revealed that the thermoresponsive segments play the dominant role to determine the deswelling behavior at the temperature below $T_{\rm C}$. When $T > T_{\rm C}$, a further deswelling behavior of the hydrogel is presented in the temperature range from 25°C to 40°C. A two-stage deswelling behavior is also found for these PEG/PEMGE hydrogel, as reported in Ref. [19]. On the other hand, the

divergences between the analytical and experimental results of the PEG/PEMGE hydrogels are calculated using the correlation index (\mathbb{R}^2), which are 93.53%, 96.17%, 98.08%, 98.39% and 98.70% for r=0.1, 0.2, 0.3, 0.4 and 0.5, respectively, as shown in Figure 4(b). In Figure 4, the apparent errors of the simulation curves mainly occur at the temperature near T_C , which is mainly because the thermoresponsive segments experience an apparent hydrophilic-to-hydrophobic transition, and the correpsonding large volume change resultes in a large experimental error. Meanwhile, as shown in equation (11), the effects of temperature and hydrophilic-to-hydrophobic transition on the interaction parameters χ^0_H and χ^0_T have not been considered, thus resulting in the apparent divergence between experimental data and simulation results around the temperature of T_C .



Figure 4. Comparisons of analytical and experimental results [19] for the swelling ratio as a function of temperature in PEG/PEMGE hydrogels with various content ratios of PEG to PEMGE, where r= 0.1, 0.2, 0.3, 0.4 and 0.5. (a) For the swelling ratio-temperature curves. (b) Divergences of the analytical and experimental results.

$N_{_{el}} u$	$\chi^0_{_H}$	$\chi^0_{\scriptscriptstyle T}$	$C_{_{HT}}$
0.006	0.1	0.2	2.1
$A_{HT}(K)$	$A_{T}(K)$	$T^*(K)$	Q_0
-600	-4	301.5	400%

Table 2. Values of parameters used in equation (11) for PEG/PEMGE hydrogels.

3. Theoretical modelling and experimental verification of local micellization

Due to the local micellization of thermoresponsive segments, a significant change of condensed molecular structures occurs and enables the hydrogel with a distinct mechanical behavior. However, the working principles and thermodynamics behind the effects of condensed molecular structures on mechanical properties are not fully understood.

As reported in Ref. [18] for the hydrogel of PNIPAm/PDMA (PNIPAm: poly(N -isopropylacrylamide); PDMA: poly(N,N-dimethylacrylamide)), the thermoresponsive PNIPAm acts as the main chain and the PDMA works as the grafted side chain. Above $T_{\rm C}=30^{\circ}$ C, the hydrogel undergoes a microphase separation between the PNIPAm and PDMA-water phases, which is mainly resulted from the increased hydrogen bonding strength between hydrophilic PDMA and water [18]. Meanwhile, the microphase separation between PNIPAm and PDMA-water phases has also been reported, in which the PDMA acts as the main chain and thermoresponsive PNIPAm acts as the grafted side chain [31]. These experimental results demonstrate that the local micellization of thermoresponsive segments is originated from the microphase separation between the hydrophilic and thermoresponsive segments, due to the enhanced hydrogen bonding between the

hydrophilic segments and water.

3.1 Dynamic modeling of microphase separation

According to the interfacial free-energy equation of microphase separation, the free-energy functions can combine those of both the ordered (F_{ORD}) and disordered phases (F_{DIS}) [7,33], which are used to describe the thermoresponsive and hydrophilic segments, respectively. The chemical potential of thermoresponsive segment is equal to that of the hydrophilic segment/water phase, and can be obtained as,

$$F_{ORD} = \gamma_{HT} \Sigma + \frac{3}{8} \frac{k_B T d^2}{N_T l_b^2} = k_B T \left(\sqrt{\frac{\chi_{HT}}{6}} \frac{N_T l_b}{d/2} + \frac{3}{8} \frac{d^2}{N_T l_b^2} \right)$$
(12a)

$$\chi_{HT} = \frac{A_{HT}}{T}$$
(12b)

$$\frac{\Delta\mu_{DIS}}{RT} = \frac{C_0}{N_T}\phi_2 + A_2 C_0^2 \phi_2^2$$
(12c)

where $\gamma_{HT} = \frac{k_B T}{l_b^2} \sqrt{\frac{\chi_{HT}}{6}}$ is the interfacial tension [33] and $\Sigma \frac{d}{2} = N_T l_b^3$ is the interfacial area between the microphases [7]. χ_{HT} is the interaction parameter between hydrophilic and thermoresponsive segments, d is the interfacial thickness of the ordered and disordered phases, l_b is the segment length, R is gas constant, N_H and N_T are the numbers of hydrophilic and thermoresponsive segments, respectively. A_{HT} is the material constant [33], C_0 is the concentration coefficient, A_2 is the second virial coefficient and ϕ_2 is the volume content of hydrophilic segment in a polymer chain ($\phi_2 = \frac{N_H}{N_H + N_T}$). If the lowest free-energy of ordered

phase is achieved, where $\frac{\partial F_{ORD}}{\partial d} = 0$ and $d = l_b N_T^{\frac{2}{3}} \chi_{HT}^{\frac{1}{6}}$ [7,33], the free-energy of

ordered phase can therefore be expressed as,

$$F_{ORD} \approx 1.2k_B T \left(N_T \chi_{HT}\right)^{\frac{1}{3}} = 1.2k_B T \left(N_{HT} \chi_{HT}\right)^{\frac{1}{3}} \phi_1^{\frac{1}{3}}$$
(13)

where ϕ_1 is the volume content of thermoresponsive segments in a polymer chain (ϕ_1

$$=\frac{N_T}{N_H+N_T}=1-\phi_2$$
; and $N_{HT}=N_H+N_T$).

During the microphase separation, the chemical potentials of ordered and

disordered phases are equal to each other at their interfaces, e.g., $\frac{\partial (\frac{\partial F_{ORD}}{\partial N_T})}{\partial T} = \frac{\partial \Delta \mu_{DIS}}{\partial T}$

[7,33]. Therefore, the volume content of thermoresponsive segments involved in the microphase separations a function of temperature $(\phi_1(T))$ can be obtained below,

$$\phi_{1}(T) = \left(\frac{3}{0.8k_{B}}\frac{\partial\Delta\mu_{DIS}}{\partial T}\right)^{3}\frac{N_{HT}^{2}}{\chi_{HT}}(T-T_{C})$$
(14a)

$$\frac{\partial \Delta \mu_{DIS}}{\partial T} = \frac{RC_0}{N_T} \phi_2 + RA_2 C_0^2 \phi_2^2 \tag{14b}$$

Furthermore, the constitutive relationship between stress and elongation ratio has been investigated for the hydrogel, which undergoes a microphase separation due to the transition of thermoresponsive segments from a hydrophilic state to a hydrophobic one. Based on the extended Maxwell model [34], the constitutive relationship between stress (σ) and elongation ratio (λ) for the hydrogel undergoing a microphase separation can be expressed as,

$$\sigma + \tau \frac{d\sigma}{dt} = E_T (\lambda - 1) + (E_T + E_M) \tau \frac{d(\lambda - 1)}{dt}$$
(15)

where E_T is the modulus of thermoresponsive segment, E_H is the modulus of microphase, t is instant time and τ is relaxation time. It should be noted that a group of thermoresponsive segments have not been involved into microphase

separation but simply act as independent networks. On the other hand, those thermoresponsive segments involved into microphase separations have acted as different types of networks as reported in Ref. [35]. These two different networks will have their contributions to the properties of hydrogel.

Figure 5 shows the thermodynamics of hydrogels with various network structures. When the polymer network is composed of two hydrophilic segments, an inevitable swelling effect can be observed. This type of swelling behavior is a typical phenomenon for the conventional hydrogel. When the polymer network is composed of the hydrophilic and thermoresponsive segments, and the main and side chains are made from the hydrophilic and thermoresponsive segments, respectively, a microphase separation will occur as shown in Figure 5. This results in a local micellization due to the existence of thermoresponsive side chains. The swelling behavior has been experimentally investigated for the PNIPAm/PDMA hydrogel [18].



Figure 5. The schematic illustration of the dynamics of gel networks with various temperatures and molecular structures.

Whereas if the polymer network is incorporated from the thermoresponsive and hydrophilic segments, and the main and side chains are made from the thermoresponsive and hydrophilic segments, respectively, a microphase separation has also been observed. In this case, a local micellization is formed due to the existence of thermoresponsive main chains. This type of swelling behavior has been experimentally investigated for the PDMA/PNIPAm hydrogel [31].

According to the equation (15), the shear elastic modulus (G') and loss modulus (G') can be written as a function of loading frequency (ω),

$$G' = \frac{E_T + \tau^2 \omega^2 (E_T + E_M)}{1 + \tau^2 \omega^2}$$
(16a)

$$G'' = \frac{E_M \tau \omega}{1 + \tau^2 \omega^2} \tag{16b}$$

According to the rubber elastic theory [32], the elongation ratio (λ) is determined by the uniaxial tension loading rate ($\dot{\lambda}$), e.g., $\lambda - 1 = \dot{\lambda}t$. The constitutive relationship of stress as a function of elongation ratio can then be written as,

$$\sigma = E_T (\lambda - \frac{1}{\lambda^2}) + E_M \dot{\lambda} \tau [1 - \exp(-\frac{\lambda - 1}{\dot{\lambda}\tau})]$$
(17)

The microphase is composed of two parts, i.e., thermoresponsive segment (ϕ_1) and hydrophilic segment (ϕ_2) . By combining equations of 14(a) and 14(b), the modulus $(E_M = E_H (1-\phi_1) + E_t \phi_1)$ of the microphase can be obtained as,

$$E_{M} = E_{H} \left[1 - \left(\frac{3\frac{\partial\Delta\mu_{DIS}}{\partial T}}{0.8k_{B}}\right)^{3} \frac{N_{HT}^{2}}{A_{HT}} (T - T_{C})\right] + E_{t} \left(\frac{3\frac{\partial\Delta\mu_{DIS}}{\partial T}}{0.8k_{B}}\right)^{3} \frac{N_{HT}^{2}}{A_{HT}} (T - T_{C})$$
(18)

where $0 \le \phi_1 \le 1$. E_t and E_H are the moduli of thermoresponsive PNIPAm and

PDMA-water phases in the microphases of the hydrogel, respectively. The thermodynamics of microphase separation is determined by the interfacial free-energy,

which is mainly influenced by the interfacial area (e.g., $\Sigma = \frac{N_T l_b^3}{d/2}$). The interfacial

thickness $(d = l_b N_T^2 \chi_{HT}^{\frac{2}{3}})$ is much smaller in comparison with the interfacial area $(\Sigma = \frac{N_T l_b^3}{d/2})$, which is not influenced by the complex shape of microphase separation.



Figure 6. The constitutive stress-elongation ratio relationships of hydrogels, of which the mechanical behavior is governed by the rubber elasticity and microphase separation. (a) For the constitutive stress-elongation ratio relationship at $T < T_{\rm C}$. (b) For the constitutive stress-elongation ratio relationship at $T > T_{\rm C}$.

Figure 6 shows the analytical results using our newly proposed model for hydrogels. The parameters used in equation (17) are $E_T = 0.01$ MPa, $E_H = 1$ MPa and $\lambda \tau = 0.33$ [29]. Figure 6(a) shows that the hydrogel obeys the rubber elasticity rule because the thermoresponsive segments are hydrophilic when $T < T_C$. These analytical results reveal that the stress is gradually increased from 0.04 MPa to 0.28 MPa with an increase in the volume content of gel from 10% to 70%. From Figure 6(b), we can also observe that the microphase separation causes the increase of the modulus, when $T>T_{\rm C}$. According to Ref. [35], the critical value associated to the volume content of thermoresponsive segments during the microphase separation was determined by the equation of $\frac{N_{HT}(\phi_1)^2 \chi_{HT}}{\phi_1 + \chi_{HT}/\pi^2} = C$, where $\chi_{HT} = 0.8$, $N_{HT} = 20$ and C = 10 [5-6,35]. Results show that there is a critical value of $\phi_1 = 62.5\%$ (volume content of gel.) for the microphase separation, and the mechanical behavior is governed by the equation

(15). These analytical results reveal that the stress is significantly enhanced from 0.28 MPa to 0.49 MPa due to the microphase separation at $\phi_1 = 70\%$.

3.2 Experimental verification

To verify the proposed model of effect of microphase separation on the mechanical behavior of hydrogels, equations (16) and (18) were applied to predict the dynamic mechanical properties of PNIPAm/PDMA hydrogel [18]. The obtained results are shown in Figure 7. Values of parameters used in equations (16) and (18) during calculation are listed in Table 3. During the heating and cooling processes, the critical temperatures are T_c^+ and T_c^- , respectively. Due to the microphase separation, the shear elastic moduli (G^+) of the PNIPAm/PDMA hydrogel are significantly increased from 0.96 kPa to 11.22 kPa with an increase in the temperature from T=310 K to T=329 K, whereas the shear loss moduli (G^+) are increased from 0.076 kPa to 1.07 kPa. Moreover, the divergences between the analytical and experimental results are calculated based on their correlation index (R^2), and the values are 98.96%, 99.14%, 88.89% and 96.98% for the hydrogels, respectively, as shown in Figure 7(b). These results indicate that good agreements between the analytical and experimental results have been achieved, where the error ratio is limited to ±12%. The divergence of

analytical and experimental results of loss moduli becomes much larger because the loss modulus (G'') is more sensitive to the time and temperature than the elatic modulus (G'). Furthermore, experimental measurement of loss modulus (G'') is significantly influenced by the relaxation behavior and hysteresis phenomenon, thus resulting in a much larger experimental error.

Table 3. Values of parameters used in equations (16) and (18) for PNIPAm/PDMA hydrogel.



Figure 7. Analytical results and experimental data [18] of dynamic mechanical analysis curves of PNIPAm/PDMA hydrogel. (a) For the elastic and loss modulus curves. (b) Error ratio of elastic and loss moduli.

The experimental results of PNIPAm/PDMA hydrogels (reported in Ref. [18]) were then used to further verify the constitutive relationship of stress-elongation ratio using our newly proposed model. The data for the parameters in the calculation using

equations (17) and (18) are listed in Table 4. Figure 8(a) shows that the proposed model can well predict the experimental results. By increasing the temperature from 20°C to 60°C, the stress is increased from 3.15 kPa to 18.4 kPa, e.g., an increase rate of 484.2% has been achieved. This is mainly due to the contribution of microphase separation in the PNIPAm/PDMA hydrogel, of which the hydrogen bonding between PDMA and water is significantly enhanced. Above $T_C = 30^{\circ}$ C, the PNIPAm/PDMA hydrogel undergoes microphase separations of PNIPAm and PDMA-water phases, whereas the PNIPAm turns into hydrophobic [18]. With a further increase in temperature, the degree of microphase separation increases and the moduli are increased significantly due to shrinkage of the thermoresponsive PNIPAm segments, thus resulting in a significant enhancement in the mechanical properties of the hydrogel. Figure 8(b) shows the divergences between the analytical and experimental results of the PNIPAm/PDMA hydrogel using the correlation index (R^2), and the obtained results are 95.41%, 99.56%, 95.32% and 99.79% at 20°C, 35°C, 50°C and 60°C, respectively. Clearly, good agreements between the analytical and experimental results are achieved, where the error ($\Delta \sigma$) is less than ±1.5 kPa.

Table 4. Values of parameters used in equations (17) and (18) for PNIPAm/PDMA hydrogel.

$E_{_{H}}$ (kPa)	E_t (kPa)	E_T (kPa)
8.54	52.9	1.80
$\left(\frac{3}{0.8k_B}\frac{\partial\Delta\mu_{DIS}}{\partial T}\right)^3\frac{N_{HT}^2}{A_{HT}}(\mathrm{K}^{-1})$	τ (s)	$T_{c}(\mathbf{K})$
0.03	5.5	303.5



Figure 8. Analytical results and experimental data [18] of stress-elongation ratio curves of PNIPAm/PDMA hydrogel at $\dot{\lambda} = 0.06s^{-1}$. (a) For the stress-elongation ratio curves. (b) Error ratio of stress.

Furthermore, the effect of graft length (e.g., x (kg/mol) which is the average molar mass of PNIPAm grafted onto the PDMA in PDMA/PNIPAm hydrogel [31,36]) of side chains on constitutive relationship of stress-elongation ratio has been evaluated and the obtained data are plotted in Figure 9. The input parameters for the calculation of equation (17) are listed in Table 5. Figure 9(a) presents the stress-elongation ratio curves of the PDMA/PNIPAm hydrogels as a function of the average molar mass of PNIPAm of x=30 kg/mol, 55 kg/mol, 90 kg/mol and 120 kg/mol, respectively. Both the analytical and experimental results reveal that the stress is gradually increased with an increase in the average molar mass of PNIPAm, and the experimental data have agreed well with the analytical results. Figure 9(b) shows the calculated divergences between the analytical and experimental results of the PDMA/PNIPAm hydrogel using the correlation index (R^2), which are 98.63%, 98.79%, 97.54% and 98.54% at x=30kg/mol, 55kg/mol, 90kg/mol and 120kg/mol, respectively. A good agreement between the analytical and experimental results has been found, where the error ($\Delta\sigma$) is limited to ±2 kPa.



Table 5. Values of parameters used in equation (17) for PDMA/PNIPAm hydrogel.

Figure 9. Analytical results and experimental data [31] of stress-elongation ratio curves of PDMA/PNIPAm hydrogel at various average molar mass of PNIPAm of x=30 kg/mol, 55 kg/mol, 90 kg/mol and 120 kg/mol, at $T=60^{\circ}$ C and $\dot{\lambda} = 0.06s^{-1}$. (a) For the stress-elongation ratio curves. (b) Error ratio of stress.

4. Conclusion

In order to develop thermo-toughening hydrogels that combine hydrophilic polymer networks with thermoresponsive segment, this study is focused to explore the working principles for generating new network topologies with varied hydrophilic, hydrophobic and thermoresponsive segments, which undergo a microphase separation above a critical temperature. The mechanical properties of the hydrogels can be then significantly enhanced due to the microphase separation between the hydrophilic segments. Analytical thermoresponsive and and experimental measurements reveal that the thermoresponsive hydrogels have different structure/properties relationships with perfectly reversible behaviors and anomalous toughness mechanisms, whereas the mechanical strengths are enhanced with an increase in the temperature. A local conservation law and interfacial free-energy equation are firstly formulated to describe the microphase separations and rubber elasticity in hydrogels. The working principles of condensed molecular structures, swelling/deswelling behaviors, interfacial equilibrium of microphase separation and dynamic mechanical properties are then investigated and discussed using the proposed models. Finally, the analytical results have been well verified by the experimental ones reported in literature. The constitutive relationships of stress, dynamic modulus and swelling ratio are established using the proposed models, and the mechanical performance of hydrogels can be adjusted according to the swelling and deswelling behaviors, based on the microphase separation. This study is expected to provide a fundamental model strategy to formulate the mechanical performances of hydrogels undergoing microphase separation, based on the constitutive relationships of stress, dynamic modulus and swelling ratio.

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