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Untangling the mechanics of entanglement in slide-ring gel towards both super-deformability and toughness

Ziyu Xing^a, Dong-Wei Shu^b, Haibao Lu^{a,*} and Yong-Qing Fu^c

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Entanglement plays a critical role in determining dynamic properties of polymer systems, e.g., resulting in slip links and pulley effects for achieving their large deformation and high strength. Although it has been studied for decades, the mechanics of entanglement for stiffness-toughness conflict is not well understood. In this study, a topological knot theory incorporating an extended tube model is proposed to understand the entanglements in slide-ring (SR) gel, which slips over a long distance to achieve large deformation and high toughness via the pulley effect. Based on the topological knot theory, the sliding behavior and pulley effect of entanglement among molecular chains and cross-linked rings are thoroughly investigated. Based on the rubber elastic theory, a freeenergy function is formulated to describe mechanical toughening and slipping of topological knots, while the SR gel retains the same binding energy. Finally, effectiveness of the proposed model is verified using both finite element analysis and experimental results reported in literature.

1 Introduction

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Polymer gels are regarded as mechanically soft matters,¹⁻⁴ which have great potentials for tissue engineering,⁵ artificial muscle,⁶ wearable sensors⁷ and soft robots.^{8,9} However, their poor mechanical properties often restrict their practical applications which require high mechanical strength and large deformation recoverability.¹⁰ In order to toughen these gels, multi-networks,^{11,12} phase-separation,¹³ ion bonding¹⁴ and nanoparticles¹⁵ incorporated into them to increase energy dissipation during deformation, thus enhancing their toughness. However, these network structures are easily damaged, which results in the rupture of the gels. Although their reversible covalent and ionic bonds have been widely employed to generate self-healing effects. $^{\rm 2,6,14}\ {\rm The}$ reconstruction of network structures is usually time-consuming, thus leading to a serious deterioration in their mechanical strengths when the gels undergo continuous and multiple loading-unloading cycles.^{10,16} Therefore, it is critically required to toughen these gels in order to withstand the repeated deformation and achieve good stretchability and recoverability.

Slide-ring (SR) gels have good mechanical performance which is quite different from the conventional gels.¹⁷⁻²¹ They have been constructed based on a strategy via threading the molecular chains into cross-linked rings, which are able to dynamically slip along the chain axis, thus retaining the same binding energy.¹⁷⁻²¹ SR gels present a low mechanical strength because the sliding could proceed without much energy consumption.^{22,23} Both experimental

and analytical results reveal that a pulley effect can enable the chains not only slip over a long distance but also resist the high loading stress, thus achieving a high mechanical performance for the SR gels.²⁴⁻³⁰

Currently, it is agreed that entanglement plays an effective role in the deformation of gels, but the sliding behaviors and pulley effects due to the collective tangled chains are less well understood. In this study, a topological knot theory³¹⁻³³ is proposed to understand the mechanics of entanglements in the SR gel. Polymer chains can slip over a long distance through these topological knots. These knots, explained using the extended tube model,^{23,34-36} can help to achieve the good deformability and toughness via the pulley effect. Based on the rubber elastic theory,^{34,35} a free-energy function is formulated to explore toughening effects of these topological knots in the SR gel. Finally, effectiveness of the proposed model is verified using both finite element analysis (FEA) and experimental results of the SR gels reported in literature.

2. Theoretical framework

In the SR gels, cross-linked rings can help the molecular chains to slide freely and thus improve their mechanical properties without much energy dissipation. Based on the rubber elasticity theory, ^{34,35} the probability of distribution (Ω) of molecular chains can be obtained,

$$\Omega(h) = (\frac{3}{2\pi nb^2})^{\frac{3}{2}} \exp(\frac{-3h^2}{2nb^2})$$
(1)

where *h* is end-to-end distance of molecular chain, *n* is the number of monomers between cross-linked rings and *b* is the length of monomer. According to the Boltzmann theorem, ^{22,34} the entropy (*S*) and free energy (F_{el}) of the polymer chains can be written as,

$$S = k_B \ln \Omega \tag{2a}$$

$$F_{el} = -TS \tag{2b}$$

^a State Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, P.R. China.

^{b.} School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

^{c.} Smart Materials and Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, UK. † E-mail: luhb@hit.edu.cn

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where k_B is the Boltzmann constant (1.38×10⁻²³ J/K) and T is the temperature. The free energy (F_{el}) of a polymer chain can be expressed as,

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$$\frac{-2F_{el}}{3k_nT} = \ln\frac{3}{2\pi b^2} - \ln n - \frac{h^2}{nb^2}$$
(3)

In the SR gel, the chains will be constrained by the cross-linked rings, thus resulting in the formation of a homogeneous gel. Here, the numbers of monomers, n can be scaled as,^{22,23}

$$\frac{\partial F_{el}}{\partial n} = 0 \Longrightarrow n = \frac{h^2}{b^2} \tag{4}$$

Accordingly, the equilibrium conformational distribution (Ω_{eq}) can be written as,

$$\Omega_{eq}(h) = \left(\frac{3}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{-\frac{3}{2}}$$
(5)

Under a stretching loading, the end-to-end distance of molecular chains between two adjacent rings is increased from *h* to *h*+*r*, where *r* represents the sliding distance.³⁴⁻³⁶ The conformational distribution probability, Ω_{sr} , can be modified into a rectangular distribution as,³⁵

$$\Omega_{sr}(h) = \frac{e^{3/2}}{2r_{\max}} \int_{-r_{\max}}^{r_{\max}} dr [\frac{3}{2\pi (h+r)^2}]^{\frac{3}{2}}$$

= $\frac{1}{4r_{\max}} (\frac{3e}{2\pi})^{\frac{3}{2}} [\frac{1}{(h-r_{\max})^2} - \frac{1}{(h+r_{\max})^2}]$ (6)
= $(\frac{3e}{2\pi})^{\frac{3}{2}} \frac{h}{(h^2 - r_{\max}^2)^2}$

where r_{max} is the maximum sliding distance, and e=2.718 is the Euler constant. When the SR gel is composed of N_{sr} molecular chains, the free energy (ΔF_{el}) can be obtained from equation 2(b),

$$\frac{-\Delta F_{el}}{N_{sr}k_BT} = \ln\Omega_{sr} - \ln\Omega_{sr}|_{h_0} = \ln\frac{h}{h_0} - 2\ln\frac{h^2 - r_{\max}^2}{h_0^2 - r_{\max}^2}$$
(7)

According to the continuum mechanics, 3^{7-39} the end-to-end distance (*h*) of polymer chains can be further written as,

$$h = \sqrt{(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)/3} = \sqrt{(\lambda^2 + \frac{2}{\lambda})/3}$$
(8)

where λ_1 , λ_2 and λ_3 represent the stretching ratios along three directions, respectively. The relationships of $\lambda_1 = \lambda$ and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$ are used in the uniaxial tensile stretching, according to the assumption of volume invariance of isotropic material, i.e., $\lambda_1 \lambda_2 \lambda_3 = 1$. In combination of equations (7) and (8), the constitutive relationship of stress (σ_{sr}) as a function of elongation ratio (λ) for the SR gel can be obtained,

$$\sigma_{sr} = -\frac{\partial \Delta F_{el}}{\partial \lambda} = 2N_{sr}\Gamma k_B T \left(\frac{1}{\sqrt{\lambda^2 + \frac{2}{\lambda}}} + \frac{4\sqrt{\lambda^2 + \frac{2}{\lambda}}}{3r_{\max}^2 - \lambda^2 - \frac{2}{\lambda}}\right) \frac{\lambda - \frac{1}{\lambda^2}}{\sqrt{\lambda^2 + \frac{2}{\lambda}}} (9)$$

where Γ is the circulation numbers between the molecular chain and cross-linked ring in the SR gel based on the knot theory. $^{31\text{-}33}$

According to the tube model, 23 the end-to-end distance (*h*) can be expressed as,

$$h \cong \frac{CN_{re}}{d^2} \tag{10}$$

where *C* is the concentration of molecular chains, and N_{re} is the repulsive monomer number. The repulsive free energy (ΔF_{re}) can be then written as,²³

$$\Delta F_{re} = \frac{N_{re}^2 V_{ex}}{2d^2 h^2} = \frac{d^2 V_{ex}}{2C^2} \text{ DOI: 10.1039/D1SM013572}$$

where V_{ex} is the excluded volume.

In the SR gel, diffusion of the molecular chain is essentially restricted by the cross-linked rings, where the extended tube model is introduced to characterize the diffusion behavior as illustrated in Fig. 1(a). It can be seen that the size of the cross-linked ring, *D* (the dimensionless diameter of the cross-linked ring in the SR model of unit volume gel) will play a decisive role in the chain diffusion, $^{30-32}$ which is determined by the orientation and rotation of the cross-linked rings. $^{17-21}$ Here, the dimensionless diameter of the tube is *d* and the diameter of a cross-linked ring is *D*. For a tube formed by a single ring, *d=D*, whereas for a tube formed a double ring, *d=2D*.



Fig. 1 (a) Illustrations of diffusion behaviors of molecular chains in terms of the extended tube model. (b) Diameter of the tube (d) is determined by the diameter of cross-linked ring (D) and stretching ratio (λ).

As can be seen from Fig. 1(b), the diameter of tube (d) becomes maximum when the ring is perpendicular to the longitudinal axis of the tube during the chain movement. As the chains slide through the ring, the sliding chain will cause the ring to tilt relative to the longitudinal axis of the tube. This causes the tube to dilate or constrict along the axial direction, and in turn causes deformation of the tube. According to the affine motion principle,³⁴ this microscopic deformation will cause а macroscopic dilation/constriction of λ -1. This is a gross simplification but an initial attempt to understand how the SR gel is deformed. The actual situation is likely to be more complicated. Different from the better understood chemical cross-linked point model, the movement of the ring cross-linked is directional. Here, in order to express the rotation and orientation, a new parameter, which is borrowed from topology theory, moment $M(=\pm 1)$, is introduced in Fig 1(b). For a chain passing through the horizontally positioned ring, both the downward sliding on the left of the ring and the upward sliding of the chain on the right of the ring, causes the ring to rotate counter-clockwisely, which is defined as M = +1. Whereas its sliding in the opposite direction is defined as M = -1. The number of times a chain passes through a ring is defined as circulation number Γ , and the mechanical enhancement caused by Γ has been treated as the equivalent crosslinking in our current model. However, the actual microscopic orientation caused by the chain's sliding is complex. Here, a net moment, M_{b0} = $\Sigma \pm 1$, summed over Γ times, represents the effect of the direction that a chain passes through a ring. Consequently, the macroscale deformation caused by such entanglement and crosslink can be averaged as $M_b = M_{b0}(\lambda - \lambda)$ 1)/Г. The name moment was chosen to reflect the rotation of polymer chain.

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The tilting of the cross-linked rings has a net macroscale stretching of $M_{b0}(\lambda-1)/\Gamma$, as shown in Fig. 1(b). This causes the variation of diameters of the tube (*d*),

$$d = D - \frac{M_{b0}^2 (\lambda - 1)^2}{2D\Gamma^2}$$
(12)

Substituting equation (12) into (11), the repulsive free energy (ΔF_{re}) can be obtained as a function of diameter of the cross-linked ring (*D*). The repulsive stress can be further obtained as,

$$\sigma_{re} = -\Gamma \frac{\partial \Delta F_{re}}{\partial \lambda} = \frac{M_{b0}^2 V_{ex}}{\Gamma C^2} [1 - \frac{M_{b0}^2 (\lambda - 1)^2}{2D^2 \Gamma^2}] (\lambda - 1)$$
(13)

By combinating equations (9) and (13), the constitutive stressstrain relationship of the SR gel is finally written as,

$$\sigma = \sigma_{sr} + \sigma_{re} = 2N_{sr}\Gamma k_B T \left[\frac{\lambda - \frac{1}{\lambda^2}}{\lambda^2 + \frac{2}{\lambda}} + \frac{4\left(\lambda - \frac{1}{\lambda^2}\right)}{3r_{max}^2 - \lambda^2 - \frac{2}{\lambda}} \right] + \frac{M_{b0}^2 V_{ex}}{\Gamma C^2} [1 - \frac{M_{b0}^2 (\lambda - 1)^2}{2D^2 \Gamma^2}] (\lambda - 1)$$
(14)

As illustrated in Fig. 2, the cross-linked rings are subjected to the moment (M_{b0}), which is expressed as $M_{b0}(\lambda-1)/\Gamma$ based on the circulation numbers (Γ). Fig. 2(a) shows the entanglement between one molecular chain and one cross-linked ring. Meanwhile, Fig. 2(b) shows the entanglements between one molecular chain and two cross-linked rings. We can conclude that the entanglements between the molecular chains and cross-linked rings can be described using two parameters, i.e., M_{b0} and Γ . There is an equivalent relationship between entanglement and topological knot, both of which are governed by the knot theory.³¹⁻³³



Fig. 2 Schematic illustrations of the entanglements between molecular chains and cross-linked rings, where the mechanical behaviors of entanglements are determined by the net direction of entanglement (M_{b0}) and circulation numbers (Γ). (a) For the entanglement with one chain and one ring. (b) For the entanglement with one chain and two rings.

element, C3D10, was used to perform the FEA simulation. About 10,000 elements were used to model the whole that The S(A) profess and compares the FEA simulation results of stress-strain relationship for entanglement and various knots. The minimum elements are used to reveal the entanglement topology, in which two loading points are needed to set a chain. The divergences in simulation results between the entanglement (Γ =3) with those of Reef knot (Γ =3) Carrick knot (Γ =3), Hunter knot (Γ =3) and Zeppelin knot (Γ =3) are calculated, ³¹⁻³³ and they are -5.2%, 5.2%, 16.2 and 28.9%, respectively, as shown in Fig. 3(b).



Fig. 3 Comparison of the mechanical behaviours between entanglements and topological knots. (a) Simulation results of the entanglements and knots with one molecular chain and multiple cross-linked rings. (b) Difference in simulation results between the entanglement (Γ =3) and knots (Γ =3). (c) Simulation results of the entanglement and knots with two molecular chains with multiple cross-linked rings.

To further investigate effects of entanglements and knots, we incorporated both entanglements and knots within multiple crosslinked rings and two chains. The obtained FEA results of stressstrain are shown in Fig. 3 (c). As revealed from the topological structure of Reef and Zeppelin knots based on topological knot theory, as shown in the Fig. 3(c), different circulation numbers (Γ) will be generated according to the specific knot and moving directions of the different chains.³¹⁻³³ The main purpose of this paper is to characterize the interactions between chains and rings, which can be obtained based on the knot theory and verified by FEA simulation results. Here, it is assumed that using the same Γ will lead to similar interaction between the chain and cross-linked ring.

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FEA simulation results of the entranglements are compared with those obtained using the topological knot theory, under a constant strain of 25%. It is assumed that both the molecular chains and cross-linked rings are amorphous polymers. The Young's modulus of the SR gel is chosen as 2 MPa, and its Poisson's ratio and density are chosen as 0.45 and 0.9 g/cm³, respectively. A 10-node tetrahedron

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For example, Reef knot is formed by two chains (i.e., circulation number=4³¹⁻³³), which is equivalent to two chains passing through four rings, and Γ =4/2 for one chain. The difference in simulation results between the entanglement (Γ =4/2) and Reef knot (Γ =4/2) is 21.1%, while that between the entanglement (Γ =5/2) and Zeppelin knot (Γ =5/2) is 2.2%. These FEA simulation results support our hypothesis that the mechanical behaviors of entanglements in the SR gels can be characterized by their topological knots, which are governed by the knot theory.

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3. Mechanical behaviors of the topological knot

We further investigate the effects of circulation number (Γ), which is used to characterize the entanglement, on the mechanical properties of the SR gel. The obtained results are summarized in Fig. 4. When the SR gels are stretched by the tensile loading under a constant strain of 300%, the deformation behavior of the knots can be obtained based on the proposed knot theory, and the results are shown in Fig. 4(a). With the change of the circulation number from Γ =1, Γ =2 to Γ =3, the FEA simulation results reveal that the deformation of the knot becomes more uniform along the chain axis, resulting in the reduced stress concentration.⁴⁰⁻⁴¹ Accordingly, the strengths of topological knots are enhanced from 28.81 N, to 46.04 N, and then to 50.43 N.



Fig. 4 (a) Schematic illustrations of deformations of topological knots with Γ =1, 2 and 3 under the constant strain of 300% by FEA simulations. (b) Analytical results of equation (14) for the topological knots with various circulation numbers of Γ =1, Γ =2, Γ =3, Γ =4 and Γ =5.

Fig. 4(b) shows the analytical results of the stress-strain curves for the knots with various circulation numbers (Γ =1, Γ =2, Γ =3, Γ =4 and Γ =5), calculated using equation (14). Results show that the stress values at the knots are increased from 0.17 MPa, 1.21 MPa, 1.58 MPa to 1.84 MPa at the same elongation ratio of 1500%, as the circulation number Γ increased from 2, 3, 4 to 5. On the other hand, the stress value of the knot with a circulation number of Γ =1 is 0 MPa at the fracture elongation ratio of λ_{max} =700%. The analytical results shown in Fig. 4(b) clearly reveal that the SR gel becomes very deformable but also much tougher with an increase in the circulation number. Its fracture elongation ratio (λ_{max}) has been increased from 700% to 1500%, and the stress has also been increased from 0.17 Mpa to 1.84 MPa. Based on both the knot theory $^{31-33}$ and equation (14), the circulation number (Γ) plays a key role indetermining the mechanical behavior of entanglement and topological knots. A higher value of Γ results in an increased coupling strength between the molecular chain and cross-linked ring, thus resulting in the increases of both elongation ratio and

fracture strength. All these make the SR gel highly deformable and tough. DOI: 10.1039/D1SM01737C

On the other hand, effects of the maximum sliding distance (r_{max}) and the diameter of a cross-linked ring (*D*) on the mechanical behaviors of topological knots have been studied based on equation (14). The results are plotted in Fig. 5. Parameters used in the calculations using the equation (14) are $N_{sr}k_BT$ =0.125 MPa, M_{b0} =1.5, V_{ex}/C^2 =0.1, Γ =4 and *D*=15 for Fig. 5(a); whereas they are $N_{sr}k_BT$ =0.125 MPa, M_{b0} =1.5, V_{ex}/C^2 =0.1, Γ =4 and r_{max} =10 for Fig. 5(b).

As illustrated in Fig. 5(a), the stresses are gradually decreased from 2.42 MPa, 1.75 MPa, 1.21 MPa, 0.98 MPa to 0.86 MPa at the same elongation ratio of λ =1500% and circulation number of Γ =4, with the maximum sliding distance (r_{max}) is increased from r_{max}^2 =85, 90, 100, 110 to 120. By increasing the maximum sliding distance of r_{max} , the free energy (ΔF_{el}) in the SR gel is reduced according to equation (7), thus resulting in the decrease of its stress.



Fig. 5 (a) Analytical results of stress as a function of elongation ratio for the SR hydrogel with various r_{max}^2 . (b) Analytical results of stress as a function of elongation ratio for the SR hydrogel with various *D*.

Meanwhile, effects of the diameters of the ring (*D*) on the mechanical properties of the SR gel are shown in Fig. 5(b), which is obtained based on equation (14). The analytical results reveal that the stress is gradually increased from 0.34 MPa, 0.94 MPa, 1.21 MPa, 1.36 MPa to 1.46 MPa with an increase of the diameter of the ring (*D*) from *D*=9, *D*=12, *D*=15, *D*=18 to *D*=21. With an increase in the value of *D*, the diameter of the tube (*d*) is also increased based on the tube model,³⁴⁻³⁶ thus resulting in the significantly reduced diffusion of the chains. This reduced diffusion of chains helps the gel to resist the externally mechanical loading, resulting in a significantly enhanced mechanical strength of the SR gels.

4. Experimental verification

Experimental data reported in Refs. [18] for PEG/CD SR gels (PEG: polyethylene glycol and CD: hydroxypropyl-acyclodextrin) are used to verify the analytical results generated from the proposed model. As reported in Ref. [18], the entanglement of the PEG/CD SR gels is originated from the PEG molecular chains and CD cross-linked rings. Levenberg-Marquardt optimization algorithm is adopted here for all the calculation parameters. The corresponding termination condition is that the value of residual sum of squares does not decay for at least 100 times, at a given Γ =3. Published on 10 January 2022. Downloaded by Northumbria University Library on 1/10/2022 4:32:38 PM.

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As can be seen from the curves shown in Fig. 6(a), with an increase in the PEG volume fractions from 0.18, 0.30 to 0.38, the stress is gradually increased from 0.85 MPa, 2.64 MPa to 5.04 MPa at the same elongation ratio of λ =1300%. All the parameters used in calculations are listed in Table 1. According to the experimental results,¹⁸ the PEG works as the molecular chain and CD acts as the cross-linked ring. Both the analytical and experimental results reveal that the cross-linked ring is able to improve the mechanical properties of the SR gel via the pulley effect, while the molecular chains are helpful to connect the cross-linked rings. More cross-linked rings are involved in the molecular chains, and a higher mechanical properties of the SR gel is achieved due to the higher Γ value based on the knot theory.³¹⁻³³ In Fig. 6(b), the correlation index R^2 between the analytical and experimental results are calculated to be 92.57%, 95.44% and 94.95% for SR-0.18, SR-0.30 and SR-0.38 gels, respectively. It can be clearly seen that the analytical results agree well with the experimental data ($|\Delta\sigma|$ < 0.6 MPa). Furthermore, results from the classical Mooney-Rivlin (M-R) equation³⁴ ($\sigma = (2C_1 + 2C_2/\lambda)(\lambda - 1/\lambda^2)$, where C_1 and C_2 are material constants) are also plotted in Fig. 6(a), and it is shown that the results obtained from our newly proposed model are more close to the experimental results.¹⁸ All these strongly support our proposed mechanical enhancement mechanism of complex network topology in SR hydrogel, which have various stages of knot entanglement, pulley effect, the sliding and ultimate stretching of the SR network.

	$N_{sr}k_{B}T$ (MPa)	$r_{\rm max}^2$	$\frac{M_{b0}^2 V_{ex}}{C^2}$ (MPa)	C1(MPa)	C ₂ (MPa)	$\frac{M_{b0}^2}{D^2}$
SR-0.18	0.0348	84.47	0.15	0.045	-0.149	0.0018
SR-0.30	0.0904	68.93	0.39	0.117	-0.322	
SR-0.38	0.2069	65.11	0.57	0.211	-0.668	



Fig. 6 Numerical results and experimental data¹⁸ of stresselongation ratio curves of PEG/CD SR hydrogel, at given PEG volume fractions of 18%, 30% and 38%. (a) The stress-elongation ratio curves to show the difference of models. (b) Divergences of analytical and experimental results of stress.

Fig. 7(a) plots both the calculated and experimentally obtained stress-elongation ratios of the PEG/CD SR gels with PEG volume fractions of 18%, 30% to 38%.¹⁸ All the parameters used in the calculation using the equation (14) are listed in Table 1. Fig. 7, which shows the loading-unloading stress-elongation ratio curves, is different but linked with Fig. 6, which shows the stress-elongation

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ratio curves of SR gels. Both these two figures are obtained during a uniaxial stretching of the PEG/CD SR gels until breaking! With the increase in the PEG volume fraction from 18%, 30% to 38%, the stress value is increased from 0.69 MPa, 1.91 MPa to 3.21 MPa at the same elongation ratio of λ =1100%. These analytical and experimental results reveal that the strength of PEG/CD SR gel can be significantly enhanced from 0.69 MPa to 3.21 MPa (an increase of 365%), with an increase in the PEG volume fraction from 18% to 38%. Fig. 7(b) also shows that the analytical results agree well with the experimental data,¹⁸ where the divergence of stress is limited to $|\Delta\sigma|<0.4$ MPa.

The working principle of the pulley effect for the PEG molecular chain in the PEG/CD SR gel is illustrated in Fig. 7(c). With an increase in the PEG volume fraction, the end-to-end distance (h) of molecular chains is increased, resulting in the increase of elongation ratio (λ) based on equation (8). According to the constitutive stresselongation ratio relationship in equation (14), the stress of the SR gel is enhanced with an increase in the elongation ratio (λ). Meanwhile, the content of the cross-linked rings of CD is kept a constant, although that of the PEG molecular chain is increased. The pulley effect in the SR gel is therefore enhanced with an increase in the moment of force (M_b) , which is determined by the sliding behavior and elongation ratio (λ). For the PEG/CD SR gel in this study, the increase in end-to-end distance (h) of PEG molecular chain causes the increase of both the moment of force (M_b) and elongation ratio (λ), thus resulting in the increased strength of the SR gels.



Fig. 7 Analytical results from current model and experimental data¹⁸ of stress-elongation ratio curves of PEG/CD SR hydrogel, at given PEG volume fractions of 18%, 30% and 38%. (a) The stress-elongation ratio curves. (b) Divergences of analytical and experimental results of stress. (c) Schematic illustration of the pulley effect, which is determined by the molecular chain and cross-linked ring in SR gel.

We use the experimental results of PEG/CD SR gels (reported in Ref. [18]) to verify the analytical results of mechanical stress-strain, obtained using equation (14). The parameters used in the calculations are listed in Table 2.

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During the mechanical loading, a tensile stress is applied to the PEG/CD SR gel with a maximum elongation ratio of 800%, and then the loading is removed and the gel is left for recovery. This has been repeated for many cycles. Fig. 8(a) plots the analytical results of the constitutive stress-elongation ratio relationships for the SR gels undergoing cycles of 1, 20, 40, 60, 80 and 100. It shows that our newly proposed model can predict well the experimental results.¹⁸ The correlation index of R^2 between the analytical and experimental results are 98.21%, 98.76%, 98.83%, 99.13%, 98.86% and 98.91% for 1, 20, 40, 60, 80 and 100 cycles, respectively, as shown in Fig. 8(b).



Fig. 8 Analytical results and experimental data¹⁸ of stresselongation ratio curves of PEG/CD SR gel undergoing 1, 20, 40, 60, 80 and 100 cycles. (a) The stress-elongation ratio curves. (b) Divergences of analytical and experimental results of stress.

(a)

Elongation ratio

R2= 98.86%

 $R^2 = 98.91\%$

Elongation ratio 2

(b)

To further verify the model, another group of experimental data of PEG/CD SR hydrogel, in which the molar concentrations of SR gels are 16%, 20% and 25%,¹⁹ have also been employed. For this case, the parameters used in the calculation using equation (14) are listed in Table 3. Analytical results clearly show that the stress is gradually increased from 0.11 MPa, 0.37 MPa to 0.55 MPa, with an increase in the molar concentration of PEG/CD SR gels from 16%, 20% to 25%, at the same elongation ratio of λ =1300%. On the other hand, the fracture elongation (λ_{max}) is also increased from 1350%, 1680% to 1710%. It can be clearly seen from Fig. 9(a) that the analytical results agree well with the experimental data. Both these results prove that the maximum elongation ratio and fracture strength of the PEG/CD SR hydrogel have been significantly enhanced with an increase in the molar concentration of the gel. The correlation index (R^2) between the analytical and experimental results are calculated as 97.50%, 93.78% and 88.30% for the hydrogels with the molar

The stress-elongation ratio curve of the SR hydrogel¹⁹ is close to a straight line³⁴. During stretching, certain number of cross-linked points may be generated instead of cross-linked rings, due to different concentrations of cross-linkers and different environments. These might cause that the mechanical properties of cross-linked points cannot support $N_{\rm sr}$. During the analysis, tube model is used to characterize the mechanical properties of polymer chain and cross-linked ring. The excluded volume (Vex) of the chains is increased due to the formation of more cross-linked rings.²³

The working principle of PEG/CD SR gel in the hydrogel is illustrated in Fig. 9(c). Based on the rubber elasticity theory,³⁴⁻³⁵ the mechanical strength can be improved with an increase in the molecule density in hydrogel, which enables a large number of molecules involved in resisting the externally mechanical force, resulting in the significantly enhanced stress. Meanwhile, the fracture elongation (λ_{max}) of hydrogel is increased due to the PEG/CD SR gel, which is super deformable and tough, achieving the hydrogel soft and tough.





Fig. 9 Analytical results and experimental data¹⁹ of stresselongation ratio curves of PEG/CD SR hydrogels, at molar concentration of PEG/CD SR gel of 16%, 20% and 25%. (a) The stress-elongation ratio curves. (b) Correlation between the analytical and the experimental stresses. (c) Schematic illustration of working principle of PEG/CD SR gel in the

hydrogel.

5. Conclusions

A new model of topological knots is proposed to represent the mechanics of the collective entanglements in the SR gels. A topological parameter, the circulation number (Γ), is proposed and applied to estimate the entanglement of polymers chains through the rings, together with the concept of moment M accounting for the phenomena when the polymer chains pass through the rings/knots. From a broader conceptual and practical perspective, this framework combining the entanglement and topological knot is well suited for the design of desired sliding behavior and pulley effect of the SR gels. These results in a super deformability and a good toughness simultaneously, which resolves the difficulties for the balance of deformability, stiffness and toughness in the gel.

Conflicts of interest

There are no conflicts to declare.

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