1 Introduction

Elastomer, one of the most popular soft matters, has been widely used for sensors, wound dressing, piezoelectric devices and artificial muscles, attributed to their abilities to integrate adaptive coloration and mechanical properties. Mechanochromic properties of the elastomers enable them with great potentials in applications of biological tissues and living organisms such as chameleons. Furthermore, great effort has been made in order to achieve good mechanical properties through molecular interactions and to improve biocompatibility and stimulus-responsibility. However, there are few theoretical investigations or models to understand the working mechanisms and design principles for molecular self-assembly, which are essential for the guidance of chemical synthesis, understanding of structure-property relationships and practical applications.

So far, much effort has been made to enhance the mechanical properties of elastomers, e.g., using multi-networks and self-assembly methods. Previously Davis et al. has successfully made mechanoochemical polymers, which have the capability of translating macroscopic forces into chemical reactions by covalently connecting mechanophore molecules to polymers. Most of these studies are focused on the optimization of elastomers’ mechanical properties by designing the self-assembly of polymer networks using different components and compositions.

Recently, chameleon-like elastomers have been fabricated through molecularly encoding strain-adaptive stiffening and coloration, and their functional properties can be regulated by the polymer network of self-assembled macromolecules. However, topological dynamics, which plays an essential role to determine the microstructures and macroscale properties of these self-assembled elastomers, has not been well investigated. Furthermore, modelling the couplings of multi-fields has not been widely studied due to the extremely complex constitutive relationships.

In this work, a ternary “rock-paper-scissors” model is employed to characterize the anchoring-mediated topology signature of the self-assembled elastomers, of which the topology network synchronously undergoes topological dynamics of self-assembly, mechanochromic coupling and mechanoresponsive stiffening. Based on the constrained molecular junction model, a free-energy function is formulated to identify the topological dynamics and coupling effect in these self-assembled elastomers. The constitutive relationships are then proposed to predict the mechanoresponsive stiffening and mechanochromic coupling/decoupling. Finally, the proposed models are verified using the experimental results reported in the literature.

2. Theoretical framework

The topological structure of a cross-linked network has a decisive influence on the mechanical properties of polymer. As the elastomers were synthesized through the self-assembly of...
triblock copolymers, the dynamic networks therefore had various topology signatures due to the increase in numbers of chains involved as shown in Fig. 1. Self-assembly of triblock copolymers yields cross-linked networks, which show the topological network junctions (ψ) of ψ=2, ψ=3, ψ=4 and ψ=6. For example, ψ=3 means that there are three chains self-assembled into a crosslink point in the network. Therefore, the regular hexagon network is formed due to a large number of chains self-assembled to form the network, in which one crosslink point is incorporated of three chains.

**Fig. 1** Illustration of cross-linked topology networks in terms of self-assembly of triblock copolymers in elastomers.

To explore the working principles and topological dynamics of cross-linked network, the elastic free-energy function (ΔFrel) is introduced based on the constrained junction model,31

\[
\Delta F_{el} = \Delta F_{ph} + \Delta F
\]

\[
\Delta F_{ph} = \frac{1}{2}(1 - \frac{2}{\psi})N_{i}k_{B}T(\lambda_{i}^{2} + \lambda_{i}^{2} + \lambda_{i}^{2} - 3)
\]

\[
\Delta F = \frac{1}{\psi}N_{i}k_{B}T\sum_{i=1,2,3}[B_{i} + D_{i} - \ln(B_{i} + 1) - \ln(D_{i} + 1)]
\]

where \(\Delta F_{ph}\) is the free-energy of the phantom network, \(\Delta F_{el}\) is the constraint-free energy, \(\psi\) is the average functionality of the network junctions, \(N_{i}\) is the cross-linking density of elastic phantom network, \(T\) is the temperature, \(k_{B}\) is the Boltzmann constant, \(B_{i}\) and \(D_{i}\) are two parameters representing the degrees of the constraints, \(\kappa\) is a given parameter for the entanglement constraint in the phantom network, \(\lambda_{1}\), \(\lambda_{2}\) and \(\lambda_{3}\) represent the stretching ratios of the elastomers along three directions, respectively. According to this constrained junction model,31 the mechanical properties of the elastomer can be described using the parameter,

\[
\lim_{\kappa \to 0} B_{i} = 0 \quad \text{and} \quad \lim_{\kappa \to 0} D_{i} = 0
\]

\[
\lim_{\kappa \to 0} \Delta F_{el} = \lim_{\kappa \to 0} \Delta F_{ph} = \frac{1}{2}(1 - \frac{2}{\psi})N_{i}k_{B}T(\lambda_{i}^{2} + \lambda_{i}^{2} + \lambda_{i}^{2} - 3)
\]

\[
\lim_{\kappa \to 0} B_{i} = \lambda_{i}^{2} - 1 \quad \text{and} \quad \lim_{\kappa \to 0} D_{i} = 0
\]

\[
\lim_{\kappa \to 0} \Delta F_{el} = N_{i}k_{B}T\left[\frac{1}{2}(\lambda_{i}^{2} + \lambda_{i}^{2} + \lambda_{i}^{2} - 3) - \frac{2}{\psi} \ln \lambda_{i} \lambda_{i} \lambda_{i}\right]
\]

(Equation 6) can be used to describe the mechanical properties of the elastomer that is governed by the free-energy of the phantom network (\(\Delta F_{ph}\)), where the weak constraint (\(\kappa \to 0\)) results in \(\Delta F_{el}=0\). Meanwhile, equation (7) is used for describing mechanical properties of the elastomer that is governed by the elastic free-energy function (\(\Delta F_{el}\)), where the strong constraint (\(\kappa \to 0\)) results in \(\Delta F_{el}=0\). To simplify the expressions of equations (6) and (7), the function of \(\psi = \lambda_{1}\lambda_{2}\lambda_{3}(h_{f}/h_{b})^{2.5}\) (\(h_{f}\) is the tensor of end-to-end distance of a polymer chain and \(h_{b}\) is the initial end-to-end distance of polymer chain) is introduced, as reported in Refs. [24-31]. Under a uniaxial tension (e.g., \(\lambda_{1}=\lambda_{2}\) and \(\lambda_{3}=\lambda_{1}(h_{f}/h_{b})^{2.5}\) where \(\lambda_{3}/\lambda_{1}\) is the uniaxial elongation ratio), the constitutive relationship of true stress for the elastomer as a function of elongation ratio can be written as,

\[
\sigma_{true} = \lambda_{1} \frac{\partial \Delta F_{el}}{\partial \lambda_{1}} = N_{i}k_{B}T\left[\frac{(\lambda_{1}^{2} - 1)}{\lambda_{1}^{2} + \lambda_{1}^{2} + \lambda_{1}^{2} - 3} - \frac{2}{\psi} \ln \lambda_{1} \lambda_{1} \lambda_{1}\right] + p
\]

where \(p\) is the hydrostatic pressure. According to the rubber elasticity theory,17 the change of end-to-end distance (\(\Delta h\) and \(h=\Delta h+h_{0}\)) of the polymer chains caused by the external force \((f)\) can be written as,

\[
f = \frac{3k_{B}T}{h_{0}} \Delta h
\]

\[
f = E_{r}(\lambda - \frac{1}{\lambda^{2}}) = 3G_{r}(\lambda - \frac{1}{\lambda^{2}})
\]

where \(E_{r}\) is the modulus of the polymer chain. According to the rubber elasticity theory, there is a constitutive relationship between modulus \((E_{r})\) and shear modulus \((G_{r})\) of \(E=3G_{r}\), because the Poisson’s ratio is approximately 0.5. Based on the boundary conditions of \(\sigma_{true}(\lambda=1)=0\), equation (8) can be rewritten as,

\[
I_{i} = \frac{h_{f} + \Delta h}{h_{b}} = 1 + \frac{E_{r}h_{f}}{3k_{B}T}(\lambda - \frac{1}{\lambda^{2}})
\]

\[
\sigma_{true} = \lambda_{1} \frac{\partial \Delta F_{el}}{\partial \lambda_{1}} = N_{i}k_{B}T\left[\frac{(\lambda_{1}^{2} - 1)}{\lambda_{1}^{2} + \lambda_{1}^{2} + \lambda_{1}^{2} - 3} - \frac{2}{\psi} \ln \lambda_{1} \lambda_{1} \lambda_{1}\right] + p
\]

\[
\sigma_{true} = \lambda_{1} \frac{\partial \Delta F_{el}}{\partial \lambda_{1}} = N_{i}k_{B}T\left[\frac{(\lambda_{1}^{2} - 1)}{\lambda_{1}^{2} + \lambda_{1}^{2} + \lambda_{1}^{2} - 3} - \frac{2}{\psi} \ln \lambda_{1} \lambda_{1} \lambda_{1}\right] + p
\]

Fig. 2 shows the analytical results obtained using equation (11), which are compared with experiment data of EAMA (EA: ethyl acrylate and MA: methyl acrylate) elastomers reported in Ref. [6]. The parameters used in calculations using the equation (11) are \(N_{i}k_{B}T=5.72\) MPa, \(E_{r}h_{f}/k_{B}T=2.2\) and \(\psi=4\). The classical rubber elasticity theory mainly includes two models: the phantom model and the affine model.17 The affine model is the earlier version of the rubber model. Cross-linking points are the main parts in the affine model, and they are randomly distributed and can move in the same proportion according to macroscopic deformation. According to these assumptions, Flory established the affine model based on Gaussian chain (the free energy of the affine network \(\Delta F_{af} = N_{i}k_{B}T(\lambda_{1}^{2} + \lambda_{2}^{2} + \lambda_{3}^{2})/2\).17 It is found that the analytical results obtained from the constrained junction model are in good agreements with the experimental data, if compared with those obtained using the phantom and affine models.17 The constrained junction model is suitable to characterize the plasticity of the EAMA elastomer due to the distinct differences in mechanical behaviors of two components of EA and MA, besides of rubber elasticity.6 Furthermore, the contribution of junction to the mechanical behavior has also been considered by the constrained junction model. Whereas for the phantom and affine models, the cross-linking point has not been considered to influence the mechanical
behavior. Therefore, our theoretically analytical results fit well with the experimental ones.

Fig. 2 Comparisons between analytical results using equation (11) and experimental data of the EAMA elastomer reported in Ref. [6], based on the constrained junction, phantom and affine models. During the uniaxial extension, the EAMA elastomer undergoes mecanochemical reaction, and the stretchable network is strongly constrained by the broken chains, which is well predicted by the constrained junction model.

2.1 Topological dynamics and transition

As reported in Ref. [9], PMMA-PDMS-PMMA (PMMA: poly(methylmethacrylate); PDMS: polydimethylsiloxane) elastomers were synthesized through the self-assembly of linear-bottlebrush-linear (PMMA works as the linear block and PDMS acts as the bottlebrush) triblock copolymers. To investigate topological dynamics and mecanochromic coupling, the constitutive relationship between molecular topology structure and mecanochromic property is proposed for the self-assembled elastomers.

According to the interfacial free-energy equation, the free-energy function of microphase (\(F_A\)) is introduced as,

\[
F_A = \frac{1}{k_B T} \left( \frac{3N \chi^2 l_b^3}{6d_i} + \frac{3d_i^2}{2N \chi^3 l_b} \right) \tag{12}
\]

where \(l_b\) is the segment length, \(\chi\) is the interaction parameter, \(N_A\) is the segment number and \(d_i\) is the diameter of the self-assembled domain. According to the principle of minimized interfacial free-energy function \((\partial \Delta F_A/\partial d_i = 0)\), the diameter can then be obtained as,

\[
\frac{\partial F_A}{\partial d_i} = 0 \Rightarrow d_i = \left( \frac{2\chi}{3} \right)^{\frac{1}{2}} N_A^{\frac{1}{2}} l_b \tag{13}
\]

Fig. 3A illustrates the physically cross-linked and topology networks. \(d_2\) is the diameter of spherically shaped PMMA domain. \(d_3\) represents the distance between two PMMA domains and it determines the morphochromism of elastomer, which can be obtained from the ultra-small-angle x-ray scattering (USAXS) measurements. Meanwhile, Fig. 3B describes the working principles of mecanochromic coupling for the self-assembled network. Under a tensile loading, the distance between two PMMA domains \((d_3)\) is gradually decreased due to the increase in the elongation ratio \((\lambda)\). Therefore, the ternary coupled “rock-paper-scissors \((d_i(h_0)\alpha, d_i(h_0)\beta, \lambda)\)” model is then employed to describe the topological dynamics and transition of self-assembly, mecanochromic coupling and mecanoresponsive stiffening, in which there are three fractal geometry components in the topology network.35

The item of \(\psi\) is the average functionality of the network junctions and plays an essential role to determine the microphase separation of PMMA-PDMS-PMMA elastomers.36 As revealed in Fig. 3, the microphase is originated from spherically shaped PMMA domain, of which the volume is determined by the intra-domain distance \((d_3)\) and obtained from \(4/3\pi(d_3/2)^3 = \pi(\chi/54)^{0.5}N_s^2l_b^3\), whereas the volume of each chain is \(N_s^2l_b^3\). Based on the Flory-Huggins theory for microphase separation,20-22 the number of self-assembled chains undergoing the microphase separation can be obtained based on \(\psi = \pi(\chi/54)^{0.5}N_s^2l_b^3/N_b\lambda\alpha\beta = \pi(\chi/54)^{0.5}N_A\beta = 4\), whereas \(\chi = 1\) and \(N_A = 10.5, 20-22, 32, 33\)

![Image](https://example.com/image1.png)

![Image](https://example.com/image2.png)

**Fig. 3** Schematic illustrations of mecanochromic coupling in terms of domains \((d_2\) and \(d_3\) and elongation ratio \((\lambda)\) in elastomer. A) For dynamic transition of molecular networks. B) Topological transition of topology networks.

The mass ratio \((<\chi\alpha\beta>)\) of each site is used to characterize the effect of \(d_2\) on the topology network, and it has the following expression,

\[
<\chi\alpha\beta> = \exp\left(\frac{\beta}{2} \ln \left( \frac{1}{d_i - d_2} \right) \right) (\beta = 1,2,\ldots,N) \tag{14}
\]

where \(\beta\) is the number of chains with a unique diameter of \(d_3\), and \(N\) is the number of chains in a spherically shaped domain.

Then, the molecular weight distribution \((<M_\beta>)\) of the domains is given as,

\[
<M_\beta> = M_0 <\chi\alpha\beta> (\beta = 1,2,\ldots,N) \tag{15}
\]

where \(M_0\) is the molecular weight of one chain. According to the rubber elastic theory,17,20 the initial end-to-end distance \((h_0)\) can then be obtained,

\[
h_0 = \sum_{\beta=1}^{N} \frac{C_{\beta}}{N_\beta} = \sum_{\beta=1}^{N} \frac{C_{\beta}M_0(d_i - d_2)^{\beta}}{M_0 <\chi\alpha\beta>} \tag{16}
\]
where \( C_\text{ct} \) is a scaling constant, \( N_\text{av}=\rho N_\text{av}/M_M > > N_\text{av}, \rho \) is the density of the elastomer, \( N_\text{av} \) is the Avogadro’s constant and \( d_\beta=(2\chi/3)^{1/2}N_\text{av}^{1/3}h_\text{av}. \)

Substituting equations (11) and (13) into (16), the end-to-end distance of a polymer chain \((h_0)\) and the true stress functions can be obtained as,

\[
h_\text{h} = \sum_{\beta=1}^{\infty} \frac{C_\beta M_\beta}{\rho N_\text{av}} (d_\beta - d_\beta) \quad \text{and} \quad \sigma_{\text{true}} = \frac{C_\beta E_\beta}{h_0} \left[ \frac{kT}{E_\beta h_0} (\lambda^2 - 1) \right] + \frac{1}{1+\frac{\lambda^2-1}{3kT}} + \frac{2}{\psi}
\]

(17a)

(17b)

where \( N_\text{av}=V_\text{av}\phi_a, V_\text{a} \) is the number of chains and \( \phi_a \) represents the volume fraction of one chain in the domain.

To verify equation (17b), the analytical results of stress as a function of elongation ratio have been plotted for the elastomer, of which the topology networks undergo dynamic transitions, at a given parameter of \( E_0/h_0A_\beta T=2 \) and \( C_\beta E_\beta/h_0=1.0\text{MPa}. \) As shown in Fig. 4A, the constitutive stress-elongation ratio relationship has been investigated at different topological network junctions \((\psi)\) of \( \psi=2, \psi=3, \psi=4 \) and \( \psi=6 \) for the self-assembled elastomer.

![Fig. 4 A](image1.png)

**Fig. 4 A** Analytical results based on equation (17) for the stress as a function of elongation ratio of elastomer, at a given constrained junction of \( \psi=2, 3, 4 \) and \( \infty \). B) FEA of the dynamic deformation and transition of topology networks, at a given \( \psi=3, 4 \) and \( 6 \).

With an increase in the junctions \((\psi)\) from \( \psi=2, \psi=3, \psi=4 \) to \( \psi=6 \) in the topology networks, the stress is gradually increased from 2.74 MPa, 2.95 MPa, 3.05 MPa to 3.16 MPa at the same elongation ratio of \( \lambda=3.0. \) In theoretical analysis, the value of \( \psi \) can be infinity, which means each chain is crosslinked to an infinite number of other chains, and the theoretical maximum can help scientists to determine the enhancement effect of physical crosslinking and prevent blind application. These analytical results indicate that the topology structure has a significant influence on the mechanical properties of the self-assembled elastomer, which is attributed to the increased cross-linking density in the polymer network based on the rubber elastic theory. On the other hand, the finite-element analysis (FEA) method is also applied to analyze the dynamic transitions of these topology networks, and the obtained results are shown in Fig. 4B. As designed, the mechanical behavior of self-assembled elastomer is critically determined by the constrained junction \((\psi)\), which determines the cross-linking density. With an increase in the constrained junctions from \( \psi=3, \psi=4 \) to \( \psi=6 \), the mechanical stress of topology network is then gradually increased owing to the increased cross-linking density. According to the constrained junction model, topological dynamics of the cross-linked network is resulted from the increased constrained junctions due to the externally mechanical loading, which causes that the topology network shows an enhanced mechanical performance and the elastomer shows a classical plasticity. These analytical results provide a working principle in topological dynamics and transition of self-assembled elastomers, which undergo strain-adaptive stiffening as the experimental results revealed.9

### 2.2 Mechanochromic coupling and decoupling

Optical properties of the elastomer are also determined by the dynamic transition of topology network due to the mechanochromic coupling, where the inter-domain distance \((d_i)\), which is linked with the optical property) is determined by the strain-adaptive elongation ratio \((\lambda)\, (\lambda)\) which is linked with the mechanical property). Here, the refractive index \((n)\) can be described as,\(16,37 \)

\[
n = n_0 \left| \frac{h \cdot h_0}{h_0} \right| = n_0 \left[ 1 + \frac{E_0 h_0}{3kT} (\lambda - 1)^2 \right]^{-1/2}
\]

(18)

where \( n_0 \) is the initial value of refractive index parameter without stress.

To identify the working principles in mechanochromic coupling and decoupling of self-assembled elastomer, the effects of strain-adaptive elongation ratio \((\lambda)\) on the mechanical stress and optical refractive index have been investigated, and the results are shown in Fig. 5. The analytical results of stress as a function of elongation ratio \((\lambda)\) have been firstly plotted in Fig. 5A. It is revealed that the stress is gradually increased from 1.94 MPa, 2.45 MPa, 2.89 MPa, 3.62 MPa to 4.63 MPa with an increase in the diameter of spherically shaped domain \((d_j)\) from 30 nm, 35 nm, 40 nm, 45 nm to 50 nm, at a given elongation ratio of \( \lambda=3.0 \). With a given value of the diameter of spherically shaped domain \((d_j)\), the inter-domain distance \((d_i)\), which determines the optical property of elastomer, is decreased with an increase in the elongation ratio \((\lambda)\). Here the end-to-end distance of a polymer chain \((h_0)\) is decreased, thus resulting in the increase of stress according to the equation (17b). These analytical results can be explained by the rubber elastic theory, e.g., the constrained junctions \((\psi)\) is increased with an increase in the diameter of spherically shaped domain \((d_j)\), which results in more chains self-assembled into the domain. Furthermore, the cross-linking density of polymer network is increased to achieve an enhanced mechanical property of the elastomer.

On the other hand, the mechanochromic coupling of the self-assembled polymer network has been further investigated for the

---

4 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx

---
elastomer, and the obtained results are shown in Fig. 5B. Firstly, the analytical results of refractive index as a function of elongation ratio (λ) have been plotted at a given value of $E_{f}h_{0}/k_{0}T=0.1, 0.2, 0.3, 0.4$ and 0.5, in order to identify the working principles of mecanochromic coupling and decoupling during the dynamic transition of topology network. It is revealed that the refractive index is increased from 1.08, 1.28, 1.49, 1.72 to 1.96 with an increase in the $E_{f}h_{0}/k_{0}T$ from 0.1, 0.2, 0.3, 0.4 to 0.5, at a given elongation ratio of λ=3.0. Here the end-to-end distance of a polymer chain ($h_{0}$) is kept a constant in order to maintain the value of $E_{f}h_{0}/k_{0}T$ a constant. These analytical results reveal that the refractive index is gradually increased with an increase in the $E_{f}h_{0}/k_{0}T$ from 0.1 to 0.5. The strain-adaptive coloration is determined by the end-to-end distance of a polymer chain ($h_{0}$), which is originated from the inter-domain distance ($d_{s}$) as the diameter of spherically shaped domain ($d_{2}$) is kept a constant. The analytical results can be verified by the experimental ones reported in Ref. [9], in which the strain-adaptive coloration is determined by the inter-domain distance ($d_{s}$) based on the experimental USAXS measurements. 

**Fig. 5** Mechnochromic coupling and decoupling of self-assembled elastomer. A) Analytical results of equation (17) for the stress as a function of elongation ratio at a given value of $d_{2}=30$ nm, 35 nm, 40 nm, 45 nm and 50 nm, whereas $C_{w}E_{f}/k_{0}T=0.5$ MPa, $\psi=4$ and $E_{f}C_{w}M_{0}/N_{w}k_{0}T=0.2$ nm$^{-0.5}$. B) Analytical results of equation (18) for the refractive index as a function of elongation ratio at a given value of $E_{f}h_{0}/k_{0}T=0.1$, 0.2, 0.3, 0.4 and 0.5, whereas $n_{w}=0.9$.

According to these analytical results, the mecanochromic coupling can be therefore characterized using our newly proposed model. The mecanochromic decoupling is determined by the strain-adaptive elongation ratio (λ, for the mechanical property) and inter-domain distance ($d_{s}$, for the optical property), respectively, whereas the mecanochromic coupling and decoupling are both governed by the "rock-paper-scissors ($d_{s}(h_{0}) \cdot d_{2}(h_{0}) \cdot \lambda$)" model in the topology network. 

3.1 Constitutive stress-elongation ratio relationship

According to the interfacial free energy and the thermodynamics of microphase separation, $\psi=4$ can be determined as shown in Section "2.1 Topological dynamics and transition". Moreover, according to equation (17), the nonlinear terms are tended to be constants when λ is large (1/λ$^{3}$→0, λ+2/λ$^{3}$→λ and 1-λ$^{3}$→λ), where the modulus can be estimated according to the end point. After these two parameters are determined, the data can be processed and the remaining two thermodynamic parameters which are difficult to obtain through experiments can be obtained by the least square method.

To experimentally verify the proposed model of equation (17), the analytical results have been plotted in Fig. 6 to predict the mechanical stress-elongation ratios of the PMMA-PDMS-PMMA elastomers,$^{9}$ whereas the effect of volume faction of PMMA ($\phi_{A}$) has been investigated at a given segment number of PDMS ($N_{0}$). During the analysis, the following parameters are used in equation (17), e.g., $E_{f}C_{w}M_{0}/N_{w}k_{0}T=2.2$, $E_{f}C_{w}M_{0}/N_{w}k_{0}T=0.2$ nm$^{0.5}$, $\psi=4$ and $E_{f}C_{w}M_{0}/N_{w}k_{0}T=180$ kPa. The obtained analytical results shown in Fig. 6A reveal that the stress is increased from 274 kPa, 361 kPa to 410 kPa, with an increase in the volume faction of PMMA ($\phi_{A}$) from 0.03, 0.06 to 0.17.

<table>
<thead>
<tr>
<th>$\phi_{A}$</th>
<th>$\sigma_{m}(10^{5} Pa)$</th>
<th>$\sigma_{m}(10^{5} Pa)$</th>
<th>$R^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>4.10</td>
<td>3.23</td>
<td>96.69%</td>
</tr>
<tr>
<td>0.06</td>
<td>3.61</td>
<td>2.85</td>
<td>92.94%</td>
</tr>
<tr>
<td>0.17</td>
<td>2.74</td>
<td>2.42</td>
<td>92.02%</td>
</tr>
</tbody>
</table>

**Fig. 6** Comparisons of analytical (using equation (17)) and experimental results for the stress as a function of elongation ratio in PMMA-PDMS-PMMA elastomers with various volume faction of PMMA ($\phi_{A}$) of $\phi_{A}=0.03, 0.06$ and 0.17, at a given segment number of PDMS ($N_{0}$) of $N_{0}=302$. $^{9}$ A) For the constitutive stress-elongation ratio curves. B) Divergences of the analytical and experimental results.

As discussed above for the topology network of self-assembled elastomers, the increase in volume faction of PMMA ($\phi_{A}$) results in the increased diameter of spherically shaped domain ($d_{2}$), and the decreased end-to-end distance of a polymer chain ($h_{0}$, $h_{0}=\sqrt{(d_{2} \cdot d_{s})}$). Therefore, the stress is increased due to the decrease in end-to-end distance of a
polymer chain ($h_o$), based on the equation (17). Furthermore, the divergences between the analytical and experimental results$^9$ of the PMMA-PDMS-PMA elastomers are calculated using the correlation index ($R^2$), which are 96.69%, 92.94% and 92.02% for $\phi_A=0.03$, 0.06 and 0.17, respectively, as shown in Fig. 6B. Meanwhile, the comparisons between analytical results and experimental data are listed in Table 1, where $\sigma_{t\max}$ is the true stress at the maximum elongation ratio for experimental data and $\sigma_{t\max}$ is the true stress at the maximum elongation ratio for analytical results.

On the other hand, the analytical results of stress as a function of elongation ratio for the PBMA-PDMS-PMA elastomers have been plotted and compared with the experimental results reported in literature.$^{15}$ Effects of volume faction of PBMA ($\phi_A$) and the chain number of PDMS ($N_0$) have also been investigated, and the results are shown in Fig. 7.

**Table 2. Comparison between analytical results and experimental data of the maximum true stress in Fig.7.**

<table>
<thead>
<tr>
<th>$\phi_A$</th>
<th>$\sigma_{t\max}(10^5$Pa$)$</th>
<th>$\sigma_{t\max}(10^5$Pa$)$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.38</td>
<td>0.37</td>
<td>94.76%</td>
</tr>
<tr>
<td>0.10</td>
<td>0.72</td>
<td>0.44</td>
<td>84.92%</td>
</tr>
<tr>
<td>0.25</td>
<td>0.98</td>
<td>0.95</td>
<td>97.15%</td>
</tr>
</tbody>
</table>

Fig. 7 Comparisons of analytical and experimental results for the stress as a function of elongation ratio in PBMA-PDMS-PMA elastomers with various volume faction of PBMA ($\phi_A$) of $\phi_A=0.05$, 0.10 and 0.25, at a given segment number of PDMS ($N_0$) of $N_0=1000$. A) For the constitutive stress-elongation ratio curves (using equation (17)). B) Divergences of the analytical and experimental results.

The following parameters are used in equation (17), e.g., $E_{\mathrm{C}}C_0M_0d^2/3/N_{\mathrm{Av}}k_8T_p=3.1$, $E_{\mathrm{C}}C_0M_0^{1/3}l_{\mathrm{Av}}V_{\mathrm{A}}^{1/3}/N_{\mathrm{Av}}k_8T_{\mathrm{p}}=9.9$, $\psi=4$ and $C_0E_f/k_8T=60$ kPa. The obtained analytical results show good agreements with the experimental data of self-assembled PBMA-PDMS-PMA elastomers. It is found that the stress is increased from 38 kPa, 72 kPa to 98 kPa, with an increase in the volume faction of PBMA ($\phi_A$) from 0.05, 0.10 to 0.25. As discussed above for the topology network of self-assembled elastomer, the increase in volume faction of PBMA ($\phi_A$) results in the increased diameter of spherically shaped domain ($d_i$) and the decreased end-to-end distance of a polymer chain ($h_o \propto (d_i-d)^{1/5}$). Therefore, the stress is increased due to the decrease in end-to-end distance of a polymer chain ($h_o$). The divergences between the analytical and experimental results$^{15}$ of the PBMA-PDMS-PMA elastomer are calculated using the correlation index ($R^2$), and the results are 94.76%, 84.02% and 97.15% for $\phi_A=0.05$, 0.10 and 0.25, respectively, as shown in Fig. 7B. Moreover, the comparisons between the analytical results and experimental data are listed in Table 2.

Effect of the chain number of PMMA ($N_0$) on the constitutive stress-elongation ratio relationship of the PMMA-PDMS-PMA elastomers has further been investigated, and the results are shown in Fig. 8. The analytical results have been plotted as a function of elongation ratio in order to predict the experimental results of stress, whereas the chain number of PMMA ($N_0$) is chosen as 365, 480, 810 and 930. The following parameters are used in the calculation using equation (17), e.g., $E_{\mathrm{C}}C_0M_0d^2/3/N_{\mathrm{Av}}k_8T_p=4.9$, $E_{\mathrm{C}}C_0M_0^{1/3}l_{\mathrm{Av}}V_{\mathrm{A}}^{1/3}/N_{\mathrm{Av}}k_8T_{\mathrm{p}}=0.06$, $\psi=4$ and $C_0E_f/k_8T=2.8\times10^5$ Pa. The analytical results in Fig. 8A reveal that the stress is decreased from 369 kPa, 297 kPa, 276 kPa to 200 kPa, with an increase in the chain number of PMMA ($N_0$) from 365, 480, 810 to 930.

**Table 3. Comparison between analytical results and experimental data of the maximum true stress in Fig.8.**

<table>
<thead>
<tr>
<th>$N_0$</th>
<th>$\sigma_{t\max}(10^5$Pa$)$</th>
<th>$\sigma_{t\max}(10^5$Pa$)$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>365</td>
<td>3.69</td>
<td>3.09</td>
<td>93.05%</td>
</tr>
<tr>
<td>480</td>
<td>2.97</td>
<td>2.35</td>
<td>90.83%</td>
</tr>
<tr>
<td>810</td>
<td>2.76</td>
<td>2.76</td>
<td>91.23%</td>
</tr>
<tr>
<td>930</td>
<td>2.00</td>
<td>2.08</td>
<td>94.07%</td>
</tr>
</tbody>
</table>

Fig. 8 Comparisons of analytical and experimental results$^{15}$ for the stress as a function of elongation ratio in PMMA-PDMS-PMA elastomers with various segment numbers of PMMA, $N_0=365$, 480, 810 and 930. A) For the constitutive stress-elongation ratio curves (using equation (17)). B) Divergences of the analytical and experimental results.

As discussed above for the topology network of self-assembled elastomer, increase in the chain number of PMMA ($N_0$) results in increases of the diameter of spherically shaped domain ($d_i$), whereas the end-to-end distance of a polymer chain ($h_o \propto (d_i-d)^{1/5}$) is then decreased as the chain number of PDMS ($N_0$) is kept at a constant of $N_0=1065$. With the decrease in the end-to-end distance of a polymer chain ($h_o$), the modulus is therefore increased as revealed in equation (17). It is worthwhile to note that the high modulus of the self-assembled elastomer is resulted from the smaller value of $h_o$. 

6 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx
leading to a larger true stress under the same elongation ratio. Meanwhile, the divergences between the analytical and experimental results of the PMMA-PDMS-PMMA elastomers are calculated using the correlation index ($R^2$), which are 93.05%, 90.83%, 91.23% and 94.07% for NaSS365, 480, 810 and 930, respectively, as shown in Fig. 8B. The comparisons between analytical results and experimental data are listed in Table 3.

3.2 Self-healing behavior in elastomer

The self-healing behavior plays an essential role to determine the mechanical properties of elastomer, where the broken polymer chains produce free radicals and the reaction rates of self-healing ($k_h$) are governed by the Fick’s second diffusion law. Therefore, the reaction rate of self-healing ($k_h$) can be expressed by,

$$
\frac{\partial k_h}{\partial t} = D \frac{\partial^2 k_h}{\partial z^2}
$$

(19)

where $t$ is the time, $D = k_B T/6 \pi \eta R_i$ is the diffusion coefficient, $z$ is the distance, $R_i$ is the hydrodynamic radius and $\eta$ is the viscosity. The value of $\eta$ can be further expressed as,

$$
\eta = \eta_0 N_{ela}^2
$$

(20a)

and

$$
N_{ela} = N_z \left( \frac{k_h}{k_d} \right)
$$

(20b)

where $\eta_0$ is the initial viscosity, $N_{ela}$ is the segment number of elastomer and $N_z$ is initial segment number of the elastomer.

Substituting equations (14) and (20) into $D = k_B T/6 \pi \eta R_i$, the diffusion coefficient can be obtained,

$$
D = \frac{k_B T}{6 \pi \eta R_i N_z^2} \sum_{i=1}^{z^d} \left( d_i - d_{i-1} \right) \frac{z^d - z}{z^d - z}
$$

(21)

In combination of equations (19) and (21), the reaction rate of self-healing ($k_h$) of elastomer can be obtained as,

$$
k_h = k_{i0} \left( k_z - k_i \right) \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left( -\frac{z^2}{4Dt} \right) dz
$$

(22)

where $k_{i0}$ is the initial constant of reaction rate and $k_z$ is the constant of reaction rate under the mechanical loading.

Figure 9 shows the analytical results of self-healing ratios as a function of waiting time, which are also compared with the experimental results reported in Ref. [38,39]. Experimental data of PEA-co-IBA (PEA: phenyl ether acrylate; IBA: isobornyl acrylate) elastomers are used to compare with the analytical results of self-healing ratio as shown in Fig. 9A. The following parameters are used in equations (21) and (22), e.g., $k_{i0}$=0.45, $N_z=11$, $d_1-d_2$=1.1 and $z(3\pi \eta R_i N_z^2/2k_B T)^{0.5}$=71.64. While the experimental data of NaSS-co-MPTC (NaSS: sodium p-styrenesulfonate; MPTC: 3-(methacryloylamino) propyltrimethylammonium chloride) elastomers reported in Ref. [39] are used to compare with the analytical results of self-healing ratio, as shown in Fig. 9B, whereas the following parameters are used in equations (21) and (22), e.g., $k_{i0}$=1.15, $k_{i0}$=0.2, $N_z=11$, $d_1-d_2$=1.1 and $z(3\pi \eta R_i N_z^2/2k_B T)^{0.5}$=58.45. It is found that the analytical results from our models are in good agreements with the experimental data of PEA-co-IBA and NaSS-co-MPTC elastomers, which undergo self-healing as a function of waiting time. Meanwhile, the divergences between the analytical and experimental results of the elastomers are calculated using the correlation index ($R^2$), which are 93.77% and 99.03% for PEA-co-IBA and NaSS-co-MPTC elastomers, respectively.

![Fig. 9 Comparisons of analytical and experimental results for the self-healing ratio as a function of waiting time.](a) For the PEA-co-IBA elastomer, (b) For the NaSS-co-MPTC elastomer.

4 Conclusions

In this study, we propose a topological dynamic framework to investigate the working principle of strain-adaptive stiffening and coloration in self-assembled elastomers. The anchoring-mediated topology signature is explored to describe the topological dynamics and transition of self-assembly, mechanoresponsive stiffening and mechanochromic coupling, in terms of three fractal geometry components, respectively. A free-energy equation is firstly developed based on the extended constrained molecular junction model, in order to formulate the constitutive stress-elongation ratio relationship, identify the topological dynamics in mechanochromic coupling and decoupling of elastomers, in terms of ternary “rock-paper-scissors (d_1(h_i)-d_2(h_i)-\lambda)” model, whereas diameter of domain (d_1) for self-assembly, inter-domain distance (d_2) for morphochromism and elongation ratio (\lambda) for mechanical elongation. Finally, the proposed framework is proved to be able to well predict topological dynamics, mechanochromic coupling and self-healing behaviors of self-assembled elastomers, and the accuracy of analytical results has then been verified using the experimentally obtained data reported in literature, which have been well fitted. This newly proposed model provides a new mechanism of topology dynamics in self-assembled elastomers and also critical insights into the physical principles which govern the constitutive relationship between molecular self-assembly and mechanochromic coupling.

Conflicts of interest

There are no conflicts to declare.

Author contributions

This journal is © The Royal Society of Chemistry 20xx...
ZY conceived and designed the analysis, collected data and contributed data and performed the analysis. HB conceived and designed the analysis, performed the analysis and wrote the paper. YQ performed the analysis and wrote the paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC) under Grant No. 11725208, and International Exchange Grant (IEC/NSFC/201078), through Royal Society and NFSC.

References