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Article

Keywords: self-healing strengthening elastomer, thermal activation, elastomeric ionomers

Posted Date: October 21st, 2020

DOI: https://doi.org/10.21203/rs.3.rs-90772/v1

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Version of Record: A version of this preprint was published at Materials Horizons on January 1st, 2021. See the published version at https://doi.org/10.1039/D1MH00638J.
Thermal and Mechanical Activation of Dynamically Stable Ionic Interaction toward Self-Healing Strengthening Elastomers

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Abstract: Biological tissues can grow stronger after mechanical damage and self-healing. However, artificial self-healing materials usually show decreased mechanical properties after repairing mechanical damage. Here, a self-healing strengthening elastomer (SSE) is developed by engineering kinetic stability in elastomeric ionomers through introduction of large steric hindrance. Elastomeric ionomers are usually thermodynamically instable due to the none-directionality and none-saturation of electrostatic interaction and the high mobility of molecular chains; thus, their mechanical properties change with time in an uncontrollable manner. However, the large steric hindrance on the cationic groups prevents the formation of new ionic bonds and rearrangement of ionic aggregates under room temperature, thus SSE is kinetically stable. Once heat or external force is applied, the kinetic stability is disrupted and the material becomes stronger driven by the thermodynamic instability. Consequently, the self-healing efficiency of fractured SSE is as high as 143%. This work provides controllable and universal strategy to fabricate biomimetic self-healing strengthening materials.
Introduction:

Supercompensation is a unique healing feature for biological tissues to build strength over the original after being subjected to a repeated mechanical force; this allows the biological tissues to adapt to the changes in external circumstance.\textsuperscript{1,2} For example, when suffering from repeated mechanical force, the myofibrils get fatigue damage firstly and then become more and thicker after a period of healing. During this healing process, the muscles become stronger and can withstand greater stress. Taking this advantage, the supercompensation is usually used for training athletes to reach an extra recovery of their physical strength. However, artificial materials typically fail after mechanical damage, leading to resource wasting and serious environment pollution.

To address this issue, two main strategies are proposed. One strategy is to develop self-growing materials relying on \textit{in situ} chemical reactions during the mechanical destruction.\textsuperscript{3,6} For example, Gong’s group\textsuperscript{6} fabricated a self-growing hydrogel on basis of double network, which becomes stronger after repeated mechanical training. The underlying principle is the external-force induced breaking of the brittle network, thereby producing free radicals which lead to polymerization of the pre-permeating monomers. Consequently, a new brittle network is formed which makes the material stronger than the original. This strategy is effective to strengthen the material and can be repeatedly carried out. Nevertheless, it suffers from the complicated fabrication process, requirement of continuous supply of external monomers and limited damage scale (the strategy will fail once a macro notch is formed). Alternatively, significant efforts have been invested into the development of the intrinsic self-healing materials based on reversible bonds such as Diels-Alder (D-A) crosslinks,\textsuperscript{7,8} hydrogen bonds,\textsuperscript{9,12} ionic interactions,\textsuperscript{13,17} metal-ligand coordination,\textsuperscript{18,24} \textit{\pi}–\textit{\pi} stacking,\textsuperscript{25,26} disulfide bonds\textsuperscript{27,30} and so forth. It is well established that the healing process proceeds in the order of molecular diffusion and reunion of reversible bonds. Therefore, this strategy is effective for damages of both micro- and macro-scale, and even complete disconnection of the materials. However, the healing process is easily influenced by insufficient diffusion of molecular chains, incomplete recovery of molecular network, and the rebinding of functional groups within respective fracture surface. These factors decrease the connect links between the fracture surfaces of the healed samples. Hence, the materials after healing are usually weaker
than the original ones, and thus the healing efficiency is usually lower than 100%.\textsuperscript{19,31} In conclusion, these two solutions to resolve the mechanical failure of manmade materials have their own strengths and limitations. It is a challenge to combine their advantages together to achieve self-healing strengthening materials which manifest higher mechanical properties after repairing mechanical damage.

Here, we develop a kinetically stable while thermodynamically instable elastomer with the inherent ability of self-healing strengthening. Such elastomer is based on ionomers with two key molecular designs: 1) the thermodynamic instability of the ionomers derived from none-directionality and none-saturation of electrostatic interaction, which endows the ionomers with driving force for self-healing strengthening; 2) the kinetical stability originated from the large steric hindrance effect which serves as a switch for self-healing strengthening. Owing to the thermodynamic instability, conventional elastomeric ionomers constantly change their physical and mechanical properties under room temperature, as unpaired cationic and anionic groups gradually form new ionic bonds and meanwhile ionic aggregates slowly undergo rearrangement, resulting an unstable and uncontrollable material at room temperature. However, due to the large steric hindrance, the unpaired cationic and anionic groups in our material are difficult to form new ionic bonds under ambient conditions, and thus the material is kinetically stable at room temperature. Once heat or mechanical force is applied to enhance molecular mobility, the kinetic stability is disrupted and the thermodynamic instability drives the unpaired groups to form more ionic bonds, which then phase separate into bigger and denser ionic aggregates (Figure 1a). Such microstructural change results in a stronger material after healing, mimicking the biological supercompensation (Figure 1b). As a result, the fracture occurs other than the position of damage and the healing efficiency can reach 143% after self-mending of cut samples (Figure 1c). By analyzing the viscoelastic properties through UCM-Gent model, it is revealed that the material becomes more elastic induced by the microstructural change after heat or mechanical treatment.

\textbf{Results and discussions:}

The synthesis of the polymer is carried out through the random copolymerization of butyl acrylate (BA), acrylic acid (AA) and 2-(Diisopropylamino)ethyl (DPA) (Experimental section for the details, Scheme S1 in Supporting Information). According to our previous
the molar ratio between AA and DPA is fixed to 1:1. The choice of these monomers are dictated by several essential reasons: 1) BA is neutral and its long alkyl side group can impart the material with high molecular mobility which is essential for the self-healing ability; 2) the oppositely charged monomers (AA and DPA) are chosen for their ability to form ionic bonds and ionic aggregates which can serve as crosslinks to strengthen the material; 3) especially, DPA is selected as the positively charged monomer since its amino group bears two bulky isopropyl groups with large steric hindrance. Based on the above design principles, a series of self-healing strengthening elastomers (SSEs) are synthesized denoted as SSE-x, where the x is the molar ratio of ionic monomers. To highlight the important role of the large steric hindrance, DPA is replaced by dimethylaminoethyl methacrylate (DMA) which owns much smaller steric hindrance than the DPA and the resulting material is denoted as p(BA-AA-DMA). The chemical structure, components and molecular weight of the polymers are examined by Fourier transformation infrared spectroscopy (FTIR), proton nuclear magnetic resonance (1HNMR) and gel permeation chromatography, and the results are displayed in Figure S1, Figure S2 and Table S1 in Supporting Information.

Owing to the electrostatic attraction, the positively and negatively charged groups interact with each other to form ionic bonds. The ionic bonds further segregate into aggregates, due to the none-directionality and none-saturation of electrostatic interaction. However, the kinetic factors such as thermal history and environmental conditions (pH, water, temperature, etc.) during material fabrication usually lead to incomplete formation of ionic bonds and metastable aggregates. For these reasons, the ionic network rearrangement readily takes place accompanied with evident changes in the number and morphology of ionic aggregates, given enough chain mobility. Such changes usually lead to variation in mechanical and thermal properties of the materials. Therefore, ionomers are usually thermodynamically instable and own incomplete ionic network. To illustrate the incomplete formation of ionic bonds, the on-line FTIR is carried out and the result is compared with that of the unpolymerized monomers with the same composition as that in the polymer (Figure 1d and Figure S3). The ratio between the intensity of the ionized COOH (peak at 1594 cm\(^{-1}\) for monomers and 1570 cm\(^{-1}\) for polymer) to that of the unionized COOH (peak at 1725 cm\(^{-1}\)), \(I_{\text{ionized}}/I_{\text{unionized}}\), represents the formation degree of ionic bonds in the system. \(I_{\text{ionized}}/I_{\text{unionized}}\) is
quite low immediately after mixing the monomers or drying the thin film of SSEs, suggesting that most amino groups and carboxyl groups do not have enough time to form ionic bonds. However, $I_{\text{ionized}}/I_{\text{unionized}}$ increases with time due to the slow formation of ionic bonds and then levels off. The variation percentage of ionic bonds (defined as the $(I_t - I_0)/I_0$, where $I_t$ represent the $I_{\text{ionized}}/I_{\text{unionized}}$ at time $t$, while $I_0$ is the initial $I_{\text{ionized}}/I_{\text{unionized}}$) versus time is exhibited in Figure1d and S3. For the monomers, the ionic bonds form gradually and more than 18 hours are needed for $(I_t - I_0)/I_0$ to level off to a value of 0.34 (Figure 1d), indicating numerous ionic bonds are formed. On contrary, only 4 hours are required for $(I_t - I_0)/I_0$ to flatten out in the polymer and the final plateau reaches a value of 0.03, which is one order of magnitude lower than that in the monomer system. The different $(I_t - I_0)/I_0$ plateau values between the monomer system and the polymer system indicate that during the solvent molding of the polymer, many amino groups and carboxyl groups do not interact with each other through electrostatic interaction, and thus the ionic network is not fully formed.

The thermodynamic instability and incomplete ionic network of ionic system could result an unstable material at room temperature. As exhibited in Figure 1e and Figure S4, the tensile strength of p(BA-AA-DMA), which represents a typical elastomeric ionomer, evidently increases with time which indicates that the material is unstable at room temperature. This instability is undesirable for practical applications of the materials. By sharp contrast, the tensile strength of SSE-23 is nearly unchanged after 2 days or 4 days at room temperature. This inconsistent behavior results from the different steric hindrance of DPA and DMA. The steric hindrance of DPA is much higher than that of DMA due to the two bulky isopropyl groups, which impedes the unpaired cationic and anionic groups to form ionic bonds under ambient conditions. Therefore, the SSE is kinetically stable at room temperature.
Figure 1: Design concept of SSEs. a) Schematic diagram of self-healing strengthening elastomers. Owing to the steric hindrance, some of the oppositely charged monomers segregate into small and sparse aggregates, which become bigger and denser after exposure to external stimuli such as heat or mechanical force. Thus, the material changes from weak to strong, as muscle works. b) Diagram of the supercompensation during destroy and healing. c) The cut position before healing and the fracture position of the healed sample. d) The variation percentage, \( \frac{(I_t - I_0)}{I_0} \), as a function of time of the SSE-23 and monomers. e) The tensile strength of SSE-23 and p(BA-AA-DMA) after storage in desiccator for different time at RT.

Since the material is thermodynamically instable, the ionic bonds and phase structure can be changed after disrupting the kinetic stability under external stimuli. To trigger such changes, an SSE-35 sample is subjected to multi cycles of heating at 60 °C for 20 minutes and then cooling down to room temperature, during which FTIR is used to monitor the change of ionic
bonds. Clearly, the peak intensity at 1570 cm\(^{-1}\) (ionized carbonyl of COOH in polymer) decreases at 60 °C; nevertheless, the intensity increases rapidly during the subsequent cooling process, as exhibited in Figure 2c. After each heating and cooling cycle, the peak intensity at 1570 cm\(^{-1}\) shows a step-wise increase both at room temperature and at 60 °C. This phenomenon fully indicates that more ionic bonds are formed after each cycle. The underlying mechanism is that the applied heating destroys the weak ionic bonds, leading to higher molecular mobility of network chains; thus, the free COOH is easier to bond with free tertiary amine to form more ionic bonds.

The increased number of ionic bonds can result in a change in microphase. Hence, atomic force microscope (AFM) tests are carried out. To accelerate the change, a thin film of SSE-15 is heated at 130 °C for 20 minutes which destroy the ionic network and then annealed at 25 °C for 4 hours to heal. As shown in Figure 2a and Figure S5, AFM images exhibit that the SSE phase separates into aggregates with wide range of size distribution. Before the thermal treatment, the aggregates are rather sparse and small (Figure 2a(i) and Figure S5(i)). Interestingly, they become denser and bigger after the thermal heating and annealing (Figure 2a(ii) and Figure S5(ii)). The big aggregate is composed of a number of small aggregates (inset picture of Figure 2(ii)). In order to decrease the occasionality, three random positions on the thin film are observed to detect the change of aggregates. The results reveal that all of the positions present denser and bigger aggregates after the thermal treatment (Figure S5). To compile the statistics of large aggregates, the aggregates with the size larger than 0.3 μm are counted and shown in Figure 2b. The Gaussian fitting results clearly reveal that the statistic mode of the size changes from 0.46 μm to 0.60 μm after the heat treatment. Meanwhile, the small angle X-ray scattering (SAXS) test is carried out to study the aggregates in the small size range (Figure S6). The result manifests that the thermal heating and annealing lead to a new peak at q=0.042 Å\(^{-1}\), corresponding to an inter-particle spacing of 15 nm, indicating that more and regular aggregates with size less than 15 nm are formed. The increased number and size of the aggregates exert stronger confinement on the molecules, consequently the glass transition temperature (\(T_g\)) of the SSE-23 increases from -6.02 °C to -4.92 °C after thermal treatment (Figure S7).

Since both the ionic bonds and aggregates can be changed by external stimuli, the
material will become stronger. To confirm this, two kinds of stimuli including heat or mechanical treatments are used to induce microscopic network damage instead of macroscopic damage. In one heat treatment, the SSE-35 is heated at 60 °C and then allowed to recover at room temperature. Rheological tests show the storage modulus exhibits an augment across the whole frequency range after the heat treatment. For both the pristine and thermal treated samples, the storage modulus of the material decreases with frequency, demonstrating that the physical nature of the network is unchanged upon thermal treatment (Figure 2d). In another heat treatment, the material is subjected repeated cyclic heating and cooling processes at a rate 3 °C/min, and dynamic mechanical analysis (DMA) is used to monitor the storage modulus change (Figure S8a). After each heating and cooling cycle, the storage modulus becomes higher spanning from 0 °C to 130 °C and the $T_g$ increases. In the mechanical treatment, a shear strain of 50% is applied to SSE-35 within 60 s by the rheometer. As shown in Figure 2e, it is found that the storage modulus decreases upon applying the strain, indicating a gradual destroy of the ionic network; after the withdraw of the strain, the storage modulus gradually increases with healing time and eventually excesses the original modulus. At the same time, the different recovery behaviors of $G'$ under different shear strain (Figure S8b) confirm that the recovery rate decreases as the shear strain increases. Collectively, the increased storage modulus and $T_g$ after heat and mechanical treatments reveals the formation of stronger network, which imposes more restriction on the molecular mobility. This is the underlying mechanism for self-healing strengthening.
Figure 2 **Damage and recovery of microscopic network.** a) AFM height images of SSE-15 before (i) and after (ii) heat treatment, the inset picture in (ii) is the amplification area of the marked area which shows that the big aggregate consists of many small aggregates. b) The corresponding bin center of aggregates with the size larger than 0.3 \( \mu \text{m} \) before and after heat treatment. c) The intensity of absorption peak variation at 1570 cm\(^{-1}\) during cyclic thermal training. d) The storage modulus before and after heat treatment. e) The normalized storage modulus versus time at room temperature after shear force treatment of SSE-35. Inset picture is the amplification of the initial storage modulus.

To investigate the influence of microscopic network damage and recovery on the mechanical properties, uniaxial tensile tests are carried out with a rate of 0.067 s\(^{-1}\). The representative stress-strain curves of all pristine materials are shown in Figure 3a. By changing the molar ratio of the ionic bonds, the stress, Young’s modulus and toughness which is defined as the integral area of the stress-strain curve can be tuned in a wide range (Figure S9). The mechanical properties of the pristine materials are then compared with those after heat or mechanical treatments. As shown in Figure 3b and Figure S10, the stress-strain curve of the SSE-23 after heat treatment (60 °C for 2 hours and 25 °C for 25 hours, inset picture of Figure 3b) shows higher Young’s modulus, more obvious strain hardening behavior and higher fracture stress. The fracture stress and Young’s modulus of the heat-treated SSE-23 are respectively 1.41 and 1.49 times of the pristine ones, indicating stronger crosslinks are formed after heat treatment. In addition, the influence of mechanical treatment is also explored. The SSE-23 samples are pre-stretched with the strain rate 0.067 s\(^{-1}\) to strains at 50% and 100% respectively (inset picture of Figure 3c). After one day at room temperature to heal, the sample is stretched again with the same strain rate. Astonishingly, the pre-stretched samples reveal stronger strain hardening behavior (Figure 3c). Moreover, the fracture stress increases from 2.33 MPa to 3.39 MPa without sacrificing the elongation after the pre-extension to 100% strain and self-healing. As such, the toughness after mechanical treatment reaches 1.34 times of the original (Figure S11).

In addition to the microscopic damages, macroscopic damages can also induce self-healing strengthening behavior. To demonstrate this, the dumbbell-shaped SSE samples are cut into two pieces (inset picture of Figure 3d). After treating the mended pieces at 60 °C for
5 hours and room temperature for 25 hours, the samples are stretched with the same strain rate. Interestingly, the samples after cutting and healing breaks beyond the cut position (Figure 1c) and all the samples exhibit improved strength after healing (Figure 3d and Figure S12). By qualifying the ratio of the average fracture stress of the repaired sample to that of the pristine one, the average healing efficiency is obtained. The healing efficiency is highest (118%) when the ionic content is 23%, which represents a balance between number of dynamic bonds and chain mobility. Nevertheless, SSE-35 with the highest content of ionic units still has the healing efficiency of 107%. To increase the healing efficiency, the time to destroy the ionic network is increased to guarantee enough molecular mobility. As shown in Figure 3e, the representative stress-strain curves of SSE-35 with different treating time at 60 °C are exhibited. With the increasing treating time at 60 °C, both the fracture strength and elongation increase (Figure 3f and Figure S13). A highest healing efficiency in terms of the ratio between the toughness of the mended sample and that of the pristine sample reach 143%. Collectively, the SSE materials can be healed with tensile strength and toughness higher than that of the original, despite the microscopic (heat and mechanical force) or macroscopic damages, as shown in Figure 3f.

Figure 3. Mechanical properties of SSEs. a) Representative stress-strain curves for SSEs. b) Stress-strain curves of SSE-23 before and after heat treatment. c) Stress-strain curves of SSE-23 before and after different strain treatment. d) Fracture stress of SSEs before and after cut and healing. e) Stress-strain curves of SSE-35 after cut and thermal treatment for different time at 60 °C. After treatment at 60 °C, all the sample is stored at room temperature for 25
hours before characterization.  

f) Fracture strength of SSE-23 before and after microscopic damages (heat or mechanical force) and SSE-35 before and after macroscopic damage.

To study the self-healing strengthening performance from the perspective of network structure. The stress relaxation experiment is conducted on DMA. A strain of 5% is rapidly applied to SSE-23 and remained unchanged at different temperature, and the stress versus time is recorded. As shown in Figure 4a and Figure S14a, the stress relaxes with time evolution, demonstrating that the physical crosslinks are gradually dissociated. The characteristic relaxation time $\tau_0$, obtained from the time required for the stress to relax to the $1/e$ (37%) of the max stress, follows an Arrhenius law (Figure 4b and Figure S14b), by which the activation energy ($E_a$) is calculated. As shown in Figure 4c, $E_a$ increases from 43.44 KJ/mol to 56.25 KJ/mol after heat treatment, indicating the formation of stronger crosslinks.

Since the strong crosslinks contribute to the entropic elasticity and the weak interaction leads to viscoelasticity, the ratio of strong and weak interactions can be discriminated from the stress-strain curves of the materials before and after heat or mechanical treatment. For this purpose, a complex model which combines Gent strain hardening model (GSH, describing elasticity) and upper convected Maxwell model (UCM, describing the viscoelasticity) is used to fit the stress-strain curve and shown as follows

$$\sigma_N(\lambda) = \sigma_{N,e}(\lambda) + \sigma_{N,e}(\lambda)$$

where GSH is written as:

$$\sigma_{N,e}(\lambda) = \left( \frac{G_v}{\mu^2 + \lambda^2} \right) \lambda^{-1}$$

and UCM is written as:

$$\sigma_{N,e}(\lambda) = \left[ \frac{2G_vD_e}{1 - 2D_e} \left( 1 - \exp \left( \frac{(1-2D_e) (\lambda - 1)}{D_e} \right) \right) \right] \lambda^{-1}$$

In these models, $\lambda$ is the extension ratio and equal to $\varepsilon + 1$; and $G_v$ and $G_e$ are the modulus contributed by the viscoelasticity (weak interaction) and that contributed by the elasticity (strong interaction) respectively; $D_e$ and $J_m$ are the Deborah number and the limited elongation of molecular chain respectively. Since the Young’s modulus, which equals to $3(G_v + G_e)$, can be obtained from the tensile curve directly, the complex model Eqn (1) can be used
to simulate the stress-strain curves with three independent parameters.

The representative fitting curve and the separated contribution of UCM and GSH are shown in Figure 4d. The good fitting demonstrates a good compatibility between the combined model and the experimental data. The influence of thermal or mechanical treatments on the fitted parameters including \( G_v \), \( G_e \), \( D_e \) and \( J_m \) are shown in Table 1. The ratio of \( G_v \) (UCM) to \( G_e \) (GSH) represents the ratio between weak interaction and strong interaction in the polymer network. As exhibited in Table 1, the \( G_v/G_e \) value of pristine SSE-23 is 3.82. After mechanical treatment or heat treatment, the value decreases to 2.70 and 2.93 respectively, demonstrating an evident ascending of the proportion of strong interactions in the SSE-23. Accordingly, the thermal or mechanical treatments make the materials become stronger with more obvious strain hardening behavior (Figure 3b and Figure 3c).

Figure 4. a) Normalized stress relaxation curves at different temperature with strain of 5%. b) Arrhenius fitting of the relaxation time from (a) for SSE-23. c) Activation energy of SSE-23 before and after heat treatment. d) Representative tensile behavior, simulate curve of complex model and their individual contributions from the UCM (viscosity) and GSH (elasticity).
is the diagram of the complex model.

Table 1 the fitted parameters including $G_v$, $G_e$, $D_e$ and $J_m$ of SSE-23 before and after microscopic damages (heat or mechanical force).

|        | $G_v$     | $D_v$     | $G_e$     | $J_m$     | $G_v/G_e$ | 3($G_v+G_e$) |
|--------|-----------|-----------|-----------|-----------|-----------|--------------|
| original | 0.677(±0.288) | 0.065(±0.024) | 0.174(±0.046) | 643.6(±277.3) | 3.82(±0.99) | 2.55(±0.99)   |
| After force treatment | 0.887(±0.070) | 0.052(±0.005) | 0.329(±0.016) | 825.6(±273.0) | 2.70(±0.34) | 3.64(±0.16)   |
| After heat treatment  | 0.613(±0.113) | 0.0686(±0.0331) | 0.216(±0.035) | 382.5(±251.6) | 2.83(±0.24) | 2.49(±0.43)   |

**Conclusion:**

Inspired by the supercompensation of nature, a self-healing strengthening material is prepared by cooperating thermodynamic instability with kinetic stability in polyampholytes. The thermodynamic instability, an inherent property of ionomers, serves as the driving force for self-healing strengthening; while the kinetic stability, derived from the large steric hindrance of the cationic group, acts as a switch to control the self-healing strengthening. At room temperature, the material is stable. Once heat or mechanical damage is applied, the kinetic stability is destroyed, leading to enhanced molecular mobility. In this scenario, the unpaired cationic and anionic groups form more ionic bonds and denser aggregates, thus resulting in a stronger physical network. Consequently, the toughness and tensile strength of the cut and self-healed material are larger than those of the original one, and the healing efficiency of the material is as high as 143%. Meanwhile, the combination of UCM and Gent model reveals that a more elastic material is obtained after damage and healing. The design strategy in this work can be extended to other supramolecular materials with similar assembling behavior. At the same time, the concept of self-healing strengthening will promote the development of a new generation of self-healing materials, which hold significant promise as smart materials.

**Method**

Materials: Butyl acrylate (BA), acrylic acid (AA) were from TCI and the purity
is >99.0%. 2-(Diisopropylamino)ethyl (DPA, 97%) was from Aldrich. 2-(dimethyl amino)-ethyl methacrylate (DMA, 99%), 2, 2-azobisisobutyronitrile (AIBN, 98%+), methyl benzoate (MB, 99%+) were all from Adams. All the solvents including methyl alcohol, petroleum, n-hexane, ethyl acetate, were purchased from Tansoole.com (China). The inhibitor in BA was removed through a basic alumina column and other materials were directly used.

Polymer synthesis: Typically, quantitative BA (0.076 mol), AA (0.013 mol), DPA (0.013 mol), AIBN (0.0001 mol), MB (one drop) and ethyl acetate (20 ml) were mixed and then the solution was added into a 100 ml three-neck round-bottom flask which was filled with argon, equipped with a magnetic stirrer and an economical allihn condenser. The mixture was heated under 70°C for 8 h after bubbled with argon for 20 minutes. After the polymerization, the precipitation by petroleum (or n-hexane) and dissolution in ethyl acetate were repeated three times. Finally, the precipitated product was dried in a vacuum oven until reaching constant weight.

Film preparation: Typically, 4 g of SSE-23 was dissolved in 100 ml methanol, and then the solution was added into a square Teflon mold. After 3 days for the solvent to slowly evaporating at room temperature, the sample was dried in a vacuum oven until reaching constant weight. Take the slow formation of ionic bonds into consideration, all the samples are stored under room temperature for 2 days before characterization.

Measurements: the molecular information were characterized by GPC (DMF as dilute solvent, HLC-8320GPC), FTIR (both reflection mode and transmission mode, Thermo Scientific Nicolet iS50) and ¹H NMR (CDCl₃ as solvent, Advance III HD 400 MHz spectrometer (Bruker)). Dynamic mechanical analysis (tension mode with a heating rate of 3 °C/min on Q800), differential scanning calorimeter (Q2000 (TA instrument)), rheology (Anton Paar (MCR302), in torsion mode with strain of 0.2%), small angle X-ray scattering (Xeuss 2.0 (Xenocs), \( \lambda = 0.154 \) nm, sample-to-detector distance = 2.47 m) and AFM experiment (tapping mode, SmartSPMTM-1000 (AIST-NT SPM)) were used to character the micro network. Uniaxial tensile measurements were carried out on an Instron 5967 at room temperature. The tensile curves were fitted by the specific equations of UCM-Gent. The stress relaxation is carried out on DMA with a strain of 5%. The specific characterization information was shown in SI. every sample was tested at least 3 times for mechanical
measurements.

Data availability

The data supporting the findings of this work are available within the paper and its Supplementary Information files and from the corresponding authors on request.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant Nos. 51873110 and 51673120), and State Key Laboratory of Polymer Materials Engineering (Grant No. sklpme2019-2-14) and the Fundamental Research Funds for Central Universities.

Author contributions

The experiments were designed by Jinrong Wu and Yan Peng. Experimental work was conducted by Yan Peng and Yujia Hou. Data analysis was performed by Jinrong Wu, Yan Peng and Qi Wu. Yan Peng wrote and edited the manuscript under supervision of Jinrong Wu.

Conflict of Interest

The authors declare no conflict of interest.

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Design concept of SSEs. a) Schematic diagram of self healing strengthening elastomers. Owing to the steric hindrance, some of the oppositely charged monomers segregate into small and sparse aggregates, which become bigger and denser after exposure to external stimuli such as heat or mechanical force. Thus, the material changes from weak to strong as muscle works. b) Diagram of the supercompensation during destroy and healing. c) The cut position before healing and the fracture position of the healed sample. d) The variation percentage, (I_t / I_0), as a function of time of the SSE 23 and monomers. e) The tensile strength of SSE 23 and p(BA AA DMA) after storage in desiccator for different time at RT.
Figure 2

Damage and recovery of microscopic network a) AFM height images of SSE 15 before (i) and after (ii) heat treatment, the inset picture in (ii) is the amplification area of the marked area which shows that the big aggregate consists of many small aggregates. b) The corresponding bin center of aggregates with the size larger than 0.3 μm before and after heat treatment. c) The intensity of absorption peak variation at 1570 cm⁻¹ during cyclic thermal training. d) The storage modulus before and after heat treatment. e) The normalized storage modulus versus time at room temperature after shear force treatment of SSE 35. Inset picture is the amplification of the initial storage modulus.

Figure 3

Macroscopic damages: Stress (MPa) vs. Strain (%) for SSE-15, SSE-23, and SSE-35. a) Stress-strain curves for SSE-15, SSE-23, and SSE-35. b) Strain hardening observed for SSE-15. c) Stress-strain curves for SSE-23 with 0%, 50%, and 100% strain hardening. d) Tensile stress-strain curves for SSE-15, SSE-23, and SSE-35 with 0%, 50%, and 100% strain hardening. e) Stress-strain curves for SSE-35 with 0%, 50%, and 100% strain hardening. f) Macroscopic and microscopic damages: SSE-23 and SSE-35 under cut&30h, cut&24h, cut&6h, cut&2h, and 100% ε conditions.
Mechanical properties of SSEs. a) Representative stress-strain curves for SSEs. b) Stress-strain curves of SSE-23 before and after heat treatment. c) Stress-strain curves of SSE-23 before and after different strain treatment. d) Fracture stress of SSEs before and after cut and healing. e) Stress-strain curves of SSE-35 after cut and thermal treatment for different time at 60 °C. After treatment at 60 °C, all the sample is stored at room temperature for 25 hours before characterization. f) Fracture strength of SSE-23 before and after microscopic damages (heat or mechanical force) and SSE-35 before and after macroscopic damage.

Figure 4

a) Normalized stress relaxation curves at different temperature with strain of 5%. b) Arrhenius fitting of the relaxation time from (a) for SSE 2323. c) Activation energy of SSE-23 before and after heat treatment. d) Representative tensile behavior, simulate curve of complex model and their individual contributions from the UCM (viscosity) and GSH (elasticity). Inset is the diagram of the complex model.

Supplementary Files

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