

Super Tough Hydrogels with Self-adaptive Network Facilitated by Liquid Metal

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 Electronic Supplementary Information

Abstract Liquid metals (LM) refer to Ga-based alloys with low melting points such as Eutectic GalnSn alloys (EGalnSn), which have excellent fluidity, flexibility and low toxicity at room temperature. In this work, by incorporating EGalnSn into poly(acrylic acid) (PAA) hydrogels as dynamic crosslinkers and effective energy-dissipating units, tough and strong PAA-LM hydrogels are prepared through the interactions between the oxide layers on the surface of LM and carboxyl groups of PAA chains. Moreover, owing to the fluidity of LM, one LM droplet as a cross-linking point may change its shape or break into more and smaller droplets in the hydrogels upon stretching. Then hydrogels with self-adaptive networks can be fabricated by mechanical training through cyclic stretch at a certain elongation. Thus, the networks of the hydrogels are further homogenized, and the hydrogels are significantly toughened during the training due to the increased cross-linking density from the larger number of smaller LM droplets. After a 5-cycle training at the maximum strain of 500% and 24 h recovering, the tensile strength and initial modulus of the PAA-LM hydrogels can be increased from 355 kPa to 597 kPa and 71 kPa to 166 kPa, respectively, while the elongation at break only decreases from 1491% to 1034%.

Keywords Poly(acrylic acid) hydrogel; Liquid metal; Physical cross-linking; Tensile strength; Self-adaptive

Citation: Gao, R. Z.; Li, Y. X.; Yan, J. H.; Ma, X. R.; Xie, X. M. Super tough hydrogels with self-adaptive network facilitated by liquid metal. *Chinese J. Polym. Sci.* 2023, 41, 866–873.

INTRODUCTION

Hydrogels with considerable flexibility and biocompatibility are promising materials as flexible electronics and biomedical devices.^[1–4] However, traditional hydrogels are weak and fragile. Their poor tensile strength (usually 1–100 kPa) limits their applications.^[5] To enhance the mechanical properties of hydrogels, multi-bond network (MBN) design has been put forward.^[6–11] MBN means a single network which is cross-linked by hierarchical bonds with different binding energies. When an MBN hydrogel is under stretching, the weaker cross-linking points break first to dissipate energy, while the stronger bonds maintain the network structure. The MBN strategy offers hydrogels with energy dissipating mechanism, which highly enhances their mechanical strength, providing an enlightening approach for the preparation of strong and tough hydrogels.

Liquid metals (LMs), particularly Ga-based eutectic alloys, have special properties such as low melting points, low viscosity, low vapor pressure^[12] and high fluidity.^[13] They are promising materials to be applied in flexible electronics,^[14] soft robotics^[15,16] and electronic skins^[17] because of their high conductivity.^[18–20] Galinstan, eutectic GalnSn (EGalnSn), with

a low melting point of 11 °C, is normally in its liquid state at 25 °C. It is noteworthy that Ga in GalnSn tends to be oxidized under quite low oxygen pressure and generate a thin gallium oxide (Ga₂O₃) layer on its surface,^[21] forming a core-shell structure.^[22] This oxidized layer is barely crystallized and does not cover the liquid droplet completely.^[23] Therefore, the Ga₂O₃ layer can act as a protection layer which provides higher rigidity and helps LM maintain its shape.^[24]

Ga LM has a high surface tension of $624 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$, which is 8.7 times that of deionized water at 25 °C, and tends to coalesce,^[25,26] making it difficult to disperse in water. Even though a uniform suspension can be obtained by virtue of sonication, the LM-water suspension is unstable, and sediment can be seen in only a few minutes in water once the sonication assistance is removed. While organic molecules containing hydroxyl or amido groups, such as acrylic acid (AA),^[27,28] acrylamide (AM), poly(vinyl alcohol) (PVA)^[29] and so on, can stabilize LM via hydrogen bonds between the oxide layers on LM and the functional groups of the organic molecules.^[30,31] Moreover, LM can promote the generation of free radicals from vinyl monomers, thereby accelerating their polymerization in the presence of water.^[32] For instance, AA^[33] and AM^[34] monomers can polymerize rapidly with the assistance of LM. The viscosity of the suspension increases rapidly and gelation happens within 10 min at room temper-

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Received August 16, 2022; Accepted September 19, 2022; Published online November 18, 2022

ature. Meanwhile, LM are stabilized in the hydrogel networks and can further act as cross-linking points to reinforce the hydrogels.

When under stretching, LMs with splendid flexibility and deformability may change the shape and separate into more droplets to adapt to the stretching and dissipate energy. This phenomenon has been reported in the elastomer-liquid metal composites,^[35–37] while there is little interaction between LMs and the elastomer matrix. Since the Ga in LM could be easily oxidized by the dissolved oxygen in the water in hydrogels, new Ga₂O₃ layers can quickly form on the surface of the more and smaller LM droplets.

Therefore, in this work, based on the MBN design, the EGaInSn LMs are used as dynamic cross-linking points to fabricate tough PAA-LM hydrogels. The PAA-LM hydrogels can be facilely synthesized by *in situ* free-radical polymerization with LM in the AA solution. The PAA-LM MBN hydrogels are cross-linked with hydrogen bonds between Ga₂O₃ layers on LM and hydroxyl groups of PAA chains, ionic bonds between Ga³⁺ on LM and carboxyl groups of PAA chains, as well as hydrogen bonds among PAA chains. These multiple cross-linking points are expected as effective energy dissipation units to enhance the mechanical properties of the PAA-LM hydrogels. Furthermore, the fluidity of multifunctional LM cross-linkers can endow the obtained hydrogels with self-adaptive and self-strengthening abilities after cyclic stretch training.

EXPERIMENTAL

Materials

Acrylic acid (AA) was purchased from Energy Chemical Co., Ltd., and purified by distillation under reduced pressure before use. Ammonium persulfate (APS) was purchased from Beijing Chemical Reagent Co., Ltd. Eutectic GaInSn (Galinstan) was purchased from Dingsheng Dongguan Co., Ltd. The weight percents of Ga, In, Sn are 60.5%–70%, 20%–25%, 10%–15%, respectively. All reagents were of analytical grade.

Preparation of PAA-LM Hydrogels

The PAA-LM hydrogels were prepared through *in situ* free-radical polymerization of AA monomer in the presence of LM and initiator APS. LM, eutectic GaInSn alloy was oxidized at room temperature to form a thin Ga₂O₃ layer. H₂O (5.6 g) and AA monomer (2.4 g) were successively added and put under 100 W sonication to form a uniform and temporarily stable suspension. Then the initiator APS (0.012 g, 0.5 wt% with respect to AA) was added for *in situ* free-radical polymerization. The precursor was controlled at 17–20 °C under sonication until the polymerization and gelation were complete.

In cyclic stretch trainings, to prevent water loss, the samples were covered with silicon oil. In the self-adapting process, they were then sealed in plastic sample bags and put in a container with a fixed humidity for a given time. In all these processes, there was negligible loss in water content (70.0 wt% to 68.2 wt%).

Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded by attenuated total reflection (ATR) using a Nicolet 560 spectrometer from 4000 cm^{−1} to 400 cm^{−1}. The morphology and element distribution of the dried hydrogels was observed by

scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) with a Bruker XFlash detector 410-M. The accelerating voltage was 10 kV when using SEM only and 25 kV when using EDS accessory.

Mechanical Tests

The mechanical properties of PAA-LM hydrogels were tested by Shimadzu AGS-X tensile tester. Tensile tests were conducted on cylinder samples (diameter: 2.6 mm), and the sample length between jaws was 15 mm. For uniaxial tensile tests, the tensile rate was 100 mm·min^{−1}. Initial modulus was calculated from the slope of the initial linear section (5%–15% strain) in the stress-strain curve. For cyclic tests, the samples were stretched to a 500% strain at 100 mm·min^{−1} and then returned to their original length at the same velocity. The tensile load (*F*) and displacement (*x*) were recorded.

The tensile stress (*σ*) was calculated by the following equation:

$$\sigma = F/S \quad (1)$$

The tensile strain (*ε*) was calculated by:

$$\varepsilon = x/l_0 \quad (2)$$

The toughness (*E*) was estimated by the area under the stress-strain curve from 0% strain to the fracture strain (*ζ_f*) by:

$$E = \int_0^{\zeta_f} \sigma(\zeta) d\zeta \quad (3)$$

where *F* is the tensile load, *S* is the cross-sectional area, *x* is the displacement and *l₀* is the original length between the jaws.

RESULTS AND DISCUSSION

By incorporating EGaInSn LMs into AA solution, the PAA-LM hydrogels were fabricated by *in situ* free-radical polymerization. As shown in Fig. 1, hydrogen bonds between Ga₂O₃ layers on the LM and hydroxyl groups of PAA chains, ionic bonds between Ga³⁺ on the LM and carboxyl groups of PAA chains, as well as hydrogen bonds among PAA chains formed a multi-bond network. In the PAA-LM hydrogels, the LMs served as multifunctional cross-linking points, which could deform and separate into more and smaller droplets under stretching. Meanwhile, the Ga in LM could be easily oxidized by the dissolved oxygen in the hydrogels, and the newly formed Ga₂O₃ protection layers would stabilize the newly formed smaller LM droplets, making it possible for generating tough hydrogels with self-adaptive and self-strengthening networks.

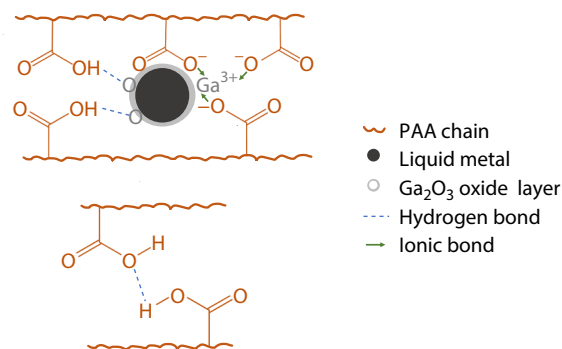


Fig. 1 Multi-bond networks of LMs as cross-linking points in PAA-LM hydrogels.

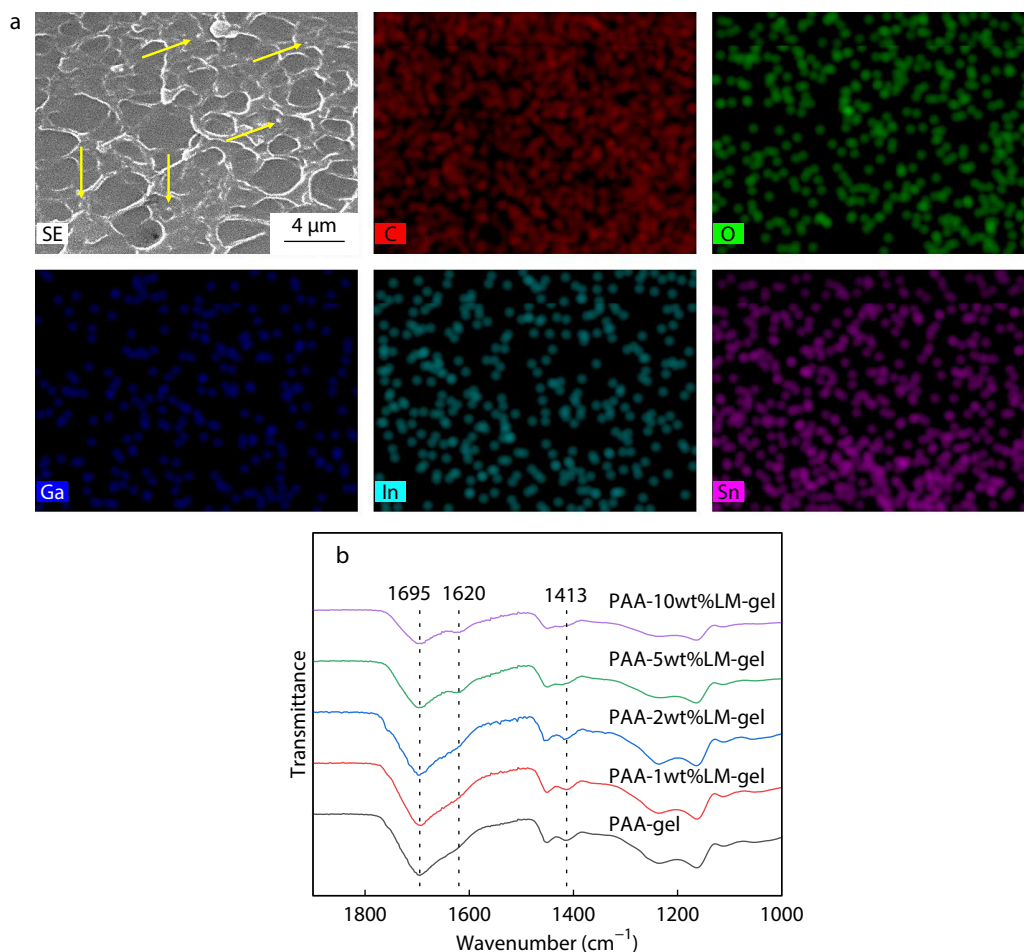


Fig. 2 Characterizations of the composition and bonding of PAA-LM hydrogels: (a) SEM micrographs and element mapping of the dried PAA-LM hydrogel with 2 wt% LM; (b) FTIR spectra of the dried PAA hydrogel and the dried PAA-LM hydrogels with different contents of LM.

The characterizations of the chemical composition and bonding of the PAA-LM hydrogels are shown in Fig. 2. Fig. 2(a) shows the SEM micrograph and element mapping of the dried PAA-LM hydrogel (2 wt% LM with respect to AA). The structure of the dried hydrogel could be seen clearly with bright GaInSn LM particles in the PAA matrix. The signals of Ga, In and Sn elements in LMs in the dried hydrogel were uniform, indicating the homogeneous distribution of LM droplets in the PAA hydrogels. The dynamic laser scattering (DLS) measurement also shows that the sizes of LM droplets in the gel precursor were uniform and obeyed unimodal distribution, with an average size of ~420 nm (Fig. S1, in the electronic supplementary information, ESI), which was consistent with the SEM results.

The interactions between the LMs and the functional groups of PAA were studied by means of FTIR spectroscopy. Fig. 2(b) shows the FTIR spectra of the dried PAA hydrogels and the dried PAA-LM hydrogels with different contents of LM. The band at 1695 cm^{-1} was ascribed to the stretching vibration of C=O groups of PAA, while when LMs were incorporated, a shoulder band appeared at 1620 cm^{-1} , indicating the formation of ionic bonds between Ga^{3+} on LM and COO^- of PAA. The band at 1413 cm^{-1} was ascribed to the bending vibration of —OH groups of PAA, which became smaller with

the addition of LM, mainly attributed to the interactions between carboxyl groups of PAA and the Ga_2O_3 layer on the surface of LM. Therefore, these strong interactions could endow the hydrogels with high strength and toughness.

Mechanical Properties of the Hydrogels Strengthened by LMs

Fig. 3 shows the mechanical properties of the PAA-LM hydrogels (70 wt% water content) with varied LM contents from 1 wt% to 10 wt% related to AA. As shown in Figs. 3(a) and 3(b), with the increasing amount of LM, the tensile strength of the hydrogels increases while the elongation at break decreases gradually. As increasing the LM from 1 wt% to 10 wt%, the tensile strength of the hydrogels is improved from 153 kPa to 549 kPa, while the elongation at break decreases from 1946% to 700%. In this case, as LM could interact with carboxyl groups in PAA, the PAA hydrogels were multi-bond cross-linked via the hydrogen bonds between carboxyl groups in PAA chains and Ga_2O_3 layers on the surface of LM, the ionic bonds between COO^- in PAA chains and Ga^{3+} on LM, as well as the hydrogen bonds among PAA chains. With the increasing amount of LM, the density of the dynamic multifunctional cross-linking points increases, which could dissipate more energy under stretching, so as to enhance the strength and toughness of the hydrogels. While, the higher cross-linking density meant shorter network chains between the

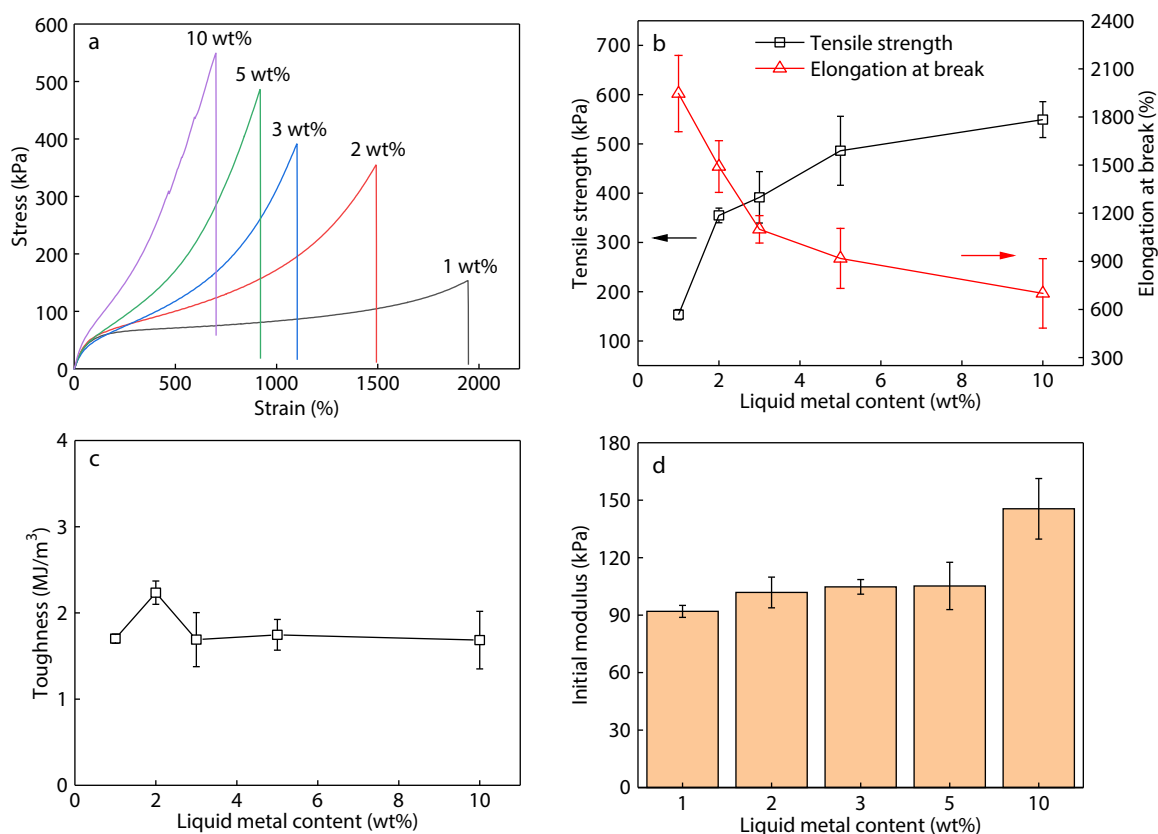


Fig. 3 Mechanical properties of PAA-LM hydrogels (70 wt% water content) with varying LM from 1 wt% to 10 wt%. (a) The tensile stress-strain curves, (b) tensile strength and elongation at break, (c) toughness, and (d) initial modulus of PAA-LM hydrogels.

cross-linking points, which would limit the stretchability of the hydrogels and cause a decrease in the elongation at break. Fig. 3(c) shows the toughness of the hydrogels, which is estimated by the area under the stress-strain curves in Fig. 3(a) from 0% to the fracture strain, and demonstrates the energy dissipated under stretching. The hydrogels with 2 wt% LM possessed the highest toughness of 2.29 MJ/m³ since they had relatively high tensile strength of 355 kPa and large elongation at break of 1491%. The initial modulus of PAA-LM hydrogels in Fig. 3(d) also increased with the increasing in LM, which was a result of the higher cross-linking density.

Mechanical Behaviors after Cyclic Stretch Training

Cyclic stretch on the same PAA-LM hydrogel samples was conducted to study the training effects based on the deformation of LM and the reformation of dynamic bonds. As shown in Fig. 4, continuous cyclic stretch on the PAA-LM hydrogels (70 wt% water content, 2 wt% LM) was carried out at a maximum strain of 500% (one third of the elongation at break). Then the samples were sealed in plastic bags and put in a container with a fixed humidity to prevent water loss. After a certain time, the deformed and teared LM particles in the hydrogels would self-adapt into more and smaller LM droplets as new cross-linking points.

The PAA-LM hydrogels could completely dissolve in water (Fig. S2 in ESI), indicating no covalent cross-linking in the hydrogels. Therefore, the PAA-LM hydrogels are physically cross-linked by dynamic bonds, which are reversible and self-healable. Fig. 4 shows the tensile stress-strain curves and the

dissipated energy of the PAA-LM hydrogels with 2 wt% LM at 70% water content. During the process of cyclic stretch at a maximum strain of 500%, obvious hysteresis loops could be observed in the stress-strain curves, indicating the large amount of energy dissipated due to the breakage of cross-linking bonds. When the cyclic stretch was carried out continuously, the broken dynamic cross-linking points hardly had time to reform, thus causing an obvious decrease in the tensile stress and less energy dissipation in comparison to the previous cycle, as shown in Figs. 4(a) and 4(b). However, when the cyclic stretch was performed with a 5-min interval, the maximum stress increased slightly with the increase in cycle numbers after the 2nd cycle and finally recovered to almost the same as that of the 1st cycle. Besides, the dissipated energy was only slightly decreased and then became almost stable after the second cycle, attributed to the reformation of some reversible bonds and the more homogenized networks after the 5-min rest (Figs. 4a and 4b). Moreover, the hydrogels have similar performance when they are stretched at different maximum strains (Fig. S3 in ESI).

The influence of the number of cycles and recovery time after cyclic stretch was further studied. The PAA-LM hydrogels were trained at a maximum strain of 500% continuously for different cycles, and were then sealed in plastic bags and put in a container with a fixed humidity at room temperature for 24 h. It is obvious that the tensile strength of the hydrogels increased with increasing the number of cycles until the 5th cycle (Figs. 5a and 5c). The decrease in the elongation at

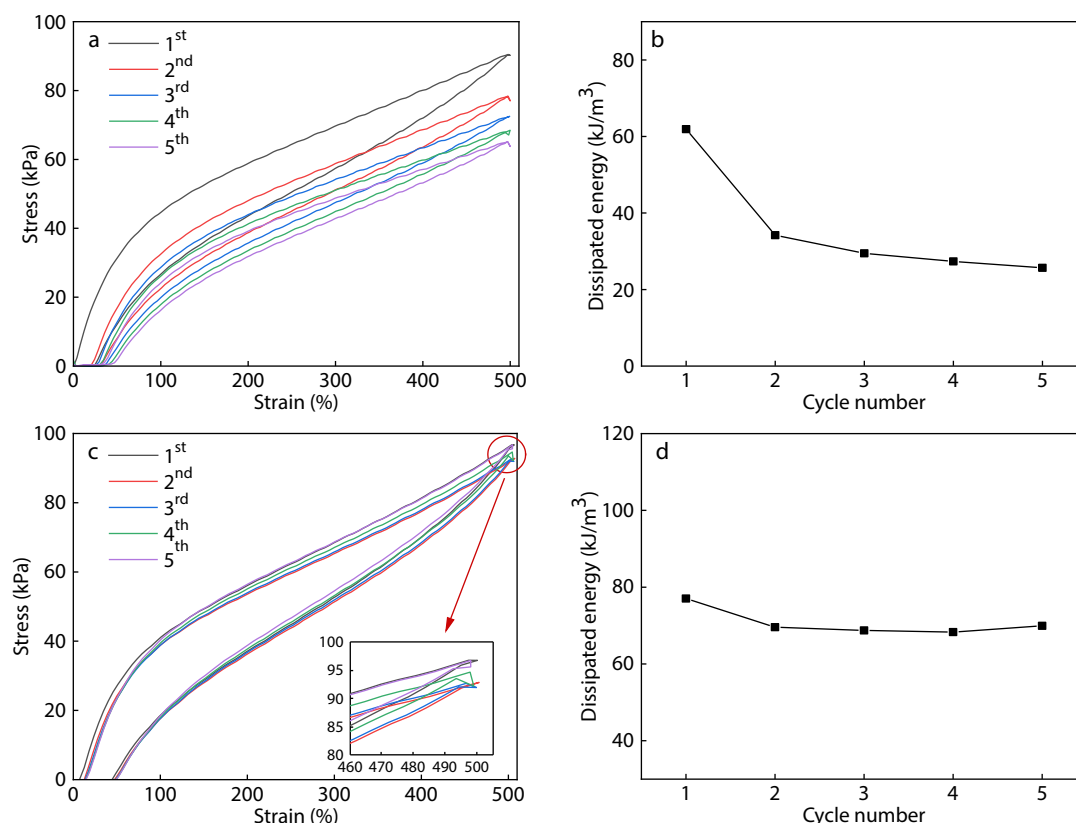


Fig. 4 Mechanical behaviors of PAA-LM hydrogels under cyclic stretch (70 wt% water content, 2 wt% LM): (a) cyclic stress-strain curve, (b) energy dissipation of hydrogels after continuous stretch; (c) Cyclic stress-strain curve and (d) energy dissipation of hydrogels after stretching with an interval of 5 min between every two cycles.

break (Fig. 5c) and the increase in the initial modulus (Fig. 5e) were also observed, which indicated the formation of denser networks. This is because the LM particles were teared into more and smaller LM droplets under stretching, and thus forming more cross-linking points. However, when more training of 10 cycles was conducted, the tensile strength of the excessively trained hydrogels decreased instead. Some irreversible damage might be introduced in the hydrogels, thus the bonds in the networks could not recover completely, causing a decrease in the mechanical properties.

To study the effect of recovery time on the mechanical properties of the hydrogels, the PAA-LM hydrogels were trained at a maximum strain of 500% for 5 cycles without interval, and were then sealed in plastic bags and put in a container with a fixed humidity at room temperature for different time. When the hydrogels recovered for only 1 h, the tensile strength could not recover to the initial value and was only 285 kPa, yet the elongation at break was larger of 1568%, indicating that the polymer network was less densely cross-linked because of the inadequate time for the dynamic bonds to recover. However, after recovering for over 8 h, the tensile strength increased to 488 kPa in comparison to the control hydrogels without cyclic training, and the elongation at break slightly decreased to 1081%. After further recovering for 24 h, the tensile strength of the PAA-LM hydrogels increased obviously from 355 kPa to 597 kPa, and the elongation at break only decreased slightly from 1491% to 1034% due to the

higher cross-linking density (Figs. 5b and 5d). The initial modulus also increased from 71 kPa to 166 kPa (Fig. 5f), owing to the denser polymer networks formed after cyclic training. This is because during stretching, the flexible and deformable LMs were broken into more and smaller droplets to form more new cross-linking points. It is clearly revealed that the PAA-LM hydrogels with self-adaptive networks can be enhanced through the deformation of LMs and the reformation of reversible bonds.

Fig. 6 shows the comparison of the structures in the micrographs of the hydrogels without and with cyclic training. Continuous cyclic stretch training on the PAA-LM hydrogels (70 wt% water content, 5 wt% LM) was carried out at a maximum strain of 500% (half of the elongation at break), and the hydrogel without training was conducted in the same condition as a control sample. The PAA-LM hydrogels were cryo-fractured and observed by SEM. It was obvious that the LM droplets after training are smaller and more uniformly distributed in the hydrogel. So, it can be recognized that the flexible LMs were deformed and broke into two or more droplets under stretching. The newly formed smaller LM droplets could be quickly oxidized and act as new cross-linking points, and therefore creating a more homogeneous and denser network.

The self-adaptivity and self-strengthening of the PAA-LM hydrogels are attributed to the deformability of LMs and the reversible bonds between the LMs and the PAA chains. Fig. 7 shows a schematic illustration of such self-adaptive process of

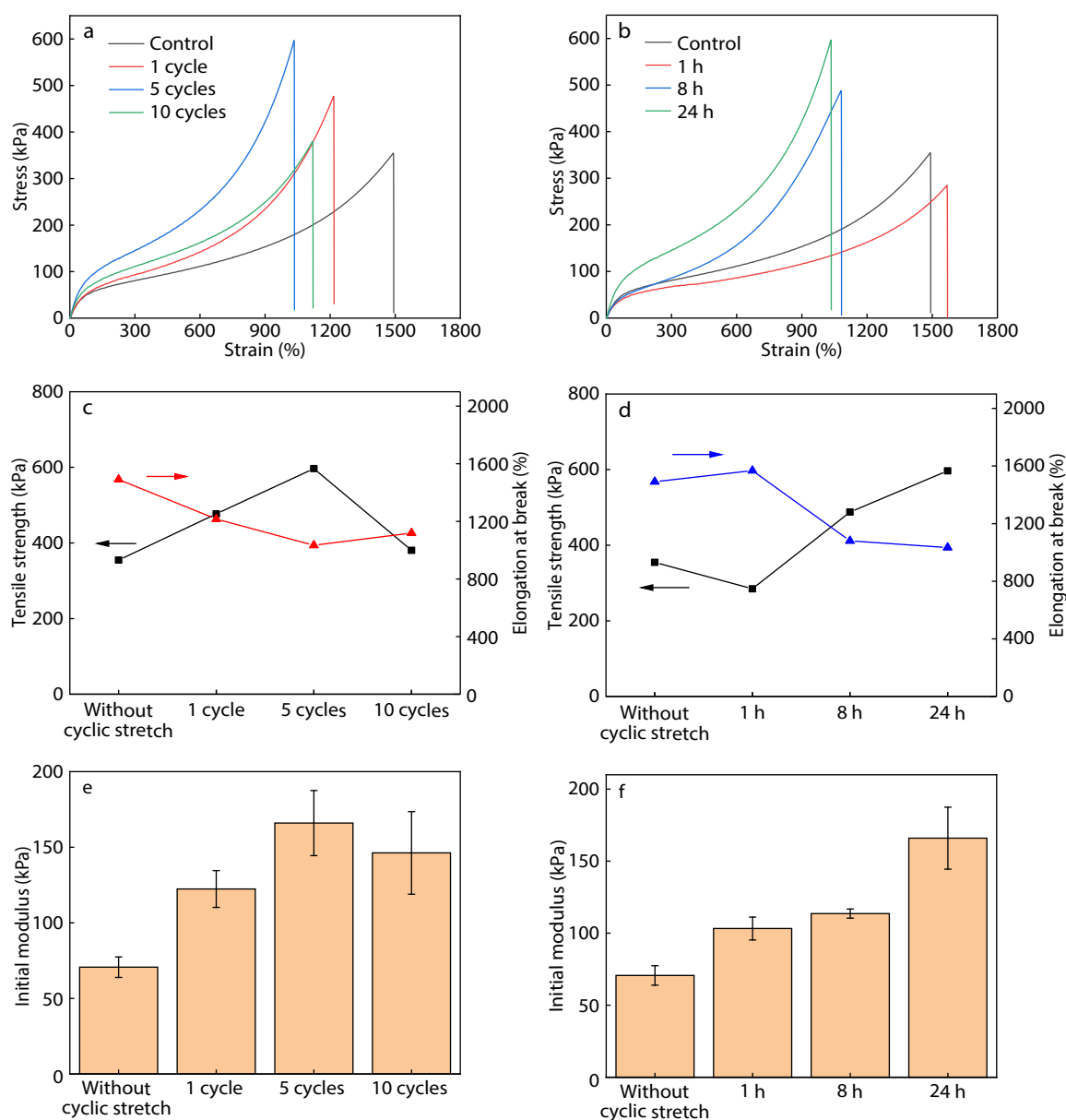


Fig. 5 The mechanical properties of PAA-LM hydrogels (70 wt% water content, 2 wt% LM) after cyclic stretch. (a) The tensile stress-strain curves, (c) tensile strength and elongation at break (e) initial modulus of PAA-LM hydrogels with different numbers of training cycles after 24 h recovering; (b) The tensile stress-strain curves, (d) tensile strength and elongation at break (f) initial modulus of PAA-LM hydrogels with different recovery time after 5 training cycles.

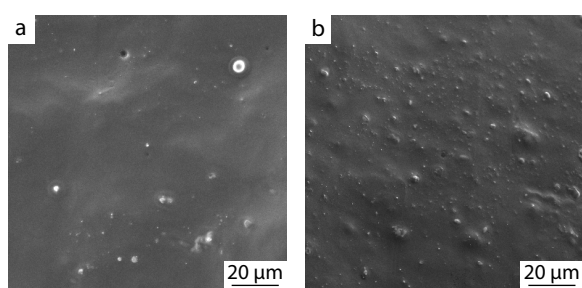


Fig. 6 SEM images of cryo-fractured PAA-LM hydrogels without and with training (a) without training, (b) with training (5 wt% LM).

the PAA-LM hydrogel network. Compared with the rigid particles, flexible LMs can deform or separate into more droplets under stretching due to their good deformability. The reformation of reversible hydrogen bonds between the carboxyl groups of PAA and the oxide layers on the smaller LM droplets as well as ionic bonds between the carboxyl groups of PAA and Ga^{3+} on LM led to new and denser networks. Thus, super tough PAA-LM hydrogels with self-adaptive networks were obtained, showing greatly increased tensile strength and initial modulus. Such adaptive hydrogels with excellent self-enhancing properties may have promising applications in biological treatments such as surgery of bone injury.

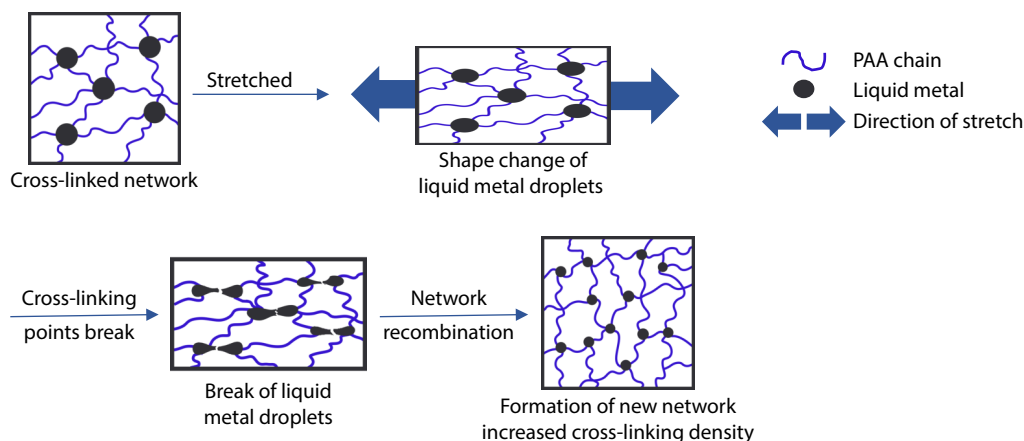


Fig. 7 Schematic illustration of the self-adaptivity of PAA-LM hydrogels.

CONCLUSIONS

In this work, super tough PAA-LM hydrogels with self-adaptive networks were fabricated, with GaInSn liquid metals as reversible and flexible physical crosslinkers. High tensile strength and toughness were achieved *via* hydrogen bonds between Ga_2O_3 layers on LM and hydroxyl groups of PAA chains, ionic bonds between carboxyl groups of PAA chains and Ga^{3+} on LM, as well as hydrogen bonds among PAA chains. Due to its fluidity and deformability, LM could deform or separate into more droplets under stretching. With the denser hydrogel networks, the mechanical properties of the PAA-LM hydrogels could recover or even be enhanced greatly after cyclic training. Thus, hydrogels with high mechanical strength, self-adaptive and self-strengthening networks were simultaneously obtained.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2874-2>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52273023, 21774069, 51633003 and 21474058).

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