Silicone-based tough hydrogels with high resilience, fast self-recovery, and self-healing properties

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Tough hydrogel is prepared from two monomers via photopolymerization of hydroxyethyl acrylate and sol-gel of methyltrimethoxysilane. Constitution and water content could be tuned easily because of the good water solubility of both monomers and two non-interfering polymerization processes. The hydrogels exhibit excellent integrated performance with toughness, high resilience, fast self-recovery, and self-healing.

High-strength polymer hydrogels have received growing attention as one of the “soft and wet” materials because of their great potential in load-bearing soft tissue applications, such as in muscles, bio-actuators, tendons, and cartilages.[1] Natural hydrogel-like bio-tissues, such as heart valves, possess both high resilience (>80%) and toughness (>1200 J/m^2) that could deform more than 3×10^9 cycles over their lifetime. By contrast, conventional hydrogels always exhibit poor mechanical strength and/or low limited extensibility and recoverability, which severely limit their potential applications as load-bearing biomaterials.[2] Therefore, designing and fabricating a hydrogel with biocompatibility and mechanical properties, including toughness, strength, recoverability, resilience, and self-healing, are crucially important.

In the last several decades, many efforts have been made to develop new polymerization methods for preparing strong hydrogels. These developments have led to the generation of diverse and tough hydrogels, including nanocomposite, sliding ring, tetrapolyethylene glycol, macromolecular microsphere composite, and dual-component polymer hydrogels. Dual-component polymer hydrogels are represented by interpenetrating network, semi-interpenetrating, and double-network hydrogels.[3] These dual-component polymer hydrogels are also characterized by a special network structure that comprises two polymer networks.[4] The mechanical properties between their strength and toughness could be balanced by tuning the inter/intramolecular interactions and structures within and between two networks that employ a wide variety of polymeric monomers, cross-linkers, and cross-linked methods. A dual-component polymer hydrogel is usually formed via a multi-step sequential polymerization process, which is briefly described as follows: the first step is the formation of a polymer network, followed by the immersion of the first network into a precursor solution that contains monomers, cross-linkers, and initiators of the second polymer. The second polymerization is performed in the first network.[5] Different tough hydrogels are achieved using a multi-step sequential polymerization process. However, the following limitations are still encountered:[4, 6] tedious and time consuming process, long swelling and diffusion times, difficulty in controlling and measuring the quantity of the second polymer network, a high precursor solution concentration for the second polymer, difficulty in forming different or complex hydrogel shapes, and formation of a hydrogel with negligible fatigue resistance, among others.

The one-pot method of synthesizing hydrogels has recently been reported.[7] This method aims to overcome the abovementioned limitations of the multi-step polymerization process used to form the dual-component polymer hydrogel. The precursor of the first polymer is polymerized in the liquid solution mixture of the other polymer and the precursor. Zheng et al.[6] synthesized agar/polyacrylamide (agar/PAM) hydrogel in a single water pot via a heating–cooling–photopolymerization process. The agar forms into gel through the sol-gel transition. The acrylamide then photopolymerizes in the agar gel, and the gel is formed. Wang’s group[8] formed polyvinyl pyrrolidone (PVP)-in situ-PAM hydrogels by polymerizing acrylamide in a mixture water solution of PVP and acrylamide. The preparation procedure of hydrogels is simplified using the one-pot method.

Notably, many tough hydrogels have achieved a variety of performances at the expense of other properties. Some hydrogels have extremely high strength and toughness without

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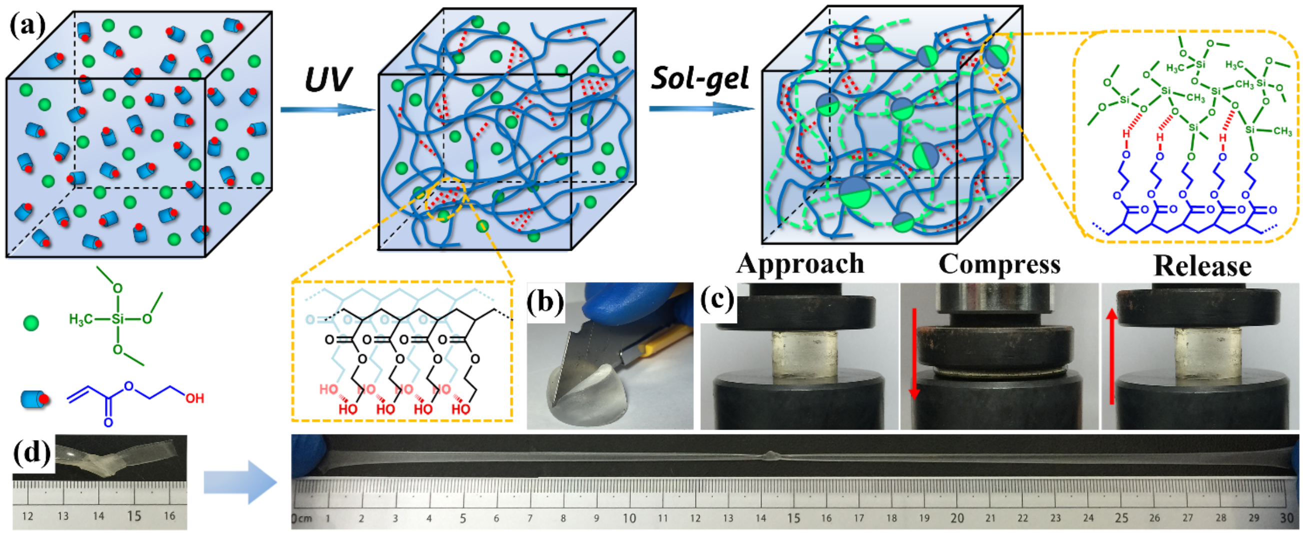

Fig. 1 (a) Formation of silicone/PHEA hydrogel via photopolymerization and sol-gel process. (b) The resultant hydrogel is tough enough that even a sharp knife could not destroy it. (c) The hydrogel rapidly reverts to its original shape after undergoing a series of compressive deformations > 90% and subsequently releasing force. (d) The hydrogel could also be stretched to extreme elongations even after being knotted.

negligible fatigue resistance and poor recovery, which are limitations in many practical applications.[9] Other hydrogels could be recovered after first loading. However, their recovery takes a long time or requires an external factor, such as moisture and heating.[10] Moreover, the hydrogels with strong mechanical performance might lack self-healing or good resilience.[11]

We report the new and simple one-pot method in this paper to synthesize a tough, highly resilient, fast-recovering, and self-healing hydrogel composed of silicone and polyhydroxyethyl acrylate (PHEA) using photopolymerization and sol-gel transition processes. The design is inspired by silicone, which is a good elastomer and has high extensibility level and good resilience for the Si–O bond with high bond energy and outstanding flexibility. However, silicone is hydrophobic and difficult to use as a hydrogel source. Some silicone monomers, such as tetramethoxysilane and methyltrimethoxysilane (MTMS), have good water solubility. Therefore, a silicone monolith that is hydrophobic and has high crosslink density could be achieved through the sol-gel process of water-soluble silicone monomers, such as MTMS.[12] Accordingly, some features (e.g., hydrophilicity/hydrophobicity, crosslink density, and self-healing) should be modified and balanced to form hydrogels that contain silicone through the sol-gel process. This study chooses the water soluble monomer hydroxyethyl acrylate (HEA), which is a precursor of the water-soluble polymer, PHEA, to tune the performance of the hydrogel-containing silicone for four reasons. First, the water solubility of PHEA could mediate the hydrophilicity/hydrophobicity of the hydrogel. Second, PHEA has many hydroxyl groups that could form hydrogen bonds among hydroxyl groups or between hydroxyl groups and Si–O–Si bonds. The hydrogen bond could form reversible physical crosslinking and possibly endow the hydrogel with recovery or self-healing performance.[13] Third, a few PHEA hydroxyl groups may be condensed with –Si–O–CH_3, which could promote silicone and PHEA interaction in the hydrogels.[14] Lastly, PHEA could be prepared from the photopolymerization of monomer HEA, which helps in forming different hydrogel shapes. The silicone/PHEA hydrogel could be synthesized successively in one pot because of the non-interfering reaction between HEA photopolymerization and the MTMS sol-gel process. Both silicone and PHEA precursors are non-toxic[15] and water soluble. Therefore, the ratio of the two precursors and the water content could be changed easily in the broad range. Consequently, the hydrogels are readily produced and optimized in a fast and controllable manner.

Figure 1 shows all reactants of HEA, photoinitiator 2959, MTMS, urea, and cetyltrimethyl ammonium bromide (CTAB). CTAB is employed to avoid phase separation between PHEA and the silicone network.[16] These reactants are added to a single water pot to synthesize silicone/PHEA hydrogels via photopolymerization and sol-gel process. The detailed synthesis procedure is described in the supplementary materials (Fig. S1 and S3, ESI†). HEA is first photopolymerized in the water solution, and the shape of the gel is fixed, the network that is physically linked by the hydrogen bond between hydroxyl groups is formed. Urea decomposes into NH_3 and CO_2 during the sol-gel process at 80 °C. $NH_3 \cdot H_2O$ also catalyzes the sol-gel process, and then the chemically crosslinked silicone network is formed. Accordingly, Attenuated Total Reflectance Spectroscopy(ATR-IR), dynamic mechanical thermal analyses(DMTA), and scanning electron microscope(SEM) have proven that the dual-component polymer networks are compatible, while the silicone gel is composed of nanoparticles and the particles are discontinuous (Fig. S4–6, ESI†). The hydrogel has only one glass transition temperature, and the gel morphology is uniform. The obtained results and referenced abstracts[14] suggest that intermolecular hydrogen bonds exist between the chains of PHEA or PHEA and silicone, and covalent bonds, Si–O–C bonds, which are condensed between silicone and PHEA (Fig. S4, ESI†). Using this polymerization strategy avoids both uncontrollable swelling and time-consuming diffusion processes for the precursor. The method also resolves the problem of hydrogels having low density of polymer chains, which is induced by the limited polymer solubility, lowered by the swelling process, or eliminated by the limited precursor diffusibility. The gels can be shaped freely, which contributes to the no-swelling process. By contrast, the silicone gel is brittle and easily crushed without PHEA which may be induced by the discontinuous microstructure (Fig. S6, ESI†). The PHEA gel without a cross linker is soft (Fig. S7, ESI†). Both gels could not be tested by mechanical experiments. However, the silicone/PHEA gels appear strong and tough. Not even knife cutting, high compression, or stretching using a knot could destroy them (Fig. 1).

The ratio of the two precursors, HEA and MTMS, could be tuned easily (Fig. 2). Both precursors could be mixed with water at any proportion. Therefore, the optimal condition could be obtained easily. The water content of all samples in Fig. 2(a) is 55%. The mole ratio of HEA to MTMS is different. Accordingly, H4M2 refers to the HEA to MTMS mole ratio of 4:2. Strain and stress first increase then decrease with the mole ratio increase of HEA to MTMS [Fig. 2(a)]. This reaction may contribute to the harmonious proportion of PHEA and silicone. The area of the strain–stress curves is calculated. The gel toughness is also obtained [Fig. 2(b)]. The H6M2 sample is the toughest among these gels. Unless otherwise stated, we mainly focus on the H6M2 sample with a stress that could achieve 1.75 MPa and an elongation of up to 970%. The sample has achieved a high compression stress of more than 20 MPa. The normal compression stress is more than 95%. The sample could also bear car pressure (Fig. S8, ESI†) and has better fatigue resistance than H5M2 (Fig. S9, ESI†).

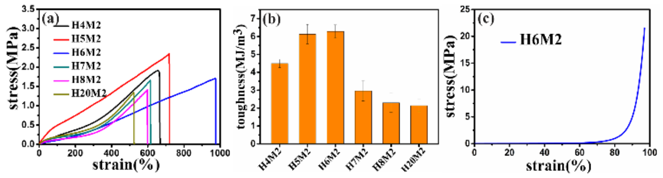

Fig. 2 Mechanical properties of HEA/MTMS hydrogels with different mole ratios of HEA to MTMS. (a) Tensile stress–strain curves, (b) toughness, and (c) compressive stress of H6M2.

Silicone/PHEA hydrogels are quite tough, which could be demonstrated by the fracture energy. The fracture energy was tested by tearing measurement which was performed according to standard ASTM D624-00. The detailed test procedure is described in the supplementary materials (Fig. S2, ESI†). The tearing test result indicates the fracture energy of H6M2 is about 339 J/m^2, while, the tearing tests of the silicone gel and PHEA gel couldn't be conducted for they are too brittle or weak.

The internal evolution on loading–unloading cycles are investigated further to understand the hydrogels' fatigue resistance, resilience, and self-recovery capabilities. Typical tensile (100 mm min^{-1}) and compressive (5 mm min^{-1}) loading–unloading tests are implemented to achieve this purpose(Fig.3b-i). During the consecutive compressive mode, the hydrogel shows favourable resilience and fatigue resistance which each cycle nearly coincides with others (Fig.3b). Even increasing the cycle times to 50 or the frequency of the force, the samples still show good anti-fatigue behaviour (Fig. S10, ESI†). Silicone/PHEA shows a small hysteresis loop under 300% strain and exhibits a rubber elastic behavior (Fig. 3d–f). Only a slight decrease has been observed from the second cycle with the consecutive tensile loading–unloading tests with five cycles. The elastic modulus ratio (second loading vs. first loading) is 0.983, which indicates that the gel network structure shows negligible change under 300% strain.

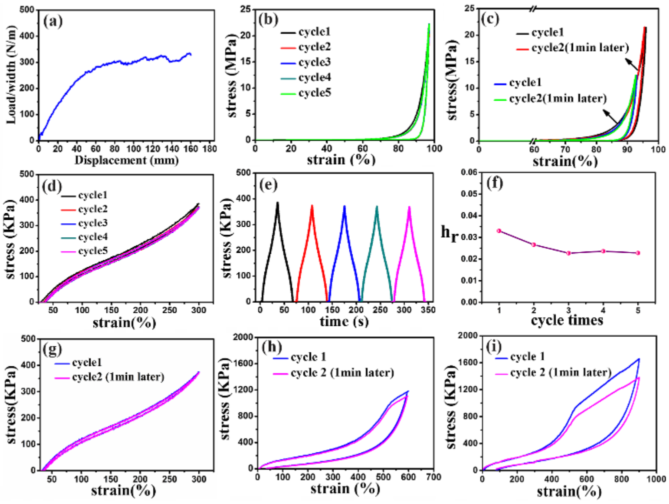

Fig. 3 (a) the load–displacement curve of tearing test result of H6M2 hydrogel (Sample shape (w=15 mm, L=150 mm, d=2 mm, the length of the initial notch is 40 mm) and pulling velocity is 50 mm/min). Loading–unloading tests of H6M2 hydrogels (b-i). (b) typical successive loading–unloading compression tests for five runs; (c) self-recovery behavior at approximately 90% and 95% compression strains; (d) typical successive loading–unloading tensile tests for five runs; (e) stress–time tensile curves at 300% strain; (f) hysteresis ratio (***h****$_r$*) with five run cycles at 300% tensile strain; and (g, h, and i) self-recovery behavior at 300%, 600%, and 900% tensile strains, respectively.

The time-evolution recovery properties of the silicone/PHEA gels are further evaluated with different strains. The hysteresis loop recovers completely when the gels are compressed to 90% or 95% after a 1 min rest (Fig. 3c). This result indicates that the gels recover well and quickly under high compression. The same outstanding recovery property is observed when the tensile loading–unloading test is conducted at 300% strain (Fig. 3g). The hysteresis loop could not recover completely when the strain increases (600%, 900%) after a 1 min rest. The recovery rates are 94.25% and 83.16% (Fig. 3h–i).

The silicone/PHEA hydrogels have different recovery ratios at different strains. Therefore, understanding the recoverable energy dissipating mechanism is crucial. The silicone/PHEA hydrogels also possess multiple polymer chain entangled forces and hydrogen and covalent bonds. These kinds of interaction have different energy dissipating mechanisms. Fig. 3g–i show that the gels exhibit different shapes of stress–strain curves at different strains. The hysteresis loop is small when the gel is stretched to 300%. Furthermore, the stress–strain curve exhibits a rubber elastic behavior. The gel transformation is the contribution of the polymer chain elongation from curl to linear because the external force is minimal. The polymer chain tends to curl once the stress is released, which is intrinsic. This transformation could recover completely as long as no polymer chain slides (the hydrogen bonds and covalent bonds). Therefore, the hysteresis loop at 300% strain could recover completely after resting for 1 min. The hydrogen bonds, which dissipate more energy, begin to break with deformation increase (600%). Therefore, the hysteresis loop enlarges. However, the hydrogen bonds could recombine once the stress stops, which causes the hysteresis loop to recover almost entirely after resting for 1 min. The covalent bonds are fractured when stretched further (900%). These fractured bonds could not be recombined and induces a gel recovery ratio, which is not as good as it previously was. Meanwhile, the further dissipated energy leads to an expanding hysteresis loop.

In vitro cytotoxicity and compatibility tests are also conducted to prove that the resultant hydrogels are cytocompatible materials (Fig. S11, ESI†).

Figure 4 demonstrates the self-healing performance of the silicone/PHEA hydrogel. The gels could self-heal when the fractured ones are reconnected and stored in a Ziploc plastic bag for several days. This self-healing capability is attributed to abundant hydrogen bonds in the network. The mechanical property of the healed gels is not as good as it previously was. However, the extent of this self-healing property increases with the increase in healing time.

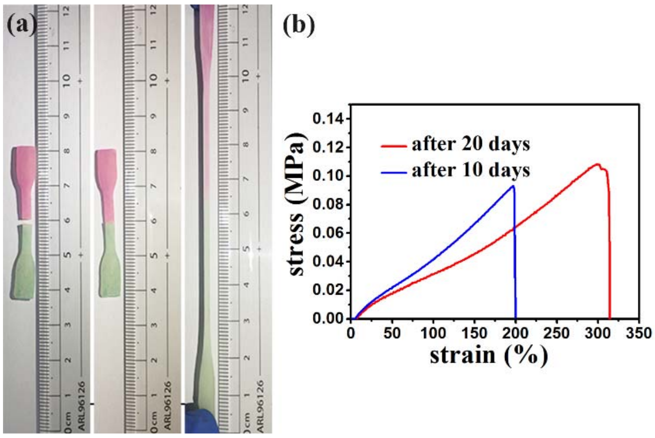

Fig. 4 Self-healing properties of the HEA/MTMS hydrogel. (a) The hydrogel is cut into two pieces and recombined. The fractured hydrogel with an alternative color can be immediately spliced together at room temperature and stretched without failure after a few days. (b) Tensile stress–strain curves of the healed H6M2 hydrogel after 10 and 20 days.

We developed a facile strategy to fabricate a hydrogel with toughness, high resilience, fast self-recovery, and self-healing properties via photopolymerization and sol-gel processes. The integrated characteristics of the prepared silicone/PHEA hydrogels make them potential fatigue-resistant materials in the biological material fields.

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Notes and references

1 (a)M. Nakahata, Y. Takashima, H. Yamaguchi and A. Harada, *Nat Commun*, 2011, 2, 511; (b)Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara and T. Aida, *Nature*, 2010, 463, 339; (c)D. Seliktar, *Science*, 2012, 336, 1124.

2 (a)M. He, Z. Wang, Y. Cao, Y. Zhao, B. Duan, Y. Chen, M. Xu and L. Zhang, *Biomacromolecules*, 2014, 15, 3358; (b)M. Krogsgaard, M. A. Behrens, J. S. Pedersen and H. Birkedal, *Biomacromolecules*, 2013, 14, 297; (c)S. Lin, Y. Zhou and X. Zhao, *Extreme Mechanics Letters*, 2014, 1, 70.

3 (a)K. Haraguchi and T. Takehisa, *Adv.mater*, 2002, 14, 1120; (b) T. L. Sun, T. Kurokawa, S. Kuroda, A. B. Ihsan, T. Akasaki, K. Sato, M. A. Haque, T. Nakajima and J. P. Gong, *Nat Mater*, 2013, 12, 932; (c)Y. Okumura and K. Ito, *Adv. Mater*, 2001, 13, 485; (d)T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M.Shibayama and U. Chung, *Macromolecules*, 2008, 41, 5379; (e)T. Huang, H.G. Xu, K.X. Jiao, L.P. Zhu, H. R. Brown, and H. L. Wang, *Adv. Mater*, 2007, 19, 1622.

4 J. P. Gong, *Soft Matter*, 2010, 6, 2583.

5 J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv.Mater*, 2003, 15, 1155.

6 Q. Chen, L. Zhu, C. Zhao, Q. Wang and J. Zheng, *Adv. Mater*, 2013, 25, 4171.

7 (a)X. Hu, M. Vatankhah-Varnoosfaderani, J. Zhou, Q. Li and S. S. Sheiko, *Adv. Mater*, 2015, 27, 6899; (b)Q. Chen, H. Chen, L. Zhu and J. Zheng, *J. Mater. Chem. B*, 2015, 3, 3654.

8 G. S. Song, L. Zhang, C. C He, D. C Fang, P. G. Whitten and H. l. Wang, *Macromolecules*, 2013, 46, 7423.

9 X. Zhao, *Soft Matter*, 2014, 10, 672.

10 (a)J. Hao and R. A. Weiss, *ACS Macro Letters*, 2013, 2, 86; (b) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, *Adv. Mater*, 2012, 24, 362; (c)P. Lin, S. Ma, X. Wang and F. Zhou, *Adv. Mater*, 2015, 27, 2054; (d) J. Yang, C. R. Han, X. M. Zhang, F. Xu and R. C. Sun, *Macromolecules*, 2014, 47, 4077.

11 (a)G. Du, F. Wu, Y. Cong, L. Nie, S. Liu, G. Gao and J. Fu, *Chem. Commun*, 2015, 51, 15534; (b)F. K. Shi, X. P. Wang, R. H. Guo, M. Zhong and X. M. Xie, *J. Mater. Chem. B*, 2015, 3, 1187; (c)J. H. Lee, J. Park, J. W. Park, H. J. Ahn, J. Jaworski and J. H. Jung, *Nat. Commun*, 2015, 6.

12 G. Hayase, K. Kanamori, G. Hasegawa, A. Maeno, H. Kaji and K. Nakanishi, *Angew. Chem. Int. Ed*, 2013, 52, 10788.

13 (a)X. J. Zhang and J. H. He, Sci. Rep, 2015, 5, 9227; (b) R. P.Wool, *Soft Matter*, 2008, 4, 400.

14 (a)S. Deng, H. Xu, X. Jiang and J. Yin, *Macromolecules*, 2013, 46, 2399. (b)F.B.Peng, L.Y. Lu, H.Lei. Sun, Y.Q. Wang, J.Q. Liu, and Z.Y. Jiang, *Chem. Mater*, 2005, 17,6790; (c)Q. G. Zhang, Q. L. Liu, A. M.Zhu, Y. Xiong and X. H. Zhang, *J. Phys. Chem. B,* 2008, 112, 16559; (d)Q.G.Zhang, Q. L. Liu, Y. Chen and J. H. Chen, *Ind. Eng. Chem. Res*, 2007, 46, 913.

15 (a)J. Cui, M. A. Lackey, A. E. Madkour, E. M. Saffer, D. M. Griffin, S. R. Bhatia, A. J. Crosby and G. N. Tew, *Biomacromolecules*, 2012, 13, 584; (b)A. Arun and B. S. R. Reddy, *Biomaterials*, 2005, 26, 1185.

16 G. Hayase, K. Kanamori and K. Nakanishi, *Microporous Mesoporous Mater*, 2012, 158, 247.