Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

POSS Based Hydrogel with Mechanical Robust, Cohesiveness and Rapid Self-Healable without healing for times by Electrostatic Interaction

Pu Wanfen, Feng Jiang*, Pei Chen and Bing Wei*

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest P etroleum University, Chengdu, Sichuan, 610500, China
E-mail: dandanfeng2940@163.com

Acrylamide (AM), acrylic acid (AA), N,N,N',N'-tetramethylenediamine (TEMED), ammonium persulfate (APS), N,N'-methylenebisacrylamide (MBA), (3-Aminopropyl)triethoxysilane (KH-550), ethanol were purchased from .Kelong Chemical Reagent Factory. Tetraethylammonium hydroxide (Et4NOH, 25% aqueous solution) was purchased from National Chemical Group. N-[3-(Dimethylamino)propyl]methacrylamide (DMAPMA) was obtained from Aladdin Company.

The Fourier transform infrared (FT-IR) spectra of POSS-NH_2-AA and hydrogel were performed with KBr pellets on a WQF-520 infrared spectroscopy (Figure S2, Suplementary Information). The microstructures of the hydrogels were observed using a scanning electron microscope (SEM). The tensile tests were conducted on a Sans Universal Testing System with a 200 N sensor at a stretch velocity of 50 mm min^{-1}. All the samples were cut into a rectangle shape with the size of length 30 mm, thickness 6 mm, width 15 mm. The length of the hydrogel between the two fixtures is 15 mm.

The synthesized hydrogel was cut into pieces and dried in a vacuum oven at 50 °C to constant weight. The dried particles were fully swollen in water. They were taken out after some intervals, gently wiped with filter paper, and immediately weighted on a microbalance. The WSR is defined as:

$$WSR = (\mathrm{m}_t - \mathrm{m}_0) \times 100\% / \mathrm{m}_f \quad (1)$$

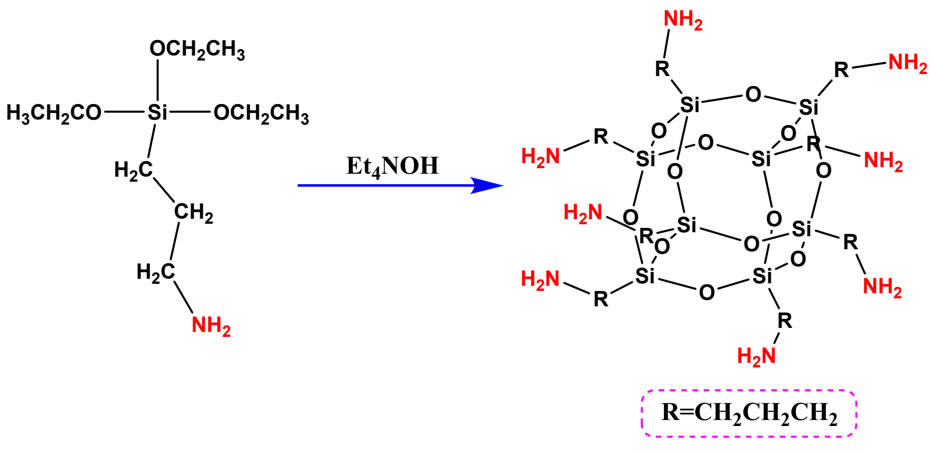
Where m_t is the weight of the hydrogels at different time, m_0 is the dry weight of the particles and m_f is the final weight of the hydrogels.[1]

The hydrogel was dried in an oven at 80 °C to a constant weight. The dried hydrogel was shattered by a pulverizer and then immersed into fresh water to swelling balance. The swollen hydrogel was placed in a device to test the breakthrough pressure.[2]

Cohesiveness and Self-healing Test

In this part, hydrogel was prepared with a cylindrical shape and the diameter of the hydrogel was 20 mm. The cohesiveness was conducted using different materials, including glass, iron, polytetrafluoroethylene (PTFE) and high density polyethylene (HDPE). In the self-healing test, the hydrogel was cut into two parts and adhere to bottle A and bottle B, respectively (Figure S4, supplementary information). Then, the two cut surfaces were brought together and the mass of the bottle B was recorded without waiting, which is used to evaluate the self-healing property of the hydrogel. The mass of the glass bottle can be changed by adding water. It is worth mentioning that the self-healing time is not taken into accounted in the self-healing property test for the rapid self-healing property.

POSS-NH_2 was synthesized according to the literature. The exist of -NH_2 is harmful to the stability of the POSS, especially in water condition.[3] Usually, POSS-NH_2 should be stored carefully at low temperature with a short period. However, the stability of the POSS can be enhanced by reacting with AA, by which -NH_2 was neutralized and POSS-NH_3^+ was formed. By this way, a molecular dispersed POSS with a good water solubility was synthesized, which can be used to reinforce the mechanical property of hydrogel.



Scheme S1. Synthesis of POSS-NH_2

As shown in Figure S1, the POSS-NH2-AA is clear and transparent absolutely. A good compatibility with monomer is beneficial to construct a hydrogel system without structure defect.

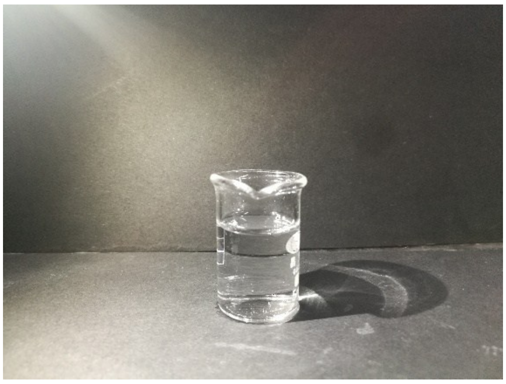


Figure S1. The picture of molecular dispersed POSS-NH_2-AA solution (5 wt%)

The formula of hydrogels can be found in Table S1. APS/TEMED system was used as initiator, which was good for the hydrogel formation. [4]

Table S1. The formula of hydrogels

Entry	AA (g)	DMAPMA (g)	POSS/AA (mL)	APS (mL)	TEMED (mL)	water (mL)
1	0.7	1.65	0	0.8	1	3.5
2	0.8	1.65	1	0.8	1	2.2
3	0.8	1.65	0	0.8	1	3.2
4	0.7	1.65	0.5	0.8	1	2.7
5	0.7	1.65	1	0.8	1	2.2
6	0.7	1.65	1.5	0.8	1	1.7

The structures of POSS-NH_2 and POSS based hydrogel are confirmed by Fourier transform infrared spectroscopy (FTIR). As shown in Figure S2, the peaks at 1108 cm^{-1} can be assigned to Si-O-Si from cage-structured POSS.[5] The band observed at 782 cm^{-1} is attributed to the -NH. The two peaks can be found in the curve fo POSS based hydrogel. Therefore, the presence of the POSS-NH_2 can be confirmed. The two peaks at 3406 and 1685 cm^{-1} are attributed to -OH and -C=O of AA and DMAPMA respectively. Therefore, the groups of AA, DMAPMA and POSS-NH_2 can be found in the structure of POSS based hydrogel, for which the structure of the hydrogel is confirmed.

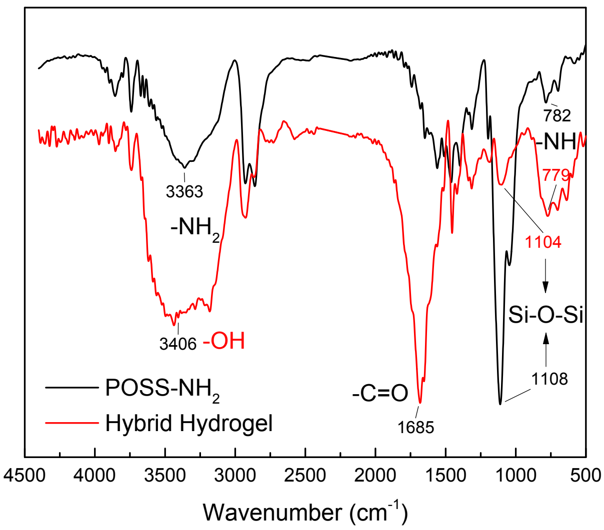


Figure S2. FTIR spectra of POSS-NH_2 and hybrid hydrogel

POSS-NH_2-AA was dispersed molecularly in the hydrogel system. Eight arms of POSS-NH_3^+ served as a physical cross linker, for which the mechanical property of hydrogel was enhanced significantly.

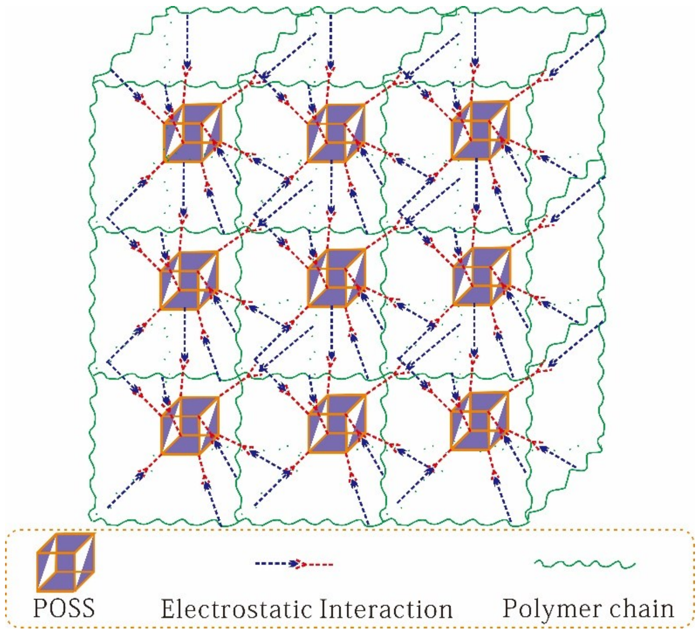


Figure S3. Diagram of POSS based hydrogel

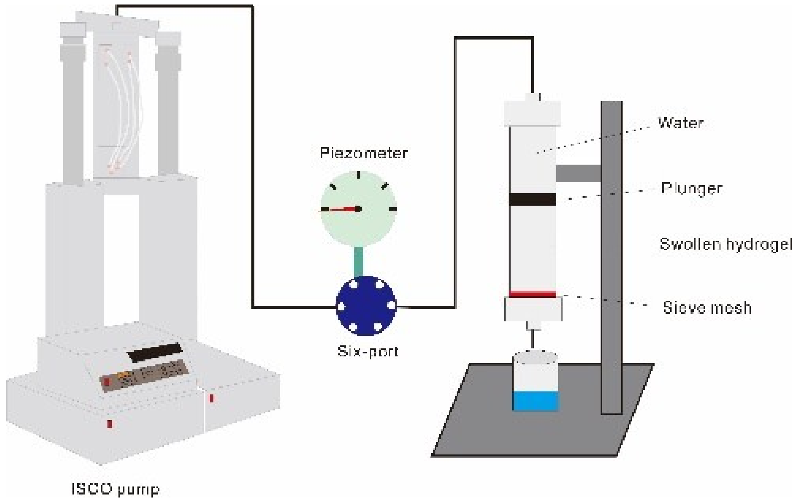


Figure S5. Breakthrough pressure chart

The self-healing test device was design simply according the good adhesiveness to glass. The two hydrogels were adhered to bottle A and B, respectively. Then, the two hydrogels were contact with each other. Beneficial from the rapid self-healing property, the mass of the Bottle B can be measured without waiting.

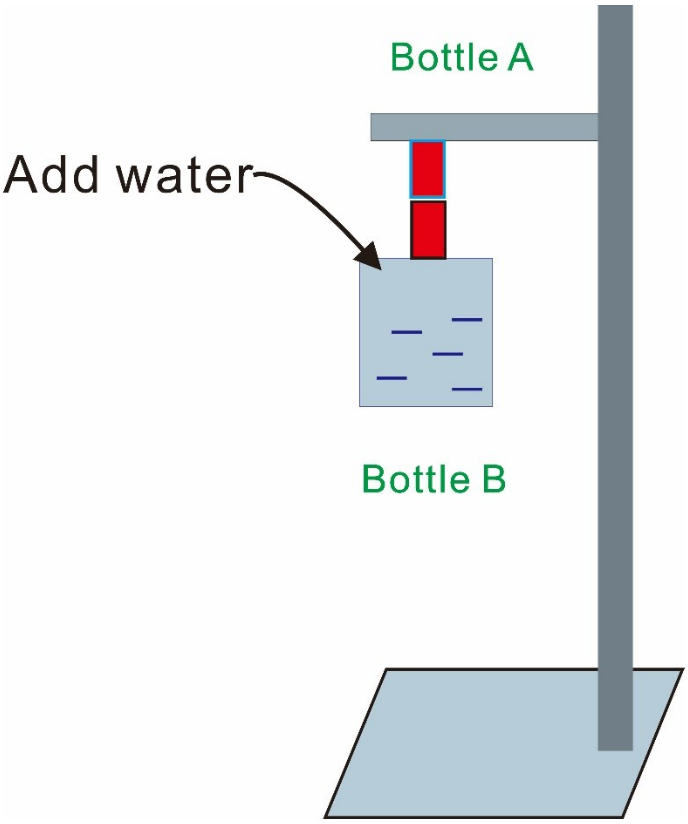


Figure S5 Diagram of self-healing property test device

References:

1. M. Xia, W. Wu, F. Liu, P. Theato and M. Zhu, *Eur. Polym. J.*, 2015, **69**, 472-482.
2. L. Zhang, C. Pu, L. Zheng and X. Gu, *J. Pet. Explor. & Prod. Technol.*, 2016, **6**, 433-440.
3. S. Neyertz, D. Brown, M. Pilz, N. Rival, B. Arstad, F. Männle and C. Simon, *J. Phys. Chem. B*, 2015, **119**, 6433-6447.
4. I. Jeon, J. Cui, W. R. Illeperuma, J. Aizenberg and J. J. Vlassak, *Adv. Mater.*, 2016, **28**, 4678-4683.
5. B. P. Nair and C. Pavithran, *Langmuir the Acs J. Surf. Colloids*, 2010, **26**, 730-735.