

## Supporting Information

### Simultaneous superior lubrication and high load bearing by dynamic weak interaction of lubricant with mechanically strong bilayer porous hydrogels

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## Experimental Section

### Materials

Acrylic acid (AAc), acrylamide (AAm), N,N'-methylene diacrylamide (MBA) and sodium alginate (SA) were purchased from Sigma-Aldrich. 2-(methacryloyloxy)ethyl trimethylammonium chloride (METAC, 80% in water, TCI), methacrylic acid sodium (MAA, 99.5%, Aldrich) and polyacrylamide (PAAm, Aldrich) were used as received. Ammonium persulphate (APS), sodium chloride (NaCl) and ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were purchased from Tianjin Chemical Reagents Corp. and used without further purification. Deionized water was applied for all polymerization and treatment processes.

### Preparation of dual-crosslinked bilayer porous hydrogels

The bilayer porous hydrogels were prepared using a two-step method. First, monomer AAm (4.2 g, 0.06 mol), different molar ratios of AAc (25%, 30%, 33%, 35%, molar ratio of AAc/AAm), 0.15% (molar ratio of AAc and AAm) chemical cross-linker MBA, 1wt% initiator APS were added into 20 ml saturated NaCl solution. The monomer was dissolved in water, followed by the precipitation of supersaturated NaCl as a pore template (porogen). After vigorously stirred for 1 min with nitrogen, the resulting suspension was poured into a petri dish and plenty of NaCl deposited in the bottom. The radical polymerization reacted at 60 °C for one hour to form a covalently cross-linked hydrogel (S-hydrogel). Then the covalently cross-linked hydrogel was immersed in the 0.15 mol/L  $\text{Fe}^{3+}$  solution for 16 hours to form the secondary ionic

cross-linking, along with the dissolution of NaCl particulates. After that, the hydrogel was immersed in deionized water for 48 hours to remove superfluous Fe<sup>3+</sup>. The dual-crosslinked bilayer porous hydrogel (P-hydrogel) was obtained. The preparation of nonporous hydrogel (N-hydrogel) was similar with the bilayer porous hydrogel just without the addition of NaCl. The reactants were added into 20 ml deionized water to initiate polymerization at high temperature. Then the chemically cross-linked hydrogel was immersed in Fe<sup>3+</sup> solution to proceed the secondary ionic cross-linking, followed by 48 hours' immersion in deionized water to remove superfluous Fe<sup>3+</sup>.

### **Characterization**

The surface morphology of bilayer porous hydrogels were obtained on a JSM-5600LV scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The testing hydrogel samples were prepared by freeze-drying method. The sample was frozen in liquid nitrogen for 2 min, and then dried at -40 °C for 12 h in freeze-drying machine.

The swelling tests were conducted to evaluate the water content of hydrogels. First, hydrogel pieces with different molar ratio of AAc/AAm were immersed in deionized water for more than 24 h in order to ensure their saturation with water. The water flowing on the surface of samples was removed with filter paper, and then the weights of wet gels ( $m_{wet}$ ) were measured by an analytical balance. The weights of dry gels ( $m_{dry}$ ) were obtained after the samples were dried for 24 h at 60 °C in vacuum. The equilibrium water content (EWC) was calculated by equations as following:

$$EWC = \left[ \frac{(m_{wet} - m_{dry})}{m_{wet}} \right] \times 100\%$$

### **Mechanical Measurement**

Tensile tests and compressive tests of the porous and nonporous hydrogels were measured by an electrical universal material testing machine with a 500 N load cell (EZ-Test, SHIMADZU). The samples were cut into a rectangular shape (length 30mm\* width 3mm\* thickness 1.5~2.0mm) for tensile tests and square shape (~1mm\*1mm\* thickness ~1mm) for compressive tests. The crosshead velocity was kept at 100 mm/min for tensile tests and 0.5 mm/min for compressive tests. The nominal tensile

and compressive stress ( $\sigma$ ), nominal strain ( $\epsilon$ ), elastic modulus ( $E$ ) were achieved from the stress-strain curve. The nominal stress and nominal strain of hydrogels were determined by the rupture point of the stress-strain curve and the elastic modulus was calculated from the slope over 5~15% of strain ratio of the stress-strain curve.

### **Friction Characterization**

The bilayer porous hydrogels were immersed in 3% sodium alginate (SA) solution for friction tests. First, the porous hydrogels need to be dehydrated to store and transport lubricant. They were dehydrated by placing them in 20 mL of absolute ethanol several times to ensure replacement of all the water by ethanol. During the dehydration process, the porous hydrogels became much harder. After the dehydration was completed, the porous hydrogels were dried at 70 °C for 1 h. Then the dried porous hydrogels were immersed in 3% SA solution for friction tests, wherein the pores were filled with lubricant through vacuum extraction. For comparison, the other three kinds of lubricants were prepared as follows: 1 g PAAm (2%) was dissolved into 100 mL deionized water and stirred for 2 h at room temperature until the solution became homogeneous; 10 g MAA (or METAC) and 0.1 g APS were mixed together in 100 mL distilled water and the reaction mixture was polymerized in 60 °C for 12 h. Then, the porous hydrogels were immersed in the three polymeric solutions for friction tests.

The friction tests of hydrogels were conducted on a conventional pin-on-disk reciprocating tribometry (UMT-2, CETR) by recording the friction coefficient versus time under different test conditions. Stainless steel ball with a diameter of 6 mm was employed as a pin to slide against bilayer porous hydrogels in 3% SA solution. The distance of one sliding was 10 mm and the friction coefficient was calculated by dividing the friction force by applied normal load. Unless wear-resisting tests, the time of the other friction tests was 5 min and at least two friction tests were repeated for each sample. Normally, friction tests were carried out by sliding a steel ball at a sliding velocity of 0.01 m/s under the load of 10 N.

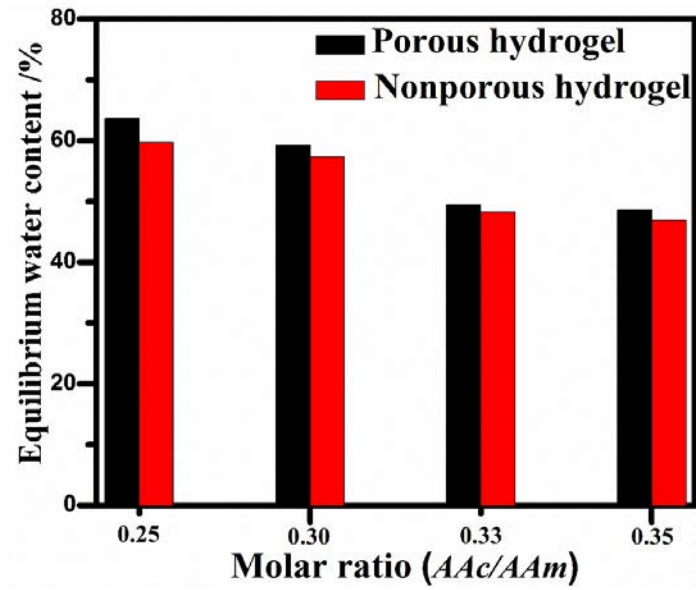


Figure S1. Water content of hydrogels with different AAc/AAm ratios

Table S1. The viscosity of different SA concentration at the shear rate of  $10 \text{ s}^{-1}$ .

Concentration (%)	0.1	0.5	1	3	5
Viscosity (mPa·s)	1.17	3.89	9.60	31.64	184.9

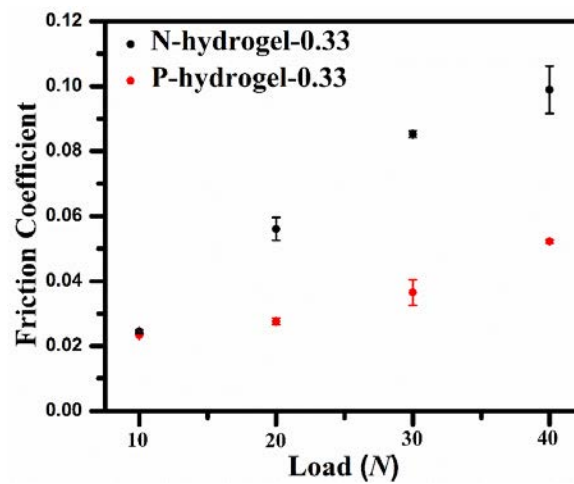


Figure S2. Friction coefficients of nonporous and porous hydrogels for different loads (at  $F=1 \text{ Hz}$ ).