1 # Supporting information

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3 **An impact resistant hydrogel enabled by bicontinuous phase structure and**

4 **hierarchical energy dissipation**

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Synthesis of hydrogels for comparison in impact resistance:

Alginate/PAAm double network hydrogel: The sodium alginate and acrylamide powders were stirred and dissolved in DI water to form a homogeneous solution. Subsequently, the aqueous solution of 3wt% $CaSO_4 \cdot 2H_2O$ was added under vigorous stirring. Finally, the above solution was poured into PTFE mold and polymerized under UV light for 120 min to obtain Alginate/PAAm double network hydrogels.[1]

PAMPS/PAAm double network hydrogel: PAMPS/PAAm double network (DN) hydrogels were synthesized by two-step methods. The aqueous solution containing 1M 2-acrylamido-2-methylpropanesulfonic acid (AMPS), 4mol% N,N'-methylenebis(acrylamide) (MBAA) and 0.1mol% 2-oxodlutaric relative to the amount of AMPS was polymerized under UV for 120 min. Then, the obtained PAMPS hydrogel was immersed in the aqueous solution containing 2M AAm, 0.1mol% MBAA and 0.1 mol% 2-oxodlutaric relative to the amount of acrylamide (Aam) for 24 h. The immersed PAMPS sample was moved into UV light to polymerize AAm, and further form the PAMPS/PAAm double network hydrogel.[2]

PVA hydrogel: 4g Poly(vinyl alcohol) (PVA) was added in 40 mL DI water and the solution was heated at 100℃ for 6h under stirring to form a homogeneous solution. PVA hydrogel was obtained by immersing the PVA aqueous solution in liquid nitrogen until it was completely frozen, and then thawing at room temperature for about 3 hours. This freeze-thaw cycle was repeated three times, then the PVA hydrogel was prepared.[3]

Polyampholyte (PA) hydrogels: Polyampholyte hydrogel were prepared by the polymerization of Sodium p-styrenesulphonate (NaSS) and (methacryloylamino)propyl-trimethylammonium chloride (MPTC). The prepolymer solution contained 2.5M monomers (molar fraction=0.52:0.48), 0.25 mol% APS and 0.1mol% MBAA (relative to the total monomer molar concentration). In addition, 0.5M NaCl was poured to obtain transparent solution. The polymerization was finished at 60 °C for 6h, followed by dialysis with deionized water for 1 week.[4]

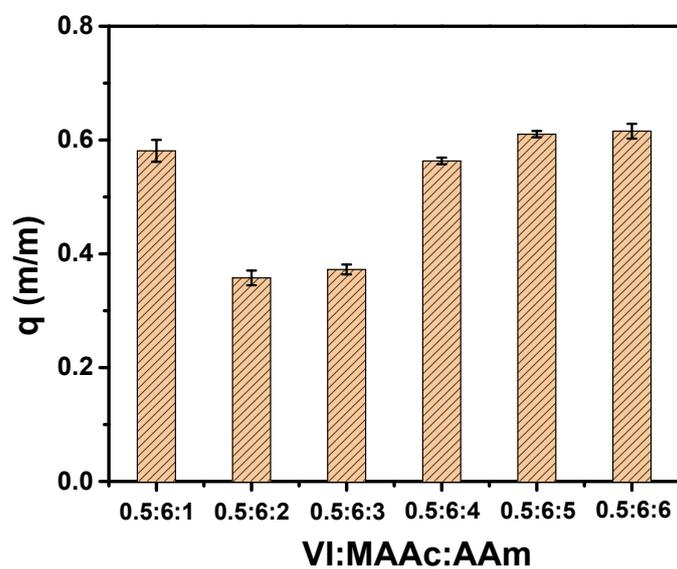These hydrogels were prepared as cylinders with a height of 2.5 mm and a diameter of 5 mm for SHPB tests.

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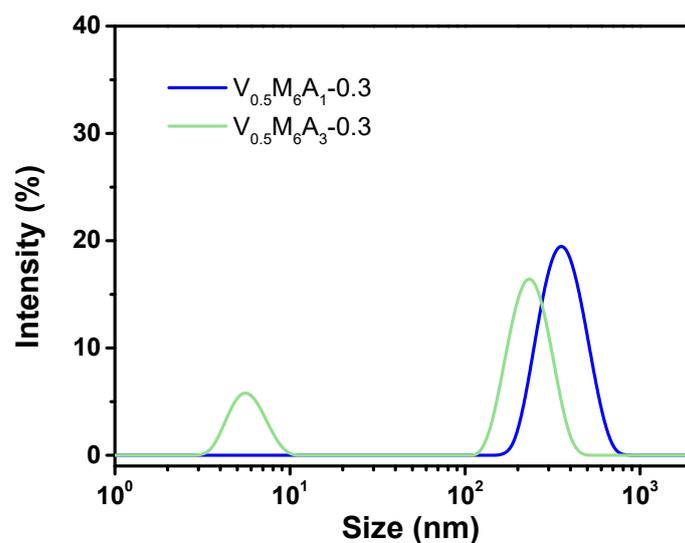
Figure S1. Dynamic light scatting (DLS) measurements for $V_{0.5}M_6A_1$-0.3 and $V_{0.5}M_6A_3$-0.3
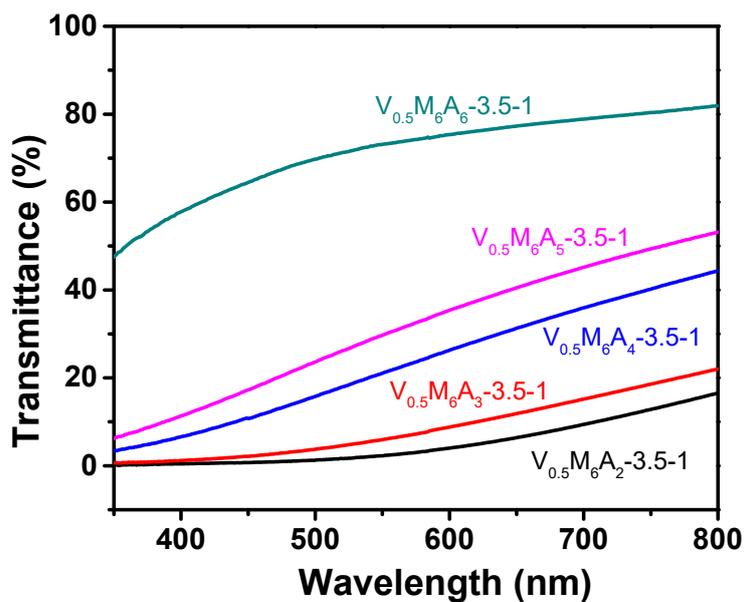
copolymers in aqueous solution.

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Figure S2. Water contents of P(VI-co-MAAc-co-AAm) copolymer hydrogels at the various

molar ratios of VI:MAAc:AAm, where C_m = 3.5 M and f_{MBAA} = 1 mol%.
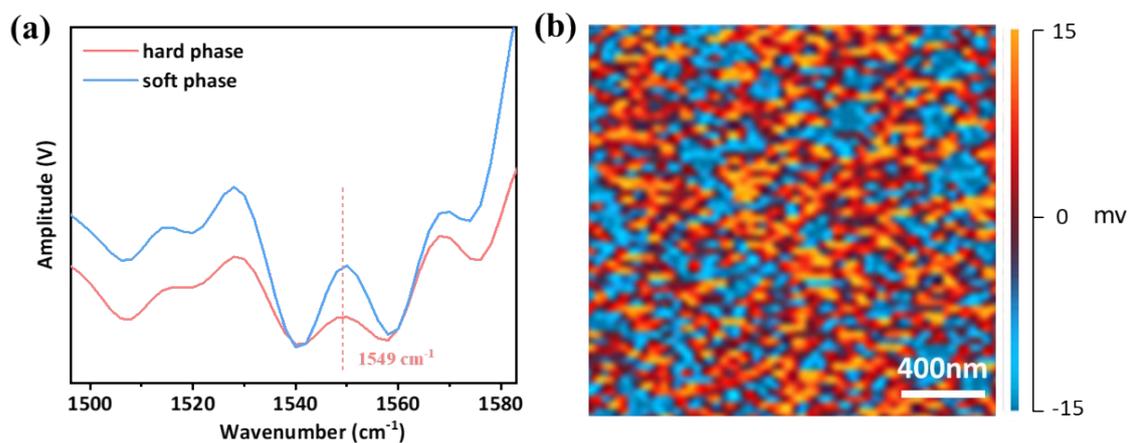
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49 **Figure S3.** Transparency of P(VI-co-MAAc-co-AAc) copolymer hydrogels with various molar
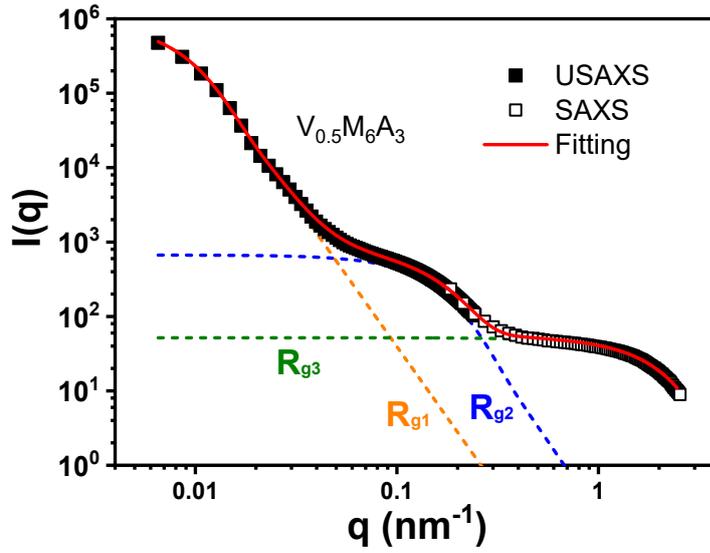
50 ratio of VI:MAAc:AAm.

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54 **Figure S4.** (a) The localized IR spectrum collected at the polymer-hard phase and polymer-

55 soft phase. (b) The chemical mapping at fixed wavenumber of 1549 cm^{-1} highlighting the

56 distributions of VI in the various phases of the $V_{0.5}M_6A_3$-3.5-1 sample.

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Figure S5. SAXS and USAXS profiles of the $V_{0.5}M_6A_3$-3.5-1 hydrogel. The dash line denotes the fitting results using the unified Guinier/power-law approach,[5-7]

$$I(q) = \sum_{i=1}^{N} \left(G_i \exp\left(\frac{-q^2 R_{g,i}^2}{3} \right) + exp\left(\frac{-q^2 R_{g,i+1}^2}{3} \right) B_i q_i^{* -P_i} \right)$$

where G is the Guinier prefactor and B is a prefactor specific to the type of power law scattering, specified by the regime in which the exponent P, falls. $R_{g,i}$ and $R_{g,i+1}$ describe average size of large-scale and small-scale structures. And q_i^* is defined by,

$$q_i^* = \frac{q}{erf\left(\frac{kqR_{g,i}}{\sqrt{6}} \right)^3}$$

and the value of k is 1 for solid structural levels and 1.06 for mass fractal levels. It is apparent that the scattering curve can be well fitted by the above equation, and three characteristic sizes were obtained. In the low-q region, the characteristic size R_{g1} ~410.4 nm, which closes to the distance between adjacent polymer-hard phase (or polymer-soft phase) from AFM nanomechanical mapping, The specific size R_{g2} (~31.1 nm) and R_{g3} (~3.01 nm) may stem from

70 the hydrogen bond aggregates in the polymer-hard phase and polymer-soft phase, respectively.
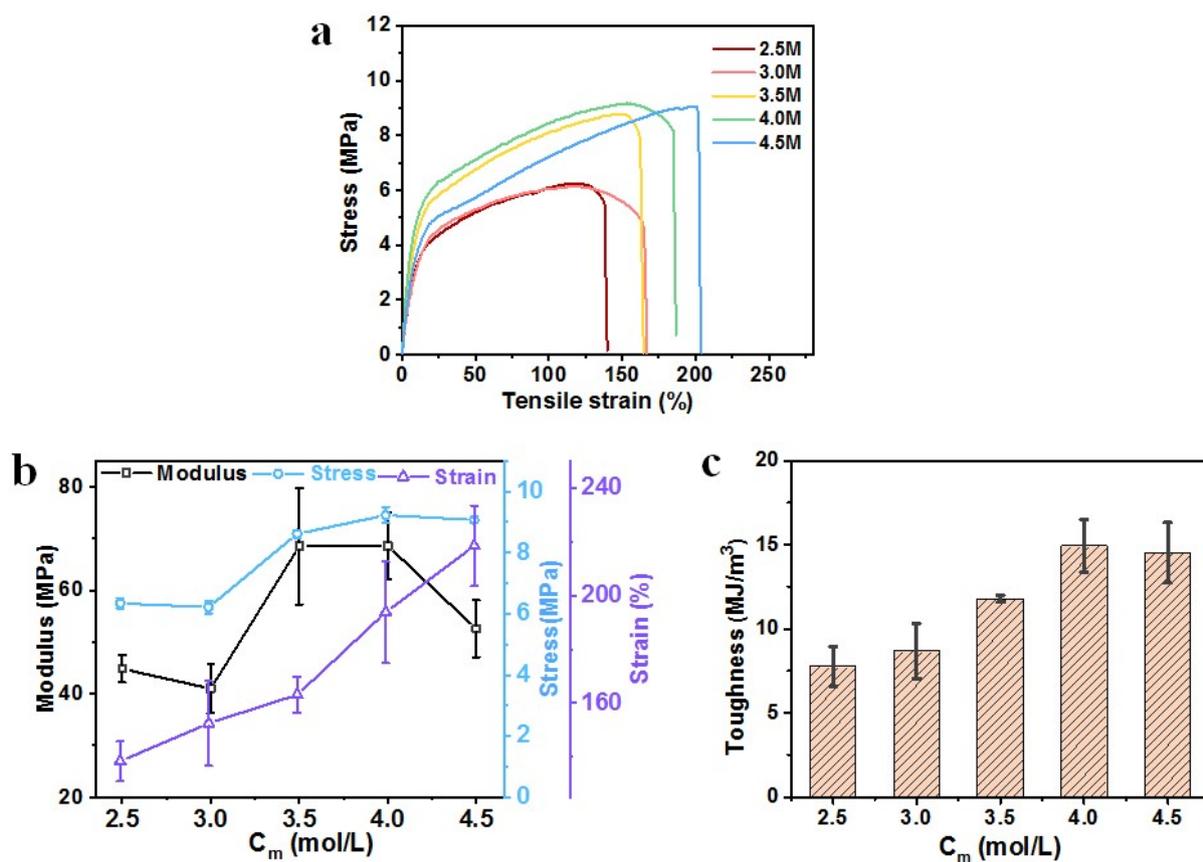
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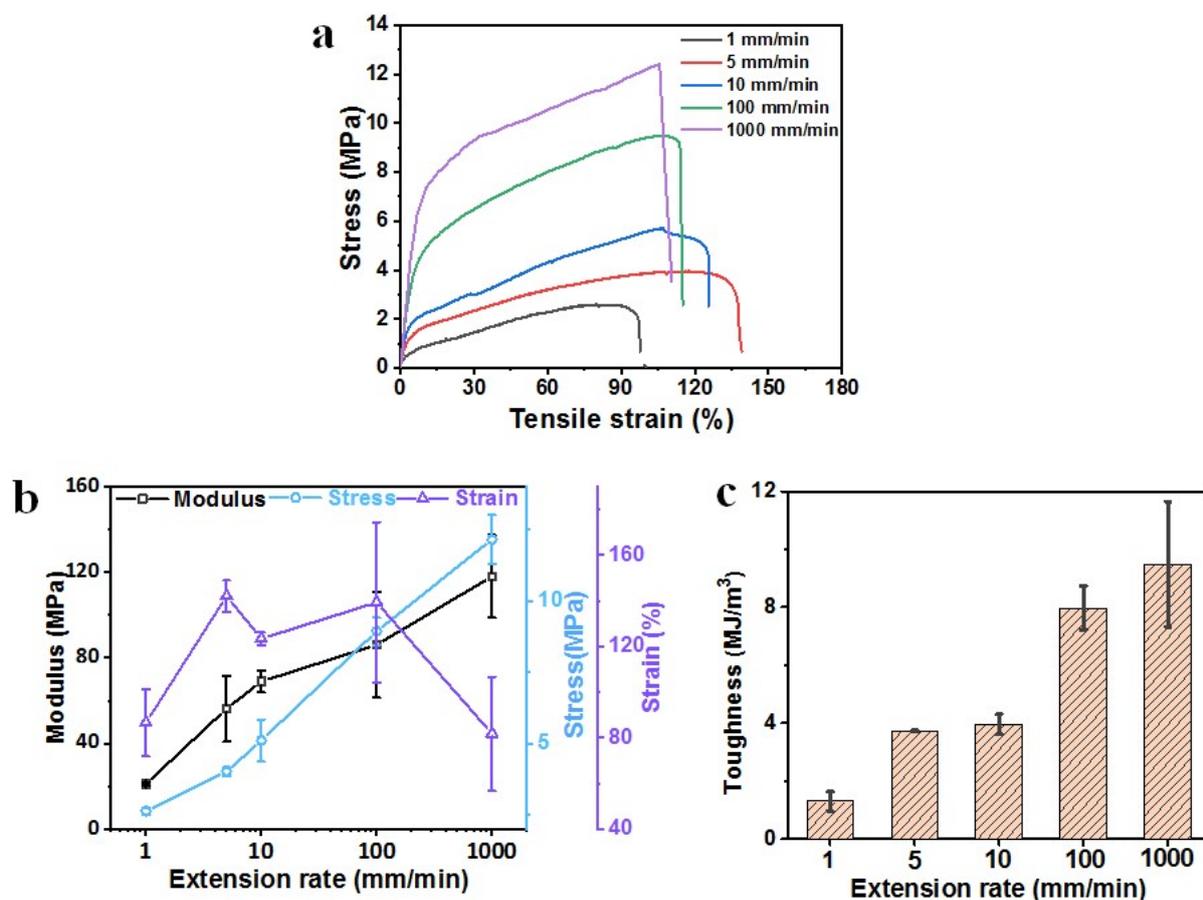
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73 **Figure S6.** (a) Tensile stress-strain curves of $V_{0.5}M_6A_3$-3.5-1 hydrogel at various extension

74 rates. Effects of extension rates on (b) Young's modulus, fracture strength, fracture strain, and
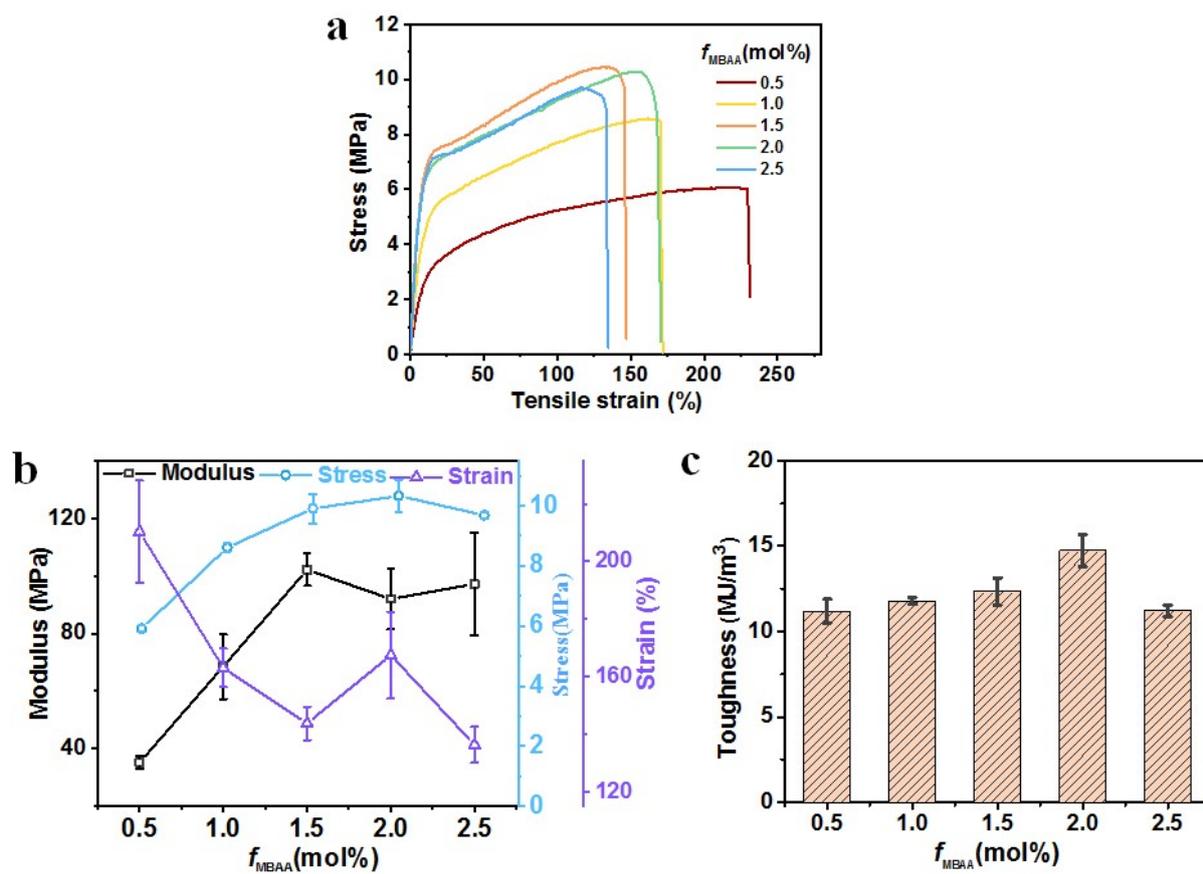
75 (c) toughness.

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Figure S7. (a) Tensile stress-strain curves of the $V_{0.5}M_6A_3$ hydrogels with varying monomer amounts from 2.5 M to 4.5 M. The effects of various monomer amounts on (b) Young's modulus, fracture strength, fracture strain, and (c) toughness, where the crosslinking agent was fixed at 1 mol% based on the monomer contents.
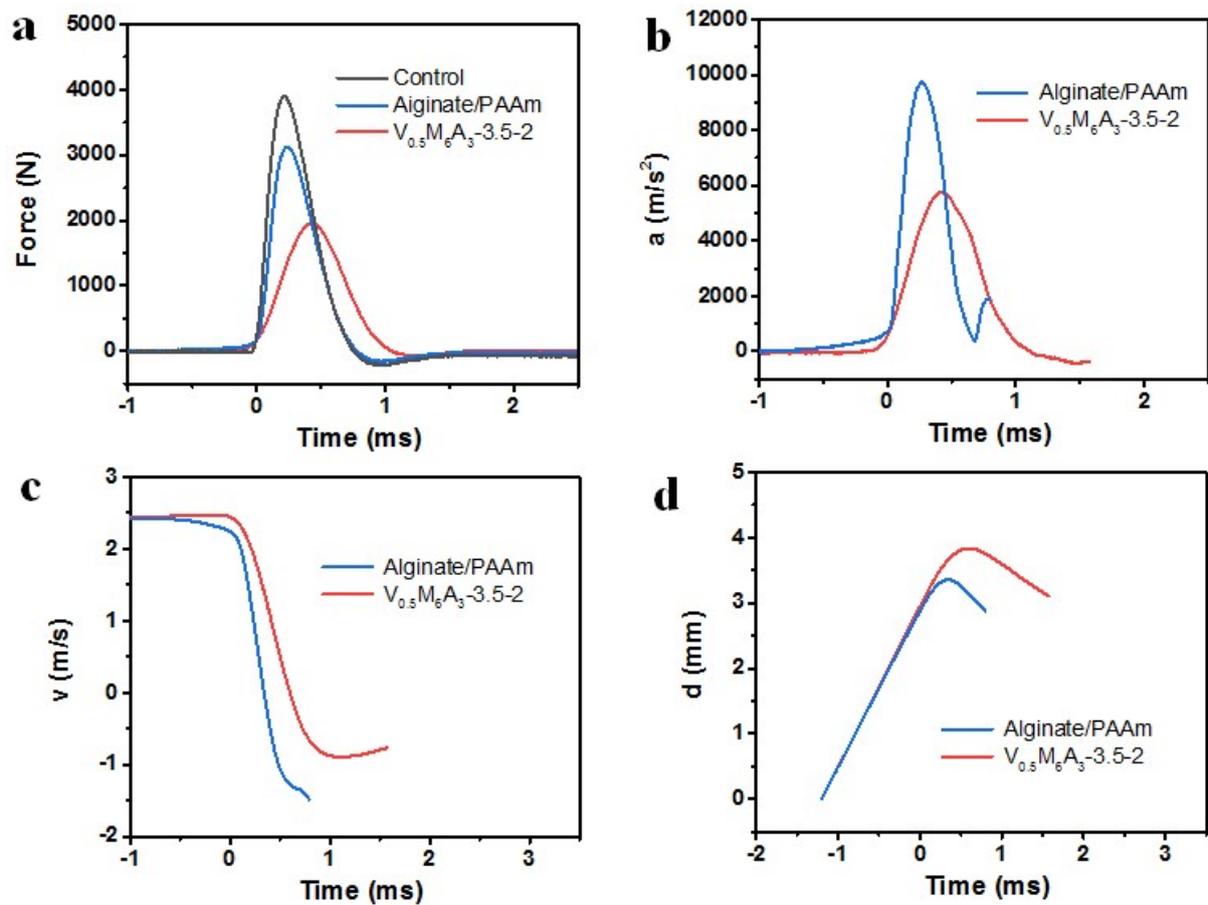
Figure S8. (a) Tensile stress-strain curves of the $V_{0.5}M_6A_3$ hydrogels with varying crosslinking agent contents from 0.5 to 2.5 mol% based on the total monomer amounts. The effects of various crosslinking agents on (b) Young's modulus, fracture strength, fracture strain, and (c) toughness, where the total monomer amount was fixed at 3.5 M.

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92 **Figure S9.** The falling hammer tests, (a) force–time, (b) mass acceleration–time, (c) velocity–

93 time and (b) displacement–time curves for the $V_{0.5}M_6A_3$-3.5-2 and alginate/PAAm double

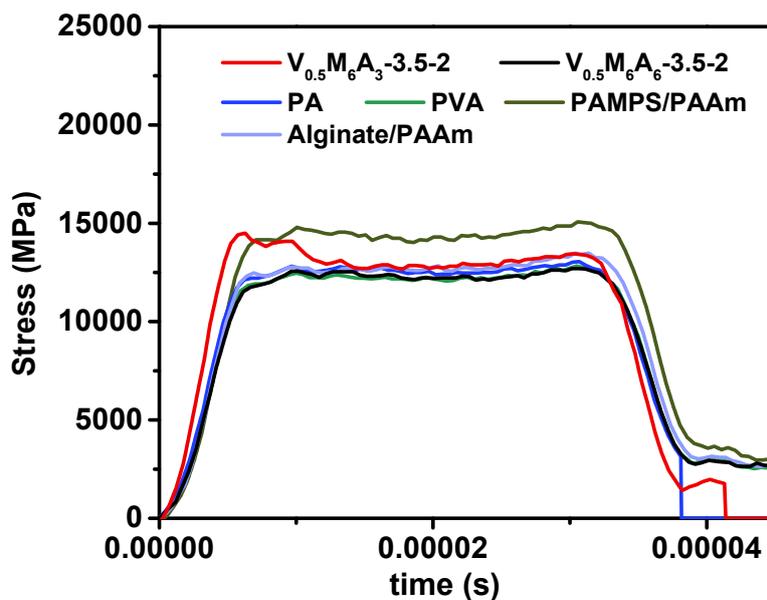94 network hydrogel, where the height of falling hammer is 30 cm.

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Figure S10. Strain rate of SPHB tests.

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