Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Physical hydrogels constructed on macro-cross-linking cationic polysaccharide with tunable, excellent mechanical performance

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Contents:

Experimental Section

Materials

Chitosan (Degree of deacetylation >90.0% and viscosity<100.0cps, Shanghai Lanji Technology Development Co., Ltd), potassium persulfate (KPS, A.R., Shanghai Chemical Reagent Corporation, Shanghai) and N,N'-methylene bisacryl- amide (BA, Aldrich, 99+%, electrophoresis grade) were bought from reagent supplier.

Methacrylic acid (MAA, purity>99.0%), acrylic acid (AA, purity>99.0%), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, purity>98.0%), 2-hydroxylethyl acrylate (HEA, purity 96.0%) and 2-hydroxylethyl methacrylate (HEMA, purity 96.0%) were purchased from Aladdin Industrial Corporation. N,N-dimethylacrylamide (DMAM, purity>99.0%) was bought from TCI (Shanghai) Development Co., Ltd. All were used as received without further purification.

Preparation of hydrogels

Chitosan, MAA (or AA or AMPS), hydrophilic monomer was mixed with water under magnetic stirring until a transparent solution was obtained. Then KPS was fed in and the solution was transferred to cylindrical glass vessels with different diameters of 15mm and 10mm respectively. N_2 was bubbled into the vessels for at least 30 min to purge O_2. Afterwards, the reaction was kept at 25°C for 24h. For comparison, traditional chemically crosslinked hydrogel was prepared using BA as a bifunctional crosslinker instead of chitosan.

Characterization

IR characterization. CMAA was obtained by dropping MAA into an aqueous dispersion of chitosan firstly till complete dissolution of chitosan, and then freeze-drying the solution for 48h. The prepared PMAA-CMAA hydrogels were soaked in distilled water for 48h to remove unreacted monomers and KPS, with water being changed every 12h. Afterwards, the purified hydrogels were freeze-dried for 48h. MAA, chitosan, CMAA and PMAA-CMAA hydrogels was embedded in KBr disks respectively. The IR spectrogram was recorded on a Nicolet 5700 spectrometer.

Compressive tests. The uniaxial compressive measurements were performed on a WDW-5T electronic universal testing machine (Jinan Heng Rui Jin Testing Machine Co., Ltd, China) equipped with a 5000N load cell. Samples with a diameter of 15mm and a height of ~10mm were coated with a layer of silicon oil before testing to prevent water evaporation. The compressing rate was 5 mm·min-1 in all measurements. The stress (σc) and strain (εc) were obtained respectively according to equations (1) and (2).

$$\sigma_c=F_c/A \qquad (1)$$

$\varepsilon c=(H_0-H_i)/H_0\times100\%$ (2)

where Fc was the applied froce (N). A was the initial cross-sectional area of hydrogel sample. Hi was the height after compression and H0 the height at initial stage (mm). For each sample, a minimum of three measurements was taken, and the average result was calculated.

Cyclic compressive tests were carried out by performing subsequent trials immediately following the initial loading with the same specimen at a crosshead speed 5mm min^{-1}.

Tensile Tests. The uniaxial tensile tests were carried out on a WDW-5T electronic universal testing machine (Jinan Heng Rui Jin Testing Machine Co., Ltd, China) equipped with a 100N load cell using cylindrical specimens with a diameter of 10mm and a length of 80mm at a crosshead speed of 100mm·min^{-1}. Samples were coated with a layer of silicon oil before testing. The gauge distance was kept at ~10mm. The tensile stress σ_t is defined as F_t/A (A is the initial cross-sectional area of hydrogel sample, F_t is the applied force.). The tensile strain ε_t is defined as the ratio of length change to the initial gauge length, $\varepsilon_t= [(l-l_0)/l_0] *100\%$ (l_0 is the initial gauge length, l is the gauge length during testing). Tensile strength (σ_b) and tensile fracture elongation (ε_b) is the tensile stress and strain at which the specimen breaks, respectively. The tensile elastic modulus (or Young's modulus) is estimated as the slope between 10~30% ε_t. The fracture energy is estimated by the integrated area under stress-strain curve.

Cyclic loading-unloading tests were carried out on the same sample after different recovering time at a crosshead speed of 100mm·min^{-1}.

Decisive role of ionic association. To verify the role of ionic association inside the hydrogel network, polymerization of acrylamide (AM) was conducted in aqueous solution of chitosan complex with acetic acid under the same condition as in the preparation of PAM-$CMAA_{0.22-4.17-20}$ hydrogel, except that unsaturated MAA was substituted by acetic acid. After reaction, the obtained product (coded as PAM-CHAc) was soaked in distilled water to examine its change with time for comparison with PAM-$CMAA_{0.22-4.17-20}$ hydrogel.

Results and discussion

Supporting Figures

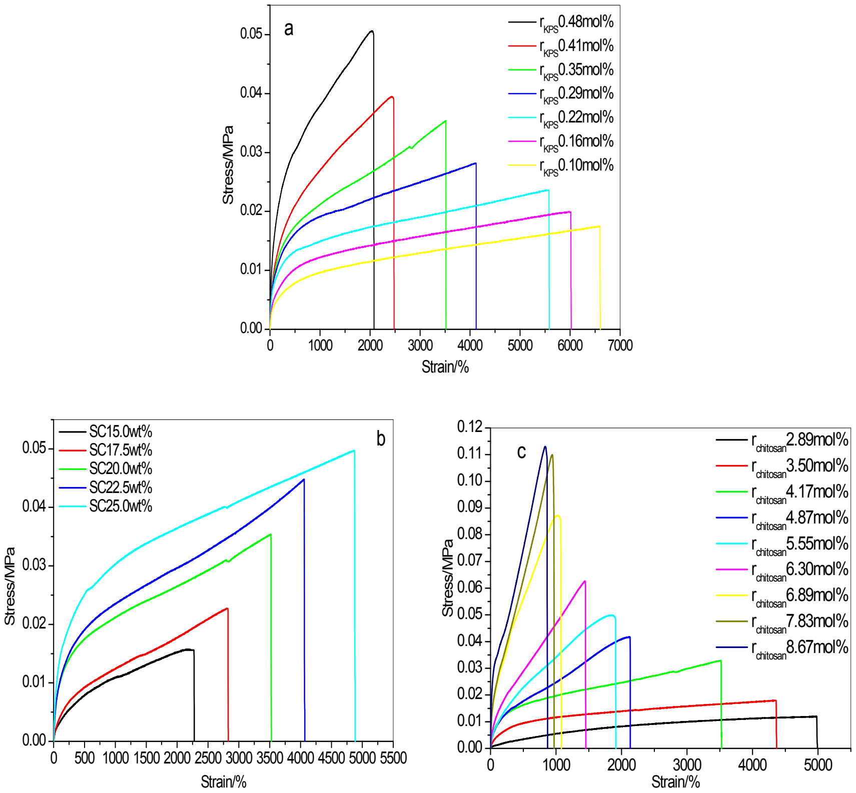

Figure SI 1 Tensile stress-strain curves of hydrogels prepared with different a) KPS content (SC20wt% and $r_{chitosan}$ 4.17mol%), b) solids content (KPS0.22mol% and $r_{chitosan}$ 4.17mol%), c) chitosan ratio (SC20wt% and KPS0.22mol%)

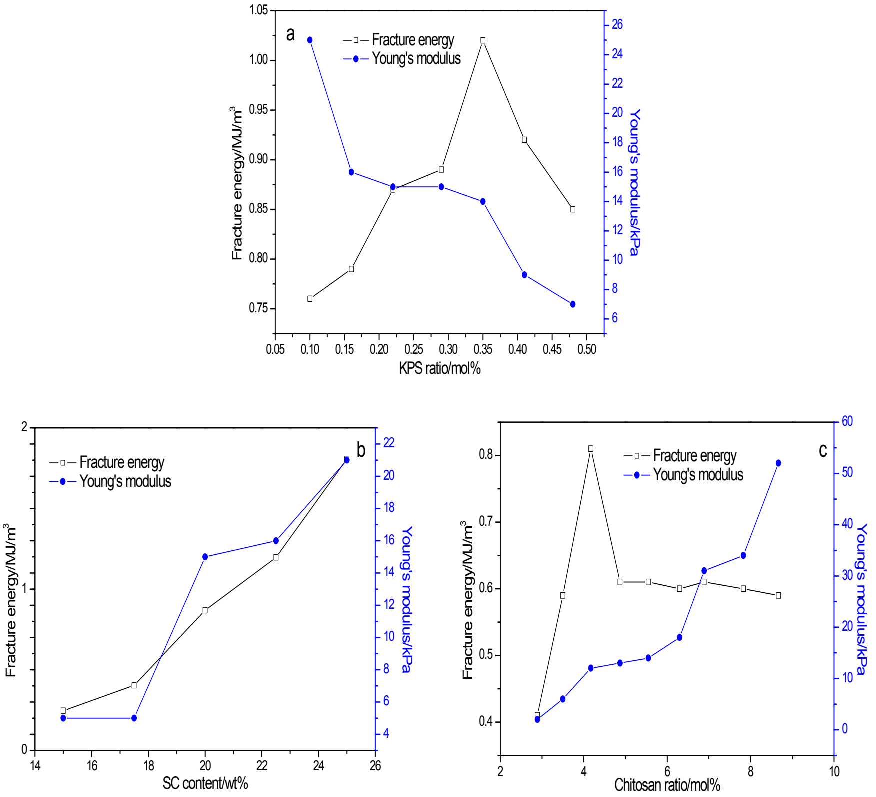

Figure SI 2 Influence of a) KPS content, b) solids content and c) chitosan ratio on the fracture energy and Young’s modulus

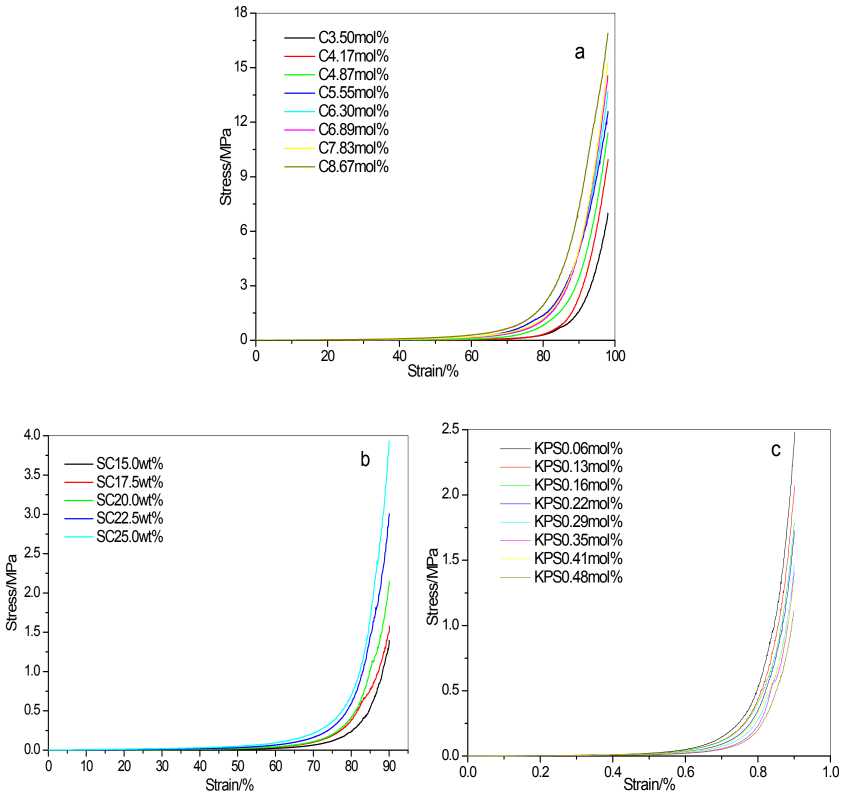

Figure SI 3 Compressive stress-strain curves of the prepared hydrogels with different a) chitosan ratio (compressed to 98% strain, SC20wt% and r_{KPS} 0.22mol%), b) solids content (compressed to 90% strain, r_{KPS}0.22mol% and $r_{chitosan}$ 4.17mol%), c) KPS content (compressed to 90% strain, SC20wt% and $r_{chitosan}$ 4.17mol%)

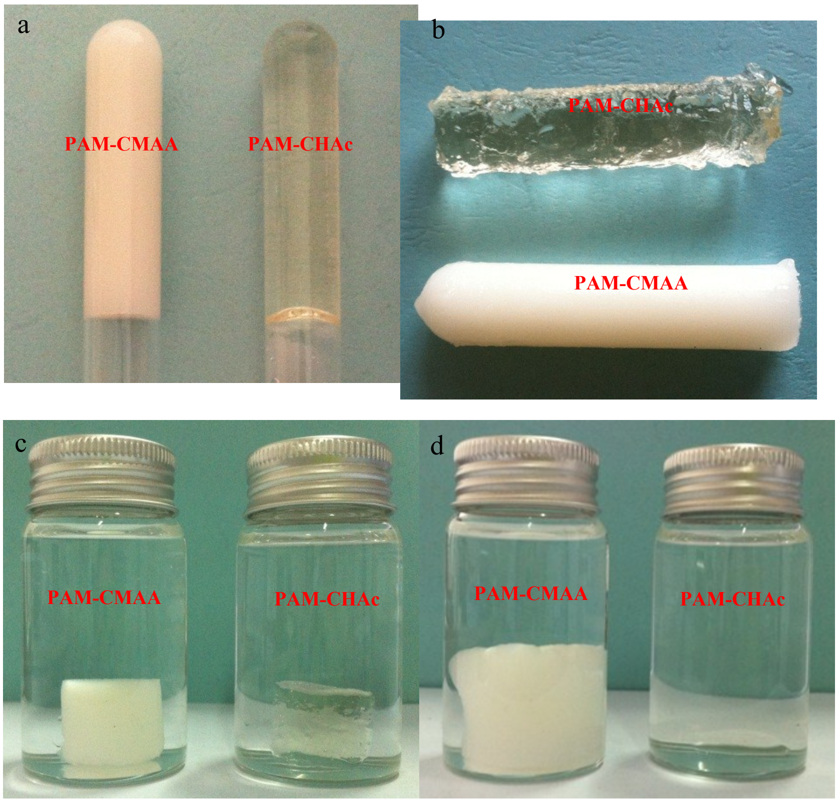

Figure SI 4 a) and b) The appearance of prepared PAM-CHAc and PAM-CMAA; c) Initial samples of PAM-CHAc and PAM-CMAA hydrogel soaked in water; d) PAM-CHAc and PAM-CMAA samples after 24h’s soaking in water.

PAM-CHAc obtained appeared in gel-state like PAM-CMAA hydrogel. However, unlike the tough and slippery PAM-CMAA hydrogel, the obtained PAM-CHAc is viscous and soft (Fig. SI 4a and 4b). The volume of PAM-CMAA hydrogel soaked in distilled water enlarges due to swelling, while the size of PAM- CHAc decreases gradually as a result of dissolution in water (Fig. SI 4c and 4d). The gel-state of PAM-CHAc can be attributed to the strong intermolecular H-bondings among high concentration of PAM and chitosan, which is apt to disrupt in water. In contrast, PAM-CMAA hydrogel doesn’t dissolve in water but retains the gel state as there are strong electrostatic interactions inside the network except for H-bondings, indicating the decisive role of ionic association inside the hydrogel.