Soft Matter



SUPPORTING INFORMATION

Tough dual nanocomposite hydrogels with inorganic hybrid crosslinking

Received 00th January 20xx, Accepted 00th January 20xx

Juan Du, Shimei Xu*, Shun Feng, Lina Yu, Jide Wang*, and Yumei Liu

DOI: 10.1039/x0xx00000x

www.rsc.org/

Supporting Information

SI 1: Experimental procedures

Preparation of dual nanocomposite hydrogels:

Poly(AAm-co-MAA)/Laponite/SiO₂ dual nanocomposite hydrogel was prepared by in-situ radical polymerization and sol-gel technique simultaneously. Typically, a transparent dispersion consisting of water (5.0 g), Laponite (0.1 g), AAm (2.5 g) was prepared under continuous stirring for 20 min at room temperature, then a mix dispersion of MPTMS (0.5 g) and MAA (4.3 g) ultrasonated for 3 min before was added into the Laponite dispersion and stirred for another 20 min, followed by 0.37 wt% of initiator KPS (relative to the weight of MAA and AAm). Finally, the solution was transferred to a sealed glass tube and the polymerization was carried out at 50°C for 48 h to obtain the dual nanocomposite hydrogel.

As a control, nanocomposite hydrogel poly(AAm-co-MAA)/SiO₂ and poly(AAm-co-MAA)/Laponite were fabricated in the same procedure mentioned above in the absence of Laponite or MPTMS respectively. Organically crosslinking gel was prepared according to the identical procedure above except 8.82 wt% N,N'-methylene-bisacrylamide (relative to the weight of MAA and AAm) was used instead of MPTMS and Laponite. Characterization:

FTIR measurements were performed on a Bruker EQINOX55 FTIR spectrometer. All spectra in the range 400-4000 cm⁻¹ with 2 cm⁻¹ spectral resolution were obtained from compressed KBr pellets in which the samples were

Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, People's Republic of China; Fax: + 86 991 8581018; Tel: + 86 991 8583972; E-mail: <u>xushmei@hotmail.com</u>, <u>awangid@xju.edu.cn</u>

 $[\]dagger$ Electronic Supplementary Information (ESI) available: Experimental procedures; Retention time dependence of transparence and viscosity; TEM images of poly(AAm-co-MAA)/SiO_ nanocomposite hydrogel; TEM images of poly(AAm-co-MAA)/Laponite/SiO_ dual nanocomposite hydrogel treated by NaOH. See DOI: 10.1039/x0xx00000x

SUPPORTING INFORMATION

Soft Matter

evenly dispersed. XRD was carried out using a Rigaku D/max 2000 H X-ray diffractometer (40 kV, 30 mA) and a curved graphite crystal monochromator Cu K α at a scanning rate of 0.5°/min. ²⁹Si solid-state NMR experiments were carried out on a Bruker AVANCE III 400 WB spectrometer operating at 79.5 MHz by use of cross-polarization from proton: the spin rate was 10 kHz, the contact time was 5 ms, and the recycle delay was 1 s. The ²⁹Si chemical shift was referenced to tetramethylsilane (TMS). TEM was conducted on a Hitachi H-600 transmission electron microscope with an accelerating voltage of 100 kV. Ultrathin films were prepared for TEM observation by cutting dried gels embedded in epoxy resin using an ultramicrotome. The HRTEM (JEM-2100, JEM) was used to further observe the microstructure of poly(AAm-co-MAA)/Laponite/SiO₂ dual nanocomposite hydrogel and HRTEM coupled with EDS was used to evaluate the elemental compositions of this hydrogel. HRTEM measurements were performed at the accelerating voltage of 200 kV. Prior to the HRTEM measurement, the hydrogel samples were ground and dispersed in acetone followed by ultrasonication, then dropped a few drops of dispersions onto holey copper grids and dried in the ambient condition. To further classify the dispersion of inorganics, the hydrogels were treated by HF (20 wt%) or NaOH (30 wt%) solutions for a certain time, then washed with deionized water for several times, finally dried on an oven at 80°C until a constant weight were obtained. The samples were subsequently ground and dispersed in acetone followed by ultrasonication prior to TEM observation. The morphology of the mixture of AAm/MAA/Laponite/SiO₂ was investigated by FESEM (S-4800, Hitachi) at the accelerating voltage of 20 kV and the samples were prepared by drop casting a few drops of dispersions onto glass slides and dried in the ambient condition.

Compression strength of as-prepared dual nanocomposite hydrogel (7 mm diameter×10 mm length) was evaluated using a H5KT testing system (Tinius Olsen) at room temperature and the crosshead speed was 10 mm/min. The residual deformation of dual nanocomposite hydrogel was performed on the same testing system at room temperature. The gel was firstly compressed to 100% of strain by a speed of 10 mm/min, and then the gel was unloaded for 1 h. The residual deformation set was calculated by measuring the variation in height across the original height and the height of the gel after released for 1h. The residual deformation (%)= [(initial height of the gel (mm)-the height after release (mm))/initial height of the gel (mm)]*100%. Cyclic compression-recovery test was conducted with 5 N preforce and 5 mm/min compression rate.

Tensile measurements were also performed on as-prepared gels of the same size (5.5 mm diameter × 60 mm length) with above-mentioned testing system at room temperature. The sample length between the jaws was 20 mm and the crosshead speed was 100 mm/min. The tensile strain was taken as the length change related to the original length and the tensile strength was estimated on the cross section of the original sample. All the samples were performed in triplicate, and the average values are reported.

SI 2: Retention time dependence of transparence and viscosity



Fig. S1 Retention time dependence of transparence (I) and viscosity (II) for: a-Laponite dispersion (2 wt%, against to water), b-Laponite/AAm dispersion, c-Laponite/MPTMS/AAm/MAA mixture.

SI 3: TEM images of poly(AAm-co-MAA)/SiO₂ nanocomposite hydrogel



Fig. S2 TEM images of poly(AAm-co-MAA)/SiO₂ nanocomposite hydrogel.

SI 4: TEM images of poly(AAm-co-MAA)/Laponite/SiO $_2$ dual nanocomposite hydrogel treated by

NaOH



Fig. S3 TEM images of poly(AAm-co-MAA)/Laponite/SiO₂ dual nanocomposite hydrogel treated by NaOH (30 wt%).