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Research paper

Stretchable dual nanocomposite hydrogels strengthened by physical interaction between inorganic hybrid crosslinker and polymers

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ABSTRACT

Stretchable hydrogels have been developed by fabricating a dual nanocomposite structure by polymerization of hydrophilic monomers and sol-gel reaction of tetraethyl orthosilicate (TEOS) in the presence of Laponite. The mechanical enhancement of the hydrogels was markedly influenced by monomer structure and contents of TEOS and Laponite. The strong interaction between *N*-isopropylacrylamide (NIPAM) and inorganic hybrid crosslinker was examined by dyeing experiment, transparency and fluorescence measurement of Laponite/SiO_2/monomer dispersions. This accounted for the excellent mechanical properties of Laponite/SiO_2/PNIPAM dual nanocomposite hydrogel. Uniaxial tensile tests showed improved tensile property (elongation at break: 1845 ± 3.46%; fracture stress: 271.41 ± 6.26 kPa), and elastic modulus of the hydrogel significantly increased with TEOS contents and reached 26.69 ± 6.13 kPa at 10:1.0 of $m_{Laponite}$:m_{TEOS}. Fracture compression strength could reach 7.06 ± 1.25 MPa (fracture energy: 1185.53 ± 5.57 J m^{-2}), meanwhile it showed remarkable fatigue resistance. The embedded nano-SiO_2 accounted for the significantly improved stiffness of the hydrogels. Moreover, the dual nanocomposite mechanism (the covalent bonding of SiO_2 with Laponite and strong physical interaction of polymer chains with inorganic hybrid crosslinker) made a big contribution to the toughness of the gels. The noncovalent entanglements between SiO_2 and polymer chains could promote both strength and elongation of the hydrogel, but the effect is not as notable as the covalent one.

1. Introduction

Nanocomposites of polymer and inorganic particles have been drawing extensive research enthusiasm and efforts (Kao et al., 2013; Kumar et al., 2013; Lu and Yin, 2012). Upon incorporation of inorganic particles, the reinforcement of nanocomposite produces increased elastic modulus compared with the pristine polymer (Lin et al., 2012; Mu and Winey, 2007; Wan and Chen, 2012). Nanocomposite hydrogels, comprising unique organic/inorganic network structures by introduction of multifunctional crosslinker (e.g., Laponite layers), is commonly considered as one of the most promising strategies for mechanical enhancement of hydrogels (Chang et al., 2010; Chen et al., 2013; Du et al., 2015a, 2015b, 2016; Haraguchi and Takehisa, 2002; Li et al., 2009; Shen et al., 2014; Wang et al., 2010, 2012a; Xavier et al., 2015; Yang et al., 2006, 2016). In the nanocomposite hydrogels, multiple polymer chains with nonuniform lengths strongly adsorb on adjacent Laponite surfaces and the Laponite work as physical crosslinking junctions. In general, each Laponite layer may adsorb several polymer chains, while a single ultralong polymer chain (about 10^6 g mol^{-1}) may adhere onto several Laponite layers, resulting in the formation of physical networks (Haraguchi et al., 2010). Therefore, as the polymer networks are deformed, relatively short chains may be ruptured or detached from the multifunctional crosslinkers but the long chains can still maintain the elasticity of the hydrogels. However, the Laponite-based nanocomposite hydrogels usually lack of high stiffness and toughness due to sole enhancement mechanism (Du et al., 2016; Zhao, 2014). Besides, owing to the special colloid property of Laponite, gelation or aggregation may be caused when ionic monomers are added into Laponite dispersion. As a result, it is hard to proceed the polymerization process to obtain mechanically strong and optically transparent ionic nanocomposite hydrogels due to heterogeneous dispersion. More efforts are needed to enrich the current understanding of the toughening mechanism in order to boost the development of novel tough hydrogels (with fracture energy above 1000 J m^{-2}) that meet demands from industrial and

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biomedical applications (Henderson et al., 2010; Sun et al., 2012). Silica nanoparticles have usually been used as reinforcing agents by acting like weak physical crosslinks within a strong chemical network (Ashraful et al., 2013; Lin et al., 2011; Petit et al., 2014; Rose et al., 2013; Shi et al., 2009, 2014; Yan et al., 2015; Yang et al., 2012, 2013a, 2013b). The resultant silica-based nanocomposite hydrogels exhibited high stress due to the strong interaction between polymer chains and silica particles, but the silica-based hydrogel was generally brittle due to poor compatibility and heterogeneous distribution. Recently a tough hydrogel with an inorganic hybrid crosslinking network was prepared through simultaneous sol-gel technique of vinyl-functionalized silane and free radical polymerization of monomers in the presence of Laponite (Du et al., 2016). Covalently bonded Laponite and SiO_2 were used as multifunctional hybrid crosslinker, in which the exfoliated nano-Laponite absorbed polymers through noncovalent bonds while the nanoscaled SiO_2 was embedded into the polymer matrix by covalent bonds. The resultant dual nanocomposite hydrogel showed both high stress and toughness.

In order to further explore the effect of physical interaction between polymers and SiO_2 on mechanical property of the dual nanocomposite hydrogel indeed, in this paper, this line of investigation by choosing TEOS (without vinyl group) as silane to construct inorganic hybrid crosslinking network was extended. In this case, SiO_2 absorbed polymers through noncovalent bonds instead of covalent bonds in previous work. For this purpose, dual nanocomposite hydrogels were obtained by simply mixing an aqueous solution of hydrophilic monomer and TEOS in presence of Laponite. Laponite acts not just a functional physical crosslinking agent, but also works as a catalyst for the hydrolyzation of TEOS (Chen et al., 2014). The influences of monomer structure and contents of Laponite and TEOS on the mechanical behavior of the hydrogel were addressed.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) was purchased from Sigma-Aldrich Co., *N*-isopropylacrylamide (NIPAM) was bought from J & K Scientific, acrylamide (AM) was supplied by Tianjin Yongsheng Fine Chemicals Co., pyrene and *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were provided by Aldrich Chemical Co., potassium peroxydisulfate (KPS) was purchased from Beijing Beihua Fine Chemicals Co., Laponite XLG [$Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$] was provided by Rockwood Ltd. and tetrasodium pyrophosphate ($Na_4P_2O_7$) was provided by Shanghai Kechang Fine Chemicals Company. All reagents were used as received without any further purification. Deionized water was used in all experiments.

2.2. Hydrogel synthesis

The dual nanocomposite hydrogels were prepared by simultaneous free radical polymerization and sol-gel technique. Typically, water (10.0 g), Laponite (0.5 g), $Na_4P_2O_7$ (0.0384 g), NIPAM (1.0 g) and TEOS (0.5 g) were mixed under stirring magnetically at room temperature for 24 h until a transparent and uniform dispersion was obtained. Then, initiator KPS (2 wt%, 1.0 mL) and catalyst TEMED (50.0 μL) were added into the dispersion with stirring, respectively. Afterwards, the pre-polymerization dispersion was transferred to a sealed glass tube and the polymerization was carried out at room temperature for 72 h to obtain the Laponite/SiO_2/PNIPAM dual nanocomposite hydrogel. Laponite/SiO_2/PAM dual nanocomposite hydrogel was fabricated in the same way aforesaid. As a control, Laponite/PNIPAM nanocomposite hydrogel was synthesized in a similar manner except for the free of TEOS. The as-prepared hydrogels were soaked in excess deionized water, which was exchanged daily for 1 week, then dried until a constant mass was obtained.

2.3. Characterization

Dispersion stability and transmittance changes of Laponite/SiO_2/NIPAM and Laponite/SiO_2/AM dispersions were characterized by transmittance at wavelength 610 nm for 60 min with a built-in temperature controlling set, and all recorded on a spectrophotometer (TU-1810, Pgeneral). The transmittance, zeta potential, and viscosity of the dispersions were measured with UV spectrophotometer (722N, Shanghai Precision & Scientific), zetasizer (Nano-ZS90, Malvern), and viscosity meter (DV-II + PRO, Brookfield), respectively. The morphology and dispersion of the dispersions were investigated by field emission scanning electron microscopy (FESEM, S-4800, Hitachi) and transmission electron microscopy (TEM, H-600, Hitachi). FESEM measurements were performed at the accelerating voltage of 20 kV, while TEM were conducted with an accelerating voltage of 100 kV. The dispersions were added dropwise onto copper wire mesh and dried at room temperature, then coated with gold prior to TEM and FESEM analysis. The high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEM) was used to observe the microstructure of Laponite/SiO_2/PNIPAM dual nanocomposite hydrogel at the accelerating voltage of 200 kV. Ultrathin films were prepared for HRTEM observation by cutting dried gels embedded in epoxy resin using an ultramicrotome. Fourier transform infrared (FTIR) spectra of the dual nanocomposite hydrogels were performed by Fourier transform infrared spectroscopy (EQINOX55, Bruker). All spectra in the range 400–4000 cm^{-1} with 2 cm^{-1} spectral resolution were obtained in transmission mode from compressed KBr pellets in which the samples were evenly dispersed. The sample concentration was about 0.7%, and 128 scans were accumulated. Dynamic rheological measurement was performed with a stress-controlled rheometer (Discovery HR-1, TA) in the oscillation mode. The gelation processes were carried out in the rheometer between the parallel plates (25 mm) with a gap size of 1000 mm at 25 °C. Deformation amplitude and frequency were set to 1% and 1 Hz, to ensure that the oscillatory deformation was within the linear viscoelastic regime, where the dynamic storage modulus (G') and loss modulus (G'') were independent of strain. Scanning electron microscopy (SEM) images of the hydrogels were obtained using a scanning electron microscope (TM3030, Hitachi) at an accelerating voltage of 20 kV. The samples were immersed in deionized water to reach equilibrium prior to freeze drying (FD-1C-50) for 48 h. Afterwards, the dry hydrogels were coated with gold prior to SEM analysis. The hydrogel powders were completely dried before ^{29}Si solid-state NMR and X-ray diffraction experiments. ^{29}Si solid-state NMR experiments were carried out at $B_0 = 9.4$ T on a spectrometer (Avance III 400 WB, Bruker) operating at 79.5 MHz. Samples were packed in a 7 mm ZrO_2 rotor and spun at the magic angle (54.7°) with the spin rate of 8 kHz. ^{29}Si MAS NMR spectra were acquired using direct excitation with ^1H high power decoupling using a 90° pulse of 2 ms and a recycle delay of 3 s. The ^{29}Si chemical shift was referenced to neat tetramethylsilane (TMS). X-ray diffraction (XRD) patterns were performed using a Bruker D8 Advance X-ray diffractometer with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Sollers slits and 0.2 mm receiving slit. XRD patterns from 2° to 25° 2θ were recorded using ($\lambda = 0.154$ nm) with the following measurement conditions: tube voltage of 40 kV, tube current of 100 mA, step scan mode with a step size of 0.02° 2θ and a counting time of 1 s per step.

2.4. Fluorescence measurement

A 1.0×10^{-3} mol/L (0.02 wt%) solution of pyrene was prepared in acetone beforehand, then 120.0 μL of this solution in a beaker were left to evaporate the solvent, whereafter 10 mL water was added followed by ultrasonication for 10 min to make the solution uniform. Next, Laponite (0.1 g), NIPAM (1.0 g) and TEOS (0.1 g) were successively mixed under stirring magnetically at room temperature for 8 h until a uniform dispersion was obtained. The fluorescence emission spectra of