



Highly magnetic sensitivity of polymer nanocomposite hydrogels based on magnetic nanoparticles



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ARTICLE INFO

Article history:

Received 8 November 2016

Received in revised form

3 January 2017

Accepted 9 January 2017

Available online 11 January 2017

Keywords:

Functional composites

Magnetic properties

Mechanical properties

Rheology

ABSTRACT

A new polymer nanocomposite hydrogels (polymer NC gels) consisted of triblock copolymers and Fe₃O₄ nanoparticles were synthesized by the in-situ polymerization method. The polymer NC gels showed good mechanical properties and high sensitivity to magnetic field. The tensile and compression strength of polymer NC gel with low content of 1.0 wt% was about 64.0 KPa and 3.1 MPa, respectively. Moreover, the relative sensitivity (8.1 kPa/mT), high absolute (ca. 4.87 MPa), and relative magnetorheological effect (6600%) of the polymer NC gels with low content of 1.0 wt% were also observed, respectively. These results were attributed to unique multiple hierarchical structure of polymer NC gel, which was composed of cross-linking polymer network and micro magnetic fluid unit. The character provided its magnetic sensitivity of magnetorheological fluids and rubber-like elasticity of magnetorheological elastomers, together. The work did not only synthesize a new polymer gels with good mechanical properties, but also provided a universal route for the rational design of magnetorheological materials with high magnetic sensitivity for various applications.

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1. Introduction

Magnetorheological (MR) materials were belonged to a family of so-called smart material, and their physical properties (eg, mechanical, optical, electrical and others properties) could be controlled continuously, rapidly and reversibly by the application of an external magnetic field [1–4]. So, the MR materials have been widely used in the vibration and noise control, sensor, artificial muscle, soft actuators and so on. According to the difference in matrix, MR materials were classified as MR fluids, MR elastomers and MR polymer gels [5]. MR fluids were consisted of micron-sized magnetic particles and a liquid carrier medium. However, the settlement of the particles due to the density mismatch between the magnetic particles and the liquid carrier medium was a serious problem [5]. MR elastomers were consisted of micron-sized magnetic particles and a non-magnetic polymeric matrix [5]. The obvious advantages of using elastomers were that the particles could not settle with time and there was no need to use extra containers to keep the MR material in its place. However, MR elastomers showed the low magnetic sensitivity, which restricted

its application in industry [3–5]. For example, Gong et al. reported the synthesis of conductive magnetorheological elastomers consisting of carbonyl iron particles, polydimethylsiloxane matrix and carbon nanotube covered polyurethane sponge, in which the shear storage modulus increased from 0.49 MPa to 0.64 MPa under magnetic field [3]. Gong et al. reported also a new kind of magnetically responsive shear-stiffening gel, in which the elastic modulus also increased from 116.5 MPa (no magnetic field) to 255.5 MPa under a 0.3T magnetic field [4]. Recently, MR polymer gels consisted of magnetic particles, liquid carrier medium and polymer have attracted lots of interesting due to high stabilization and high magnetic sensitivity [6–15]. For example, Alan et al. reported the synthesis and rheological properties of a new MR polymer gels consisted of micron-sized iron particles, oil and polyurethane [6,7]. Dynamic yield stress significantly increased with an external magnetic field up to 2.3 KPa under 0.35T [7]. Mendes, Srinivasa, et al. reported the rheological response of MR polymer gels consisted of polystyrene hydrogenated polybutadiene-polystyrene triblock copolymer, oil and micron sized carbonyl iron particles [8–11,14,15]. The storage modulus was improved to be about 6000% under magnetic field [10]. Mitsumata et al. reported the preparation and rheological properties of the magnetic polymer gels consisted of cross-linked poly (vinyl alcohol), iron oxide particles and water. The initial storage modulus

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(ca. 210.0 Pa) increased to be 2300 Pa under 0.5T [12]. Despite all the studies done so far in this field, it was still a high challenge for MR polymer gels with high mechanical properties, high stabilization and high magnetic sensitivity, together.

Based on the above considerations, a new kind of MR polymer NC gels was designed and synthesized. The MR polymer NC gels were composed of cross-linking polymer network and Fe₃O₄ nanoparticles aqueous fluid unit. Owing to the unique cross-linking polymer network matrix, the MR polymer NC gels showed high mechanical properties and high stabilization. At the same time, the micro magnetic fluid unit consisted of Fe₃O₄ nanoparticles and water was well dispersed in cross-linking polymer network matrix, resulting in improvement of magnetic sensitivity. The MR polymer NC gel with high performance was expected to be applied in artificial muscle, soft actuators and so on.

2. Experimental

2.1. Materials

Acrylamide (AM), acrylic acid (AA), 2-acrylamido methyl-propane sulfonic acid (AMPS) Ammonium persulfate (APS) and N, N, N', N'-tetramethylethylenediamine (TEMED) were supplied by Sigma. And the inorganic clay, synthetic Laponite (LT-HS) was purchased from Rockwood. FeCl₃ and FeCl₂ were supplied by Shanxi Wanhua chemical Company, Potassium hydroxide (KOH) were kindly provided by Wanhua chemical Company.

2.2. Preparation of MR polymer NC gels

Stable Fe₃O₄ suspension solution (0.1 g/ml) was prepared by co-precipitation method according to previous work [16], in which the average size and magnetization saturation of Fe₃O₄ was ca. 27.3 nm and ca. 66.4emu/g, respectively. The MR polymer NC gels were synthesized by in-situ free-radical polymerization as shown in Scheme 1. Firstly, the 1.0 g acrylamide (AM), 0.3 g acrylic acid(AA), 0.07 g 2-acrylamido-2-methyl-1-propan-essulfonic acid (AMPS) and 0.6 g Laponite were dispersed in deionized water (8.0 ml) under stirring in an ice-water bath for 2.0 h. And then the tetramethylethylenediamine (TEMED) (20.0 μL), the ammonium persulfate (APS) aqueous solution (20.0 mg/ml) and stable Fe₃O₄ suspension solution was added into the mixing solution under stirring. Finally, the mixing solution was moved directly into the test tube and polymerization at 40.0 °C for 24 h and at 60.0 °C for 12.0 h after evacuation to form the MR polymer NC gels. In a typical experiment, the Fe₃O₄ content of 1.0 wt%, 3.0 wt% and 5.0 wt% was controlled by adjusting the volume of Fe₃O₄ suspension solution.

2.3. Characterization

An XRD diffractometer (Bruker) was employed with a radiation source of Cu Kα and wave length $k = 0.154$ nm operated at 40 kV and 40 mA. The incidence angle (2θ) was fixed between 10° and 80°, in which the scan rate was 0.01°/s.

The microstructure of MR polymer NC gels was examined by an Inspect scanning electron microscopy (SEM) instrument (Su-4700) with energy-dispersive spectra.

The magnetic properties of MR polymer NC gels were investigated at room temperature by vibrating sample magnetometer (VSM; Lake Shore 7410), supplied by the Lake Shore Co. Ltd (USA).

The tensile and compression measurement of mechanical properties was conducted on a universal testing machine (Instron 5567, US) at room temperature with a cross-head speed of 100.0 mm/min.

The dynamic shear storage modulus was measured using a rheometer (MCR301, Anton Paar) under magnetic fields. The field direction was perpendicular to the strain. The samples were disks of 20.0 mm diameter and 1.3 mm thickness. The absolute sensitivity or MR effect (ΔG , Pa), relative sensitivity (R_s , Pa/T) and relative MR effect (%) can be defined as:

$$\Delta G = G_T - G_0$$

$$R_s = \frac{\Delta G}{T_1 - T_0}$$

$$\text{MR effect(\%)} = \frac{\Delta G}{G_0} \times 100\%$$

G_0 and G_T are the zero magnetic field and extend magnetic field storage modulus (Pa), respectively, T_1 and T_0 are magnetic flux density corresponding to G_T and G_0 , respectively.

3. Results and discussion

3.1. Synthesis and properties of the MR polymer NC gels

Fig. 1 shows the FT-IR spectra of polymer NC gels with and without Fe₃O₄ nanoparticles. The two samples showed similar FT-IR spectra. The absorption band at around 1000.0 cm⁻¹ was ascribed to Si–O stretching of Laponite. The characteristic absorption peaks at around 1702.0 cm⁻¹ and 1333.0 cm⁻¹ were assigned to carboxylate anion of AA groups [17]. The characteristic absorption peaks at around 1460.0 cm⁻¹ and 808.0 cm⁻¹ were attributed to the stretching of C–N and N–H plane bending vibration of AM group, respectively [18]. At the same time, the strong peaks around 1652.0 cm⁻¹ and 1189.0 cm⁻¹ were assigned to –CONH– and –SO₂ symmetrical stretching vibration of AMPS, respectively [19]. In a comparison, the absorption peak (ca. 1702.0 cm⁻¹) assigned to C=O of carboxyl group was almost disappear, and the absorption peak assigned to AM and AMPS were all almost shift as shown in Fig. 1B. Furthermore, the increase in intensity of absorption peak (ca. 1000.0 cm⁻¹) assigned to Si–O bending vibration was also observed. These results indicated the formation of MR polymer NC gels consisted of Fe₃O₄, Laponite and P(AM-co-AA-co-AMPS), in which the chemical interaction between Fe₃O₄ and P(AM-co-AA-co-AMPS) was formed.

The XRD patterns of polymer NC gels with and without Fe₃O₄ nanoparticles were characterized and compared as shown in Fig. 2. Fig. 2B clearly showed a broad diffuse-like peak at 28.5° for the pure polymer NC gel, which was attributed to the amorphous structure of polymer NC gel matrix [20]. In a comparison, excluding the strong diffraction peaks of polymer NC gel matrix, there presented three new diffraction peaks at 35.5°, 57.1° and 62.8° for all MR polymer NC gels, which were assigned to (311), (511) and (440) planes of Fe₃O₄ (JCPDS card No. 44-0141), respectively [16]. And the intensity of these diffraction peaks was relatively low due to be low doping contents of Fe₃O₄. These results further confirmed the formation of MR polymer NC gels based on Fe₃O₄ nanoparticles.

The microstructure of polymer NC gels with and without Fe₃O₄ nanoparticles were examined by the SEM as shown in Fig. 3. To avoid the collapse of pore shape, the hydrogel samples were freeze drying at –60.0 °C. It was found that all polymer NC gels showed similar porous structure and dense architecture like card rooms as shown in Fig. 3A–E. This was due to that a lot of water molecules within the gel precursors were removed by sublimation, and the polymer chains could not move and remained in the same conformation to form macrospores during freeze drying. These

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