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PAPER

Physically crosslinked poly(vinyl alcohol) hydrogels with magnetic field controlled modulus

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Physically cross-linked isotropic and anisotropic poly(vinyl alcohol) (PVA) hydrogels containing micron-sized carbonyl iron particles were prepared through a cyclic freezing–thawing process. The PVA hydrogel can respond to a magnetic field and shows a magnetorheological (MR) effect, *i.e.*, the modulus of the PVA hydrogel can be adjusted under a magnetic field. The chain-like structures of carbonyl iron are formed in the PVA hydrogel after orientation under a magnetic field of 1.5 T. Also some magnetic field induced oriented pores with a tunable diameter are observed in the dried PVA gel. The MR effect can be adjusted by changing the carbonyl iron content, the initial concentration of PVA solution and test frequency. The formation of aligned chain-like structures of carbonyl iron in the anisotropic PVA MR hydrogel improves the compression properties and the MR effect. At a carbonyl iron content of 70 wt%, the maximum absolute and relative MR effect of anisotropic PVA MR hydrogels are ~ 1.24 MPa and $\sim 230\%$, respectively. The PVA hydrogels with good MR effects and moderate mechanical strength have potential applications in artificial muscle, soft actuators and drug release.

1. Introduction

Poly(vinyl alcohol) (PVA), a water-soluble semicrystalline polymer with plenty of applications in packaging, textiles, and so on, is able to form hydrogels by different methods. PVA hydrogels can be prepared using chemical crosslinking agents such as epichlorohydrin,¹ glutaraldehyde,² and sodium borate.³ It can also be chemically crosslinked by γ -irradiation.⁴ PVA in aqueous solution can gelatinize and result in physically cross-linked hydrogels when subjected to several freezing–thawing cycles.^{5,6} The gelation arises from the hydrogen bonding followed by crystallization, which leads to the formation of a porous network structure in which PVA crystallites serve as junction points.^{5,7} Compared with other methods, the cyclic freezing–thawing method has several advantages: (1) the procedure is simple; (2) it does not require any additional chemicals; and (3) the obtained PVA hydrogels are thermoreversible and show many useful properties such as high mechanical strength, rubberlike elasticity, stability at room temperature, ability to retain their original shape, high water content, biocompatibility and nontoxicity.^{8,9} PVA hydrogels have potential applications as soft tissue replacements, articular cartilage, artificial skin, and so on. Kokabi *et al.* incorporated clay into PVA hydrogel and used it for wound dressing.¹⁰ When magnetic particles (Fe_3O_4) are

incorporated, PVA hydrogel composites can be used as a kind of smart ferrogel which can respond to a magnetic field. PVA ferrogels can be used in drug release, artificial muscle, and actuators.^{11–14}

Magnetorheological (MR) materials belong to a family of so-called smart material whose rheological properties can be controlled continuously, rapidly and reversibly by the application of an external magnetic field. According to the difference in matrix, MR materials can be mainly classified as MR fluids, MR foams, and MR elastomers.¹⁵ MR fluids are the most common MR materials whose yield stress and apparent viscosity can be changed from a Newtonian liquid to a non-Newtonian liquid when subjected to a magnetic field.¹⁶ However, the settlement of the particles due to the density mismatch between the magnetic particles and the liquid carrier medium is a serious problem. MR elastomers, a new kind of MR material, consist of micron-sized magnetic particles suspended in a non-magnetic polymeric matrix. The obvious advantages of using elastomers are that the particles are not able to settle with time and there is no need to use extra containers to keep the MR material in its place. MR elastomers have been applied in adaptive tuned vibration absorbers,¹⁷ stiffness tunable mounts, and suspensions¹⁸ for their controllable mechanical properties. It was reported that the maximum increase in the shear modulus due to the MR effect was $\sim 133\%$ of the zero-field modulus for a plasticized natural rubber based MR elastomer.¹⁹ The application of MR elastomers has been limited by the lower MR effect to some extent. A softer matrix is desirable in order to improve the MR effect. Polymer gels possess rubberlike elasticity as elastomers and can be softer than normal elastomers. So, polymer gel may be one good

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candidate for MR materials. Previously, polymer gels were used as carrier medium for MR fluids.^{20–22} However, investigations on MR gel have been seldom documented.^{23,24} Recently, a polystyrene-hydrogenated polybutadiene–polystyrene triblock copolymer based gel was used for an isotropic MR gel with a maximum MR effect of 59%.²³ An *et al.* made a big progress in MR effect. They showed that the relative MR effect of the anisotropic polystyrene-*block*-poly (ethylene-*stat*-butadiene)-*block*-polystyrene (SEBS) based MR gel can be as high as 6000%. However, the mechanical properties were not so good, which may limit its applications.²⁴

In this study, isotropic and anisotropic PVA MR hydrogels were prepared through a cyclic freezing–thawing process for the first time. Compared with conventional rubber based MR elastomers, the procedure for physically crosslinked PVA MR hydrogels is simple. Moreover, the stiffness of PVA hydrogels could be easily tuned by changing the initial PVA concentration to obtain a higher MR effect. The PVA MR hydrogels with good MR effect and moderate mechanical strength have potential applications in drug release, artificial muscle and soft actuators.

2. Experimental

2.1 Materials

PVA with a saponification value of 99% and polymerization degrees of 1000 (PVA-1099), 1700 (PVA-1799) and 2400 (PVA-2499) were purchased from Sinopec Sichuan Vinylon Factory (China). Carbonyl iron particles with sizes of $d_{10} \sim 2 \mu\text{m}$, $d_{50} \sim 4 \mu\text{m}$, and $d_{90} \sim 9 \mu\text{m}$ were provided by BASF (OM model). Distilled water was used to prepare all aqueous solutions.

2.2 Preparation of PVA MR hydrogels

PVA (60 g) and distilled water (240 g) were added into a three-necked flask equipped with a condenser and a mechanical stirrer. The PVA solution with a concentration of 20 wt% was obtained by dissolving PVA in water for 2 h at 110 °C under reflux. Bubbles were removed by refluxing the solution with a lower stirring speed for 2 h at 90 °C, obtaining a homogeneous PVA solution. The anisotropic PVA MR hydrogels with carbonyl iron contents of 50, 60 and 70 wt% were prepared under a magnetic field. The procedures for preparing the anisotropic PVA MR hydrogel sheet with 70 wt% carbonyl iron at a thickness of $\sim 3 \text{ mm}$ are as follows: carbonyl iron (140 g) and PVA solution (60 g) were mixed by ball milling for 10 min to obtain the PVA-Fe dispersion. The dispersion was vacuum-degassed for 3–5 min to remove the bubbles. PVA-Fe dispersions obtained from a 20 wt% PVA solution with 50, 60 and 70 wt% carbonyl iron were designated as D-2050, D-2060 and D2070, respectively. Thereafter, the viscous dispersion was poured into an O-ring mold and oriented under a 1.5 T magnetic field along the thickness direction for 5 min. The anisotropic structure of carbonyl iron was frozen by pouring plenty of liquid nitrogen onto the mold. Then, the frozen sample was kept at $-20 \text{ }^\circ\text{C}$ for 10 h and thawed at room temperature for 1 h. The above freezing–thawing process was repeated for 5 times. Finally, the anisotropic PVA MR hydrogel sample was obtained. The anisotropic PVA MR hydrogels cylinder samples for compression tests, with dimensions of 12.5 mm in height and 29.0 mm in

diameter, were prepared under a 1 T magnetic field along the height direction. The anisotropic PVA MR hydrogel prepared from a 20 wt% PVA solution with 50, 60 and 70 wt% carbonyl iron were designated as Aniso-2050, Aniso-2060 and Aniso-2070, respectively. As a contrast, the blank PVA and isotropic PVA MR hydrogels were prepared with the same procedures without magnetic field. The isotropic PVA MR hydrogels with 50, 60 and 70 wt% carbonyl iron were designated as Iso-2050, Iso-2060 and Iso-2070, respectively. Anisotropic PVA MR hydrogels with 70 wt% iron prepared from 10 wt% and 15 wt% PVA solutions were designated as Aniso-1070 and Aniso-1570, respectively.

2.3 Characterization

2.3.1 Viscosity measurement. The rheological behavior of the PVA-Fe dispersions prepared by ball milling with different iron contents was investigated using a RH7D rheometer (Bohlin Instruments Ltd.) with 40-mm diameter parallel plates. The gap between the plates was 0.15 mm. The sample was allowed to equilibrate at the test temperature for at least 3 min prior to steady shear measurement. The viscosity as a function of shear rate was obtained in the shear rate range of $0.1\text{--}100 \text{ s}^{-1}$ at 40 °C.

2.3.2 Scanning electron microscope (SEM). For SEM observation, PVA MR hydrogels were firstly transformed into xerogels by the removal of water in methanol for 24 h and subsequently drying under vacuum at 80 °C. An Inspect F SEM instrument (FEI Company) was employed to observe the morphology of the carbonyl iron particles with an acceleration voltage of 20 kV. The samples were cryogenically fractured in liquid nitrogen and coated with a thin gold layer prior to observation.

2.3.3 Mechanical properties measurement. The measurement of mechanical properties was conducted on a universal testing machine (Instron 5567, USA) at room temperature. For the tensile tests, the dumbbell-shaped specimens with a thickness of $\sim 3 \text{ mm}$ were stretched until breaking at a crosshead rate of 50 mm min^{-1} . The stress–strain curves were recorded. The tensile strength, elongation, and stress at the 50%, 100% and 200% strain were the average values of five specimens. For compression tests, the cylinder specimens were compressed to the maximum strain of 25% at a rate of 10 mm min^{-1} according to the China Standard GB/T 7757-1993. Four compression cycles were carried out and the last cycle was selected to determine the compressive properties. The dimensions of the cylinder sample were 12.5 mm in height and 29.0 mm in diameter.

2.3.4 Magnetorheological effect analysis. The MR effect was measured on a modified dynamic mechanical analyzer with a shear mode under magnetic field (Triton Technology Ltd., UK, model Tritec 2000B)^{25,26} at room temperature. A shaft connects the sample and the motor in DMA. The motor drives the shaft and the sample moves at a given amplitude and frequency. The stress in the sample was measured with the sensor and the strain was taken as the displacement amplitude. The shear modulus was computed from the data of strain and stress. During the test, a magnetic field which can vary from 0 to 1 T was applied to the sample. The dimensions of the sample were $10 \times 10 \times 3 \text{ mm}$.

The dynamic strain amplitude was set as 0.3%. The MR effect was tested at three different frequencies, *i.e.*, 1, 5 and 10 Hz.

3. Results and discussion

3.1 The preparation of PVA hydrogels

The macroscopic properties of PVA hydrogels prepared by freezing–thawing cycles depend on the starting materials components (*e.g.* concentration of PVA in water, molecular weight, degree of saponification, tacticity) and the processing steps (number of freezing–thawing cycles, temperatures and times of both freezing and thawing steps).⁶ They are largely determined by the organization and interactions of the chains in the gel state. Table 1 shows the mechanical properties of PVA hydrogels prepared with polymerization degrees of 1000, 1700 and 2400 at an initial PVA concentration of 20 wt%. It should be noted that the sample prepared with PVA-1799 has the highest tensile strength and elongation at breaking among the three samples. For preparation of PVA hydrogels, PVA should have a proper molecular weight. If the molecular weight is too low, the entanglement of PVA chains is too weak to form physically crosslinked network; if the molecular weight is too high, bubbles cannot be removed completely from the PVA solution. Therefore, PVA-1799 was chosen to prepare PVA MR hydrogels in the this study. Table 2 shows the influence of the freezing–thawing cycles on the mechanical properties of PVA hydrogels prepared with PVA-1799. As the number of freezing–thawing cycles increases from 1 to 5, the tensile strength increases from 0.38 to 1.68 MPa, and the elongation at breaking increases from 182% to 366%. This should be attributed to the improvement of the crystallinity after more freezing–thawing cycles. As the freezing process goes on, the viscosity increases quickly and the mobility of the PVA molecular chains decreases, which means a part of the PVA chain segments cannot accomplish an ordered arrangement. When the PVA hydrogels thaws at room temperature, some PVA chain segments can be activated at room temperature and thus have the ability to rearrange upon freezing once again, leading to an improved crystallization. As confirmed, the first five or six freezing–thawing cycles play a very important role in determining the hydrogel structure since they improve the crystallinity of the samples to a limiting value.²⁷ So, five freezing–thawing cycles was utilized to prepare PVA MR hydrogels.

3.2 The rheological behavior of PVA-Fe dispersion

The introduction of the micron-sized carbonyl iron has a significant influence on the viscosity of the PVA-Fe dispersion, which will further affect the orientation of iron in the PVA matrix. So the viscosity of the PVA-Fe dispersion was tested prior to orientation and gelation. The effects of the shear rate

and carbonyl iron content on the viscosity of the PVA-Fe dispersion are shown in Fig. 1. Under double-logarithmic coordinates, the viscosity is nearly proportional to the shear rate. The data can be fitted with the Herschel–Bulkley model:^{28,29} $\eta = \tau_0/\dot{\gamma} + k\dot{\gamma}^{n-1}$, where $\dot{\gamma}$ is the shear rate, k and τ_0 are constants, n is the flow behavior index or shear thinning parameter. The viscosity at a low shear rate of 1.1 s⁻¹ and a high shear rate of 70.0 s⁻¹, and the fitted shear thinning parameter n are listed in Table 3. The PVA-Fe dispersion shows a shear-thinning behavior. The viscosity of the PVA-Fe dispersion increases significantly with the increase of the iron content. At a shearing rate of 1.1 s⁻¹, the viscosities of blank PVA solution, D-2050, D-2060 and D-2070 at 40 °C are 34.3, 61.0, 131.2 and 344.7 Pa s, respectively. The shear thinning parameter n shows an obvious decrease from 0.82 to 0.45. Therefore, for the PVA-Fe dispersion, a higher carbonyl iron content will result in more obvious shear-thinning behavior. The sensitivity of the PVA-Fe viscosity to the shear rate can be utilized in the sample preparation process. So, ball milling was used to assure the complete mixing of high content of carbonyl iron powders with PVA solution in a short time.

3.3 The morphology of PVA MR hydrogel

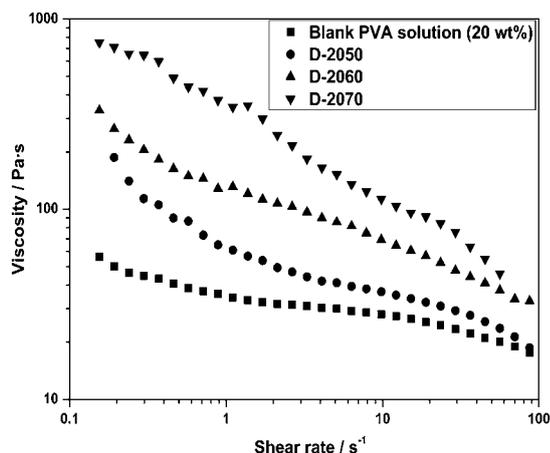
PVA MR hydrogels were transformed into xerogels before SEM observation. If the samples are dried directly, the shrinkage of the samples is serious due to the loss of water. SEM images of blank PVA hydrogel and isotropic PVA MR hydrogel with 70 wt% carbonyl iron are shown in Fig. 2. There are many irregular aggregates on the fracture surface of the blank PVA gel (Fig. 2(b)), which may be ascribed to the crystallization of PVA. For isotropic PVA MR hydrogels, the carbonyl iron particles are dispersed randomly in the fracture surface (Fig. 2 (c) and (d)). The carbonyl iron particles are possibly enwrapped with PVA layers and partially connected with each other. The pore structure can be seen on the fractured surface, which is formed by the evaporation of water after drying. Fig. 3 shows SEM images of anisotropic PVA MR hydrogels with 50, 60 and 70 wt% carbonyl iron particles. After orientation under a 1.5 T magnetic field, the carbonyl iron particles form chain-like structures along the direction of the magnetic field, which are frozen by liquid nitrogen. During the freezing–thawing process, the chain-like structures of the carbonyl iron are fixed in the gel as the physically crosslinked PVA networks form. The density of the chain-like structures increases with the increase of iron content from 50 to 70 wt%. Interestingly, some oriented pores can be observed in the anisotropic PVA MR hydrogel along the direction of the magnetic field, while they do not appear in the blank PVA hydrogel and isotropic PVA MR hydrogel. It has been confirmed that the PVA hydrogel consists of plenty of free

Table 1 The effect of molecular weight of PVA on the mechanical properties of PVA hydrogels prepared with five freezing–thawing cycles

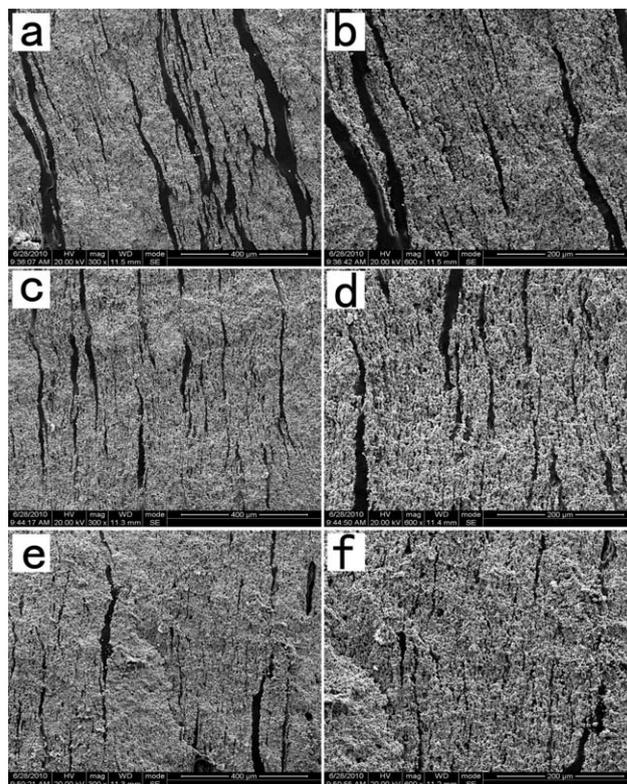
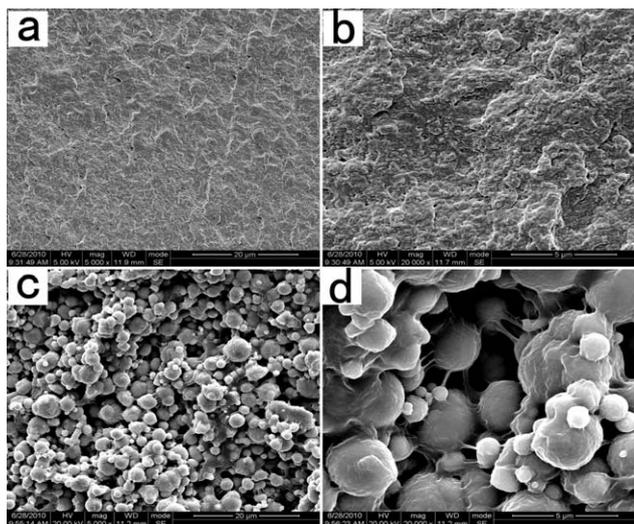
Sample	Tensile strength/MPa	Elongation at breaking/%	Stress at 50% strain/MPa	Stress at 100% strain/MPa	Stress at 200% strain/MPa
PVA-1099	0.41 ± 0.02	190 ± 13	0.11	0.21	—
PVA-1799	1.68 ± 0.12	366 ± 16	0.09	0.28	0.70
PVA-2499	0.52 ± 0.03	248 ± 18	0.10	0.17	0.41

Table 2 The influence of the freezing–thawing cycles on the mechanical properties of PVA hydrogels prepared with PVA-1799

Number of freezing–thawing cycles	Tensile strength/MPa	Elongation at breaking/%	Stress at 50% strain/MPa	Stress at 100% strain/MPa	Stress at 200% strain/MPa
1	0.38 ± 0.04	182 ± 15	0.14	0.23	—
3	0.99 ± 0.06	193 ± 13	0.22	0.47	—
5	1.68 ± 0.12	366 ± 16	0.09	0.28	0.70

**Fig. 1** The viscosity of PVA-Fe dispersions with different iron contents at 40 °C.**Table 3** The viscosity of PVA-Fe dispersions at a low shear rate of 1.1 s⁻¹ (η_L) and a high shear rate of 70.0 s⁻¹ (η_H) and the shear thinning parameter n

Dispersion	η_L /Pa s	η_H /Pa s	n
Blank PVA solution (20 wt%)	34.3	18.9	0.82
D-2050	61.0	21.3	0.80
D-2060	131.2	33.7	0.75
D-2070	344.7	40.2	0.45

**Fig. 3** SEM of anisotropic PVA MR hydrogels with different carbonyl iron contents after removing the water: (a) and (b) with 50 wt% iron, (c) and (d) with 60 wt% iron, (e) and (f) with 70 wt% iron.**Fig. 2** SEM of blank PVA hydrogel ((a), (b)) and isotropic PVA MR hydrogel with 70 wt% carbonyl iron ((c), (d)) after removing the water.

water, a small part of non-freezing and freezing bound water.⁴ The pores in the fracture surface should be the evaporation trace of free water in the PVA hydrogel. The phase separation during gelation may result in the aggregation of water. The orientation of carbonyl iron particles along the direction of the magnetic field generates some gaps between the chain-like structures. The free water separated from the PVA gel will fill in the gaps. Once the water in the gaps is removed by drying, pores will form in the gel. With the increase of iron content from 50 to 70 wt%, the maximum pore diameter decreases from ~ 110 to ~ 37 μm (Fig. 3(a), (c) and (e)) and the amount of pores also decreases. This should be attributed to the increase of carbonyl iron content and the decrease in the water content in the composite hydrogels. This also suggests a good way for the tuning of the oriented pore size. Recently, Zhao *et al.*¹⁴ revealed that the ferrogel with porous structure could be remotely controlled by a magnetic field to deliver various biological agents. So, PVA MR hydrogels with tunable oriented pores may also be used for drug release.

3.4 Mechanical properties

Generally, MR materials are highly filled with magnetic particles so as to obtain a good MR effect. In such a case, the mechanical properties become worse. The deterioration of mechanical properties is a key issue for the practical application of the MR materials. The mechanical properties of the blank PVA hydrogel, isotropic and anisotropic PVA MR hydrogels with 50, 60, and 70 wt% carbonyl iron are shown in Table 4. The tensile strength and elongation at breaking of the blank PVA hydrogel are 1.68 MPa and 366%, respectively. The tensile strength of Iso-2050 and Iso-2060 is improved to some extent compared with the blank PVA gel. As the iron content increases to 70 wt%, both tensile strength and elongation at breaking decrease. At higher iron contents, the stress concentration and poor load transfer will deteriorate the mechanical properties. For anisotropic PVA MR hydrogels, the tensile strength and elongation at breaking are lower than those of isotropic one with the same iron content. The formation of chain-like structures along the thickness direction in the hydrogel may act as stress concentration points, resulting in the decrease in tensile properties. The tensile strength of the PVA MR gel with 70 wt% carbonyl iron still can be as high as ~ 1 MPa, which is close to that of a natural rubber MR elastomer with the same iron content (~ 2.27 MPa).¹⁹ It should be mentioned that for MR gels, it is difficult to obtain good mechanical properties compared to rubber or elastomer based MR materials. For example, An *et al.* reported that the shear modulus of SEBS based MR gel with 30 vol% carbonyl iron is only ~ 10 KPa.²⁴ The improvement of mechanical properties of PVA MR gel should be mainly attributed to the presence of the physically crosslinked network structure in which PVA crystallites serve as junction points.

The compressive stress–strain curves of the blank PVA gel, and isotropic and anisotropic PVA MR hydrogels are shown in Fig. 4. The compression stress at 10% and 20% strains are shown in Table 5. With the incorporation of iron particles, the compression properties are significantly improved. The compression stress at a strain of 10% for Iso-2070 and Aniso-2070 are 56.0 and 83.8 kPa, ~ 2.3 and ~ 3.5 times that of blank PVA hydrogel (23.8 kPa), respectively. Compared with the isotropic PVA MR hydrogel, the anisotropic one has a higher compression stress due to the formation of aligned chain-like structures along the direction of compression.

3.5 Magnetorheological effect

The MR effect originates from the interaction of magnetic particles. When MR hydrogels are subjected to a magnetic field,

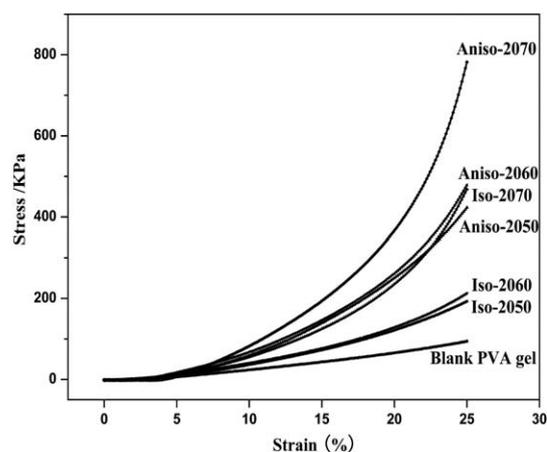


Fig. 4 Compressive curves of isotropic and anisotropic PVA MR hydrogels with different iron contents.

magnetic particles tend to align in the direction of the magnetic field for the ferrous particles can be magnetized easily. The field-induced magnetic forces between the magnetic particles provide an ability of anti-deformation, resulting in the change of shear modulus. The relative MR effect can be defined as $\Delta G/G_0 \times 100\%$, G_0 is the zero-field shear modulus, and ΔG is the increment of field-induced shear modulus, *i.e.*, absolute MR effect. The influence of the aggregate structure and content of magnetic particles, the initial PVA concentration, and the test frequency on the MR effect of PVA MR hydrogels were examined.

Fig. 5 shows the change of shear modulus with magnetic field strength for the isotropic and anisotropic PVA MR hydrogels with different carbonyl iron contents. Table 6 lists the zero-field modulus and the MR effect of the samples. The zero-field modulus increases with the increase of the carbonyl iron content, which is consistent with normal filled composites. The anisotropic PVA MR hydrogel has a higher zero-field modulus compared with the isotropic one with the same iron content due

Table 5 Compression stress of PVA MR hydrogels at 10% and 20% strains

Sample	Stress at 10% strain/kPa		Stress at 20% strain/kPa	
	Isotropic	Anisotropic	Isotropic	Anisotropic
Blank PVA gel	23.8		65.6	
50 wt% Fe	37.2	59.0	122.0	250.3
60 wt% Fe	40.7	68.1	128.5	261.9
70 wt% Fe	56.0	83.8	235.3	368.4

Table 4 Mechanical properties of PVA MR hydrogels with different iron contents

Sample	Tensile strength/MPa	Elongation at breaking/%	Stress at 50% strain/MPa	Stress at 100% strain/MPa	Stress at 200% strain/MPa
Blank PVA gel	1.68 \pm 0.12	366 \pm 116	0.09	0.28	0.70
Iso-2050	2.62 \pm 0.23	393 \pm 14	0.28	0.60	1.11
Aniso-2050	1.33 \pm 0.10	290 \pm 12	0.17	0.41	0.87
Iso-2060	2.23 \pm 0.05	354 \pm 15	0.33	0.63	1.13
Aniso-2060	1.26 \pm 0.29	213 \pm 39	0.33	0.69	1.00
Iso-2070	1.27 \pm 0.10	255 \pm 16	0.27	0.60	1.05
Aniso-2070	0.93 \pm 0.09	199 \pm 17	0.24	0.53	—

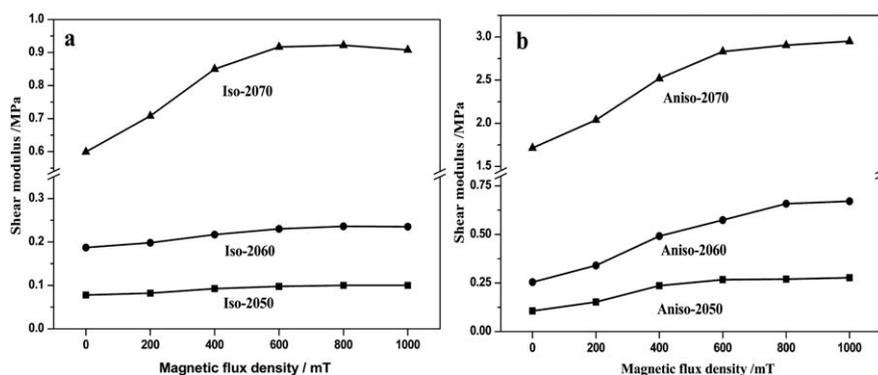


Fig. 5 Magnetic field induced shear modulus increment of isotropic (a) and anisotropic (b) PVA MR hydrogels with different iron contents.

Table 6 The zero-field modulus and MR effects of PVA MR hydrogels with different iron contents

Sample	Zero-field modulus/MPa		Absolute MR effect/MPa		Relative MR effect/%	
	Isotropic	Anisotropic	Isotropic	Anisotropic	Isotropic	Anisotropic
50 wt% Fe	0.078	0.10	0.022	0.17	28	170
60 wt% Fe	0.19	0.25	0.047	0.42	25	168
70 wt% Fe	0.60	1.71	0.31	1.24	52	73

to the formation of chain-like structures. For isotropic PVA MR hydrogels, the absolute MR effect appears when the iron content is 50 wt%, and increases to ~ 0.31 MPa at an iron content of 70 wt%. For anisotropic PVA MR hydrogels, the absolute MR effects of Aniso-2050, Aniso-2060 and Aniso-2070 are ~ 0.17 , ~ 0.42 and ~ 1.24 MPa, respectively. It is obvious that the orientation of iron particles also greatly improves the relative MR effect. The alignment of carbonyl iron reduces the distance of iron particles, which subsequently enhances the interaction of iron particles under a magnetic field, and results in a higher MR effect for anisotropic samples. The chain-like structures in the PVA hydrogel with 70 wt% carbonyl iron is the densest, so the interaction between iron particles under the magnetic field is the strongest. A surprising point is that at 70 wt% iron content, the relative MR effect is much lower than those samples at 50 wt% and 60 wt% iron contents. This can be explained as follows: the increase in the relative MR effect, *i.e.*, $\Delta G/G_0 \times 100\%$, is related to the increase in the zero-field modulus and the absolute MR effect. For samples with 50 wt% and 60 wt% carbonyl iron, the magnitude of the increase in the absolute MR effect is much higher than that of zero-field modulus, so the relative MR effect of the anisotropic sample is much higher. For samples with 70 wt% carbonyl iron, the magnitude of the increase in the absolute MR effect is close to that of the zero-field modulus, the relative MR effect of the anisotropic sample is not improved so much. Compared with our previous study on an anisotropic polyurethane (PU) based MR elastomer with 70 wt% carbonyl iron (the absolute and relative MR effects are ~ 1.3 MPa and 21%, respectively),²⁶ the absolute MR effect of PVA MR gel with 70 wt% carbonyl iron is almost equal to that of PU MR elastomer, while the relative MR effect of the PVA MR gel is ~ 3.5 times that of the PU MR elastomer. The dramatic relative MR effect of the PVA MR gel should be attributed to the lower hardness of the PVA gel matrix. The mechanical strength of PVA hydrogels

prepared by the freezing–thawing method depends on microcrystalline regions of PVA macromolecules as the physical crosslinked point to form the three-dimensional network, and the elasticity depends on the amorphous phase of PVA and the free water which acts as the external plasticizer in the hydrogel networks.

The effect of initial PVA concentration on the MR effect of the anisotropic PVA MR hydrogel with 70 wt% carbonyl iron is shown in Fig. 6. It can be seen that the zero-field modulus decreases from ~ 1.71 to ~ 0.46 MPa (by $\sim 73\%$) when the initial PVA concentration decreases from 20 wt% to 10 wt%. The absolute MR effect nearly remains constant, while the relative MR effect increases from 73% to 230%. The absolute MR effect of PVA MR gels with different initial PVA concentrations is independent of the

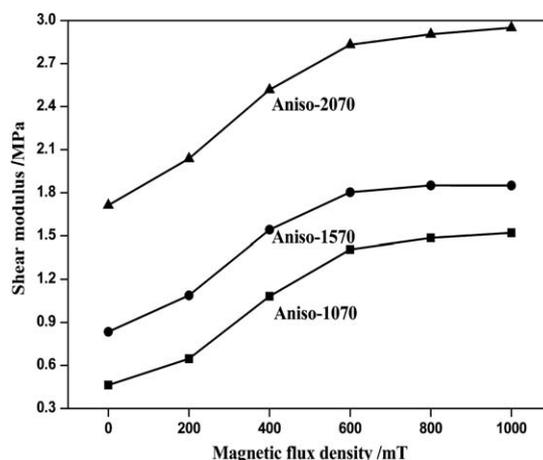


Fig. 6 The effect of PVA concentration on the magnetic field induced shear modulus increment of anisotropic PVA MR hydrogel with 70 wt% carbonyl iron.

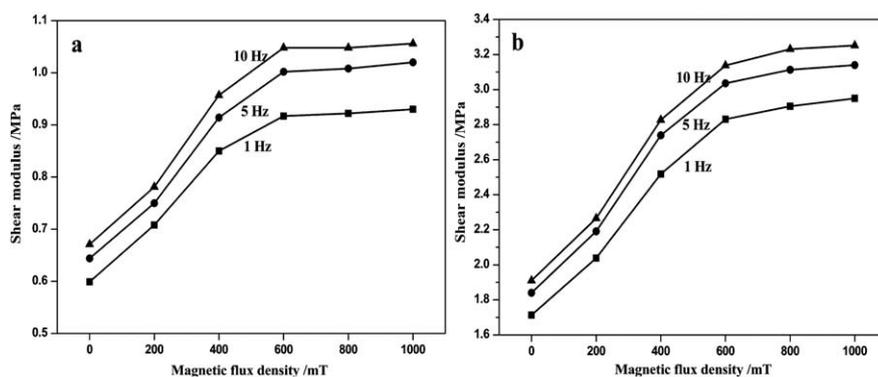


Fig. 7 The effect of test frequency on the magnetic field induced shear modulus increment of isotropic (a) and anisotropic (b) PVA MR hydrogel with 70 wt% carbonyl iron.

hardness of the matrix, which is in accordance with the dipole model. The dipole model for an anisotropic MR elastomer developed by Jolly³⁰ is deduced from the dipole–dipole interactions of magnetic particles. Thus, this model is also suitable for a MR gel. According to the dipole model, the maximum absolute MR effect can be calculated as: $\Delta G_{\max} = \phi J_s^2 / 2\mu_1 \mu_0 h^3 (\varepsilon < 0.1)$, where ϕ is the volume fraction of particles, J_s is the dipole moment magnitude per unit particle volume as magnetically saturated, μ_1 is the relative permeability of the matrix, μ_0 is a constant, h is the ratio of particle distance to the particle diameter, ε is the shear strain. Therefore, the absolute MR effect relies on the type, the arrangement and the volume fraction of magnetic particles. At a given iron content, the relative MR effect is in inverse proportion to the hardness of PVA MR gel. The hardness of PVA MR hydrogels can be adjusted easily by changing the initial PVA concentration. With a lower initial PVA concentration, the higher content of water will bring about the increasing plasticization effect of water for PVA. The highest relative MR effect reported in a previous study¹⁹ is $\sim 133\%$ based on plasticized natural rubber MR elastomers (the ratio of plasticizers to natural rubber is set as 1). Compared with that, the PVA MR hydrogel has a higher relative MR effect. The above result shows that the relative MR effect can be easily adjusted by changing the initial PVA concentration.

The frequency dependence of the MR effect for PVA MR hydrogels was also investigated. The MR effects of isotropic and anisotropic PVA MR hydrogels with 70 wt% carbonyl iron at 1, 5 and 10 Hz are shown in Fig. 7. It should be noted that the zero-field modulus increases with increasing the test frequency due to the frequency dependence of the polymer matrix. With increasing the frequency, the motion of PVA molecular chains cannot keep up with the external stimuli. The molecular chains tend to be rigid which results in an enhancement of zero-field modulus. With increasing the frequency from 1 to 10 Hz, the absolute MR effect changes little, while the relative MR effect of the isotropic and anisotropic PVA MR hydrogel decreases. So, the operating frequency should be considered in the application of MR hydrogels.

PVA MR gel is a kind of new intelligent material as MR fluids and MR elastomers. It not only has good processability and quick responsiveness to the magnetic field as MR fluids, but also possesses moderate mechanical strength as MR elastomers.

Moreover, the lower hardness of the PVA gel results in a better relative MR effect. So the PVA hydrogels with a good MR effect and moderate mechanical strength may have potential applications in drug release, artificial muscle and soft actuators.

4. Conclusion

The physically crosslinked PVA MR hydrogels with anisotropic structure and good magnetic responsiveness were prepared through a cyclic freezing–thawing process. It has been proved that PVA hydrogel is a good matrix for MR material. The chain-like structures of carbonyl iron particles can be formed in the PVA hydrogel after orientation under a magnetic field. The orientation of carbonyl iron particles greatly enhances the compressive strength of the composite. The tensile strength of the PVA MR gel with 70 wt% carbonyl iron is close to that of a natural rubber MR elastomer. The MR effect of PVA MR hydrogels can be easily adjusted by changing the carbonyl iron content, the initial PVA concentration, and the test frequency. At a carbonyl iron content of 70 wt%, the maximum absolute and relative MR effect of anisotropic PVA MR hydrogels are ~ 1.24 MPa and $\sim 230\%$, respectively.

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References

- 1 B. Jiang, *J. Appl. Polym. Sci.*, 1992, **46**, 783.
- 2 H. S. Mansur, C. M. Sadahira, A. N. Souza and A. A. P. Mansur, *Mater. Sci. Eng., C*, 2008, **28**, 539.
- 3 G. Park, E. J. McLaurin and L. E. Faidley, *Conference on Behavior and Mechanics of Multifunctional and Composite Materials*, San Diego, 2008.
- 4 T. Hatakeyama and A. Yamauchi, *Eur. Polym. J.*, 1984, **20**, 61.
- 5 E. Yokoyama, I. Masada, K. Shimamura, T. Ikawa and K. Monobe, *Colloid Polym. Sci.*, 1986, **264**, 595.
- 6 R. S. Stauffer and A. P. Nikolaos, *Polymer*, 1992, **33**, 3932.
- 7 R. Ricciardi, F. Auriemma, C. Gaillet, C. D. Rosa and F. Lauprêtre, *Macromolecules*, 2004, **37**, 9510.
- 8 C. M. Hassan and N. A. Peppas, *Adv. Polym. Sci.*, 2000, **153**, 37.
- 9 R. Ricciardi, F. Auriemma, C. Gaillet, C. D. Rosa and F. Lauprêtre, *Macromolecules*, 2004, **37**, 1921.

- 10 M. Kokabi, M. Sirousazar and Z. M. Hassan, *Eur. Polym. J.*, 2007, **43**, 773.
- 11 T. Liu, S. Hu, T. Liu, D. Liu and S. Chen, *Langmuir*, 2006, **22**, 5974.
- 12 R. V. Ramanujan and L. L. Lao, *Smart Mater. Struct.*, 2006, **15**, 952.
- 13 G. Park, E. J. McLaurin and L. E. Faidley, *Conference on Behavior and Mechanics of Multifunctional and Composite Materials*, San Diego, 2008.
- 14 X. Zhao, J. Kim, C. A. Cezarb, N. Huebsch, K. Lee, K. Bouhadird and D. J. Mooney, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 67.
- 15 J. D. Carlson and M. R. Jolly, *Mechatronics*, 2000, **10**, 555.
- 16 W. Li, G. Chen and S. H. Yeo, *Smart Mater. Struct.*, 1999, **8**, 460.
- 17 H. Deng, X. Gong and L. Wang, *Smart Mater. Struct.*, 2006, **15**, 111.
- 18 J. M. Ginder, M. E. Nichols, L. D. Elie and J. L. Tardiff, *Smart Structures and Materials 1999 Conference*, Newport Beach, 1999.
- 19 L. Chen, X. Gong, W. Jiang, J. Yao, H. Deng and W. Li, *J. Mater. Sci.*, 2007, **42**, 5483.
- 20 A. Fuchs, M. Xin, F. Gordaninejad, X. Wang, G. H. Hitchcock, H. Gecol, C. Evrensel and G. Korol, *J. Appl. Polym. Sci.*, 2004, **92**, 1176.
- 21 A. Fuchs, B. Hu, F. Gordaninejad and C. Evrensel, *J. Appl. Polym. Sci.*, 2005, **98**, 2402.
- 22 B. Hu, A. Fuchs, S. Huseyin, F. Gordaninejad and C. Evrensel, *J. Appl. Polym. Sci.*, 2006, **100**, 2464.
- 23 P. V. Rao, S. Maniprakash, S. M. Srinivasan and A. R. Srinivasa, *Smart Mater. Struct.*, 2010, **19**, 085019.
- 24 H. An, S. J. Pickenab and E. Memdes, *Soft Matter*, 2010, **6**, 4497.
- 25 J. Wu, X. Gong, L. Chen, H. Xia and Z. Hu, *J. Appl. Polym. Sci.*, 2009, **114**, 901.
- 26 J. Wu, X. Gong, Y. Fan and H. Xia, *Smart Mater. Struct.*, 2010, **19**, 105007.
- 27 R. Ricciardi, C. Gaillet, G. Ducouret, F. Lafuma and F. Lauprêtre, *Polymer*, 2003, **44**, 3375.
- 28 G. Matijašić and A. Glasnović, *Chem. Biochem. Eng. Q.*, 2002, **16**, 165.
- 29 H. Xia and M. Song, *J. Mater. Chem.*, 2006, **16**, 1843.
- 30 M. R. Jolly, J. D. Carlson and B. C. Munoz, *Smart Mater. Struct.*, 1996, **5**, 607.