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The mechanical behavior of smart magnet–hydrogel composites

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Abstract
Micron sized magnetic particles (Fe_3O_4) were dispersed in a polyvinyl alcohol (PVA) hydrogel. This multiferroic ferrogel combines the elastic properties of PVA gel and the magnetic properties of Fe_3O_4 particles. The response of the ferrogel (with Fe_3O_4 concentration in the range of 1–10 wt%) to the application of a static magnetic field (up to a maximum of 40 mT) was investigated. The results showed that the extent of deflection depended strongly on the Fe_3O_4 content and the magnetic field strength. For each Fe_3O_4 concentration there existed a threshold value of magnetic field strength before large deflection occurred. This implied that the ferrogel system can be used as an 'on–off' type transducer. The threshold value decreases with an increase in Fe_3O_4 content. Finally, two approaches were used to evaluate this ferrogel system for artificial muscle or soft actuator applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There have been various attempts to synthesize artificial muscles, these attempts [1–3] range from a robot-like metallic actuator to a more advanced soft actuator. Hydrogels, which are crosslinked polymer networks swollen with water, turn out to be one of the most promising materials for making soft actuators. However, most gels are relatively homogenous materials that shrink or swell uniformly, with no dramatic change in shape. Therefore there is a need to improve the response of gels and their suitability as soft actuators. Li and co-workers [4] made gels whose composition was engineered so that, in response to a specific stimulus, they spontaneously bent or curled into a predetermined shape such as a letter of the alphabet, a spiral, etc. Two polymers, such as poly(*N*-isopropyl acrylamide) (PNIPA) and polyacrylamide, were employed. The gels (bigel strips) were synthesized side-by-side in such a way that across the thickness of the gel its composition changed gradually from pure polyacrylamide to a mixture of polyacrylamide and PNIPA and finally to pure PNIPA.

The two polymers respond differently: PNIPA shrinks drastically when warmed above 37 °C, whereas polyacrylamide shrinks much more than PNIPA when the acetone concentration of the aqueous medium increases beyond 34%. Thus, by choosing the appropriate temperature and solvent conditions, the bigel strips can be made to bend into a predetermined shape. The shape changes are reversible. Several of these bigel strips can be joined to make a gel 'hand' that grasps objects with its bigel 'fingers' and releases them in response to stimuli.

Zrinyi *et al* [5, 6] developed magnetic field sensitive gels in which magnetic particles of colloidal size are dispersed and incorporated into the gels. These ferrogels combine the magnetic properties of magnetic fillers and the elastic properties of hydrogels. Thus shape distortion occurs instantaneously and disappears abruptly when the external magnetic field is applied and removed. When the gels were placed into a spatially non-uniform magnetic field, forces act on the magnetic particles and as a result of strong interaction between magnetic particles and polymer chains, they all move together as a single unit. The *coupling* of hydrogel and magnetic particles has applications in soft actuators. Since the magnetic particles have been incorporated within the hydrogel, the response of the magnetic particles to the magnetic field is that of the ferrogel as a whole. The effect of uniform magnetic fields and magnetic field gradients on magnetic particles has been well established by many investigators.

A polyvinyl alcohol (PVA)–iron oxide composite was prepared and characterized. PVA gel was selected for its biocompatibility [7] and elastic behavior, e.g. PVA gel has been used as a synthetic vitreous body to treat retinal

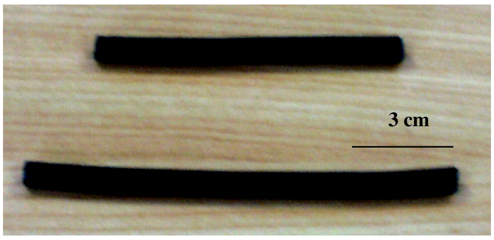

Figure 1. Picture of a ferrogel made of PVA + Fe_3O_4.

detachment [8]. The ability of this magneto-elastic multiferroic ferrogel to deflect in the presence of a magnetic field was explored in this study. The dependence of deflection on the iron oxide concentration and magnetic field strength was also investigated. The elasticity and flexibility of the system are presented. Finally, two approaches on how to make a soft actuator and artificial muscle are discussed.

2. Experimental procedure

The (PVA + Fe_3O_4) ferrogel was prepared. PVA powder (99% hydrolyzed supplied by Aldrich Chemicals Inc.) was dissolved in water with a weight composition of 23:100. The solution was stirred and heated to 70–90 °C to increase the solubility of PVA in water. Depending on the weight ratio, Fe_3O_4 powder (supplied by Aldrich Chemicals Inc.) of size $\approx 5\ \mu$m was added to the solution and mixed homogenously. Complete gelation was done by a conventional freezing/thawing method [9]. The ferrogels were long cylinders with a diameter of 4.5 mm (figure 1).

The samples were exposed to a static magnetic field of an NdFeB magnet, which is able to generate a magnetic field up to 360 mT. The response of the ferrogel was measured by the extent of deflection; a schematic and the actual experimental setup are presented in figure 2. The top end of the sample was fixed to a rod while the lower end was free to deflect upon application of a magnetic field. Variation in the magnetic field was obtained by moving the magnet towards or away from the lower end of the ferrogel. The Young's modulus was measured using an Instron 5567 universal mechanical tester.

3. Results and discussion

3.1. Magnetic response of ferrogels as a function of iron oxide concentration

Using the experimental setup mentioned in the previous section, the following results were obtained. Figure 3(a) shows the deflection of the ferrogel in response to a static magnetic field, as a function of iron oxide content. A greater maximum deflection was observed with an increase in concentration of iron oxide particles. For a given concentration of iron oxide, deflection increased with magnetic field strength. Interestingly, deflection increased slowly up to a certain threshold magnetic field strength; once this threshold field was crossed, a large increase in deflection occurred. Thus there is a threshold value which is the minimum magnetic field strength required to trigger large, instantaneous deflection.

The dependence of threshold magnetic field on iron oxide concentration is illustrated in figure 3(b). It is clear that as the iron oxide concentration increases, the threshold magnetic field required to impart a large deflection decreases. The magnetic particles and the hydrogel moved together as a system in response to the attractive magnetic force exerted by the magnet; the samples responded and recovered instantaneously upon application and subsequent removal of the magnetic field. Viscous flow of the hydrogel was not observed.

All these findings imply that the correct coupling of iron oxide content and magnetic field can result in large, instantaneous motion of the ferrogel, desirable for soft actuators and artificial muscle applications. This is similar to the mechanoelectric effects observed in ionic gels by Gennes *et al* [10]. The difference is that the spontaneous curvature of their ionic gels was driven by an electric field instead of a magnetic field.

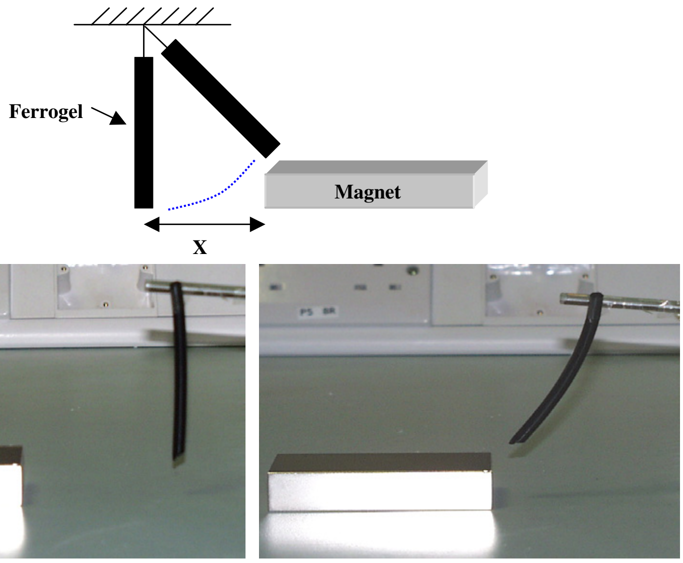

Figure 2. Experimental setup.

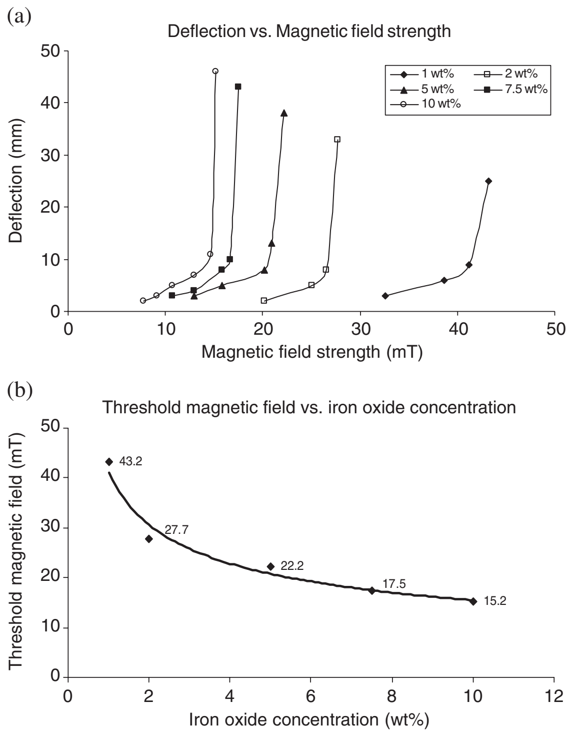

Figure 3. (a) Deflection versus magnetic field strength for different Fe_3O_4 contents. (b) Threshold magnetic field strength versus iron oxide concentration.

Zrinyi *et al* [11, 12] investigated the elongation of a ferrogel in response to a spatially non-uniform magnetic field. The iron oxide content ranged from 2.75 to 12.6% and magnetic fields up to 840 mT were employed. A schematic of the experimental setup and the main result are presented in figure 4. When there is no magnetic field (figure 4(a)), no deformation occurs; in the presence of an applied magnetic field, a field gradient develops parallel to the gel axis and results in elongation (figure 4(b)). The schematic in figure 4(c) [11–13] shows the dependence of elongation on the current density required by the electromagnets to produce a magnetic field. At small current intensities, displacement increases slightly. At a critical current density, a large displacement occurs. Further increase in current density results in further small extension. However, as the current density is reduced, the recovery does not follow the same path. A significant hysteresis characterizing the extension–contraction processes was observed [13].

A difference between the present work and that of Zrinyi's is that our results do not appear to exhibit hysteresis, which is ascribed to the difference in the experimental setup. Deflection and recovery followed the same path when magnetic field was applied and removed. Furthermore, Zrinyi *et al* were studying the non-instantaneous elongation of the ferrogel in response to a magnetic field while our work focuses on the instantaneous deflection of the ferrogel in the presence of a magnetic field. Thus 'on–off' actuator can be obtained by applying a magnetic field above the threshold value. The flexibility and elasticity of this ferrogel is assessed in the next section.

3.2. *Elasticity and flexibility of the ferrogel*

Figure 5 demonstrates the elasticity and flexibility of the ferrogel; it can be repeatedly bent and will recover smoothly, unlike a metallic robotic muscle which moves in a stiff fashion.

The elastic behavior of the ferrogel was qualitatively assessed by tensile testing. The result (figure 6) shows that the ferrogel was elastic—an extensive linear region was observed. A change in iron oxide concentration from 1% to 10% does not appear to significantly change the elasticity or stiffness of the ferrogel. The average Young's modulus, measured as a tangent of the stress–strain curve, was 0.75 MPa, which is in the range for rubbery materials such as polyisoprene with a shear modulus of 0.43 MPa [14]. Elastic moduli ranging from 0.17 to 0.75 MPa were obtained for magnetoactive elastomers studied by Bossis *et al* [15].

3.3. *Development of artificial muscle from ferrogel*

As mentioned earlier, ferrogel derives its elasticity from PVA gel and its magnetic behavior from iron oxide particles. Thus, there is a coupling effect between the magnetic and elastic

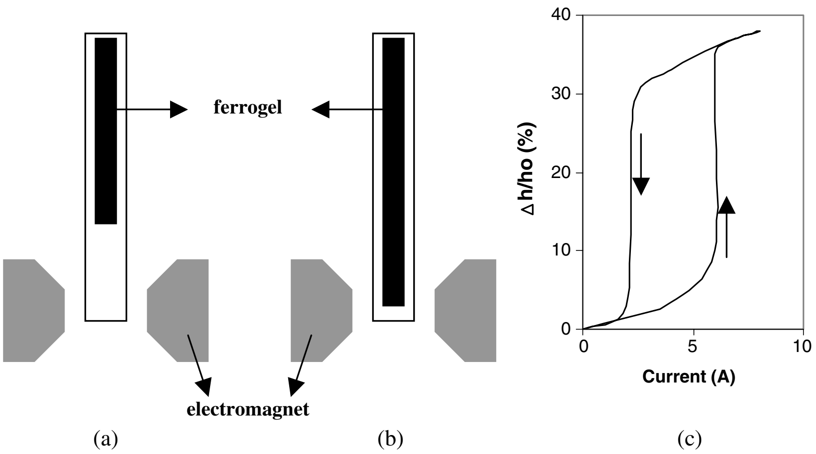

Figure 4. Elongation of ferrogel: (a) no magnetic field; (b) maximal magnetic field at the lower end of the ferrogel; (c) elongation versus current density (hysteresis) [11–13].

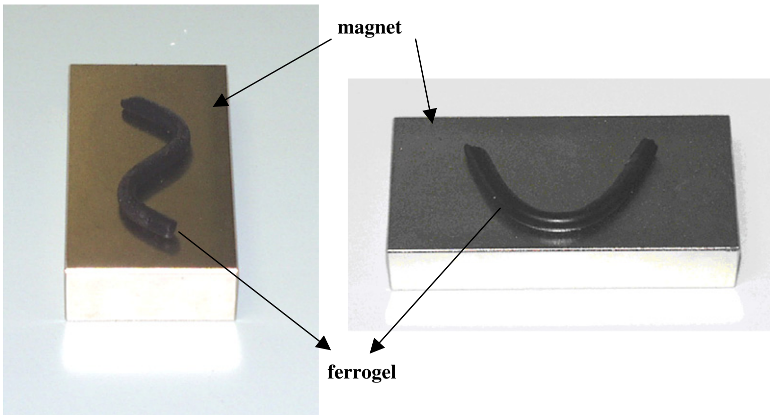

Figure 5. Flexibility of (PVA + Fe_3O_4) ferrogel.

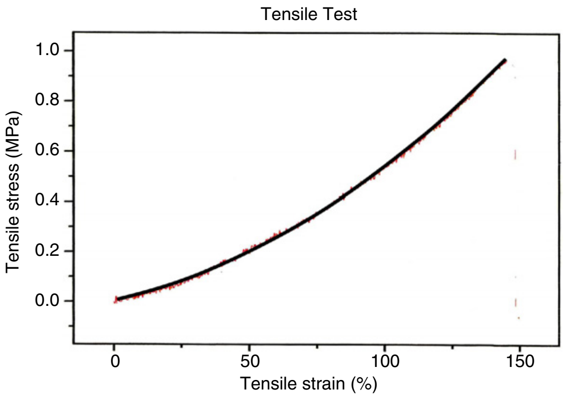

Figure 6. Stress–strain curve of (PVA + Fe_3O_4) ferrogel.

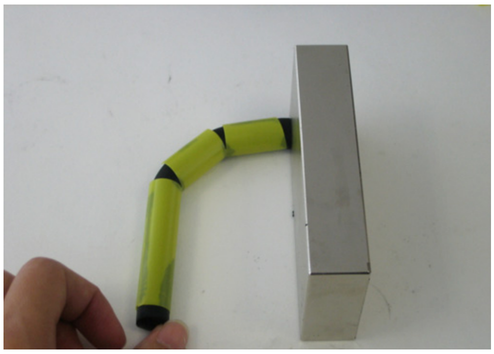

Figure 7. Concentration graded ferrogel, the concentrations are 25, 15 and 3 wt% of iron oxide in the three regions; the highest concentration is closest to the magnet.

properties of the two constituents. This peculiar magneto-elastic behavior is the basis for the development of such actuators for biomechanics and biomimetic applications.

Two possible approaches were proposed to develop a prototype of an artificial finger from the (PVA + iron oxide) composite.

(a) As discussed previously, the deflection of the system depends sensitively on the concentration of the magnetic carrier. Significant deflection can only occur when the applied magnetic field is above the threshold value. Therefore, by constructing a concentration-graded ferrogel with coatings to form joints, different portions of the ferrogel will undergo different extents of deflection when the ferrogel is subjected to a uniform magnetic field (figure 7). The uncoated portions will serve as the joint that facilitates the bending action necessary for each finger. The coating also serves to impart a higher mechanical strength that might be required for actuator applications. When the magnetic field is adjusted to create a magnetic field that is above the threshold value of the most concentrated portion but below the threshold value of the least concentrated portion, bending or 'finger bending' movement can be obtained. In short, the portion with the highest concentration bends/deflects the most while the portion with the lowest concentration deflects the least or not at all.

(b) Another approach is to coat a ferrogel of uniform concentration but to manipulate the coating properties. An example is the encapsulation of a ferrogel containing 10 wt% Fe_3O_4 with a transparent plastic material (figure 8). The ferrogel can be made to bend in a finger-like motion by applying a magnetic field of approximately 21 mT to one end of ferrogel and fixing the other end.

4. Conclusions

A study of multiferroic magneto-elastic magnetic and hydrogel composite materials was conducted. Iron oxide (Fe_3O_4) in the concentration range of 1–10 wt% was added to PVA gel and subjected to a magnetic field of up to 40 mT. The following results were obtained:

(1) (PVA + Fe_3O_4) ferrogel showed instantaneous deflection and recovery upon application and removal of a magnetic field.

(2) The extent of deflection strongly depends on the iron oxide content. There was a threshold value of magnetic field associated with each concentration, above which large deflection was obtained.

(3) The ferrogel was elastic and flexible. Finger-like motion was successfully mimicked by ferrogel partially encapsulated in rigid transparent plastic. The exposed

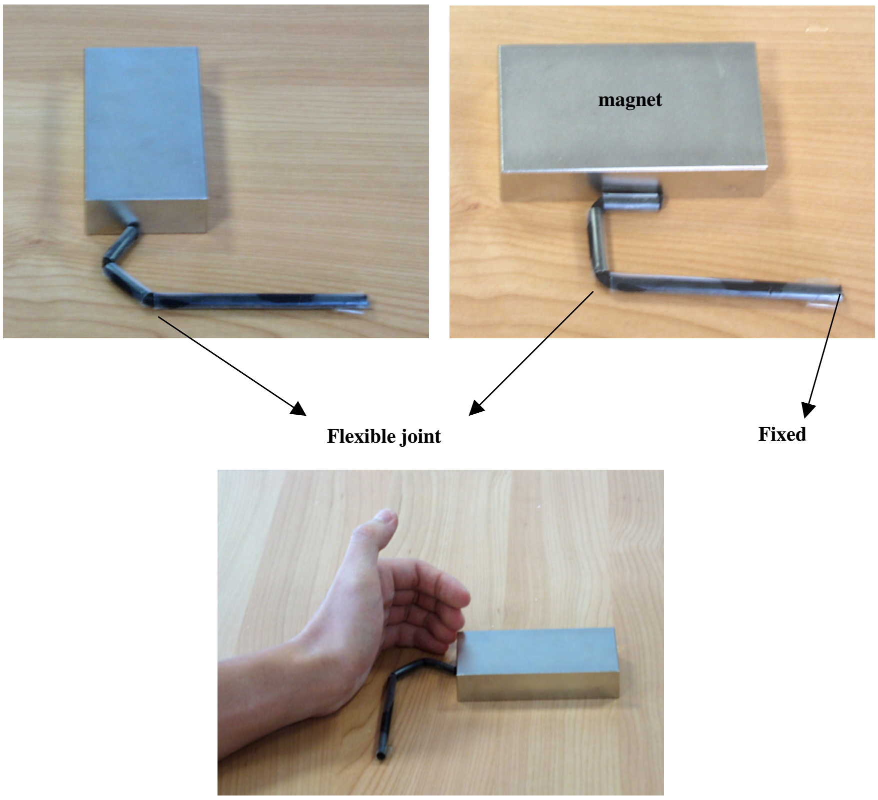

Figure 8. Artificial finger made of ferrogel with iron oxide content of 10 wt% and a magnetic field of 21 mT.

ferrogel parts serve as the joints that allow smooth and repeated finger bending.

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