Smart Nanocomposite Polymer Gels

*Zsolt Varga, József Fehér,Genovéva Filipcsei, Miklós Zrínyi**

HAS-BUTE Laboratory of Soft Matters, Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary
Email: zrinyi@mail.bme.hu

Summary: The combination of polymers with nanomaterials displays novel and often enhanced properties compared to the traditional materials. They can open up possibilities for new technological applications. The magnetic polymer gel represents a new type of composites consisting of small magnetic particles, usually from the nanometer range to the micron range, dispersed in a highly elastic polymeric gel matrix. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effects, high elasticity, anisotropic properties, temporary reinforcement and quick response to magnetic field open new opportunities for using such materials for various applications.

Keywords: anisotropic properties; gels; magnetic gels; nanocomposites; smart materials

Introduction

Composite materials consisting of rather rigid polymeric matrices filled with magnetic particles have been known for a long time and are called magnetic elastomers or magnetoelasts. These materials are successfully used as permanent magnets, magnetic cores, connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and practically do not change their size, shape and elastic properties in the presence of external magnetic field.

The new generation of magnetic elastomers represent a new type of composite, consisting of small (mainly nanosized) magnetic particles, having superparamagnetic behaviour, dispersed in a highly elastic polymeric matrix. These materials are relatively new and our knowledge of the magnetoelastic behaviour depending on the composition, external conditions and the synthesis processes is still rather poor.

 DOI: 10.1002/masy.200351009

Composite Gels

Many useful engineering materials, as well as living organisms, have a heterogeneous composition. The components of composite materials often have contradictory, but complementary properties. We use the term composite gel to indicate that in addition to the polymer network and swelling agent a third component is present as filler. Fillers are usually solid additives that are incorporated into the polymer networks to modify the physical properties. Fillers can be divided into three categories: those that reinforce the polymer gel and improve its mechanical performance, those that are used to take up space, and thus reduce material cost. The third, less common, category is when filler particles are incorporated into the gel to improve its electrical or magnetic properties. The size of the filler material varies from several nanometers to micrometers. They can be built into a network either as individual particles, or aggregates. Filler particles can also form ordered structures. If there are strong attractive interactions between the network polymers and the surface of the solid particles, this provides a coupling between forces acting on the solid particles and conformational change of the surrounding macromolecules.

Magnetic interactions are strong in certain solids, but rather weak in fluid systems. In order to enhance the influence of external fields on solution and/or gel properties it is necessary to combine solid-like and fluid-like behaviour. Magnetorheological fluids and ferrofluids contain small, dispersed particles in the size range from nanometers to micrometers.[1] These fluids respond to an applied field by rapidly changing their apparent viscosity and yield stress. Since polymer gels contain substantial amounts of liquid as swelling agent, it is possible to fabricate magnetic field sensitive gels by using a polymer network swollen by a complex fluid. The incorporated colloidal particles, characterized by strong adsorptive interactions with the polymer chains, couple the shape and physical properties of the gel to the external field. Since the particles are attached to the gel matrix, all forces acting on the particles are transmitted directly to the polymer chains, resulting either in locomotion or in macroscopic deformation of the gel. Here we consider such filler loaded gels, in which the filler particles have strong magnetic properties. The stronger field attracts the particles and, due to their small size and strong interactions with molecules of dispersing liquid and polymer chains, they all move together. Because of the cross-linking bridges in the network, changes in molecular

conformation can accumulate and lead to macroscopic shape changes or/and motion. In this case the polymer network plays the role of a mechanical amplifier.

Preparation of Magnetic Gels

A magnetic field sensitive gel is a special type of filler loaded polymer network, where the finely divided filler particles in the swelling agent have strong magnetic properties. Preparation of a magnetic gel does not require a special polymer or a special type of magnetic particle. As a polymer network one may use every flexible macromolecules that can be cross-linked. The filler particles can be obtained from ferri- and ferromagnetic materials.

Preparation of a magnetic gel is similar to that of other elastomeric networks. One can precipitate well dispersed particles in the polymeric material. The "in situ" precipitation can be made before, during and after the cross-linking reaction. According to another method the preparation and characterization of colloidal magnetic particles are made separately, and the cross-linking takes place after mixing the polymer solution and the magnetic particles together.

A critical point of the synthesis is the stabilisation of solid magnetic particles. It can be done either by surfactants or by strong adsorptive interactions bonding the particles to polymer chains. A highly responsive magnetic gel should have low elastic modulus and high initial susceptibility as well as high saturation magnetisation. In order to increase the magnetoelastic response to external field it is possible to decrease the elastic modulus by swelling. We have prepared magnetic gels made of poly(dimethyl-siloxane) containing randomly distributed magnetite particles. These gels are abbreviated as m-PDMS gels.

The Principles of Magnetoelasticity

The solid particles incorporated in the elastic matrix are the elementary carriers of a magnetic moment. In the absence of an applied field the magnetic moments are randomly oriented, and thus the polymer as a whole has no net magnetization. As soon as an external field is applied, the magnetic moments tend to align with the field to produce a bulk magnetic moment. With ordinary field strengths, the tendency of the dipole moments to align with the applied field is partially overcome by thermal agitation, such as the molecules of paramagnetic gas. As the strength of field increases, all the particles eventually align their moments along the direction of

the field, and as a result, the magnetization saturates. If the field is turned off, the magnetic dipole moments quickly randomise and thus the bulk magnetization is again reduced to zero. In a zero magnetic field a magnetoelast presents a mechanical behaviour very close to that of filler loaded network.

In a uniform magnetic field a magnetoelast experiences no net force. When it is placed in a gradient of a magnetic field, forces act on the superparamagnetic particles and the magnetic interactions are enhanced. The stronger field attracts the particles and due to their small size and strong interactions with molecules of polymer chains they all move together. Because of the cross-linking bridges in the network, changes in molecular conformation can accumulate and lead to macroscopic shape changes, which go together with motion. The force density, $\mathbf{f}_m$ on a piece of magnetoelast can be written as

$$\mathbf{f}_m = (\mathbf{M} \bullet \nabla)\mathbf{H} \qquad (1)$$

where **M** represents the magnetisation and $\nabla\mathbf{H}$ is the gradient of the magnetic field, **H**. It should be kept in mind that the magnetic force density vector varies from point to point in accordance with the position dependence of the product $(\mathbf{M} \bullet \nabla)\mathbf{H}$. The orientation of $\mathbf{f}_m$ is parallel to the direction of the magnetic field gradient. In a non-accelerating system the force density manifests itself as a stress distribution, which must be balanced by the network elasticity. A completely balanced set of forces is in this respect equivalent to no external force at all. However, they affect the gel internally, tending to change its shape or size or both. In general the deformation induced by magnetic field cannot be considered as a homogeneous deformation, since the driving force $(\mathbf{M} \bullet \nabla)\mathbf{H}$, varies from point to point in space. However one can find a special distribution of magnetic field, where the deviation from the homogeneous case is not significant. In this case the condition for uniaxial deformation of a ferrogel sample can be written as follows:[2-8]

$$\lambda^3 - \beta\left(H_t^2 - H_b^2\right)\lambda - 1 = 0 \qquad (2)$$

where λ stands for the deformation ratio, H_b and H_t represent the magnetic field strength at the bottom and the top of a magnetic gel sample, the parameter β is defined as

$$\beta = \frac{\mu_0 \chi}{2G} \qquad (3)$$

where μ_0 is the magnetic permeability of free space, χ stands for the initial susceptibility of the magnetic gel, and G is the elastic modulus. It must be mentioned that Eq.2 was derived on the basis of following assumptions: homogeneous deformation, a linear dependence between magnetisation and field strength and a Gaussian-type strain energy function were considered.

Eq.2 can be considered as a basic equation for describing the unidirectional magnetoelastic properties of a magnetic gel. It says if we put a gel in a non-homogeneous magnetic field in such a way that $H_t > H_b$ then elongation $\lambda > 1$ occurs. Figure1 demonstrates this effect. A m-PDMS gel was glued to a glass surface. The condition of $H_t > H_b$ was realized by placing a permanent magnet above the upper surface of the m-PDMS gel. It is seen on the figure that due to the field gradient (pointing from down to up) significant extension of the sample occurs.

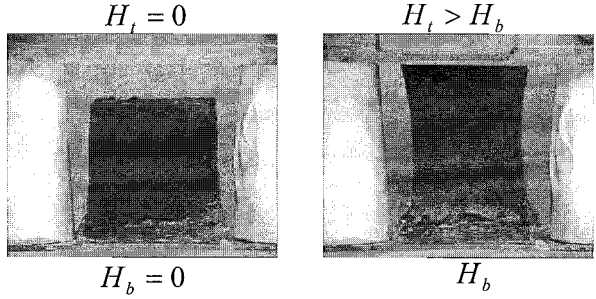

Fig. 1. Extension of magnetite loaded m-PDMS gel due to nonuniform magnetic field. $H_t > H_b$.

Preparation of Gels with Anisotropic Mechanical Behaviour

Synthesis of elastomers in uniform magnetic field can be used to prepare anisotropic samples. In a uniform field – due to the lack of a field gradient – there are no attractive or repulsive field-particle interactions, therefore particle-particle interactions become dominant. In liquids the imposed field orients the magnetic dipoles. If the particles are spaced closely enough, so that their field can reach their neighbours, mutual particle interactions are present. These interactions can be very strong leading to significant change in the structure of the particle ensemble.

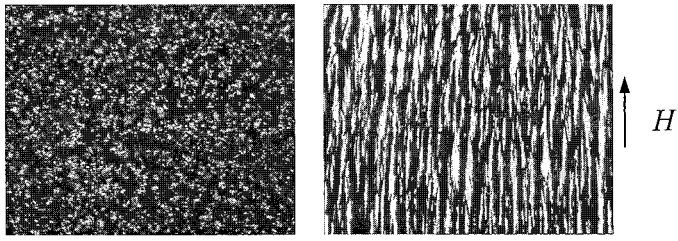

Fig. 2. Formation of bundles of magnetite particles parallel to the field direction in silicon oil as seen under a microscope. The concentration of magnetite in the mixture is 5m%. A; no external magnetic field, B; The magnetic induction in uniform magnetic field is 50 mT.

The particles attract each other when aligned end to end, and repel each other when placed side by side. Due to the attractive forces pearl chain structure develops as shown in Figure 2.

If the chemical reaction proceeds not too fast, then there is enough time to induce the pearl chain structuring of the filler particles by applying a uniform external field before the reaction is completed. The first step is to mix the filler particles with the reaction mixture, which contains the monomers, the cross-linking agent and the catalyst. The second step is to stabilize the system in order to avoid aggregation and sedimentation. Surfactant or polymers can do this.

Applying the uniform field and inducing the chemical reaction by raising the temperature is the next step. The formation of chain-like structures takes a few minutes and as a result, particle aggregates aligned parallel to the field direction are fixed in the network. The anisotropy manifests itself both as a direction dependent elastic modulus as well as direction dependent swelling. Figure 3. (A) shows a magnetite loaded PDMS gel in three different states. The magnetite content of the m- PDMS gel is 40 m%. On the left side of figure (A) the sample is

stress free. The arrow indicates the direction of the chain-like particle orientation. On the middle, a load is placed on top of the sample. Due to this load a slight compression occurs. If the same sample is rotated by 90 degree and the same load is placed on the perpendicular surface of sample as shown on the right side of figure (A), the compression is larger. This finding indicates mechanical anisotropy, since the elastic modulus is direction dependent. The anisotropy manifests itself during swelling. Figure 3. (B) shows the effect of swelling on the same m-PDMS sample. We increased the swelling degree by replacing the silicon oil with n-hexane. This latter is a better solvent for PDMS than silicon oil. Due to the solvent exchange the swelling degree increases. However the swelling shows anisotropy. The swelling degree parallel to the chain-like particle orientation is less than in the perpendicular case.

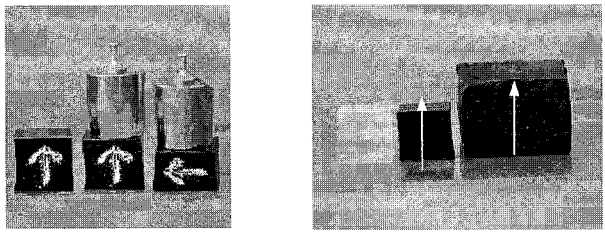

Fig. 3. Anisotropic mechanical (A) and swelling (B) behaviour as seen by the naked eye.

Future Aspects

The ability of magnetic-field-sensitive gels to undergo a quickly controllable change of shape can be used to create an artificially designed system possessing sensor and actuator functions internally in the gel itself. The peculiar magneto-elastic properties may be used to create a wide range of motion and to control shape change and movement that are smooth and gentle similar to that observed in muscle. Thus, application of magnetic field sensitive gels as a soft actuator for robots and other devices like switches, seals, micromachines, active vibration control and biomimetic energy-transducing devices has special interest.

Acknowledgements

This research was supported by the Széchenyi NRDP No. 3/043/2001 and the Hungarian National Research Fund (OTKA, Grant No. T038228). This research is sponsored by NATO's Scientific Division in the framework of the Science for Peace Programme.

[1] R.E. Rosenweig, "*Ferrohydrodynamics*", Cambridge University Press, Cambridge, 1985.
[2] M.Zrínyi, L.Barsi, A.Büki, *Polymer Gels and Networks* **1997**, 5, 415.
[3] M.Zrínyi, L.Barsi, A.Büki, *J. Chem. Phys.* **1996**, *104*, 8750.
[4] M.Zrínyi, *Trends in Polymer Science*, **1997**, *5*, 280.
[5] M.Zrínyi, L.Barsi, D.Szabó, H.-G.Kilian, *J.Chem Phys*, **1997**, *108*, 5685.
[6] D.Szabó, G.Szeghy, M.Zrínyi, *Macromolecules* **1988**, *31*, 6541.
[7] M.Zrínyi, D.Szabó, L.Barsi, in: "*Polymer Sensors and Actuators*" Eds. Y.Osada, D.E.Rossi, Springer, Berlin 1999, p. 385.
[8] M. Zrínyi , D. Szabó, G. Filipcsei, J. Fehér, in: "*Electric and Magnetic Field-Sensitive Smart Polymer Gels Polymer Gels and Networks*", Marcel Dekker., New York, Eds. Y. Osada , A. Khokhlov 2001, Ch 11, p. 309.