Electric and Magnetic Field-Structured Smart Composites

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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 electric- and magnetic- field-sensitive elastomers represent a new type of composites consisting of small particles, usually from nanometer range to micron range, dispersed in high elastic polymeric matrix. Coupling of electric and/or magnetic fields with elastic properties leads to a number of striking phenomena that are exhibited in response to impressed external fields.
The ability of such materials to change their size and mechanical properties in a reversible manner has inherent interest, if for no other reason than the uniqueness having giant elastic response to polarization. The giant deformational effect, high elasticity, anisotropic properties, and quick response to either electric or magnetic fields open new opportunities for using such materials for various applications. Since electric and magnetic fields are convenient stimuli from the point of signal control, it is of great importance to develop and study such flexible, smart polymeric systems.

Keywords: anisotropic magnetic elastomers; Einstein-Smallwood parameter; electrorheology; field-sensitive elastomers; magnetorheology

Introduction

Many useful engineering materials, as well as living organisms have a heterogeneous composition. The hybridization of organic and inorganic matter on the colloidal scale provides new and sometimes surprising properties. Fillers are usually solid additives that are incorporated into the polymer to modify its physical properties. Fillers can be divided into 3 categories: those that reinforce the polymer and improve its mechanical performance; those that are used to take up space, and thus reduce material cost; and a less common category, those that are incorporated into the material to improve its responsive properties. The new generation of polymer composites contains electric- and/or magnetic-field-sensitive particles and enables a coupling of external field and mechanical properties. Application of field-sensitive filler particles provides a unique ability for such materials to modify mechanical and thermodynamical properties.

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Composite materials consisting of rather rigid polymeric matrices filled with magnetic particles have been known for a long time. These materials are successfully used as permanent magnets and magnetic cores, connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and hardly change their size, shape, and elastic properties in the presence of an external magnetic field.

The new generation of smart elastomers represents a new type of composites consisting of small magnetic- or electric- field-sensitive particles, usually in the nanometer range, dispersed in a highly elastic polymeric matrix. A giant deformational effect, high elasticity and quick response to external fields open new opportunities for using such materials for transducers, actuators, and fast artificial muscles. The main purpose of the present paper is to report on recent advances in the development of uniaxially- and biaxially-ordered composites by using electrorheological and magnetorheological effects. The influence of the ordered structure on the elastic modulus has been studied.

Preparation of field-sensitive polymer gels

Field-sensitive gels are a special type of filler-loaded polymer network, where the finely divided filler particles have a strong response to either electric or magnetic fields. Any flexible polymer, which can be crosslinked can be used for a polymer network. The filler particles can be obtained from magnetic- and electric-field responsive materials.

Preparation of field-sensitive gels is similar to that of other filler-loaded networks—well-dispersed particles are precipitated in the polymeric material. The *in situ* precipitation can be made before, during, and after the crosslinking reaction. In another method, the preparation and characterization of colloidal magnetic particles are made separately, and the crosslinking takes place after the polymer solution and the magnetic particles are mixed together. The preparation can also be realized in the presence of an external magnetic field. In this case, ordered particle aggregates are incorporated into the elastic matrix. A critical point of the synthesis is the stabilisation of solid particles which can be done either by surfactants or by strong adsorptive interactions, bonding the particles to polymer chains. A more detailed description of the preparation procedure can be found in other papers. [1-7]

Polymer gels in non-uniform electric or magnetic field

All materials experience forces or torques when subjected to electric or magnetic fields. These interactions are strong for certain solid materials, but rather weak for fluid systems. In order to enhance the influence of external fields on solution and/or gel properties solid- and fluid-like behaviours must be combined. New colloidal solutions, termed *complex fluids* have been introduced. Electrorheological fluids, magnetorheological fluids, and ferrofluids contain dispersed small particles ranging in size from nanometers to micrometers.[8] 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 a swelling agent, it is possible to fabricate field-sensitive gels by using a polymer network swollen by a complex fluid.[1-7] The incorporated colloidal particles, characterized by strong adsorptive interactions between solid particles and polymer chains, couple the shape and physical properties of the gel to the external field. These field-sensitive gels can be exploited to construct new types of soft actuators, sensors, micromachines, biomimetic energy transducing devices, and controlled delivery systems.

If a field-sensitive gel is exposed to an external field, two distinct types of interactions can be identified: a *field–particle* interaction and a *particle–particle* interaction.[8,9] If the field is nonuniform, then the field-particle interactions are dominant. Particles experience a dielectrophoretic (DEP), or magnetophoretic (MAP) force, respectively. As a result, the particles are attracted to regions of stronger field intensities. Because of the crosslinking bridges in the network, changes in molecular conformation due to either DEP or MAP forces can accumulate and lead to macroscopic shape changes and/or motion. The main features of the DEP and MAP forces are summarized in Table I.

Table I. Particle–field interactions in nonuniform fields. R is the radius of solid particles, ε and μ are the respective permittivity and permeability. The index 2 refers to the colloidal particle; the index 1 denotes the swelling agent.

ELECTRIC FIELD	MAGNETIC FIELD
dielectrophoretic force $f_{DEP} = 2\pi\varepsilon_1 R^3 K \nabla E_0^2$	*magnetophoretic force* $f_{MAP} = 2\pi\mu_1 R^3 K \nabla H_0^2$
permittivities $K = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}$	***permeabilities*** $K = \frac{\mu_2 - \mu_1}{\mu_2 + 2\mu_1}$
field gradient ∇E_0	***field gradient*** ∇H_0

Field-sensitive gels can be made to bend and straighten, as well as elongate and contract repeatedly without damage to the gel.[5,6] The response time for obtaining the new equilibrium shape was found to be less than a second and seems to be independent of the size of the gel. This is demonstrated for magnetic-field-sensitive as well as electric-field-responsive gels in Figures 1 and 2.

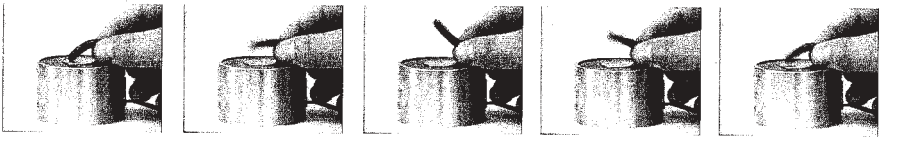

Figure 1. Snapshot of shape change of a magnetite-loaded polyvinyl alcohol hydrogel due to modulated magnetic field. The frequency of the field is 40 Hz.

The magnetoelastic response time is rather quick, one cycle requires a half-second. It is noteworthy that up to 40 Hz, the magnetic stimulus and the elastic response are strongly coupled. No phase shift, or significant mechanical (or magnetic) relaxation takes place.

The TiO_2-loaded PDMS gel cylinder, suspended into silicon oil, showed significant and rapid bending as shown in Figure 2.

In a uniform field the situation is completely different. Due to the lack of field gradient, there are no attractive or repulsive field-particle interactions. The particle-particle interaction becomes dominant. The imposed field induces electric or magnetic dipoles. As a result, mutual particle interactions occur if the particles are so closely spaced that the

local field can influence its neighbours. This mutual interaction can be very strong and influences the elastic modulus of the gel.

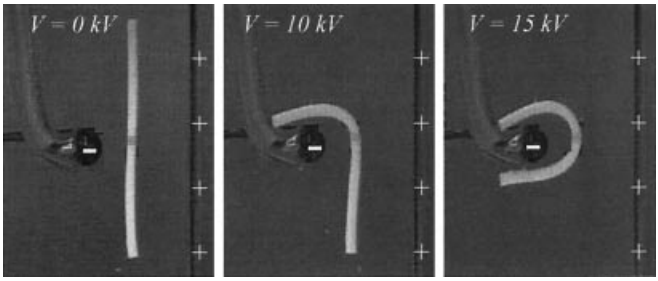

Figure 2. Bending of an electric-field-responsive PDMS gel in a non-uniform field. The polarity of the electrodes and the voltage are indicated here.

Preparation of elastomers with anisotropic mechanical behaviour

Synthesis of elastomers in a uniform magnetic field can be used to prepare anisotropic samples. In a uniform field dipoles are induced. As a result, mutual particle interactions occur if the particles are so closely spaced that the local field can influences their neighbours. This mutual interaction can be very strong, leading to significant changes in the structure of particle ensembles.

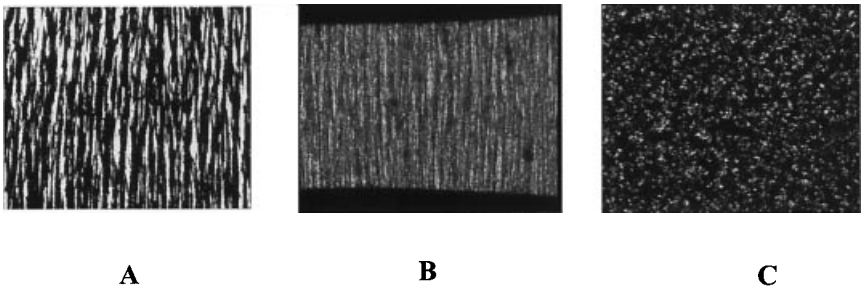

Figure 3. Magnetorheological (A) and electrorheological (B) effects of neutral particles under uniform magnetic or electric field respectively. Figure (C) shows magnetite suspension when no external field is present. The direction of chains is parallel to the field direction of the *E* or *H* fields.

The particles attract each other when aligned end-to-end, and repel each other when side-by-side. In liquids, a pearl-chain structure can develop as a consequence of electrorheological and magnetorheological effects, as demonstrated in Figure 3. Pearl-chain structuring of Fe_3O_4 particles dispersed in silicon oil in a uniform magnetic field is

shown in Figure 3A. The electrorheological effect is demonstrated in Figure 3B. The same structuring phenomena occur in the monomer mixture of PDMS. If the polymerization reaction does not proceed too quickly, then there is enough time to induce the pearl-chain structuring of the filler particles by applying a uniform external field before the reaction has been completed.

In order to prepare an anisotropic magnetic gel, the mixture of Elastosil 604 and magnetite particles were placed between the poles of a large electromagnet (JM–PE–I, JEOL, Japan) for 24 hours at room temperature. The uniform magnetic field was varied in a wide range from 10 to 400 mT. The formation of chain-like structures takes a few minutes, and as a result, aligned particle aggregates parallel to the field direction are fixed in the network. Depending on the concentration of the magnetic particles as well as on the applied magnetic field, the columnar structures of the magnetic particles built in the elastic matrix can be varied in a wide range.

Anisotropic mechanical and swelling behaviour of composite gels

The anisotropy manifests itself in both directions dependent elastic modulus as well as direction dependent swelling. Figure 4A shows a magnetite-loaded PDMS gel in 3 different states. The magnetite content of the magnetoelast is 40% m. On the left side of Figure 4A the sample is stress-free. The arrow indicates the direction of the chain-like particle orientation. In the middle, a load is placed on top of the sample and, due to this load, a slight compression occurred. When the same sample is rotated by 90° and the same load is placed on the perpendicular surface of the sample (right side of Figure 4A), the compression is larger. This finding indicates a mechanical anisotropy, since the elastic modulus is direction-dependent.

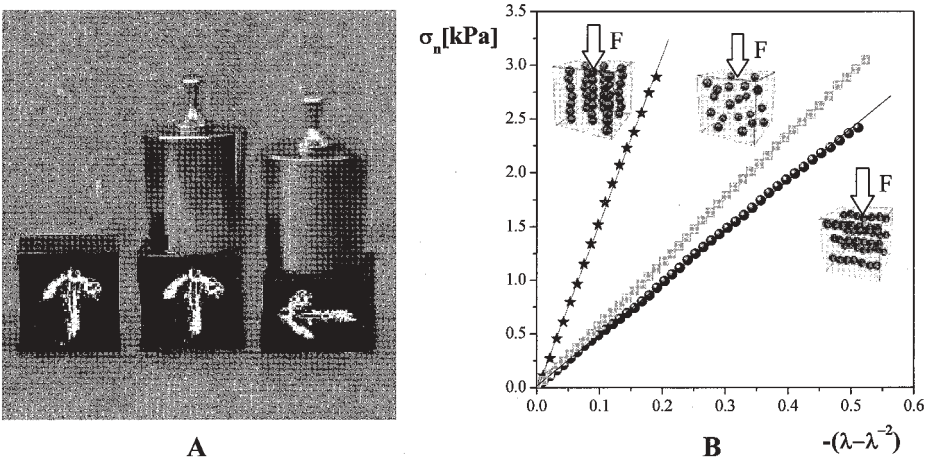

Figure 4. Anisotropic mechanical behaviour as seen by the naked eye (A) and by stress-strain measurements (B). Three samples with the same amount of filler particles but differing particle distribution, as indicated in the Figure, are compared.

The elastic modulus was determined by unidirectional compression measurements and the modulus, *G,* was calculated on the basis of the statistical theory of rubber elasticity:[10,11]

$$\sigma_n = G(\lambda - \lambda^{-2}) \tag{1}$$

where σ_n is the nominal stress defined as the ratio of the equilibrium elastic force and the undeformed cross-sectional area of the sample. The deformation ratio, λ, is the length, h, (in the direction of the force) divided by the corresponding undeformed length, h_0. G stands for the modulus which can be expressed as a function of the filler concentration by the Einstein-Smallwood equation:[10,11]

$$G = G_0(1 + k_e\phi_m) \tag{2}$$

where G_0 denotes the modulus of the elastomer without any solid particles, k_e is the Einstein-Smallwood parameter, and ϕ_m represents the volume fraction of the filler particles.

The elastic modulus of the magnetic elastomers was determined on the basis of Eq. 1 from the plot of nominal stress against $(\lambda - \lambda^{-2})$ data. The slope, *G,* was calculated by the linear

least square method. Figure 4B shows evidence that there are a significant differences in the stress-strain behaviour. On the basis of the Einstein-Smallwood equation (Eq. 2) one expects that the reinforcement is due only to the concentration of filler particles.

We have found that not only the particle concentration, but also the spatial distribution of the solid particles significantly influences mechanical behaviour. Figure 4B—as a demonstrative example—shows the strong influence of particle arrangement on the elastic modulus.

The anisotropy manifests itself during swelling. Figure 5 shows the effect of swelling on the same magnetoelast. As a swelling agent, n-hexane was used at room temperature. Since the swelling degree and elastic modulus are interrelated, the swollen gel shows anisotropy. The swelling degree parallel to the chain-like particle orientation is less in the perpendicular direction.

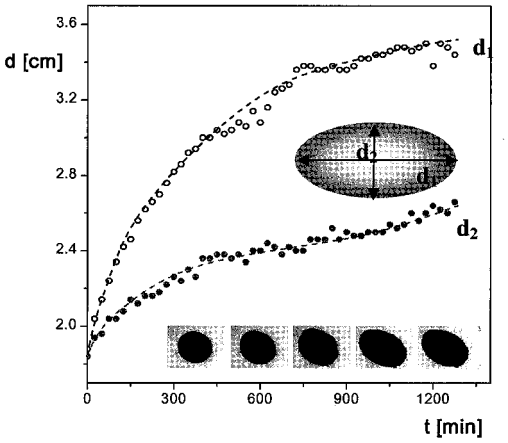

Figure 5. Anisotropic swelling of a magnetic PDMS gel in n-hexane

Temporary reinforcement due to magnetic interactions

The only process taking place when a uniform magnetic field is imposed on a magnetic gel is the rotation of the magnetic dipole moment of the individual particles, which results in a considerable macroscopic magnetization of the gel. As a consequence of the magnetization, a demagnetizing field will be formed, reducing the effective field inside the gel. Deformation of the ferrogel sample involves a change in the geometry, and thus, a change in the demagnetizing coefficient. As a consequence of the change in the

demagnetizing coefficient, both the effective field and magnetisation will change, resulting in a change of the magnetic energy. This means that deformation of ferrogel requires more energy in a uniform magnetic field since the change in elastic and magnetic energy must be overcome. In practice, the magnetic effect manifests itself as an increase in the elastic modulus. This increase due to magnetic interaction is called temporary reinforcement.

In order to study the effect of the uniform magnetic field on the elastic modulus, we prepared several types of Fe_3O_4 and iron-loaded magnetic gels without an external magnetic field and under a 400 mT uniform magnetic field. The concentration of the filler particles was varied in a wide range, from 10-40 wt%. The intensity of the external magnetic field was varied from 0 to 400 mT. The direction of the applied uniform magnetic field was parallel to the particle alignment, but the applied mechanical stress was perpendicular to the field, as indicated in Figure 6. The only difference between the samples shown in Figure 6 is due to the distribution of magnetic particles. The magnetic gel containing randomly distributed particles can be characterized by a smaller increase in the modulus. The magnetoelast containing particles with a pearl-chain structure has a larger increase in the modulus.

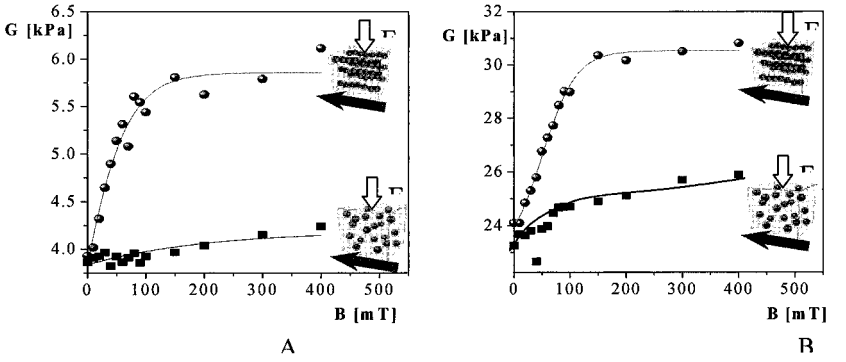

Figure 6. The effect of the uniform magnetic field on the elastic modulus. The arrows show the direction of the applied uniform magnetic field during the stress-strain measurements. a) iron content 20 wt%, b) iron content 40 wt%

At low field intensities the modulus increases; at higher fields it levels off. It is also seen that spatial distribution of magnetic particles has a decisive effect on the temporary reinforcement effect. Comparing the excess elastic modulus of the isotropic samples to the anisotropic elastomers, significant differences can also be observed. The excess elastic

modulus of the elastomers with homogeneous filler distribution is lower than that of the orientated sample. The uniform magnetic field which is parallel to the particle alignment and perpendicular to the deformation increases the modulus due to the mutual particle interaction. As the field intensity is increased, this interaction becomes stronger and stronger, up to 150 mT field intensity. At a higher field intensity the elastic modulus does no longer changes.

We have made measurements where the direction of the applied uniform magnetic field was parallel to the particle alignment and to the applied mechanical stress. The results are shown in Figure 7. When the applied uniform magnetic field is parallel to the particle alignment, the relative change in the modulus (the excess modulus) is the highest (270%). We can conclude that the parallel uniform magnetic field intensifies the effect of the particle alignment. When the iron content is increased, the mutual particle interaction also increases and, because of the stronger interaction, the elastic modulus increases.

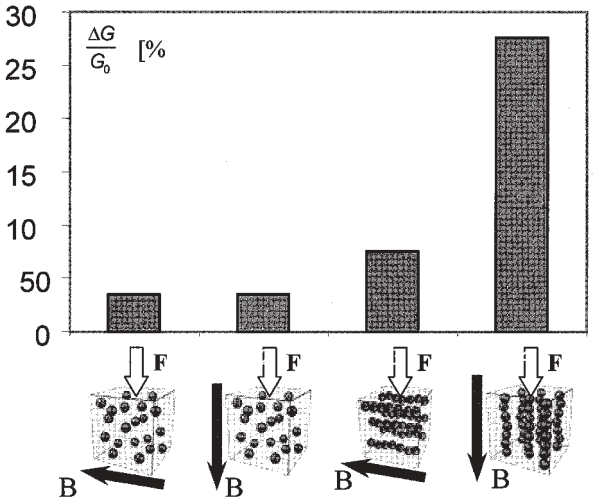

Figure 7. Relative change in the elastic modulus due to a uniform magnetic field.

Conclusion

We have demonstrated that the interactions in colloidal particles can be easily tuned by external magnetic fields, and the chemical process can fix the structured lane formation. The result is a highly anisotropic sample. We have shown that uniaxial field-structured composites consisting of magnetic particles in the elastomer exhibit a larger increase in the

modulus compared to that of random particle dispersions. According to the measurements the increase in the elastic modulus is most significant if the applied field is parallel to the particle alignment. The anisotropy manifests itself in both direction dependent elastic modulus as well as direction dependent swelling.

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