The energetics of magnetoelastic actuators is analogous to phase transformations in materials

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Received 4 September 2009; received in revised form 16 June 2010; accepted 18 June 2010
Available online 17 July 2010

Abstract

A ferrogel is a composite system comprised of a polymeric matrix and magnetic filler particles. The elastic properties of the polymer can be coupled with the magnetic properties of the particles to create novel soft actuators. Understanding the mechanical behavior of ferrogels in an external magnetic field is essential to optimize actuator performance. The energetics of the mechanical behavior of cylindrical ferrogel specimens was found to be analogous to the energetics of chemical phase transformations in materials. Depending on the sample geometry, the elongation mechanism of ferrogel cylinders in an external magnetic field was identified as either a continuous or discontinuous deformation, analogous to a second- or first-order phase transformation, respectively. In analyzing mechanical strain as a function of magnetic field, the first and second derivatives of energy can be used to predict metastability and transitions in ferrogel deformation behavior.

Keywords: Magnet–polymer composites; Phase transformations; Mechanical behavior of composites; Energetics of deformation

1. Introduction

A ferrogel [1] is a composite consisting of a polymeric matrix and magnetic filler particles. Novel deformation behavior of such composites in an external magnetic field can be obtained due to the coupling of the elastic properties of the polymer with the magnetic properties of the filler [2]. Ferrogels [1], also termed magnetoelastics [3], magnetooactive polymers [4], magnetorheological elastomers [5], magnetostrictive polymers [6] and magnetic field sensitive gels [7], have been extensively researched for a wide range of technological applications in biomedical, automotive, aerospace and robotics-based industries. These materials are lightweight, relatively inexpensive and can be cyclically deformed to high strains in three dimensions with minimal self-damage or release of byproducts into the environment [8]. Potential applications range from soft actuators [4] and micromanipulators [1] to applications such as active clothing, biologically inspired robotics [9], damping components [6], vibration/shock absorbers [7] and stiffness tunable mounts [10]. Biomedical applications include artificial tissues [2], drug carriers [1] and cancer therapeutics [11]. Understanding the mechanical behavior of ferrogels is a vital step in optimizing their performance.

Ferrogel materials require optimum coupling of the elastic properties of a polymer network with the magnetic properties of the filler component. Filler materials should be selected to maximize response, thereby limiting the amount of filler needed. Since our primary interest was biomedical applications, Fe3O4, a commonly used biocompatible magnetic compound, was selected for modeling. The relative permeability of Fe3O4 nanoparticles within a polymer matrix is reported to range from 4 to 7 [12]. In general, other magnetic alloys or processing techniques may be utilized to improve the magnetic response [13]. FeCo powders are highly magnetic, as evidenced by their position on the Slater–Pauling curve; Fe36Co62Ge2 powders in a polymer
matrix, for example, have a saturation value of 173 emu g\(^{-1}\) [14]. Synthesis techniques, such as the incorporation of flakes of metallic glass, can be used to increase the magnetic response of filler material. Ferrogel systems containing HyMu800 powders or Metglass 2705 M flakes that have been cut from ribbons have been reported to achieve relative permeability of over 100 [15]. An additional parameter to consider in maximizing magnetic response is the size of filler particles. Silicone matrices with iron oxide particulate filler material have relative permeability values ranging from 9 to 21 as the particle size changes from 2.5 to 9 \(\mu\)m [16]. The polymer component can also be tuned to increase the response of a ferrogel composite. For example, polyester systems containing nickel microparticles display a relative permeability ranging from 5 to 20 [17], whereas nickel alloy microparticles within natural rubber have a relative permeability of 3–4.5 [18].

The magnetoelastic stability of magnetic materials has been studied because of its relevance to a wide range of applications, including magnets for particle physics research, magnets for medical applications, magnetically levitated trains and magnetic forming systems [22–24]. Other applications include magnetohydrodynamic devices and fusion reactors [25]. The topic of buckling due to magnetic forces has been examined in terms of energy relationships and catastrophe theory [26]. In the case of magnetically induced deflection of cylindrical ferrogel specimens, “on–off” discontinuous deformation has been experimentally observed by Ramanujan and Lao [27].

Our work focuses on the interesting relationships between the energetics of mechanical deformations of ferrogels in an external magnetic field and the classical phase transformations that occur in metals, ceramics and polymers [19]. Examples of mechanical transitions previously studied by analogy to phase transformations include bulge propagation in a long, cylindrical balloon, neck propagation in polymeric materials, and buckle propagation in externally pressurized pipes [20]. Zrínyi et al. [21] noted the similarity between the abrupt, reversible volume change that occurs in response to an infinitesimal change in potential in pyroelectrolytic gels and a first-order phase transformation.

Raikher et al. [28] claimed that the gradual, smooth transition of ferrogel membranes is similar to a second-order phase transformation. A similar continuous transition can be elicited in the case of linear magnetostriction of cylindrical ferrogel specimens. Our work demonstrates that magnetoelastic mechanical behavior can be modeled using phase transformation concepts. Additionally, our work shows that the geometric parameters of a ferrogel specimen can be used to elicit various deformation mechanisms, including continuous and discontinuous deformations.

Ferrogel deformation modes include elongation, deflection, contraction and coiling [29]. This study focuses primarily on elongation and contraction (Fig. 1). It is shown that the energetics of the mechanical transitions that occur during magnetoelastic deformation of ferrogels are analogous to those of phase transformations in materials. For elongation, both first- and second-order transformations are feasible; however, for contraction, only second-order transformation behavior is observed for the same range of geometric parameters, consistent with experimental observations.

2. Results and discussion

Experimental studies showed that ferrogel cylinders in an external magnetic field can deform in actuation, contraction and coiling modes. Fig. 2a shows the discontinuous elongation of a cylindrical specimen suspended above an electromagnet. The deformed specimen consisted of coexisting grossly elongated and minimally elongated phases. The extent of deformation of these coexisting phases was determined by the material’s response to local values of the magnetic field. The qualitative strain differences between these regimes could be seen by visual inspection of the respective regions as indicated in Fig. 2a.
Similar behavior is observed in the bulging of a long, cylindrical balloon; noticeably different grossly expanded and minimally expanded regions of the balloon coexist [20].

The deflection of both a cylindrical ferrogel specimen (Fig. 2b) and a ferrogel membrane (Fig. 2c) exhibited continuous strain for small magnetic fields, followed by discontinuous deformation at large magnetic fields.

In our work, the energetics that govern ferrogel deformation were found to be analogous to phase transformations. Furthermore, discontinuous deformation was found to correspond to magnetic field values at which the first and second derivatives of energy with respect to strain were both zero.

2.1. Energy of deformation

The change of Helmholtz free energy ($A$) of a ferrogel in the presence of an external magnetic field ($B$) was used to model the strain ($\lambda$)–magnetic field response [1]. The linear magnetostrictive elongation of cylindrical ferrogel specimens in the presence of the magnetic field generated by an electromagnet was modeled as shown in Fig. 3a. One end of the specimen was maintained at a fixed distance ($z_0$) from the centerline of the electromagnet dipoles, while the other end was free to respond to the magnetic field. Fig. 3b shows the corresponding schematic for ferrogel contraction.

Szabo et al. suggested that the relationship between field decay ($k$) and electromagnet pole radius ($\delta$) is given by $k = \gamma/(2\delta + \gamma \delta^2)$, where $\gamma$ is a constant and is characteristic of the individual electromagnet [1]. Using this expression, the magnetic field strength as a function of distance from the center of the electromagnet poles ($z$) was determined as follows for various $B_{\text{max}}$ values, where $B_{\text{max}}$ is the maximum magnetic field strength along the centerline of the electromagnet poles:
The total Helmholtz free energy ($A_t$, Eq. (4)) of the composite is the sum of two terms [1]: the elastic energy ($A_{el}$, Eq. (5)) and the magnetic energy ($A_{mag}$, Eq. (6)):

$$A_t = A_{el} + A_{mag}$$

$$A_{el} = \frac{1}{2} G_P V \left(k z^2 + \frac{C_0}{k} \right)$$

$$A_{mag} = \frac{L_0}{2 \mu_0 \tilde{\kappa}_z} \int_{z_0}^{z} B^2(z) dz$$

where $\chi$ is the magnetic susceptibility of the ferrogel, $d_0$ is the initial cross-sectional area of the specimen, $\mu_0$ is the permeability of free space, $z_0$ is the distance from the center of the poles and $h_0$ is the initial specimen length. The Poisson’s ratio of rubber-like materials is approximately 0.5 [30]; therefore, constant volume was assumed. $G_P$ is the shear modulus of the polymer matrix, $V$ is the specimen volume and $\tilde{\kappa}_z$ is the strain of the ferrogel specimen as a function of $z$. Unless otherwise noted, all calculations were completed using values of shear modulus ($G_P$) of 60 kPa, dipole radius ($\delta$) of 1.5 cm, field intensity ($c_0$) of 40 cm$^{-1}$, and the field strength ($B_{max}$) of 2 T.

![Fig. 3. Schematic of specimen and the electromagnet position for: (a) elongation and (b) contraction studies.](image)

![Fig. 4. Schematic of energy vs. strain of a ferrogel in the presence of an external magnetic field.](image)

![Fig. 5. Equilibrium strain of ferrogel specimen as a function of magnetic field strength. The strain-relaxation profile is divided into: (a) gradual continuous strain; (b) discontinuous transition; (c) gradual continuous strain; (d) saturation behavior; and (e) hysteresis on relaxation ($h_0 = 10$ cm, aspect ratio = 3, $z_0 = 1.5h_0$).](image)

![Fig. 6. Strain-field profiles illustrating: (a) continuous ($h_0 = 1$ cm, aspect ratio = 1, $z_0 = 1.5h_0$) and (b) discontinuous ($h_0 = 10$ cm, aspect ratio = 3, $z_0 = 1.5h_0$) deformation mechanisms of ferrogel elongation.](image)
filler volumetric concentration ($\Phi_m$) of 2%, and magnetic susceptibility ($\chi$) of 21.2 $\Phi_m$ [1].

The experimental observations of maximum achievable equilibrium strain can be explained using Eqs. (4)–(6). The change in Helmholtz free energy is comprised of two terms: the elastic term ($A_{el}$) that resists deformation, and the magnetic term, ($A_{mag}$) that favors deformation (Fig. 4). Strain is determined by a balance of these two terms.

A key aspect of these two energy terms is their differing dependence on specimen geometry. The elastic energy is dependent upon the specimen volume, whereas the magnetic energy term is proportional to the cross-sectional area of the specimen integrated over the specimen length. This
differing dependence on geometry allows the specimen geometry and configuration \((d_0, h_0, z_0, \text{aspect ratio})\) to be readily altered to tune deformation behavior.

2.2. Calculation of strain vs. magnetic field

The equilibrium strain was found by determining the minimum energy value using Eqs. (4)–(6). This strain value was then paired with the corresponding value of the associated magnetic field \((B_{\text{max}})\) to generate strain–magnetic field curves. A schematic with the relevant strain regimes of a typical strain–magnetic field profile is shown in Fig. 5. The strain–field profile can be divided into the following regimes: for small magnetic fields (region a), deformation is continuous and gradual. Above a critical magnetic field (region b), the ferrogel undergoes a discontinuous change in strain, corresponding to a mechanical transition. Subsequently, the system again undergoes continuous deformation (region c), followed by saturation (region d). Ferrogels can also exhibit strain–field hysteretic relaxation (region e) as the magnetic field is reduced to zero.

The equilibrium strain was calculated as a function of magnetic field strength for various specimen configurations. Original specimen lengths \((h_0)\) ranging from 1 to 30 cm, aspect ratio (initial length divided by diameter) ranging from 1 to 7, and initial specimen distance from field source \((z_0)\) ranging from 1.5 to 2 times that of the original specimen length were studied. An initial distance of 1.5 times that of the specimen length implies that the closest end of the specimen was at a distance from the center of the electromagnet poles of half of its initial length.

By examining the effects of changes in geometric parameters on the resultant strain–magnetic field profiles, it was found that ferrogel elongation can be either continuous (Fig. 6a) or discontinuous (Fig. 6b).

2.3. Discontinuous deformation

The abrupt and discontinuous elongation of cylindrical specimens (Fig. 2a) in the presence of an external magnetic field is a mechanical transition analogous to a first-order phase transformation. Chater and Hutchinson [20] noted the existence of several mechanical transitions between uniform solution states which have features in common with phase transformations. The magnetoelastic strain of ferrogels in the presence of an external magnetic field is another such example due to the parallels between the energy–strain curves and the energetics of phase transformations.

Macroskopically, the mechanical transition observed in Fig. 2a and b included hysteretic behavior and the coexistence of more than one phase [31]. Within a deformed ferrogel, coexisting minimally deformed and grossly deformed regions (Fig. 2a) are analogous to the simultaneous presence of more than one phase within a material.

The presence of hysteresis in the strain–magnetic field profile (Fig. 5) is analogous to the discontinuous, hysteretic nature of first-order phase transformations. Analysis of the corresponding energy \((A)\) as a function of strain \((\dot{x})\) for various magnetic fields showed that as magnetic field was increased from 0.1 to 0.8 T, the number and location of energy minima changed (Fig. 7a).

In Fig. 7a, at small values of magnetic field, e.g. \(B_{\text{max}} = 0.1\) T, there was one minimum in the energy–strain plot. For values of magnetic field between 0.36 and 0.57 T, in the “two-phase region”, there were two minima in the energy curve (“minimum a” and “minimum b”, Fig. 7b). These minima can be interpreted as a metastable phase (local minimum) and a stable phase (global minimum) [32]. These minima share a common tangent (Fig. 8), corresponding to equal chemical potential in the case of phase transformations.

The magnetic field values at which discontinuous strain occurred was determined by examination of the plots of the first derivative of energy \((A')\) as a function of strain. Discontinuous strain occurred when the first and second derivatives of energy were simultaneously equal to zero [22,33]. When this condition was satisfied, the system was able to shift to the new minimum due to the absence of an energy barrier between the minima. In the example provided (Fig. 9), these magnetic field values were 0.36 and 0.57 T. At these values of \(B_{\text{max}}\), a discontinuous strain occurred, as can be clearly observed in the strain–magnetic field profile. Within the hysteretic regime, i.e. \(B_{\text{max}}\) between 0.36 and 0.57 T, \(A'\) displayed both a local minimum and a local maximum (i.e. \(A'' = 0\)). However, within this region a discontinuous strain did not occur because \(A'\) and \(A''\) were not simultaneously equal to zero, i.e. not equal to zero at
the same strain value. For discontinuous strain to occur, both first and second derivatives of energy must be equal to zero for the same value of strain.

The development of metastability and subsequent elimination of the energy barrier for the mechanical transition are shown in Fig. 10. At small field values, the strain was continuous; only one minimum was observed in the energy as a function of strain plots (Fig. 10b, $B_{\text{max}} = 0.1 \text{ T}$). Further increase in magnetic field resulted in a second minimum at higher strain than the original minimum. Initially, this new, second minimum was a local rather than global minimum (Fig. 10c, $B_{\text{max}} = 0.4 \text{ T}$). The system remained in the original minimum despite the fact that there was a lower energy state available; in other words, the system was in metastable equilibrium (Fig. 10d, $B_{\text{max}} = 0.5 \text{ T}$). With further increase in magnetic field, the trough of the second minima became deeper and the energy barrier between minima decreased in height. At a critical value of $B_{\text{max}}$, there was no barrier (Fig. 10e, $B_{\text{max}} = 0.57 \text{ T}$); the original minimum vanished and the system was thermodynamically unstable, similar to spinodal decomposition of solutions. As a result, the ferrogel underwent a discontinuous change in strain.

When this abrupt transition occurred, the slope of the energy as a function of strain curve became zero at the original minimum and increasingly negative in the space between the previously coexisting minima (Fig. 10e). This corresponded to the lack of an energy barrier between the two minima. The reverse was true for relaxation. In this case, the system was forced to reside in the second minimum ("minimum b", Fig. 7b) until there was no energy barrier. This explains why discontinuous mechanical transition occurs at higher strain values in elongation than in relaxation. This hysteretic behavior is analogous to the hysteresis observed in a first-order phase transformation.

2.4. Continuous deformation

As shown in Fig. 5, for magnetic field values preceding and following the discontinuous transition, the ferrogel underwent continuous deformation. Furthermore, for certain specimen geometric configurations, no discontinuous transition occurred and only continuous deformation was achieved. Continuous deformation corresponded to a smooth transition from the single energy minimum at a given field value to the next minimum as the magnetic field increased.

Fig. 9. Strain vs. magnetic field and corresponding first derivative of energy for specimen of initial length 10 cm and an aspect ratio of 3, initially 1.5$h_0$ away from an electromagnet of maximum field 0.3, 0.36, 0.45 and 0.57 T.
increased (Fig. 11). There was no abrupt, discontinuous strain and no hysteresis; this deformation is therefore analogous to a second-order phase transformation.

2.5. Influence of geometric parameters

The geometric parameters of a ferrogel specimen can be readily altered to tune the deformation mechanism in the presence of an external magnetic field as described in detail elsewhere [34]. Initial specimen length and distance from the field source have pronounced effects on the deformation mechanism. At small values of initial length ($h_0$ less than 7 cm, $z_0 = 1.5h_0$), ferrogels underwent continuous deformation in the presence of an external magnetic field. Further increase in length resulted in discontinuous deformation. This continuous-to-discontinuous transition occurred at smaller values of specimen length with increasing distance of the sample from the field source or with increasing aspect ratio.

2.6. Contraction

Contraction of cylindrical specimens was also examined. Specimens were modeled such that the midpoint of the specimen length was aligned with the center of the dipoles of the electromagnet (Fig. 3). With suitable limits of integration of the magnetic energy term, the same equilibrium-based approach that was used in the elongation analysis was used for generating strain profiles. The first and second derivatives of the total energy were also studied.
The same range of geometrical parameters that was considered in the case of elongation was considered for contraction. However, in contrast to elongation behavior, only continuous strain behavior was observed, consistent with experimental observations. The corresponding strain profiles are provided in Fig. 12.

3. Conclusions

The mechanical behavior of ferrogel specimens in an external magnetic field was modeled and analogies to phase transformations were examined. The following conclusions were reached:

- The energy–strain relationships during mechanical deformation of magnetoelastic soft actuators are analogous to chemical phase transformations in materials. These energy relationships can be used to mathematically predict the strain and magnetic field at which the discontinuous mechanical transition of a deformed ferrogel occurs.
- Specimen geometry can be used to alter the mechanism of linear elongation of a cylindrical ferrogel system. Changing the sample geometry provides a range of mechanical transitions that are similar to first- or second-order transformations. The mode of mechanical transition is dependent on the type of deformation (elongation, deflection, etc.).

Fig. 11. (a) Strain profile, (b–e) energy, and first derivative of energy for various magnetic field values illustrating a gradual, continuous strain mechanism ($h_0 = 1$ cm, aspect ratio = 1, $z_0 = 1.5h_0$).
For elongation, both first- and second-order transformations are predicted. In the case of contraction of cylindrical specimens, only second-order transformations are predicted.

Acknowledgements

The authors thank the Asian Office of Aerospace Research & Development, Tokyo, for financial support through grant AOARD-08-4120. R.S. performed this work under a grant provided by the Fulbright Program of IIE, funded by the Department of State, USA.

References


Fig. 11 (continued)

Fig. 12. Simulated strain profiles of the continuous contraction of a cylindrical ferrogel specimen with increasing magnetic field strength (aspect ratio = 7).