Magnetic-field Sensitive Gels with Wide Modulation of Dynamic Modulus

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A new class of magnetorheological gel that demonstrates drastic and reversible changes in dynamic modulus without using strong magnetic fields was obtained. The magnetic gel consists of carrageenan of polysaccharides and carbonyl iron particles. The magnetic gel with a volume fraction of 0.34 exhibited a reversible increase by factors of 500 of the storage modulus and 1200 of the loss modulus upon a magnetic field of 500 mT. We postulate that the particle structural change by magnetic fields leads to the drastic change in the dynamic modulus.

Functional softmaterials that respond to physical stimuli have been extensively and thoroughly investigated for the past decade. Magnetic fluid is a typical functional material for which the viscoelastic properties markedly change upon applying a magnetic field. The phenomenon is called the magnetorheological (MR) effect. Similarly, polymer gels containing magnetic fluids or magnetic particles also exhibit the MR effect. Not only MR fluids but also MR gels have been developed for use in vibration control devices because gels are easily handled and much more suitable for supporting objects than liquids. Many attempts to fabricate MR gels using synthetic polymer,[1] silicone elastomers,[2–5] and rubbers[6,7] have been performed. However, the increment in the storage modulus by magnetic fields, to the original modulus without the field, was less than double.

We found an interesting phenomenon that the dynamic modulus of magnetic gels consisting of polysaccharides and barium ferrite decreased markedly upon magnetization.[8,9] The magnetic gel exhibits reductions in the storage Young's modulus of ca. 10^7 Pa and in the loss modulus of ca. 10^6 Pa by only irradiating a magnetic field (1000 mT), not under the magnetic field. The magnetic gel contains a particle network which was made of many fragile (physical) contacts between magnetic particles, and the network is destroyed by the transitory magnetic field. This strongly suggests that the morphological changes of particles bring the drastic changes in dynamic modulus. In this study, we synthesized a magnetic gel in which the particle morphology can be altered by magnetic field and found that the gel demonstrates huge and reversible MR effects.

The magnetic gel consisted of carbonyl iron particles (BASF Japan) and κ-carrageenan ($M_w = 857$ kDa, CS-530, San-Ei Gen F.F.I.). A pre-gel solution of the magnetic gel was prepared by mixing a 0.7 wt % aqueous carrageenan solution and carbonyl iron at 95 °C using a mechanical stirrer for 30 min. The diameter of the particle was 2.7 μm, and the saturation magnetization and coercive force were 207 and 1.3 emu g^{-1}, respectively. The particle has no magnetization at synthesis, it was magnetized under magnetic fields. The dynamic shear modulus at 1 Hz, 20 °C was measured using a rheometer (MCR301, Anton Paar) under stepwise magnetic fields. The field direction was perpendicular to the strain. The samples were disks with dimensions of 20-mm diameter and 1.3-mm thickness.

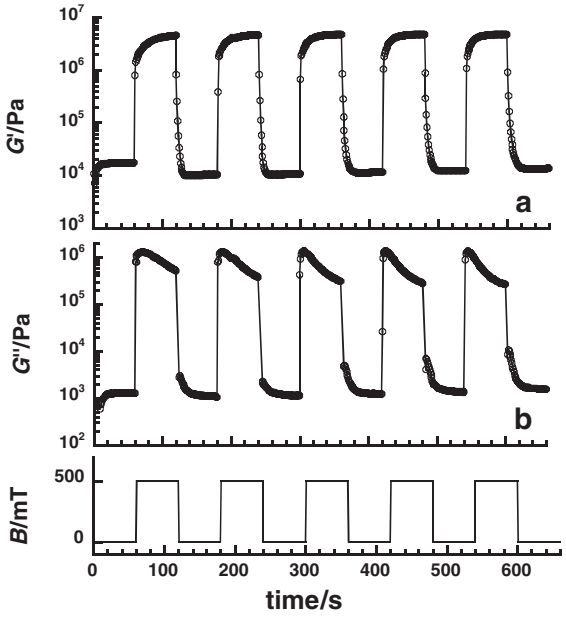

Figure 1. Change in storage modulus (a) and loss modulus (b) of magnetic gels in response to stepwise magnetic fields (carrageenan 0.7 wt %, $\gamma \approx 10^{-4}$, $\phi = 0.34$).

Figure 1a shows the storage modulus (G') at $\gamma = 10^{-4}$ of magnetic gels, in response to stepwise magnetic fields between 0 and 500 mT. The gel demonstrated huge, exceeding two orders of magnitude and reversible changes in G' synchronized with the magnetic field. The storage modulus of silicone gels with carbonyl iron particles increased by 2.5 times at 59 kA m^{-1} (from 20 to 50 kPa);[2] this may be the highest value in the past studies of MR gels and elastomers. The change in G' observed here ($\Delta G'$) was 4.5 MPa, which corresponds to 500 times ($=\Delta G'/G'_{B=0}$) the original value of G' at $B = 0$. The change in dynamic modulus was weakened when agar gel of random dispersants is used for a matrix; also it significantly decreased when iron oxide (Fe_3O_4) of weak magnetization was used for magnetic particles. Probably, the wide modulation of dynamic modulus acquires both particle network (heterogeneous dispersion) and high magnetization.

Figure 1b shows the loss modulus (G'') at $\gamma = 10^{-4}$ of magnetic gels. The magnetic gel gave nearly the same response as the storage modulus. The change in G'' was 1.3 MPa, which corresponds to 1200 times the original value of the loss modulus. It is typical that changes in G' or G'' level off at high strains; however $\Delta G/G_{B=0}$ for G' and G'' at $\gamma = 10^{-1}$ maintained high values of 180 and 730, respectively.

Figure 2 shows the magnetic field dependence of the storage modulus for magnetic gels. The G' increased with magnetic field and was saturated at high magnetic fields. Similar to the Maxwell's stress, an additional stress due to magnetic fields is

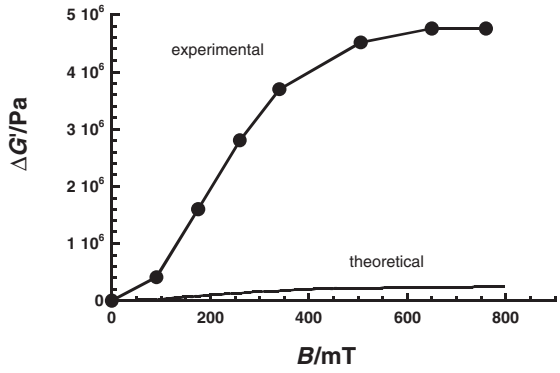

Figure 2. Experimental and theoretical values of the increment in the storage modulus as a function of magnetic fields (carrageenan 0.7 wt %, $\gamma \approx 10^{-4}$, $\phi = 0.34$).

generated by the magnetization of carbonyl iron particles. The solid line in the figure represents the theoretical value of the change in G' by magnetic fields, which was calculated with the equation $\Delta G' = \mu_0(M\phi)^2$.[9] Here, μ_0, M, and ϕ represent the magnetic permeability in vacuum, magnetization, and volume fraction of magnetic particles, respectively. The magnetization curve of carbonyl iron particles was measured by a magnetometer and the value of $\Delta G'$ was obtained. The experimental values of G' (=4.8 MPa at saturation) were far higher than the theoretical value (=0.24 MPa). This strongly indicates that the huge increase in G' cannot be explained only by the magnetic interaction between magnetic particles.

The magnetic gel presented here demonstrated enhanced Payne effect[10] before irradiating magnetic fields, indicating that the magnetic particles in the gel form a particle network, similar to previous studies.[9,11] Actually, the volume fraction of magnetic particles (=0.34) is far higher than typical values of the percolation threshold for magnetic gel[9] (=0.14) or nonmagnetic comoposite gel[12] (=0.18). Also, it was shown that the storage modulus approximately of 6 MPa increases by orientation of magnetic particles.[13] We postulate that the drastic change in the dynamic modulus is caused by the structural change of particles from isotropic network to chain structure as seen in magnetic fluids. In previous study,[9] we reported that the magnetostriction leads to the giant and negative reduction in dynamic modulus; the gel was magnetized without any restrictions. In the present experiment, the magnetic gel is difficult to deform because the gel was magnetized under a restriction of parallel plates; therefore, the influence of the magnetostriction is considered to be negligible.

Figure 3 shows a microphotograph of magnetic gels at $\phi \approx 10^{-3}$. The photograph indicates that carbonyl iron particles agglomerate with a size of ca. 10 μm in carrageenan gel. The agglomeration develops isotropic particle network when the particle volume fraction is raised, similarly to barium ferrite particles.[11] The formation of the agglomeration is considered to be caused by the hydrophobic property of particles. The MR effect increased with decreasing the storage modulus of matrix. This means that the particle structure in soft matrix is enhanced by

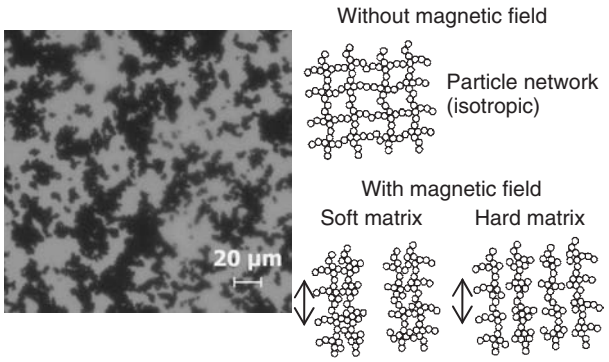

Figure 3. Photograph representing the particle dispersibility of carbonyl iron in carrageenan gels without magnetic fields (left). A possible mechanism of the MR effect observed in this study (right). Arrows represent the direction of magnetic fields.

magnetic field, oppositely, the structure in hard matrix is destroyed by the field. Schematics are shown in Figure 3.

Gels that demonstrate drastic and reversible changes in dynamic modulus of magnetic gels were presented. On further improvement of the MR performance, it could be important to optimize the particle dispersibility, particle shape, and rheological characteristics of matrix. MR gels with wide modulation range have great possibilities for use in passive vibration control devices and portable tactile sensing devices allowing tactile sensing at multiple locations.

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