

Giant Reduction in Dynamic Modulus of κ -Carrageenan Magnetic Gels

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Effects of magnetization on the complex modulus of κ -carrageenan magnetic gels have been investigated. The magnetic gel was made of a natural polymer, κ -carrageenan, and a ferrimagnetic particle, barium ferrite. The complex modulus was measured before and after magnetization of the gel by dynamic viscoelastic measurements with a compressional strain. The gels showed a giant reduction in the storage modulus of $\sim 10^7$ Pa and also in the loss modulus of $\sim 10^6$ Pa due to magnetization. The reduction increased with increasing volume fraction of ferrite, and it was nearly independent of the frequency. It was also found that the change in the modulus was nearly independent of the magnetization direction and irradiation time of the magnetic fields to the gel. The magnetic gels demonstrating the giant reduction in the dynamic modulus showed a large nonlinear viscoelastic response. It was observed that the magnetic gel was deformed slightly due to magnetization. The observed giant complex modulus reduction could be attributed to the nonlinear viscoelasticity and deformation caused by magnetization. Magnetism, nonlinear viscoelasticity, and effects of magnetization on the morphological and shape changes were discussed.

1. Introduction

A variety of functional soft materials have been widely and well investigated for the past decade. Magnetic fluid is one of the functional materials, and it demonstrates the phenomenon that viscoelastic properties change dramatically with the application of magnetic fields. The phenomenon is called the magnetorheological (MR) effect, which has attracted considerable attention for field-sensitive actuators and dampers. Polymer gels and elastomers containing magnetic fluids or magnetic fine particles also undergo the MR effect, and they have been called MR gels or MR elastomers. MR gels or elastomers are more practical than magnetic fluids for applying vibration control devices because gels or elastomers are not fluidic. So far, many kinds of polymers and magnetic substances have been examined for use as MR materials.

Silicone gels with magnetically aligned iron particles enhanced their elastic modulus by action of constant magnetic fields.¹ Both the storage and loss moduli of the gels increased under constant magnetic fields. The change in the storage modulus was ~ 18 kPa at the magnetic field $B = 43$ kA/m ($= 5.4 \times 10^{-2}$ T) when the volume fraction of iron particles $\phi = 0.28$. The increase in the modulus was diminished in large strain regime $\gamma > 0.1$. An elastomer containing carbonyl iron particles showed a 0.6 MPa increase in shear modulus at $B = 0.8$ T and $\phi = 0.3$.² The elastomer was prepared in the presence of magnetic field as well as ref 1 in order to form columnar structures. Afterward, the change in shear modulus for the elastomer made from natural rubber and carbonyl iron particles reached 2 MPa at $B = 0.6$ T and $\phi = 0.27$.³ The storage modulus of the silicone elastomer containing carbonyl iron particles, which is cured under magnetic fields, increased 4 MPa at $B =$

42 kA/m ($= 5.3 \times 10^{-2}$ T) and $\phi = 0.3$.⁴ Recently, it was reported that the elastic modulus of poly(dimethyl siloxane) elastomers containing iron particles depends strongly on particle arrangements.⁵

Elastomers and gels swollen by a solvent also demonstrate the MR effect. The compressive modulus of the poly(vinyl alcohol) (PVA) gel containing magnetic fluids increased under constant magnetic fields.⁶ The compressive modulus change at 0.4 T was 31 Pa, which is equal to 19% of the increase of that without fields. The modulus changed simultaneously with on/off switching of magnetic fields. Because the modulus change corresponds to the magnetization curve, the increase in the modulus is considered to be due to the magnetic interaction between particles. MR effects can also be seen in the frequency region of ultrasounds. The sound velocity of a PVA gel containing magnetic fine particles increased when the gel was magnetized, suggesting that the increase in the longitudinal modulus is due to magnetization.^{7–9} This result was consistent with that of the magnetic gel containing magnetic fluids. Moreover, it was clear that the change in the longitudinal modulus depends on the geometry of the strain and magnetization directions. We considered the fact that the observed anisotropy in the longitudinal modulus is ascribed to the anisotropy in magnetic interactions between magnetic particles in microscopic regions. A theoretical investigation to explain the anisotropy in the MR effect has been published in the literature.¹⁰

All of the MR elastomers and gels described above consist of a chemically cross-linked matrix. The influence of the matrix, for example, a type of cross-linking, should affect the MR properties. To clear the influence, MR response has been investigated using a κ -carrageenan matrix that is well known as a physical gel. We have briefly reported that κ -carrageenan magnetic gel underwent the giant modulus reduction due to magnetization.¹¹ First, we observed a large decrease in the storage modulus (10^7 Pa) before and after magnetization. Particularly, we stress that the change in the modulus was

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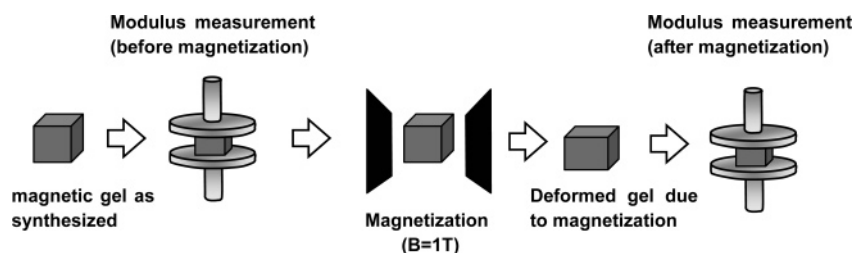


Figure 1. Schematic illustration explaining the rheological measurement.

negative, the opposite of that in past studies. This implies that the mechanism of the MR effect observed is completely different from that of a positive MR effect provoked by a constant magnetic field. It may be originated from the field-induced modification of the preexisting particle network. At maximum, the modulus after magnetization equaled a quarter of the modulus before magnetization. In this paper, details of the giant MR effect of κ -carrageenan magnetic gels are presented and a possible mechanism of the effect has been discussed.

2. Experimental Procedures

Synthesis of Magnetic Gel. Magnetic gels, which consist of a finely dispersed powder of barium ferrite and κ -carrageenan of a natural polymer, have been synthesized. A pre-gel solution of the magnetic gel was prepared by mixing the 3 wt % κ -carrageenan (CS-530, San-Ei Gen F. F. I., Inc.) aqueous solution and the barium ferrite $\text{BaFe}_{12}\text{O}_{19}$ particles (Sigma-Aldrich Co.) at 90 °C. The aqueous solution mixed with the particles was mechanically shaken at 90 °C for 20 min. We did not intentionally control particle dispersion; dispersants such as surfactants were not used for preparation of the magnetic gel. A large nonlinear viscoelasticity of the magnetic gel is intrinsically important in order to generate the giant decrease in the dynamic modulus. Barium ferrite particles formed clusters in the aqueous solution of κ -carrageenan. The large nonlinearity originates from the clusters. If magnetic particles are dispersed perfectly in the aqueous solution, then magnetic gel after solidification does not show the large nonlinearity. Accordingly, the magnetic gel now shows the giant decrease in the modulus due to magnetization. The pre-gel solution was cooled to 20 °C, and the magnetic gel was obtained. The mean diameter of a magnetic particle was determined to be $15 \pm 1.2 \mu\text{m}$ by using a particle size analyzer (Mastersizer2000, Malvern Instruments). The diameter of barium ferrite is much larger than that of magnetic fluids. A magnetic fluid does not show any remanent magnetization because the diameter is less than the size of a magnetic domain. The diameter of barium ferrite used in the present study is large enough to have a remanent magnetization. Accordingly, barium ferrite shows the magnetization only irradiating a transitory magnetic field. The weight ratio of ferrite to that of κ -carrageenan was varied up to 75 wt %, which corresponds to the volume fraction of 39 vol %. To find the magnetization effects, the gel was irradiated by a 1 T magnetic field in order to give the gel a remanent magnetization.

Rheological Measurements. Dynamic viscoelastic measurements were carried out using a Dve Rheospectra (Dve-V4, Rheology Co., Ltd). Oscillatory compressional strain $\gamma = \gamma_0 \sin 2\pi ft$ was applied to the magnetic gels, and the stress response was measured; hence, the elastic modulus obtained is Young's modulus. The frequency range varied from 10^{-1} to 10^2 Hz, and the oscillation amplitude varied from approximately 1×10^{-5} to 9×10^{-3} . The offset strain with respect to the sample thickness was kept as 3%. The temperature was maintained at 20.0 ± 1.0 °C during viscoelastic measurement.

The shape of samples for the mechanical measurement was cubic with dimensions of approximately $10 \times 10 \times 10 \text{ mm}^3$. A schematic illustration representing the rheological measurement studied here is shown in Figure 1. First we put the sample in the rheometer and measured the complex modulus of the sample before magnetization, and then the gel was replaced in the electromagnet to magnetize. Afterwards, the modulus was measured again. Note that the viscoelastic measurement was carried out in the absence of magnetic fields. Each modulus was determined from an average of three measurements using different samples. Most of the experimental errors of the modulus were smaller than the data points in the Figure.

Magnetic Measurements. Magnetization measurements up to 1 T were carried out by a vibrating sample magnetometer (VSM-P7, Toei Industrial Co., Ltd.). The shape of the sample is a disk 2 mm in diameter and 1 mm in thickness. The magnetic gel was wrapped in a thin film of poly(vinyl chloride) to avoid evaporation of water from the gel. Magnetization of the magnetic gel was calibrated by the disk-shaped Ni to eliminate the demagnetizing effect.

Microscope Observations. Microscope observations were carried out using an upright microscope (Axio Imager M1m, Carl Zeiss, Inc.). The magnetic gel with a low volume fraction of magnetic particles ($\phi \approx 3 \times 10^{-3}$) was used for the observation. The morphologies of magnetic particles were observed before and after magnetization.

Measurement of the Distortion. Dimensions, which are parallel and perpendicular to the magnetization, were measured using a laser displacement sensor with the maximum resolution of $0.01 \mu\text{m}$ (LK-G15, Keyence Co.). We measured the dimensions of a cubic shaped magnetic gel with the size of $10 \times 10 \times 10 \text{ mm}^3$ before and after magnetization.

3. Results and Discussion

Magnetism. The magnetization curves of the magnetic gels with various volume fractions of magnetic particles are shown in Figure 2a. Only major loops of the magnetization curve are presented in the Figure. The magnetization shown in the Figure appears as the mass magnetization by 1 kg of a magnetic gel. All of the magnetic gels showed magnetic hysteresis having a remanent magnetization and coercive force that is typical of magnetization curves for a ferrimagnetic substance. κ -carrageenan consists of nonmagnetic elements; therefore, it does not show any large magnetic hysteresis like magnetic gels. As the volume fraction was increased, a large hysteresis loop was observed. The magnetization for all of the magnetic gels was saturated above the magnetic field with 0.7 T. Both the saturation magnetization and the remanent magnetization increased with the volume fraction, and the coercive force was almost independent of the volume fraction. The remanent magnetization M_r , which is the magnetization with a positive value at $B = 0$, was analyzed to clear the magnetism of barium ferrite embedded in carrageenan gels.

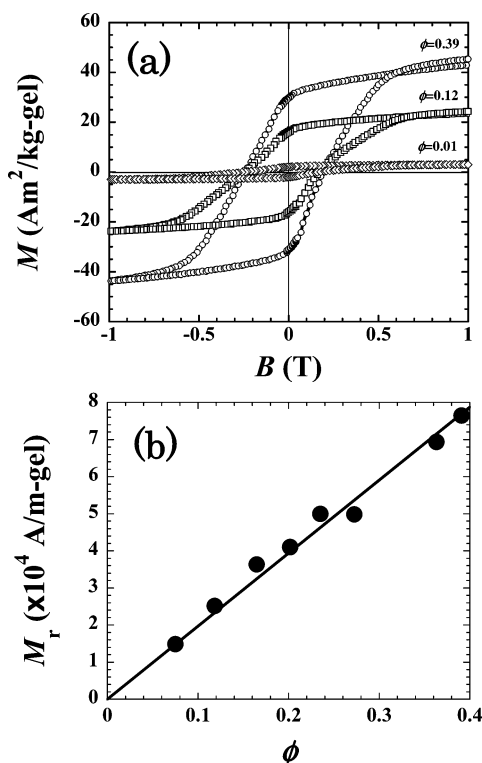


Figure 2. (a) Magnetization curves of magnetic gels with various volume fractions of magnetic particles. (b) Remanent magnetization of magnetic gels as a function of the volume fraction of magnetic particles.

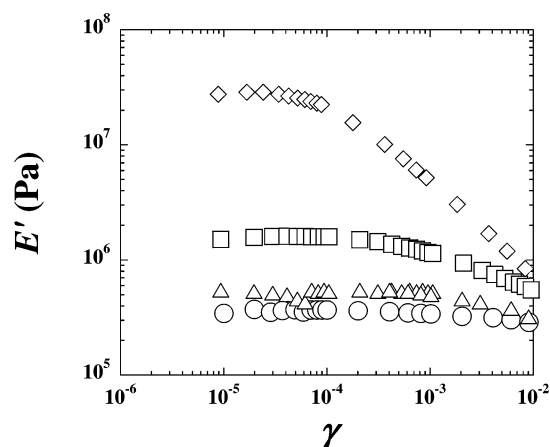


Figure 3. Strain dependence of the storage modulus at 1 Hz for magnetic gels without magnetization; volume fraction of magnetic particles (○) 0, (△) 0.12, (□) 0.14, and (◇) 0.39.

Figure 2b shows the relationship between the remanent magnetization and the volume fraction of magnetic particles. The remanent magnetization was proportional to the volume fraction with good linearity. The slope of the solid line in the Figure represents the remanent magnetization of barium ferrite in a unit volume. The remanent magnetization was estimated to be $1.97 \times 10^5 \text{ A/m}$, which is nearly equal to that of barium ferrite as a powder state ($\approx 2.10 \times 10^5 \text{ A/m}$). This strongly suggests that the magnetism of the barium ferrite is kept after the ferrite is embedded in a κ -carrageenan gel.

Rheology. Figure 3 shows the strain dependence of the storage modulus of magnetic gels with various volume fractions of magnetic particles. The storage modulus of a κ -carrageenan gel without magnetic particles is also shown in the Figure. The storage modulus of the κ -carrageenan gel without particles lied

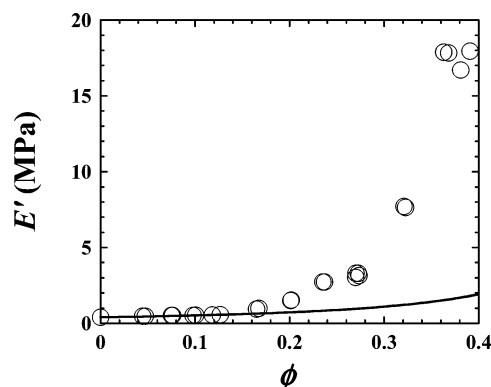


Figure 4. Storage moduli for magnetic gels without magnetization as a function of the volume fraction of magnetic particles ($f = 1 \text{ Hz}$, $\gamma \approx 2 \times 10^{-5}$).

at $\sim 3 \times 10^5 \text{ Pa}$, and it was nearly insensitive to the strain. The storage modulus of the magnetic gels increased with increasing volume fraction. Simultaneously, the nonlinear viscoelastic response was significant in a higher volume fraction of magnetic particles. The strain dependencies of the modulus for $\phi = 0.12$ and 0.14 were completely different from each other; however, the difference in the volume fraction was very small. This indicates that a particle's dispersion changes greatly at a boundary between the fractions $\phi = 0.12$ and 0.14 . When the volume fraction was 0.39 , the linear viscoelastic region was only below the strain $\gamma < 4 \times 10^{-5}$ and the storage modulus decreased over 1 order of magnitude. A similar phenomenon was reported for a filled rubber such as carbon black,¹² and it has been called the Payne effect. We considered the fact that the magnetic particles in the gel connect to each other with a weak force, which is easy to temporarily destruct by very small strains.

Figure 4 shows the storage modulus of magnetic gels as a function of the volume fraction of magnetic particles. The storage modulus increased with the volume fraction, and the modulus at $\phi = 0.39$ was 45 times higher than that of a carrageenan gel without particles. The solid line in the Figure represents the modulus, E' , calculated by the Krieger–Dougherty equation as follows¹³

$$E' = E'_0 \left(1 - \frac{\phi}{\phi_m} \right)^{-5/2\phi_m} \quad (1)$$

where E' and E'_0 show the storage modulus of the magnetic gel and carrageenan gel, respectively. ϕ_m stands for the maximum volume fraction of magnetic particles, which is nearly equal to 0.63 for hard spheres.¹⁴ The storage modulus below the volume fraction with 0.12 obeyed the above equation. This means that magnetic particles are dispersed randomly in the magnetic gel. The storage modulus above the volume fraction with 0.15 did not follow the equation, suggesting that magnetic particles are not dispersed randomly in the gel. We considered the fact that magnetic particles come in contact with each other and make a structure with a high modulus. This consideration coincides with the data shown in Figure 3. The nonlinear viscoelastic response was very weak ($\phi < 0.12$) and was suddenly enhanced ($\phi > 0.14$).

Figure 5 shows the strain dependence of the storage modulus and loss tangent at 1 Hz before and after magnetization. The geometry of the magnetization and strain is perpendicular. After the magnetic gel was magnetized, the storage modulus was observed to be lower than that before magnetization. The change in the modulus at the linear regime reached $1.78 \times 10^7 \text{ Pa}$, which corresponds to 65% of the modulus before magnetization.

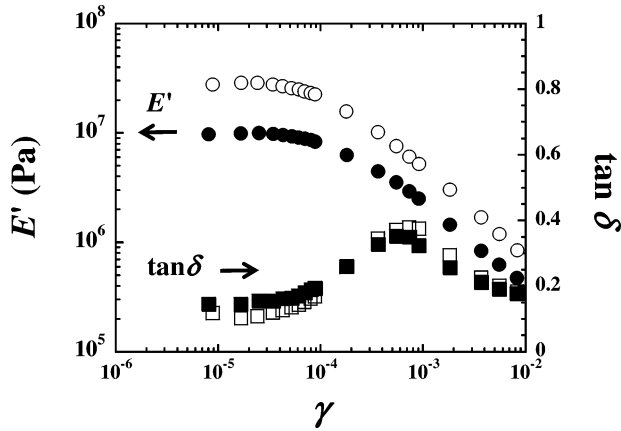


Figure 5. Strain dependence of the storage modulus at 1 Hz (\circ , \bullet) and loss tangent (\square , \blacksquare) for magnetic gels with $\phi = 0.39$. Open and closed symbols represent before and after magnetizing at 1 T, respectively.

Generally, magnetorheological materials show an increase in the elastic modulus by magnetic fields. For example, the storage modulus of the magnetic gel consisting of magnetic fluids increased in the presence of magnetic field.⁶ Elastomers containing magnetic particles that were cured under magnetic fields also show the increase in the modulus by applying magnetic fields.^{1–5} However, the carrageenan magnetic gel presented here showed a decrease in the storage modulus, which is called a “negative magnetorheological effect”. This is the first time that the negative MR effect for magnetic gels was observed. Another importance seen in the MR effect is the quantity of the effect. Normally, MR materials shows the increase in the modulus of 10^3 – 10^6 Pa caused by magnetic fields. According to the literature,⁴ the silicone elastomers containing iron particles shows that the modulus changes to 3×10^6 Pa in the presence of magnetic field with ~ 0.05 T. The modulus change is probably the maximum in past studies. κ -Carrageenan magnetic gel underwent the modulus change at 1.78×10^7 Pa only due to remanent magnetization, in the absence of magnetic fields. The mechanism of the MR effect observed here is considered to be completely different from that in the past, which is explained by the magnetic dipole–magnetic field interactions.

Loss tangent curves had a peak in the vicinity of the strain $\gamma \approx 10^{-3}$ due to the nonlinear viscoelastic properties. A similar peak in the loss tangent has been reported for carbon-filled elastomers.¹² We considered the fact that the peak in the loss tangent originates from a temporary destruction of the structure of magnetic particles. Remarkable change in the peak was not observed before and after magnetization. However, the loss tangent tends to increase after magnetization in a smaller strain region.

Figure 6 shows the frequency dependence of the complex modulus and loss tangent at $\gamma \approx 2 \times 10^{-5}$ before and after magnetization. The geometry of magnetization and strain is perpendicular. The storage modulus before magnetization increased gradually with increasing frequencies, which is similar to the behavior of a weak gel. It was observed that both the storage and loss moduli after magnetization were lower than those before magnetization at all frequencies. Change in the moduli due to magnetization was nearly insensitive to the frequency. The loss tangent decreased in the low-frequency region and was almost independent of the frequency in the higher-frequency regime. The loss tangent after magnetization tended to be higher than that before magnetization, which might have originated from the change in the state of contact between the magnetic particles.

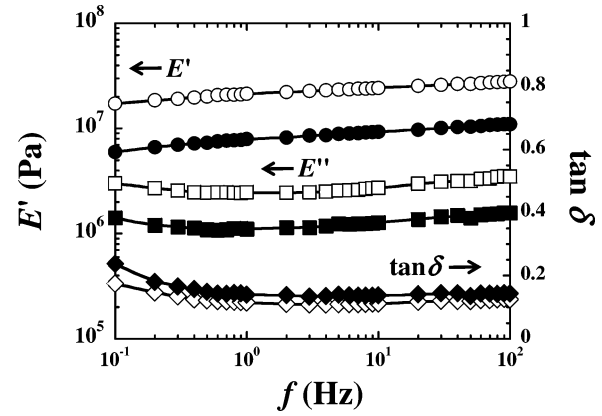


Figure 6. Frequency dependence of the storage modulus (\circ , \bullet) and loss modulus (\square , \blacksquare) and loss tangent (\diamond , \blacklozenge) for magnetic gels ($\phi = 0.39$, $\gamma \approx 2 \times 10^{-5}$). Open and closed symbols represent before and after magnetizing at 1 T, respectively.

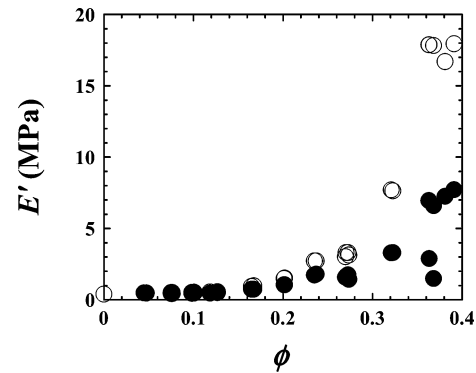


Figure 7. Volume fraction dependence of the storage modulus for magnetic gels; (\circ) before and (\bullet) after magnetizing at 1 T ($f = 1$ Hz, $\gamma \approx 2 \times 10^{-5}$).

Figure 7 shows the volume fraction dependence of the storage modulus for magnetic gels before and after magnetization. The geometry of magnetization and strain is perpendicular. It was clearly observed that the storage modulus for the gels with $\phi > 0.16$ decreased because of magnetization. Gels showing the giant storage modulus reduction are the ones that do not follow eq 1 ($\phi > 0.16$) or the ones showing a large nonlinear viscoelasticity ($\phi > 0.14$). This evidence strongly indicates that the giant MR effect is strongly related to the structure of magnetic particles characterized by the Payne effect.

If the observed modulus reduction is caused mainly by magnetic interactions, then the reduction in storage modulus should be anisotropic. We have also investigated the reduction of the modulus for a parallel geometry; the magnetization direction is parallel to that of the strain. Figure 8 shows the reduction of the storage modulus of magnetic gels before and after magnetization as a function of the volume fraction of magnetic particles. The giant modulus reduction also occurred in the parallel geometry. The change in the modulus for the perpendicular geometry is also presented in the Figure. In both geometries, the change in the modulus, $\Delta E'$, increased exponentially with the volume fraction. The change in the modulus with respect to the modulus before magnetization, $\Delta E'/E'_0$, was defined by the following equation

$$\frac{\Delta E'}{E'_0} = \frac{E' - E'_0}{E'_0} \quad (2)$$

where $\Delta E'$ is the change in storage modulus and E'_0 represents the modulus without magnetization. Below the volume fraction

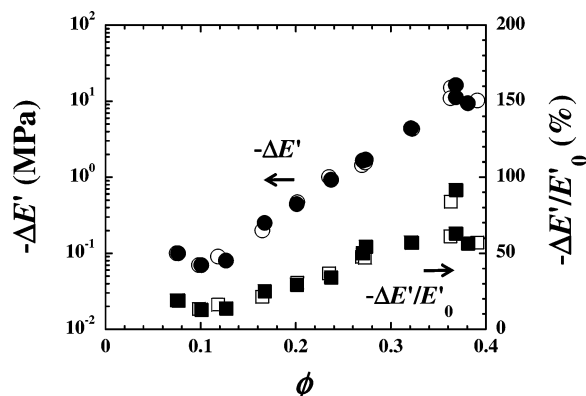


Figure 8. Change in the storage modulus in perpendicular (\circ , \square) and parallel (\bullet , \blacksquare) geometries and as a function of volume fractions ($f = 1$ Hz, $\gamma \approx 2 \times 10^{-5}$). Open and closed symbols represent before and after magnetizing at 1 T, respectively.

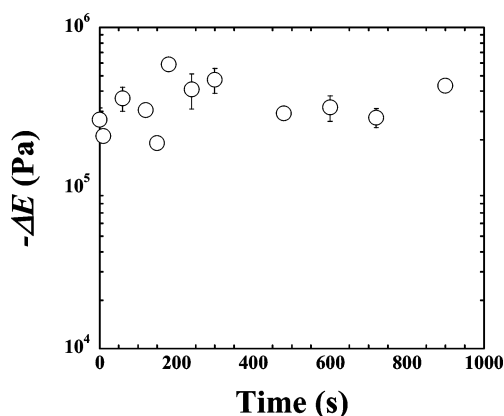


Figure 9. Relationship between the change in the storage modulus and the irradiation time of the magnetic field with 1 T to the gel ($\phi = 0.14$, $f = 1$ Hz, $\gamma \approx 4.3 \times 10^{-5}$).

0.12, the change in storage modulus was almost constant around 10%, and it increased suddenly with increasing volume fraction. The change in the modulus reached 76.5% at the maximum. No clear difference in the change in the modulus was found for the perpendicular and parallel geometries. We considered the fact that the giant modulus reduction is caused by destruction of an isotropic structure, not an anisotropic structure such as the columnar one by magnetic fields. Figure 9 shows the relationship between the change in the storage modulus and the irradiation time of the magnetic field with 1 T. The magnetization direction is perpendicular to that of the strain. The change in the modulus lied around 3×10^5 Pa, and it was nearly independent of the irradiation time. The change in the modulus beyond 10^5 Pa took place by the irradiation time with only 1 s; however, it took approximately 10 s to raise the magnetic field with 1 T. It is well known for magnetic fluids that a columnar structure between parallel plates of a rheometer induced by magnetic fields changes the viscosity of the fluid. It is impossible for a nonfluidic gel matrix to form a macroscopic structure such as a columnar one; if possible, it needs a considerable time. Hence, the giant modulus reduction may be caused by a slight change in the contact between magnetic particles.

If a magnetic gel having remanent magnetization is put under a certain negative magnetic field (that is, the point of coercive force, i.e., the cross point of the x axis in the negative magnetic field in Figure 2a), then the magnetization of the gel disappears. If the giant modulus reduction originates from the quantity of the magnetization, then the gel should not show any reduction in the modulus. However, this gel also showed the giant modulus

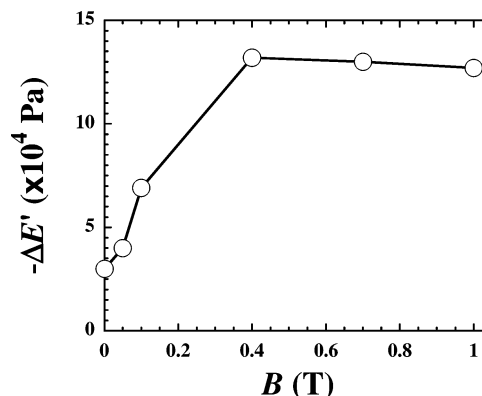


Figure 10. Relationship between the change in the storage modulus and the maximum strength of the magnetic fields ($\phi = 0.14$, $f = 1$ Hz, $\gamma \approx 4.3 \times 10^{-5}$).

reduction on the order of 10^7 Pa as well as the results shown in Figure 5. Accordingly, we concluded that the magnetic interaction between magnetic particles is less important for the giant modulus reduction observed here. Figure 10 shows the relationship between the reduction of the storage modulus before and after magnetization and the strength of magnetic fields applied to the gel. The geometry of the magnetization and strain is perpendicular. Considerable change in the modulus ($\sim 10^4$ Pa) occurred only at 1 mT. In general, it is quite difficult for MR elastomers to change their modulus by such a small field. The modulus change was saturated to 0.13 MPa above the magnetic field with 0.5 T.

We have theoretically estimated the modulus change due to magnetic interactions acting on the magnetic particles. Similar to Maxwell's stress, the magnetic amount of substance having the same dimension of a storage modulus should be only $\mu_0 M^2$, with μ_0 being the magnetic permeability in a vacuum and M being the magnetization. Accordingly, we obtained the following equation taking into account for the volume fraction, ϕ

$$\Delta E' \approx \mu_0 (M\phi)^2 \quad (3)$$

When the volume fraction of magnetic particles was the maximum fraction with 0.39, the magnetization was determined to be 1.97×10^5 A/m. Hence, the change in the storage modulus was estimated to be 7×10^3 Pa. This value is 4 orders of magnitude lower than the observed modulus reduction of $\sim 10^7$ Pa. This reveals that the observed modulus change cannot be explained only by magnetic interactions between dispersed magnetic particles.

Figure 11 shows the deformation and corresponding strain, γ_m , as a function of magnetic fields. Both geometries (the deformation direction is parallel and perpendicular to that of the magnetization) are presented in the Figure. As expected, a macroscopic deformation was observed for the gel after magnetization. In the parallel geometry, the deformation increased proportionally with the magnetic field. On the contrary, in the perpendicular geometry the deformation decreased proportionally with the field. The deformation in the parallel geometry was approximately 2 times larger than that in the perpendicular geometry. The deformation at the magnetic field of 1 T reached several tens of micrometers, which corresponds to the strain on the order of 10^{-3} because the sample thickness was nearly 10 mm. The strain is enough to decrease the storage modulus with 10^7 Pa according to the nonlinear viscoelasticity shown in Figure 3. The giant reduction in the storage modulus can be explained by the deformation induced by magnetization and the Payne effect of magnetic gels.

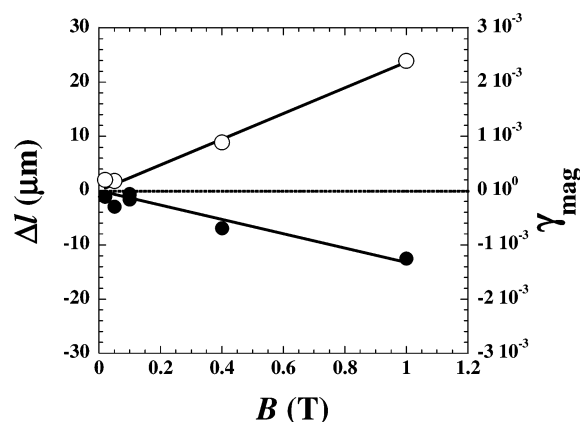


Figure 11. Deformation (left axis) and corresponding strain (right axis) induced by magnetization as a function of magnetic fields for the magnetic gel with $\phi = 0.14$; ○, parallel; ●, perpendicular.

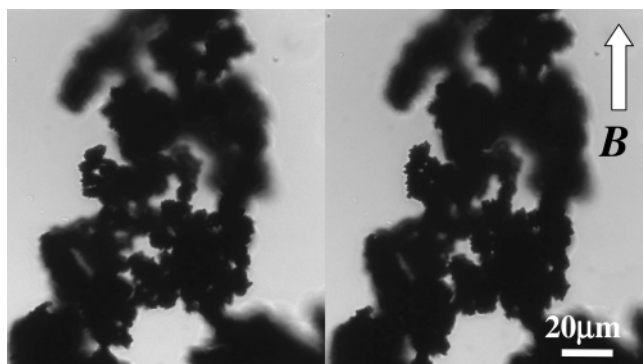


Figure 12. Microphotographs of the magnetic gel with $\phi = 3 \times 10^{-3}$ before (left) and after (right) magnetizing at 1 T. The field direction is indicated by an arrow.

We have further investigated the reason that the anisotropic deformation occurs when the gel was magnetized. Figure 12 shows microphotographs of the magnetic gel before and after magnetization. It is impossible to observe the morphology of the gel with $\phi = 0.39$ because the color of the gel is deep black. To observe the morphology of magnetic particles, the gel with a low volume fraction ($\phi \approx 3 \times 10^{-3}$) was used. The diameter

of the magnetic particles was approximately $15 \mu\text{m}$, as described in the Experimental Section. The magnetic particles were observed to aggregate and connect to each other in the magnetic gel. When the magnetic field was applied to the gel, the length of aggregates, which is perpendicular to the magnetic field, decreased by several micrometers. This result coincides with the deformation shown in Figure 11. For the magnetic gel with a high volume fraction of magnetic particles, the small deformation with several micrometers would lead to macroscopic deformation.

Figure 13 shows schematic illustrations representing a possible explanation for the giant reduction in the dynamic modulus of κ -carrageenan magnetic gels. Magnetic particles are aggregated in the carrageenan gel as seen in Figure 12. We considered the fact that changes in the contact between aggregated particles bring the giant reduction in the modulus. Magnetic particles have a nature to align with the magnetic line of force under magnetic fields. Indeed, magnetic particles in a liquid make a columnar structure bridging between magnetic poles. The magnetic force acting on magnetic particles in a gel should be the same as that in a liquid. Unlike the liquid, the particles that are dragged into a gel probably cannot move because the gel is not fluidic. In addition, the gel is not a rigid body like a metal; it is an elastic substance that can be deformed by an external stress. Hence, we can consider the fact that the particles change their location through deformation of the gel. This leads to the macroscopic deformation seen in Figure 11. Accompanied with the deformation, the state of contact between magnetic particles should be changed. This change in the contact would be small; however, it brings a large decrease in the storage modulus. It is because the magnetic gel studied here has a large nonlinear viscoelasticity that the storage modulus decreased at very small strains.

4. Conclusions

The effects of magnetization on the complex modulus of κ -carrageenan magnetic gels have been investigated by dynamic viscoelastic measurements. The magnetic gel showed a large nonlinear viscoelastic response, suggesting that the magnetic particles in the gel connect to each other with a weak force. The storage modulus of the gel above $\phi > 0.16$ increased

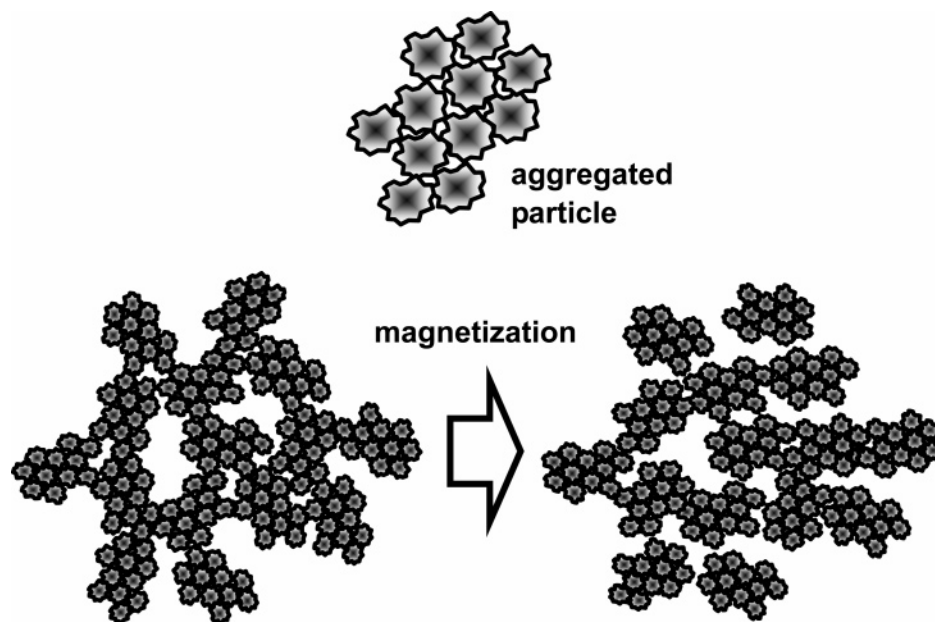


Figure 13. Schematic illustrations representing the giant negative magnetorheological effect seen in κ -carrageenan magnetic gels.

significantly with the volume fraction, which is not satisfying with the Krieger–Dougherty equation. This strongly suggests that the magnetic particles come in contact with each other and make a structure with a high modulus. These gels showed the giant and negative magnetorheological effect. The magnetorheological effect increased with the volume fraction of magnetic particles, and it was nearly independent of magnetization directions. At maximum, the modulus after magnetization equaled to $1/4$ of the modulus before magnetization. The modulus reduction due to magnetization was theoretically estimated from magnetic energies acting on the dispersed magnetic particles. The estimation revealed that the modulus reduction observed was much larger than that calculated (10^4 times). The macroscopic deformation with the strain of 10^{-3} was observed. Both the viscoelastic feature characterized by the Payne effect and the macroscopic deformation may bring on the giant and negative magnetorheological effect. The phenomenon observed is a general effect. We have also carried out a series of experiments for agar gels and urethane elastomers and observed the giant decrease in the modulus ($\Delta E' > 0.1$ MPa) before and after magnetization. Effects of matrixes on the giant magnetorheology will be presented in a subsequent paper. The modulus reduction observed so far is irreversible; however, this could be applied for dampers with a wide range of modulation.

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References and Notes

- (1) Shiga, T.; Okada, A.; Kurauchi, T. *J. Appl. Polym. Sci.* **1995**, *58*, 787.
- (2) Jolly, M. R.; Carlson, J. D.; Munoz, B. C.; Bullions, T. A. *J. Int. Mater. Sys. Struct.* **1996**, *7*, 613.
- (3) Ginder, J. M.; Clark, S. M.; Schlotter, W. F.; Nichols, M. E. *Int. J. Mod. Phys. B* **2002**, *16*, 2412.
- (4) Bossis, G.; Bellan, C. *Int. J. Mod. Phys. B* **2002**, *16*, 2447.
- (5) Varga, Z.; Filipcsei, G.; Zrinyi, M. *Polymer* **2005**, *46*, 7779.
- (6) Mitsumata, T.; Ikeda, K.; Gong, J. P.; Osada, Y.; Szabo D.; Zrinyi, M. *J. Appl. Phys.* **1999**, *85*, 8451.
- (7) Mitsumata, T.; Juliac, E.; Furukawa, K.; Iwakura, K.; Taniguchi, T.; Koyama, K. *Macromol. Rapid Commun.* **2002**, *23*, 175.
- (8) Mitsumata, T.; Furukawa, K.; Juliac, E.; Iwakura, K.; Koyama, K. *Int. J. Mod. Phys. B* **2002**, *16*, 2419.
- (9) Juliac, E.; Mitsumata, T.; Taniguchi, T.; Iwakura, K.; Koyama, K. *J. Phys. Chem. B* **2003**, *107*, 5426.
- (10) Taniguchi, T.; Mitsumata, T.; Sugimoto, T.; Koyama, K. *Physica A*, in press.
- (11) Mitsumata, T.; Nagata, A.; Sakai, K.; Takimoto, J. *Macromol. Rapid Commun.* **2005**, *26*, 1538.
- (12) Payne, A. R. *J. Appl. Polym. Sci.* **1960**, *3*, 127.
- (13) Krieger, I. M.; Dougherty, T. J. *Trans. Soc. Rheol.* **1959**, *3*, 137.
- (14) Onoda, G. Y.; Liniger, E. R. *Phys. Rev. Lett.* **1990**, *64*, 2727.