

# Rheological Characteristics and Magnetization Effects of Magnetic Gels

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Magneto-rheological effects of  $\kappa$ -carrageenan magnetic gels have been investigated. The magnetic gel was made of a natural polymer of  $\kappa$ -carrageenan and a ferromagnetic particle of barium ferrite. The complex modulus of the magnetic gel was measured by dynamic viscoelastic measurements with a compressional strain. It was observed that the magnetic gels showed giant storage modulus reduction  $\sim 10$ MPa before and after magnetization. The reduction increased with increasing the volume fraction of the ferrite and it reached 14.9 MPa at maximum. No volume change was observed during magnetization. Strain and frequency dependences of the dynamic modulus and a possible mechanism of the modulus reduction have been discussed.

Key words: gels, magnetic gel, modulus, rheology, carrageenan

## 1. INTRODUCTION

The polymer gel containing magnetic fluids or magnetic fine particles is able to respond to magnetic fields and it is called as the magneto-rheological gel<sup>[1]</sup>. Compressive modulus of the magnetic gel with the matrix of a poly(vinyl alcohol) (PVA) swollen by a magnetic fluid, increased under uniform magnetic fields<sup>[2]</sup>. The modulus change occurred simultaneously with an application of the magnetic field; it increased with increasing magnetic field strength and saturated above 2 kOe. It was considered that the modulus change was brought by the strong coupling between polymer networks and magnetic fluids. The change in the modulus at 4 kOe was 31 Pa, which equals to 19% increases of that without fields.

We have studied the magneto-rheological effect of chemically cross-linked PVA gel containing ferromagnetic fine particles. The mean diameter of the particle is approximately 20  $\mu\text{m}$ . Relationship between magnetization direction and the longitudinal modulus change was investigated using 10 MHz ultrasonic waves<sup>[3-5]</sup>. The longitudinal modulus of the magnetic gel after magnetization was higher than that before magnetization, which is consistent with the results of the magnetic gel containing magnetic fluids. Moreover, it was cleared that the change in the longitudinal modulus depended on the geometry of strain and magnetization directions. It was considered that the observed anisotropy in the longitudinal modulus is ascribed to the anisotropy in magnetic interactions between magnetic particles in microscopic regions. Dynamic viscoelastic measurements of the PVA magnetic gel at  $10^{-1}$  Hz- $10^2$  Hz cleared that the gel did not show any volume change before and after magnetization, i.e. without magnetostriction<sup>[6]</sup>. However, the mechanism of the modulus

change and the effect of gel matrix on the modulus change are still unclear.

Recently, we reported that  $\kappa$ -carrageenan magnetic gel undergoes the giant modulus reduction due to magnetization<sup>[7,8]</sup>. In this paper, strain and frequency dependences of the dynamic modulus and a possible mechanism of the modulus reduction have been discussed.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Synthesis of Magnetic Gel

Magnetic gels, which consist of a finely dispersed powder of barium ferrite and  $\kappa$ -carrageenan of a natural polymer, have been synthesized. A Pre-gel solution of the magnetic gel was prepared by mixing the 5 wt.%  $\kappa$ -carrageenan (CS-530, San-Ei Gen F.F.I., Inc.) aqueous solution and the barium ferrite  $\text{BaFe}_{12}\text{O}_{19}$  (Sigma-Aldrich Co.) at 90 °C. The pre-gel solution was cooled down to 20 °C, and the magnetic gel was obtained. The mean diameter of a magnetic particle was determined as 20  $\mu\text{m}$ . The diameter of barium ferrite is much larger compared to magnetic fluid, so it enables the gel to have a remanent magnetization even though the magnetic field is not applied. The weight ratio of ferrite to that of  $\kappa$ -carrageenan  $c_f$  was varied up to 75 wt.% which corresponds to the volume fraction of 39 vol%. To find out magnetization effects, the gel was put under a uniform magnetic field of 1 T in order to give the gel a remanent magnetization.

### 2.2 Rheological Measurements

Dynamic viscoelastic measurements were carried out using a Dve Rheospectra (Dve-V4, Rheology Co., Ltd). Oscillatory compressional shear  $\gamma = \gamma_0 \sin 2\pi ft$  was applied to magnetic gels and the stress response was measured; hence

elastic modulus obtained stands for Young's modulus. The frequency range was varied from  $10^{-1}$  Hz to  $10^2$  Hz, and the oscillation amplitude was varied from  $1 \times 10^{-5}$  to  $9 \times 10^{-3}$ . The offset strain with respect to the sample thickness was kept as 3%. The temperature was maintained at  $20.0 \pm 1.0$  °C during viscoelastic measurement. The shape of samples for the mechanical measurement was cubic with dimensions of approximately  $10 \times 10 \times 10$  mm. Each modulus was determined from an average of three measurements.

### 2.3 Magnetic Measurements

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

### 2.4 SEM Observations

Surface morphologies of wet gels were investigated using a variable-pressure scanning electron microscope (VP-SEM S-2460N, Hitachi, Ltd). An accelerating voltage and chamber pressure of 15 kV and 50 Pa, respectively, were used to operate the VP-SEM.

## 3. RESULTS AND DISCUSSIONS

Figure 1 shows the strain dependence of the storage modulus at 1 Hz of magnetic gels with and without magnetization. The geometry of magnetization and strain directions is perpendicular. The storage modulus of a  $\kappa$ -carrageenan gel without magnetic particles lied approximately  $\sim 10^5$  Pa. The storage modulus below  $\gamma \sim 3 \times 10^{-5}$  was almost constant and it largely decreased with strain indicating non-linear viscoelastic response. In contrast, the  $\kappa$ -carrageenan gel without magnetic particles did not show such large decreasing in the modulus. This indicates that the magnetic particles in the

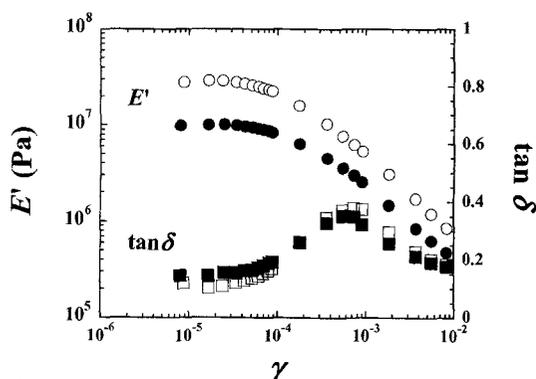


Fig. 1 Strain dependence of the storage modulus and loss tangent at 1 Hz before ( $\circ, \square$ ) and after ( $\bullet, \blacksquare$ ) magnetization ( $\phi=0.39$ ).

gel form a weak structure, which is easy to break by very small strains. It was obvious that the storage modulus after magnetization was lower than that before magnetization. The change in the modulus reached  $1.78 \times 10^7$  Pa, which corresponds to 65% of the modulus before magnetization. It is firstly observed in magnetic gels that the storage modulus decreased during magnetization. For example, the storage modulus of the magnetic gel consisting of magnetic fluids increased in the presence of magnetic field [2]. Elastomers containing magnetic particles that were cured under magnetic fields also show the increase in the modulus by applying magnetic fields [9]. Loss tangent curves have a peak around the strain  $\gamma \sim 8 \times 10^{-4}$  due to the non-linear viscoelastic response. Remarkable change in the peak was not observed before and after magnetization.

Figure 2 shows the frequency dependence of the storage modulus at  $\gamma \sim 2 \times 10^{-5}$  of magnetic gels before and after magnetization. The geometry of magnetization and strain directions is perpendicular. The storage modulus before magnetization gradually increased with increasing frequencies, which is similar to the behavior of a weak-gel. It was also cleared that the storage modulus after magnetization was lower than that before magnetization at all frequencies. Change in the modulus due to magnetization tended to decrease in a high frequency region. The loss tangent was almost insensitive to the frequency in higher frequency regime, and it increased in a low frequency region. It had a tendency that the loss tangent after magnetization is higher than that before magnetization.

Figure 3 shows the change in the storage modulus of magnetic gels before and after magnetization as a function of the volume fraction of ferrite. The change in modulus  $\Delta E'/E'_0$  was defined by the following equation:

$$\frac{\Delta E'}{E'_0} = \frac{|E' - E'_0|}{E'_0} \quad (1),$$

where  $\Delta E'$  is the change in storage modulus,  $E'_0$

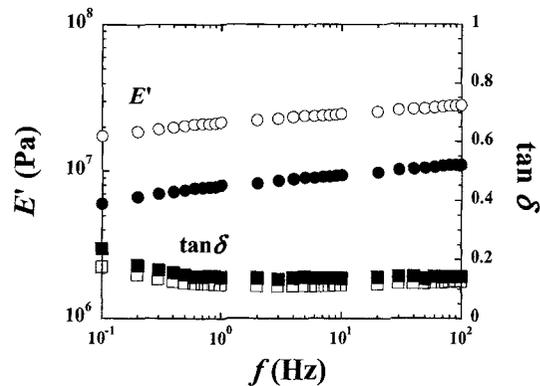


Fig. 2 Frequency dependence of the storage modulus and loss tangent for magnetic gels before ( $\circ, \square$ ) and after ( $\bullet, \blacksquare$ ) magnetization.

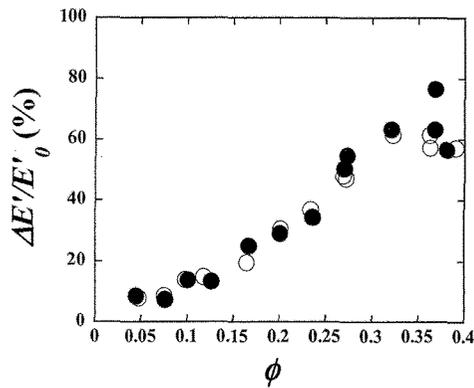


Fig. 3 Change in the storage modulus before and after magnetization as a function of volume fraction of magnetic particles; (○): Perpendicular geometry, (●): Parallel geometry.

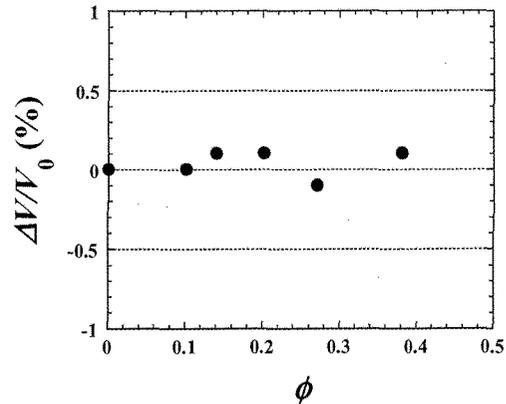


Fig. 4 Change in the volume before and after magnetization as a function of volume fraction of magnetic particles.

represents the modulus without magnetization. Below the volume fraction of 0.1, the change in storage modulus lied around 10%, and it rapidly increased with increasing the volume fraction. The change in the modulus reached 76% at maximum. The results showed that there is no geometry effect of magnetization and strain directions.

Figure 4 shows the change in volume during magnetization as a function of volume fraction of magnetic particles. The change in volume was defined by the following equation,

$$\frac{\Delta V}{V_0} = \frac{|V - V_0|}{V_0} \quad (2).$$

Here,  $\Delta V/V_0$  is the change in volume,  $V_0$  and  $V$  represent the volume before and after magnetization, respectively. The volume was calculated by the mass and density of magnetic gels. The maximum change in the volume was approximately 0.1%, which is much lower than the experimental error of density measurements. Therefore, we concluded that the volume change is not a major reason for the giant modulus reduction.

Considering the mechanism of the observed modulus change, we have theoretically estimated the change in the storage modulus due to magnetization. The magnetic energy is originated from a pair of magnetic momentum, and the energy density  $U$  is proportional to  $(M\phi)^2$ ;  $M$  and  $\phi$  stand for the magnetization and the volume fraction of magnetic particles. According to the dimension analysis, the change in the modulus should correspond to the energy density  $U$ , that is

$$\Delta E' \sim (M\phi)^2 \quad (3).$$

When the volume fraction of magnetic particles was 0.39, the magnetization was 198 emu/cm<sup>3</sup> determined by magnetic measurements. Hence, the change in the storage modulus was estimated

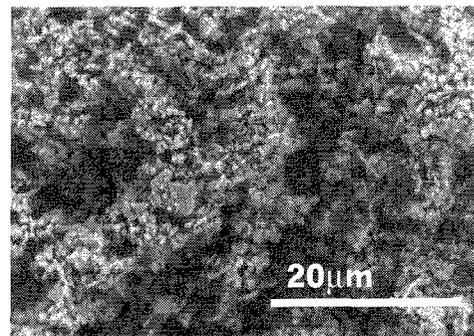


Fig. 5 SEM photograph of a surface of  $\kappa$ -carrageenan magnetic gel ( $\phi \sim 0.14$ ).

as  $6 \times 10^3$  Pa. This value is four orders of magnitude lower than the observed modulus change of  $\sim 10^7$  Pa. This strongly suggests that the observed modulus change cannot be explained by only magnetic interactions between dispersed magnetic particles.

Figure 5 shows SEM photograph of a surface of the magnetic gel before magnetization. Magnetic particles were aggregated, suggesting the primary particles form a cluster in the gel. According to the rheological measurements, particles connect each other with weak forces. The weak connection would be broken by a small strain induced by magnetization, as a result, the dynamic modulus decreased.

#### 4. CONCLUSION

Rheological characteristics and magnetization effect of  $\kappa$ -carrageenan magnetic gels have been investigated by dynamic viscoelastic measurements. The giant modulus reduction was observed due to magnetization. Changes in the modulus increased with increasing ferrite concentrations, and it was nearly independent of the frequency and magnetization directions. This anomalous decrease in the modulus can be explained by neither volume change nor magnetic interactions between nearest neighbor magnetic particles. Structures made of magnetic particles would be closely related to the observed giant

modulus reduction of the  $\kappa$ -carrageenan magnetic gels.

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#### References

- [1] For example, M. Zrinyi, "Polymer Gels and Networks", Ed. by Y. Osada and A. R. Khokhlov, Marcel Dekker (2002) pp. 309-55.
- [2] T. Mitsumata, K. Ikeda, J. P. Gong, Y. Osada, D. Szabo, and M. Zrinyi, *J. App. Phys.* **85**, 8451-55 (1999).
- [3] T. Mitsumata, E. Juliac, K. Furukawa, K. Iwakura, T. Taniguchi, and K. Koyama, *Macromol. Rapid Commun.* **23**, 175-78 (2002).
- [4] T. Mitsumata, K. Furukawa, E. Juliac, K. Iwakura, and K. Koyama, *Int. J. Modern Phys. B* **16**, 2419-25 (2002).
- [5] E. Juliac, T. Mitsumata, T. Taniguchi, K. Iwakura, and K. Koyama, *J. Phys. Chem. B* **107**, 5426-31 (2003).
- [6] T. Mitsumata, A. Nagata, K. Sakai, and T. Taniguchi, *Jpn. J. Appl. Phys.* **43**, 8203-07 (2004).
- [7] T. Mitsumata, A. Nagata, T. Taniguchi, and J. Takimoto, *Theoretical and Applied Mechanics Japan* **54**, 269-74 (2005).
- [8] T. Mitsumata, A. Nagata, K. Sakai, and J. Takimoto, *Macromol. Rapid Commun.* **26**, 1538-41 (2005).
- [9] T. Shiga, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **58**, 787-92 (1995).

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