Magnetroviscoelastic Behavior of Composite Gels

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SYNOPSIS

Dynamic viscoelasticity of silicone gels having many lines of dispersed iron particles under the influence of external magnetic fields was studied. The particulate composite enhanced its elastic modulus by action of magnetic fields. The magnetroviscoelastic behavior was caused by the cohesive forces between magnetically polarized particles and was analyzed using a simple model of induced dipole-induced dipole interactions. The presented results provide insight into the relationship between macroscopic viscoelastic behavior of the composite gels and the microscopic bondings between dispersed particles.

INTRODUCTION

The phase morphology and microscopic interactions between dispersed phases in an immiscible polymer blend have been investigated extensively since they greatly affect mechanical properties of the blend. Recently, Moriya et al. demonstrated that anisotropic structures in blend could be generated by applying ac electric fields to solvent-free blends.[1] Krause, Wnek, and co-workers also reported the use of dc electric fields to control the shape and orientation of the dispersed phases.[2-4] These works suggest a new approach for the modulation of polymer blend morphology. In a previous paper,[5] we reported that silicone gel containing polyelectrolyte particles enhanced its elastic modulus by action of electric fields. The electroviscoelastic effect was caused by microscopic bondings between electrically polarized particles. It offers the possibility of an electrical control of viscoelasticity of an immiscible polymer blend. The electric fields may thus give us advanced polymer materials having unique mechanical properties.

The electroviscoelastic effect transpires in polymeric materials with many lines of adjacent particles spanning between two electrodes before application of electric fields (Fig. 1).[6,7] The electric field induces a dipole in a particle and yields adhesive forces between dispersed particles. Since the adhesive forces change the lines of particles into chains, the particulate composite apparently increases its elastic modulus. As shown in Figure 1, the induced dipole-induced dipole interaction between particles plays an important role in the electroviscoelastic effect. As the dipole is induced also by external magnetic fields, it is expected that composites of particles which may polarize in external magnetic fields display an interesting phenomenon similar to the electroviscoelastic effect (magnetroviscoelastic effect). This paper aims at demonstrating the magnetroviscoelastic effect of particulate composites. We discuss the magnetroviscoelastic effect theoretically as well as experimentally.

THEORETICAL APPROACH

Straight lines of particles are more effective compared to winding lines of them to design a large electroviscoelastic effect.[7] Here we discuss viscoelasticity of a cubical blend having many straight lines of dispersed particles under magnetic fields.

We start the induced magnetic dipole moment of a sphere in unbounded continuous medium which is not influenced by external magnetic fields. The magnetized sphere may be considered as a point dipole of magnetic moment M [eq. (1)].[8,9]

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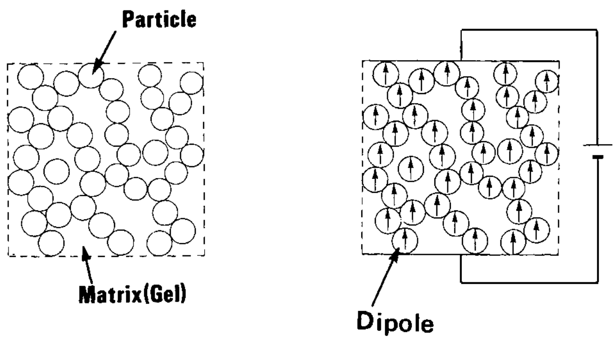

Figure 1 Schematic illustration of the electroviscoelastic effect in polymer gel.

$$M = (\tfrac{4}{3})\pi r^3 xH \quad (1)$$

where r is radius of a sphere, x is magnetic susceptibility of a sphere per unit volume, and H is the intensity of applied magnetic field. We next consider the magnetrostatic potential about an isolated pair of spheres with dipole moments of $\mathbf{M}_1$ and $\mathbf{M}_2$. $\mathbf{M}_1$ and $\mathbf{M}_2$ are vectors. The magnetrostatic potential ϕ between $\mathbf{M}_1$ and $\mathbf{M}_2$ separated by the distance R is given by eq. (2).

$$\phi = (\tfrac{1}{4}\pi\mu_0 R_3) \times [\mathbf{M}_1 \cdot \mathbf{M}_2 - (\tfrac{1}{3})(\mathbf{M}_1 \cdot R)(\mathbf{M}_2 \cdot R)] \quad (2)$$

Here μ is magnetic permeability. When the two spheres are aligned in the direction of external magnetic fields and touched each other, ϕ is written by eq. (3).

$$\phi = -\mathbf{M}_1 \cdot \mathbf{M}_2 / 2\pi R^3 \quad (3)$$

Since the magnetrostatic force between two adjacent spheres at a short range is calculated by $F = -d\phi/dR$, F is obtained using eq. (1) and eq. (3) at $R = 2r$.

$$F = -d\phi/dR = 3\mathbf{M}_1 \cdot \mathbf{M}_2 / 2\pi\mu_0 R^4 = \pi r^2 x^2 H^2 / 6\mu_0 \quad (4)$$

We consider a cubical blend having many straight lines which remain parallel to the direction of the applied magnetic field, and discuss the deformation of the cube by a shear strain from the perpendicular direction of the applied field (see Fig. 3). It is assumed that macroscopic mechanical properties such as storage and loss moduli are estimated easily by multiplying the magnetrostatic force F by the number of the line n. Since the magnetrostatic force changes the lines of dispersed particles into chains, the apparent shear modulus of the cube increases in magnetic fields. An increment of shear modulus ΔG induced by external magnetic fields is given by eq. (5).

$$\Delta G = nF \sin\theta / \gamma_0 L^2 \quad (5)$$

where γ_0 is the applied strain, θ is the lean angle of chain, and L is the length of the cube.

$$n = (\text{vol of particle in a cube}) / (\text{vol of particle in one line}) = 3CL^2 / 2\pi r^2 \quad (6)$$

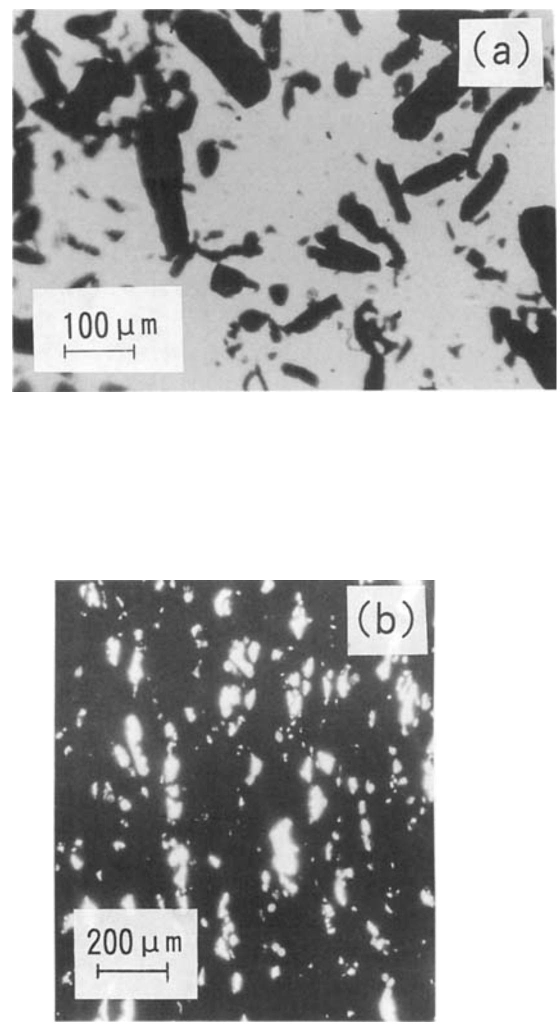

Figure 2 (a) Optical photograph of iron particles; (b) optical photograph of straight lines of the particles in the gel prepared under the influence of a magnetic field. The particle content in (b) is 5.6 vol %.

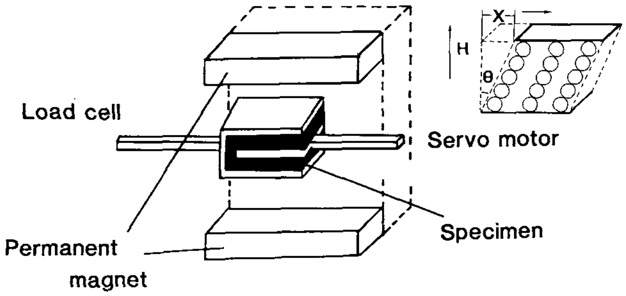

Figure 3 Schematic illustration of a test apparatus for viscoelastic measurements in external magnetic fields.

Substituting eq. (6) into eq. (5), we get

$$\Delta G = Cx^2H^2 \sin\theta / \gamma_0\mu_0 \qquad (7)$$

Since $\sin\theta = X/(X^2 + L^2)^{1/2}$, $X/L = \gamma_0$,

$$\sin\theta = \gamma_0/(\gamma_0^2 + 1)^{1/2}$$

So ΔG is reduced to eq. (8).

$$\Delta G = Cx^2H^2/\mu_0(\gamma_0 + 1)^{1/2} \qquad (8)$$

Equation (8) suggests that the changes of macroscopic mechanical properties of the particulate composite in external magnetic fields are qualitatively related to the microscopic interaction between induced-dipole moments.

EXPERIMENTAL

Preparation of Samples

The composite gels used experimentally were silicone gels with many straight lines of iron particles. They were prepared by heating a mixed solution of iron particles (Waco Chemical Ltd. Saturation magnetization 2.02 Wb/m^2) and a prereaction solution of silicone gel (Toray Dow Corning. SE1886) at 70°C for 5 h under the influence of a magnetic field of 27 kA/m. Iron particle contents in the composite gels were 1.1 vol % (No. 1), 5.6 vol % (No. 2), 12 vol % (No. 3), 20 vol % (No. 4), and 28 vol % (No. 5). The diameter of the iron particle was found to be roughly 100 μm by means of an optical micrograph [Fig. 2(a)]. Figure 2(b) indicates an optical photograph of dispersion of iron particles in the composite gel (Specimen No. 2). It was found that the gel had many straight lines of adjacent particles spanning the space between upper and lower surfaces.

Measurement of Magnetization Curve of Iron Particles

The magnetization curve of the iron particles was measured by a magnetometer (Toei Kogyo Ltd. VSM-3S). The particle weight for the measurement was 87 mg.

Measurement of Viscoelasticity

The experiments were performed on a viscoelastic spectrometer (Iwamoto Seisakusho Ltd. VES-F) at room temperature. Figure 3 shows a schematic illustration of a test apparatus for viscoelastic measurement in the presence of magnetic fields. The specimen was sandwiched between an inner alu-

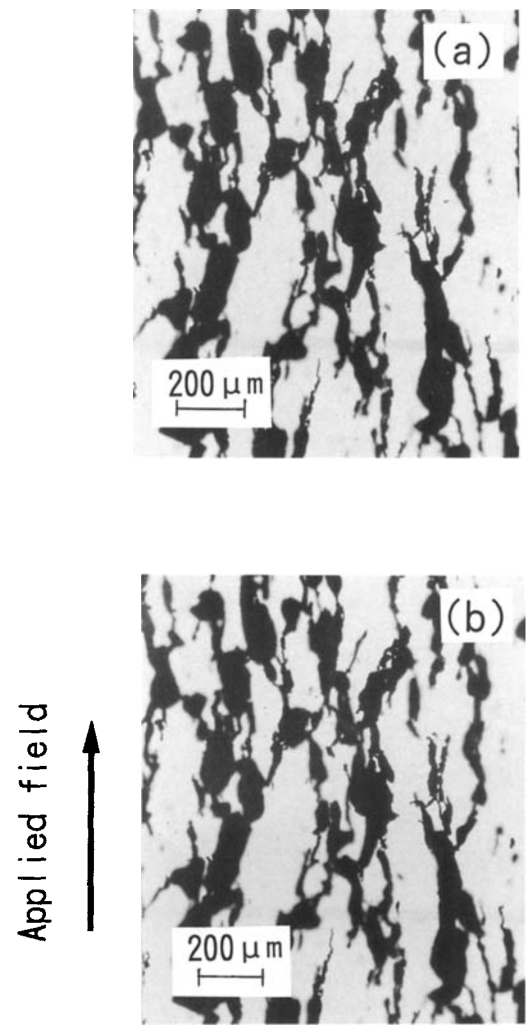

Figure 4 Optical photographs of lines of the particles under magnetic fields of 0 kA/m (a) and 43 kA/m (b). The particle content is 1.1 vol %.

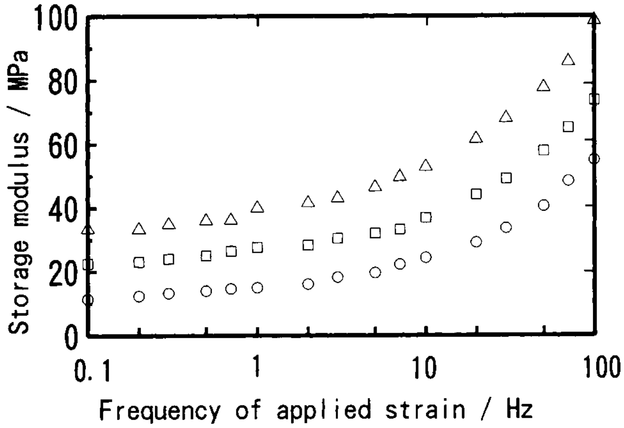

Figure 5 Storage modulus–strain frequency curves in various magnetic fields. (○) 0 kA/m, (□) 43.2 kA/m, and (△) 59.2 kA/m. The experiments were carried out at $\gamma_0 = 0.1$ using the specimen (No. 5).

minum plate (size 8 × 8 mm) and two outer plates (gap between the inner and outer plates 1 mm). The test apparatus was set between two permanent magnets in a test chamber of the viscoelastic spectrometer. The specimen was placed so as to arrange the straight lines along the external magnetic fields. The inner plate was vibrated by sinusoidally varying strains, $\gamma = \gamma_0 \sin 2\pi f t$($\gamma_0$, 0.025 to 0.6; f, 0.1 to 100 Hz). Torque acting on the two outer plates was measured through a load cell. Shear storage and loss moduli G' and G'' were calculated automatically by a personal computer.

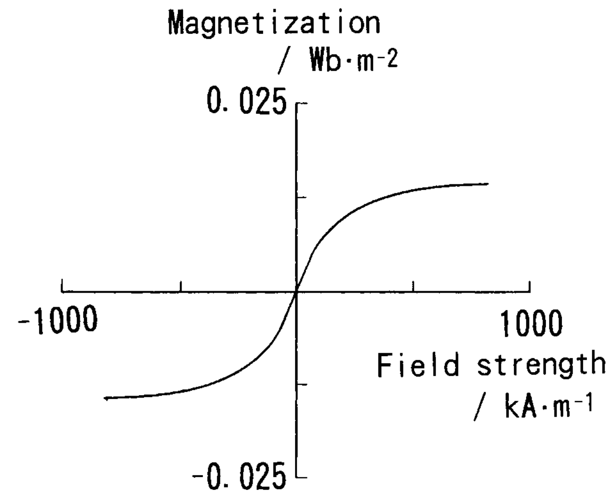

Figure 7 Magnetization curve of iron particle.

Measurements of Magnetic Fields

The intensity of magnetic fields between two permanent magnets in Figure 3 was measured by a gauss meter (ADS Ltd. HGM-8200). The field intensity was varied using various permanent magnets.

RESULTS AND DISCUSSION

Packing of Particles Under Magnetic Fields

We investigated the packing of iron particles in the gel under magnetic fields by means of an optical micrograph. The gel used in this work was specimen

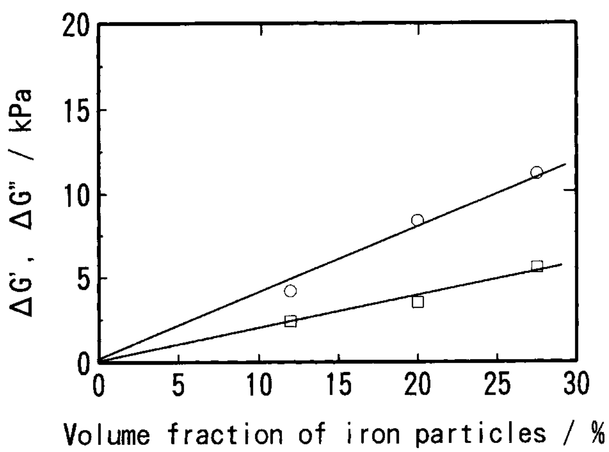

Figure 6 Effect of volume fraction of iron particle on the magnetroviscoelastic effect. In Figures 6, 8, and 10, $\Delta G'$ (○) and $\Delta G''$ (□) represent the increments of storage and loss moduli induced by magnetic fields, respectively. The experiments were made at $f = 10$ Hz, $\gamma_0 = 0.1$, and $H = 59$ kA/m.

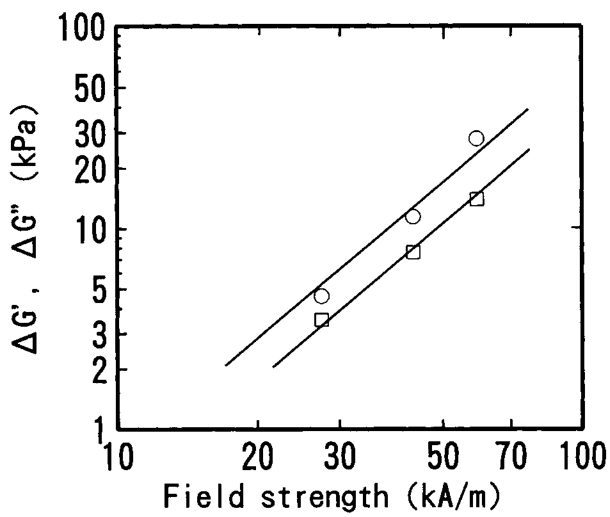

Figure 8 Field intensity dependences of $\Delta G'$ and $\Delta G''$. In Figures 8 and 9, the measurements were made at $f = 10$ Hz and $\gamma_0 = 0.1$ using the specimen (No. 5).

(No. 1). Figure 4(a) and (b) indicates the packings of the particles before and after application of a magnetic field of 43 kA/m. Distortion or deformation of the lines and realignment of the particles by action of the magnetic field were not detected in the silicone gel.

Magnetroviscoelastic Effect

We first measured viscoelasticity of the composite gels with or without magnetic fields to examine whether the composite gels show the magnetroviscoelastic effect. Figure 5 indicates strain frequency dependence of G' in various magnetic fields. In the absence of magnetic fields, G' increases with increasing strain frequency. The G' frequency curve is shifted to the upper side by the action of magnetic fields on the order of 10 kA/m. Comparing the values of G' with or without magnetic fields, G' at 10 Hz doubles in a magnetic field of 59 kA/m. In other words, the magnetroviscoelastic effect has been observed in the composite gels. The increment of G', indicating the value of the magnetroviscoelastic effect, is affected by the frequency of applied strain. When it was measured using a thermometer (Tsuruga Electric Works Ltd. Model 3527), the temperature at the surface of the gel was not changed by action of magnetic fields. Thermal effects may not be associated with the magnetroviscoelastic effect.

Effect of the Particle Content

According to the above point-dipole model, the change of macroscopic elastic modulus in external magnetic fields is connected with the magnetroviscoelastic effect using eq. (8). The increment of shear modulus induced by magnetic fields may be determined by C, H, and γ_0. Viscoelasticity of the composite gels with various volume fractions of iron particle was first measured under a field of 59 kA/m. Relationships between the increments of G' and G'' induced by the magnetic field ($\Delta G'$, $\Delta G''$) and the volume fraction of particle are displayed in Figure 6. Both $\Delta G'$ and $\Delta G''$ increase with the volume fraction, and are related to following equations: $\Delta G' = 0.41C$ and $\Delta G'' = 0.21C$, respectively. It is found that the magnetroviscoelastic effect reflects strongly on the storage modulus than on the loss modulus. The experimental results are in agreement with the point-dipole model.

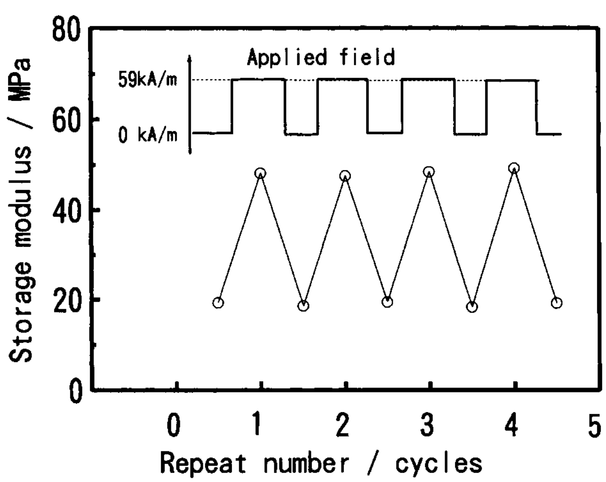

Figure 9 Repeatability of the magnetroviscoelastic effect.

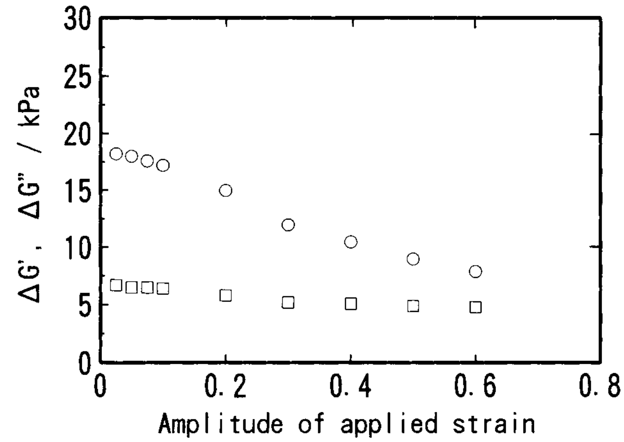

Figure 10 Effect of amplitude of applied strain on the magnetroviscoelastic effect. The experiments were carried out at H = 43 kA/m and f = 10 Hz using the specimen (No. 5).

Field Intensity Dependence

Figure 7 shows a magnetization curve of iron particle. The slope of the curve, indicating x, remains constant in the intensity range from 0 to 80 kA/m. Equation (8) indicates that the increments of G' and G'' are proportional to H^2 if x is independent of H. So the experiments were carried out between 0 and 59 kA/m. The experimental results are shown in Figure 8. The solid lines in Figure 8 represent $\Delta G = AH^2$(A is a constant). Both $\Delta G'$ and $\Delta G''$ show quadratic dependences on the field intensity. The storage modulus of the gel under a periodically varying magnetic field is displayed in Figure 9. It is found that the repeatability of the magnetroviscoelastic effect is good. The obtained result says that a permanent residual affect after dipole induction is negligible.

Effect of the Strain Amplitude

According to eq. (8), ΔG remains constant for small γ_0 whereas it decreases with increasing γ_0 for large γ_0. Figure 10 indicates the influence of the amplitude of applied strain on the magnetroviscoelastic effect. In the amplitude range of less than 0.1, $\Delta G'$ roughly remains constant. When the amplitude is more than 0.1, $\Delta G'$ decreases gradually with increasing amplitude. On the other hand, the dependence of the amplitude on $\Delta G''$ is ambiguous. This may perhaps be caused by weak reflection of the magnetroviscoelastic effect on G''.

From the experimental results in Figures 6, 8, and 10, it is concluded that the magnetroviscoelastic effect is qualitatively explained by a simple model due to the induced dipole-induced dipole interactions.

CONCLUSION

We demonstrated the magnetroviscoelastic effect using iron particle-filled silicone gels. We analyzed experimental results of the magnetroviscoelastic effect using the point-dipole approximation model. It was found that the changes of macroscopic mechanical properties were roughly related to the microscopic interactions between induced-dipole moments. The magnetroviscoelastic and electroviscoelastic effects offer the possibility of electromagnetical control of the adhesion between dispersed phases in an immiscible polymer blend. A polymeric material which can vary elastic modulus in external electromagnetic fields is expected to be designed.

REFERENCES

1. S. Moriya, K. Adachi, and T. Kotaka, *Polym. Commun.*, **26**, 235 (1985).
2. J. M. Serpico, G. E. Wnek, S. Krause, T. W. Smith, D. J. Luca, and A. Van Laeken, *Macromolecules*, **24**, 6879 (1991).
3. G. Venugopal, and S. Krause, *Macromolecules*, **25**, 4626 (1992).
4. J. Serpico, G. E. Wnek, S. Krause, T. W. Smith, D. J. Luca, and A. Van Laeken, *Macromolecules*, **25**, 6373 (1992).
5. T. Shiga, T. Ohta, Y. Hirose, A. Okada, and T. Kurauchi, *Koubunshi Ronbunshu*, **48**, 47 (1991).
6. T. Shiga, T. Ohta, Y. Hirose, A. Okada, and T. Kurauchi, *J. Maters. Sci.*, **28**, 1293 (1993).
7. T. Shiga, A. Okada, and T. Kurauchi, *Macromolecules*, **26**,(25), 6958 (1993).
8. R. Plonsey and R. E. Collin, *Principles and Application of Electromagnetic Fields*, McGraw-Hill, New York, 1961.
9. N. Kumagai, *Dengikigaku Kisoron*, Ohm Book Company, Tokyo, 1987.

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